

ORIENTATION PROCESSES IN CRYSTALLINE AND AMORPHOUS REGIONS OF POLYPROPYLENE DURING YARN SPINNING

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The influence of the spinneret draw ratio and subsequent solid-state stretching of polypropylene multifilament yarns (PMY) on changes in the orientation of crystallites and molecular chains in the polymer amorphous regions was studied using x-ray structure analysis. It was shown that crystallites and molecular chains of amorphous polypropylene (PP) became significantly more oriented already for a yarn spinneret draw ratio of 2400% and changed little if it was increased further. Additional solid-state stretching of yarns at elevated temperature had practically no effect on the orientation of PP crystallites but did halve the misorientation angle of molecular chains in the polymer amorphous regions. This phenomenon suggested that the substantial decrease of the elongation at break and increase of PMY physicomechanical parameters could be attributed to distribution of the applied load onto a larger number of continuous chains.

X-ray structure analysis of the influence of preparation conditions for polypropylene multifilament yarns (PMYs) on the supramolecular structure of isotactic polypropylene (PP) showed that crystallites become highly oriented in the fibers already during spinning with apparent spinneret draw ratio $\Phi_a = 1400\%$ [1]. It was found that increasing Φ_a to 16,300% had little effect on the orientation of polymer crystallites but prevented a^* -oriented folded-chain lamellae in which the molecular chains were perpendicular to the fiber axes [1, 2].

These crystalline folded-chain lamellae were practically completely converted into fibrillar crystallites of stretched chains during orientational drawing of PMY in the range 4.2-5.6 with heating [2]. It is noteworthy that the crystallites did not become significantly more oriented during this. Thus, orientation processes in the polymer crystalline phase could not explain the changes of the yarn physicomechanical parameters. In our opinion, the orientation of molecular chains in the PP amorphous phase should play an important role in deformation of the yarns.

Therefore, the goal of the work was to study the effect of the spinneret draw ratio and subsequent PMY deformation on the orientations of crystallites and molecular chains in the polymer amorphous regions.

Yarns were produced using Balen isotactic PP 01250 (Ufaorgsintez Corp., TU 2211-015-00203521—99). The PP melt flow index as measured on an IIRT-5M apparatus was 25 g/10 min (230°C/2.16). The PP melting temperature as determined using a heating stage was 169°C.

Freshly spun PMY were produced on an SFPV-1 laboratory test bench [3] equipped with an extruder, melt conduit, spinneret with 24 orifices (diameter 0.4 mm), and take-up device. The spinning temperature was 220°C. The melt feed rate and take-up speed were controlled during the experiment. Orientational drawing of the yarns used an OSV-1 test bench at a speed of 16-20 m/min and temperature in the drawing zones increasing from 130 to 150°C. The apparent spinneret drawing ratio (Φ_a) of the yarns was calculated as before [1]. The orientational drawing ratio was determined using the formula

$$B = d_{fr}^2 / d_{or}^2,$$

where d_{fr} and d_{or} are the filament diameters of freshly spun and oriented yarn, respectively.

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Table 1. Preparation Conditions and Main Characteristics of PMY

Φ_a , %	B	T , tex	ϵ_b , %
2400	0	150	923.0
16300	0	27	607.0
2400	5.56	27	33.7

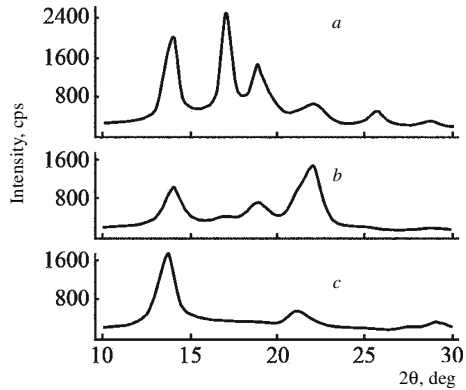


Fig. 1.

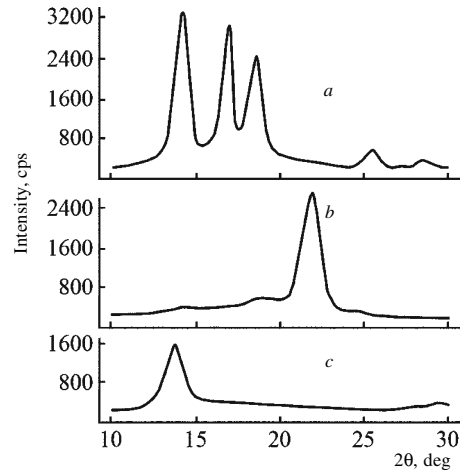


Fig. 2.

Fig. 1. Equatorial (a), azimuthal (b), and meridional (c) x-ray scattering curves for freshly spun PMY fibers at $\Phi_a = 2400\%$ and $B = 0$.

Fig. 2. Equatorial (a), azimuthal (b), and meridional (c) x-ray scattering curves for freshly spun PMY fibers at $\Phi_a = 16300\%$ and $B = 0$.

Filament diameters were measured on a Lanotester-2 instrument. The linear density (T) of yarns was calculated according to GOST 6611.1-73. The relative elongation at break (ϵ_b) of the PMY was determined using a 2099P-5 tensile tester with elongation rate 250 mm/min and specimen working length 100 mm. Table 1 presents the characteristics of the studied yarns.

Ground PP granules in both the initial condition and after heat treatment at 150°C for 1 h were used as additives.

X-ray structure analysis of the samples used a DRON-3 diffractometer and Cu $K\alpha$ -radiation isolated by balanced Ni and Co filters. Exposures were taken in transmission mode in the 2θ range 10-30° with rotating crystal and detector. Filament texture was studied using a special cell that formed a flat sample from yarns laid parallel [4, 5] and a goniometer enabling their controlled rotation. Equatorial and meridional scatterings were studied for a vertical and horizontal arrangement, respectively, of the yarns; radial (azimuthal), by diffraction with the yarn axes tilted 45° from the vertical. Powdered materials were analyzed using a flat cell with 5- μ m thick polyethyleneterephthalate film windows that was installed in an attachment for rotating samples and averaging scattered intensity.

Quantitative measurements of the sample scattering intensity took into account the background and differential filtration of the radiation [6, 7]. The sample scattering intensities were normalized to an external standard in order to adjust the results to a single scale [6-8].

Figures 1 and 2 show intensity curves for equatorial, meridional, and azimuthal x-ray scattering by freshly spun PMY produced at $\Phi_a = 2400$ and 16,300%.

Reflections for 110, 040, and 130 at 2θ 14.1, 16.9, and 18.65° on the equatorial curves (Fig. 1a and 2a) were characteristic of the α -form of isotactic PP and suggested that the yarns contained c -axial-oriented crystallites for which the unit-cell c -axis was directed along the fiber axis [2, 9]. The insignificant effect of equatorial reflection 040 at $2\theta = 16.9^\circ$ on the azimuthal scattering (Fig. 1b and 2b) indicated that crystallites were considerably oriented already at spinneret draw ratio 2400%. A quantitative estimate of the average polymer crystallite misorientation angle (α_{avg}) using the 040 reflection

Table 2. Misorientation Angles of Crystallites of PMY Fibers Prepared Under Various Conditions

PMY spinning conditions	α_{avg} , deg
$\Phi_a = 2400, B = 0$	15.0
$\Phi_a = 16300, B = 0$	13.5
$\Phi_a = 2400, B = 5.56$	13.5

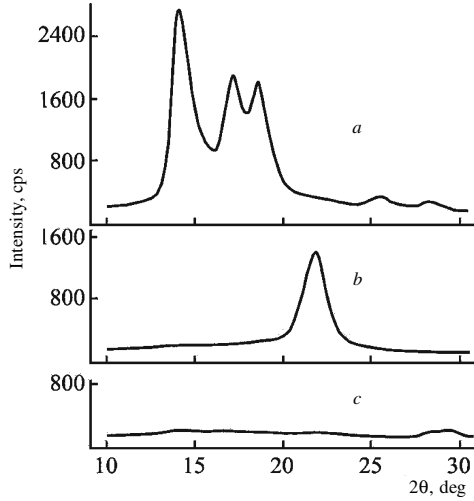


Fig. 3.

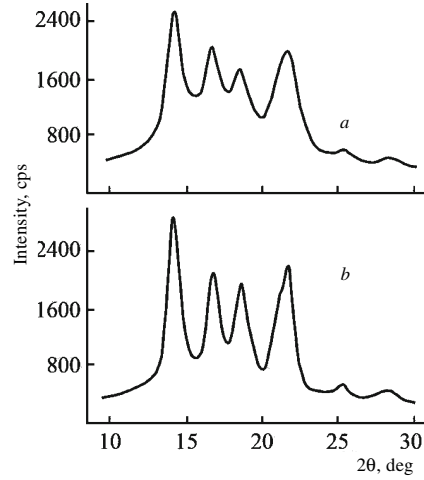


Fig. 4.

Fig. 3. Equatorial (a), azimuthal (b), and meridional (c) x-ray scattering curves for freshly spun PMY fibers at $\Phi_a = 2400\%$ and $B = 5.56$.

Fig. 4. X-ray diffraction patterns of initial powdered isotactic PP (a) and that heated to 150°C (b).

and the literature method [1, 5] showed that α_{avg} decreased from 15.0 to 13.5° as the yarn draw ratio increased from 2400 to 16,300% (Table 2).

Figure 3 shows intensity curves for equatorial, azimuthal, and meridional scattering by PMY filaments prepared by solid-state stretching by 5.56 times of freshly spun yarns of 150 tex. The filament crystallite misorientation angle depended weakly on thread stretching (Table 2). This agreed with previous results [2].

The specifics of the equatorial, azimuthal, and meridional scattering curves (Figs. 1-3) indicated that the dependence of polymer diffuse scattering intensity on azimuthal rotation angles of oriented filaments could be analyzed and that an angular parameter characterizing the orientation of molecular chains in the PP amorphous phase could be determined from it. An important feature of this analysis was the judicious selection of diffraction angles at which PP crystallites had little effect on the polymer diffuse halo.

This problem was solved by analyzing spherically symmetric scattering by isotactic PP powders in both the initial condition and after heat treatment at 150°C (Fig. 4).

Diffuse scattering at $2\theta = 10^\circ$ was previously proven to belong to isotactic PP. The degrees of crystallinity of initial and heated PP were 50.3 and 71.6%, respectively [10]. The low scattering intensity at $2\theta = 10^\circ$ did not allow a reliable quantitative analysis of oriented filaments (Figs. 1-3).

The diffraction patterns shown in Fig. 4 indicated that PP crystallization was accompanied by a significant weakening of scattering intensity at $2\theta = 15.4^\circ$, which was close to the diffuse halo maximum of isotactic PP [11]. Table 3 presents normalized diffraction intensities (I_{refl}^n) at $2\theta = 10$ and 15.4° for powdered PP with different amounts of amorphous phase (A_M). The coefficient of variation of the data was 1.5%.

Normalized scattering intensities of samples were corrected for incoherent scattering, which was determined using data for polycrystalline carbamide [6] taking into account differences of chemical composition and total mass attenuation coefficient of the radiation by the samples. Calculations showed that the ratio of coherent normalized diffuse

Table 3. Normalized Diffraction Parameters for Powdered Polypropylene Samples

Parameters	PP sample		K_{coh}
	initial	heated	
I_{refl}^n (10°), counts/s	203	139	1.75
I_{refl}^n (15.4°), counts/s	969	590	1.75
A_M	0.497	0.284	1.75

Table 4. Misorientation Angles of Molecular Chains in the Amorphous Phase of PMY Fibers Prepared Under Various Conditions

PMY spinning conditions	β , deg
$\Phi_a = 2400, B = 0$	42
$\Phi_a = 16300, B = 0$	38
$\Phi_a = 2400, B = 5.6$	22

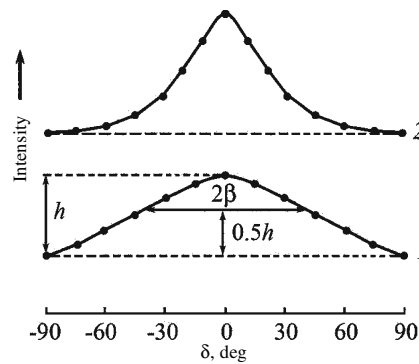


Fig. 5. Azimuthal intensity profile of the diffuse halo at $2\theta = 15.4^\circ$ for PMY fibers spun under different conditions: $\Phi_a = 2400\%$, $B = 0$ (1) and $\Phi_a = 2400\%$, $B = 5.56$ (2).

scattering intensities for initial and heated PP (K_{coh}) at $2\theta = 10^\circ$ agreed with the same parameter for $2\theta = 15.4^\circ$ (Table 3). This indicated that this point belonged to the PP diffuse halo. Strong scattering intensity at $2\theta = 15.4^\circ$ increased the analytical accuracy.

Figure 5 shows azimuthal profiles of diffuse scattering at $2\theta = 15.4^\circ$ for PMY fibers produced under different conditions. The diagram shows the determination of the average misorientation angle β of molecular chains in the polymer amorphous phase relative to the fiber axis using freshly spun yarns as an example (curve 1). Azimuthal angle $\delta = 0$ corresponded to filaments with vertical axes; $\delta = 90^\circ$ and -90° , horizontal. Table 4 presents the results for parameter β for filament yarns spun under different conditions.

The results indicated that the PP amorphous phase became considerably textured because polymer chains became oriented relative to the filament axis already during production of freshly spun PMY. Increasing the spinneret draw ratio from 2400 to 16,300% decreased parameter β by only 10%. This indicated that Φ_a had little effect on chain orientation in the fiber amorphous phase.

The studies found that solid-state stretching of freshly spun yarns at elevated temperature decreased the misorientation angle of molecular chains in the filament amorphous phase from 42 to 22° . This property and the aforementioned practically complete conversion of lamellar folded-chain crystallites to fibrillar crystallites of stretched chains [2] explained the substantial reduction of elongation-at-break of the yarns during solid-state stretching (Table 1) and their increased physicomechanical parameters due to distribution of the applied load over more continuous chains.

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