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STRUCTURAL CHARACTERIZATION OF HIGHLY REDRAWN ISOTACTIC POLYPROPYLENE FILMS*

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Abstract

The preoriented isotactic polypropylene (iPP) film, which was prepared by drawing and annealing, was redrawn at the angles of α ($\alpha=0, 30, 45$ and 60°) to the preoriented direction (named the first draw direction FDD). By high redrawing, the preoriented iPP films were highly reoriented to the redrawing direction (named the second draw direction SDD). The films had the high crystal and amorphous orientation factors; such as $f_c=0.992$ and $f_{am}=0.714$. The dependence of T_m on DSC scan speed was examined and it was found that the degree of superheating increased with f_{am} . A history of the preorientation remained in the highly redrawn films and it appeared during thermal shrinkage at higher temperatures.

1. INTRODUCTION

In the previous papers^{1,2}, we studied the deformation behavior of the preoriented isotactic polypropylene (iPP) films by the redrawing performed at the angles of α ($\alpha=0, 30, 45, 60$, and 90°) to the preoriented direction (named the first draw direction, FDD). Further, we studied the structural changes of the highly reoriented films by thermal shrinkage³, and found that the crystal c -axis which had reoriented highly to the deformation direction (named the second draw direction, SDD) rotated to the FDD by thermal shrinkage at higher temperatures. That is, the history of the preorientation remains even in the highly redrawn films and it appears during thermal shrinkage. The crystal reorientation may be mainly caused by the relaxation of the strained amorphous chains and the partial melting of crystallites. On the other hand, it is expected that the development of the strained amorphous chains leads to the increment of crystal and amorphous orientations in highly redrawing. In addition, it is an interesting problem whether the crystals having higher orientations to the SDD rotate or not to the FDD by thermal shrinkage.

The high values of crystal orientation factor f_c and amorphous orientation factor f_{am} have been

reported in the literatures: 0.95^4 , 0.996^5 , 0.9968^6 , 0.9947^7 , and 0.9978^8 for f_c and 0.7163^9 , 0.72^4 , 0.75^6 , and 0.657^8 for f_{am} . However, there are few reports on the films or fibers which have high values of f_c and f_{am} concurrently. For example, Desper⁶ obtained the values; $f_c=0.9968$, $f_{am}=0.64$ and $f_c=0.9963$, $f_{am}=0.75$ for the thin highly drawn polypropylene films.

We obtained the films which had high values of crystal and amorphous orientation by highly redrawing of the preoriented iPP films. In the present paper, the structural characterization of the highly redrawn iPP films was investigated by means of x-ray diffraction methods and DSC measurements.

2. EXPERIMENTAL

2.1 Sample preparation

The used material was a iPP film (supplied Chisso Co. Ltd., $M_n=30 \times 10^4$). The sample was moulded into film about $400 \mu\text{m}$ in the thickness at 220°C for 10 min and subsequently quenched in ice-water. The film was drawn at 80°C with necking and annealed at $T_a=140^\circ\text{C}$ for 30 min. in an air bath, keeping the film ends free. Thus obtained film was used as an original sample (A film named in the previous paper¹) and the x-ray diffraction patterns of it are shown in Fig. 1. The long period estimated from small angle x-ray scattering (SAXS) was 244 Å. The original film was redrawn to the draw ratios as high as possible

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Fig. 1 Wide-angle x-ray diffraction (WAXD) and small-angle x-ray scattering (SAXS) patterns of the original film. The directions of incident x-ray beam are normal to the film surface (thru view) and parallel to it (edge view).

at 110°C in the direction of angles α ($\alpha=30, 45$ and 60°) to the FDD. The obtained draw ratios λ were 4.2, 5.0, and 6.0 for $\alpha=30, 45$, and 60° , respectively. The sample film drawn to $\lambda=2.5$ at $\alpha=0^\circ$ was also prepared.

As in the previous paper¹⁾, the films redrawn to λ at α were denoted by $A_{\alpha, \lambda}$.

2.2 X-ray diffraction patterns

Rota flex RU-3 instrument (Rigaku Denki Co.) was employed. The radiation used was Ni filtered $\text{CuK}\alpha$ of wavelength 1.542 Å. X-ray diffraction photographs were obtained using a point collimation Rigaku Denki small-angle camera and a flat wide-angle camera.

The diffraction intensity of the (hkl) crystal plane was recorded by a scintillation counter.

2.3 Crystallite sizes

Crystallite sizes were estimated from wide-angle x-ray diffraction (WAXD) patterns using Scherrer's equation

$$D_{\text{hkl}} = K \lambda / \beta \cos \theta_{\text{hkl}} \quad (1)$$

where D_{hkl} is the average dimension of the crystallites normal to the diffraction planes (hkl); λ is the wavelength (1.542 Å); β is the integral breadth of the reflection in radians; θ is the Bragg angle; and K is a shape factor depending on the method of determining β and is taken as 1.05 for integral breadth of diffraction. The observed diffraction breadths (B) were corrected for instrumental broadening by Warren's method

$$\beta^2 = B^2 - b^2 \quad (2)$$

where b is the integral breadth of a standard silicon powder.

2.4 Orientation

The end view of the WAXD patterns (incident x-ray beam is parallel to the SDD) of the highly redrawn films show nearly uniform rings and the refractive index of the direction of the film thickness is nearly equal to that of the direction of perpendicular (parallel to the film surface) to the SDD. Accordingly, it is considered that these films have an orientation of cylindrical symmetry to the SDD.

The crystal orientation factors f_c , f_b and f_a were estimated from the azimuthal intensity distributions of the (110) and (040) reflections using Wilchinsky's method. Here, f_c , f_b and f_a are represent the orientation factors of the crystal c -, b - and a' -axis, respectively.

Amorphous orientation factor f_{am} was estimated from the birefringence and x-ray crystal orientation data according to the relation

$$\Delta n = f_{\text{am}} (1 - \chi_v) \Delta n_a^\circ + f_c \chi_v \Delta n_c^\circ \quad (3)$$

where Δn is the birefringence obtained from an Abbe refractometer¹⁰⁾ and the value is corrected to the value at the density of 0.900 g/cm³ as Okajima et al. already reported¹¹⁾; χ_v is the degree of crystallinity in volume fraction estimated from the density. Densities were determined by refractive index using Okajima's equation¹²⁾; Δn_a° and Δn_c° are the intrinsic birefringence of the amorphous and crystalline regions, respectively and $\Delta n_a^\circ = 38.5 \times 10^{-3}$ and $\Delta n_c^\circ = 41.5 \times 10^{-3}$ ¹³⁾ are used here.

2.5 DSC measurements

Melting points T_m were determined using a Perkin-Elmer DSC-2. Standard correction was made for change in apparent melting points. As a

standard, indium ($T_m = 156.4^\circ\text{C}$) was used. The highest temperatures at the maxima of the endotherms were taken as the T_m of samples. Heating rates were varied in the range of $2.5^\circ\text{C}/\text{min}$ to $80^\circ\text{C}/\text{min}$.

2.6 Thermal shrinkage

Thermal shrinkage was carried out in an air bath at 160°C for 10 min and the degree of thermal shrinkage S was calculated according to

$$S = \frac{l_0 - l}{l_0} \times 100 \quad (4)$$

where l_0 and l are the length of the sample before and after thermal shrinkage, respectively.

3. RESULTS AND DISCUSSION

3.1 Morphology of the highly redrawn films

Typical WAXD and SAXS patterns of the highly redrawn films are shown in Fig. 2. The sharpness of the WAXD spots indicates a very high degree of crystal orientation. On the other hand, the SAXS patterns do not show any long period spacing but only give a central diffuse scattering (thru view) or a streak (edge view). That is, by highly redrawing, the original lamellar structure seems to be destroyed and the crystallites highly reorient around the SDD.

The orientation factors, the crystallite sizes, and the crystallinity of the original and the highly redrawn films are summarized in Table 1. The orientation factor of the crystal c -axis f_c is very high for the redrawn films. The amorphous orientation factor f_{am} is also high, especially for $A_{45,5.0}$ and $A_{60,6.0}$. For $A_{60,6.0}$, the values of f_c and f_{am} are 0.991 and 0.714, respectively. $f_c = 0.991$ means approximately perfect orientation of the crystal c -axis to the SDD. The value $f_{am} = 0.714$ is comparable to the very high value $f_{am} = 0.75$ reported by Desper⁶⁾ for thin, highly drawn polypropylene

film that prepared by a continuous process involving drawing between rollers in a radiant heat oven near the melting point. (The value of $f_{am} = 0.75$ was obtained using a $\Delta n_a^o = 60 \times 10^{-3}$ and $\Delta n_c^o = 29.1 \times 10^{-3}$ ¹⁴⁾ These are different from the values used in our study. But, by changing Δn_a^o and Δn_c^o , the value of f_{am} almost remains unchanged.)

The crystallite sizes D_{110} , D_{040} and D_{130} for the redrawn films are smaller than those of the original film in the each directions. But the α dependency of the crystallite size reduction is not clear. The degree of crystallinity χ_v , also, decreases by redrawing. The crystallites seems to be destroyed by redrawing and this may lead to the reduction of crystallinity.

Fig. 2 WAXD and SAXS patterns of $A_{60,6.0}$ film. SDD: second draw direction, FDD: first draw direction, α : redrawing angle.

Table 1 Characteristics of the sample films.

	Orientation Factor				Crystallite Size ($\text{\AA}$)			Crystallinity χ_v (%)
	f_c	f_b	$f_{a'}$	f_{am}	D_{110}	D_{040}	D_{130}	
Original	0.968	-0.482	-0.486	0.337	94	91	87	50.8
$A_{0,2.5}$	0.992	-0.496	-0.496	0.428	86	84	78	46.7
$A_{30,4.2}$	0.993	-0.497	-0.496	0.574	87	84	80	46.1
$A_{45,5.0}$	0.992	-0.496	-0.496	0.714	80	80	78	46.8
$A_{60,6.0}$	0.991	-0.497	-0.494	0.714	84	79	80	45.4

3.2 Differential scanning calorimetry

Fig. 3 shows the DSC thermograms of the original and the redrawn films. The melting endotherm of the original film has a double melting peaks in a narrow temperature range. As the original film is annealed at 140°C, it seems that the lower temperature melting peak corresponds to the melting of crystals developed during annealing.

For $\alpha = 0^\circ$ ($A_{0,2.5}$), the melting curve is similar to that of the original film but the low temperature peak sharpens and shifts to a higher temperature. For $\alpha = 30^\circ$ ($A_{30,4.2}$), 45° ($A_{45,5.0}$) and 60° ($A_{60,6.0}$), they do not show the double melting peaks which appear on that of the original or $A_{0,2.5}$ films, but show irregular profiles. By redrawing, the melting temperature, generally, shifts to higher temperatures and the width of the endotherm broadens.

As in Table 1, the crystallite sizes of the redrawn films are smaller than those of the original film, however, the melting temperature becomes higher by redrawing. In general, the melting temperature increases with an increase in crystal size and/or crystal perfection. If both of them do not increase so much with the highly redrawing, the shifts of T_m to higher temperatures is due to a superheating effect by the entropy loss imposed by chain constraints given by redrawing in the amorphous

Fig. 3 DSC thermograms of the original and redrawn films. $\alpha = 0^\circ$ $A_{0,2.5}$; $\alpha = 30^\circ$ $A_{30,4.2}$; $\alpha = 45^\circ$ $A_{45,5.0}$; $\alpha = 60^\circ$ $A_{60,6.0}$

phase. Taking into account the reduction of crystallinity and width of crystallites, the speculation may be reasonable. Then, to investigate the superheating effect, the melting temperature was measured at different heating rates for the original, the redrawn and a melt-quenched films.

Fig. 4 shows the dependence of the melting temperature, T_m on DSC scan speeds. T_m of the highly redrawn films is higher than that of the original and a melt-quenched films at any heating rate. For all sample films, T_m decreases with the heating rate and has a minimum at the heating rate of 10 to 40°C/min. But for the melt-quenched film, T_m remains unchanged at above the heating rate of 20°C/min. The heating rate at the minimum of T_m shifts to 10°C/min for $\alpha = 45$ and 60° from 40°C/min for the original film. That is, the minimum shifts to lower heating rates with increasing

Fig. 4 Plot of the melting temperature of the original, redrawn and melt quenched films as a function of the heating rate. (●) original; (∇) $A_{0,2.5}$; ($\square$) $A_{30,4.2}$; ($\triangle$) $A_{45,5.0}$; ($\circ$) $A_{60,6.0}$; ($\times$) melt quenched film

Fig. 5 Plot of the difference between T_m at the heating rate of 80°C/min and that of 2.5°C/min as a function of the amorphous orientation factor f_{am} .

the amorphous orientation factor f_{am} . On the other hand, the degree of superheating depends on the redrawing angle α of sample films. This result, also corresponds to the values of the amorphous orientation factor f_{am} . That is, the superheating effect increases with f_{am} . In Fig. 5, the difference between T_m at the heating rate of 80°C/min and that of 2.5°C/min is plotted against the f_{am} . As expected, the difference increases with f_{am} . The difference of T_m at $f_{am} = 1.0$, which is estimated by the extrapolation of the straight line, is 7.6°C and then T_m becomes 172.7°C at the heating rate of 80°C/min. For the melt-quenched film, the crystallite sizes and the crystal perfection may be appreciably different from those of the other sample films. Consequently, it seems that the data for the melt-quenched film is not on the straight line. Thus, the observed superheating effect can be understood in terms of the increasing constraints on the amorphous regions by the redrawing.

Wunderlich¹⁵⁾ has shown that superheating depends on the width of crystals as well as on the crystal thickness and molecular weight. On the other hand, Zachmann has shown that conditions for superheating can occur either when all the chain ends are concentrated on the crystal surface (extended chain crystals) or when a stack of conventional crystals is connected by strained amorphous material^{16,17)}. And Hellmuth and Wunderlich has shown that the melting temperature of extended-chain crystals increases, whereas metastable folded-chain crystals display a lowering of the melting temperature as the heating rate is increased¹⁸⁾. Then, if a number of extended-chain crystals are produced by highly redrawing, T_m may increase with heating rate. But, as seen in Fig. 4, as the decrease of T_m is seen for all sample films, the existence of a number of extended-chain crystals is not supported experimentally even for the highly redrawn films. Hence, it is presumed that the minimum of T_m , as seen in Fig. 4, appears by the coupling of the two effects: the one is the increase of T_m by strained amorphous chains and the other is the decrease of T_m caused by folded-chain crystals accompanied by the increase of the heating rate. As f_{am} becomes higher values, the former effect appears preferentially and the heating rate at the minimum of T_m shifts to slower

heating rates. On the contrary, the latter effect appears preferentially in such a case of the original film or the melt-quenched film and superheating is scarcely shown.

3.3 Structural change by thermal shrinkage

Fig. 6 shows the typical WAXD and SAXS patterns of one of the films. The WAXD pattern of the highly redrawn films rotates back towards the first draw direction, FDD, even in the case of the film having a high degree of crystal and amorphous orientation, by thermal shrinkage of the sample film at $T_s = 160^\circ\text{C}$ in a similar manner as described in the previous paper³⁾. The SAXS pattern shows a diffuse two-point reflection on the diagonal and this means that the lamellar structure stacked to the direction between the FDD and the SDD appears. By thermal shrinkage, the crystal c -axis tilts about 25° to the SDD for the samples of $A_{30,4.2}$, $A_{45,5.0}$ and $A_{60,6.0}$ and then the lamellar normal, also, tilts about 25° to the SDD. This fact shows that the crystal c -axis is parallel to the lamellar normal. That is, by thermal shrinkage, the strain energy stored by highly redrawing is relaxed and the rotation of crystals accompanying the chain slips along the chain axis may occur.

Fig. 6 WAXD and SAXS patterns of $A_{60,6.0}$ film shrunk at 160°C for 10 min.

Thermal shrinkage is about 75% for the redrawn films and this value is comparable to the values obtained for the samples redrawn to $\lambda = 4.0$ in the previous paper³⁾.

4. CONCLUSION

The preoriented isotactic polypropylene (iPP) film was redrawn at the angles of α ($\alpha = 0, 30, 45$ and 60°) to the preoriented direction. By high

redrawing, the preoriented iPP films were highly reoriented to the redrawing direction, SDD and the redrawn films had the high crystal and amorphous orientation factors; such as $f_c = 0.992$ and $f_{am} = 0.714$.

The dependence of T_m on DSC scan speed was examined and it was found that the degree of superheating increased with f_{am} . The plot of the difference between T_m at the heating rate of $80^\circ\text{C}/\text{min}$ and that of $2.5^\circ\text{C}/\text{min}$ against f_{am} was linear.

A history of the preorientation remained in the highly redrawn films and it appeared during thermal shrinkage at higher temperatures: the crystal c-axis approached to the lamellar normal.

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高度に再延伸されたアイソタクチック ポリプロピレンフィルムの構造特性

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延伸-熱収縮によって作られた初期配向をもったアイソタクチックポリプロピレン(iPP)フィルムが初期配向軸(first draw direction FDD)に対し α ($\alpha = 0, 30, 45, 60^\circ$)の角度で再延伸された。高度に再延伸されたiPPフィルムは高度に再延伸軸(second draw direction SDD)に再配向する。高度に再延伸することにより, 結晶配向および非晶配向がそれぞれ $f_c = 0.992$,

$f_{am} = 0.714$ のような高い値をもつフィルムが得られた。 T_m の昇温速度依存性が検討され, superheatingは f_{am} に依存することがわかった。昇温速度 $80^\circ\text{C}/\text{min}$ と $2.5^\circ\text{C}/\text{min}$ における T_m の差はオリジナルフィルムと再延伸フィルムでは直線になる。

初期配向の履歴は高度に再延伸されたフィルムにも残っており, 高温での熱収縮によりそれは現れる。