Stretchability and Properties of Biaxially Oriented Polypropylene Film

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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.

J.L.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 polyamide-6, while S.Ree [22] investigated the DBTF process-processability and the structure development of polyamide-612. K.Song [23] researched the processability of the blending of PBT and PET. Recently M.Takashige [24-27] 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[28-30].

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   , and cooled by water at a temperature of about 15   . 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].

$$\sigma_{MD} = \frac{F_L}{2\pi R_L H_L} \qquad\qquad 1$$

$$\sigma_{TD} = \frac{R_L \cdot \Delta P}{H_L} \qquad\qquad 2$$

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. 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.

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-dichlorobenzen, the flow speed was 1.0 ml/min, with the cooling temperature rate being 10 K/hr from 135   to 0   and the heating rate, 40 K/hr from 0   to 135   . An infrared detector was used and the TREF column size was   4.2mm× 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 stretchablility 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.

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

Maximum Stretching Stress in MD

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.
 2. U.S.Patent 3,510549(1970), Tsubosita,K.,Kano,T.
 3. U.S.Patent 3,260,776(1966), Lindstrom,C.
 4. U.S.Patent 3,300,555(1967), Bild,F.,Robinson,W.
 5. U.S.Patent 4,112,034(1978), Nash,J.L.,Polish,S.J.,Carrico,P.H.
 6. U.S.Patent 4,156709(1979), Kondo,K.,Wano,T
 7. U.S.Patent 3,260,776 (1966), Lindstrom, C.A., William,M.A., Baird,G., Bosse,A.L.
 8. U.S.Patent 3,510,549 (1970), Tsuboshima, K., Kanho, T.
 9. U.S.Patent4,112,034 (1978), Nash, J.L., Polich,S.J.
10. U.S.Patent 4,279,580 (1981), Hayashi, K., Morihara, K., Nakamura, K.
11. U.S.Patent 4,597,920(1986), Ralph,G..
12. U.S.Patent 5,904,964(1999), Douglas,J.
13. U.S.Patent 5,298,202(1994), Schirmer,H.
14. U.S Patent 4,801,652 (1989), Mizutani,T.,Isozaki,H
15. U.S Patent 3,663,662 (1972), Ostapchenko,J.,Williamsville)
16. U.S.Patent 5,589,561 (1996), Barry,R.,Pellereau,B.
17. U.S.Patent 4,551380 (1984), Jurian.H.
18. Japan Patent 2,688,827 (1988), Isozaki,H.,Fukushima.H.
19. U.S.Patent 09/846,218 (2001), Uehara,H., Matsuda,Y., Sakauchi,K.
20. White,J.L, :Film Processing, Hanser Publishers, p.412 (1999)

21. Takashige,M., and Kanai, T. :Int. Polym. Process. V, p.287 (1990)

22. Ree, S. and White, J.L. :Int. Polym. Process. XVI, p.272 (2001)

23. Song, K. ,White J.L. :Antec proceeding 57 p.1650 (1999)

24. Takashige,M., Kanai,T., Yamada,T. : Int.Polym.Process. 18, p.368 (2003)

25. Takashige,M., Kanai,T., Yamada,T.:Int.Polym.Process.19, p.147 (2004)

26. Takashige,M., Kanai,T., Yamada,T. : Int.Polym.Process. 19, p.47 (2004)

27. Takashige,M., Kanai,T., Yamada,T. : Int. Polym.Process. 19, p.56 (2004)

28. Uehara,H., Sakauchi,K., Kanai,T., Yamada,T. Intern.Polym.Process. 19(2),155(2004)

29. Uehara,H., Sakauchi,K., Kanai,T., Yamada,T. Intern. Polym. Process. 19(2),163(2004)

30. Uehara,H., Sakauchi,K., Kanai,T., Yamada,T. Intern. Polym. Process. 19(2),172(2004)

31. Kanai,T., Campbell,G.A.: Film Processing. Hanser Publishers, Munich, p.386 (1999)

32. Housaki,T.:Bunseki 9 (Japanese), p.518 (2000)

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 ; B) No.2 m.p.=159 ; C) No.3 m.p.=143 ;

  D)No.4 m.p.=138 ; E) No.5 m.p.=133

  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

Table 1. Material characteristics of PP films

Film No.		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.	( )	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		4.25	5.27	3.91	3.45	3.78	3.65	3.66	3.68	3.67
Gradient[*] of the Region 40-70 in TREF	( )	4.6	15.1	6.0	4.4	3.5	3.4	2.9	3.8	3.0

Weight average molecular weight
Number average molecular weight
Calculated from TREF data

Table 2. Stretching stress range of double bubble tubular films

Film No.		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
Stretching stress $_{MD}$ (MPa)	Min	16.0	13.9	12.0	12.1	10.4	14.3	12.3	12.1	13.5
	Max	44.9	20.8	36.2	40.1	32.4	39.1	33.4	18.3	17.9
	R=(Max-Min)	28.9	6.9	24.2	28	22	24.8	21.1	6.2	4.4
Stretching stress range index (SSRI)	$R / \dfrac{Min + Max}{2}$	0.95	0.40	1.00	1.07	1.03	0.93	0.92	0.41	0.28

Table 3. Properties of the double bubble tubular films

Film No.		1		2		3		4		5		6		7		8		9	
MI	(g/10min)	1.7		2.1		2.1		2.2		2.7		3.1		3.3		6.0		7.0	
Stretching Stress MD	(MPa)	33.2		20.8		32.8		32.0		32.4		32.6		34.1		18.3		17.9	
Stretching strength	(MPa)	170	200	200	210	210	210	180	170	170	220	170	180	170	150	160	163	160	180
Elongation	(%)	110	130	120	120	100	120	120	140	100	120	130	130	120	100	120	140	120	110
Young's modulus	(MPa)	970	1090	1520	1630	1350	1480	960	840	1010	1120	840	870	810	840	900	920	870	1020
Tear strength	(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	90	12	16	3	6	8	14	12	20	14	19	16	21	14	18	10	18	10	15
	100	19	23	6	9	13	18	21	28	22	28	27	33	25	28	18	27	17	24
	110	31	35	8	11	20	27	34	41	37	39	42	44	38	42	31	42	29	37
MD TD	120	47	50	11	18	36	41	51	56	57	58	58	60	54	56	54	61	45	52
	130	61	62	17	28	58	62	66	68	74	72	76	71	69	70	77	71	64	65
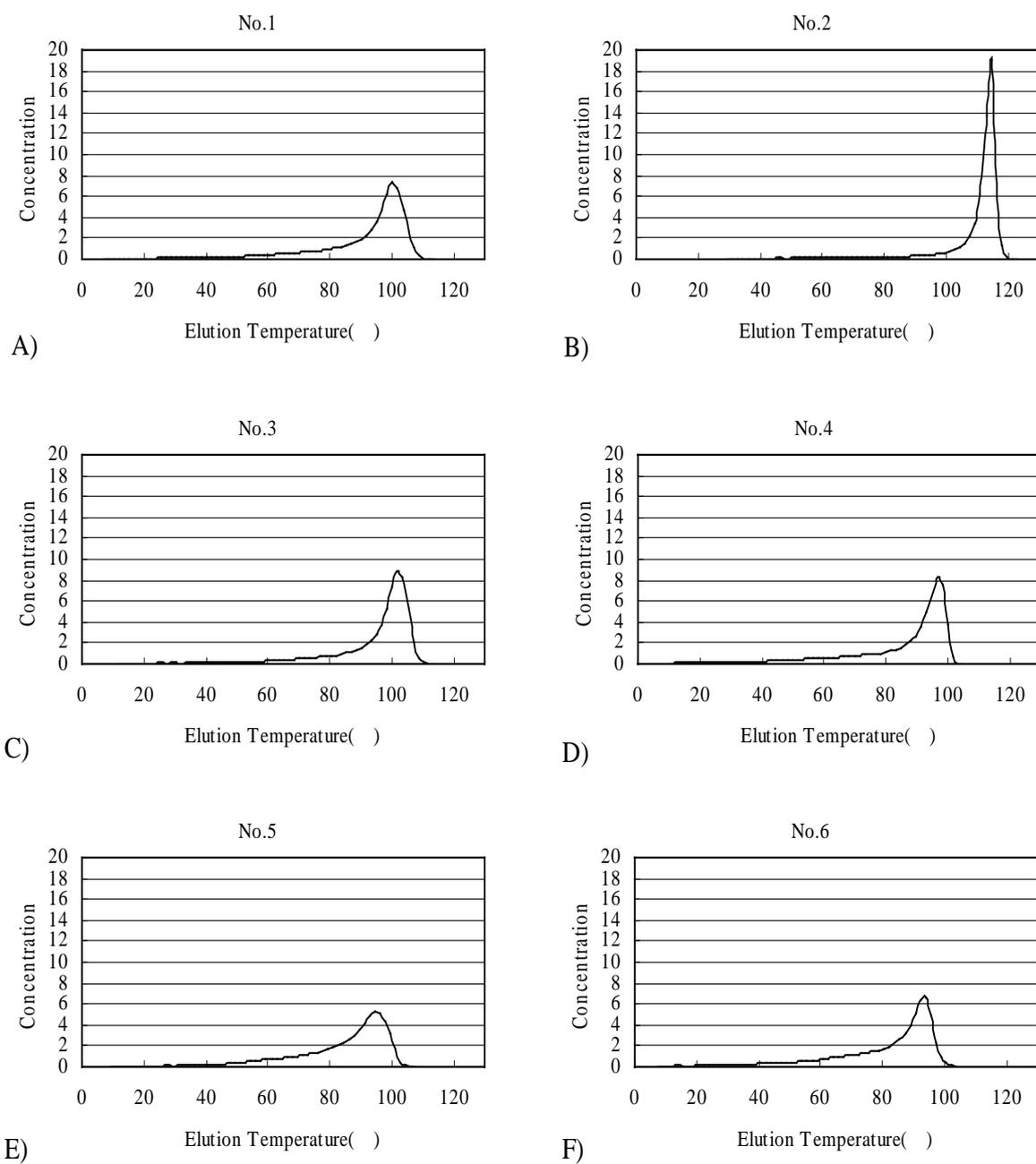
Fig.1-1. Polymer separation results in TREF:
(A)No.1 MI=1.7g/10min ;(B)No.2 MI=2.1g/10min; (C)No.3 MI=2.1g/10min;
(D)No.4 MI=2.2g/10min; (E)No.5 MI=2.7g/10min; (F)No.6 MI=3.1g/10min

No.7

G)

No.8

H)

No.9
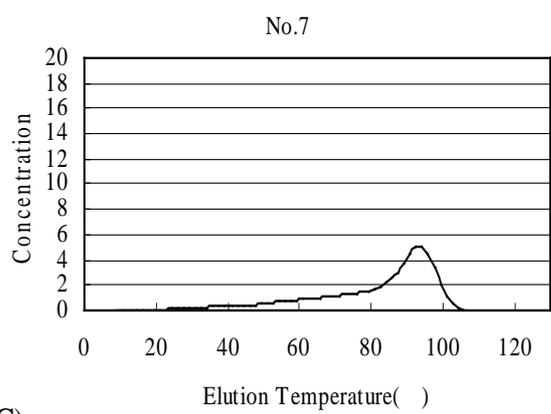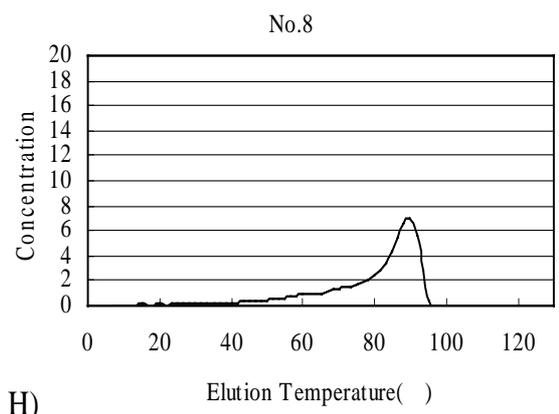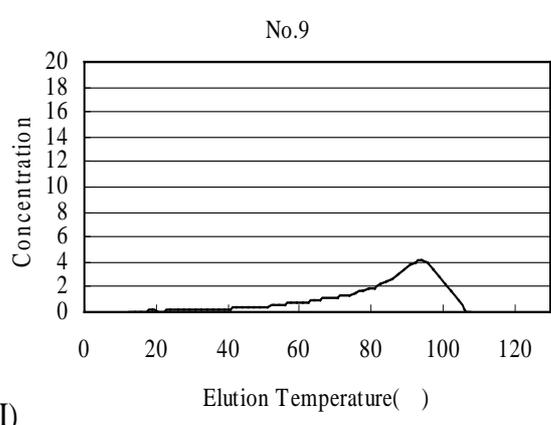
I)

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
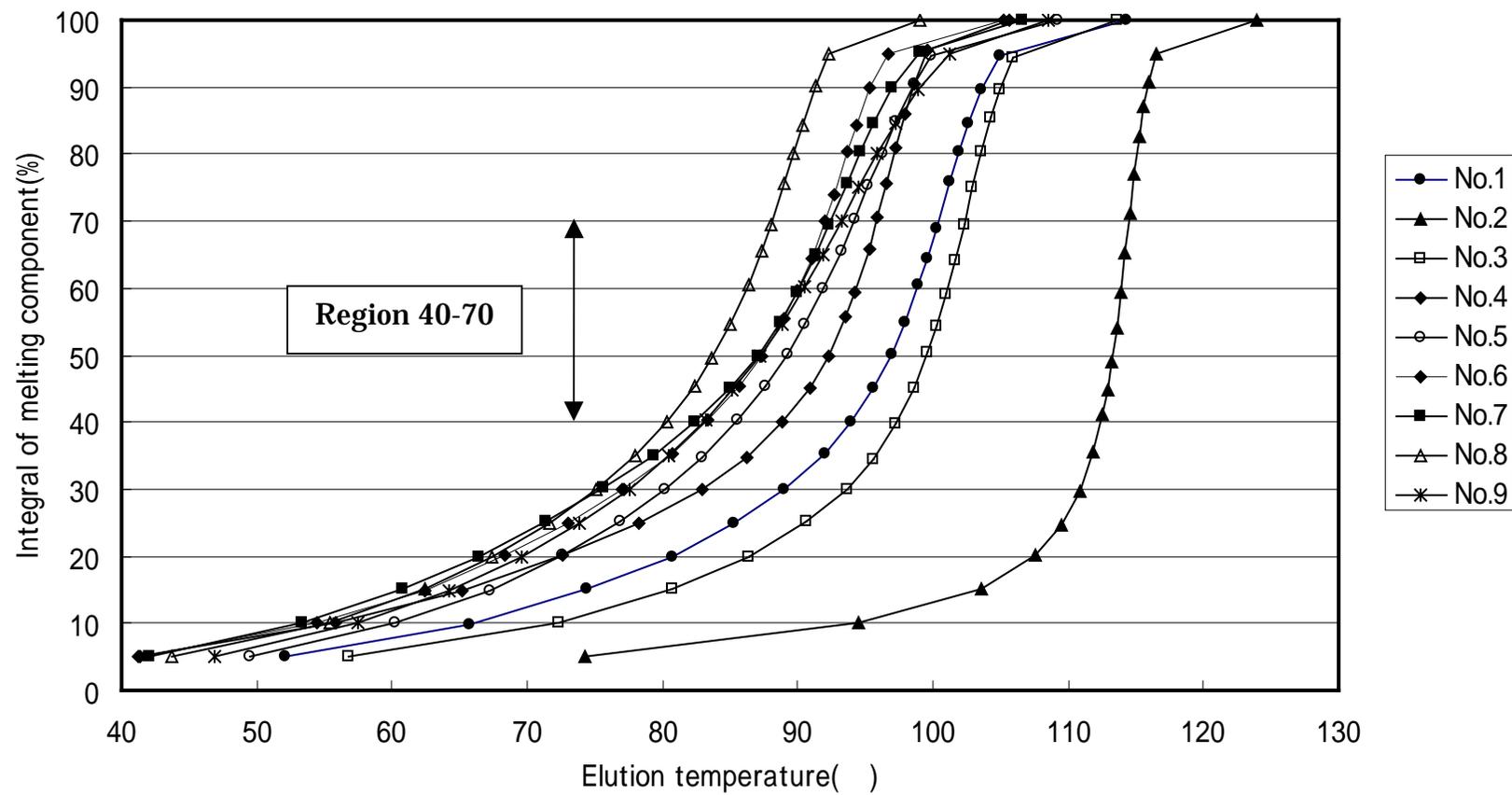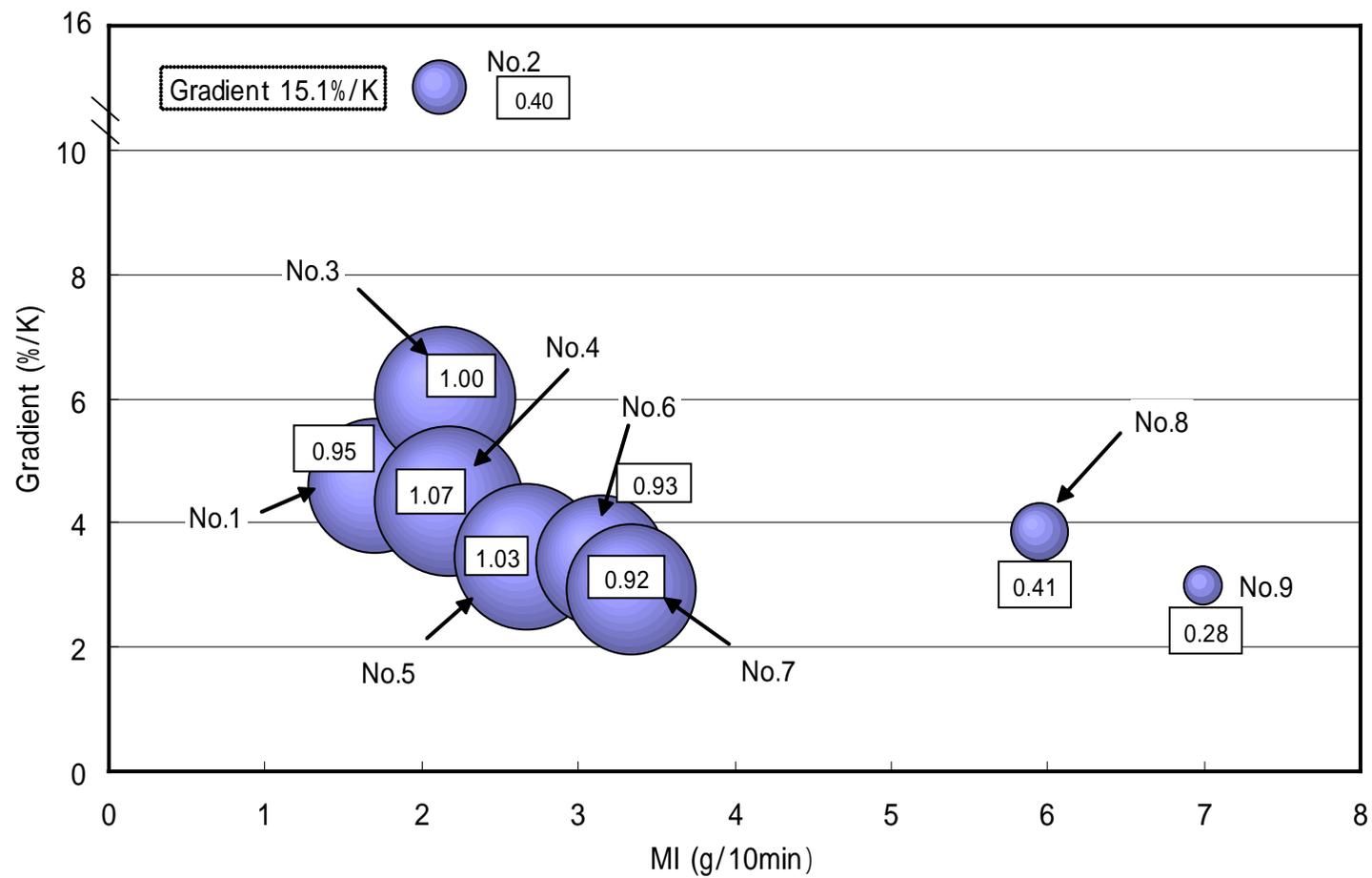
Fig.2. Integral of melting component of TREF

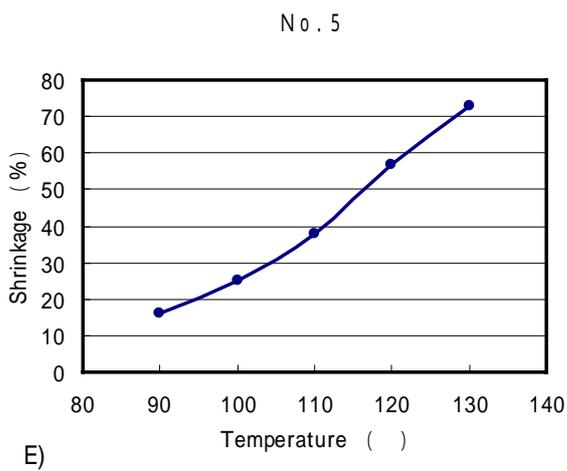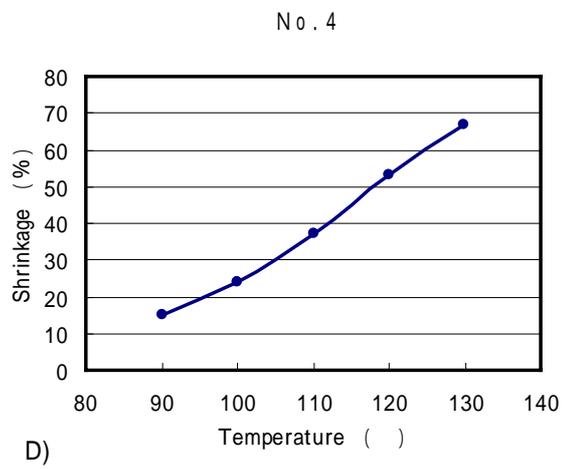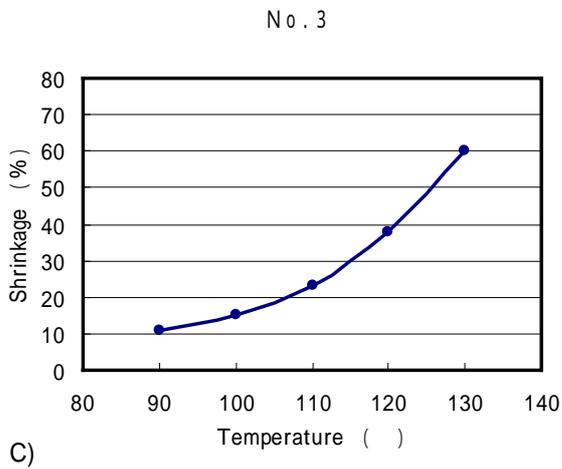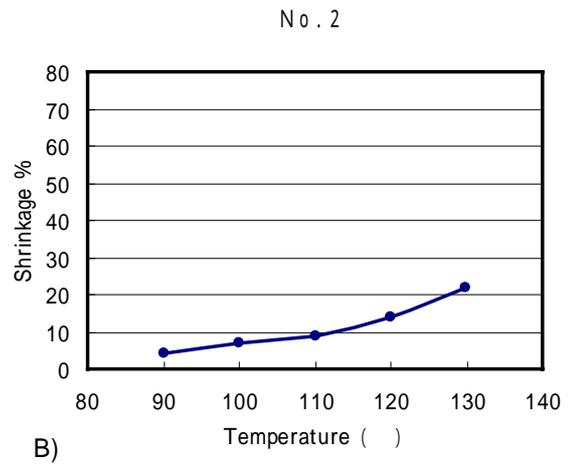**Fig.3. Relationship among MI, Gradient of TREF 40-70 and stretching stress range index (SSRI)**
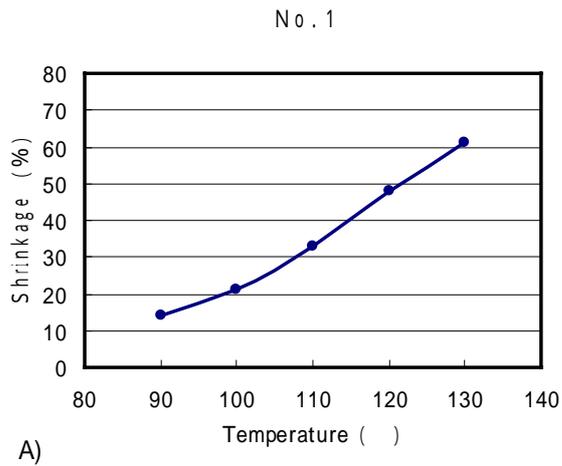
Fig.4-1 Shrinkage (geometric average of MD and TD) of PP films:
A) No.1 m.p.=140 ; B) No.2 m.p.=159 ; C) No.3 m.p.=143 ;
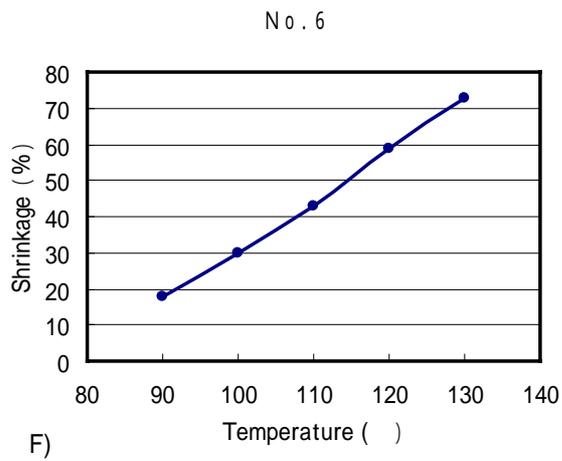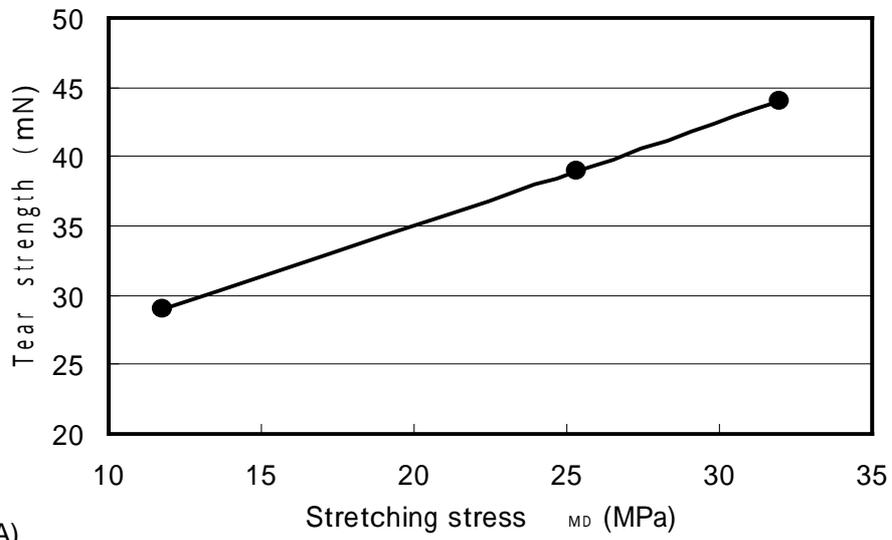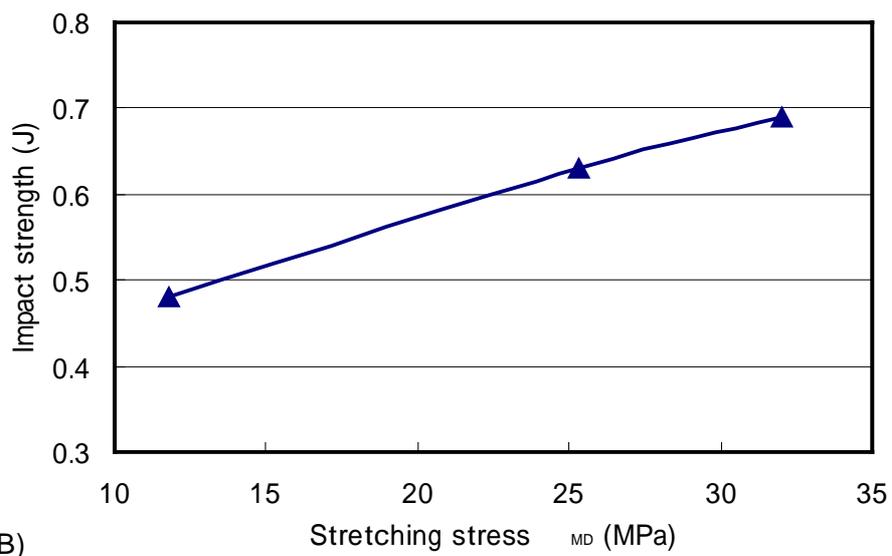D) No.4 m.p.=138 ; E) No.5 m.p.=133
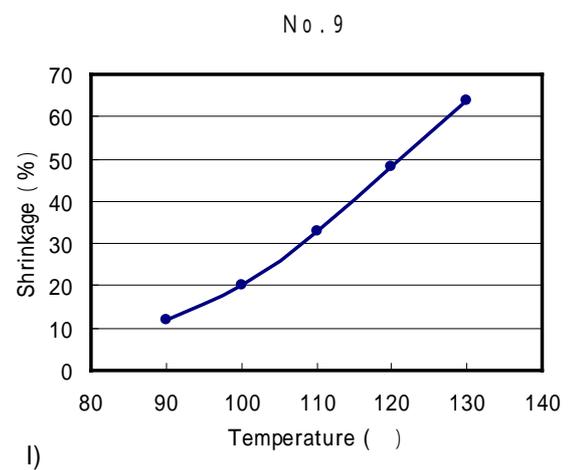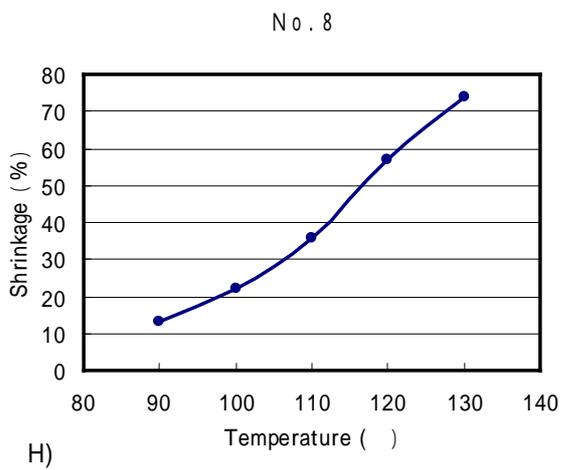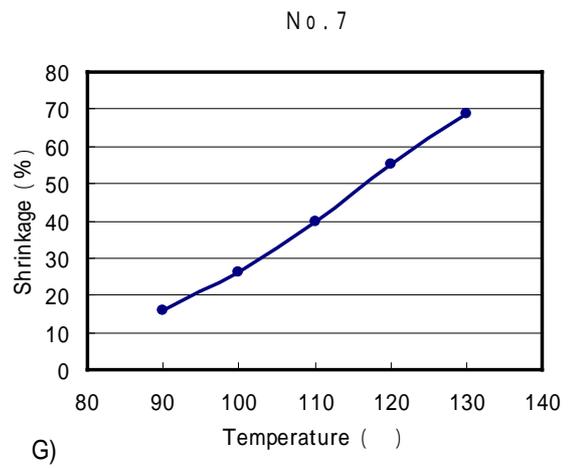
Fig. 4-2 Shrinkage (geometric average of MD and TD) of PP films:
F) No.6 m.p.=132   ; G) No.7 m.p.=132   ;
H) No.8 m.p.=134   ; I) No.9 m.p.=133

A)

B)

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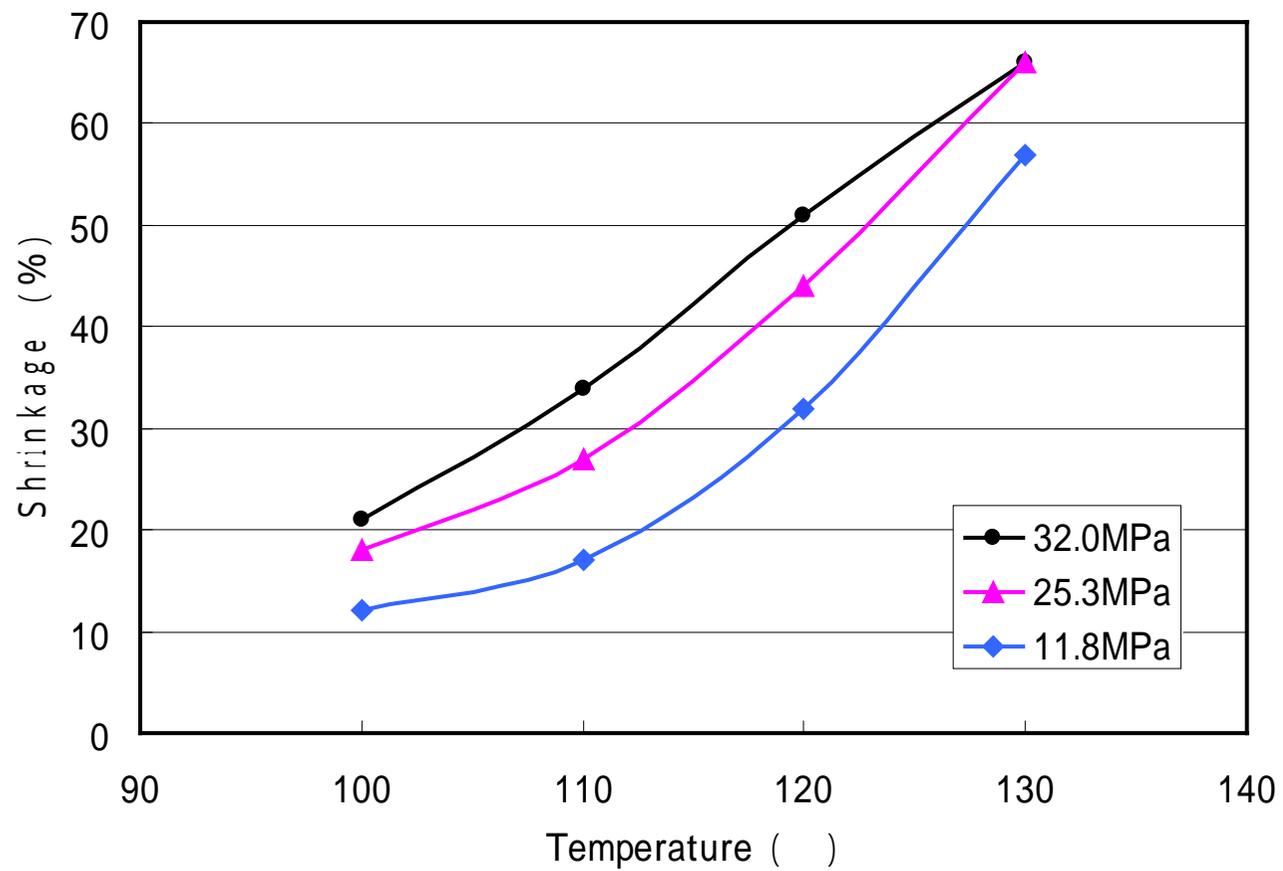**(A) Tear strength, (B) Impact strength**

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