

Oriented Isotactic Polypropylene Structure and Morphology

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Abstract. Structure, morphology and mechanical properties of uniaxially oriented in the solid state and subsequently annealed isotactic polypropylene sheets were examined by X-ray diffraction, electron microscopy, differential scanning calorimetry (DSC) and mechanical testing. The sheet structure and morphology showed parallel fibrils with orientation degree, crystal size, crystallinity, melting temperature and mechanical properties depending on draw ratio and annealing temperature.

1. Introduction

Isotactic polypropylene (iPP) is a widely applied technical material mainly due to its versatility and relatively low price. The low mechanical strength is often improved by sample preferred orientation [1 - 3]. There are several types of orientation, one, two or more directional drawing, with or without subsequent annealing at temperatures near but below the melting point. [7, 8]. For instance, unidirectional drawing leads finally to a microfibrillar morphology with increased tensile strength and Young's modulus [1 - 3, 8] and different melting behaviour [12].

According to the classical model proposed by Peterlin [11], drawn films and fibres consist of aligned small lamellar blocks mutually connected through non-crystalline molecules and/or crystalline bridges. Several reports do not support his model and the proposed transition scheme of original crystal lamellae into microfibrils and a longitudinal sliding motion of these microfibrils [10,11]. Those studies describe the melting of crystalline lamellae under tension followed by the recrystallisation into the oriented fibrillar structure. At present, there is no accepted general model for the drawing behaviour of crystalline polymer samples.

In this contribution, we describe the preparation and characterisation of iPP sheets unidirectionally oriented and subsequently annealed taut at various temperatures below the melting temperature. The relations between structural changes and mechanical properties owing to preferred orientation and annealing are discussed.

Experimental

1.1. Samples

Isotactic polypropylene, Mosten TB002, was obtained as pellets from Unipetrol RPA, Czech Republic, with isotacticity 98.3%, number molecular weight 67 935 g/mol and weight molecular average 428



800 g/mol. Sheets of this iPP were prepared in the Polymer Institute Brno (Czech Republic). In the first step the pellets were extruded at 125°C as sheets. The sheets were cut to 10 mm wide bands and extended uniformly at 145°C to extension ratios 5, 8 and 11. Annealing, was performed either 30 min in an oven while bands were held taut, or moved slowly (10 min in contact with plates and a roller heated to annealing temperature (T_a)). The sample speed and thickness were continuously monitored. The sheets with various elongation ratio, λ , and annealing treatments, with the samples held taut, are listed in Table I. All further measurements were done at room temperature.

1.2. X-ray diffraction

The wide angle diffractogram scans were taken in the longitudinal and radial directions in the 2Θ range 5 - 30° in transmission and reflection modes. Scans were collected on a horizontal goniometer HZG-6 (Freiberg Präzisionsmechanik Holding GmbH, Germany) and the diffractometer A1P1 (AREM PRO, s.r.o., Czech Republic) using $\text{CuK}\alpha$ Ni filtered line shape radiation. The measuring conditions were: 0,05° step size, hold time 5s at room temperature.

Crystal size - The sample crystal size, L_{110} , was calculated from the 110 crystal diffraction peak profiles according to the Scherrer equation [12].

Crystallinity - The sample crystallinity (X) was calculated from the X-ray scans as the ratio of areas of crystalline peaks and total scan area over background.

Orientation degree - The most important characteristic of preferentially oriented samples is the type and, primarily, the degree of orientation. The orientation degree was characterized by the azimuthal 2Θ angle where the original 110 peak intensity on the equator decreased to one half (Or).

1.3. Morphology

Transmission electron microscopy (TEM) was performed using a Tesla 500 (TESLA ELMI, a.s., Czech Republic) at 90kV using replicas of selectively etched sample surfaces. After selective etching the samples were vacuum shadowed with gold or platinum and vertically coated with an evaporated carbon film. The magnification of the micrographs is indicated by 1 μm bars and the extension direction by an arrow.

1.4. DSC-measurements

Disc shaped specimens, 1 to 5 mg in weight, were cut from the sheets and measured in a DSC (TA Instruments Inc., Q100, USA). The scan conditions were heating rate 10 °C/min in nitrogen atmosphere. From the scans the fusion enthalpy (ΔH), peak temperature (T_m), melting range and crystallinity (X) were evaluated. For crystallinity calculation as a standard for 100% iPP the $\Delta H_0 = 209$ J/g was taken according to Mezghani and Phillips [13].

1.5. Mechanical properties measurements

The tensile properties of the original and annealed polypropylene film strips were tested using an Instron 4302 (Illinois Tool Works Inc., USA).

2. Results and Discussion

2.1. X-ray diffraction – crystal structure

Figure 1 shows the transmission X-ray diffraction scans of the non-oriented sample, TB, after annealing at various T_a . The scans show 7 reflections corresponding to the (110), (040), (130), (111), (031) and (041) superimposed, (060) and (220) crystallographic planes, respectively. The diffraction patterns belong to the stable α monoclinic unit cell of isotactic polypropylene with cell dimension $a = 6.65$, $b = 20.96$ and $c = 6.50$ Å [10]. Annealing at higher temperature increased the peak intensity, and decreased the peak width so that the two peaks (111 and superimposed 131 and 041) in the range $2\Theta = 21 - 22^\circ$ could be better resolved. Annealing the TB samples (Fig. 1) at higher T_a tended to increase the (040) and (130) intensities relative to that of (110). In non-annealed, oriented samples ($T_a = 23^\circ\text{C}$) the

ratio of $I(040) / I(110)$ decreased with growing extension ratio λ from 0.55 of the non-oriented sample ($\lambda = 1$) to 0.34 for the temperature and sample 11/10 with $\lambda = 11$. This is in accord with increasing sample orientation.

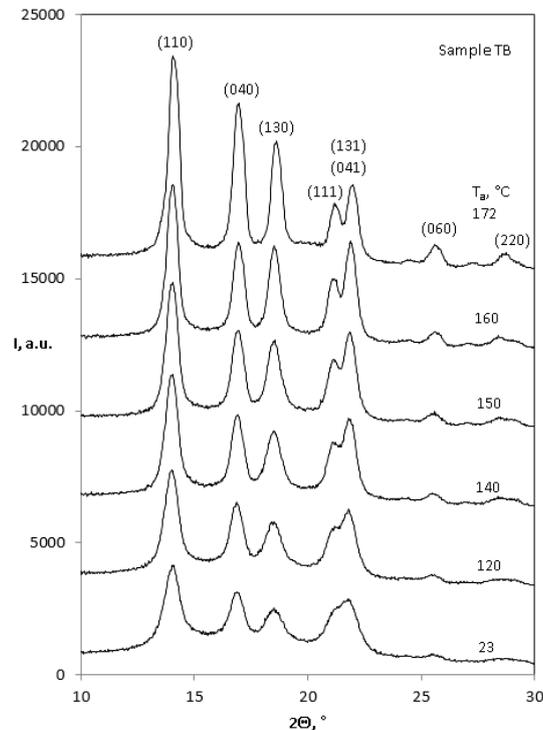


Figure 1. Typical equatorial WAXS diffractograms of the TB samples non-oriented and annealed at various T_a .

Increasing T_a had an opposite effect, the ratio $I_{(040)}/I_{(110)}$ increased with growing T_a . Annealing, though in a fixed position, slightly decreased the sample orientation degree. A hypothetical explanation of this effect (higher 040 peak intensity) would be the formation of a small amount of the γ – phase in the α -phase matrix, however, this is improbable because the main γ -phase characteristic peak (117) at $\sim 21^\circ 2\theta$ was not detected in any of our samples.

The crystallinity increased with elongation degree λ and annealing temperature T_a as expected.

2.2. Crystal size

The tendency for the L110 values to increase with increasing T_a was apparent for sample TB annealed for a relatively long time (30 min), while in oriented samples, annealed for a shorter time (10 min), the L110 values growth was less pronounced. The L110 value at $T_a = 23^\circ \text{C}$ for the non-oriented sample, TB, was slightly higher (107 Å) than for the oriented samples (101-104 Å) indicating that the extension process resulted in decrease of the original crystal size or changed the tilt of molecules in the crystals. With increasing T_a the L110 values increased for the non-oriented sample TB up to 143 Å. In the oriented samples the L110 values also increased with T_a , but to a lesser extent. Although the L110 values might also be affected by crystal defects, it is often accepted that they reflect mainly the crystal size. Thus, we suggest that the crystal size's growth during annealing depended on two factors: the original sample extension and the annealing temperature.

2.3. Orientation degree

The orientation degree values O_r were close to 4° and increased with increasing T_a only slightly. Thus annealing decreased the orientation degree (increase of the O_r or of I_{040}/I_{110}) a little with growing T_a . Sample annealing, mainly above 140°C , led to structure changes, including increased crystallinity and crystal size but on the other side, to lower orientation. Annealing of the drawn samples at higher T_a brought two types of effects: 1. Increasing crystallinity and crystal size. 2. Decreasing of the orientation degree and sample volume which, the latter in samples in taut position increased the internal tension and resulted in perpendicular crack formation, leading to the tensile strength decreasing in samples annealed at $T_a = 150^\circ\text{C}$ and higher.

2.4. Melting

For the non-oriented and non-annealed sample TB the melting scan (Fig. 2) shows only one broad melting peak ($T_m = 165,4^\circ\text{C}$). Besides of the main peak in the TB samples, annealed at higher T_a , a second lower melting peak (or shoulder in sample with $T_a = 160^\circ\text{C}$) appeared. The oriented and annealed samples had more complicated melting scans, showing 2-3 lower melting peaks or shoulders. The melting peaks and shoulders also had the tendency to shift to higher T_m with growing \square and T_a . The melting behavior was influenced by two factors: extension and annealing. The sample extension and annealing increased the melting temperature of the sample. Also lower melting peaks or shoulders shifted to higher temperatures.

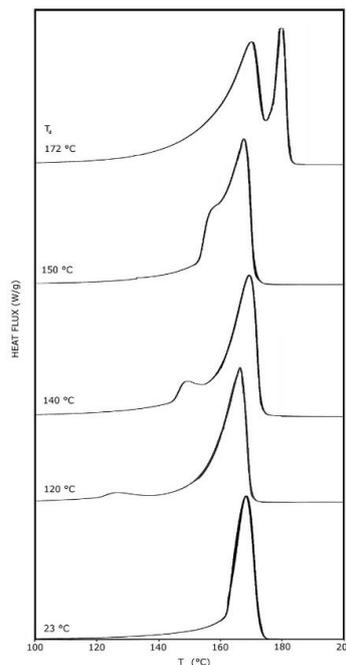


Figure 2. DSC melting curves of non-oriented (TB) and oriented samples iPP annealed at various T_a . a – non-oriented sample, b – sample 5/10, c – sample 8/10, d – sample 11/10.

2.5. Morphology

The examination of oriented iPP sheets by SEM and TEM has shown that the spherulitic structure was transformed by orientation and annealing to a system of parallel fibrils oriented along the orientation direction.

In Fig. 7a of the sample 5/10, the fibrils form 10 ~ 100 μm long pointed elongated sections of probably emerging and sinking fibrils parts. It appears that the fibrils are not straight but slightly waved up and down in extension direction. The fibril diameter lies in the range 2 - 6 μm . Similar picture shows of the sample 8/10 Fig. 7b, where the emerging parts are longer (50 – 150 μm) and thicker (4 – 8 μm).

Fig 3c of the sample 11/10 has a different appearance. There are two features: the elongated fibrils in orientation direction such as in Fig. 3a and b and a system of perpendicular lines or cracks (10 – 20 μm apart) that are visible as a silvering effect. The silvering effect (opacity) was observed only in the sample 11/10 not annealed or annealed at T_a below 170°C. In the sample 11/10 annealed at 170°C the opacity decreased.

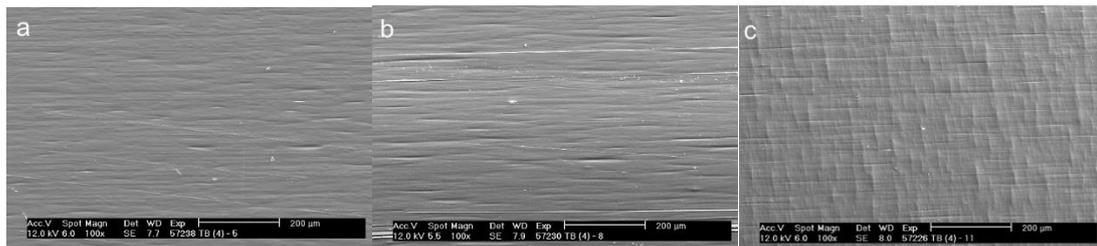


Figure 3. SEM micrographs of iPP parallel oriented fibrils : a – sample 5/10 annealed at $T_a = 140^\circ\text{C}$, b –sample 8/10 annealed at $T_a = 150^\circ\text{C}$, c – parallel fibrils and perpendicular cracks in sample 11/10 annealed at 120°C . Orientation direction horizontal.

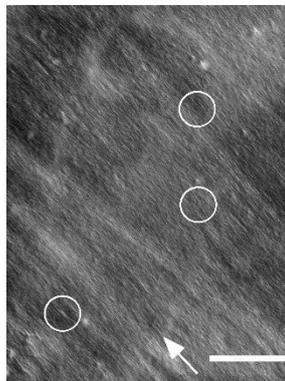


Figure 4. SEM micrographs of iPP parallel oriented fibrils : a – sample 5/10 annealed at $T_a = 140^\circ\text{C}$, b –sample 8/10 annealed at $T_a = 150^\circ\text{C}$, c – parallel fibrils and perpendicular cracks in sample 11/10 annealed at 120°C . Orientation direction horizontal.

The figure 4 of the sample 8/10 annealed at 120°C shows that the fibrils consist of thin parallel (120-160 \AA) lamellae oriented in the extension direction and perpendicular or slightly inclined to the sheet surface (marked by circle). Fig. 5a, b of the highest oriented not – annealed sample 11/10 disclosed details of iPP oriented structure.

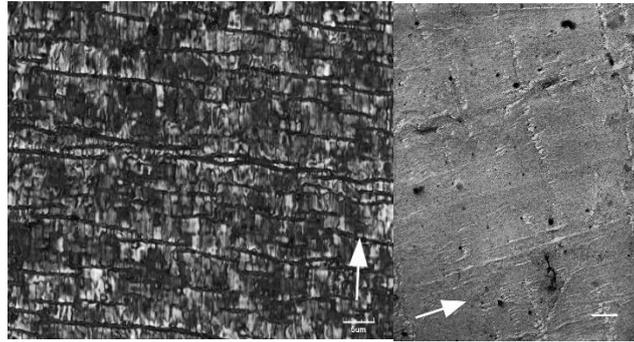


Figure 5. SEM micrographs of iPP parallel oriented fibrils : a – sample 5/10 annealed at $T_a = 140^\circ\text{C}$, b –sample 8/10 annealed at $T_a = 150^\circ\text{C}$, c – parallel fibrils and perpendicular cracks in sample 11/10 annealed at 120°C . Orientation direction horizontal.

Polymer chain breaking releases the local superheating and partial melting of broken chains ends parts (Fig. 10a). Annealing of highly oriented samples disclosed details of the cracked surface with lamellar parts extended to fibrils, melted fragment or voids and crazes (Fig. 10b). After annealing at $T_a = 140$ or 160°C the amount of such material increased. In those samples the individual fibrils and thin lamellae were clearly resolved. In some locations was evident that from their longitudinal fibrils or thin lamellae short branches grow in a perpendicular direction (marked R in Fig.10b).

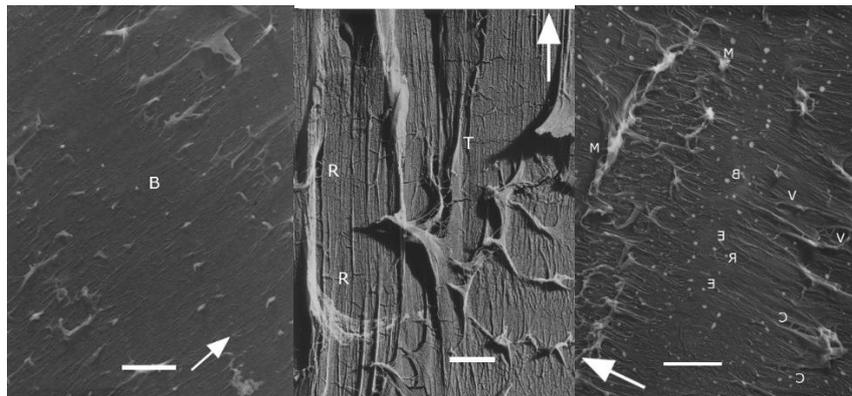


Figure 6. TEM micrographs of the 11/10 not annealed iPP sample.

Perpendicular bands (B) to extension direction formed by lamellar twisting and traces of chain breaking and local surface melting (M) are visible. 6b Details of the 11/10 surface after annealing at 140°C with twisted lamellae (T) and lamellae with short branches (R).

6c TEM micrograph shows details of the sample surface of a iPP sample 11 /10 after annealing at 160°C . In band parts with lamellae perpendicular to sample surface cracks and voids appeared (marked C and V). Perpendicular bands are marked (B), short branches (R), lamellar parts extended to fibrils (E), melted fragments (M).

2.6. Mechanical properties - *Tensile strength (TS)*

The tensile strength of the starting, not-annealed sample (35 MPa) increased with the elongation degree λ . In the direction perpendicular to the sample elongation the TS decreased an order of magnitude as shown for the sample with $\lambda = 5$ in Fig. 2. The substantial increase of the tensile strength in oriented samples was due mainly to the molecular orientation (Or) in the elongation direction. Sample annealing at Ta up to 140°C had only a negligible effect; the tensile strength decreased only slightly. Increasing the Ta to 170°C resulted in a sharp decrease of tensile strength and final sample failure. The main reason for the relative sharp TS decrease is the presence of growing number or depth of the perpendicular crazes formed initially in the extension process and further enlarged by annealing at Ta above 140°C.

3. Conclusion

The samples consisted of 63-83% crystalline, highly oriented, iPP α -modification. The structure and property changes, compared to the initial nonoriented spherulitic material, were due to 1. the elongation and 2. the annealing process.

In the elongation process the original lamellar spherulites transformed to a system of parallel fibrils (ca 2 – 6 μm diameter) oriented in the extension direction. During this conversion also elongated parallel cracks and voids and finally also perpendicular cracks formed in high oriented samples.

The crystallinity and crystal size values of oriented samples were slightly lower than in the nonoriented samples (TB) annealed at the same Ta. The void and cracks formed in highly oriented samples resulted in an anomalously low sample density. Annealing of the extended samples in taut position brought further structure changes mainly at Ta above 140°C. Annealing increased the sample crystallinity, crystal size, melting temperature and mechanical strength. Annealing tended to decrease the crack and void content (crack healing).

The elongation process obviously represents a relatively drastic breaking up of the original lamellar spherulitic structure to smaller crystalline blocks of different size and lower Tm. During this transformation a small number of voids and cracks formed. After extending further structural changes occurred and their extent depended on Ta.

The sample fixation during annealing obviously partially hindered the chain segments mobility at Ta values below 150°C. At higher Ta the segmental mobility increased and the conformational changes took place similar as in the non-oriented sample. The enhanced segmental mobility at Ta above 160°C was confirmed by the decrease of silvering, which was observed in highly oriented samples 11/10. The silvering was due to cracks oriented perpendicular to the extension direction

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Acknowledgment

This work was supported by an internal grant of UTB in Zlín IGA/FT/2018/004 financed from Funds of specific academic research.