Structure and Mechanical Properties of Nylon 6.12
Prepared by Temperature Slope Crystallization II.
Rolling Deformation and Microhardness of the
Oriented Negative Spherulite.

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ABSTRACT

The oriented negative spherulite of nylon 6.12 was crystallized by the temperature slope method. Rolling deformation of the negative texture was performed in the three different directions. The deformation mechanism of the negative spherulites was investigated by X-ray diffraction and microhardness measurements. Slip deformation between crystalline lamellae (interlamellar slip) is observed in the first stage of the deformation. The results are compared with the rolling deformation of other polymer textures such as the positive spherulites of nylon 6.12 and the β -phase isotactic polypropylene. In the rolling deformation of nylon 6.12, the hydrogen bonded (010) planes play an important role. For large deformations ($\lambda > 1.5$), the preferential slip between (010) planes appears, resulting in a lamellar inclination of 60° and a decrease of the lamellar thickness by $1/\sqrt{2}$. Microhardness measurements after rolling deformation of the oriented negative texture show good agreement with the structural analysis. The rapid decrease in the microhardness with increasing deformation can be explained by the lamellar thickness decrease which is brought about the preferential slip between the (010) planes.

Running Title : Rolling deformation and microhardness of nylon 6.12.

I. INTRODUCTION

In previous papers, the deformation mechanisms of lamellar crystals of β -phase isotactic polypropylene were reported [1,2,3]. In these studies, we used unidirectionally oriented lamellae prepared by the temperature slope crystallization (TSC) method. The TSC method was developed by Fujiwara et al. and has been applied to various polymers such as polyethylene, polypropylene, polyvinylidene fluoride and paraffin [4 - 10]. Lovinger reported the directional solidification of even-even nylons such as nylon 66, 6.10 and 6.12 [11,12].

Recently, we have prepared oriented nylon 6.12 lamellae by the TSC method [13,14]. The mechanical properties of nylon are specially of interest in relation to the behavior of the hydrogen bonded planes, which may show different deformation mechanisms from those of polyethylene or polypropylene.

Microhardness measurements of polymers have been shown to provide information about changes in morphology and microstructure of these materials during crystallization and deformation [15 - 19]. It is known that microhardness represents a bridging property between microstructure (crystal thickness, etc) and macroscopic properties (yield stress, elastic modulus, etc), furnishing in addition, an excellent method for investigating the deformation mechanism [20].

In the present paper, rolling deformation of negative spherulites is investigated by X-ray diffraction and microhardness measurements. The results are compared with the rolling deformation of other polymer textures such as the positive spherulites of nylon 6.12 and the β -phase isotactic polypropylene, discussed in previous papers [1,2,3,13].

II. EXPERIMENTAL

1) Sample Preparation

Poly(hexamethylene dodecane diamide), generally known as nylon 6.12 was used in this work. The sample was purchased from Scientific Polymer Products INC. with the sample number of #313, and a specific gravity of 1.06. The crystalline structure of nylon 6.12 is known to be triclinic with $a=4.97 \text{ \AA}$, $b=5.37 \text{ \AA}$, $c=25.1 \text{ \AA}$, $\alpha=51.1^\circ$, $\beta=77.1^\circ$, $\gamma=63.5^\circ$ [13].

Nylon 6.12 has three kinds of spherulites: positive spherulites, negative spherulites and

spherulitic aggregates. These textures have the same crystalline structure, whereas they may have different crystalline orientations. The thermal analysis of the original sample shows a melting temperature (T_m) of 218 °C when the sample was heated at 0.5 °C/min.

2) *Temperature Slope Crystallization (TSC)*

In this experiment, nylon 6.12 sample was crystallized by the specially designed apparatus using the TSC method which is described in the preceding paper [14]. A rod shaped nylon 6.12 sample with diameter 2.0 mm was mounted on the TSC apparatus, in between the heater and the cooler. The oriented negative texture was crystallized when the growth rate less than 0.1 mm/hour. The orientation and microhardness of the as grown negative texture before the deformation was reported in the preceding paper [14].

3) *Rolling method*

The rod shaped negative sample was cut into slices with a thickness of 0.5-0.6 mm. To define the rolling deformation, let us introduce a Cartesian coordinate system as shown in Fig.1, where the Z-axis is parallel to the growth direction G . The sample was rolled in the different three ways. For A- and B-rolling deformations, the sample was cut into strips parallel to the YZ-plane. In case of A-rolling, the rolling plane is parallel to the YZ-plane and the rolling direction is parallel to the Y-axis. On the other hand in B-rolling, the rolling plane is parallel to the YZ-plane and the rolling direction is parallel to the Z-axis. For the C-rolling deformation, the sample was cut in the XY-plane in such a way that the C-rolling plane is parallel to the XY-plane and the rolling direction is parallel to the X-axis.

Rolling deformation was carried out at room temperature. The sample was deformed by repeated rolling, leading to a gradual decrease of the sample thickness. The degree of deformation was defined by the draw-ratio

$$\lambda = t_0/t$$

where t_0 and t are the sample thickness before and after the rolling deformation, respectively. After deformation, WAXS and SAXS experiments were carried out at room temperature. The X-ray

patterns with the incident beam parallel to the X-, Y-, and Z-axes will be denoted as X-, Y-, and Z-pattern, respectively. In the nylon textures, the direction of the hydrogen bonded planes is important in the deformation mode. Furthermore, we define **N** as the direction normal to the (010) planes.

4) *Microhardness Measurement*

The microhardness (**H**) was measured at room temperature using a Leitz tester adapted with a square based pyramid indenter. A loading cycle of 0.1 min was used to minimize the creep, and different loads 0.15, 0.25, 0.5 and 1 N were employed. The microhardness value was obtained by dividing the peak contact load, **P**, by the projected area of impression:

$$H = KP/d^2,$$

where **d** is the impression diagonal, and **K** a geometrical factor equal to 1.854.

III. RESULTS

1. ROLLING DEFORMATION OF THE NEGATIVE TEXTURES

1) *A-rolling deformation*

For $\lambda=1.5$, the 010 reflections appear on the equator, showing the normal **N** parallel to the X-axis (see Fig.2a). Since the original orientation of the negative texture had the direction **N** parallel to the Z-axis, **N** is turned 90° from Z to X. On the other hand, the 100 reflection appearing as a ring in the X-pattern indicates a random distribution of the c-axis in the YZ-plane (Fig.2b). From the SAXS pattern (Fig.2c), one can deduce that the normal of the layer inclines 30° from the rolling plane. For deformations $\lambda=2.0$ and 4.0, the Z-WAXS patterns indicate a sharp orientation of **N** parallel to Z. For $\lambda=4.0$, the X-pattern shows that the c-axis becomes parallel to the Y- axis. The SAXS reflections remain present up to $\lambda=2.0$, but disappear for $\lambda=4.0$.

2) *B-rolling deformation*

For $\lambda=1.5$, both WAXS and SAXS patterns have nearly the same features as the original patterns before the deformation ($\lambda=1.0$). In the X-pattern for $\lambda=2.0$ (Fig.3a), the maximum intensity of 100 arc is located on the meridian, showing the c-axis perpendicular to the Z-axis. While in the Y-

pattern (Fig.3b), the 010 reflection appears on the equator, indicating that direction **N** is parallel to the X-axis. The Y-SAXS pattern (Fig.3c) indicates that the lamellae incline 30° from the YZ-plane.

After further deformation for $\lambda=4.0$, the c-axis becomes parallel to the Z-axis, as evidenced by the equatorial 100 reflection (see Fig.3d). At this stage, the 010 reflections (Fig.3e) show a broadening on the equator. The SAXS maximum disappears at $\lambda=4.0$ (Fig.3f).

3) C-rolling deformation

From the meridional 010 and equatorial 100 reflections (Fig.4a), one can deduce that the normal **N** and the c-axis are parallel and perpendicular to the Z-axis, respectively, for $\lambda=1.5$. If we consider the original structure of the oriented negative texture, it turns out that both, **N** and the c-axis remained unchanged during the deformation. However the SAXS pattern for the sample drawn at $\lambda=1.5$ indicates that the lamellar normal is rotated by 60° (Fig.4c). For higher deformations ($\lambda=2.0$ and 4.0), the 010 reflection shows a broadening (Fig.4b) and the SAXS reflections disappeared.

4) Rolling deformation mechanism of the negative texture

The rolling deformation has two effects on the polymer: pressing and drawing. The direction of pressing is perpendicular to the rolling plane. If we denote both directions as **P** (pressing) and **D** (drawing), the vectors are parallel to the coordinate depending on the three rolling deformations shown in Table 1. The results of the three rolling deformations are also summarized in Table 1, which indicates that **N** approaches to **P** in the deformation mode.

2. MICROHARDNESS STUDIES AFTER ROLLING DEFORMATION

Microhardness was measured after rolling deformation of the negative sample. The H values after deformation, measured after a drying treatment are shown in Table 2. The value of the B-rolling for $\lambda=1.5$ was missed due to the surface inclination of the sample with reference to the microindenter. The variation of H as a function of λ for the A- and B-rolling deformations is shown in Fig.8. The results for the C-rolling deformation are shown in Fig.9. The values of $\lambda=1.0$ are

those of the side- and end-surfaces of the as grown negative texture before deformation. In all cases, H decreases with increasing rolling deformation. In the A- and C-rolling deformation, H decreases for the initial rolling stage ($\lambda=1.5$). While in the B-rolling, the H value for $\lambda=2.0$ is nearly the same at $\lambda=1.0$. The lowest H value is obtained in the A-rolling deformation ($\lambda=4.0$).

IV. DISCUSSION

1) Mechanisms of Deformation

From the above observations, the three rolling deformations of the oriented negative texture can be described as follows:

(a) A-rolling Deformation: For $\lambda=1.5$, the original lamellar structure is rotated and inclined by 30° , where the normal $\mathbf{N}$ is rotated 90° from Z to X . The features of the A-rolling deformation are schematically depicted in Fig.5, where, both, the growth direction $\mathbf{G}$ and the normal $\mathbf{N}$ of the original lamellae are perpendicular to the pressing $\mathbf{P}$ and drawing $\mathbf{D}$ directions. During deformation, the hydrogen bonded planes become nearly parallel to the rolling plane ($\mathbf{N}/\mathbf{P}$), and the oriented lamellar texture becomes aligned to the draw direction ($\mathbf{G}/\mathbf{D}$). As a result, the original lamellae are strongly damaged by the A-rolling deformation.

(b) B-rolling Deformation: For $\lambda=1.5$, the original lamellar structure is stable. For a larger deformation ($\lambda=2.0$), the normal $\mathbf{N}$ is rotated 90° from Z to X , and for $\lambda=4.0$ the c -axis is oriented parallel to Z . In the B-rolling deformation, $\mathbf{D}$ is parallel to the growth direction $\mathbf{G}$. The lamellar texture along $\mathbf{G}$ is deformed for $\lambda=1.5$ by an interlamellar slip, and for $\lambda=2.0$ by intralamellar slip between (010) planes as shown in Fig.6.

(c) C-rolling Deformation: The original lamellae soon incline 60° by the (010) slip deformation. In the C-rolling deformation, $\mathbf{P}$ is parallel to $\mathbf{N}$, and $\mathbf{D}$ is perpendicular to $\mathbf{G}$. In this case, the deformation proceeds preferentially by (010) slip as indicated in Fig.7.

2) Comparison of the rolling deformation of the negative nylon texture with other polymer textures.

Using the TSC method, β -phase polypropylene textures and positive nylon 6.12 have been

investigated by rolling deformation [1,2,3,13]. In the rolling deformation of β -phase isotactic polypropylene, the deformation proceeds at first by interlamellar slip. As a result of the slip between the lamellar textures, the direction of the lamellar normal is rotated without changing their thickness and inclined 45° from the rolling plane. In the next stage, deformation is performed by intralamellar slip between the crystalline molecules. Owing to the slip between the molecules within the lamellae, the lamellar thickness decreases due to the inclination of c-axes in the lamellae. By these two mechanisms of inter- and intralamellar slips, the β -phase texture is aligned to the rolling direction. Further deformation makes destruction of the original β -phase crystal producing the c-axis oriented α -phase texture.

In the case of rolling of the positive nylon 6.12 texture, we can distinguish among three stages of rolling deformation : (1) the first stage is performed by the rotation of lamellae around the orientation axis, accompanied with the slip deformation between the hydrogen bonded sheets, (2) the second stage involves the slip between the neighbouring hydrogen bonded planes without hard destruction of the lamellae, (3) the third stage entails the destruction of the original lamellae mainly by the large slip or cleavage between the neighbouring hydrogen bonded planes. In all cases, the hydrogen bonded planes significantly affect the deformation behaviour. The broadening of the 010 reflections shows that the coherence of the (010) planes is reduced by the large slip deformation.

In the rolling deformation of the positive nylon 6.12, the hydrogen bonded (010) planes play an important role in the deformation mechanism. In the first stage of the deformation, a preferred orientation of the (010) planes emerges. The lamellae rotate so as to adjust the orientation of the (010) plane.

In the second and third stages of the deformation, crystals are deformed mainly by the slip or cleavage between the neighbouring (010) planes. The resultant crystals lose the crystalline coherence in the direction perpendicular to the (010) plane, which causes the observed broadening of 010 reflections.

By comparing the deformation of the above textures, the oriented negative textures also have the interlamellar slip in the first stage of A- and B-rolling. During the A-, B- and C-deformations, the

normal $\mathbf{N}$ becomes parallel to the pressing direction $\mathbf{P}$. Especially in the C-rolling deformation, the preferential slip between (010) planes occurs for $\lambda=1.5$, resulting in a lamellar inclination of 60° . This is due to the fact that the direction of $\mathbf{N}$ is perpendicular to the growth direction $\mathbf{G}$ in the original texture before the deformation.

3) Microhardness and structural changes of the negative texture

If we use the parallel model of hardness additivity which applies for semicrystalline polymers [12], we can write:

$$H = \omega_c H_c + (1 - \omega_c) H_a$$

where H_c and H_a are the intrinsic hardness values of the crystalline and the amorphous phases and ω_c is the volume fraction of crystalline material.

From the above equation, it is clear that ω_c controls the microhardness value of a polymer.

However, the structure of the semicrystalline polymer is characterized by stacks of crystalline lamellae. The direct influence of crystal thickness, l_c , upon microhardness in the case of chain-folded and chain-extended PE samples has been also evidenced [14]. The hardness of the crystals can be described by ;

$$H_c = H_c / (1 + b/l_c)$$

where H_c is the hardness of an infinitely thick crystal and b is a parameter related to the basal surface free energy, σ_e , of the crystal and to the energy, h , required for plastic deformation of the crystals through formation of a great number of shearing planes. The b parameter is equal to ;

$$b = 2\sigma_e / h.$$

Let us now discuss the H changes during rolling deformation of the negative nylon 6.12 texture in the light of the above conditions. After the C-rolling deformation, the value of l_c decreases due to the slip deformation between the (010) planes. If we consider the inclination of the lamellar normal

of 60° as shown in Fig.7 for $\lambda=1.5$, the lamellar thickness showed decrease to $l_c \cos 60^\circ = l_c/2$.

Accordingly, the rapid decrease in H at $\lambda=1.5$ can be mainly ascribed to the decrease of the thickness by $l_c/2$.

In the case of the B-rolling deformation, the deformation proceeds mainly by the interlamellar slip without any change in l_c . Consequently the H value remains nearly the same in the first stage until $\lambda=2.0$. In the A-rolling deformation, both N and G are perpendicular to P and D . Therefore, the lamellae are strongly damaged during the deformation. This surface damage will probably cause an increase in σ_e . The lowest value in H in the A-rolling for $\lambda=4.0$ is presumably due to a combination of both effects: a decrease in l_c and an increase in σ_e .

The microhardness results can be thus explained by the specific deformation mechanisms in the oriented negative nylon 6.12 texture. The consistency of the both sets of results confirms the above analysis.

IV. CONCLUSIONS

1. Deformation of the oriented negative textures has been investigated by the rolling in three different directions. In the first stage of deformation, slip between crystalline lamellae (interlamellar slip) is observed in A- and B-rolling. During A-, B- and C-rolling, the hydrogen bonded (010) planes are oriented parallel to the rolling plane. In the rolling deformation of the nylon 6.12 texture, the hydrogen bonded planes play an important role. Specially in the C-rolling deformation, the preferential slip between (010) planes appears, and give rise to a lamellar inclination of 60° and a decrease of the crystal thickness by $1/2$.
2. Microhardness measurements during rolling deformation of the oriented negative texture are in agreement with the microstructural changes. The rapid decrease in the microhardness in the C-rolling has been explained by the decrease in the lamellar thickness induced by the predominant slip between the (010) planes.

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Table 1

Pressing (**P**) and drawing (**D**) direction for the three rolling deformations.

Direction of the normal of the (010) plane (**N**) during the deformation

	P	D	N			
			$\lambda=1.0$	$\lambda=1.5$	$\lambda=2.0$	$\lambda=4.0$
A-rolling	X	Y	Z	X	X	X
B-rolling	X	Z	Z	Z	X	X
C-rolling	Z	X	Z	Z	Z	Z

Table 2

Variation of microhardness (H) in the three rolling deformations as a function of draw ratio.

Deformation	Draw Ratio (λ)	H (MPa)
Original (Side-face)	1.0	106
Original (End-face)	1.0	137
A-rolling	1.5	100
A-rolling	2.0	86
A-rolling	4.0	69
B-rolling	1.5	---
B-rolling	2.0	105
B-rolling	4.0	81
C-rolling	1.5	91
C-rolling	2.0	86
C-rolling	4.0	81

FIGURE CAPTIONS

Figure 1 Scheme of the three rolling deformations with reference to the trirectangular coordinate system of deformation. The growth direction $\mathbf{G}$ is here parallel to the Z-axis.

Figure 2 WAXS and SAXS patterns of the A-rolling deformation for $\lambda=1.5$.

(a) Z-pattern, (b) X-pattern, (c) Z-pattern (SAXS).

Figure 3 X-ray diffraction patterns of the B-rolling deformation. (a) X-pattern for $\lambda=1.5$,

(b) Y-pattern for $\lambda=1.5$, (c) Y-pattern for $\lambda=1.5$ (SAXS), (d) X-pattern for $\lambda=2.0$, (e) Y-pattern for $\lambda=2.0$, (f) Y-pattern for $\lambda=2.0$ (SAXS).

Figure 4 X-ray diffraction patterns for the C-rolling deformation. (a) Y-pattern for $\lambda=1.5$,

(b) Y-pattern for $\lambda=2.0$, (c) Y-pattern for $\lambda=1.5$ (SAXS).

Figure 5 Schematic representation of the structural change during A-rolling.

(a) Before the deformation: $\mathbf{P} / \mathbf{G}$, $\mathbf{D} / \mathbf{G}$, (b) For $\lambda=1.5$, $\mathbf{N}$ turns 90° inducing the fracture of the original lamellae and the (010) slip: $\mathbf{N} // \mathbf{P}$.

Figure 6 Schematic representation of the structural change during the B-rolling.

(a) Before the deformation: $\mathbf{P} / \mathbf{G}$, $\mathbf{D} // \mathbf{G}$, (b) Interlamellar slip for $\lambda=1.5$ and (010) slip for $\lambda=2.0$, then $\mathbf{N} // \mathbf{P}$.

Figure 7 Schematic representation of the structural change during the C-rolling.

(a) Before the deformation: $\mathbf{P} // \mathbf{G}$, $\mathbf{D} / \mathbf{G}$, (b) (010) slip for $\lambda=1.5$, $\mathbf{N} // \mathbf{P}$.

Figure 8 Change in the microhardness H induced by A- and B-rolling deformation.

Figure 9 Change in the microhardness H induced by C-rolling deformation.

Fig.1

Fig.2

Fig.5

Fig.6

Fig.7

Fig.8

Fig.9