Stretchability and Properties of Various LLDPE for Biaxially Oriented Film

1 Introduction

The double bubble tubular polypropylene film is used for pack- age stationary, groceries, foods and so on because of its comparatively easier processability [2 to 7] and relatively cheaper resin cost. But recently shrink film for this usage is required to have a superior shrinkage, film strength and packaging ma- chinability. The double bubble tubular film (DBTF) of LLDPE has greater shrinkage, tear strength and seal ability than the shrink film made from polypropylene (PP). For this reason the demand for DBTF of LLDPE has been increasing [8 to 10]. However the stretching temperature range of LLDPE is narrower than PP, and the bubble stability is also worse than that of PP. In order to improve the stretchability and film properties of LLDPE, the blending of different densities of LLDPE [11 to 13] or co-extrusion of the different densities of LLDPE [14 to 16] have been carried out. But the biaxial stretchability of LLDPE has not been reported in any detail. In the previous re- port, the relationship among stretchability, film density and the composition distribution was investigated by blending the LLDPE. In this report, various LLDPE resins with wide ranges of density and MFI were selected from the commercialized resin, and the relationship between stretchability and material properties was investigated.

2 Experimental

2.1 Materials

Various LLDPEs were chosen from commercialized resins. Ta- ble 1 shows the material characteristics of these LLDPE films. LL-A, LL-B and LL-C were used in the previous report [1]. In this report, only LL-A and from LL-D to LL-H were examined. These material characteristics were evaluated by using the pri- mary films of the double bubble tubular process, in order to compare with the previous report [1], which dealt with blended LLDPE films.

2.2 Laboratory Tenter

The laboratory tenter is type BIX-703 made by Iwamoto Seisa- kusho Co. which is the same machine as used in the previous report [1].

2.3 Double Bubble Tubular Film Machine

The DBTF process consists of two stages of bubbles. In the first stage, the bubble is blown from a molten state. The first bubble is flattened out by a set of nip rolls and re-inflated into a larger second stage bubble at a temperature higher than a soften- ning temperature. The second bubble is stretched biaxially in an infrared heater oven, and after stretching, the bubble is cooled by air. The second bubble is also flattened out by a set of nip rolls and is slit along both edges, and each film is wound separately. The double bubble tubular film machine was also the same as in the previous report [1].

The DBTF line has been constructed by our company with a 65 mm extruder from Modern Machinery Company and a 180 mm annular die from Tomi Machinery Manufacturing Corporation. A torque measurement instrument SS201 made by Ono Sokki Co. in Japan was set between the take-up nip roll and driving motor to measure the stretching force or stress from the stretching torque.
The maximum stretching stresses can be calculated following Eqs. 1 and 2 as reported in the previous report [17], $\sigma_{MD}$ was used as a parameter representing overall of stretching stress in this report. Here, stretching range was defined as the range of stress from the onset of bubble stability to the bubble burst. With more than 5 Nm of stretching torque fluctuations, the bubble visibly moved, and as such was judged as bubble instability.

2.4 Evaluation Methods of Material and Film Properties

The melt index of polymer materials was evaluated by the measurement method of ASTM D 1238, and the melting point was measured by a DSC (Seiko Instruments Inc., EXSTAR DSC6200R). The composition distribution was measured by the temperature rising elution fractionation (TREF) method using an equipment made by Idemitsu Petrochemical Co., Ltd [19]. The measuring conditions were as follows. The solvent was ortho-dichlorobenzen, the flow speed was 1.0 ml/min, with the cooling temperature rate being 10 K/h from 135 to 0 °C and the heating rate, 40 K/h from 0 to 135 °C. An infrared detector was used and the TREF column size was 4.2 mm × 150 mm, Chromosorb P was used as the filler and the pour quantity was 0.5 ml with a concentration of 4 mg/ml. TREF relies on the crystallization and re-dissolution process to separate polymers having different degrees of branching.

The film densities were measured by a densimeter Accupyc 1330 made by Micromeritics Instrument Corporation. Principle of the densimeter is based on the evaluation of sample volume by measuring the pressure variation of charged gas upon the change of the volume of a chamber system filled with the sample. This equipment can measure the density faster than the density gradient tube method, while maintaining the same measurement accuracy. The shrinkage, tear strength, haze and Young’s modulus were evaluated by the measurement method of ASTM D 2732, ASTM D 1922, ASTM D 1003 and ASTM D 882, respectively.

3 Results

3.1 Material Characteristics

Material characteristics are shown in Table 1. The film densities are from 0.903 to 0.922 g/cm$^3$. In order to compare with

<table>
<thead>
<tr>
<th>Material</th>
<th>LL-A</th>
<th>LL-B*6</th>
<th>LL-C*7</th>
<th>LL-D</th>
<th>LL-E</th>
<th>LL-F</th>
<th>LL-G</th>
<th>LL-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm$^3$)</td>
<td>0.915</td>
<td>0.902</td>
<td>0.935</td>
<td>0.903</td>
<td>0.913</td>
<td>0.913</td>
<td>0.916</td>
<td>0.922</td>
</tr>
<tr>
<td>MFI (g/10 min)</td>
<td>1.0</td>
<td>1.0</td>
<td>2.5</td>
<td>1.2</td>
<td>1.3</td>
<td>1.3</td>
<td>2.0</td>
<td>0.9</td>
</tr>
<tr>
<td>$M_w$</td>
<td>120000</td>
<td>96000</td>
<td>86000</td>
<td>103000</td>
<td>100000</td>
<td>99000</td>
<td>90000</td>
<td>111000</td>
</tr>
<tr>
<td>$M_n$</td>
<td>38000</td>
<td>49000</td>
<td>33000</td>
<td>41000</td>
<td>33000</td>
<td>36000</td>
<td>34000</td>
<td>33000</td>
</tr>
<tr>
<td>$\text{MW/MN}$</td>
<td>3.17</td>
<td>1.96</td>
<td>2.61</td>
<td>2.51</td>
<td>3.06</td>
<td>2.77</td>
<td>2.69</td>
<td>3.34</td>
</tr>
<tr>
<td>Gradient*4 of the Region 40 to 70 in TREF %/K</td>
<td>3.19</td>
<td>6.60</td>
<td>8.43</td>
<td>2.45</td>
<td>2.92</td>
<td>2.95</td>
<td>2.95</td>
<td>3.75</td>
</tr>
<tr>
<td>HDPE composition*5 (%)</td>
<td>22.9</td>
<td>0</td>
<td>62.4</td>
<td>8.0</td>
<td>15.8</td>
<td>11.0</td>
<td>18.7</td>
<td>31.0</td>
</tr>
</tbody>
</table>


Table 1. Material characteristics of LLDPE films

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the results of blended films in the previous report [1], the film densities (not resin densities) were used as a parameter. Mw/Mn means the molecular weight distribution (MWD). LL-D, LL-F and LL-G have a comparatively narrow MWD. The relationship between the MWD and the stretchability is described in the following section. The composition distributions in TREF are shown in Fig. 1, and the integrated composition of the melting component from the TREF results are shown in Fig. 2. The relationship between the slope of the integrated composition versus melting temperature curve in the range of integrated composition of 40 to 70% (Region 40 to 70) and the stretchability was reported in the previous report [1], and the same analytical process was used in this report. The gradients of the Region 40 to 70 in TREF are shown in Table 1. There are two peaks in the composition distribution in Fig. 1. The higher temperature peak is for the high density polyethylene (HDPE) composition. In order to analyze in more detail than the previous report [1], the composition for the component melted at a temperature higher than 92 °C in TREF was used as an additional parameter, and that was defined as the HDPE composition in this report. The LL-D has a very small quantity of HDPE composition. The LL-E and LL-F are of the same film density, but the shape of composition distribution is different. The relationship among the stretchability, the composition distribution and the quantity of the HDPE composition was investigated.

3.2 Stretchability

3.2.1 Laboratory Tenter Stretched Film (LTSF)

Results of laboratory tenter stretching conducted at various temperatures are summarized in Table 2. In this table, the data for each film were arranged in the order of density. Properties of the LTSFs at the lowest stretching temperature are shown in Table 3. The relationship between stretch ratio and stretching force of LTSF is shown in Fig. 3. The relationship among the stretchability and each parameter, film density, MFI, MWD, gradient of the Region 40 to 70 in TREF and the quantity of HDPE composition were investigated. In these results, the film density and gradient of the Region 40 to 70 in TREF have a strong correlation with the stretchability. The film which has a lower gradient of the Region 40 to 70 in TREF has a better stretchability.
stretchability. Furthermore, these data show that the MWD of film is not so well correlated with the stretchability. It is considered that the composition distribution is more important than the molecular weight distribution in the stretching. The films with lower density also have a greater maximum stretching stress. Especially, the lowest density film in this test has a very wide stretching temperature range and a high maximum stretching stress. The film density 0.903 g/cm$^3$ is classified as a very low density polyethylene (VLDPE). A Young’s modulus of a VLDPE film is very low. Hence, the tenter stretching which utilizes clips is more applicable to the VLDPEs.

The hatched area in Table 2 is the prediction of the stable bubble stretching range of DBTF, when considering the deterioration of film transparency and stretching stress (Haze range was determined as that from the lowest haze to a 50\% increase in such. The minimum stretching stress is not less than 7.5 MPa.)

Table 2. The relationship between stretching temperature and stretching stress and haze of the films stretched by laboratory tenter

Table 3. Properties of films stretched at the lowest stretching temperature by laboratory tenter
stretching temperature depends on the film density. The stretchability, which means corresponds to stretching temperature range (STR), and the stretching stress range of DBTF are shown in Table 4. The STR was in proportion to the stretching stress range. A wider STR corresponds to better stretchability. The STR of the DBTF was very difficult to measure because stretching is taking place non-isothermally, and observation of the bubble was hindered by infrared heaters. The STR was defined as the following Eq. 4. The increment of stretching stress by stretching temperature was calculated by using the data of LTSF.

\[
\text{Increment of stretching stress (MPa/K)} = \frac{r_{\text{max}} - r}{D_{\text{t}}}, \quad (3)
\]

\[
\text{STR (K)} = \frac{\text{Stretching stress range (MPa)}}{\text{Increment of stretching stress (MPa/K)}}. \quad (4)
\]

The \( r_{\text{max}} \) is the stretching stress obtained under the conditions of a 5 × 5 stretching ratio at the lowest temperature of LTSF, and \( r \) is the stretching stress obtained under the condi-

<table>
<thead>
<tr>
<th>Material</th>
<th>1 LL-D</th>
<th>2 LL-E</th>
<th>3 LL-F</th>
<th>4 LL-A</th>
<th>5 LL-G</th>
<th>6 LL-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stretching torque (Nm)</td>
<td>–</td>
<td>min</td>
<td>30.4</td>
<td>35.5</td>
<td>39.1</td>
<td>35.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>max</td>
<td>57.2</td>
<td>59.4</td>
<td>71.0</td>
<td>67.4</td>
</tr>
<tr>
<td>Stretching stress (MPa)</td>
<td>min</td>
<td>8.2</td>
<td>15.4</td>
<td>16.0</td>
<td>19.1</td>
<td>9.6</td>
</tr>
<tr>
<td></td>
<td>max</td>
<td>15.4</td>
<td>16.0</td>
<td>19.1</td>
<td>18.2</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>7.2</td>
<td>6.4</td>
<td>8.6</td>
<td>–</td>
<td>8.6</td>
</tr>
<tr>
<td>Increments of stretching stress in LTSF (MPa/K)</td>
<td>–</td>
<td>1.5</td>
<td>1.35</td>
<td>1.48</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.75</td>
</tr>
<tr>
<td>Stretching temperature range (K)</td>
<td>–</td>
<td>–</td>
<td>5.33</td>
<td>4.34</td>
<td>7.17</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.80</td>
</tr>
</tbody>
</table>

Table 4. Stretching stress range and calculated stretching temperature range (STR) of the double bubble tubular films
tions of a $5 \times 5$ stretching ratio \(2 \, ^\circ\text{C} \times \Delta t\) higher than the lowest stretching temperature. This STR was used as the parameter for judging the stretchability of DBTF.

It was reported in the previous report [1] that the gradient of the total melting component of Region 40 to 70 in TREF correlated with the stretchability of DBTF. Fig. 4 shows the relationship among the film density, the gradient (%/K) of the Region 40 to 70 in the TREF, and the STR. Further more, the blended LLDPE types in the previous report [1] were calculated from stretching stress range to the STR in the same way, and plotted in Fig. 4. The size of the circle expresses the STR, with a larger displaying greater stretchability. This data shows that a better stretchability was achieved around 0.915 g/cm\(^2\) of the film density, and from 2.0 to 3.3 %/°C of the gradient.

In order to analyze in more detail the relationship among the HDPE composition in the TREF, the gradient (%/K) of the Region 40 to 70 in the TREF and the STR is shown in Fig. 5. This data shows that a good stretchability occurs from about 14 % to 27 % of HDPE composition in the TREF, however the best results were achieved in the 20 % to 27 % range. The film with a HDPE composition of less than 8 % can not be stretched, because stretching stress is not large enough to make a stable bubble. When the HDPE composition is more than about 30 %, it needs a very high stress in order to stretch, hence the bubble is easily susceptible to bursting.

Although LL-G has an 18.7 % HDPE composition and a Gradient is 3.3 %, it could not be stretched successfully. This is because the MFI of LL-G is 2.0 g/10 min, which means that the melt tension is not high enough to hold a bubble. When the results of LLDPE blends that have a MFI from 1.0 to 1.4 g/10 min were considered, a better stretchability range was achieved from about 0.5 to 1.5 g/10 min of MFI.

There was not such a strong correlation between stretchability of DBTF and MWD of the film. It was also considered that the stretchability of DBTF was greatly affected by the composition distribution of the film. This is because the balance of melted component to non-melted component is very important in achieving bubble stability for the DBTF.

When comparing the results of LTSF and DBTF an important point to consider in the case of DBTF is the required melt tension to support the bubble, hence it is not good for the DBTF if the film density falls below 0.910 g/cm\(^2\) due to a lack of HDPE composition. Over a 0.910 g/cm\(^2\) film density, it is possible to predict the DBTF stretchability using the LTSF results, taking into consideration the deterioration of film transparency and stretching stress as written in previous report [1]. Fig. 6 shows the comparison between the predicted stretching temperature range for DBTF with a density over 0.910 g/cm\(^2\), when considering the deterioration of film transparency and stretching stress of LTSF, and the stretching temperature range for DBTF. This data was compiled from both current research and the previous report [1] of LLDPE blended films. It is possible to predict the stretchability of DBTF relatively by using LTSF, however the results in this report evaluating the TREF and MFI of the film enable a more accurate prediction of the stretchability for DBTF.

### 3.3 Film Properties

The properties of LTSF that have the highest stretching stress (stretched by the lowest temperature) are shown in Table 3. The lower density film has a lower temperature stretchability.
and a lower temperature shrinkability. LL-D film has a good shrinkability, but generally Young’s modulus is too low for packaging film.

The properties of the DBTF that have the minimum and maximum stretching stresses are shown in Table 5. The higher stretching stress film of each material has a better shrinkability, greater Young’s modulus and a better tear strength balance in MD and TD. The relationship between stretching stress and film properties was discussed in detail in the previous report [17].

The comparison between the DBTF and the LTSF properties are shown in Figs. 7 and 8. The shrinkability of the DBTF was better than the LTSF for each film. This means that the DBTF was oriented more effectively than the LTSF. This is because the DBTF was stretched non-isothermally, while the LTSF was stretched isothermally. In addition the strain rate for the DBTF was higher than the strain rate of the LTSF. This was also reported in detail in the previous report [17].

4 Conclusions

A suitable LLDPE for DBTF must satisfy the following conditions. The gradient of the total melting component from 40 to 70 % in TREF is from 2.0 to 3.3 %/K, because a wider composition distribution is better for stretchability. However a LLDPE with a too wide composition distribution (below 2.0 %/K ) is not good for stretchability, because the entirely melted composition and unmelted composition exists in the stretching temperature range.

A film with a density of about 0.915 g/cm³ is the best for stretchability. Further more, a percentage between 14 % to

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness (µm)</th>
<th>Film density (g/cm³)</th>
<th>Stretching stress σ_{MD} (MPa)</th>
<th>Young’s modulus MD (MPa)</th>
<th>Tear strength MD/TD (mN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LL-E</td>
<td>15</td>
<td>0.913</td>
<td>8.2</td>
<td>260</td>
<td>13/19</td>
</tr>
<tr>
<td>LL-F</td>
<td>140/110</td>
<td>0.913</td>
<td>15.4</td>
<td>300</td>
<td>19/21</td>
</tr>
<tr>
<td>LL-H</td>
<td>160/140</td>
<td>0.915</td>
<td>9.6</td>
<td>290</td>
<td>13/19</td>
</tr>
<tr>
<td>LL-D</td>
<td>130/80</td>
<td>0.922</td>
<td>16.0</td>
<td>300</td>
<td>19/23</td>
</tr>
</tbody>
</table>

Table 5. Properties of the double bubble tubular films

![Fig. 7. Comparison of shrinkage between DBTF and LTSF](image1)

![Fig. 8. Comparison of Young’s modulus between DBTF and LTSF at the highest stretching stress](image2)
27% of HDPE composition which melts at a temperature higher than 92°C in TREF, is necessary in order for the bubble to remain stable and so its shape can be fixed at the end of the stretching process. A too higher percentage disrupts the stretching. The melt index of the film is from 0.5 to 1.5 g/10 min, because in order to achieve a stable bubble, a high melt tension is necessary.

In the case of LTSF, the film which has a lower density and lower gradient in the Region 40 to 70 in TREF, has a better stretchability, because there is no need for supporting the bubble.

References

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