Study on Rough-Surface Biaxially Oriented Polypropylene Film. II. Influence of Stretching Conditions

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Synopsis

The production of rough-surface biaxially oriented polypropylene film (BOP) has been studied by means of casting a polypropylene which contained γ-quinacridone, a β-crystal nucleator, with a T-die extruder into a sheet which has subsequently been stretched successively in the machine direction (MD) and the transverse direction (TD) with a roll-type stretching machine and a pantograph-type stretching machine, respectively. For roughening of BOP using β-form crystals in a successively stretching tenter method, it is preferable to roughen in the MD-stretching process, with suppression of the recrystallization into the α crystals after melting of the β crystals being the most important objective. By rapid heating of a cast sheet in the MD-stretching process, a rough-surface BOP with a crater-like roughness was obtained. Theoretical proof for the effectiveness of the rapid heating in the MD-stretching process was obtained from experiments on the melt-transformation of the β crystals by differential scanning calorimetry (DSC) measurements.

INTRODUCTION

The method of stretching a cast sheet, in which β crystals are formed, at a temperature between the melting point of the β crystals and that of the α crystals is known to induce roughening of biaxially oriented polypropylene film (BOP).[1-16] Nakatani et al.[15] and Hobbs and Pratt[16] studied roughening of BOP by the tubular method and found that BOPs with crater-like surface roughness were obtained by biaxially stretching stalks, in which β crystals were formed, in a temperature range between the melting point of the β crystals and that of the α crystals and by inducing melt and collapse of the β crystals.

Generally, in the production of BOP by the successively stretching tenter method, a sheet is cast with a T-die extruder, stretched in the machine direction (MD) with a roll-type stretching machine, and then stretched and thermally set in the transverse direction (TD) with a tenter, producing a BOP.[17] Several patents[2,4,7-10,12-14] which are more or less concerned with the production of rough-surface BOPs utilizing β crystals in the successively stretching tenter method have been applied for. Sato et al.[4] and Nakamura et al.[8] claim in their patents to rapidly heat a cast sheet containing β crystals in the MD-stretching process. The present article reports the study on the

influence of stretching conditions (mainly MD-stretching conditions) on the roughness of rough-surface BOP produced by utilizing the β crystals in a successively stretching tenter method, and theoretical proof for the effectiveness of the rapid heating in the MD-stretching process will be proposed.

EXPERIMENTAL

Raw Resin

Tokuyama Polypro Grade FB110 powder [melt flow index (MFI) = 1.8 dg/min], which was a homoisotactic polypropylene (PP) produced by Tokuyama Soda Co., Ltd. was mixed with 10 ppm γ-quinacridone as a β-crystal nucleator, 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 approx. 3 mm with an automatic cutter.

Casting of Sheet

Sheets 800 μm and 500 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 chill roll temperatures of 30°C, 60°C, and 90°C. The casting conditions were hereafter represented by the extrusion temperature—the chill roll temperature (ex. 220−90).

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) and crystallinities were calculated from the diffraction curves according to Turner-Jones et al.[18, 19] and Weidinger and Hermans,[20] respectively. K value is a nonlinear function of the fraction of crystallites present which have the β form. The α and β crystals were equally included in the crystallinity.

The morphologies of β crystals in the surfaces of the cast sheets were analyzed by a toluene immersion method as follows[5]: The cast sheets were immersed in toluene at 92°C for 3 min and the β crystals in the sheet surfaces were dissolved. Since the spaces previously occupied by the β crystals appear as depressions or basins, they were observed with a reflection-type differential interference microscope (NIKON OPTIPHOT AFM manufactured by Nihon Kogaku Kogyo Co., Ltd.) and the diameter and density of the β crystals were measured.

MD Stretching

The cast sheets were stretched five times in the machine direction (MD) with a roll-type stretching machine shown in Figure 1 under the following conditions: preheating oven temperature: room temperature, 130°C, and 140°C; temperature of oil which circulated the heating rolls: 130°C (below the melting point of the β crystals) and 170°C (above the melting point of the β crystals); roll rotation speed: heating rolls (low speed)/cooling rolls (high speed) = 1 m/min/5 m/min (1/5), 2/10, and 3/15. The cast sheets were passed so that the surfaces opposite to the chill roll-touched surfaces touched
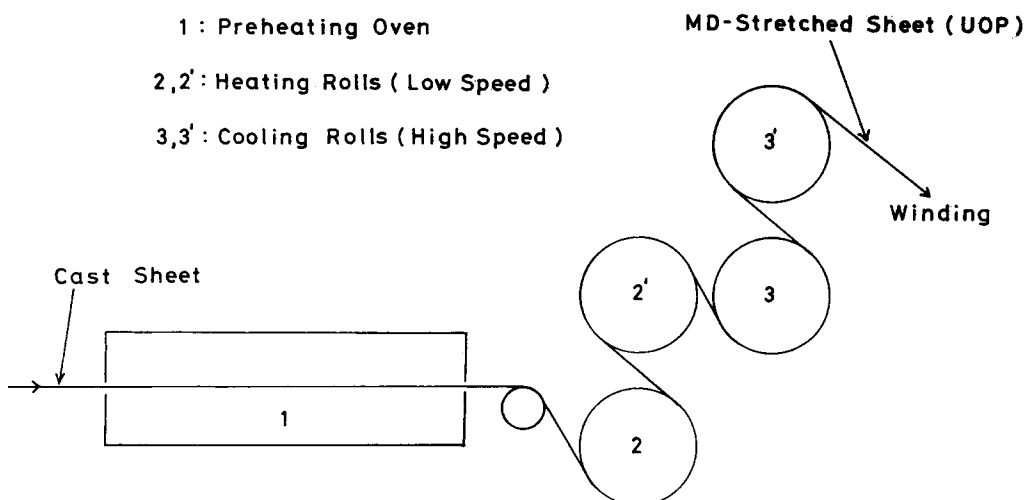
1 : Preheating Oven

2,2′: Heating Rolls (Low Speed)

3,3′: Cooling Rolls (High Speed)

MD-Stretched Sheet (UOP)

Cast Sheet

Winding

Fig. 1.   MD-stretching process.

the 2′ roll. When the setting temperatures of the heating rolls were 130°C and 170°C, the surface temperatures of the heating rolls were 115°C and 145°C, respectively.

With the MD-stretched sheets (UOP) obtained, their surface states were observed with the reflection-type differential interference microscope and their K values and crystallinities were measured by X-ray diffraction.

TD Stretching

The UOPs were stretched 10 times in the transverse direction (TD) with a pantograph-type stretching machine, Brückner-Laboratory Unit Type KARO 1500/60, manufactured by Brückner Maschinenbau under the following conditions: preheating time: 1 min; stretching temperature: 150°C and 155°C; stretching rate: 3000%/min.

Surface states of the biaxially stretched films (BOP) obtained were observed with the reflection-type differential interference microscope. Their average roughnesses, R_a, were measured with a Surfcorder Model TDF-3A manufactured by Kosaka Laboratory Ltd. according to the JIS B0601. Their hazes were measured with a Direct Reading Haze Meter manufactured by Toyo Seiki Seisakusho Ltd. according to the ASTM B1003.

Analysis of Melt-Transformation of β Crystals by DSC

Using the 220-90 cast sheet, the melt-transformation behaviors of the β crystals were studied using a Perkin-Elmer DSC BI. The purpose of this experiment was to study the relations between the heating conditions of the cast sheet and the melt-transformation behaviors of the β crystals contained therein, and obtain information about the heating conditions at the MD-stretching process.

First, in order to study the influence of the preheating temperature and the preheating time, the temperature of the sample was rapidly raised from room

temperature to 140–160°C and maintained for an appointed time, and then lowered at a rate of 20°C/min, and the exotherm for crystallization was measured. Next, to study the influence of the heating rate, the temperature of the sample was raised to 150°C at rates of 5–80°C/min and then immediately decreased at a rate of 20°C/min and the exotherm for crystallization was measured. Since the exotherm measured in these experiments originates from the recrystallization of the part which has not been recrystallized after melting of the β crystals, it decreases as the recrystallization proceeds. Accordingly, the behaviors of melt-transformation of the β crystals were studied by analyzing the data obtained from these experiments.

RESULTS AND DISCUSSION

Analysis of Cast Sheet

Figure 2 shows the variation of β-crystal content (K value) with the extrusion temperature using the chill roll temperature as a parameter. As in the case of the previous article,[19] the K value decreases with increasing extrusion temperature and depends to a lesser extent on the chill roll temperature.
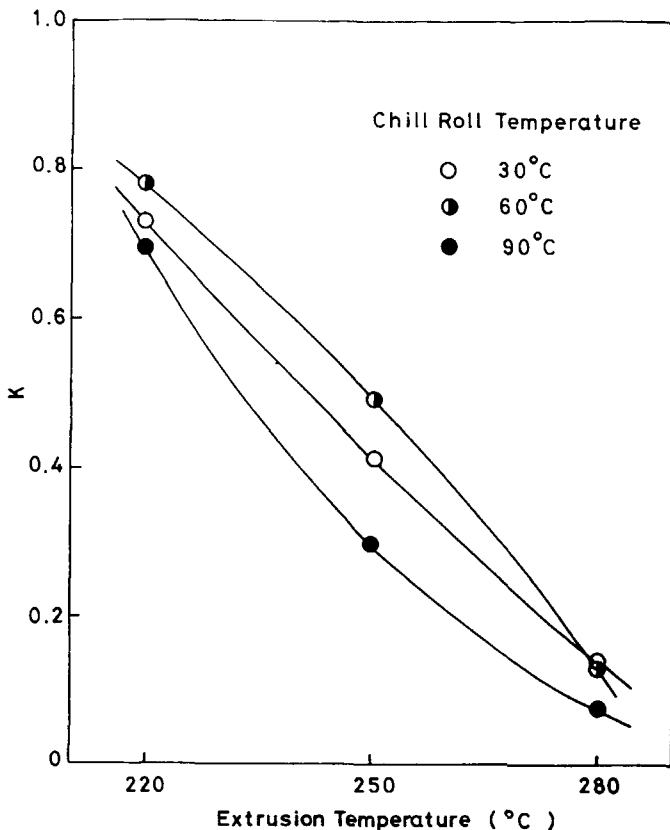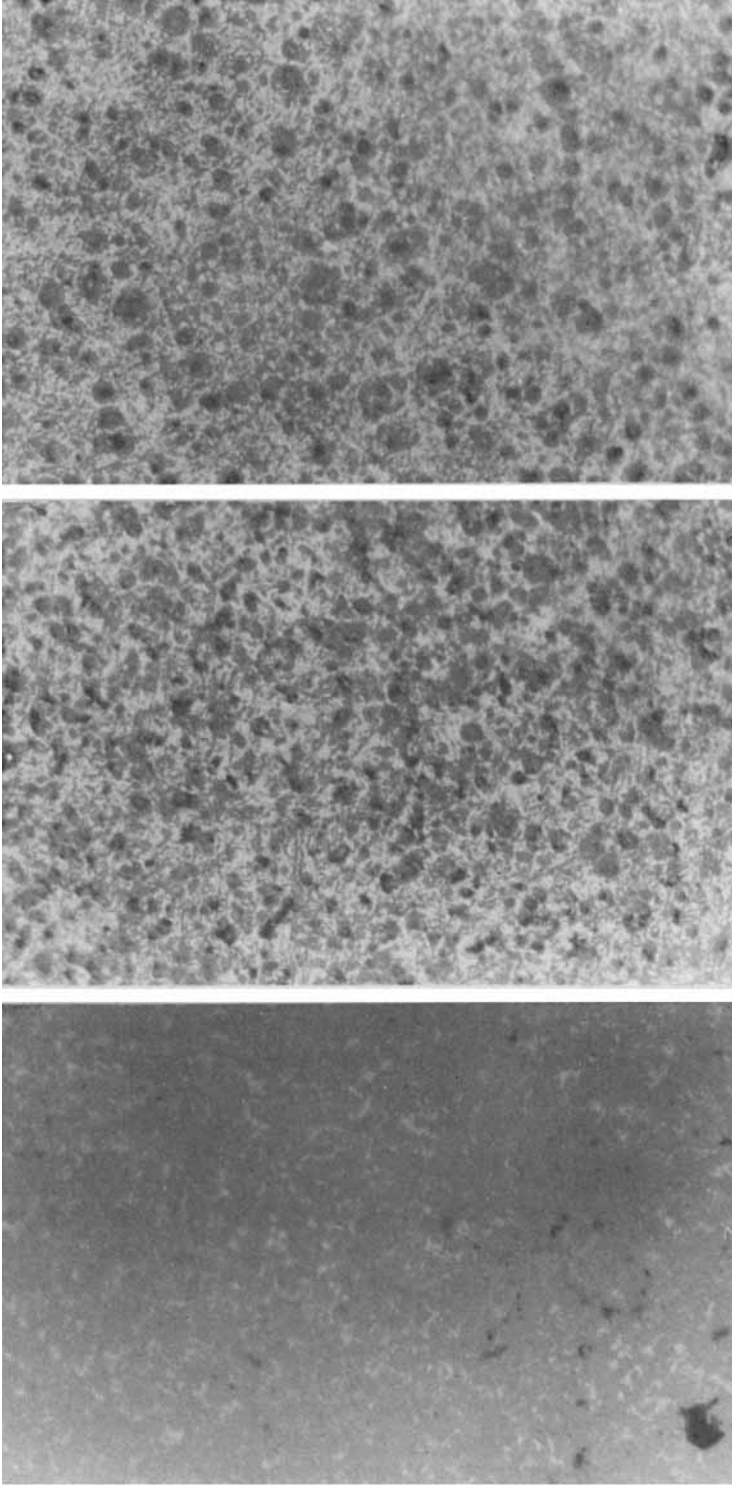

Fig. 2.   Variation of K value with extrusion temperature. Chill roll temperature: (○) 30°C; (◑) 60°C; (●) 90°C.

Fig. 3. Surfaces of cast sheets treated with toluene immersion. Opposite side of chill roll-touched surface.

TABLE I
Analysis of β-Form Crystals in Cast Sheet Surface

Cast sheet	Spherulite diameter (μm)	Spherulite density (number/cm²)
220–90	Unanalyzable	Unanalyzable
250–90	3–6	700,000
280–90	3–6	450,000

Figure 3 shows photographs of the surfaces opposite to the chill roll-touched surfaces of the cast sheets treated with the toluene immersion. Basins, the spaces previously occupied by the β crystals, are observed. No basin was observed on the chill roll-touched surfaces and they were smooth. The diameters and densities of the β spherulites measured from the photographs are shown in Table I. Since the basins were not clear for the 220–90 sheet, the diameter and density could not be analyzed. It is considered that since the 220-90 sheet contained large amounts of β crystals, particularly in the surface, as can be seen from the K value, and consequently almost all the β crystals in the sheet surface were dissolved by toluene immersion, the basins became indistinguishable. Taking these facts into consideration, it is assumed that the density of the β spherulites increases with decreasing extrusion temperature and the diameter of the β spherulites changes very little with the extrusion temperature.

Stretching

In order to leave or melt the β crystals in the cast sheets in the MD-stretching process, the MD stretchings were carried out at a roll rotation speed of 1/5 and at a roll-setting temperature of 130°C (a roll surface temperature of 115°C), which is below the melting point of the β crystals, or at a roll setting temperature of 170°C (a roll surface temperature of 145°C), which is above the melting point of the β crystals, respectively. The K values and crystallinities of the cast sheets and MD-stretched sheets are shown in Figure 4 and Table II, respectively. It can be seen from Figure 4 that the K values of the MD-stretched sheets decrease considerably from those of the cast sheets even in the case of the MD-stretching temperature of 130°C and the K values of the MD-stretched sheets are nearly zero in the case of the MD-stretching temperature of 170°C. Since the crystallinities of the 130°C MD-stretched sheets decrease considerably from those of the cast sheets as shown in Table II, it is considered that the main cause of the large decrease in the amount of the β crystals in the MD-stretching process is the mechanical collapse of the β crystals by the stretching operation rather than the melt-transformation of the β crystals. Because the crystallinities of the 170°C MD-stretched sheets are nearly equal to or slightly higher than those of the cast sheets and the K values of the 170°C MD-stretched sheets are nearly zero, it is assumed that almost all the β crystals have been melt-recrystallized into the α crystals.

Figure 5 shows photographs of the surfaces of these UOPs and those of the BOPs obtained by stretching the UOPs in the TD at 150°C. In the case of
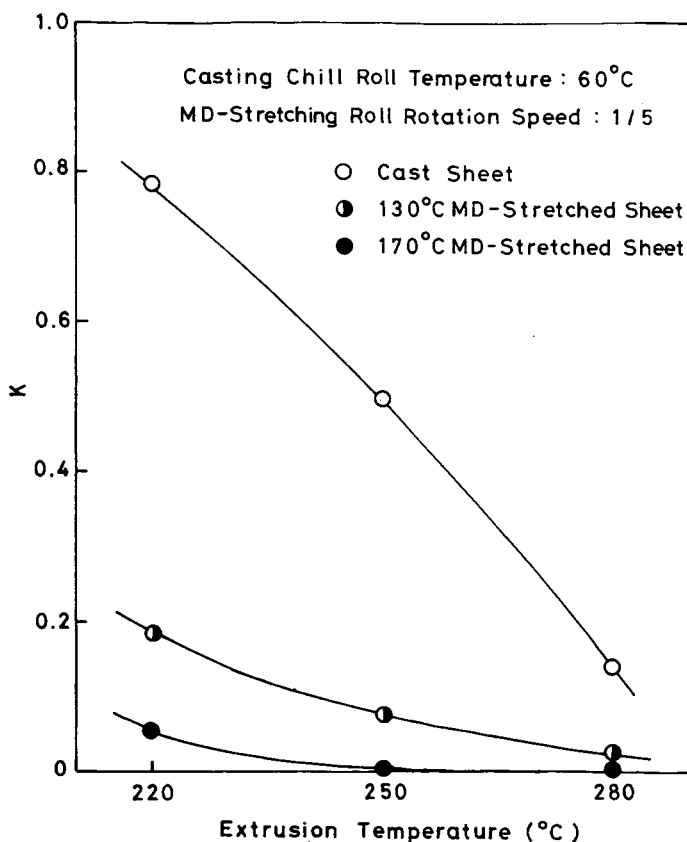
Fig. 4.   K value of cast (○) and MD-stretched (◑, 130°C; ●, 170°C) sheets.

the 130°C MD stretching, the UOP shows streaks extended in the MD while the BOP obtained is smooth. In the case of the 170°C MD stretching, the UOP shows small ellipsoidal basins extended in the MD and the BOP obtained shows unclear craters.

By the method in which a cast sheet is stretched in the MD below the melting point of the β crystals and subsequently melted in the TD-stretching process, only a smooth surface BOP was obtained as shown in Figure 5. By stretching a cast sheet in the MD at a temperature where the β crystals are partially melted, ellipsoidal basins were observed in the UOP and signs of a

TABLE II
Crystallinities of Cast and MD-Stretched Sheets

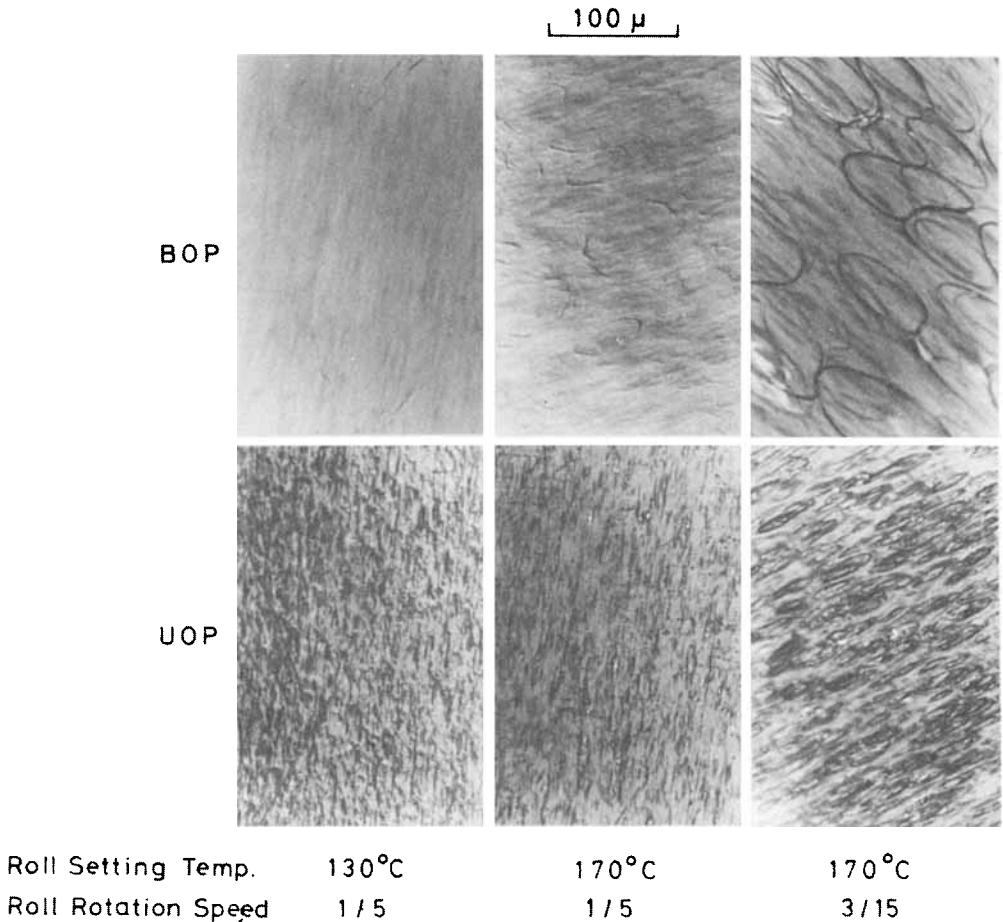| Sample	Cast sheet	130°C MD-Stretched sheet	170°C MD-Stretched sheet
220–60	48.4	41.9	46.7
250–60	48.8	44.3	49.0
280–60	51.1	42.0	51.7
250–90	50.0	42.2	53.2

MD-stretching roll rotation speed: 1/5.

Fig. 5.   Surfaces of MD-stretched sheets (UOP) obtained from 280–60 cast sheet 800 μm thick at various roll-setting temperatures and roll rotation speeds and biaxially stretched films (BOP) made from them at stretching temperature of 150°C.

crater-like surface appeared with the obtained BOP. Accordingly, it is thought appropriate to roughen in the MD-stretching process as shown by Nakamura et al.[8] However, although the BOP obtained in this manner showed a crater-like roughness, its degree of roughness was not sufficient. Since the K values of the UOPs MD-stretched at 170°C are nearly zero as shown in Figure 4, it is assumed that the β crystals in the cast sheets have been melt-recrystallized into the α crystals. It is supposed that the β crystals had been melt-recrystallized when the cast sheets touched the heating rolls of the MD-stretching machine, no melted part existed at the critical moment of the stretching, and hence no collapse occurred: an unfavorable situation for roughening. Accordingly, we considered, as shown by Nakamura et al.,[8] that it is preferable to heat the cast sheet rapidly and then to MD stretch it while the β crystals are melted but before they are recrystallized into the α crystals. In order to suppress the melt-recrystallization of the β crystals at the preheating stage, MD stretching was carried out using a preheated oven and

TABLE III
MD- and TD-Stretching Conditions and Surface Properties of Obtained BOPs

Cast sheet		MD-stretching conditions			TD-stretching conditions		BOP	
Thickness (μm)	Casting conditions	Setting temperature of heating roll (°C)	Preheating oven temperature (°C)	Roll rotation speed (m/min)	Preheating temperature (°C)	Preheating time (min)	Ra (μm)	Haze (%)
	280–60	130	Room temperature	1/5	150	1	0.09	2.4
	280–60	130	Room temperature	1/5	155	1	0.10	2.4
	280–60	170	Room temperature	1/5	150	1	0.09	0.8
	280–60	170	Room temperature	1/5	155	1	0.07	0.9
800	250–90	170	130	2/10	150	1	0.15	2.6
	250–90	170	130	2/10	155	1	0.11	2.5
	280–60	170	140	3/15	150	1	0.13	9.5
	280–60	170	140	3/15	155	1	0.18	10.1
500	250–90	170	140	3/15	150	1	0.21	18.8
	250–90	170	140	3/15	155	1	0.12	18.1

by increasing the rotation speed of the rolls. The purpose of the preheated oven was to preheat the cast sheet up to a temperature below the melting point of the β crystals before it touched the heating roll. The purpose of increasing the rotation speed of the rolls was to reduce the time during which the cast sheet touched the heating rolls. Furthermore, since the heating of the cast sheet was considered to be affected by its thickness, cast sheets 500 μm and 800 μm thick were studied.

Examples of the photographs of the surfaces of a UOP and a BOP obtained in this manner are shown at the right-hand side of Figure 5. Ellipsoidal basins extending into the MD are clearly observed on the UOP stretched with rapid heating. A clear crater-like roughness is observed on the BOP which was obtained by stretching the UOP in the TD. This crater-like roughness is presumed to be formed by extending the ellipsoidal basins in the TD. Since the UOP stretched at rapid heating differs clearly from the UOP stretched with slow heating, it seems likely that, in the former, the recrystallization into α crystals after melting of the β crystals was suppressed at the preheating stage and the melted parts of the β crystals were collapsed at the time of stretching. The casting conditions of the sheets, MD- and TD-stretching conditions, and the surface characteristics of the BOPs obtained are shown in Table III. In the case of the 800 μm thick cast sheet, R_a and haze increase with increasing roll rotation speed. In the case of the 500 μm thick cast sheet, the hazes are still higher.

Analysis of Melt-Transformation of β Crystals by DSC

Since the melt-transformation of the β crystals in the MD-stretching process is the important point in the roughening of BOP by the successively stretching tenter method, the melt-transformation behaviors of the β crystals were studied by DSC measurements.
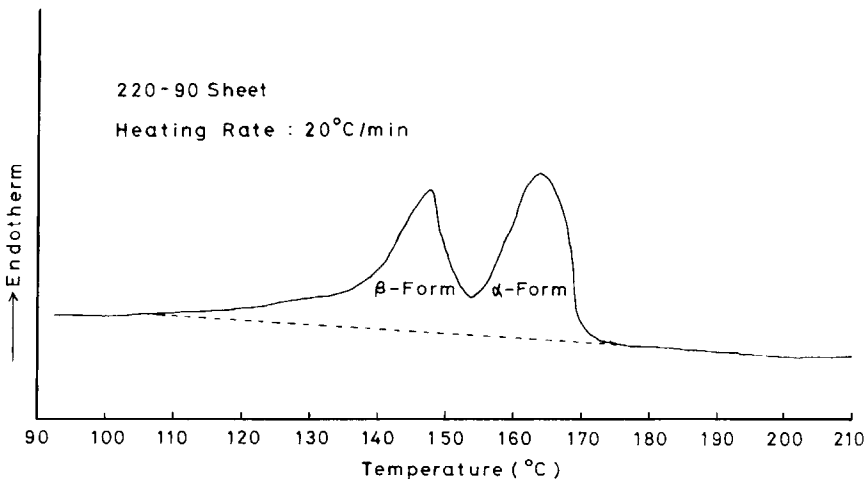

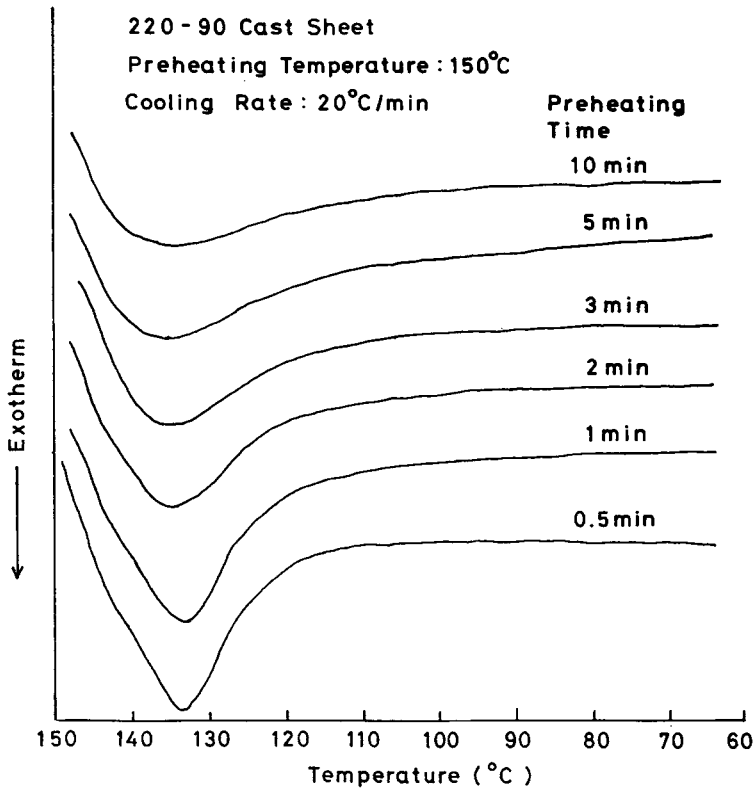Fig. 6. DSC melting thermogram of 220–90 cast sheet measured at heating rate of 20°C/min.

Fig. 7. DSC crystallization thermograms of 220–90 cast sheet measured at cooling rate of 20°C/min after preheating at 150°C for various times.

Figure 6 shows a DSC melting thermogram of the 220–90 cast sheet. Two peaks originated from the β crystals and the α crystals appear at 147°C and 164°C, respectively. A base line was drawn on the thermogram and the area which was enclosed by the thermogram and the base line was regarded as the heat of fusion. After the temperature of the sample was raised to 205°C in Figure 6, it was lowered at a rate of 20°C/min, and the sample was crystallized. An exothermic peak appeared at 114°C, and the area of the peak which was the latent heat of crystallization was the same as the heat of fusion.

Figure 7 shows examples of the DSC crystallization thermograms of the 220–90 cast sheet which was cooled at a rate of 20°C/min just after preheating at 150°C for various times. Since the crystallization peak originates from the part which remains uncrystallized after partial melting at the preheating temperature for a fixed time, the ratio of the crystallization peak area to the melting peak area in Figure 6 was regarded as the residual melting amount, R. The variations of R's at various preheating temperatures with the preheating time are shown in Figure 8. The relation between R and the preheating time is linear when plotted double logarithmically as shown in Figure 9. The slopes of these straight lines are regarded as recrystallization rates and are plotted against the preheating temperature in Figure 10. The rate of the melt-recrys-
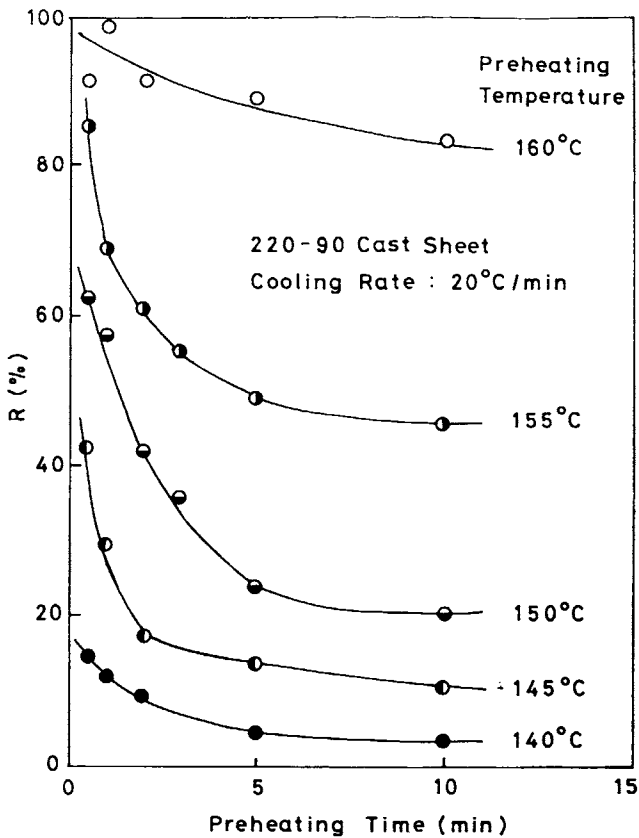
Fig. 8.   Variations of residual melting part, R, with preheating time at various preheating temperatures. (○) 160°C; (◑) 155°C; (◓) 150°C; (◒) 145°C; (●) 140°C. Cooling rate: 20°C/min.

tallization into the α crystals of the β crystals is low at the temperature near to the melting point of the α crystals and increases with decreasing temperature. From this, it can be said that in order to suppress the recrystallization after melting of the β crystals in the cast sheet, it is preferable to MD stretch the cast sheet at as high a temperature as possible. However, when the temperature is too high, the sheet breaks in the stretching process due to the melting of the α crystal parts, and hence there is an upper limit of the MD-stretching temperature.

The dependence of R on the heating rate is shown in Figure 11. R increases as the heating rate increases, and hence it can be seen that rapid heating suppresses recrystallization into α crystals after melting of β crystals. As mentioned above, although recrystallization is slower at higher heating temperatures, there is an upper limit for the heating temperature since the sheet breaks in the MD-stretching process due to α-crystal melting. In order to effectively suppress the recrystallization within the limitation, it is preferable to heat the sheet rapidly. Thus, the experimental results mentioned previously suggesting that it was favorable to heat the cast sheet rapidly in the MD-stretching process in the roughening of BOP by the successively stretching tenter method have been theoretically supported.
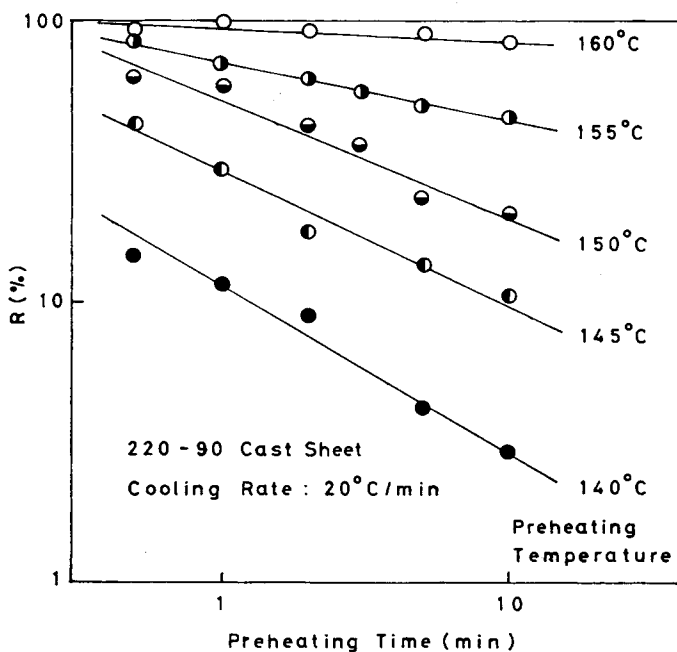
Fig. 9. Log–log plots of residual melting part, R, and preheating time at various preheating temperatures. (O) 160°C; (◐) 155°C; (◓) 150°C; (◖) 145°C; (●) 140°C. Cooling rate: 20°C/min.
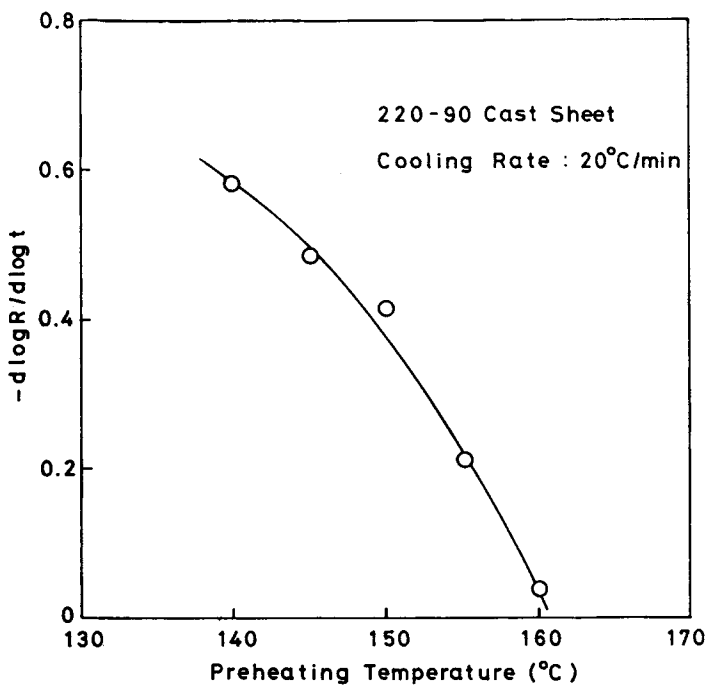

Fig. 10. Dependence of recrystallization rate $-d \log R/d \log t$ on preheating temperature. Cooling rate: 20°C min.
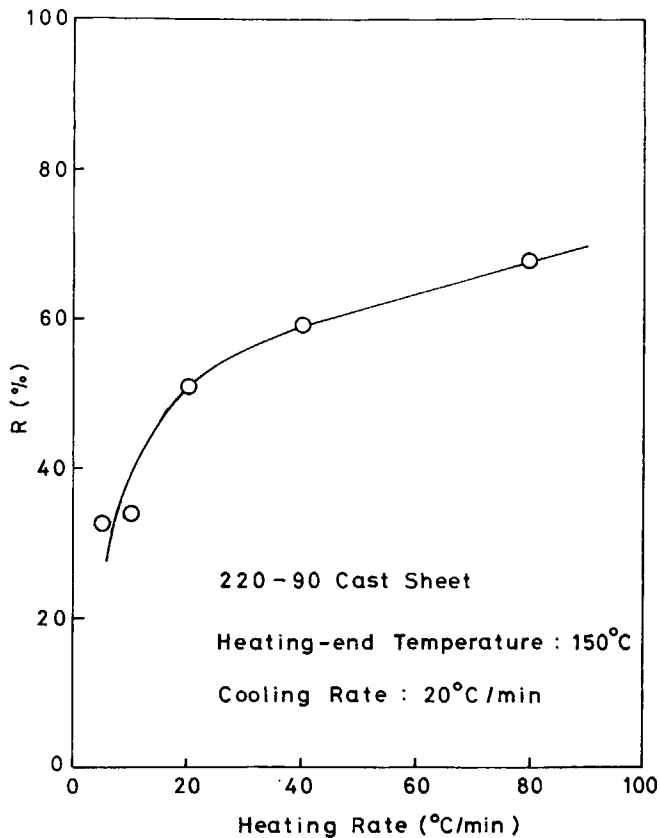
Fig. 11. Dependence of residual melting part, R on heating rate. Heating end temperature: 150°C; cooling rate: 20°C/min.

CONCLUSIONS

In the roughening of BOP by the successively stretching tenter method, the method in which a cast sheet is MD stretched at a temperature between the melting point of the the β crystals and that of the α crystals is favorable and the preheating conditions prior to stretching is the important point. BOPs with a crater-like roughness have been obtained by suppressing the recrystallization into the α crystals after melting of the β crystals by a rapid heating in the MD-stretching process. In order to support these experimental results, the melt-recrystallization behaviors of a cast sheet which contained the β crystals have been studied by DSC measurements. The recrystallization proceeded more slowly at higher heating temperature, and hence it can be said that it is preferable to perform MD stretching at as high a temperature as possible. However, at too high temperatures, the sheet broke in the MD-stretching process, and hence there is an upper limit to the MD-stretching temperature. As for the heating rate, the recrystallization into the α crystals after melting of the β crystals was more suppressed at higher heating rates. Accordingly, it is preferable to heat a cast sheet rapidly to a temperature as high as possible at which the sheet does not break in the MD-stretching process and then to MD stretch at that temperature.

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