

Intrinsic Birefringence of Nylon 6

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Synopsis

Different values are reported in the literature for the intrinsic birefringence of the crystalline (Δn_c^0) and the amorphous (Δn_a^0) phases in nylon 6. Mostly, these values have either been determined by extrapolation (and then it is assumed that $\Delta n_c^0 = \Delta n_a^0$) or calculated theoretically. In this study, intrinsic birefringence values Δn_c^0 and Δn_a^0 for nylon 6 were determined using the Samuels two-phase model which correlates sonic modulus with structural parameters. Three series of fiber samples were used: (1) isotropic samples of different degrees of crystallinity for estimation of $E_{l,a}^0$ and $E_{l,c}^0$ moduli at two temperatures. The following modulus values were obtained: 1.62×10^9 and 6.66×10^9 N/m² for 28.5 °C, and 1.81×10^9 and 6.71×10^9 N/m² for -20 °C; (2) anisotropic, amorphous fiber samples for estimation of $\Delta n_a^0 = 0.076$ and $E_{l,a}^0 = 1.63 \times 10^9$ N/m² at 28.5 °C; (3) semicrystalline samples of various draw ratios for estimations of $\Delta n_c^0 = 0.089$ and $\Delta n_a^0 = 0.078$. All measurements were carried out with carefully dried samples to avoid erroneous results caused by moisture.

INTRODUCTION

Recently, attempts have been made to correlate quantitatively mechanical properties of fibers with their structures.¹⁻⁶ This requires knowledge of the intrinsic birefringence of the crystalline (Δn_c^0) and the amorphous (Δn_a^0) phases. The same value, $\Delta n_c^0 = \Delta n_a^0 = 0.073$, is frequently used for nylon 6 and nylon 66.^{3,4,7} This value was estimated by Culpin and Kemp⁸ 25 years ago by extrapolating to infinity the birefringence versus draw ratio dependence for nylon 66 fibers. Acceptance of this value for the intrinsic birefringence seems to be questionable for many reasons.

Kunugi et al.⁹ have recently attempted to estimate intrinsic birefringences for nylon 6 fibers by the method of Orito et al.¹⁰ They have found $\Delta n_c^0 = 0.078$ for the fibers of draw ratios from 2 to 4.5; however, for lower draw ratios they obtained $\Delta n_c^0 = 0.03$. The values are hardly to be accepted because the applied method assumed some simplifications, such as equality of the orientation functions of amorphous and crystalline phases ($f_a = f_c$) for high draw ratios as well as equality of the ratios of amorphous and crystalline densities and their intrinsic birefringences ($d_a/d_c = \Delta n_a^0/\Delta n_c^0$). The latter relation is very unlikely due to the internal field effects¹¹ which have a strong influence on chain anisotropy and hence on the intrinsic birefringences of phases.

Owen and Ward¹² have determined maximum birefringence for so-called ideally oriented nylon 6 fiber and found $\Delta n_{\max} = 0.067$. Nearly the same value was reported by Jambrich and Diacik.¹³ Some attempts of theoretical calculation of intrinsic birefringences of nylons were also undertaken.^{9,14,15} Kunugi et al.⁹ have reported $\Delta n_c^0 = 0.094$ for the α -form of nylon 6. Their calculations were based on bond polarizability data estimated by Bunn et al.¹⁶ as well as on the crystallographic parameters of nylon 6 found by Holmes et al.¹⁷ Based on

the same data, Matsumoto and Kiyodu¹⁴ calculated $\Delta n_c^0 = 0.096$ and $\Delta n_a^0 = 0.083$ for nylon 6. Next, Urbańczyk¹⁵ calculated for the same nylon $\Delta n_a^0 = 0.084$, that is, an equivalent of birefringence of ideally oriented fiber after the definition of Hermans.¹⁸

It is thus seen that the values for crystalline and amorphous intrinsic birefringences of nylon 6 are indeed very scattered and of little reliability. It is evident that there is need for more work in this area. The main aim of our present investigation was to determine experimentally Δn_c^0 and Δn_a^0 , paying great attention to dryness of the nylon 6 samples. Although it has been well known that moisture affects strongly the properties of nylons, this fact was very seldom taken into account in the past studies.

THEORY

The applied method correlates parameters of morphological structure of a polymer, such as degree of crystallinity β , orientation function of crystalline f_c , and amorphous phases f_a , with its properties, i.e., birefringence Δn and the sonic modulus E . The method was elaborated by Samuels^{1,2} for isotactic polypropylene and then used by Dumbleton¹⁹ and by Gupta and Kumar²⁰ for poly(ethylene terephthalate). The method is founded on works of Moseley²¹ and Ward²² who correlated molecular orientation of a fiber sample with its sonic modulus.

According to the Samuels procedure, the intrinsic birefringences are given by the equation

$$\Delta n = \Delta n_c^0 \beta f_c + \Delta n_a^0 (1 - \beta) f_a \quad (1)$$

providing the contribution of form birefringence was neglected, as has been the practice with work in this field. In this equation, Δn , β , and f_c are easily measurable by commonly known methods, while f_a is determined from sonic measurements, using the following relation:

$$\frac{1}{E} = \frac{2}{3} \left[\frac{\beta(1 - f_c)}{E_{t,c}^0} + \frac{(1 - \beta)(1 - f_a)}{E_{t,a}^0} \right] \quad (2)$$

where $E_{t,c}^0$ and $E_{t,a}^0$ are the intrinsic transverse sonic moduli of the crystalline and amorphous phases, respectively. Then, the intrinsic transverse sonic moduli are determined from the expression

$$\frac{3}{2} \frac{1}{E} = \frac{\beta}{E_{t,c}^0} + \frac{(1 - \beta)}{E_{t,a}^0} \quad (3)$$

which relates the sonic modulus of isotropic sample to its degree of crystallinity.

In the case of amorphous anisotropic samples ($\beta = 0$), eqs. (1) and (2) lead to

$$\frac{1}{E} = \frac{2}{3} \frac{1}{E_{t,a}^0} - \frac{2}{3} \cdot \frac{\Delta n}{\Delta n_a^0 E_{t,a}^0} \quad (4)$$

The procedures described above were followed in our investigation, and the appropriate values were determined graphically using suitable equations. The determination of Δn_c^0 was performed assuming that $(\Delta n_c^0)_\alpha = (\Delta n_c^0)_\gamma$, because

the investigated samples varied to a great extent with regards to α and γ crystalline forms.

At last, it should be mentioned that correct determination of molecular orientation of polyamide fibers can only be achieved by the sonic modulus, providing the measurements are carried out with absolutely dry fibers as was shown by Richter²³ and us.²⁴ This is due to the fact that water acts as a strong plasticizer for polyamides and changes their properties to a great extent. Thus, determination of correct values of intrinsic birefringence is possible only when measurements are performed with dry samples. Such special dry conditions of work were provided. They enabled us to prepare amorphous samples of nylon 6 fibers as well and to use them for investigation. This special care was necessary because even small quantities of moisture lower considerably the glass transition temperature of nylon 6, which, in the case of amorphous samples, induces their crystallization already at ambient temperature.^{25,26}

EXPERIMENTAL

Samples

Three series of experimental fiber samples were investigated: (a) isotropic samples of different degrees of crystallinity, (b) amorphous anisotropic samples, and (c) crystalline anisotropic samples. Extracted nylon 6 pellets $\eta_{rel} = 2.97$; measured in 96% H_2SO_4 at 25°C with an Ubbelohde viscosimeter capillary no. 1) were used for fiber spinning. The amorphous isotropic and anisotropic fibers were spun under moisture-free conditions and without any lubricant finish.

The amorphous isotropic, 60- μ m-diameter monofilament sample was spun from the melt at 285°C using a small laboratory device. A take-up speed of 30 m/min and a side-blowing of dry air (0.3 m/s) at 3–5°C were used. To avoid moisture sorption from the atmosphere, the fibers were taken up into a chamber at reduced humidity (ca. 15% RH) and formed into very small packages (ca. 0.1 g) so that the as-spun monofilaments were in contact with the chamber air no longer than 45–60 s. The packages were kept at room temperature in hermetically closed boxes over molecular sieves as drying agents. The samples had a density of 1.090 g/cc and showed both glass ($T_g = 47^\circ C$) and cold crystallization ($T_{cc} = 69^\circ C$) transitions as measured in differential scanning calorimeter DSC-1B at a heating rate of 16°C/min. The above characteristics are typical for amorphous nylon 6.²⁷ Samples of varied degrees of crystallinity were prepared from the isotropic amorphous monofilaments by thermal or hydrothermal annealing.

Noncrystalline anisotropic fiber samples were formed in a laboratory Fourné spinning machine. The melted nylon 6 was spun at 280°C; take-up velocities varied from 300 to 2800 m/min, while side-blowing air at 3–5°C flowed at 0.5 m/s. The moisture-free conditions as described above were maintained.

Semicrystalline anisotropic fiber samples were prepared by drawing on a hot plate at 90°C the fibers spun from the melt at 285°C, at a take-up velocity of 350 m/min and side-blowing air at 0.5 m/s. The high degrees of crystallinity were realized in anisotropic samples by subjecting them to thermal annealing in evacuated ampoules.

TABLE I
Structural and Mechanical Data Measured at -20 and $+28.5^\circ\text{C}$ on Isotropic Nylon 6 Monofilaments

Sample	Sound velocity, km/s		d , g/cc	$\frac{1}{E} \times 10^9, \text{m}^2/\text{N}$		β
	At -20°C	At $+28.5^\circ\text{C}$		At -20°C	At $+28.5^\circ\text{C}$	
	Amorphous M_{iso}	1.578		1.488	1.090	
M_{iso} stored at room temperature for 30 days at 65% RH ^a	1.767	1.650	1.1227	0.285	0.327	0.30
M_{iso} annealed 1 h at 110°C	1.779	1.674	1.1276	0.280	0.316	0.33
M_{iso} annealed 1 h at 200°C	1.849	1.797	1.1467	0.255	0.270	0.42
M_{iso} boiled in water for 2 h ^b	1.990	1.812	1.1476	0.220	0.265	0.53

^a Dried after storage.

^b Dried after boiling.

Measurements

A Geigerflex x-ray diffractometer was used for the measurement of the degree of crystallinity and orientation function of the crystalline phase. The degree of crystallinity was determined by the procedure of Stepaniak et al.,²⁸ while the orientation function f_c was measured by the Hermans method adapted to nylon 6 fibers by Urbańczyk.²⁹

Densities were measured at 20°C in a gradient tube using mixtures of *n*-heptane and freshly distilled carbon tetrachloride; the latter has to be free from photodegradation products to avoid liquid-induced crystallization of the amorphous nylon 6 samples.

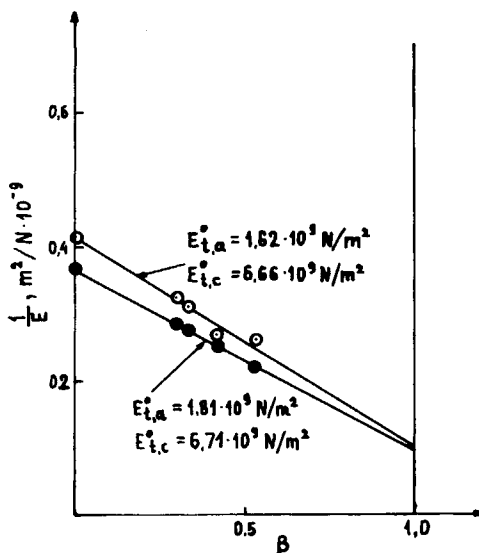


Fig. 1. Plot of $1/E$ vs. degree of crystallinity β measured at -20°C (—●—●—) and $+28.5^\circ\text{C}$ (—○—○—) in dry isotropic monofilaments. Estimated values of intrinsic moduli are given in the figure.

TABLE II
Structural and Mechanical Data Measured at 28.5°C in Noncrystalline Nylon 6 Monofilaments

Take-up velocity of sample, m/min	Density, g/cc	Sound velocity, km/s	Birefringence Δn	$E \times 10^{-9}$, N/m ²	$\frac{1}{E} \times 10^9$, m ² /N
30	1.0904	1.488	0.0000	2.414	0.414
250	1.0952	1.510	0.0010	2.497	0.400
400	1.0960	1.541	0.0044	2.602	0.384
650	1.0968	1.595	0.0081	2.790	0.358
950	1.0972	1.666	0.0143	3.045	0.328
1020	1.0987	1.655	0.0150	3.009	0.332
1750	1.1086	1.722	0.0194	3.287	0.304

Birefringence was measured with a Polish interference-polarizing microscope Biolar PI using the striated field method.³⁰⁻³² As stated earlier,²⁴ the birefringence of nylon 6 fibers changes very moderately with temperature; e.g., from +30 to -20°C, the change is within measurement error ($\pm 3.10^{-4}$), so the Δn values determined at room temperature were also used for low-temperature calculations.

The sonic modulus was determined using a Dynamic Modulus Tester PPM-5R which had been specially adapted²⁴ for measurements at controlled temperatures (from room to -25°C) and humidities (from 0 to 100% RH). The modulus was calculated from the expression

$$E = dC^2 \tag{5}$$

where d and C are sample density and sound velocity, respectively.

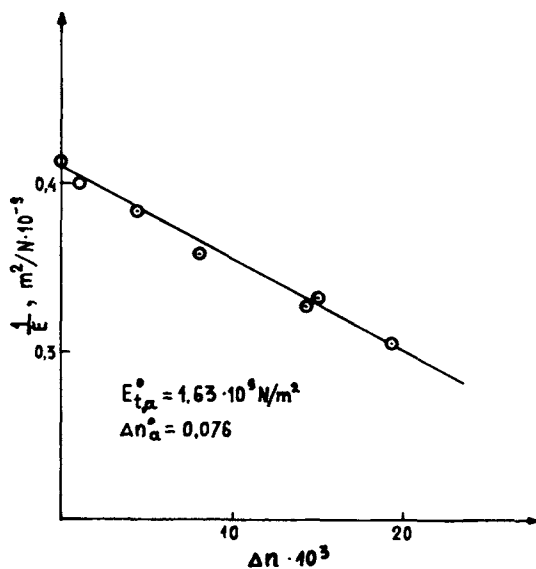


Fig. 2. Plot of $1/E$ vs. birefringence Δn measured at 28.5°C in dry, amorphous anisotropic samples. Estimated values are given in the figure.

TABLE III
Structural and Mechanical Data Measured at -20 and $+28.5^\circ\text{C}$ on Semicrystalline Nylon 6 Fiber Samples

Draw ratio	Sound velocity, km/s		d , g/cc,	Δn	β	f_c	f_{am}	
	At -20°C	At $+28.5^\circ\text{C}$					At -20°C	At $+28.5^\circ\text{C}$
1.0		1.761	1.1309	0.0061	0.34	0.10		0.062
1.5	1.899	1.816	1.1314	0.0112	0.35	0.205	0.092	0.101
2.0	2.089	2.020	1.1337	0.0310	0.356	0.60	0.208	0.237
3.0	2.401	2.348	1.1380	0.0447	0.409	0.80	0.337	0.377
4.0		2.442	1.1395	0.0508	0.422	0.90		0.389
4.4	2.581	2.543	1.1427	0.0529	0.447	0.91	0.375	0.422
1.0 ^a		1.881	1.1430	0.0098	0.459	0.18		0.058
1.5 ^a	2.060	1.993	1.1436	0.0264	0.462	0.59	0.055	0.090
2.0 ^a	2.294	2.164	1.1480	0.0438	0.499	0.82	0.151	0.140
3.0 ^a	2.521	2.483	1.1519	0.0518	0.529	0.92	0.237	0.295
4.0 ^a		2.525	1.1536	0.0550	0.533	0.94		0.308
4.4 ^a	2.616	2.560	1.1547	0.0565	0.553	0.942	0.251	0.299

^a Annealed for 1 h at 200°C under vacuum.

RESULTS AND DISCUSSION

The measured data used for determination of $E_{t,c}^0$ and $E_{t,a}^0$ are collected in Table I, and the relation $1/E = f(\beta)$ is plotted in Figure 1. As is seen, the relation is linear for both -20°C and $+28.5^\circ\text{C}$. The moduli $E_{t,c}^0$ and $E_{t,a}^0$ were estimated by extrapolation of $1/E$ to $\beta = 0$ and to $\beta = 1$. They were found to be 1.81×10^9 and 6.71×10^9 N/m² for -20°C and 1.62×10^9 and 6.66×10^9 N/m² for $+28.5^\circ\text{C}$, respectively. The results refer to dry nylon 6 fibers because in the case of moist samples, the modulus $E_{t,a}^0$ falls, as expected.²⁴ Then, at 28.5°C and equilibrium moisture sorption at 65 and 100% RH, the $E_{t,a}^0$ is equal to 0.88×10^9 and 0.34×10^9 N/m², respectively, while the $E_{t,c}^0$ rests unchanged and is the same as for the dry sample (6.7×10^9 N/m²). This fact seems to be due to the intercrystalline

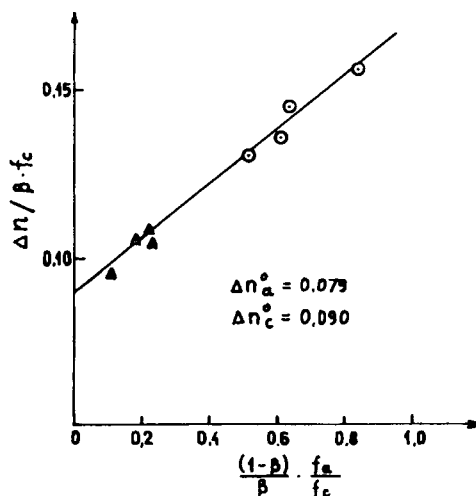


Fig. 3. Plot from the present data for calculation of intrinsic birefringence for the crystalline and amorphous phases. Measurements were made at -20°C in dry unannealed (\circ) and annealed (\triangle) samples. Estimated values are given in the figure.

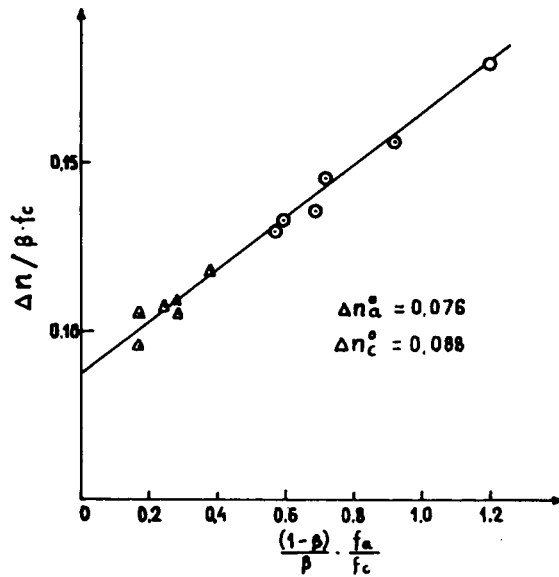


Fig. 4. Plot from the present data for calculation of intrinsic birefringence for the crystalline and amorphous phases. Measurements were made at 28.5°C in dry unannealed (—○—○—) and annealed (—Δ—Δ—) samples. Estimated values are given in the figure.

character of water sorption in nylon 6. These facts supported our decision to carry out the determinations of intrinsic birefringences in dry samples.

The data obtained for amorphous anisotropic fiber samples are presented in Table II. Densities of samples spun at rather moderate take-up velocities are nearly the same as the density of isotropic amorphous samples (1.09 g/cc)³³; only in one sample, a higher density (1.109 g/cc) was observed. All the samples exhibited cold crystallization transition as measured by DSC. This indicates that even the latter sample is partially noncrystalline. The temperature of this transition is dependent, however, on the sample anisotropy, so that the higher the anisotropy, the lower is the transition temperature, which decreases to 40–50°C.

Figure 2 represents a plot of 1/E vs. Δn, from which $E_{t,a}^0$ and Δn_a^0 were estimated according to eq. (4). The $E_{t,a}^0$ was found by extrapolation at Δn = 0 and gave the value of 1.63×10^9 N/m², which is in perfect agreement with the value reported above for isotropic samples measured at 28.5°C. The intrinsic birefringence of the amorphous phase calculated from the slope yielded the value of 0.076.

For the determination of Δn_a^0 and Δn_c^0 , two series of semicrystalline anisotropic fiber samples were used. In the first, fibers of different draw ratios were investigated, while in the second, the same fibers after thermal annealing were used. Sound wave velocities were measured at two temperatures: -20 and +28.5°C. The results are summarized in Table III, and functions of $\Delta n / \beta f_c = f[(1 - \beta)f_a / \beta f_c]$ are plotted in Figures 3 and 4 according to eq. (1) rewritten in the form

$$\frac{\Delta n}{\beta f_c} = \Delta n_c^0 + \Delta n_a^0 \frac{(1 - \beta) f_a}{\beta f_c} \tag{6}$$

The values $\Delta n_a^0 = 0.079$ and $\Delta n_c^0 = 0.090$ were obtained from measurements at -20°C . The corresponding values for $+28.5^\circ\text{C}$ read from Figure 4 are 0.076 and 0.088, respectively. Thus, the appropriate values of intrinsic birefringences of nylon 6 determined at two different temperatures are very much the same. So, one could average them, and in this case $\Delta n_a^0 = 0.078$, and $\Delta n_c^0 = 0.089$.

Finally, it is worth noting that the average value of $\Delta n_a^0 = 0.078$ is in very good agreement with the previous one (0.076) obtained from measurements performed on amorphous anisotropic fiber samples.

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