Study on Rough-Surface Biaxially Oriented Polypropylene Film. I. Formation of β-Form Crystals in Sheet Cast with T-Die Extruder

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Synopsis

Sheets were cast by extruding polypropylenes (PP) which contained γ-quinacridone, a β-crystal nucleator, at levels of 0–10 ppm using a 30 mm φ extruder with a T-die at extrusion temperatures of 200–260°C and chill roll temperatures of 30–90°C. The influences of raw resin characteristics such as γ-quinacridone content and MFI of the base PP and casting conditions such as extrusion temperature and chill roll temperature on the amount of β-crystals formed in the sheet were studied. The amount of the β-crystals formed was larger as the γ-quinacridone content was higher and the extrusion temperature was lower and almost independent of the chill roll temperature. As for the influence of MFI of the base PP, the amount of the β-crystals formed was maximum at MFI ≒ 8 dg/min.

INTRODUCTION

Because of their excellent properties in mechanical strength, transparency, chemical resistance, moisture-barrier property, and electric property, biaxially oriented polypropylene films (BOP) are widely used in the fields of wrapping uses such as foods, cigarettes, textiles, drugs, and electronic parts and electric uses such as cable wrapping, transformer, and capacitor. When BOP is used as a capacitor dielectric, its surface is usually roughened in order to improve the impregnation properties of insulating oils. As a roughening method of BOP, the mechanically embossing methods,[1-3] the methods of stretching sheets which contain different polymers,[4-9] and the method of stretching sheets in which β-crystals are formed[10-25] are known.

As production methods of BOP, there are the tubular and the tenter methods, and the tenter method is divided into the simultaneously stretching method and the successively stretching method.[26] A series of papers reported from now on are concerned with the production of the rough-surface BOP by utilizing β-crystals in a successively stretching tenter method. The production of BOP by the successively stretching tenter method is usually made as follows[26]: A sheet is cast with a T-die extruder, stretched in the machine direction with a roll-type stretching machine, and stretched and thermally set in the transverse direction with a tenter, and a BOP is obtained. The present paper reports, in the first place, the study on the formation of β-crystals in

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the sheet cast with a T-die extruder. In the following papers we will report on the influence of stretching conditions (Part II[27]), the influence of MFI of base resin (Part III[28]), and the influence of addition of crystal nucleator (Part IV[29]) on the roughening of BOP, and an analysis and control of roughness state (Part V[30]), roughening by laminated sheet (Part VI[31]), and roughening by blending low melting point polymers (Part VII[32]).

Many basic studies have been done on the formation of β-crystals.[33-50] Padden et al.[33] first found that the β-crystals were formed by quenching a polypropylene (PP) melt below 128°C. Awaya[34] reported that the β-crystals were formed by compression-molding a highly isotactic PP just after a short time melting at a temperature range of 160–180°C, which is near the melting point. Turner-Jones et al.[35] showed that the β-crystals were formed by melting a PP which is supposed to contain a β-crystal nucleator at a temperature range of 190–230°C and subsequently by quenching it into a temperature in the range of 100–120°C. Almost no β-crystal was formed when the melting temperatures were above 250°C or the quenching temperatures were below 90°C or above 130°C. Ullmann and Wendorff[39] melted a PP with a β-nucleator at a temperature range of 190–260°C and isothermally crystallized it at a temperature range of 0–140°C. They found that the amount of the β-crystals formed was independent of the melting temperature and, as for the crystallization temperature, the amount of the β-crystals was maximum at 40–60°C and no β-crystal was formed at 140°C. Moos and Tilger[41] melted PPs with various contents of β-nucleator at a temperature range of 200–300°C and isothermally crystallized them at a temperature range of 0–145°C. They found that the amount of the β-crystals was larger as the nucleator content was higher and the melting temperature was lower. In the case of PP with high nucleator content, the β-crystals were formed even at a melting temperature of 300°C. As for the crystallization temperature, the β-crystals were formed at 0–140°C, and the amount of the β-crystals was maximum at 20–123°C, where the amount of the β-crystals was independent of the crystallization temperature. Zhou et al.[48] melted a PP with a β-nucleator at 200°C and isothermally crystallized it at a temperature range of 60–145°C, and found that large amounts of β-crystals were formed at 60–140°C but no β-crystal was formed above 140°C.

From a practical viewpoint, it is reported that the β-crystals are contained in processed PP articles which have been crystallized under shear in processings such as injection molding[51-55] and extrusion molding.[54,56,57] Dragaun et al.[54,56] reported that, in the pipe extrusion molding of a PP of MFI = 0.5 dg/min with no β-nucleator, the amount of the β-crystals was larger as the mass temperature was lower and the bath temperature was higher. Since the PP they used did not contain β-nucleator, the amount of the β-crystals was small: less than 10% even in the maximum case. Nakatani et al.[57] found that there exist spherulites, pillarlike crystals, and veil-like crystals as morphologies of β-crystals, and proposed a map which shows how their formation changes with the melting temperature and the shearing temperature.

The present paper reports the study on the influences of raw resin characteristics such as the γ-quinacridone content and MFI of PP and casting conditions such as extrusion temperature and chill roll temperature on the amount of the β-crystals formed in the sheet cast with a T-die extruder. As far

TABLE I
Recipes of Raw Materials

Sample name	Base PP: Grade	MFI (dg/min)	M_w[a] ($\times 10^5$)	$\frac{M_w}{M_n}$[b]	$\eta_{\dot{\gamma}=10^2\,s^{-1}}$[b] ($10^3$ p)	γ-Quinacridone (ppm)	BHT[c] (wt %)	Irganox 1010[d] (wt %)	CaSt[e] (wt %)
FB-0	FB110	1.8	4.3	9.4	9.3	0	0.2	0.1	0.015
FB-1	FB110	1.8	4.3	9.4	9.3	1	0.2	0.1	0.015
FB-3	FB110	1.8	4.3	9.4	9.3	3	0.2	0.1	0.015
FB-10	FB110	1.8	4.3	9.4	9.3	10	0.2	0.1	0.015
RB-1	RB110	0.90	6.3	7.9	13.7	1	0.2	0.1	0.015
RB-3	RB110	0.90	6.3	7.9	13.7	3	0.2	0.1	0.015
YE-1	YE130	5.9	3.2	9.1	7.1	1	0.2	0.1	0.015
YE-3	YE130	5.9	3.2	9.1	7.1	3	0.2	0.1	0.015
FC-1	FC140	8.5	2.7	9.5	4.9	1	0.2	0.1	0.015
FC-3	FC140	8.5	2.7	9.5	4.9	3	0.2	0.1	0.015
FA-1	FA150	9.8	2.4	8.9	4.2	1	0.2	0.1	0.015
FA-3	FA150	9.8	2.4	8.9	4.2	3	0.2	0.1	0.015

[a] Measured by GPC for a sample of the same grade but different lot.
[b] Measured by a capillary rheometer with a die of $L/R = 20$ for a sample of the same grade but different lot.
[c] 2,6-Di-*tert*-butyl-4-methyl phenol.
[d] Tetrakis-[methylene-3-(3′,5′-di-*tert*-butyl-4′-hydroxy-phenyl)propionate] methane.
[e] Calcium stearate.

as the authors know, there is no systematic study on the formation of the β-crystals in the sheet cast with a T-die extruder.

EXPERIMENTAL

Raw Resin

PP resins used were Tokuyama Polypro Grades RB110, YE130, FC140, and FA150 powders which were homoisotactic PPs (produced by Tokuyama Soda Co., Ltd.). γ-Quinacridone was used as a β-nucleator. BHT, Irganox 1010, and CaSt were used as thermooxidative stabilizers. Recipes of the raw materials are shown in Table I. These raw materials were mixed with a Supermixer, and extruded with a 40 mm ϕ extruder at an extrusion temperature of 250°C into a strand which was cut into pellets of about 3 mm size with an automatic cutter.

Casting of Sheet

Sheets 600 μm thick were cast with a 30 mm ϕ extruder equipped with a 130-mm-wide T-die from FB-samples at extrusion temperatures of 200, 230, and 260°C and chill roll temperatures of 30, 60, and 90°C, and from other samples at an extrusion temperature of 200°C and a chill roll temperature of 60°C.

Measurement of β-Crystal Content

X-ray diffractions were measured on the cast sheets with a Rigaku Denki RU-200 diffractometer with Ni-filtered Cu-K_α radiation using a rotating

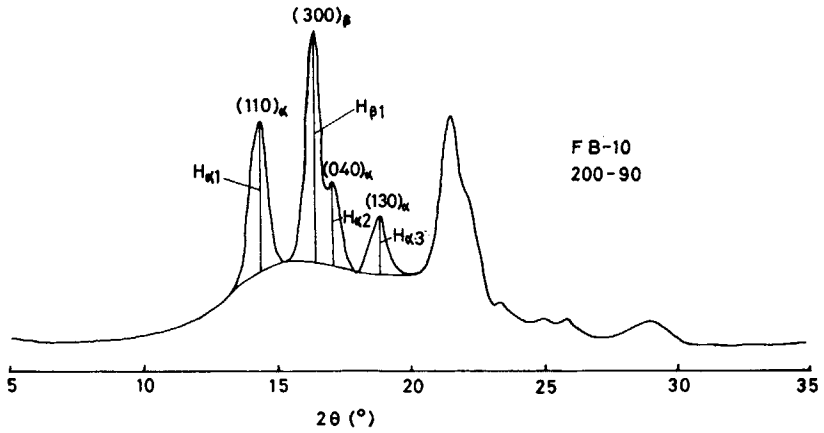


Fig. 1. X-ray diffraction diagram of FB-10 sheet cast at an extrusion temperature of 200°C and chill roll temperature of 90°C, and evaluation of β-form crystal content (K value).

specimen table, and β-crystal contents (K values) were calculated from the diffraction curves according to Turner-Jones et al.[35] as shown in Figure 1 as follows:

$$K = \frac{H_{\beta 1}}{H_{\beta 1} + H_{\alpha 1} + H_{\alpha 2} + H_{\alpha 3}}$$

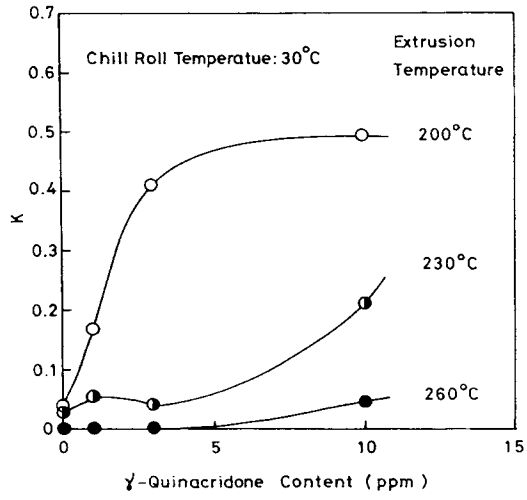
where $H_{\beta 1}$, $H_{\alpha 1}$, $H_{\alpha 2}$, and $H_{\alpha 3}$ are the reflection intensities of the (300) plane of β-crystals, (110), (040), and (130) planes of α-crystals, respectively.

RESULTS AND DISCUSSION

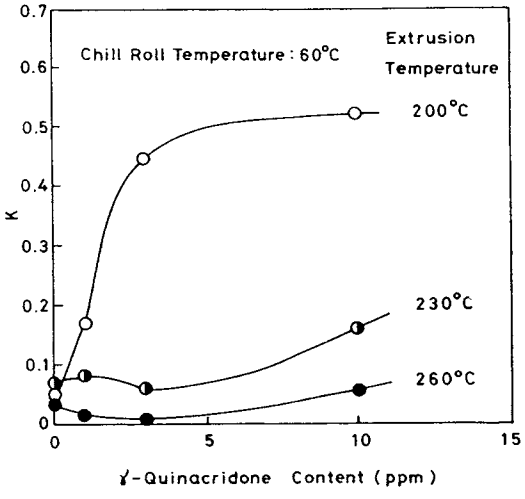
Influences of β-Nucleator Content and Casting Conditions on Formation of β-Crystals

Figure 2 shows the variation of the K value of the sheet cast from the FB sample at each chill roll temperature as a function of the γ-quinacridone content using the extrusion temperature as a parameter. Although the results in the case of the extrusion temperature of 200°C show similar tendencies to the results of Moos and Tilger,[41] where the K value increased with increasing β-nucleator content, in the cases of the extrusion temperatures of 230 and 260°C, the K values in themselves are low and almost independent of or even decreases with the nucleator content; the behaviors differ from the results of Moos and Tilger.[41]

As for the influence of the extrusion temperature, the K value decreases with the increasing extrusion temperature, and almost no β-crystal is formed above 260°C independent of the nucleator content and the chill roll temperature. These results agree with the results of Turner-Jones et al.,[35] Moos and Tilger[41] and Dragaun et al.[54,56] and differ from the results of Ullmann and Wendorff,[39] where the K value was independent of the melting temperature in a range of 190–260°C. In a low melting temperature range, the nuclei or associations of molecular chains persist in the melt, and the formation of



(a)



(b)

Fig. 2. Variations of K value with γ-quinacridone content; FB-samples. (Continuing to the next page.)

the β-crystals results from these associations.[35] It seems likely that since the associations of the molecular chains which play an assistant role in the formation or growth of nuclei by the nucleator decrease with increasing melting temperature, the formation of the β-crystals is suppressed as the melting temperature increases.

Although the influence of the chill roll temperature is generally small, the K value tends to increase with increasing the chill roll temperature for samples with low β-nucleator content, and the K value tends to decrease with increasing the chill roll temperature for samples with high β-nucleator content. These results differ from the results of Turner-Jones et al.,[35] where no β-crystal was formed below a crystallization temperature of 90°C, and agree

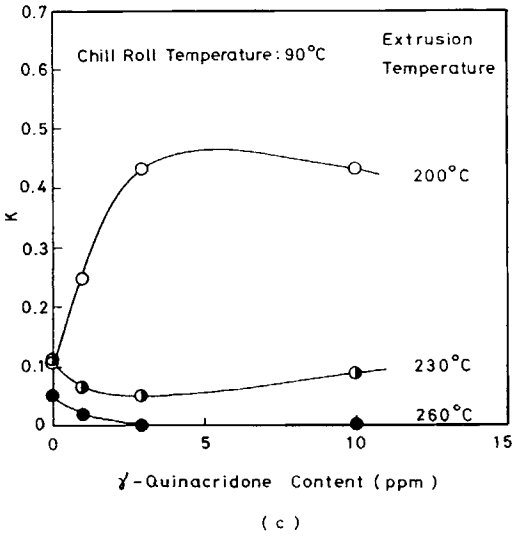


Fig. 2. *(Continued from the previous page.)*

with the results of Ullmann and Wendorff,[39] Moos and Tilger,[41] and Zhou et al.,[48] where the β-crystal content was independent of the crystallization temperature in a range of 30–90°C. Dragaun et al.[54,56] reported that in the pipe extrusion of a PP with no nucleator the amount of the β-crystals formed was larger as the bath temperature was higher. In the present experiment a similar tendency to the results of Dragaun et al. was obtained for a PP with no β-nucleator (FB-0).

Influence of MFI of Base PP on Formation of β-Crystals

There is no study on the influence of molecular weight (MFI) of the base PP on the formation of the β-crystals.

Figure 3 shows the dependence of the K value on the MFI of the base PP using the β-nucleator content as a parameter. The K value shows a maximum at MFI ≒ 8 dg/min. The K value of the PP with no β-nucleator also shows a maximum at MFI ≒ 8 dg/min as will be shown in a following paper.[28] The weight-average molecular weight, M_w, and the ratio of M_w to the number-average molecular weight, M_n, M_w/M_n, which is a measure of molecular weight distribution, are shown in Table I. The molecular weight distributions of all the samples are nearly the same. Since the extrusion temperature was the temperature set on the extruder barrel, there was a possibility that the resin temperature might decrease with increasing MFI because the melt viscosity of the resin would decrease with increasing MFI. We measured the flow curves of all the samples using a capillary rheometer with a die of length to radius of 20 at 200°C over a shear rate range of 10^1–10^4 s^{-1}. The difference between the flow curve of the FC sample and that of the FA sample was very small in comparison to those of the other samples over the shear rate range studied. The apparent shear viscosity at a shear rate of 10^2 s^{-1}, which may be regarded as the shear rate order which a polymer melt encounters in a screw extruder, is shown as a representative value of the flow curve in Table I. The

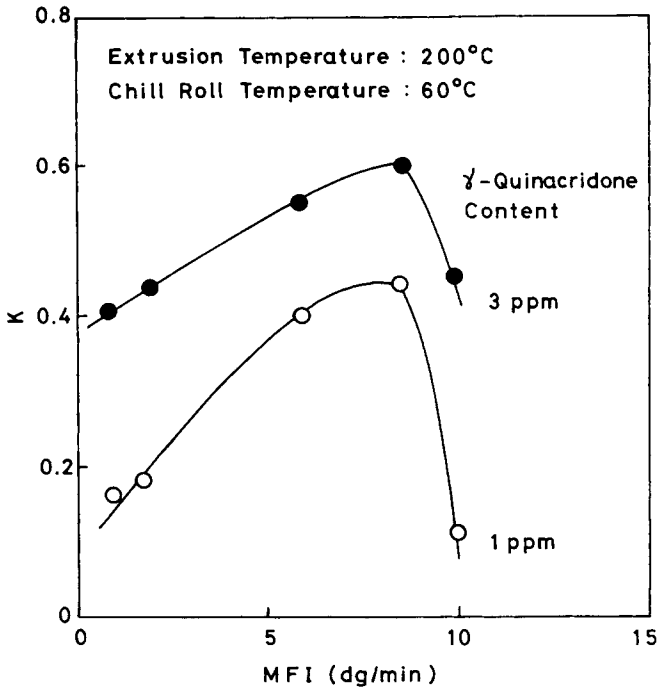


Fig. 3. Dependences of K value on MFI of base PP.

difference between the viscosity of the FC sample and that of the FA sample is very small in comparison to those of the other samples as in the case of MFI. If the melt viscosity affects the K value through the viscous heating, the K value must increase monotonously with increasing MFI because the resin temperature might increase in proportion to the melt viscosity or decrease in proportion to MFI. However, the experimental result shows a maximum of K value at MFI $\doteqdot$ 8 dg/min. The reason for this is incomprehensible now and more studies are needed. The K value is larger as the β-nucleator content is higher at all the MFI range studied.

CONCLUSIONS

The β-crystal content in the sheet cast with a T-die extruder is higher as the γ-quinacridone content is higher and the extrusion temperature is lower, and almost independent of the chill roll temperature. No β-crystal is formed at extrusion temperatures above 260°C. As for the influence of MFI of the base PP, the amount of the β-crystals is maximum at MFI $\doteqdot$ 8 dg/min.

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