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Effects of transparency on polypropylene sheets by multilayer sheet extrusion

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ABSTRACT

Isotactic polypropylene is used for the packaging of various products. However, it is difficult to be used in the high transparency field due to the characteristics of crystalline resin. To improve the transparency of polypropylene sheets, the spherulites that form in the sheet have to be controlled . When the sheets were produced under quenching conditions, spherulites with a smaller size were formed because crystallization was suppressed. In the case of the static model sheet, it was observed that a large number of spherulites were formed uniformly in the entire sheet. However, in the case of the extruded sheet, most spherulites were localized in the vicinity of the surface. It was considered that the differences in the distribution of spherulites were caused by shear stress induced crystallization during the extrusion process. In order to reduce the surface shear stress, multilayer sheets were produced using a low viscosity resin for the surface.

Comparing the multilayer sheets with single layer sheets, the number of spherulites on the surface of the multilayer sheet was found to be fewer than that of single layer sheets, so a higher transparency could be achieved.

Keywords; polypropylene, spherulite, multilayer

1. Introduction

In the previous study, in order to obtain highly transparent isotactic polypropylene sheets, various factors contributing to transparency have already been analyzed. It is well known that highly transparent sheets made from a crystalline polypropylene resin can be obtained by quick quenching molten resin sheets in the laboratory [1].

However, research into the transparency under shear stress conditions, similar to an actual manufacturing process have not been reported in detail.

First, the distribution of spherulites in the direction of the cross-section was observed. **Fig.1** shows micrographs obtained by the phase contrast microscopy of cross-section of (a) the static quenching model and (b) the extruded sheet. The spherical substances in the micrographs are spherulites [2].

In the case of (a) the static model sheet, it was observed that a large number of spherulites existed uniformly in the thickness direction. However, in case of (b) the extruded sheet, a lot of spherulites existed near the sheet surface. Even if those sheets are produced under similar cooling conditions, there was a different distribution of spherulites. It means that the reason why so many spherulites were formed mostly near the sheet surface by the exturusion process was not the spherulite nucleation mechanism caused by supercooling. It is thought that stress induced crystallization by shear stress might be the main cause of a high concentration of spherulites at the sheet surface.

In order to reduce the surface shear stress, multilayer sheet was produced using a low viscosity resin for the surface. Comparing single-layer sheets with multilayer sheets, the effects of higher transparency obtained by the multilayer sheet process were examined. In other words, the purpose of this study was to investigate the effects on multilayer sheets with regards to crystallization being the controlling factor contributing to transparency.

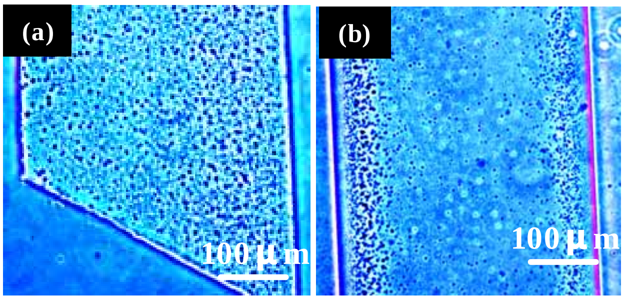

Fig.1 Micrographs obtained by phase-contrast microscopy of cross sections of (a) the static model and (b) the extruded sheet.

2. Experiments

2.1 Samples

Table 1 shows the resin characteristics of each sheet used in this experiment. The sheet structure was listed here; A is a standard resin, B is a low viscosity resin, and C is a low tacticity resin. Then, the three-layer film was composed of two different kinds of resins, whose outer layers were the same low viscosity resin and the center layer was a standard resin different from the outer layers. For example, B/A/B means three-layer films having outer layers of B and a center layer of A.

The higher order structure is very important for this resarch. It was investigated by phase-contrast microscopy, light scattering, and wide-angled X-ray diffraction (WAXD).

Table 1 Molecular characteristics of PP samples

Sheet Structure	Each layer thickness [μm]	MFR [g/10min]	mmmm [mol%]
A	344	3	92.5
B/A/B	19/309/19	20/3/20	92/92.5/92
C/A/C	22/299/27	4.5/3/4.5	70/92.5/70

2.2 Measurement of transparency

Table 2 shows the summary of the haze data of each PP sheet. Haze is an index that expresses the cloudiness of the resin. The total haze of B/A/B and C/A/C are much lower than that of A. In other words, the higher transparency could be accomplished by using multilayers. Moreover, the internal haze of B/A/B was remarkably improved. It is considered that the effect of multilayer was influenced by the internal structure.

Table 2 Comparison of various PP samples haze

Sheet Structure	Total haze[%]	Internal haze[%]	Outer haze[%]
A	14.0	13.5	0.5
B/A/B	8.3	7.6	0.7
C/A/C	12.2	11.2	1.0

3. Results and Discussion

Fig.2 shows the variation of H_v light scattering intensity distribution curves for A, B/A/B, C/A/C. The peak angle of H_v scattering means the size of the spherulites, and relative intensity means the number of spherulites. This graph shows that B/A/B sheet has markedly smaller numbers of spherulites. Also, this graph shows that the size and number of spherulites did not change substantially between single-layer sheets and multilayer sheets. From these results it was considered that multilayer sheet which was produced using a low viscosity resin for the surface decreases the number of spherulites. **Table 3** shows the size of spherulites for each sample calculated from the peak angle. Whether it was a single-layer sheet or multilayer sheet, the spherulites size were almost the same. As a result, the number of spherulites in multilayer sheets was smaller than that of single layer sheets.

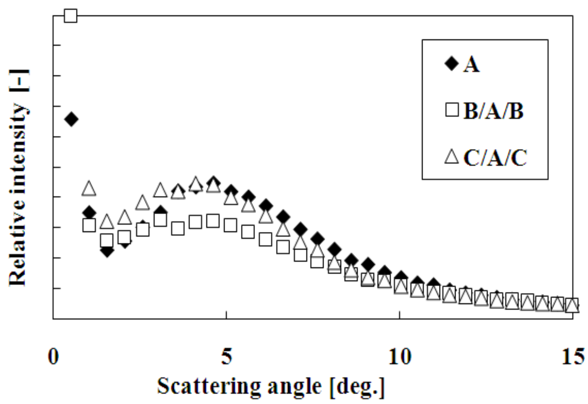

Fig.2 Relative intensity of light scattering of PP samples

Table 3 Spherulite size of PP samples

Sheet Structure	A	B/A/B	C/A/C
Spherulite size[μm]	5.1	6.6	6.6

In addition, in order to examine the number of spherulites in more detail, **Fig.3** shows micrographs obtained by phase contrast microscopy of cross-sections of A, B/A/B, and C/A/C sheet samples. On all samples, a lot of spherulites were observed especially near the sheet surface. Compared with single-layer sheets, even if the sheeting process was carried out under the same conditions, multilayer sheets generated less spherulites.

Next, the number of spherulites was counted. Micrographs obtained by phase contrast microscopy of the cross-section (**Fig.3**) were divided into ten, and then the spherulites numbers in each layer were counted.

Fig.4 shows each layer "Number density"(= number of spherulites/observed area[mm^2]). The value of "Number density" means the degree of overcrowding of spherulites. As already mentioned, a lot of spherulites were localized relatively near the sheet surface. However, as sheets were produced under quenching conditions, a low number of spherulites were formed because crystallization was suppressed at the extreme surface [Ⅰ, Ⅹ]. The left side in **Fig.4** means the belt side, and the right side of it means the chill-roll side. Comparing the chill-roll side with the belt side, the number of spherulites on the chill-roll side was fewer than that of the belt side because the chill-roll side was quenched quickly, and crystallization was more suppressed. Next, comparing the single layer sheets with multilayer sheets, it was found that the number of spherulites didn't change substantially on the inner coat [Ⅳ~Ⅶ]. However, the number of spherulites on both surfaces of the multilayer sheets [Ⅰ~Ⅲ,Ⅷ~Ⅹ] was clearly found to be smaller than that of the single layer sheets. Moreover, in the case of B/A/B sheets, a large decrease of the spherulites on the surface was observed. Judging from these results, the influence of shear stress was decreased, and as a result stress induced crystallization was suppressed.

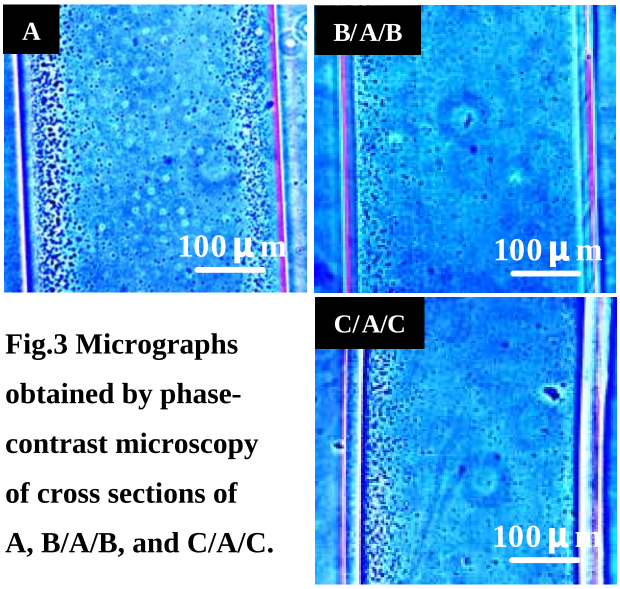

Fig.3 Micrographs obtained by phase-contrast microscopy of cross sections of A, B/A/B, and C/A/C.

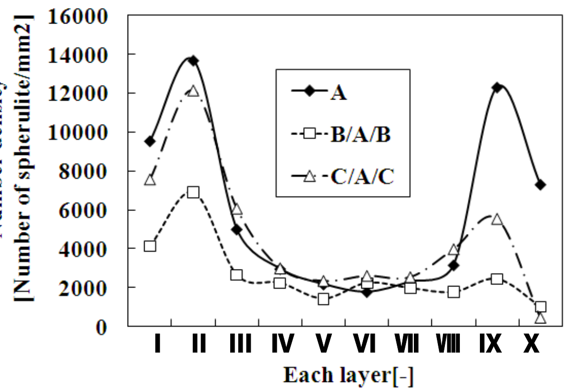

Fig.4 Distribution of spherulites

Fig.5 shows scattering patterns of WAXD of A, B/A/B and C/A/C. This graph shows that two broad peaks at around 2θ = 15 and 21°, which are known as characteristic features of mesomorphic phase of isotactic PP [3]. In previous studies, it was reported that mesomorphic phase was generated as an imperfect crystalline state that intermediates between amorphous and crystal when PP sheets were produced under quenching conditions. Therefore, mesomorphic phase peaks were observed. As a result, there were no differences in crystalline state between single-layer sheets and multilayer sheets.

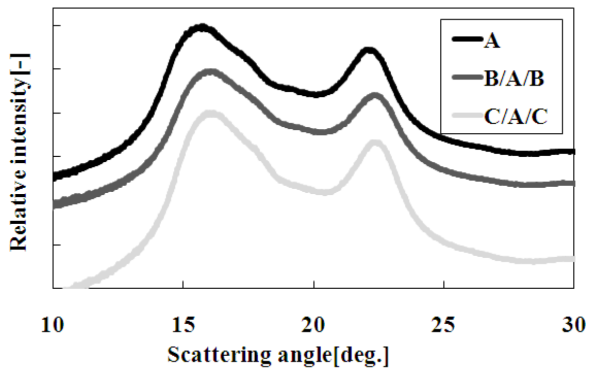

Fig.5 Relative intensity of PP samples by WAXD

4. Conclusion

To improve transparency of an isotactic PP sheet, important factors were investigated. It was found that a lot of spherulites generated mostly near extruded sheet surface, this was due to stress induced crystallization caused by shear stress. In order to reduce surface shear stress, a multilayer sheet was produced using a low viscosity resin on surface layer.

As a result, stress induced crystallization was suppressed. Even if spherulites size and crystalline state did not change substantially between single-layer sheets and multilayer sheets, number of spherulites on near surface of multilayer sheets decreased. therefore a higher transparency could be achieved.

Reference

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