Study on Rough-Surface Biaxially Oriented Polypropylene Film. IV. Influence of Addition of Crystal Nucleator

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Synopsis

In the roughening of biaxially oriented polypropylene film (BOP) by utilizing β-form crystals in a successively stretching tenter method, the influence of an α-crystal or β-crystal nucleator added to base polypropylene (PP) during roughening of BOP has been studied. Rough-surface BOPs were made from homoisotactic PPs which had a melt flow index (MFI) of 8.5 dg/min and contained the α or β nucleator at levels of 0–10 ppm. The β crystals formed in cast sheets and the roughness of the BOPs was analyzed. Degree of roughness and the diameter of craters on BOP decreased with increasing α- or β-nucleator content. This stems from the fact that the diameter of the β spherulites formed in the cast sheet decreases with increasing nucleator content. In the cases of nucleator content below 1 ppm, the diameter of the β spherulites in the cast sheet did not change significantly, and the decrease in diameter of the BOP craters was small. On the other hand, the degree of roughness of the BOP dropped significantly when nucleator content was above 10 ppm. Accordingly, a nucleator content of about 1 ppm is suitable for the roughening of BOP for both the α and β nucleators.

INTRODUCTION

Investigations of the roughening of biaxially oriented polypropylene film (BOP) using β-form crystals in a successively stretching tenter method clearly indicate that the roughening occurs in the machine direction (MD) -stretching process.[1] In studies on the influence of melt flow index (MFI) of base polypropylene (PP), highly roughened BOPs with a crater-like roughness have been obtained.[2] However, since these BOPs have craters with very large diameters, they present practical problems, such as retaining voids during the impregnation process of insulating oils and low dielectric breakdown strength due to their nonuniform roughness.

To overcome these problems, it is necessary to control the diameter of β spherulites formed in cast sheet and then to form uniform craters with an appropriate diameter on the BOP. In the present report, in order to control the diameter of the β-spherulites, α-crystal or β-crystal nucleator was added to the base PP and the relation between the roughness and the nucleator content has been studied.

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EXPERIMENTAL

Raw Resin

Tokuyama Polypro Grade FC140 powder (MFI = 8.5 dg/min) which was a homoisotactic PP produced by Tokuyama Soda Co., Ltd. was mixed with γ quinacridone as a β nucleator or PTBBAAl (*p-t*-butyl benzoic acid monohydroxy aluminium) as an α nucleator at levels of 0–10 ppm, and 0.2 wt% BHT, 0.1 wt% Irganox 1010, and 0.015 wt% calcium stearate as thermo-oxidative stabilizers in a Supermixer, and extruded with a 65 mmϕ extruder at an extrusion temperature of 250°C into a strand which was cut into pellets of about 3 mm with an automatic cutter. Sample name is represented as, for example, FC-β-1 which contains 1 ppm β nucleator, FC-α-10 which contains 10 ppm α nucleator, and so on.

Casting of Sheet

Sheets 800 μm thick were cast with a 65 mmϕ extruder equipped with a 500 mm wide T die from the pellets at extrusion temperatures of 220°C, 250°C, and 280°C, and a chill-roll temperature of 90°C.

X-ray diffractions were measured on the cast sheets with a Rigaku Denki RU-200 diffractometer with Ni-filtered Cu-Kα radiation using a rotating specimen table, and β-crystal contents (K values) were calculated from the diffraction curves according to Turner-Jones et al.[3,4]

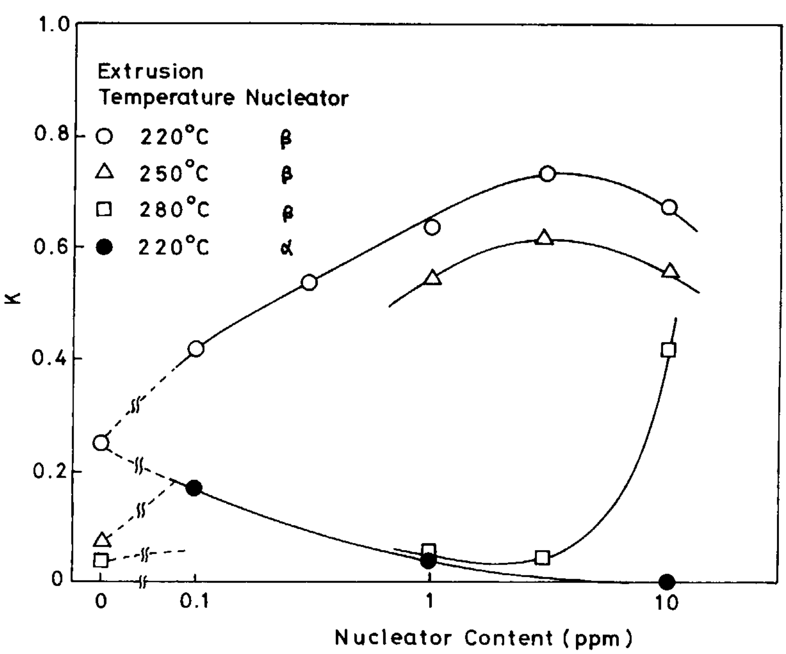

Fig. 1. Dependence of K values of cast sheets at various extrusion temperatures on nucleator content of raw PP resin. β nucleator: (○) 220°C; (△) 250°C; (□) 280°C; α nucleator (●) 220°C.

The spherulitic morphologies were observed, with a polarizing microscope (Olympus PM-6), on thin pieces about 10 μm thick sliced from the sheets cast at an extrusion temperature of 220°C normal to the MD with a micrometer.

MD Stretching

The cast sheets were stretched five times in the machine direction (MD) with a roll-type stretching machine shown in Figure 1 of the Part II of this series[1] under the following conditions: preheating oven temperature: 140°C; setting temperature of heating roll: 160°C, 170°C, and 180°C; roll rotation

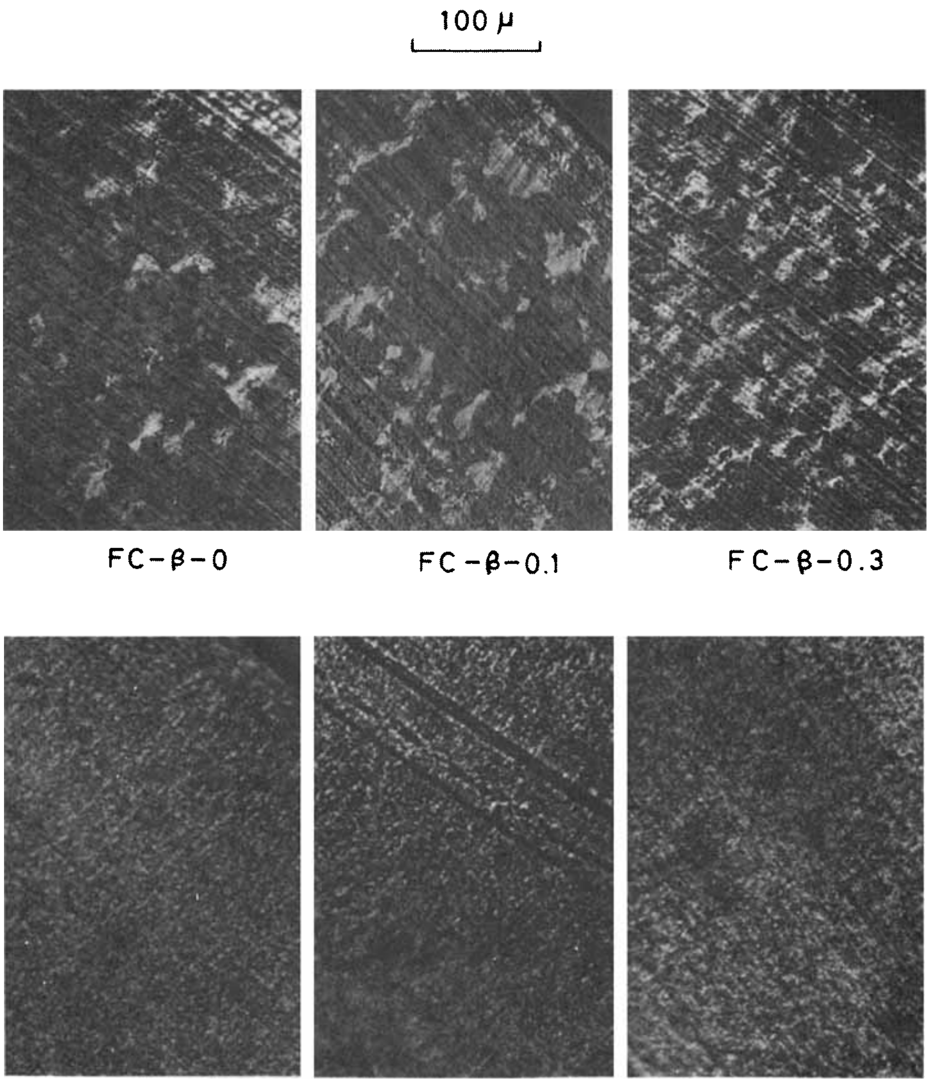

Fig. 2. Variation of spherulitic texture of cast sheet with β-nucleator content. Extrusion temperature: 220°C.

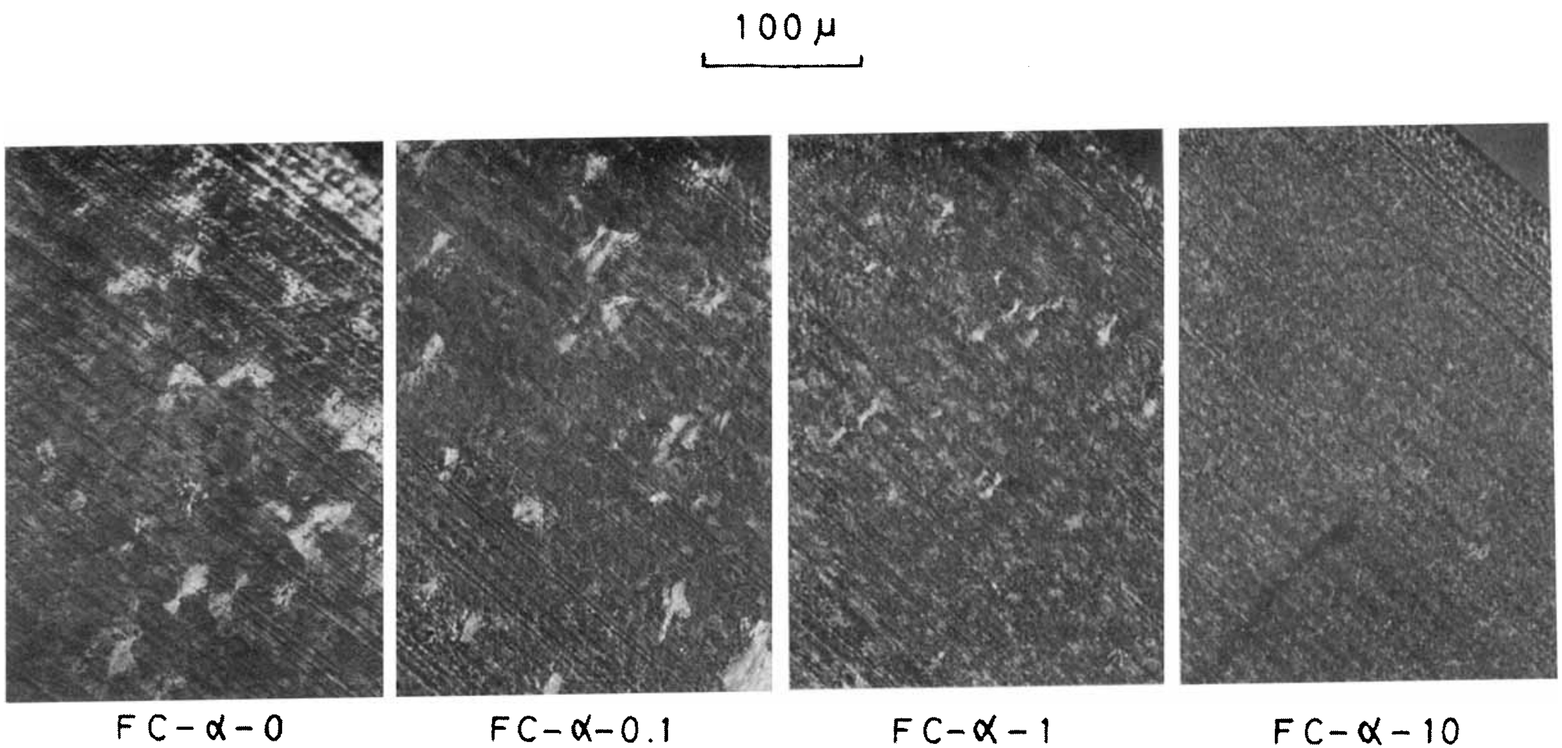

Fig. 3. Variation of spherulitic texture of cast sheet with α-nucleator content. Extrusion temperature: 220°C.

speed[1]: 3/15. The cast sheets were passed so that the surfaces opposite to the chill roll-touched surfaces touched the 2′ roll.

TD Stretching

The MD-stretched sheets were stretched ten times in the transverse direction (TD) with a pantograph-type stretching machine[1] at a preheating time of 1 min, a stretching temperature of 150°C, and a stretching rate of 3000 %/min.

The roughness of BOPs obtained was studied by observation of the surfaces with a reflection-type differential interference microscope and by the measurements of the average roughness, R_a and haze.[1]

RESULTS AND DISCUSSION

Analysis of Cast Sheet

Figure 1 shows the dependence of the K values of the cast sheets on the nucleator content. As for the β nucleator, as in the case of the Part I of this series,[4] the K values tend to increase with increasing nucleator content. In the cases of low extrusion temperatures (220°C and 250°C), the effect of the β nucleator appears from low content. In the case of a high extrusion temperature (280°C), the K value scarcely changes by the addition of the nucleator at contents below 3 ppm, and the effect of the nucleator does not appear. In the case of no nucleator, the K value increases with decreasing extrusion temperature. This is considered to be due to the fact that, in the case of low melting (extrusion) temperature, there exist nuclei or associations of molecular chains in the molten PP.[3] Accordingly, it is supposed that in the case of low extrusion temperature, the formation of the β crystals is promoted by the addition of small amounts of the β nucleator. In the case of the α nucleator, the K value decreases with increasing nucleator content and no β crystal is formed at nucleator contents above 10 ppm.

TABLE I
Characterization of Cast Sheets and BOPs

Resin/Nucleator		Cast sheet	BOP		
Kind	Content (ppm)	β-spherulite diameter (μm)	R_a (μm)	Haze (%)	Crater diameter (μm)
	0	35	0.88	18.0	340
	0.1	30	0.91	17.5	300
β	0.3	27	0.48	15.3	220
(γ-Quinacridone)	1	15	0.31	10.3	170
	3	Ca. 5	0.15	4.2	65
	10	Ca. 3	0.09	2.5	38
	0	35	0.88	18.0	340
α	0.1	33	0.86	18.4	430
(PTBBAAl)	1	22	0.38	8.5	260
	10	9	0.08	1.7	110

Extrusion temperature of cast sheet; 220°C. Setting temperature of MD-stretching roll: 170°C.

Figures 2 and 3 show the variations, with the nucleator content, of the spherulitic morphologies of the cast sheets which contain β and α nucleators, respectively. The diameter of the β spherulites decreases with increasing nucleator content in both the cases of β and α nucleators. The diameters of the β spherulites are shown in Table I. Since it is supposed that the size of the β spherulites in the cast sheet affects the degree of roughness and the diameter of craters of the BOP obtained from it, it is considered that the roughness of a BOP can be controlled to some extent by the amount of the nucleator added to the base PP.

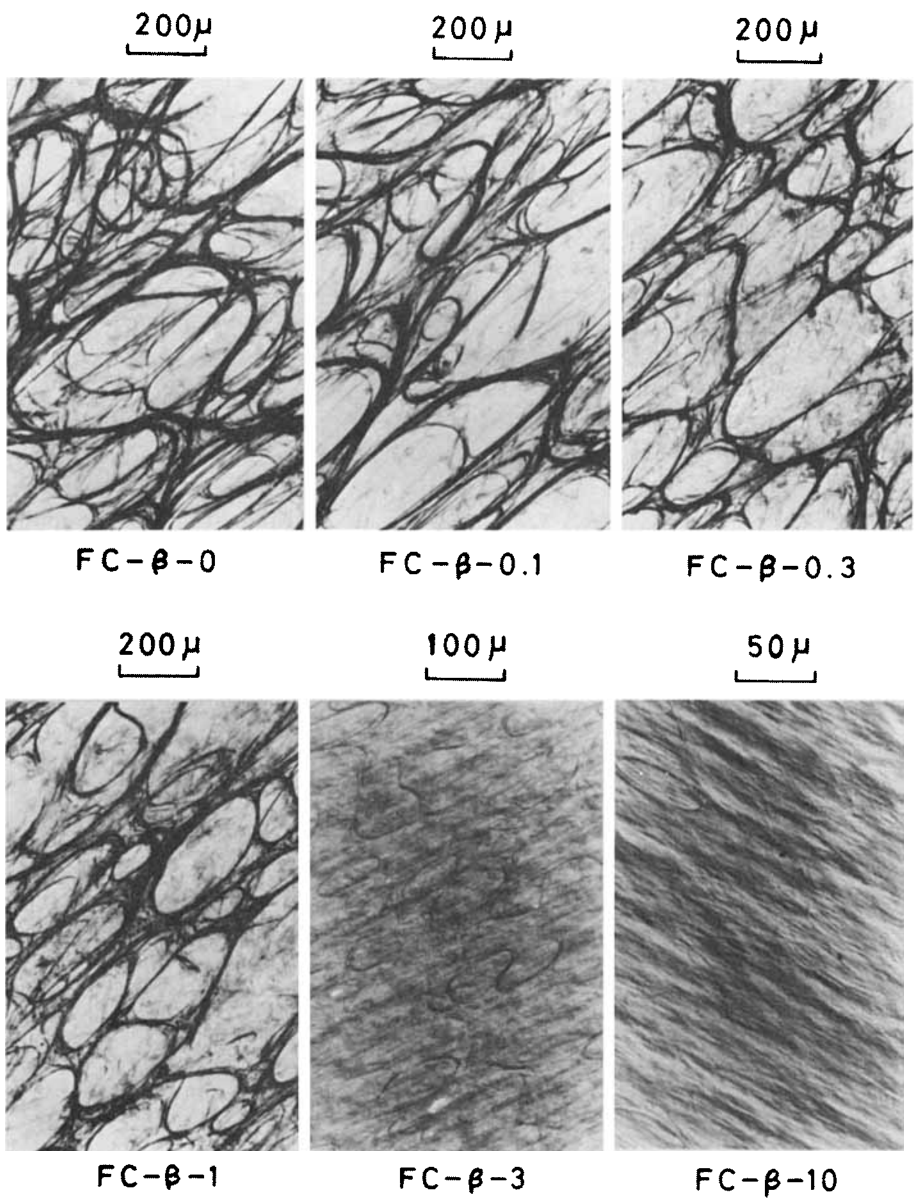

Fig. 4. Variation of surface of BOP with β-nucleator content. Extrusion temperature of cast sheet: 220°C, setting temperature of MD-stretching roll: 170°C.

Rough-Surface BOP Obtained by Addition of β Nucleator

Figure 4 shows examples of the surface photographs of BOPs obtained by extruding PPs with various β-nucleator contents at an extrusion temperature of 220°C into sheets, by MD stretching the cast sheets at a roll-setting temperature of 170°C, and then by TD stretching the MD-stretched sheets at 150°C. When the β-nucleator contents are below 1 ppm highly roughened BOPs are obtained, and when the nucleator contents are above 3 ppm the diameter of craters decreases and the degree of roughness is low. The diameters of the craters are shown in Table I.

Figure 5 shows the dependence of average roughness, R_a and haze on the β-nucleator content using the MD-stretching temperature as a parameter. As in the case of the Part III of this series,[2] R_a and haze increase with increasing MD-stretching roll temperature. In the case of an MD-stretching roll temperature of 160°C, R_a is about 0.3 μm and haze is about 5%, independent of the nucleator content. The effect of the nucleator content gradually appears as the MD-stretching temperature increases, and generally, R_a and haze tend to decrease with increasing nucleator content. However, in the cases of very low nucleator contents (0.1–0.3 ppm), the BOPs with very high R_a and haze were obtained in comparison to the case of no nucleator. The values of R_a and haze are shown in Table I. Also shown in Table I, the diameters of the β spherulites in the cast sheets and the diameters of the craters on the BOPs in the cases of very low nucleator contents (0.1–0.3 ppm) do not decrease greatly from those in the case of no nucleator. On the other hand, since the amount of

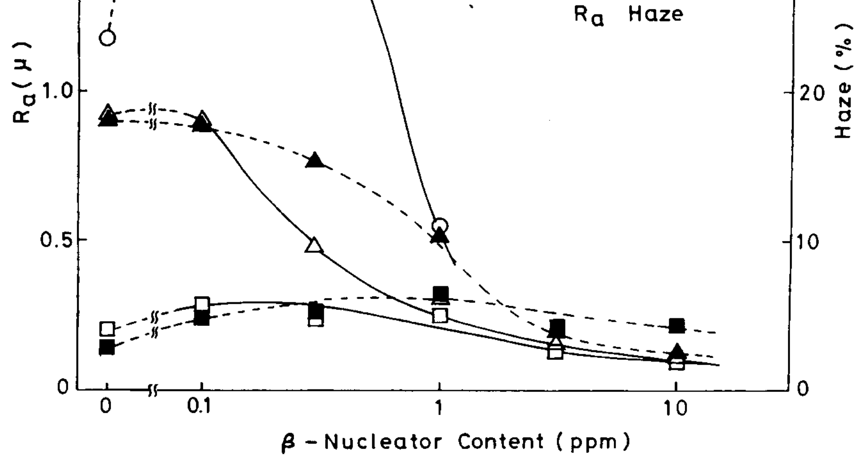

Fig. 5. Dependence of average roughness, R_a and haze on β-nucleator content. Extrusion temperature of cast sheet; 220°C. Roll-setting temperature: R_a (○) 180°C; (△) 170°C; (□) 160°C; haze: (●) 180°C; (▲) 170°C; (■) 160°C.

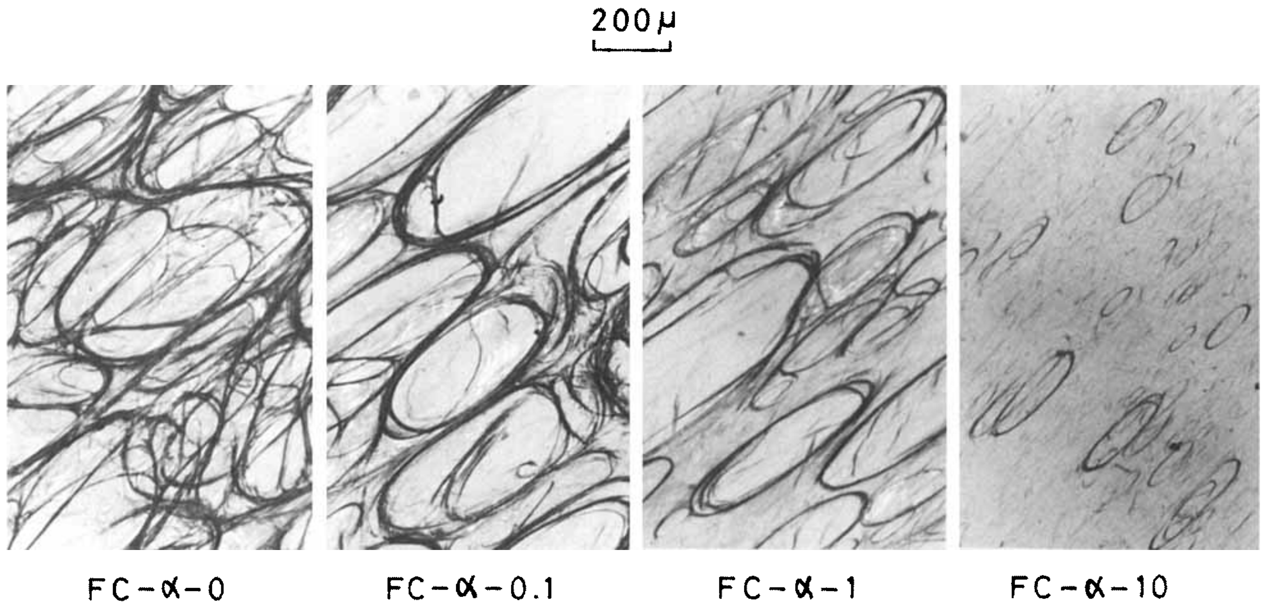

Fig. 6. Variation of surface of BOP with α-nucleator content. Extrusion temperature of cast sheet: 220°C, setting temperature of MD-stretching roll: 170°C.

the β crystals formed in the sheet increases by the addition of even very small amount of the β nucleator as shown in Figure 1, it is assumed that the degree of roughness of the BOP increases by the addition of a very small amount of the β nucleator in the case of MD stretchings at high temperatures.

Although, as mentioned above, a highly roughened BOP is obtained by adding the β nucleator to the base PP at levels of 0.1–0.3 ppm, the diameter of the craters on the BOP is very large as in the case of no nucleator as shown in Figure 4, and hence it is forecast that it must exert bad influences on the properties, such as the impregnation properties of insulating oils and dielectric breakdown strength. Taking these facts into consideration, a β-nucleator content of about 1 ppm is the most suitable for the roughening of BOP.

Rough-Surface BOP Obtained by Addition of α Nucleator

Figure 6 shows examples of the surface photographs of BOPs obtained by extruding PPs with various α-nucleator content at an extrusion temperature of 220°C into sheets, by MD stretching the cast sheets at a roll-setting temperature of 170°C, and then by TD stretching the MD-stretched sheets at 150°C. Both the clearness and diameter of the craters decrease with increasing α-nucleator content. The diameters of the craters are shown in Table I.

Figure 7 shows the dependence of average roughness, R_a and haze on the α-nucleator content using the MD-stretching temperature as a parameter. Although R_a and haze increase with increasing MD-stretching temperature as

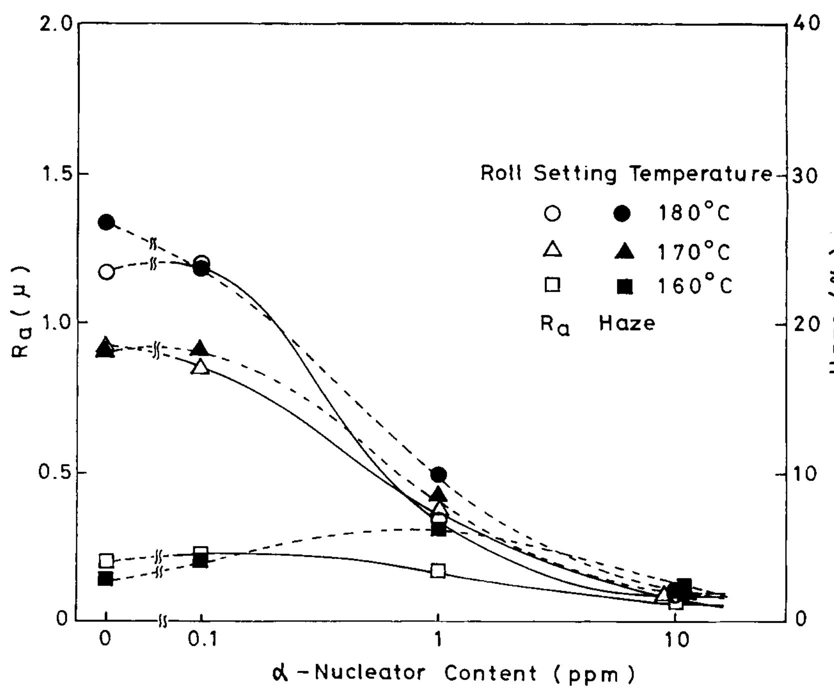

Fig. 7. Dependence of average roughness, R_a and haze on α-nucleator content. Extrusion temperature of cast sheet; 220°C. Roll-setting temperature: R_a: (○) 180°C; (△) 170°C; (□) 160°C; haze: (●) 180°C; (▲) 170°C; (■) 160°C.

in the case of the β nucleator, R_a and haze are not so high in the case of a low nucleator content (0.1 ppm). This is assumed to be due to the facts that, unlike the β nucleator the α nucleator itself has no ability to become a nucleus of the β crystal and rather suppress the formation of the β crystals, and hence the amount of the β crystals formed decreases with increasing α-nucleator content. However, since the diameter of the β spherulites in the cast sheet decreases by adding the α nucleator as shown in Figure 6 and Table I, the diameter of the craters on the BOP also decreases by adding the α nucleator. From Figures 6 and 7 it can be said that in order to obtain a BOP with a moderate roughness and a moderate diameter of craters an α-nucleator content of about 1 ppm is the best as in the case of the β nucleator.

CONCLUSIONS

In the roughening of BOP by adding the α-crystal or β-crystal nucleator, the difference between both nucleators is the variation of the amount of the β crystals formed in the cast sheet against nucleator content: In the case of the β nucleator the amount of the β crystals formed increases by adding the nucleator, and in the case of the α nucleator it decreases by adding the nucleator. Originating from the difference of the amount of the β crystals formed in the cast sheet, the variation against the nucleator content of the degree of roughness of the BOP, which has been obtained by biaxially stretching the cast sheet and has crater-like roughness on its surface, differs for both nucleators. However, for both nucleators, the diameter of the craters on the BOP in the cases of nucleator content below 0.3 ppm does not differ much from that in the case of no nucleator, and the diameter of the craters decreases with increasing nucleator content in cases of nucleator content above 1 ppm. Accordingly, in order to obtain a BOP with a sufficient roughness and moderately small craters, a nucleator content of about 1 ppm is best for both the α- and β-nucleators.

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