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Stretchability and Properties of Biaxially Oriented Polypropylene Film

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. Recently, shrinkage film for this usage is required to have good stretchability and shrinkage strength. But the biaxial stretchability changes of polypropylenes and the reasons for such have not been reported upon systematically.

In this report, the relationship between stretchability and material design of various polypropylenes (PP) for biaxially oriented film, which are most popular polymers, was investigated. Several different ethylene contents and melt flow indices (MI) of PP were examined. There was a correlation between MI, ethylene content and the stretchability of the DBTF. A random copolymer with MI 2 g/10 min and ethylene content 4.0 wt.% gave good stretchability. The most suitable composition distribution for stretching and the properties of biaxially oriented films were studied by using the temperature rising elution fractionation.

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 its comparatively easier processability [1 to 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 to 19] have been applied for the DBTF process technology.

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White [20] explained the technical trends and typical applications of those resins. Takashige and Kanai [21] reported on the DBTF process and the theoretical analysis of the stress development and the scale-up rule for PA6, while Ree [22] investigated the DBTF process-processability and the structure development of polyamide-612. Song [23] researched the processability of the blending of PBT and PET. Recently Takashige [24 to 27] studied processability, physical properties, scale-up and barrier characteristics of polyamide-6.

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 to 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 to 30].

Film No.	Unit	1	2	3	4	5	6	7	8	9
Melt index	g/10min	1.7	2.1	2.1	2.2	2.7	3.1	3.3	6.0	7.0
Density	g/cm ³	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
Ethylene content	wt. %	4.3	–	2.7	4.0	4.2	5.0	5.0	3.2	4.2
Butene content	wt. %	–	–	–	–	–	–	–	2.8	–
Melting temp.	°C	140	159	143	138	133	132	132	134	133
Mw ^{*1}	–	398 000	419 000	377 000	345 000	332 000	332 000	315 000	276 000	259 000
Mn ^{*2}	–	94 000	80 000	97 000	100 000	88 000	91 000	86 000	75 000	71 000
Mw/Mn	–	4.25	5.27	3.91	3.45	3.78	3.65	3.66	3.68	3.67
Gradient ^{*3} of the Region 40 to 70 in TREF	%/K	4.6	15.1	6.0	4.4	3.5	3.4	2.9	3.8	3.0

*1 weight average molecular weight, *2 number average molecular weight, *3 calculated from TREF data

Table 1. Material characteristics of PP films

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 to 30]. The DBTF line has been constructed by Okura Industry 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.

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 300 μm , and the stretched film thickness was 12 μm . Film size was a 95 mm square, but with allowances for clipping, the effective stretching film size became a 70 mm 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 375 μm , and the film width was 235 mm, 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 15 μm and 1180 mm, 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 Eqs. 1 and 2 as reported in detail by Kanai [31].

$$\sigma_{\text{MD}} = \frac{F_L}{2\pi R_L H_L}, \quad (1)$$

$$\sigma_{\text{TD}} = \frac{R_L \cdot \Delta P}{H_L}. \quad (2)$$

The maximum stretching stresses σ_{MD} and σ_{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 ΔP is the inside bubble pressure which was measured by inserting the needle

connected to the manometer [21]. Since σ_{MD} is closely correlated with σ_{TD} , as reported in the previous report [28], σ_{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.

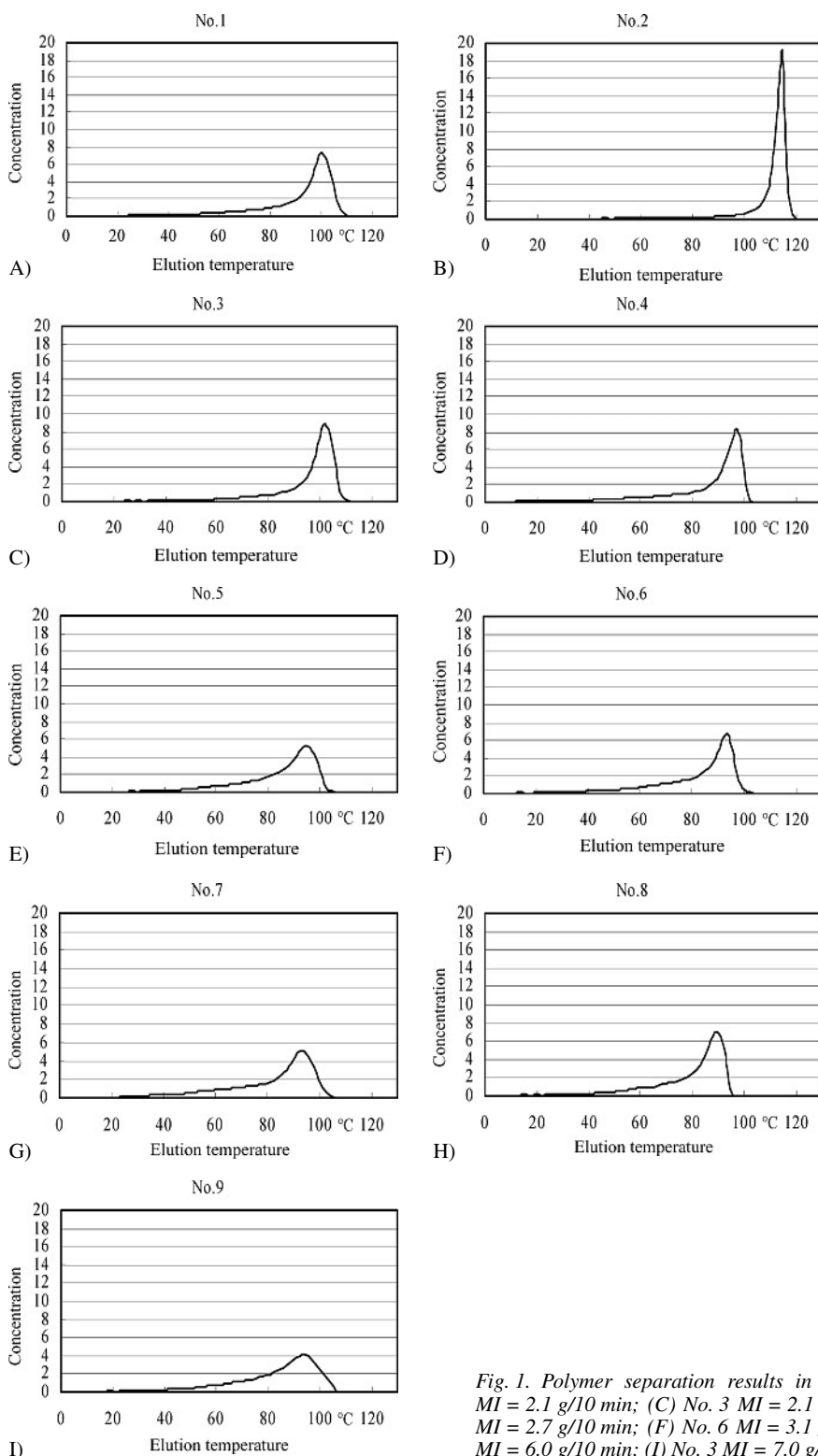


Fig. 1. Polymer separation results in TREF: (A) No. 1 MI = 1.7 g/10 min; (B) No. 2 MI = 2.1 g/10 min; (C) No. 3 MI = 2.1 g/10 min; (D) No. 4 MI = 2.2 g/10 min; (E) No. 5 MI = 2.7 g/10 min; (F) No. 6 MI = 3.1 g/10 min; (G) No. 1 MI = 3.3 g/10 min; (H) No. 2 MI = 6.0 g/10 min; (I) No. 3 MI = 7.0 g/10 min

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/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 $\varnothing 4.2 \text{ mm} \times 150 \text{ mm}$, 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 Accucy 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/10 min. The PP resins with ethylene content below 5.0 wt.% are used. Mw/Mn means the molecular weight distribution (MWD). 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 com-

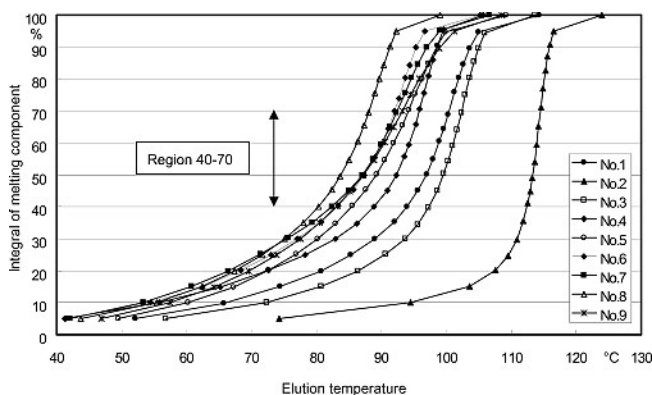


Fig. 2. Integral of melting component of TREF

position of 40 to 70 % (Region 40 to 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 to 70 in TREF are shown in Table 1.

The data of temperature raising elution fractionation (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 to 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 polypropylenes 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 Eq. 3 is used.

$$SSRI = (\sigma_{MD\max} - \sigma_{MD\min}) / \left(\frac{\sigma_{MD\max} + \sigma_{MD\min}}{2} \right), \quad (3)$$

where $\sigma_{MD\max}$ is maximum stretching stress in MD, and $\sigma_{TD\max}$ is 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/10 min 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 7.0 g/10 min 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 about 2.2 g/10 min.

Homopolymer No. 2 has high melting point and large gradient in the range of integral component from 40 to 70 in TREF,

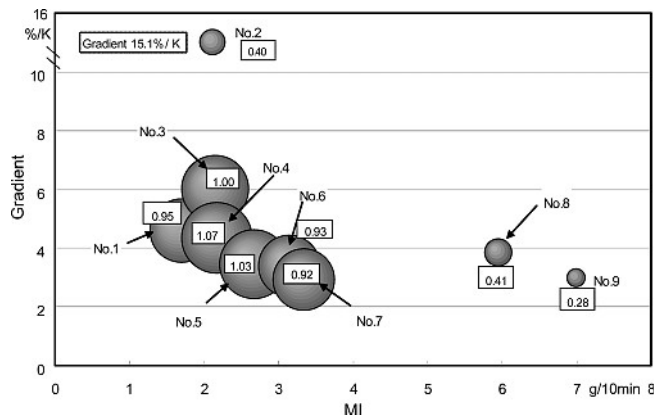


Fig. 3. Relationship among MI, Gradient of TREF 40 to 70 and stretching stress range index (SSRI)

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 0.47 MPa/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 59.6 K. On the contrary, the dependence of temperature on stretching stress for the best stretchable LLDPE was 0.90 MPa/K. The stretchable stress range was from 9.0 to 19.1 MPa and the stretchable temperature range was 11.3 K. 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.

Film No.	Unit	1	2	3	4	5	6	7	8	9
Melt index	g/10 min	1.7	2.1	2.1	2.2	2.7	3.1	3.3	6.0	7.0
Stretching stress, Min	MPa	16.0	13.9	12.0	12.1	10.4	14.3	12.3	12.1	13.5
Stretching stress, Max	MPa	44.9	20.8	36.2	40.1	32.4	39.1	33.4	18.3	17.9
σ_{MD} (MPa)	$R = (\text{Max} - \text{Min})$	28.9	6.9	24.2	28	22	24.8	21.1	6.2	4.4
Stretching stress range index (SSRI)	$R / \frac{\text{Min} + \text{Max}}{2}$	0.95	0.40	1.00	1.07	1.03	0.93	0.92	0.41	0.28

Table 2. Stretching stress range of double bubble tubular films

Film No.		1	2	3	4	5	6	7	8	9
MI	g/10 min	1.7	2.1	2.1	2.2	2.7	3.1	3.3	6.0	7.0
Stretching stress σ_{MD}	MPa	33.2	20.8	32.8	32.0	32.4	32.6	34.1	18.3	17.9
Stretching strength (MD/TD)	MPa	170/200	200/210	210/210	180/170	170/220	170/180	170/150	160/163	160/180
Elongation MD/TD	%	110/130	120/120	100/120	120/140	100/120	130/130	120/100	120/140	120/110
Young's modulus MD/TD	MPa	970/1090	1520/1630	1350/1480	960/840	1010/1120	840/870	810/840	900/920	870/1020
Tear strength MD/TD	mN	39/59	29/29	29/49	39/49	39/49	49/49	39/39	39/29	29/29
Impact strength	J	0.74	0.40	0.65	0.69	0.72	0.69	0.75	0.50	0.48
Shrinkage % MD/TD	90 °C	12/16	3/6	8/14	12/20	14/19	16/21	14/18	10/18	10/15
	100 °C	19/23	6/9	13/18	21/28	22/28	27/33	25/28	18/27	17/24
	110 °C	31/35	8/11	20/27	34/41	37/39	42/44	38/42	31/42	29/37
	120 °C	47/50	11/18	36/41	51/56	57/58	58/60	54/56	54/61	45/52
	130 °C	61/62	17/28	58/62	66/68	74/72	76/71	69/70	77/71	64/65

Table 3. Properties of the double bubble tubular films

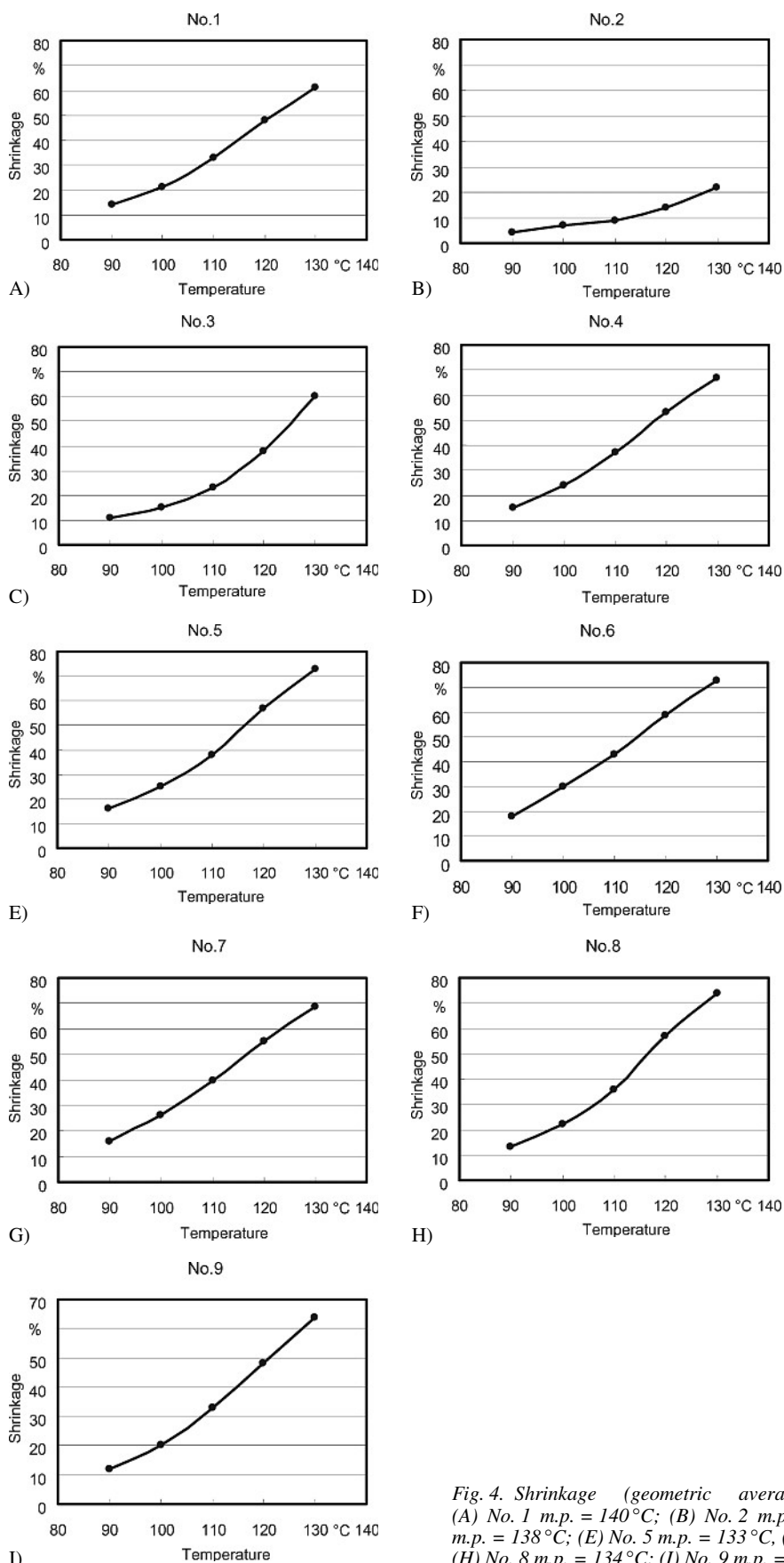


Fig. 4. Shrinkage (geometric average of MD and TD) of PP films: (A) No. 1 m.p. = 140°C; (B) No. 2 m.p. = 159°C; (C) No. 3 m.p. = 143°C; (D) No. 4 m.p. = 138°C; (E) No. 5 m.p. = 133°C; (F) No. 6 m.p. = 132°C; (G) No. 7 m.p. = 132°C; (H) No. 8 m.p. = 134°C; (I) No. 9 m.p. = 133°C

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 to 7 on the almost same stretching stress condition of 32.0 to 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, homopolymer 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. 4A to 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 and 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 stretch-

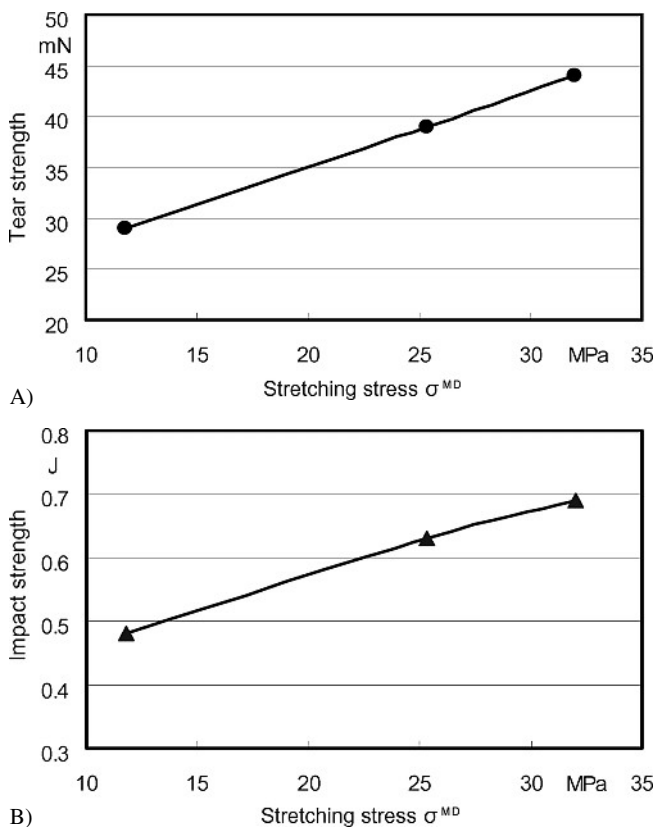


Fig. 5. Relationship between stretching stress and tear, impact strength. (A) tear strength, (B) impact strength

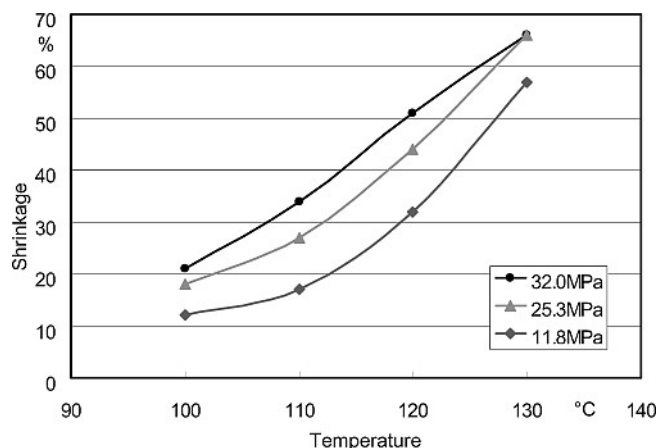


Fig. 6. Relationship between stretching stress and shrinkability of No. 4 film

ing 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. The shrinkage reaches maximum at high temperature at which shrink film relaxed most of stretching strain during double bubble tubular process.

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 2.2 g/10 min and over 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/10 min. High melt tension is necessary in order to achieve a stable bubble, but too high melt tension occurs the bubble break.

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