The evaluation of stretchability and its applications for biaxially oriented polypropylene film

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Abstract
In recent years, plastic film is essential in our daily lives. Among them, polypropylene has good physical properties, for example, tensile strength, impact strength, and transparency. Recently, it was found that the stretchability of polypropylene (PP) is improved by blending a small amount of low modulus polypropylene (LMPP) which is a low tacticity polypropylene. The purpose of this research was to investigate the effect of blending LMPP, which has different characteristic of resin such as tacticity and molecular weight, on PP and to study the mechanism of the structure formation in a biaxial stretching process. The blending of LMPP to PP reduces the spherulite size and increases the thickness of the amorphous phase in the lamella without changing the thickness of the crystal phase, namely the melting temperature. LMPP blends also reduced the yield stress during the stretching process and increased the stress buildup ratio. For these reasons, it improved film thickness uniformity of biaxially stretched film and reduced film break during the high production line. Furthermore, as the stretchable temperature window was widened to the low-temperature side, the thickness uniformity was improved in the wide stretchable temperature. As a result, improving the stretchability and the film thickness uniformity of PP were achieved by blending LMPP to PP.

KEYWORDS
biaxial stretching, crystallinity, low modulus PP, stretchable temperature width, tacticity

1 | INTRODUCTION

Polypropylene (PP) is widely used for the biaxially oriented film using the sequentially biaxial-oriented process and the supply capacity in 2014 reached over 10 million tons/year.[1] This film is mainly used in the field of food packaging and industrial usage because of the high transparency, high physical properties, heat resistance, and chemical resistance, etc. According to the increase of the demand, high production speed[1] or ultra thin film such as capacitor film[2] has been required. In the case of high-speed production, as high stress is applied during the biaxially oriented process, the film breaks and the problem of uneven film thickness occurs.

To investigate the mechanism of film break and the problem of uneven film thickness,[3] the in situ observation of the structure development during the stretching process such as birefringence, light scattering, small angle X-ray scattering (SAXS), and stress–strain buildup was studied using the equipment of the uniaxial stretching.[4,5] This in situ stretching evaluation method could observe the structure development during the uniaxial stretching at any temperature. From this experiment, stretchability, thickness uniformity, spherulite size, and molecular orientation could be obtained at the same time. The comparison of high tacticity PP with low tacticity PP suggested that high tacticity PP had a high stretching stress yield value at the initial strain, a large spherulite size in the base sheet, and high crystallinity. The stretching worsened stretching uniformity and the birefringence pattern, compared with low tacticity PP. Most of the spherulites were broken up at the yield point and then disappeared by further stretching. Even though there was very small amount of the...
sample, it was possible to know the potential of the orientation, stretchability, thickness uniformity, and spherulite deformation during the uniaxial stretching process.

However, most of stretching film is produced by the biaxial stretching machine, not the uniaxial machine. There is little research which reports on the biaxial stretching with the observation of the orientation, stretchability, thickness uniformity, and spherulite deformation during the biaxial stretching process, even though the biaxial stretched film is widely used all over the world.

For these reasons, the in situ stretching evaluation method is required to observe the structure development during the biaxial stretching which can obtain stretchability, thickness uniformity, spherulite size, and three-dimensional molecular orientations.\(^6\)

Furthermore, we also tried to improve the stretchability of PP using polymer blending. There are many papers which described polypropylene or polyethylene blends to control spherulite structure, crystallinity, rheology, and so on.\(^7\)–\(^11\) We concentrated on the crystallization control of PP which was very important for stretchability. We found that low tacticity polypropylene (LMPP)\(^12\) which has low crystallinity and low melt temperature could control the crystallization speed of polypropylene.

Our previous research reported that the addition of LMPP to PP which reduced the size of spherulites, crystallinity and decreased the yield value of the stress–strain curve gave better stretchability from the results of uniaxial stretching.\(^4\)\(^,\)\(^5\)

The purpose of this research was to observe the structure development and to investigate the mechanism of stretchability. Both the stress–strain curve and the super structure measurements such as spherulite size and three-dimensional molecular orientations during the biaxial stretching with a small amount of various resins and then to improve the stretchability of PP by adding suitable LMPP were studied.

2 | EXPERIMENT

2.1 | Samples

The samples which were used are listed in Table 1. Sample A which is isotactic polypropylene for biaxially oriented PP grade is produced by Prime Polymer. L1, L2, and L3 are LMPP grades, and L1 is a standard grade of LMPP and L2 is a lower tacticity and has a lower melting temperature (\(T_m\)) than L1. L3 has a higher molecular weight than L1.

Our previous research showed that as 5 wt % LMPP blended to PP had the best stretchability, various 5 wt % blended samples were prepared. Iso-polypropylenes A blended with 5 wt% of various LMPP, namely L1, L2, and L3, was formed into 500-μm sheets of A/L1, A/L2, and A/L3, respectively under the resin temperature of 250°C at the die exit and the chill roll temperature of 30°C. The samples were cut into 58 mm x 58 mm square sizes.

2.2 | Experimental equipment

The biaxial stretcher SDR-527K which was designed by our group and made by Etoh Corporation was used. The schematic view of this equipment is shown in Figure 1. There are three clips on each side and four clips on each corner, totaling 16 clips. Various data could be obtained at the same time such as stress–strain curve (S–S), refractive indexes in three directions, phase difference distribution, and light scattering data. The stretching conditions are shown in Table 2.

The crystallization speed was measured using the Flash DSC 1 produced by Mettler Toledo under the cooling conditions from melt temperature to solid temperature of 25°C at the speed of 2,000°C/s. Figure 2 shows the crystal growth rate at 25°C of PP and PP/LMPP blend. Blending of LMPP to PP reduced the crystallization speed of PP.

The thickness standard deviation was obtained by measuring 60 points in biaxially stretched film. The crystallinity was calculated by the following equation.

\[
\text{Crystallinity} = \frac{\Delta H}{100\% \text{ crystallinity}}
\]

\[
\Delta H \text{ of PP (} = 209 \text{ J/g)}
\]

The spherulite diameter was measured by light scattering and then was calculated by

\[
U_{\text{max}} = \frac{4.09}{[(4\pi/\lambda) \sin (\theta_{\text{SALS, max}}/2)]}
\]

where \(U_{\text{max}}\) is the average spherulite radius [μm] and \(\theta_{\text{SALS, max}}\) is the maximum scattering angle showing the maximum value 45° to the polarizing direction. The phase difference distribution was measured at 141 points, and then, standard deviation was calculated.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resin</th>
<th>mmmm</th>
<th>MFR</th>
<th>(M_w)</th>
<th>(M_w/M_n)</th>
<th>(T_m) [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>i-PP</td>
<td>90</td>
<td>3</td>
<td>3.8 × 10^5</td>
<td>4.2</td>
<td>161</td>
</tr>
<tr>
<td>L1</td>
<td>LMPP</td>
<td>–</td>
<td>60</td>
<td>1.3 × 10^5</td>
<td>2.2</td>
<td>70</td>
</tr>
<tr>
<td>L2</td>
<td>LMPP</td>
<td>–</td>
<td>60</td>
<td>1.3 × 10^5</td>
<td>2.2</td>
<td>60</td>
</tr>
<tr>
<td>L3</td>
<td>LMPP</td>
<td>–</td>
<td>7</td>
<td>2.3 × 10^5</td>
<td>2.2</td>
<td>70</td>
</tr>
</tbody>
</table>

TABLE 1 Experimental samples
2.3 | Stress–strain curve during the stretching

Figure 3 shows an image pattern of the stress–strain curve during the sequentially biaxial stretching. As the tenter process is usually used in the TD stretching, the final thickness uniformity is considered to be determined in TD stretching. From the previous research, good and poor stretchable patterns were obtained by the stress–strain curve.\(^6\) The stress pattern has the high yield point at the initial stretching stage and then reduces stress shows poor film thickness uniformity.

On the contrary, the stress pattern which has the low yield point at the initial stretching stage and then increasing stress shows good film thickness uniformity. The reduction of yield value is important to obtain good thickness uniformity.\(^2\)

3 | RESULTS AND DISCUSSION

3.1 | Stress–strain curve

Figure 4 shows stress–total stretching ratio (MD stretching ratio x TD stretching ratio) curves for various samples. Sample A has a high yield value and then the stress decreases after the yield point passes. This means the necking deformation during the stretching process occurs and is undesirable for thickness uniformity. The A/L1 and A/L2 which have much lower yield values than PP A show strain hardening. Although A/L3 shows almost the same yield value as PP A, the stress of A/L3 increases rapidly in the high stretching ratio field. L3 is high molecular weight LMPP and has molecular entanglement in the amorphous phase during the stretching process.

From these results, it is expected that LMPP blended samples create better film thickness uniformity than PP A sample, and furthermore, the film break during the stretching process can be reduced.

3.2 | Film thickness uniformity of biaxially oriented film

Table 3 shows the yield value \(\sigma_{\text{yield}}\), maximum stress \(\sigma_{\text{max}}\), stress buildup ratio \(\sigma_{\text{max}}/\sigma_{\text{yield}}\), and standard deviation of film thickness \(\sigma_t\) when the samples are stretched in TD at the stretching temperature of 159°C. The thickness uniformity

<table>
<thead>
<tr>
<th>Stretching mode</th>
<th>Sequential stretching</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stretching Speed</td>
<td>10 mm/s</td>
</tr>
<tr>
<td>Stretching Ratio</td>
<td>MD 5 x TD 7</td>
</tr>
<tr>
<td>Stretching Temperature</td>
<td>159°C</td>
</tr>
<tr>
<td>Preheating Time</td>
<td>7 min</td>
</tr>
</tbody>
</table>

Table 2 | Stretching conditions
was measured at 60 points, at 1 cm intervals by Toyo Seiki Thickness Meter B-1. Table 3 shows A/L1 and A/L2 blends have about 40% lower yield values and have rapidly increasing stress. The stress buildup parameter which is defined as the maximum stress at the final stretching ratio divided by yield stress increases for A/L1 and A/L2 blends.

Figure 5 shows the relationship between stress buildup ratio $\sigma_{\text{max}}/\sigma_{\text{yield}}$ and the standard deviation of film thickness uniformity $\sigma_t$. This result shows a good correlation between them and thickness uniformity improves with increasing the stress buildup ratio $\sigma_{\text{max}}/\sigma_{\text{yield}}$. The reduction of the yield value increases stress buildup ratio $\sigma_{\text{max}}/\sigma_{\text{yield}}$ and reduces the necking deformation. It produces uniform stretching and reduces standard deviation of film thickness.

### 3.3 Relationship between stretchable temperature window width and film thickness uniformity

The stretchable temperature window width was defined as the stretchable temperature range. A lower temperature than the stretchable temperature causes film break because of too high stretching stress. A higher temperature than the stretchable temperature melts film during the biaxial stretching.

Figure 6 shows the relationship between the stretchable temperature window width and the standard deviation of film thickness uniformity.

The stretchable temperature window of PP A is 158–163°C (6°C), and A/L1, A/L2, and A/L3 which have lower stretchable temperature windows are 156–163°C (8°C). As the blending of LMPP to PP increases lower melting components and decreases the crystallization speed during the stretching process, stretching at a lower temperature is possible.

As a result, A/L1 and A/L2 improved the film thickness uniformity and the standard deviation is about half at 159°C, compared with PP A.

A/L3 also improved thickness uniformity, but it is not as good as A/L1 and A/L2. A/L3 which has high molecular component shows molecular chain entanglement and strain hardening, but does not show the reduction of yield value at the initial stretching stage and stress buildup ratio does not become as large as A/L1 and A/L2.

These results show that lower LMPP molecular weight may produce better stretchability.

### 3.4 Three-dimensional refractive indexes

Figure 7 is the experimental data of the stretching deformation in the TD tenter oven using a production line. The film sample after MD roll stretching in the production line was marked at the same interval along TD and then was introduced to a tenter oven.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Yield stress $\sigma_{\text{yield}}$ [MPa]</th>
<th>Maximum stress $\sigma_{\text{max}}$ [MPa]</th>
<th>Stress buildup $\sigma_{\text{max}}/\sigma_{\text{yield}}$ [-]</th>
<th>SD of Thickness uniformity $\sigma_t$ [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.57</td>
<td>0.72</td>
<td>1.26</td>
<td>2.28</td>
</tr>
<tr>
<td>A/L1</td>
<td>0.35</td>
<td>0.55</td>
<td>1.57</td>
<td>1.33</td>
</tr>
<tr>
<td>A/L2</td>
<td>0.40</td>
<td>0.70</td>
<td>1.75</td>
<td>1.29</td>
</tr>
<tr>
<td>A/L3</td>
<td>0.56</td>
<td>0.83</td>
<td>1.46</td>
<td>1.53</td>
</tr>
</tbody>
</table>

**TABLE 3** Stretching properties of PP samples in TD (159°C)
After the stable stretching condition was achieved, the tenter line was suddenly stopped and the film sample was taken out from the tenter oven. The upper left picture shows the film sample after it was taken out from the tenter oven on the white paper. The upper right picture shows the copied drawing from the upper left picture. The lower picture shows the local stretching ratio as a function of distance from the entrance of the stretching zone. These data show the neck-like deformation during TD stretching in a tenter oven. In the initial stretching region, the stretching ratio is locally different and does not show uniform deformation and after a certain stretching ratio in the TD oven, the stretching ratio becomes uniform. This deformation mechanism is very much dependant on the stress–strain curve. Our previous research found that the polymer having a higher yield value at the initial stretching ratio shows this kind of neck-like deformation.

The orientation during the stretching can be obtained by measuring the three-dimensional refractive indexes using a newly developed biaxial stretching machine. The refractive index was measured at the center part of the film during the stretching. Figure 8 shows the refractive indexes of PP A and A/L1 blend samples under the stretching temperature of 166°C. MD refractive index $N_x$ increases during MD stretching ratio 5, and then, TD refractive index $N_y$ increases with increasing TD stretching ratio and the refractive index of $N_y$ becomes larger than $N_x$ over TD stretching ratio 5. ND refractive index gradually decreases during MD and TD stretching. The A/L1 blend sample reduces the neck-like stretching and

**FIGURE 6** Relationship between standard deviations of thickness uniformity and temperature

**FIGURE 7** Necking Phenomenon in the Tentering Zone
decreases fluctuation and fluctuating range, compared with PP sample. These data also show LMPP produces better thickness uniformity.

3.5 | Light scattering (LS)

The spherulite size of the sheet sample was measured by light scattering. The existence of large spherulites in a

<table>
<thead>
<tr>
<th>Samples</th>
<th>Spherulite radius[μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10.5</td>
</tr>
<tr>
<td>A/L1</td>
<td>5.0</td>
</tr>
<tr>
<td>A/L2</td>
<td>4.7</td>
</tr>
<tr>
<td>A/L3</td>
<td>10.4</td>
</tr>
</tbody>
</table>

FIGURE 8 Refractive indexes and total stretching ratio in PP and PP/LMPP1 (P/L1) 5% blend

FIGURE 9 Light scattering images of PP samples
sheet makes the stretchability worsen. He-Ne laser (wavelength $\lambda = 632.8 \text{ nm}$) was used as a light source. The polarizer and the analyzer were mutually set perpendicularly, and the Hv pattern was observed. The Hv patterns measured by the light scattering are shown in Figure 9. The radius of spherulite size $U_{\text{max}}$ was calculated by Eq. (2).

Table 4 shows the spherulite size of various samples. As $H_v$ scattering pattern of sample PP A has a small clover pattern, the spherulite size is large and reaches about 10.5 $\mu$m. On the contrary, the $H_v$ scattering pattern of samples A/L1 and A/L2 are large and the spherulite size is reduced and about half, compared with PP A. As the crystallization speed of LMPP is much slower than PP, it is considered that the blending of LMPP to PP reduces the crystallization speed and the spherulite growth speed. As the spherulite size of A/L3 is almost the same as PP A, the blending effect of L3 is weak.

### 3.6 | Differential Scanning Calorimetry (DSC)

The enthalpy of fusion $\Delta H$ and the melting temperature were measured by DSC-7 which was produced by Perkin Elmer. Figure 10 shows DSC curves on the 2nd heat data of PP A and A/L1.

Table 5 shows that the blending LMPP to PP A reduces $\Delta H$ by about 4%. The melting temperature of LMPP blends remains constant and is the same as PP A.

### 3.7 | Small angle X-ray scattering (SAXS)

The long period L was measured for 30 min using Rigaku X-ray SAXS at voltage 50 kV, Ampere 280 mA, CuKα ($\lambda = 1.5418 \text{ Å}$) and then was calculated by the maximum value of scattering pattern $2\theta_{\text{max}}$ and Bragg equation Eq.(3).

$$2L \sin \theta_{\text{max}} = \lambda$$

### Table 5 | Crystallinities of PP samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Heat of fusion $\Delta H$ [J/g]</th>
<th>Crystallinity [-]</th>
<th>Melting temperature $T_m$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>93.5</td>
<td>44.7</td>
<td>160</td>
</tr>
<tr>
<td>A/L1</td>
<td>90.4</td>
<td>43.3</td>
<td>161</td>
</tr>
<tr>
<td>A/L2</td>
<td>90.5</td>
<td>43.3</td>
<td>160</td>
</tr>
<tr>
<td>A/L3</td>
<td>90.6</td>
<td>43.4</td>
<td>160</td>
</tr>
</tbody>
</table>

### Table 6 | Higher-order structures of PP samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Long period [μm]</th>
<th>Crystallinity [-]</th>
<th>Thickness of crystal layer [μm]</th>
<th>Thickness of amorphous layer [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>12.6</td>
<td>44.7</td>
<td>5.6</td>
<td>7.0</td>
</tr>
<tr>
<td>A/L1</td>
<td>13.9</td>
<td>43.3</td>
<td>6.0</td>
<td>7.9</td>
</tr>
<tr>
<td>A/L2</td>
<td>13.4</td>
<td>43.3</td>
<td>5.8</td>
<td>7.6</td>
</tr>
<tr>
<td>A/L3</td>
<td>13.0</td>
<td>43.4</td>
<td>5.6</td>
<td>7.4</td>
</tr>
</tbody>
</table>
Figure 11 shows the relationship between the relative intensity and the scattering angle $2\theta_{\text{max}}$. From these results, the scattering peak of A/L1 and A/L2 is shifted to the small angle side. It means the long period increases, but A/L3 shows a small shift.

From the long period and $\Delta H$ obtained by DSC, the thickness of crystal phase was obtained. Table 6 shows the long period, the thickness of crystal phase and the amorphous phase. The increase of LMPP blend samples’ long period is caused by penetrating LMPP into the amorphous phase, not the crystal phase. LMPP reduces the crystallinity of blend samples. Figure 12 shows that the superstructure is changed by inserting LMPP into the amorphous phase of the PP lamella structure.

Figure 13 shows the measurement results of phase difference distribution of PP A, A/L1, and A/L2. A/L1 and A/L2 have better uniformity than PP A and the blending of LMPP into PP can produce better film uniformity as shown in Table 3.

4  |  CONCLUSIONS

Blending of LMPP to PP was investigated in order to improve the biaxial stretchability of PP. As blending of LMPP to PP decreased the crystallization speed, LMPP blends reduced the yield values during the stretching process and increased the stress buildup ratio. As a result, they improved film thickness uniformity of biaxially stretched film and reduced film break during the production line. Furthermore, as the stretchable temperature window was widened to the low-temperature side, the thickness uniformity was improved in the wide stretchable temperature. The blending of LMPP to PP reduces the spherulite size and increases the thickness of the amorphous phase in the lamella without changing the thickness of the crystal phase, namely the melting temperature. As a result, reducing crystallinity and improving the stretchability and the film thickness uniformity of PP were achieved.

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How to cite this article: Kanai T, Egoshi K, Ohno S, Takebe T. The evaluation of stretchability and its applications for biaxially oriented polypropylene film. Adv Polym Technol. 2017;00:1–8.  
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