STUDY OF THE CRATER FORMATION MECHANISM ON THE SURFACE OF BOPP FILM

Toshitaka Kanai[1*], Satoshi Tamura[2]
[1] *Idemitsu Kosan Co.,Ltd. 1-1, Anesaki-Kaigan, Ichihara-city, Chiba, 299-0193 Japan*
toshitaka.kanai@si.idemitsu.co.jp
[2] *Prime Polymer Co., Ltd . 580-30, Nagaura, Sodegaura-city, Chiba, 299-0265 Japan*
Satoshi1.Tamura@primepolymer.co.jp

Abstract
In an attempt to clarify the formation mechanism of the crater-like surface roughness of BOPP film, various thicknesses of PP sheets were compared in this study. It was found that the thickness of PP sheet has a great effect on the crater shape of BOPP film. In addition, the crystal grains formation in the surface layer which is precursor producing crater-like surface can be predicted from the analysis of the cooling calculation. It was found that the crystal grains in the surface layer are easily created with the increase of chill-roll temperature. From the analysis of the cooling calculation, it was confirmed that more than 1.5 seconds of the crystallization time is required to produce crystal grains for the same PP. In addition, the crater formation mechanism was researched in terms of the stretching behavior of entire PP sheets. By analyzing the change of the surface roughness with the stretching ratio, the deformation of surface structure starts partially before the craters were formed on the BOPP films surface. New hypothesis of the crater-like film surface roughness formation mechanism was proposed by observing the transformation of crater from sheet to BOPP film and by investigating the relationship between the stress-strain curve and surface roughness change.
Keywords: Film, Surface, Crater-like structure, Polypropylene, Spherulite

1. Introduction

It is a well known fact that there are some crystal types of PP with different crystal systems, and surface roughness of BOPP films has been investigated in association with crystal types [1),2)].

Various studies have reported on the change of the crystal structure during the stretching process [3)-6)]. Although Koike et al. made a report on the change of PP crystal structure during the uniaxial stretching observed by the birefringence technique[7)], no information related to the surface structure was reported. Kanai et al. reported on the PP spherulites deformation and crystalline orientation during stretching in terms of the stretching stress pattern, and on the analytical results of the crystal structure changes observed by birefringence, light scattering and small-angle X-ray scattering (SAXS) [5)]. Kanai et al. also reported that there was a strong relationship between the observation results of crystal structures in PP sheets and the simulation results obtained by cooling calculations conducted with regard to the thermal transfer characteristics of PP sheets using the chill-roll cooling system [8)]. It was concluded in the report that the cooling simulation is an efficient method to control the crystallization of a PP sheet which is an important factor of stretchability of BOPP.

It was found in our previous report [9)] that the crater-like structures on BOPP film surface were related to the morphology of the surface layer of the PP sheets. This report will give some perspective on the formation mechanism of craters with regard to controlling the morphology of the surface layer of PP sheet and also on its connection to changes in the entire structure.

2. Experiments

1) Samples

In order to clarify the mechanism for the formation of the surface craters, PP-A of a high tacticitiy with a meso pentad mmmm value of 96mol% and PP-B of a low tacticity with mmmm value of 91mol% were used. Properties of PP-A and PP-B are shown in Table 1. Melting point of PP-A was 3℃ higher than that of PP-B, because stereoregularity of PP-A is higher than PP-B.

Table1. Properties of PP Resins

Properties	PP-A	PP-B
MFR(g/10min)	3.5	3.0
mmmm (%)	96	91
Tm(℃)	164	161
Mw/Mn (-)	5.2	4.5

PP sheets were produced using a sheet forming machine (GM Engineering) with a diameter of 35mm extruder. The PP resin was extruded from a T-die with a width of 200mm at 250℃. Then it was cast by a chill-roll with a diameter of 250mm at a speed of 0.8 m/min and PP sheets with various thicknesses were produced at various chill-roll temperatures. In this report, samples were named in order of resin type, chill-roll temperature, and thickness. So a sample 'A80-500' is the sheet made by PP-A at a chill-roll temperature of 80℃ with a thickness of 500μm. The BOPP film names were defined by putting 'f' at the end of PP sheet names, for example 'A80-500f'.

After PP sheets were cut into a square shape of 85×85mm in size, they were stretched to BOPP films by a table tenter (Bruckner KARO Ⅳ) in order to analyze the surface structure. And then after they were preheated at a definite temperature for 1 minute, it was stretched at maximum stretching ratios of 5 times to the machine direction (MD) at first, and next 7 times to the transverse direction (TD). On other condition, it was also stretched at maximum stretching ratios of 6 times to both the machine direction (MD) and the transverse direction simultaneously.

2) Evaluation of PP sheets and the BOPP films

The sectional structures of PP sheets were observed by an optical microscope (Nikon ECLIPSE-LV100POL). Thermal properties of Tm and ΔHm of PP sheets were measured by DSC (PerkinElmer B014-3018/B014-3003) at the heating rate of 10℃/min.

X-ray diffractions were measured on the PP sheets with a Rigaku Denki RINT-2500 diffractometer with Ni-filtered Cu-Kα radiation. The crystallinity χ_c and the β crystal content named as the K-value of PP sheets were calculated from the X-ray diffraction curves [25,26]. Spherulite size U_{max} of PP sheet was calculated from equation (1) obtained by the Hv scattering pattern which reflects the scattering of the polymer superstructure

$$U_{max} = \frac{4.09}{(4\pi/\lambda)\sin\theta_{max}} \quad \cdots\cdots (1)$$

where λ is the wavelength of He-Ne laser (632.8nm), and sin θ_{max} is the scattering angle which indicates the yield point of scattering intensity to 45°against a plane of polarization, respectively.

The surface structure of BOPP films were observed by Scanning Electron Microscope (SEM, JOEL JSM5600LV). The shapes of the craters were measured by a highly precise shape measuring machine (Kosaka Laboratory SURFCODER ET4000A) using a diamond head at a head pressure of 70μN. Ten points average roughness Rz defined by JIS B0601 [1994] was used as the parameter of depth of crater on BOPP films surface.

Moreover, in order to investigate the crater formation mechanism at the surface layer of PP sheet, the influence of cooling speed was studied at the sheet forming condition described at section 2.1). The temperature of PP resin starts to drop after PP sheet is extruded from the die and touches the chill-roll. PP crystallization starts when the sheet temperature reaches the crystallization temperature, at 115℃ in the case of PP-A. After sheet temperature is kept at the crystallization temperature until the latent heat ΔH is consumed, the sheet temperature starts to drop again. Crystallization time is defined as the time during which PP sheet temperature is kept at the crystallization temperature, and PP crystallizes during the crystallization time. In this report, it is assumed that heat is conducted by primary thermal conduction expressed in equation (2) and is transferred at the boundary condition expressed in equation (3).

$$\frac{\partial T}{\partial t} = \frac{k}{Cp \cdot \rho} \cdot \frac{\partial^2 T}{\partial x^2} \quad \cdots\cdots (2)$$

$$k\frac{\partial T}{\partial x} = h(T_w - T_\infty) \quad \cdots\cdots (3)$$

where T is sheet temperature (K), t is time (s), k is thermal conductivity (0.28W/m・K), C_p is heat capacity (1.93 J/kg・K), ρ is density of PP, x is sheet position from chill-roll (m), h is heat-transfer coefficient (756W/m^2・K), T_w is surface temperature of sheet (K), and T_∞ is chill-roll temperature (K), respectively. Although the density ρ of PP depends on temperature, the fixed value 890kg/m^3 was used in this study in order to make the calculation simple. Heat-transfer coefficient h was determined by measuring the real temperature of chill-roll and PP sheet using a touched type thermometer.

3. Results and Discussion

1) Relationship between the crystalline structure of sheet and crater shape of BOPP film surface

Properties of PP sheets made by sheet forming machine are shown in Table 2.

Table2. Properties of PP Sheets

Properties	A30-500	A80-500	B30-500	B80-500
PP Resin	A	A	B	B
Chill Roll Temp. (℃)	30	80	30	80
Thickness (μm)	500	500	500	500
Xc (%)	46	65	48	64
Chill Roll Side Rz (μm)	0.21	0.26	0.20	0.21
Opposite Side of Chill Roll Rz (μm)	2.24	2.85	1.63	1.90

It is considered that these crystal grains are giving some influence on forming the crater, because they were not observed in the surface layer on the chill-roll side with the temperature at 80℃ or lower. After measuring the diameter and the depth of these grains of PP sheet by visual inspection and a diameter and Rz of craters of BOPP films, there seemed to be a good correlation between them (Fig. 1). Therefore, it can be said that the craters were formed from the crystal grains after the PP sheets were stretched to become the BOPP films.

2) Formation behavior of crater

Formation behavior of the crater was observed with SEM using the PP films at various stretching ratios using a table tenter. A lot of apertures appeared on the surface of the opposite side of the chill-roll after being stretched at only 1.5 times in the machine direction. These apertures became precursors at the beginning of stretching process, and these apertures seemed to grow into craters after the stretching ratio got higher. As a result, craters were produced from the apertures created at the beginning of stretching process as the starting point.

SEM images of the cross-sectional view of PP sheets stretched at arbitrary stretching ratios are shown in Fig. 2. Some apertures of around 10-20μm in depth appeared in the early period of the stretching process at 1.5×1.5 times, and the diameter of the aperture increased with increasing stretching ratio. Many thick walls appeared on the stretching ratio at 1.5×1.5 times, and at the end the walls between craters were torn apart into thin walls.

The effect of the total stretching ratio on Rz of the BOPP film which is a good parameter of the crater depth was investigated in Fig.3. Rz showed a maximum value at a stretching ratio of 2.0, and then got lower as the stretching ratio got larger. After the stretching ratio of 2.0, the size of the crater became larger as the wall between craters were torn. The apertures depth that appeared at the beginning of the stretching process got deeper as the stretching temperature was raised from 153 ℃ to 159 ℃. Therefore, it is believed that there is the another crater formation mechanism other than the crystal dislocation system from β crystal to α crystal, because crater shape changed at higher stretching temperature than the β crystal melting point of 148℃.

It is considered that the transformation behavior of this crystal in the surface layer is related to the stretching behavior of the whole film. Fig. 4 shows the changes of stretching force with the stretching ratio. A yield points were observed at a stretching ratio of 1.3 and the stretching force gradually decreases at stretching ratios from 1.3 to 5. It is well known that interlamellar separation in the amorphous phase occurs at the beginning of stretching and the spherulite begins to collapse when the stretching ratio passes the yield point. Therefore, it is presumed that the grains in the surface layer of the sheet begin to collapse similarly to the spherulites in the middle layer of the sheet.

3) The influence of sheet forming conditions on the crater formation of BOPP film

A higher chill-roll temperature is required to produce craters on the BOPP film surface of chill-roll side. Furthermore, crystal grains in PP sheet are needed in order to produce craters on BOPP film.

In order to investigate the influence of the chill-roll temperature on the sheet surface temperature, calculated results of the primary sheet temperatures of the opposite side of chill-roll and chill-roll side are shown in Fig.5 (a) and (b), respectively. The crystallization time got longer as the chill-roll temperature got higher. This graph shows that a crystallization time of more than 1.5 seconds is needed to create the crater on the surface of BOPP film at our experimental method. This result obtained from the PP sheet with the different chill-roll temperatures is similar to PP sheets of different thicknesses. It was confirmed that crater formation can be controlled by the crystallization time which is a function of the thickness of PP sheet and chill-roll temperature. In addition, crater can be formed on the BOPP film surface of the chill-roll side with controlling the crystallization time suitably, while the previous reports discussed only the cases of the crater on the surface of opposite side of chill-roll.

4. Conclusion

In an attempt to clarify the formation mechanism of crater-like surface roughness, different PPs and forming conditions were used in this study. As a result, it was found that chill-roll temperature had a great effect on the shape of the crater and, the crater of the BOPP film stretched from that at 80℃ was larger than the PP sheet cast at 30℃. When chill-roll temperature rose, the crystal grain of the PP sheet at surface layer of the opposite side of the chill-roll grew larger. This means that the shape of the crater is closely related to the crystal grain shape.

It was found that the thickness of PP sheet has a great effect on the crater shape of BOPP film because the crystal grains in the surface layer of PP sheet changes accordingly to the thickness of PP sheets. In addition, the crystal grains formation in the surface layer can be predicted from the analysis of the cooling calculation. It was found that over critical crystallization time is required to produce crystal grains in the surface layer of PP sheet with β type trans-crystals.

Furthermore, the relationship between the crater on the BOPP films surface and the chill-roll temperatures at the proceeding of PP sheet was investigated. It was found that the crystal grains in the surface layer are easily created with the increase of chill-roll temperature. From the analysis of the cooling calculation, it was confirmed that more than 1.5 seconds of the crystallization time is required to produce crystal grains for the same PP.

5. References

1) Fujiyama M., Kawamura Y., Wakino T., Okamoto T., J. Appl. Polym. Sci. 36, 985(1988)
2) Fujiyama M., Kawamura Y., Wakino T., Okamoto T., J. Appl. Polym. Sci. 36, 995(1988)
3)Kanai T., Yonekawa F., and Kuramoto I ,17th Polym. Proc. Society Annual Meeting Abstracts, 17(2001)
4) Kanai T., Seikei-Kakou, 18(1), 53-66(2006)
5) Kanai T., Matsuzawa N., Takebe T., Yamada T., Polymer Processing Society Regional Meeting Europe CD-ROM Abstracts(2007)
6) Kanai T., 24th Polymer Processing Society Annual Meeting CD-ROM Abstracts (2008)
7) Koike Y., and Cakmak M., Polymer 44, 4249-4260 (2003)
8) Kanai T., Takebe T., Matsuzawa N., Yamaguchi H. Asian Workshop on Polymer Processing Plenary Lecture(2009)
9) Tamura S., Ohta K., Kanai T., J. Appl. Polym. Sci. 124,2725-2735(2012)

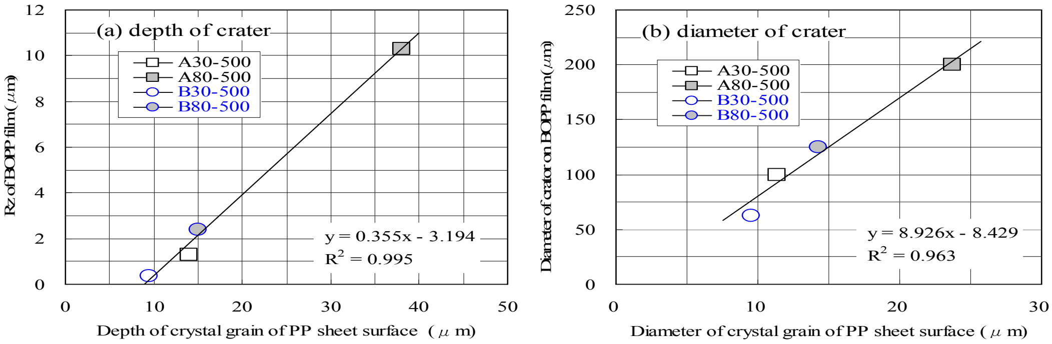

Fig.1 Relationship between the shape of crystal grain on PP sheet surface and shape of craters of BOPP film surface

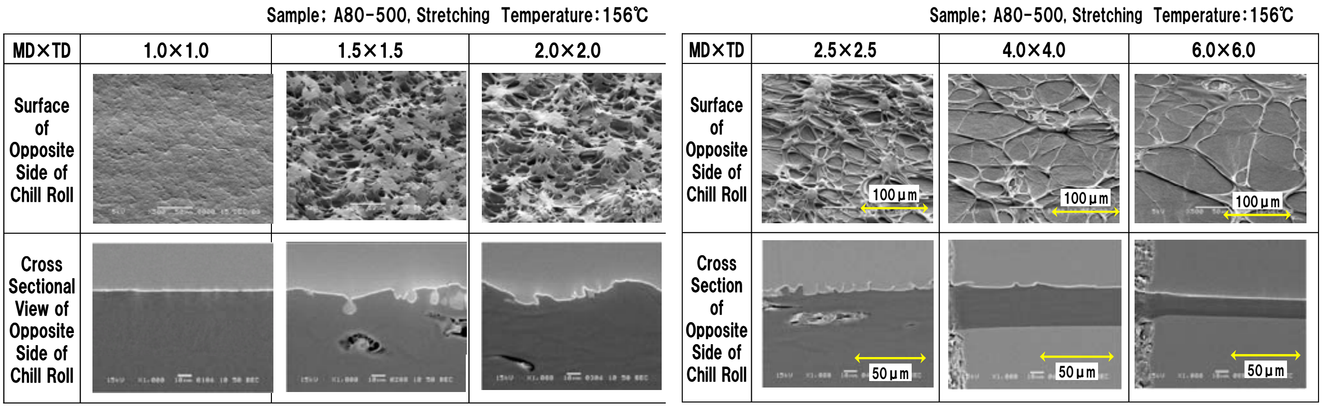

Fig. 2 SEM image of the surface of BOPP film stretched from A80-500 sheet at several Stretching Ratios at 156 ℃

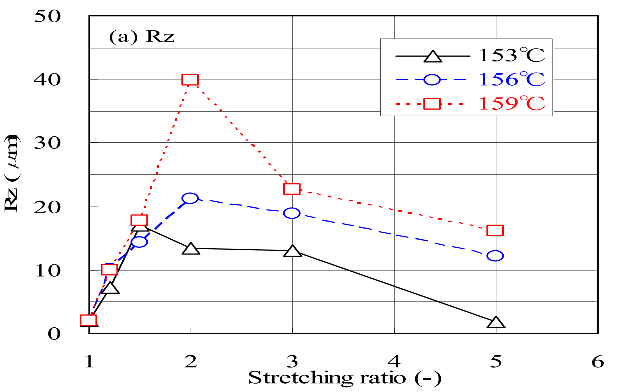

Fig. 3 Dependence of surface roughness on total stretching ratio of A80-500 at different stretching temperatures

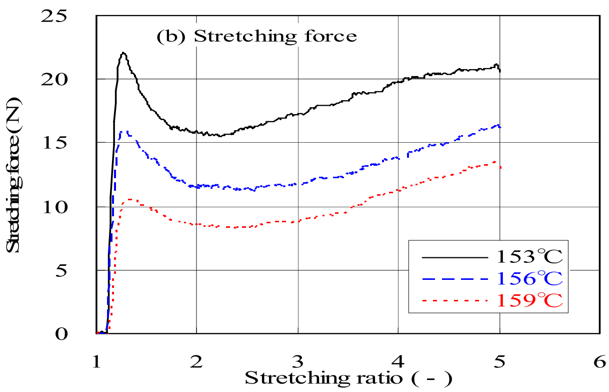

Fig. 4 Dependance of stretching force on stretching ratio of A80-500 at different stretching temperatures

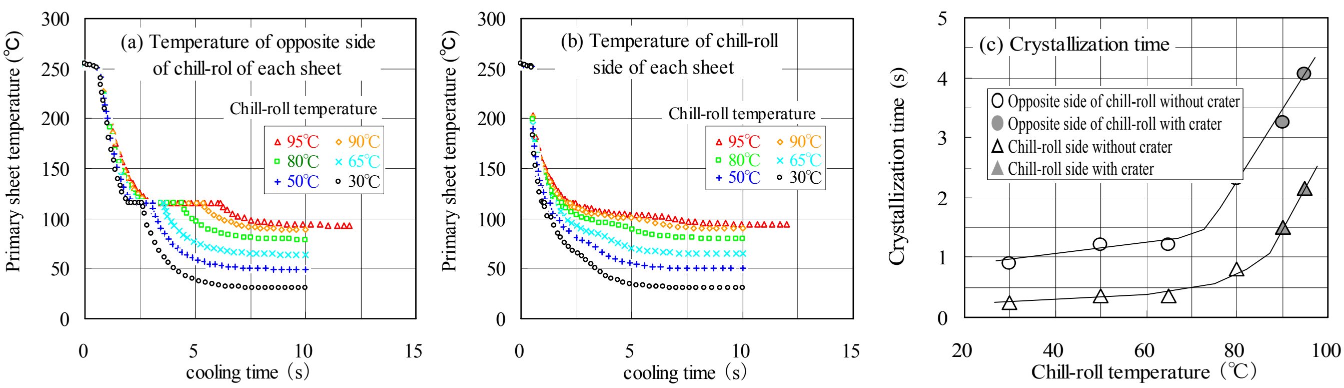

Fig.5 Calculated results of the temperature of PP sheets with different chill roll temperatures

Conditions: Die temperature 250℃, Thickness of sheets 300 μ m, Stretching Temperature 159℃, MD/TD Stretching Ratio 5/7