Stretchability and Properties of Biaxially Oriented Polypropylene Film

T.Kanai (a)*, H.Uehara (b) , K.Sakauchi (b) , T.Yamada (c)

(a)Plastics Technical Center, Idemitsu Kosan Co.,Ltd , 1-1 Anesaki-Kaigan, Ichihara, Chiba,Japn
(b) Functional Product Dept.,Okura Industrial Co.,Ltd, 1515 Nakatsu-cho, Marugame-shi ,Japan
(c)Material Engineering, Kanazawa University, Kakuma, Kanazawa, Ishikawa, Japan

Abstract
Stretchability and composition distribution of various polypropylenes (PP) for biaxially oriented film was investigated. Several different ethylene contents and melt flow indices (MI) of polypropylenes (PP) were examined. There was a correlation between MI, ethylene content and the stretchability of the DBTF. A random copolymer with MI 2 g/10min and ethylene content 4.0wt% gave good stretchability. The most suitable composition distribution for stretching and the properties of biaxially oriented films were reported.

1. Introduction
The double bubble tubular film (DBTF) process is a more economical way of producing biaxially oriented film, when compared to the tenter biaxially oriented film process. This film manufacturing technique has been widely used to produce biaxially oriented films because of good shrinkability and high physical properties.

The double bubble tubular polypropylene film was developed in 1950 [1] and it has been used to package stationary, groceries, foods and so on because of it’s comparatively easier processability [1-6], good flatness and reasonable resin cost.

The DBTF process has been studied using various resins such as polyvinylidene chloride (PVDC), poly(ethylene terephthalate) (PET), poly(phenylene sulfide) (PPS), polyamide 6 (PA6), ethylene vinyl alcohol copolymer(EVOH), polypropylene(PP), and polyethylene(PE). Many patents [7-19] have been applied for the DBTF process technology.


The double bubble tubular film (DBTF) of PP which is most popular has good stretchability, a uniform film thickness and seal ability. Recently the shrink film for this usage is required to have a superior shrinkage and packing machinability. The demand for DBTF of PP having low temperature shrinkage and wide temperature range of stretchability has been increasing. In order to improve the stretchability
and film properties of PP, various random copolymers have been carried out. The biaxial stretchability of PP has not been reported in any detail. In the previous report, the relationship among stretchability, film physical properties and the composition distribution was investigated by using various LLDPE and blending LLDPE[28-30].

In this report, various PP resins with wide ranges of ethylene contents and MI were selected from the commercialized resin, and the relationship among molecular structure, stretchability and film physical properties was investigated.

2. Experimental

2.1 Materials
Various PP were chosen from commercialized resins. Table 1 shows the material characteristics of these PP films. In this report, various PP changing ethylene contents and propylene ethylene butene terpolymer were examined. These material characteristics were evaluated by using the primary films of the double bubble tubular process.

2.2 Laboratory Tenter
The laboratory tenter is type BIX-703 made by Iwamoto Seisakusho Co. which is the same machine as used in the previous report [28-30].

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 softening 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 one in the previous report [28-30]. The DBTF line has been constructed by our company with a 65mm extruder from Modern Machinery Company and a 180mm 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.

2.4 Film Preparation

2.4.1 Laboratory Tenter Stretched Film (LTSF)
The test piece film for the laboratory tenter was the first bubble film produced by the DBTF process. The stretch ratios were set at 5 in the machine direction (MD) and 5 in the transverse direction (TD) respectively. The thickness of the first bubble film was 300µm, and the stretched film thickness was 12µm. Film size was a 95mm square, but with allowances for clipping, the effective stretching film
size became a 70mm square. The heating time prior to the stretching was 2 minutes, and the stretching speed was 30 mm/s. The stretching temperature was changed in increments of 2 degrees, and the relationship between the stretch ratio and the stretching force under each stretching temperature was investigated. Only the MD data was used here because the stretching force in MD and TD were similar as reported in the previous report [27]. Other properties of stretched film such as shrinkage, Young’s modulus and haze were measured.

2.4.2 Double Bubble Tubular Film (DBTF)

The primary film was extruded from a die at a temperature of 200 °C, and cooled by water at a temperature of about 15 °C. The thickness of the primary film was 375µm, and the film width was 235mm, hence the blow up ratio was 0.83. The MD and TD stretch ratios were 5, while the thickness and width of final stretched film were 15µm and 1180mm, respectively. The output rate was 47 kg/h. The stretching force of the DBTFs was measured by using stretching torque. The stretching stresses can be calculated by the following equations (1) and (2) as reported in detail by Kanai [31].

\[
\sigma_{MD} = \frac{F_L}{2\pi R_L H_L} \quad (1)
\]

\[
\sigma_{TD} = \frac{R_L \cdot \Delta P}{H_L} \quad (2)
\]

The maximum stretching stresses \(\sigma_{MD}\) and \(\sigma_{TD}\) are at the final stretching point, where bubble diameter reaches the final bubble diameter. \(F_L\) is the bubble tension, \(R_L\) is the final bubble radius, \(H_L\) is the final bubble thickness, and \(\Delta P\) is the inside bubble pressure. Since \(\sigma_{MD}\) is closely correlated with \(\sigma_{TD}\) as reported in the previous report [28], \(\sigma_{MD}\) 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.

2.4.3 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 Kosan Co., Ltd [32]. The measuring conditions were as follows. The solvent was ortho-dichlorobenzene, the flow speed was 1.0 ml/min, with the cooling temperature rate being 10 K/hr from 135 °C to 0 °C and the heating rate, 40 K/hr from 0 °C to 135 °C. An infrared detector was used and the TREF column size was 4.2mm x 150mm. 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. MI ranges from 1.7 to 7.0 g/10min. The PP resins with
ethylene content below 5.0wt% are used. Mw/Mn means the molecular weight distribution (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-
70 % (Region 40-70) and the stretchability was reported in the previous reports [29,30], and the same
analytical process was used in this report[29]. The gradients of the Region 40-70 in TREF are shown
in Table 1.
The data of temperature raising elution fracturation (TREF) are shown in Fig.1 and they show one
peak in the different peak positions and various composition distributions. PP having low temperature
peak corresponds to high ethylene content. Homopolymer (No.2) has narrow composition distribution
and high temperature peak. The gradient in the region 40-70 in TREF ranges from 2.9 to 6.0%/K. The
relationship among the stretchability, the composition distribution and the film physical properties was
investigated.

3.2 Stretchability of Double Bubble Tubular Film Process

The stretchable stress ranges of various polypropylene are shown in Table 2. The stretching stress
which is used as the evaluation of stretchability is also very much influenced by MI and temperature
dependence of stretching stress. In this reason, the dimensionless parameter (Stretchable Stress Range
Index SSRI) defined by the following equation (3) is used.

\[
SSRI = \left( \sigma_{MD \text{max}} - \sigma_{MD \text{min}} \right) / \left( \frac{\sigma_{MD \text{max}} + \sigma_{MD \text{min}}}{2} \right) \tag{3}
\]

\( \sigma_{MD \text{max}} \) : Maximum Stretching Stress in MD
\( \sigma_{TD \text{max}} \) : Maximum Stretching Stress in TD

The relationship among SSRI, MI and gradient in the range of integral component from 40 and 70% is
shown in Table 2. It is found that the stretchability is very much influenced by MI.
The film sample No.4 whose MI is 2.2 g/10min has the widest stretchable range. Above this MI, the
stretchable range decreases with increasing MI. The resin having high MI gives low stretching tension
and low stability. Table 2 shows the resin which has 6.0 or 7.0g/10min for MI possesses low stretching stress compared with the resin of MI 2.2. The resin which has very low MI below 1.0 is easy to break during double bubble tubular film process, because very high stretching stress is required. As the results of this research, the best MI for this process is 2.2g/10min.

Homopolymer No.2 has high melting point and large gradient in the range of integral component from 40 to 70 in TREF, which means narrow composition distribution. It has narrow stretchable temperature range and it is difficult to be stretched. Further as it has high melting temperature, it is necessary to set the high stretching temperature.

From the results of the relationship between stretchability and TREF in Table 2, the resin having small gradient of integral component from 40 and 70% in TREF and wide composition distribution obtains good stretchability. Compared with LLDPE stretchability, the stretching stress is transformed into stretching temperature. The dependence of temperature on stretching stress is obtained by laboratory tenter equipment. As a result, it was 0.47MPa/K for the best stretchable sample No.4. The stretchable stress range was from 12.1 to 40.1 MPa and the stretchable temperature range was 59.6K. On the contrary, the dependence of temperature on stretching stress for the best stretchable LLDPE was 0.90MPa/K. The stretchable stress range was from 9.0 to 19.1MPa and the stretchable temperature range was 11.3K. It is found that the stretchable temperature range for PP is much wider than one for LLDPE. PP has wide stretchable stress range and small dependence of temperature on stretching stress. PP also obtains better film uniformity than LLDPE, because it has strain hardening curve.

### 3.3 Film Physical Properties

The film physical properties of various PP is shown in Table 3. The film physical properties of sample No.1 and No.3-7 on the almost same stretching stress condition of 32.0-34.1 MPa are compared. The samples No.2 and No.8,9 have lower stretching stresses, so the film physical properties at the highest stretching stress are compared with the other results. In terms of the film physical properties, especially the impact strength is very much influenced by MI. The film of low MI has high impact strength. Compared with random copolymer, homo-polymer No.2 shows high tensile modulus, low tear strength and low impact strength.

The film shrinkage for various PP are shown in Table 3 and Fig.4 a-i. The film sample which is low MI and high ethylene content has high shrinkage at the low temperature, because it has high stretching stress and low melting point. There is good relationship between shrinkage properties and TREF data. At the same MI, the film sample having low peak temperature and wide composition distribution shows good shrinkage. As homo-polymer No.2 has high melting temperature, it shows high shrink temperature. So it is not fit for shrink film. Various stretched films were produced by changing stretching stress for the best stretchable sample No.4. The results are shown in Fig.5a, b and Fig.6. From these results, the film physical properties increase with increasing stretching stress. This result is the same as LLDPE one. This means the stretched film at the high stretching stress is produced at the low stretching temperature and has high strain at the low temperature. In order to obtain the film of
high shrinkage and high physical properties, it is important to be stretched at the low stretching temperature without bubble break. It is found that the double bubble tubular film can produce good shrink film compared with the tenter process film, because the former process can stretch at the non-isothermal and low temperature than the later one. Compared PP with LLDPE in terms of stretchability, it is clarified from this study that PP is superior to LLDPE.

4. Conclusions

A suitable PP for DBTF must satisfy the following conditions. The most appropriate MI is 2.2g/10min and over the this value has less bubble stability and below MI 2.2 shows less stretchability. The stretchability range increases with decreasing the gradient in the total melting component from 40 to 70% in TREF, which means wider composition distribution is better for stretchability. The melt index of the film is about 2.2 g/10min. High melt tension is necessary in order to achieve a stable bubble, but too high melt tension occurs the bubble break.

References

1. U.S.Patent 2,979,777(1961), Goldman,M.
6. U.S.Patent 4,156709(1979), Kondo,K.,Wano,T

Tables

Table 5-1. Material characteristics of PP films
Table 5-2. Stretching stress range of double bubble tubular films
Table 5-3. Properties of the double bubble tubular films

Figures

Fig.1. Polymer separation results in TREF:
(A) No.1 MI=1.7g/10min ; (B) No.2 MI=2.1g/10min; (C) No.3 MI=2.1g/10min;
(D) No.4 MI=2.2g/10min; (E) No.5 MI=2.7g/10min; (F) No.6 MI=3.1g/10min;
(G) No.1 MI=3.3g/10min; (H) No.2 MI=6.0g/10min; (I) No.3 MI=7.0g/10min

Fig.2. Integral of melting component of TREF

Fig.3. Relationship among MI, Gradient of TREF 40-70 and stretching stress range index (SSRI)

Fig.4. Shrinkage (geometric average of MD and TD) of PP films:
A) No.1 m.p.=140 ºC; B) No.2 m.p.=159 ºC; C) No.3 m.p.=143 ºC;
D) No.4 m.p.=138 ºC; E) No.5 m.p.=133 ºC
F) No.6 m.p.=132 ºC; G) No.7 m.p.=132 ºC; H) No.8 m.p.=134 ºC; I) No.9 m.p.=133 ºC

Fig.5. Relationship between stretching stress and Tear, Impact strength
(A) Tear strength, (B) Impact strength

Fig.6. Relationship between stretching stress and shrinkability of No.4 film
<table>
<thead>
<tr>
<th>Film No.</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt Index (g/10min)</td>
<td>1.7</td>
<td>2.1</td>
<td>2.1</td>
<td>2.2</td>
<td>2.7</td>
<td>3.1</td>
<td>3.3</td>
<td>6.0</td>
<td>7.0</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
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<tr>
<td>Ethylene content (wt%)</td>
<td>4.3</td>
<td>2.7</td>
<td>4.0</td>
<td>4.2</td>
<td>5.0</td>
<td>5.0</td>
<td>3.2</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>Butene content (wt%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melting temp. (ºC)</td>
<td>140</td>
<td>159</td>
<td>143</td>
<td>138</td>
<td>133</td>
<td>132</td>
<td>132</td>
<td>134</td>
<td>133</td>
</tr>
<tr>
<td>Mw*1</td>
<td>-</td>
<td>398,000</td>
<td>419,000</td>
<td>377,000</td>
<td>345,000</td>
<td>332,000</td>
<td>332,000</td>
<td>315,000</td>
<td>276,000</td>
</tr>
<tr>
<td>Mn*2</td>
<td>-</td>
<td>94,000</td>
<td>80,000</td>
<td>97,000</td>
<td>100,000</td>
<td>88,000</td>
<td>91,000</td>
<td>86,000</td>
<td>75,000</td>
</tr>
<tr>
<td>Mw / Mn</td>
<td>-</td>
<td>4.25</td>
<td>5.27</td>
<td>3.91</td>
<td>3.45</td>
<td>3.78</td>
<td>3.65</td>
<td>3.66</td>
<td>3.68</td>
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<tr>
<td>Gradient*3 of the Region 40-70 in TREF (ºC / %)</td>
<td>4.6</td>
<td>15.1</td>
<td>6.0</td>
<td>4.4</td>
<td>3.5</td>
<td>3.4</td>
<td>2.9</td>
<td>3.8</td>
<td>3.0</td>
</tr>
</tbody>
</table>

*1 Weight average molecular weight
*2 Number average molecular weight
*3 Calculated from TREF data
Table 2. Stretching stress range of double bubble tubular films

<table>
<thead>
<tr>
<th>Film No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
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<tbody>
<tr>
<td>Melt Index</td>
<td>g/10min</td>
<td>1.7</td>
<td>2.1</td>
<td>2.1</td>
<td>2.2</td>
<td>2.7</td>
<td>3.1</td>
<td>3.3</td>
<td>6.0</td>
</tr>
<tr>
<td>Stretching stress MD (MPa)</td>
<td>Min</td>
<td>16.0</td>
<td>13.9</td>
<td>12.0</td>
<td>12.1</td>
<td>10.4</td>
<td>14.3</td>
<td>12.3</td>
<td>12.1</td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>44.9</td>
<td>20.8</td>
<td>36.2</td>
<td>40.1</td>
<td>32.4</td>
<td>39.1</td>
<td>33.4</td>
<td>18.3</td>
</tr>
<tr>
<td></td>
<td>R=(Max-Min)</td>
<td>28.9</td>
<td>6.9</td>
<td>24.2</td>
<td>28</td>
<td>22</td>
<td>24.8</td>
<td>21.1</td>
<td>6.2</td>
</tr>
<tr>
<td>Stretching stress range index (SSRI)</td>
<td>( R/\frac{\text{Min} + \text{Max}}{2} )</td>
<td>0.95</td>
<td>0.40</td>
<td>1.00</td>
<td>1.07</td>
<td>1.03</td>
<td>0.93</td>
<td>0.92</td>
<td>0.41</td>
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</table>
Table 3. Properties of the double bubble tubular films

<table>
<thead>
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<th>Film No.</th>
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<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
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<tbody>
<tr>
<td>MI (g/10min)</td>
<td>1.7</td>
<td>2.1</td>
<td>2.1</td>
<td>2.2</td>
<td>2.7</td>
<td>3.1</td>
<td>3.3</td>
<td>6.0</td>
<td>7.0</td>
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<tr>
<td>Stretching Stress $\sigma_{MD}$ (MPa)</td>
<td>33.2</td>
<td>20.8</td>
<td>32.8</td>
<td>32.0</td>
<td>32.4</td>
<td>32.6</td>
<td>34.1</td>
<td>18.3</td>
<td>17.9</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>110 / 130</td>
<td>120 / 120</td>
<td>100 / 120</td>
<td>120 / 140</td>
<td>100 / 120</td>
<td>130 / 130</td>
<td>120 / 100</td>
<td>120 / 140</td>
<td>120 / 110</td>
</tr>
<tr>
<td>Young's modulus (MPa)</td>
<td>970 / 1090</td>
<td>1520 / 1630</td>
<td>1350 / 1480</td>
<td>960 / 840</td>
<td>1010 / 1120</td>
<td>840 / 870</td>
<td>810 / 840</td>
<td>900 / 920</td>
<td>870 / 1020</td>
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<tr>
<td>Impact strength (J)</td>
<td>0.74</td>
<td>0.40</td>
<td>0.65</td>
<td>0.69</td>
<td>0.72</td>
<td>0.69</td>
<td>0.75</td>
<td>0.50</td>
<td>0.48</td>
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<tr>
<td>Shrinkage %</td>
<td>90%</td>
<td>12 / 16</td>
<td>3 / 6</td>
<td>8 / 14</td>
<td>12 / 20</td>
<td>14 / 19</td>
<td>16 / 21</td>
<td>14 / 18</td>
<td>10 / 15</td>
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<td></td>
<td>100%</td>
<td>19 / 23</td>
<td>6 / 9</td>
<td>13 / 18</td>
<td>21 / 28</td>
<td>22 / 28</td>
<td>27 / 33</td>
<td>25 / 28</td>
<td>18 / 27</td>
</tr>
<tr>
<td></td>
<td>110%</td>
<td>31 / 35</td>
<td>8 / 11</td>
<td>20 / 27</td>
<td>34 / 41</td>
<td>37 / 39</td>
<td>42 / 44</td>
<td>38 / 42</td>
<td>31 / 42</td>
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<td></td>
<td>120%</td>
<td>47 / 50</td>
<td>11 / 18</td>
<td>36 / 41</td>
<td>51 / 56</td>
<td>57 / 58</td>
<td>58 / 60</td>
<td>54 / 56</td>
<td>54 / 61</td>
</tr>
<tr>
<td></td>
<td>130%</td>
<td>61 / 62</td>
<td>17 / 28</td>
<td>58 / 62</td>
<td>66 / 68</td>
<td>74 / 72</td>
<td>76 / 71</td>
<td>69 / 70</td>
<td>77 / 71</td>
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</table>

- 10 –
Fig. 1-1. Polymer separation results in TREF:
(A) No.1 MI=1.7g/10min ;(B) No.2 MI=2.1g/10min; (C) No.3 MI=2.1g/10min;
(D) No.4 MI=2.2g/10min; (E) No.5 MI=2.7g/10min; (F) No.6 MI=3.1g/10min
Fig. 1-2. Polymer separation results in TREF:
(G) No.1 MI=3.3g/10min ; (H) No.2 MI=6.0g/10min; (I) No.3 MI=7.0g/10min
Fig. 2. Integral of melting component of TREF

Region 40-70
Fig. 3. Relationship among MI, Gradient of TREF 40-70 and stretching stress range index (SSRI)
Fig. 4-1 Shrinkage (geometric average of MD and TD) of PP films:
A) No. 1 m.p.=140 °C; B) No. 2 m.p.=159 °C; C) No. 3 m.p.=143 °C;
D) No. 4 m.p.=138 °C; E) No. 5 m.p.=133 °C
Fig. 4-2 Shrinkage (geometric average of MD and TD) of PP films:
F) No. 6 m.p. = 132 ℃; G) No. 7 m.p. = 132 ℃;
H) No. 8 m.p. = 134 ℃; I) No. 9 m.p. = 133 ℃
Fig. 5. Relationship between stretching stress and Tear, Impact strength
(A) Tear strength, (B) Impact strength
Fig. 6. Relationship between stretching stress and shrinkability of No.4 film