INFLUENCE OF COOLING WATER TEMPERATURE ON FILM STRETCHABILITY, SUPERSTRUCTURE AND FILM PHYSICAL PROPERTIES OF RANDOM COPOLYPROPYLENE IN DOUBLE BUBBLE TUBULAR PROCESS

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ABSTRACT

It is commonly said that the molten resin of polyolefin extruded from die in the double bubble tubular process should be cooled by low temperature cooling water. This is because restraining the crystallization progress by low temperature cooling water makes it possible to obtain good stretchability and good physical properties of the stretched film. Therefore the cooling water temperature is customarily set low. However, the correlations among the cooling water temperature, the stretchability and the physical properties of stretched film have not been reported thoroughly.

This report discusses the influence of the cooling water temperature in the double bubble tubular process on the stretchability, the physical properties of the stretched film and the film superstructure of random copolypropylene (r-PP) which is commonly used for this process.

It was found that the stretchability was not influenced by the cooling water temperature in the double bubble tubular process, also the physical properties of the stretched film and the film superstructure of r-PP was slightly changed by the cooling water temperature. However such changes could be compensated by adjusting the preheating process temperature so that the stretching stress could be of the same value.
1. INTRODUCTION

The heat shrinkable film is widely used to package stationery, groceries and other goods. The heat shrinkable film produced by the double bubble tubular process has good physical properties, such as heat shrinkage and transparency. There are many materials used for heat shrinkable film such as polyethylene, polypropylene, polystyrene, polyamide 6 (PA6) and polyester. Polypropylene is the most widely used among all of them, because of the cost performance and the good stretchability. Manufacturing technologies have been investigated by many film producers over the past several decades. Many patents were registered and also technical papers were reported. The biaxially stretched film was investigated in terms of materials, superstructure, process and so on.

Superstructure change of stretched polyethylene and polypropylene were studied by Okajima and Tanaka et al /1-8/. The stretchability, processability and physical properties of linear low density polyethylene and random copolypropylene were published by Uehara et al. and Kanai et al. /9-12/. The processability of biaxially orientated PP film was investigated by Benkreira et al. /13/. The processability, scale-up rule and structure development of biaxially oriented PA6 film were reported by Takashige and Kanai et al. /14,15/. The processability and structure development of polyamide 612 (PA612) film were investigated by S. Rhee and J. L. White /16/. The heating process of BOPP was investigated by H. Benkreira /17/. Process system and theoretical analysis were written by M. Takashige and T. Kanai /18/. Process and film properties are written by J. L. White /19/. Many patents /20-25/ were applied to the manufacturing method of biaxially oriented film for various resins with the double bubble tubular process, because the technology of biaxially orientation is very important for the physical properties of stretched film.

It is commonly said that the cooling of extruded molten resin by low temperature cooling water in the double bubble tubular process gives good stretchability. However, in the factory production stage, it can be considered that WCF (Water Cooled Film) is not always sufficiently cooled in the case of seasonal factor namely summer season or increasing production speed, such as the out-put rate and increasing of line speed. Accordingly the crystallization progress of WCF can not be avoided.

In this research, the influence of cooling water temperature on film
stretchability, superstructure and film physical properties of r-PP in the double bubble tubular process was investigated by changing the cooling water temperature of molten resin, under the assumption that WCF was not cooled sufficiently in the case of summer season or high cooling water temperature due to energy saving. The process conditions for producing stretched film having constant quality were investigated in terms of cooling water temperature, the preheating temperature and stretching temperature even if the cooling water temperature is changed by the seasonal factors and so on.

2. EXPERIMENTAL

2.1. Materials

Some characteristics of random copolypropylene (r-PP) used in this research are shown in Table 1. The material properties were density of 0.91(g/cm³), melt flow index (MI) of 5.0g/10min at 230°C and ethylene cont. of 5wt%.

The final densities of WCF under various film temperatures are shown in Table 2. WCF was produced by double bubble tubular film machine under the condition cooling water temperature was 15°C.

<table>
<thead>
<tr>
<th>Material</th>
<th>r-PP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>0.91</td>
</tr>
<tr>
<td>Melt index (g/10min)</td>
<td>3.5</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>132</td>
</tr>
<tr>
<td>Ethylene content (%)</td>
<td>5.0</td>
</tr>
<tr>
<td>Mw (-) *1</td>
<td>315,000</td>
</tr>
<tr>
<td>Mn (-) *2</td>
<td>86,000</td>
</tr>
<tr>
<td>Mw/Mn (-) *3</td>
<td>3.66</td>
</tr>
</tbody>
</table>

*1 weight average molecular weight
*2 number average molecular weight
*3 polydispersity index
Influence of Cooling Water Temperature on Film Stretchability

Table 2
Final density of r-PP used in this study under various film temperatures

<table>
<thead>
<tr>
<th>Temperature(˚C)</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>108</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final density(g/cm³)</td>
<td>0.893</td>
<td>0.894</td>
<td>0.897</td>
<td>0.901</td>
<td>0.904</td>
</tr>
</tbody>
</table>

2.2. Installation of the Double Bubble Tubular Film Machine

The double bubble tubular film machine consists of two stages, as shown in Fig. 1. In the first stage, the molten resin extruded from the circular die is cooled and solidified during the water cooling process and folded by a set of nip rolls. The flattened film is re-inflated and passes the preheating process which is equipped with infrared heaters. The film heated during the preheating process is stretched biaxially in the following stretching process. The preheating process and the stretching process with infrared heaters are divided into several steps, and the surface temperature of an infrared heater in each step is controlled respectively. Stretched film cooled with a cooling air ring is folded by a set of nip rolls and cut at both edges and two films are wound respectively.

This machine had a φ65mm extruder which was used for both the outer and the inner layers (Modern Machinery Company), a φ50mm extruder which was used for the core layer (Modern Machinery Company) and a φ180mm annular die (Tomi Machinery Manufacturing Corporation). The film temperature at the stretch starting point was measured using the radiation thermometer (RAYRHP3SFWC, Raytek). A torque measurement instrument (Ono Sokki Co., SS201) was attached between the take-up nip roll and the driving motor, in order to measure the stretching force or stress from the stretching torque. The measuring method of the stretching torque was mentioned in the previous literature /9/.

The standard operating conditions in the double bubble tubular film machine of r-PP used in this study were listed in Table 3.

2.3. Installation of Laboratory Tenter Stretcher

The laboratory tenter stretcher is produced by Iwamoto Seisakusho, BIX-703. A film sample cut in square was set to the attachment and fixed all sides.
The film was heated for 2 minutes and then simultaneously stretched biaxially.

Table 3
The standard operating condition of the double bubble tubular film machine

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Preset value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Die temperature(°C)</td>
<td>200</td>
</tr>
<tr>
<td>Cooling water temperature(°C)</td>
<td>15</td>
</tr>
<tr>
<td>Take up roll 1(m/min)</td>
<td>4.8</td>
</tr>
<tr>
<td>Take up roll 2(m/min)</td>
<td>4.8</td>
</tr>
<tr>
<td>Stretch nip roll(m/min)</td>
<td>24.0</td>
</tr>
</tbody>
</table>

2.4. Film Preparation

2.4.1. Double Bubble tubular Film

There are three kinds of films in this study and each film is indicated in Fig. 1. WCF denotes water cooled film. WCF was sampled after the water cooling process. PHF denotes preheated film. PHF was sampled at the exit position of the preheating process or the stretching start position. PHF was immediately cooled with cold water. SF denotes stretched film. SF was sampled at the winder.

The MD and TD stretch ratios were 5. The thickness of WCF was 375 μm, and the film width was 235 mm. The SF’s thickness was 15 μm and the SF’s width was 1180 mm. The output rate was 46 kg/h. The line speed of WCF was 4.8m/min, and that of SF was 24.0 m/min. The stretching stress of the double bubble tubular film was measured by using a stretching torque meter. The stretching stress was changed by the stretching temperature which was controlled by the preheating equipment and the stretch heating equipment.

2.4.2. Laboratory Tenter Stretched Film

The laboratory tenter stretcher was used to investigate the stretchability of WCF produced by the double bubble tubular machine. The stretch ratios were set at 5 in the machine direction (MD) and 5 in the transverse direction (TD) respectively. The thickness of WCF was 375μm, and the stretched film thickness was 15μm. Pre-stretched film size is a 95mm square, but with
allowance for clipping, the effective stretching film size becomes a 70 mm square. The preheating time is 2 minutes, and the stretching speed is 30 mm/sec. The preheating time was determined by measuring the required time of reaching film temperature to set temperature. The correlation between the stretch ratio and the stretching force was measured after the preheating time passed 2 minutes.

2.5. Evaluation Methods of Material and Film Properties

2.5.1. Differential Scanning Calorimeter (DSC)

A Differential Scanning Calorimeter (Seiko Instruments Inc. EXSTAR DSC6200R) was used to detect the memory of resin having previous thermal history. The amount of 10±0.5mg for each sample was placed in a DSC pan. The heating rate was 10°C /min.

2.5.2. Film Density Measurement

The film density at each step was measured by a fixed volume expansion method (SHIMADZU Accupic1330). The measurement principle is based on the evaluation of the sample volume by measuring the pressure variation of charged gas upon the change in the volume of a chamber system filled with the sample. The amount of about 4.5g for WCF and PHF, and about 2.0g for SF was placed in a cell.

2.5.3. Evaluation Methods of Film Properties

The stretching strength, elongation and Young’s modulus were based on ASTM D882. The tear strength and impact strength were based on ASTM 1922 and ASTM D3420 respectively. The haze was based on ASTM D1003 (Murakami Color Research Laboratory. HM-150). The Gloss was based on ASTM D2457 (Murakami Color Research Laboratory. GM-26PRO). The shrinkage was based on ASTM D2732. These physical properties were used as average values.

2.5.4. Light Scattering

The analysis of the superstructure of the film sample was conducted by the polarized light scattering technique /26, 27/. A 15mW He-Ne gas laser (NEO-15MS, Nihon Kagaku Engineering Co., Ltd.) was used as the polarized monochromatic (λ=632.8nm) light source. The polarized incident light
irradiates to the sample, and scattered light passes through an analyzer placed behind the sample. A light scattering pattern was recorded on a photographic film with a 1/250 s exposure time, using Hv polarization condition where the polarization of the analyzer and of the incident light was perpendicular.

The measurement of the spherulite radius was based on the light scattering theory /26/ for perfect spherulites which gives

\[ R = \frac{4.09 \lambda}{4\pi \sin \left( \frac{\theta_m}{2} \right)} \]

(1)

where \( R \) is the spherulite radius, \( \lambda \) is the wavelength of the light in medium, \( \theta_m \) is the scattering angle corresponding to the maximum scattered light intensity.

2.5.5. X-ray Crystal Structure Analysis

Crystallinity and the period of the lamella stacking (long period) were calculated using the wide angle x-ray scattering (WAXS) method and small angle x-ray scattering (SAXS) method, respectively. The WAXS analysis was based on the Ruland methods /28/. X-ray diffraction profiles were obtained by a camera system connected to an imaging plate (IPR-420, Bruker AXS K. K.) using a graphite monochromatized Cu-K\( \alpha \) radiation (1.542Å) from an X-ray generator (ultraX 18, Rigaku Co. Ltd). The distance from the sample to the detector was 7 cm for WAXS and 110 cm for SAXS.

2.5.6. Thickness uniformity measurement

Film thickness was measured using the thickness gauge (Mitutoyo IDF-112). The thickness of WCF was measured at 10 cm intervals in the MD and at 1 cm intervals in the TD. The thickness of SF was measured at 50 cm intervals in the MD and at 5 cm interval in the TD. In order to evaluate the thickness uniformity, standard deviation \( \sigma \) was used.

3. RESULTS & DISCUSSION

3.1. Stretching Stress Change and Stretchability

The relationship between cooling water temperature and stretching stress is shown in Table 4. The data were obtained for samples 1, 2, 4 and 6 which means the cooling water temperature of 15°C, 25°C, 35°C and 52°C respectively. When the cooling water temperature increased from 15°C to 52°C, the stretching stress decreased slightly from 33.0 MPa to 31.0 MPa.
# Influence of Cooling Water Temperature on Film Stretchability

## Table 4
Production conditions of the double bubble tubular films and SF’s properties

<table>
<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooling water temperature (˚C)</td>
<td>15</td>
<td>25</td>
<td>35</td>
<td>52</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Film temperature of WCF (˚C)</td>
<td>16</td>
<td>24</td>
<td>34</td>
<td>51</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Film temperature at the entrance position of the preheating process (˚C)</td>
<td>22</td>
<td>24</td>
<td>25</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
</tr>
<tr>
<td>Average preset temperature of the preheating process (˚C)</td>
<td>214</td>
<td>214</td>
<td>207</td>
<td>214</td>
<td>203</td>
<td>214</td>
<td>200</td>
</tr>
<tr>
<td>Average preset temperature of the stretching process (˚C)</td>
<td>310</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Film temperature at the exit position of the preheating process (˚C)</td>
<td>107</td>
<td>108</td>
<td>108</td>
<td>107</td>
<td>106</td>
<td>107</td>
<td>106</td>
</tr>
<tr>
<td>Sample condition (Stretching stress, MPa)</td>
<td>33.0</td>
<td>31.8</td>
<td>33.2</td>
<td>31.6</td>
<td>33.7</td>
<td>31.0</td>
<td>33.5</td>
</tr>
<tr>
<td>Stretching strength (MPa)</td>
<td>MD/TD</td>
<td>190/185</td>
<td>182/185</td>
<td>180/188</td>
<td>190/180</td>
<td>188/190</td>
<td>185/195</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>MD/TD</td>
<td>118/130</td>
<td>120/136</td>
<td>115/125</td>
<td>125/128</td>
<td>120/125</td>
<td>123/136</td>
</tr>
<tr>
<td>Young’s modulus (MPa)</td>
<td>MD/TD</td>
<td>750/790</td>
<td>710/740</td>
<td>750/800</td>
<td>770/820</td>
<td>720/750</td>
<td>760/720</td>
</tr>
<tr>
<td>Tear strength (mN)</td>
<td>MD/TD</td>
<td>57/55</td>
<td>59/57</td>
<td>55/57</td>
<td>54/58</td>
<td>56/54</td>
<td>59/56</td>
</tr>
</tbody>
</table>
Table 4 (continued)

<table>
<thead>
<tr>
<th></th>
<th>Impact strength (J)</th>
<th>Haze (%)</th>
<th>Gloss (%)</th>
<th>Shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.65</td>
<td>0.57</td>
<td>0.58</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>151</td>
<td>151</td>
<td>150</td>
</tr>
<tr>
<td>90°C</td>
<td>20/19</td>
<td>22/19</td>
<td>21/19</td>
<td>20/19</td>
</tr>
<tr>
<td>100°C</td>
<td>33/29</td>
<td>32/28</td>
<td>31/28</td>
<td>31/26</td>
</tr>
<tr>
<td>110°C</td>
<td>44/42</td>
<td>45/42</td>
<td>44/42</td>
<td>45/41</td>
</tr>
<tr>
<td>120°C</td>
<td>60/59</td>
<td>60/59</td>
<td>61/59</td>
<td>59/57</td>
</tr>
<tr>
<td>WCF</td>
<td>0.83</td>
<td>1.13</td>
<td>1.22</td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td>110.3</td>
<td>113.1</td>
<td>114.6</td>
<td>119.2</td>
</tr>
<tr>
<td></td>
<td>43.8</td>
<td>43.4</td>
<td>45.5</td>
<td>52.3</td>
</tr>
<tr>
<td>PHF</td>
<td>0.93</td>
<td>1.05</td>
<td>1.13</td>
<td>1.45</td>
</tr>
<tr>
<td></td>
<td>140.1</td>
<td>140.1</td>
<td>140.1</td>
<td>140.1</td>
</tr>
<tr>
<td></td>
<td>57.1</td>
<td>55.6</td>
<td>55.2</td>
<td>56.9</td>
</tr>
<tr>
<td>SF</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>135.7</td>
<td>131.7</td>
<td>131.7</td>
<td>133.7</td>
</tr>
<tr>
<td></td>
<td>40.6</td>
<td>39.7</td>
<td>39.8</td>
<td>38.8</td>
</tr>
</tbody>
</table>

*1 Film temperature of WCF denotes the outer surface temperature of the flattened tube and was measured just after the first pinch roll.

*2,3 Average preset temperature denotes the average value of the preset temperature in each steps divided into several steps.
One of the factors to decrease the stretching stress with increasing cooling water temperature was considered to be the difference of the superstructure and the film stretching temperature. The differences of the superstructure are mentioned in section 3.4. The other factor was considered to be the difference of the film temperature, as shown in Table 4. The influence on the surface film temperature at exit position of the preheating process was not observed, but the film temperature at the entrance position of the preheating process reflected the cooling water temperature. Therefore changing the cooling water temperature may influence the average stretching temperature and then the stretching stress.

The stretchability of double bubble tubular film under various cooling water temperatures was investigated as shown in Table 5 An evaluation method of stretchability refers to the previous reports /9-12/. Stretchability was evaluated using each stable stretching stress range under various cooling water temperatures. The stable stretching stress range was from about 13MPa to 34MPa at all cooling water temperatures. Hence it was clarified that the stretchability was not influenced even if the cooling water temperature was changed.

Table 5
The stretchability of the double bubble tubular film under various cooling water temperature

<table>
<thead>
<tr>
<th>Cooling water temperature (˚C)</th>
<th>15</th>
<th>25</th>
<th>35</th>
<th>52</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stable stretching stress range (MPa)</td>
<td>min.</td>
<td>12.3</td>
<td>12.8</td>
<td>13.0</td>
</tr>
<tr>
<td></td>
<td>max.</td>
<td>33.4</td>
<td>33.7</td>
<td>34.1</td>
</tr>
<tr>
<td></td>
<td>R(max.-min.)</td>
<td>21.1</td>
<td>20.9</td>
<td>21.1</td>
</tr>
</tbody>
</table>

In addition, for reference, the stress-strain curves of WCF produced under various cooling water temperatures are shown in Fig. 2. The stretching stresses at the yield point and the maximum strain point were different in cooling water temperatures. It is considered that these phenomena result from the different crystal condition of WCF.

3.2. Physical Properties of Stretched Film

The important physical properties for shrink film, such as tensile strength,
elongation, Young’s modulus, tear strength, impact strength, optics and shrinkage were measured. The process conditions of sample 1 shown in Table 4 were standard process conditions in this study and compared with the other process conditions, such as SF1 and SF2. SF1 was sampled under the same preheating conditions with sample 1, so the stretching stress was changed by the cooling water temperature. The physical properties of SF1 are samples 2, 4 and 6 in Table 4, and shown in Fig. 3. SF2 was sampled so that stretching stress might be compensated by adjusting the preset temperature of the preheating process to the same stretching stress. Those of SF2 are samples 3, 5 and 7 in Table 4, and shown in Fig. 4. Most of the physical properties, such as stretching strength, elongation, Young’s modulus, optics and shrinkage, in both SF1 and SF2 were not influenced by the cooling water temperature. The superstructure of SF1 and SF2 were approximately the same from the results of WAXS and SAXS explained in section 3.4. Only the impact strength slightly decreases with increasing cooling water temperature, as shown in Fig. 3-e) and Fig. 4-e). The voids formed in the molecular structure of SF by the stretching force were observed by SAXS patterns as described later. It was considered that one of the factors to decrease the impact strength was the amount of a void increased with increasing cooling water temperature. However, clear data regarding the difference in the amount of a void could not be obtained, but the decreasing of the impact strength was minimal and there is no problem in practical use.

The WCF under various cooling water temperatures was stretched by the laboratory tenter stretcher as a reference. The results listed in Table 6 and Fig. 5 show that the shrinkage in MD is slightly lower when WCF is produced under high temperature cooling water.

**Table 6**

Shrinkage of SF stretched at lowest stretching temperature using laboratory tenter stretcher

<table>
<thead>
<tr>
<th>Cooling water temperature (°C)</th>
<th>15</th>
<th>25</th>
<th>35</th>
<th>52</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shrinkage (%) MD*TD</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90°C</td>
<td>24  / 24</td>
<td>25  / 24</td>
<td>24  / 23</td>
<td>22  / 23</td>
</tr>
<tr>
<td>100°C</td>
<td>35  / 34</td>
<td>35  / 34</td>
<td>33  / 34</td>
<td>33  / 33</td>
</tr>
<tr>
<td>110°C</td>
<td>48  / 48</td>
<td>48  / 47</td>
<td>46  / 46</td>
<td>45  / 46</td>
</tr>
<tr>
<td>120°C</td>
<td>62  / 60</td>
<td>61  / 61</td>
<td>60  / 59</td>
<td>60  / 60</td>
</tr>
</tbody>
</table>
The film physical properties could be controlled by the preheating temperature so that the stretching stress could be of the same value and then almost the same results for the stretchability and physical properties of film were obtained. It is found that it is possible to produce SF having approximately the same physical properties, even if the cooling water temperature is changed.

3.3. Thickness Uniformity of WCF & SF

The influence of the cooling water temperature on thickness uniformity of WCF and SF was investigated. Fig. 6 shows standard deviations of WCF and SF under various cooling water temperatures. The thickness uniformity of WCF was measured as shown in Fig. 6-a). The standard deviation of WCF under various cooling water temperatures fluctuated between 4 and 6. That of SF1 under various cooling water temperatures fluctuated between 0.5 and 1, as shown in Fig. 6-b). Also that of SF2 fluctuated between 0.5 and 1, as shown in Fig. 6-c).

High cooling water temperature did not debase the thickness uniformity of WCF and SF. Hence it is possible to produce a stretched film having constant thickness uniformity, when the cooling water temperature is changed.

3.4. Film Material Properties Change and Film Superstructure Change in Each Processing Conditions

3.4.1. Water Cooled Film (WCF)

This section deals with the relationship between cooling water temperature and superstructure of WCF.

Fig. 7 shows the relationship between film density and cooling water temperature. It was found that the density of WCF(●) increases as cooling water temperature increases.

Fig. 8 shows the relationship between film haze and cooling water temperature, because there is the relationship between density and haze. The haze of WCF(●) showed the same tendency as density, namely haze and density increased as cooling water temperature increased.

Fig. 9 shows the relationship between crystallization energy of film and cooling water temperature. The crystallization energy of WCF(●) increased
as cooling water temperature increased. As a result of the above data, it was found that the crystallization of WCF progressed with increasing the cooling water temperature. These phenomena were caused by a difference in the nucleation process of crystalline polymer.

The Hv light scattering patterns of WCF under various cooling water temperatures are shown in Fig. 10. These SALS patterns showed a clover leaf pattern at all cooling water temperatures, and indicated the typical scattering from spherulite. As a result of calculating the spherulite radius by using eq. 1, it was found that the spherulite size became larger with increasing the cooling water temperature.

Fig. 11 shows the relationship between film crystallinity and cooling water temperature. It was found that the crystallinity of WCF calculated from the wave pattern of WAXS intensity distribution increased as the cooling water temperature increased.

Fig. 12-a) shows the relationship between long period of crystalline lamella and cooling water temperature. The long period of WCF estimated from SAXS intensity distribution increased as the cooling water temperature increased.

It is thought that the difference in superstructure influenced by the cooling water temperature is caused by the difference in a crystallization mechanism such as a nucleation rate and subsequent crystal growth process.

In the case of the crystallization under different cooling water temperatures, the following mechanism can be considered. When the cooling water temperature is low, the spherulites become small. Because the nucleation rate is fast, a lot of spherulites are formed and they cannot grow large. On the contrary, when the cooling water temperature is high, the nucleation rate decreases and spherulites easily grow larger.

Fig. 13 and 15 show the photos of crystalline orientation in WCF, and they were investigated by WAXS and SAXS. As a result, the difference of crystalline orientation in each plane was not observed.

Hence it was clarified that the cooling water temperature influenced the superstructure, such as the crystallinity, the long period of crystalline lamella and spherulite size of WCF.

3.4.2. Preheated Film (PHF)

As described in section 3.2, it was clarified that the physical properties of SF were almost the same, even if the stretching stress changed due to the
difference of the cooling water temperature or the stretching stress was compensated by adjusting the preset temperature of the preheating process to constant stretching stress. However, as described in section 3.4.1, the superstructure of WCF was different when the cooling water temperature differed. The superstructure of PHF, which passed the preheating process, was important. In this section, the superstructure change from WCF to PHF is described when the cooling water temperature is different.

The relationship between film density of PHF obtained by heating WCF in the following preheating process and cooling water temperature is shown in Fig. 7. There are 2 kinds of PHF. PHF1 (▲) is the film obtained by heating WCF in the preheating process under the same preset temperature. PHF2 (△) is the film obtained by heating WCF in the preheating process under a different preset temperature. The preset temperature of the preheating process was adjusted so that the preheating conditions of PHF2 would be the same as the stretching stress of SF in the case of the cooling water temperature being 15°C. Both densities of PHF became higher than WCF by passing the preheating process and the differences in the density of PHF1 and PHF2 were negligible.

Haze of PHF could not be measured, because the PHF inside of the sample tube was wavy.

The relationship between the crystallization energy of PHF1(▲) and PHF2(△) and cooling water temperature is shown in Fig. 9. The crystallization progress of WCF was restrained by making the cooling water temperature low. However, the crystallinity restrained at the water cooling process progressed, because WCF was re-heated at the preheating process. The crystallization energy of WCF was different when the cooling water temperature was different, but that of PHF was higher than WCF and became the same value, as shown in Fig. 9. It is suggested that it is not necessary to set the cooling water temperature low, because the restrained crystallinity at the water cooling process progressed and reached almost the same level at the preheating process exit position.

The Hv light scattering patterns of PHF are shown in Fig. 10. The spherulite radius of either PHF1(No. 2, 4 and 6) or PHF2(No. 3, 5 and 7) increased slightly due to the heat treatment during the preheating process as compared with WCF. WAXS data show that the crystallinity of both PHF1(▲) and PHF2(△) increased by the heat treatment during the preheating process and the crystallinity values became almost equal.
regardless of the different cooling water temperatures of WCF as shown in Fig. 11. As shown in Fig. 7, the density difference between PHF1 and PHF2 was almost same. Also difference in the crystallinity and long period were not observed. The above results mean that the superstructure change by heat treatment during the preheating process happens mainly inside the crystal lamella.

In order to clarify the structure change inside the crystal lamella, the change of SAXS intensity distribution was analyzed. Fig. 12-b), c) and d) show SAXS intensity distributions of WCF, PHF1 and PHF2 under various cooling water temperatures. When Fig. 12-c) and d) were compared to Fig. 12-b), it was found that SAXS intensity increased due to preheating. This factor of increasing SAXS intensity can be explained by the theory based on the pseudo two phases model of lamella structure as shown in Fig. 17. Generally, a lamella structure of crystalline polymer is constructed from a crystal phase, amorphous phase and the interface region of both. Fig. 17-(a) presents the pattern diagram of crystalline polymer’s lamella structure, and its electron density profile is shown in Fig. 17-(b). SAXS intensity based on this pattern diagram can be written, with the use of the volume fraction of crystal phase and amorphous phase $\Phi_c$ or $\Phi_a$ and electron density $\rho_c$ or $\rho_a$, as follows.

$$I \propto (\rho_c - \rho_a)^2 (\Phi_c \cdot \Phi_a - \text{St} / \text{S/V})$$  \hspace{1cm} (2)

where $I$ is SAXS intensity, $t$ is interface thickness and S/V is specific surface area /28/. If based on this model, it is thought that the increasing of SAXS intensity by heat treatment during the preheating process is caused by decreasing interface thickness as shown in Fig. 17-(c). In other words, a rearrangement of molecular chains happens due to the heat treatment of crystal lamella, and the interface phase transfer to crystal phase by the quenching of disarray at interface region. The SAXS intensity of PHF1 was almost the same in spite of the different cooling water temperature, as shown in Fig. 12-c). That of PHF2 was almost the same too, and that of PHF1 and PHF2 were almost the same in spite of the different processing conditions, as shown in Fig. 12-d). It is considered that the processing temperature during the preheating process is hardly different, even if the cooling water temperature differs or the preset temperature of the preheating process is adjusted so as to compensate for the stretching stress. The difference of crystallinity in the water cooling process is compensated in the preheating
process, and the difference of the superstructure becomes smaller.

The orientation of crystal in PHF was also investigated using WAXS and SAXS, but the orientation of crystal in each plane was not observed, as shown in Fig. 13 and 15.

### 3.4.3. Stretched Film (SF)

The relationship between film density of SF and cooling water temperature is shown in Fig. 7. SF1(■) was processed under different stretching stress, since the cooling water temperature was different. SF2(□) was the film with which the stretching stress of SF was controlled to keep constant using a preset temperature adjustment of the preheating process. The stretching stress of SF was compensated so as to be the same as the stretching stress in the case of the cooling water temperature being 15°C. As shown in Fig. 7, the density of SF was not influenced, even if the stretching stress was changed due to the difference of the cooling water temperature.

A correlation between haze of SF and cooling water temperature is shown in Fig. 8. Both the hazes of SF1(■) and SF2(□) were not influenced by the cooling water temperature.

The Hv light scattering patterns of SF could not be observed, as shown in Fig. 10. This phenomenon indicates that the spherulite was broken up by stretching force. As shown in Fig.12-e) and f), a drastic reduction of SAXS intensity in both SF shows that crystal lamella is broken up and segmentalized. However, the SAXS intensity of SF1 and SF2 was almost the same despite the differences of cooling water temperature or the stretching stress. This was because the change of stretching stress was very small. Hence the crystallinities of SF1(■) and SF2(□) calculated from WAXS intensity distribution were lower than those of PHF(▲ or △) due to the broken crystalline, as shown in Fig. 11. Also the crystallinity of SF1 and SF2 became almost the same. As shown in Figs. 13 and 15, SF was oriented strongly in the MD and TD from results of the end view, the edge one and the through one. As shown in Figs. 14 and 16, the orientation of crystal in SF was almost the same, even if the cooling water temperature was different or the stretching stress was different within this range.

The spherulite size of WCF or PHF was different due to the different cooling water temperature. But the superstructure of SF was hardly different due to the cooling water temperature, because the crystal was broken even if the cooling water temperature was different. Hence it was considered that the
differences of SF’s physical properties were hardly observed.

3.5. Difference and Change of Superstructure

The influence of the cooling water temperature on the superstructure at each processing process is listed in Table 4. The differences of the growth of the spherulite and the crystal lamella in WCF were observed. The spherulite size, the crystallinity and the crystal lamella increased as the cooling water temperature increased. In the following preheating process, as the crystallization progressed by heat treatment, the crystallinity and the long period increased and reached constant values irrespective of the cooling water temperature. The spherulite size hardly changed in the preheating process, because the growth of spherulite was completed in the WCF production process. In the following stretching process, the difference of superstructure in SF was hardly observed, because the spherulite, which was influenced by cooling water temperature, was broken up. Finally the stretched film has the same superstructure and does not depend on the cooling water temperature.

4. CONCLUSIONS

The influence of cooling water temperature on the superstructure, the film physical properties, stretchability and thickness uniformity was investigated. As a result, the following results for r-PP which is one of the most popular resins as a shrink film, were obtained.

1. When the cooling water temperature increases, the stretching stress decreases slightly and the physical properties of stretched film (SF) were slightly influenced. If the stretching stress controllable by changing the preheating set temperature was set to the same value, the same film physical properties and stretchability were obtained.

2. In terms of the superstructure, the spherulite size, the long period and the crystallinity increases with increasing the cooling water temperature. The crystallinity and the long period increases during the preheating process and reach almost the same values at the exit point of the preheating process. The spherulite size hardly changes during the preheating process. But the spherulite is broken up by the stretching stress during the
3. Even though WCF shows different crystallinity, spherulite size and long period due to the cooling water temperature, SF produced under the similar stretching stress has nearly identical superstructure. The superstructure of SF is hardly influenced by the cooling water temperature.

4. From these results, the stretched film which has almost same film physical properties can be produced by controlling the stretching stress even if the cooling water temperature is changed by the seasonal factors and so on.

5. REFERENCES


Fig. 1: Schematic drawing of the double bubble tubular process

Fig. 2: The stress-strain curve stretched at 90°C

Fig. 3: The physical properties of SF with which stretching stress was not adjusted, under various cooling water temperature in double bubble tubular process a) stretching strength, b) elongation, c) Young’s modulus, d) tear strength, e) impact strength, f) optics, g) MD shrinkage, h) TD shrinkage

Fig. 4: The physical properties of SF with which stretching stress was adjusted, under various cooling water temperature in double bubble tubular process a) stretching strength, b) elongation, c) Young’s modulus, d) tear strength, e) impact strength, f) optics, g) MD shrinkage, h) TD shrinkage

Fig. 5: The shrinkage of stretched film using the laboratory tenter stretcher a) MD, b) TD

Fig. 6: Thickness uniformity of films in the double bubble tubular process a) WCF, b) SF by which stretching stress was not controlled, c) SF by which stretching stress was controlled
Fig. 7: Correlation between the cooling water temperature and the density
※ PHF1 & SF1: Pre-heating process temperature was not adjusted.
※ PHF2 & SF2: Pre-heating process temperature was adjusted

Fig. 8: Correlation between cooling water temperature and haze
※ SF1: Pre-heating process temperature was not adjusted.
※ SF2: Pre-heating process temperature was adjusted.

Fig. 9: The enthalpy of crystallization
※ PHF1: Pre-heating process temperature is not adjusted.
※ PHF2: Pre-heating process temperature is adjusted

Fig. 10: SALS patterns and the spherulite size of each film in the double bubble tubular process.

Fig. 11: Film crystallinity by WAXS analysis.

Fig. 12: SAXS analysis: a) long-period, b) SAXS intensity of WCF, c) SAXS intensity of PHF-1, d) SAXS intensity of PHF-2, e) SAXS intensity of SF-1, f) SAXS intensity of SF-2.

Fig. 13: WAXS diffraction photographs of WCF, PHF and SF under the condition that cooling water temperature is 15°C.

Fig. 14: WAXS diffraction photographs of SF

Fig. 15: SAXS diffraction photographs of WCF, PHF and SF under the condition that cooling water temperature is 15°C.

Fig. 16: SAXS diffraction photographs of SF

Fig. 17: Pseudo-two phase structure MODEL.
Fig. 3: The physical properties of SF with which stretching stress was not adjusted, under various cooling water temperature in double bubble tubular process a) stretching strength, b) elongation, c) Young’s modulus, d) tear strength, e) impact strength, f) optics, g) MD shrinkage, h) TD shrinkage

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Fig. 6: Thickness uniformity of films in the double bubble tubular process; a) WCF, b) SF by which stretching stress was not controlled, c) SF by which stretching stress was controlled

Fig. 7: Correlation between the cooling water temperature and the density ※ PHF1 & SF1: Pre-heating process temperature wasn’t adjusted. ※ PHF2 & SF2: Pre-heating process temperature was adjusted

Fig. 8: Correlation between cooling water temperature and haze; ※ SF1: Pre-heating process temperature was not adjusted. ※ SF2: Pre-heating process temperature was adjusted.

Fig. 9: The enthalpy of crystallization; ※ PHF1: Pre-heating process temperature is not adjusted. ※ PHF2: Pre-heating process temperature is adjusted

Fig. 10: SALS patterns and the spherulite size of each film in the double bubble tubular process.

Fig. 12: SAXS analysis: a) long-period, b) SAXS intensity of WCF, c) SAXS intensity of PHF-1, d) SAXS intensity of PHF-2, e) SAXS intensity of SF-1, f) SAXS intensity of SF-2.

Fig. 13: WAXS diffraction photographs of WCF, PHF and SF under the condition that cooling water temperature is 15°C.

Fig. 14: WAXS diffraction photographs of SF

Fig. 15: SAXS diffraction photographs of WCF, PHF and SF under the condition that cooling water temperature is 15°C.