Influence of Cooling-Water Temperature on Primary Film of Random Polypropylene in Double Bubble Tubular Process.

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Abstract

Stretchability, thickness uniformity and physical properties of random-polypropylene(r-PP) for double bubble tubular process is investigated under the various conditions changing cooling water temperature of primary film sampled after cooling water process(position A in Figure 1).

Conventionally the primary film is cooled by chilled water, but its influence of cooling water temperature on the stretchability and physical properties are not reported.

From our experimental results, it is found that crystallinity, superstructure and stretchability of primary film and stretched film(tertiary film, position C in Figure 1) on double bubble tubular process were influenced by cooling water temperature on primary film producing process, but the influence is adjustable by preset modification of pre-heating process. It is found that thickness uniformity of primary film or tertiary film on double bubble tubular process aren't influenced by cooling-water temperature on primary film producing process. Also the physical properties of stretched film are scarcely influenced by cooling water temperature. Considering to this investigation, it is not necessary for the double bubble tubular process to cool the primary film beyond excess.

1. Introduction

The various oriented films are used to package stationery, groceries, foods and so on, because the shrink packaging system is manageable and the packaged commodities were convenient to handle. In various resins, random-polypropylene(r-PP) and linear low density polyethylene are used for such shrink film popularly and widely. Shrink film is usually produced by double bubble tubular film process(Figure 1), because the oriented film has superior properties, such as shrinkage, tear strength and impact strength. The requirement for the shrink film is not only the mechanical properties but also the accuracy such as thickness uniformity or flatness or straightness.

Biaxially stretched film is investigated in terms of material, superstructure, process and so on. The materials for stretched films are polyethylene, polypropylene, nylon, polyethylene terephthalate and so on. The stretchability, processability and physical properties of linear low density polyethylene were published by *Uehara* et al.[1 to 3]. The processability of biaxially orientred PP film was investigated by *Benkreira* et al. [4]. The processability, scale-up rule and structure

development of biaxially oriented PA6 film was reported by Takashige et al.[5, 6]. The processability and structure development of polyamide 612 (PA612) film was investigated by S.Rhee and J. L. White [7]. The heating process of BOPP was investigated by H. Benkreira[8]. Process system and theoretical analysis is written by M.Takashige and T. Kanai[9]. Process and film character is written by J. L. White [10]. Many patents[11 to 13] were applied as to the producing method of biaxially oriented film for various resins with double bubble tubular process, because the technology of biaxially orientation is very important for the physical properties of oriented film.

Generally the molten resin extruded from die on double bubble tubular process is cooled by cooling water, in order to reduce the degree of crystallization and to obtain good stretchability. But there is no report describing the influence of cooling condition on the physical properties of biaxially oriented film. The relationship among cooling-water temperature, stretchability and mechanical properties of oriented film on double bubble tubular process have not been studied in detail.

2. Experimental

2.1 Materials

Some characteristics of r-PP used in this research is shown in Table 1.

2.2 Evaluation methods of material and film properties

2.2.1 Differential Scanning Calorimeter(DSC)

Differential Scanning Calorimeter (Seiko Instruments Inc. EXSTAR DSC6200R) was used to detect the memory of resin having previous thermal history. The amount of 10± 0.5mg for each sample was placed in a DSC pan.

2.2.2 Film density measurement

The film density in each process was measured by a fixed volume expansion method (SHIMADZU Accupic1330). The amount of about 4.5g for each sample was placed in a cell.

2.2.3 Haze measurement

The haze was measured by a hazemeter (Murakami Color Research Laboratory. HM-150) according to ASTM D1003.

2.2.4 Lightscattering

The analyses of the supermolecular structure of film sample were conducted by the polarized light scattering technique [17, 18]   A 15mW He-Ne gas laser (NEO-15MS, Nihon Kagaku Engineering Co., Ltd.) was used as the polarized, monochromatic (λ=632.8nm) light source. The polarized incident light irradiates to the sample, and scattered light is passing through an analyzer placed

after the sample. A light scattering pattern was recorded on a photographic film with a 1/250 s exposure time, using Hv polarization condition where the polarization of the analyzer and of the incident light are perpendicular.

The measurement of the spherulite radius is based on the light scattering theory[1] for perfect spherulites which gives

$$R = 4.09\lambda / \{4\pi \sin(\theta_m/2)\} \quad ,$$

where R is the spherulite radius, λ is the wavelength of the light in medium, θ_m is the scattering angle corresponding to the maximum scattered light intensity.

2.2.5 X-ray crystal structure analysis

Crystallinity and the period of the lamella stacking (long period) were calculated by the wide angle x-ray scattering (WAXS) method and small angle x-ray scattering (SAXS) method, respectively. X-ray diffraction profiles were obtained by a camera system connected to an imaging plate (IPR-420, Bruker AXS K. K.) using a graphite monochromatized Cu-Kα radiation (1.542**Å**) from an X-ray generator (ultraX 18, Rigaku Co. Ltd). The distances from the sample to detector were 7 cm for WAXS and 110 cm for SAXS.

2.3 Installation
2.3.1 Double Bubble Tubular Film Machine

The double bubble tubular film process consists of two stages(shown in Figure 1). In the first stage, the resin extruded from the circular die is cooled into solid state by cooling water process and flattened out by a set of nip rolls. The flattened film is re-inflated and pass the pre-heating process which is equipped with the infrared heater. The film which passes the pre-heating process is hereinafter called secondary film (end point of pre-heating process or starting point of stretching, position B in Figure 1). Additionally, the secondary film is stretched biaxially in the stretching process. After stretching, the stretched film(tertiary film) is cooled by a cooling air ring. The tertiary film is also flattened out by a set of nip rolls and cut both edges, and two films are wound respectively.

This machine has a 65mm extruder which is used for outer and inner layer (Modern Machinery Company), a 50mm extruder which is used for core layer (Modern Machinery Company) and a 180mm annular die (Tomi Machinery Manufacturing Corporation). A torque measurement instrument (Ono Sokki Co., SS201) is attached between the take-up nip roll and driving motor, in order to measure the stretching force or stress from the stretching torque. The measuring method of the stretching torque is mentioned in the literature[1]

2.3.2 Laboratory Stretcher

The laboratory stretcher is produced by Iwamoto Seisakusho, BIX-703. A film sample cut in square is set to the attachment and fixed all the sides. The film is heated for 2 minutes and is afterward stretched biaxially. The stretched film is cooled by air and removed from the attachment.

3. Film preparation

3.1 Double Bubble Tubular Film

Secondary film to measure a density and X-ray analysis is cooled with cold water right after it is sampled. The primary, secondary and tertiary film means a film of a position shown in Figure 1. The MD and TD stretch ratios are 5. The thickness of the primary film is 375 μm, and the film width is 235 mm. The stretched film thickness is 15 μm and the film width is 1180 mm. The output rate is 46 kg/h. The stretching stress of the double bubble tubular film is measured by using stretching torque. The stretching stress is changed by the stretching temperature which is controlled by the pre-heater and stretching heater.

3.2 Laboratory Stretcher's Film

The laboratory stretcher was used to investigate the stretchability of primary film produced by double bubble tubular film process. The stretch ratios are set at 5 in the machine direction (MD) and 5 in the transvers direction (TD) respectively. The thickness of primary film is 375μm, and the oriented film thickness is 15μm. Pre-oriented film size is a 95mm square, but with allowance for clipping, the effective stretching film size becomes a 70 mm square. The pre-heating time is 2 minutes, and stretching speed is 30 mm/sec. The relationship between the stretch ratio and the stretching force under each stretching temperature are measured. Only the MD data is used in this study, because the stretching force in MD and TD are similar as reported[1].

4. Results and discussion

4.1 Film properties and superstructure of each process produced at various water cooling condition

Properties and superstructure of PP film which is produced under various water cooling condition is investigated for each process, namely primary film, secondary one and tertiary one.

4.2 Random Polypropyrene

4.2.1 Relationship between the cooling water temperature and Density or haze or heat of crystallization (DSC)

The film density as a function of cooling water temperature for primary film and secondary one are measured. Figure 2 shows that the density of primary film increases with increasing cooling water temperature and low cooling temperature gives low density. This means that primary film density is influenced by cooling water temperature, especially low cooling water temperature. Though the primary film which is produced at different cooling water temperature has different density, the

secondary film becomes the same density with the film that cooling water temperature is different. The reason is because the preset temperature of pre-heating process is changed (Table 2) so that each tertiary film has the same stretching stress. This means that the influence of difference of the cooling water temperature on primary film by difference of the cooling water temperature can be adjusted at pre-heating process. In other word, in order to investigate the difference of cooling water temperature, only pre-heating process condition is changed in this research so that tertiary film has same stretching stress.

Referentially the density and haze as a function of cooling water temperature are shown in Figure 3. Among the results, these data mean that the haze of primary film shows a tendency like as density. Still secondary film can't be measured, because the one is wavy and rough on film surface. There is no transparency difference in tertiary film.

The heat of crystallization (ΔH) at each process is measured with DSC. Figure 4-a and b show that primary film and secondary one under various cooling water condition have shape changes in crystal melt behaviour slightly. The DSC data of heat of crystallization for tertiary film cannot be measured because of film shrinkage (Figure 4-c). From the results of DSC (Figure 4), the heat of crystallization (ΔH) is shown in Figure 5. Figure 5 shows that ΔH of primary film increases with increasing cooling water temperature and low cooling water temperature gives low ΔH. But the secondary film which passed the pre-heating zone, whose infrared temperature is adjusted to have the same stretching stress, has approximately the same heat of crystallization (ΔH). ΔH of primary film and secondary one at each process under various cooling water temperature shows the same tendency like density and haze.

$T_{mp.}$ of r-PP film for various cooling conditions are shown in Table 3. The $T_{mp.}$ of primary film and secondary one have same values under various cooling water temperature. The $T_{mp.}$ of tertiary films can't be measured correctly, because the film shrinkage occurs during DSC measurement.

4.2.2 Relationship between spherulite size and process condition

The spherulite size which is influenced by cooling water temperature is measured by light scattering for primary, secondary and tertiary films under various cooling water temperature. Figure 6 shows that the spherulite size of primary film increases with increasing cooling water temperature and low cooling water temperature gives small one. The spherulite size of secondary film is hardly changed by pre-heating process passage. Considering a spherulite size change being small and ΔH of secondary film being bigger than that of primary one by pre-heating process passage, it is suggested that crystallization is caused by microcrystal growth progresses. The spherulite size of tertiary film can't be measured, because the spherulite is crumbled by stretching force and doesn't maintain a sphere.

4.2.3 Superstructure analysis of film under various conditions by WAXS and SAXS

The superstructure of film under various process conditions is analysed by WAXS. Figure 7-a shows that the crystallinity of primary film increases with increasing cooling water temperature and the one of secondary film and tertiary one under various cooling water temperature are approximately same. From this result, it is clarified that the different crystallinity of primary film influenced by cooling water temperature is adjustable at the pre-heating process, and the crystallinity of secondary film slightly progresses to the same degree. The crystallinity of tertiary film under various cooling water temperature becomes lower than that of primary one and secondary one. This means that the crystal of secondary film is crumbled by the stretching force. In order to clarify the results of crystallinity change analysed by WAXS, a density change is investigated more in detail by SAXS. Figure 7-b shows long period of lamellae. Figure 7-b shows that lamellae's thickness of secondary film is bigger than that of primary film by the pre-heating process passage, and that of tertiary film is smaller than that of secondary film by stretching force. Figure 7-c means that the increase of peak intensity is correlate with the increase of crystallinity. Figure 7-d and e mean that superstructure of secondary film and tertiary one isn't influenced by cooling water temperature.

Judging from these results, the film superstructure change by the cooling water temperature and processing process passage is thought about as follows shown in Figure 8. At the cooling water process, the crystal consists of 3 phase. One is crystal phase, the other is amorphous one, the one more another is interface phase which is between the crystal phase and amorphous phase. In the case of primary film, the amorphous phase ratio is same. But the reason why the crystallinity increase with increasing cooling water temperature is that the interface phase changes to the crystal phase with increasing of cooling water temperature. The change of film superstructure by processing process passage is explained as follows. At the position of secondary film, the crystallinity of primary film increase to same degree by adjusted pre-heating process. The incident of crystallinity increasing is that interface phase changes to crystal phase furthermore. The individual crystal is crumbled by the stretching force, and a new amorphous phase is generated in each crumbled crystal interval. So tertiary film's crystallinity decrease than primary and secondary film.

4.3 Stretchability
4.3.1 Double Bubble Tubular Machine
The stretchability of double bubble tubular film is investigated for r-PP. The results are shown in Table 4. An evaluation method of stretchability refers to the report[1]. Stretchability is evaluated by each stretching stress range under various cooling water temperature Stretching stress range of r-PP is from about 13MPa to 34MPa at any cooling water temperature. But stretching stress and cooling water temperature is correlative under same pre-heating condition. The stretchability of r-PP isn't influenced by cooling water temperature on primary film producing process.

4.3.2 Laboratory stretching machine

The stretchability of laboratory stretching machine is investigated for r-PP. The results are shown in Figure 9. Stretchability is evaluated in terms of strain- stress data. From the results, r-PP is influenced by cooling water temperature and stretching stress with strain is slightly different in every cooling water temperature. There are slightly difference at yield point and terminal point definitely, it is considered that crumbling way of crystal (lamella or spherulite) slightly different with alteration of cooling water temperature. As the cooling water temperature is low, the early stretching stress is low, and the latter stretching stress is high. As the cooling water temperature is high, the stretching stress of yield point is high, and the late stretching stress is low. It is considered that the stretching stress change is different for its superstructure.

4.4 Thickness Uniformity of Film in each Processes

The thickness uniformity of primary films and tertiary films are measured. The thickness of primary film in MD is measured at 10 cm interval and thickness of primary film in TD is measured at 1 cm interval. The thickness of tertiary film in MD is measured at 50 cm interval and the thickness of tertiary film in TD is measured at 5 cm interval. From Figure 10, the thickness uniformity of primary films and tertiary films aren't influenced by the cooling water temperature.

4.5 Mechanical Properties of Stretched Film

4.5.2 Double Bubble Tubular Film

The mechanical properties of the tertiary films were measured. Figure 11 shows mechanical properties of several stretched film. The indispensable physical properties for shrink film is tensile strength, elongation, young's modulus, tear strength, impact strength, optics and shrinkage. In every properties of r-PP, only tear strength of r-PP shows difference value. The difference is that the impact strength decreases with increasing the cooling water temperature (Figure 11-e). It is considered that stretched film's crystal form is differ for the heat history of primary film.

4.5.1 Laboratory Tenter Stretch Film

The shrinkages of r-PP and LLDPE film stretched by labolatory stretching machine at lowest stretching temperature are measured. The results are shown in Figure 12. The shrinkabilities of both films are same at the shrink temperature from 90 to 120 . In spite of r-PP film having different stretching stress(Figure 9), the shrinkability isn't influenced by the cooling water temperature.

5. Conclusion

Stretchabilities of double bubble tubular process on r-PP isn't influenced by the cooling water temperature of primary film. Although primary film has different density and superstructure every cooling water temperature, the density at adjusted pre-heating process passage point become same.

As a result, even tertiary film under various cooling water temperature can be processed with same stretching stress by adjusting the pre-heating process.

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Tables

Table 1. Characteristics of r-PP

Table 2. Process condition for the double bubble tubular films of r-PP

Table 3. The T_{mp}. from DSC 1st run of r-PP film at each process

Table 4. The stretching stress range of r-PP for the double bubble tubular machine

Figures

Fig 1. Schematic drawing of the double bubble tubular film process

Fig 2. Relationship between cooling water temperature and density of films at each process

Fig 3. Relationship between cooling water temperature and haze of films at each process

Fig 4. DSC data of films at each process and raw material

a) 1st run of primary film, b) 1st run of secondary film, c) 1st run of tertiary film, d) 2nd run of r-PP's raw material

Fig 5. The ΔH change of films at each process

Fig 6. The photos and the spherulite size of films at each process by lightscattering

Fig 7. X-ray analysis data of films at each process or under various cooling water temperature

a) crystallinity change by WAXS, b) long-period change by SAXS, c) SAXS of primary films, d) SAXS of secondary films, e) SAXS of tertiary films

Fig 8. The schematic drawing of superstructure difference and change

Fig 9. Relationship between the stretch ratio and the stretching force during stretching of primary films in laboratory stretching machine

Fig 10. Thickness uniformity of films at each process under various cooling water temperature for the double bubble tubular machine

a) primary films, b) tertiary films

Fig 11. The properties of tertiary films under various cooling water temperature on double bubble tubular machine

a) stretching stress, b) elongation, c) young's modulus, d) tear strength, e) impact strength, f) optic, g) MD shrinkage, h) TD shrinkage

Fig 12. The shrinkage of tertiary films under various cooling water temperature stretched by laboratory stretch machine(stretched at 90   )

Table 1. Characteristics of r-PP

Material	r-PP
Density (g/cm^3)	0.91
Melt index (g/10min)	3.5
Melting point ( )	132
Ethylene content (%)	5.0
Mw (-) *1	315,000
Mn (-) *2	86,000
Mw/Mn (-) *3	3.66

*1 weight average molecular weight
*2 number average molecular weight
*3 polydispensity index

Table 2. Process condition for the double bubble tubular films of r-PP

Cooling water temperature( )	15	25	35	52
Ave. temp. of the pre-heaters( )	214	207	203	200
Ave. temp. of the stretching heaters ( )	310	310	310	310
Film temperature after the pre-heater( )	107	108	106	106
Stretching stress $_{MD}$(MPa)	33.0	33.2	33.7	33.5

Table 3. The $T_{mp.}$ from DSC 1st run of r-PP film at each process

	Cooling water temperature( )	15	25	35	52
	A : Primary film	130.0	131.1	131.5	130.7
$T_{mp.}$( )	B : Secondary film	128.8	130.8	130.5	130.7
	C : Tertiary film	129.3	135.4	131.3	132.3

Table 4. The stretching stress range of r-PP for the double bubble tubular machine

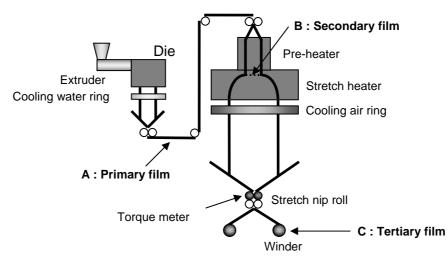|	Cooling water temperature( )	15	25	35	52
Stretching stress range (MPa)	min.	12.3	-	13.0	12.5
	max.	33.4	-	34.1	34.0
	R(max.-min.)	21.1	-	21.1	21.5

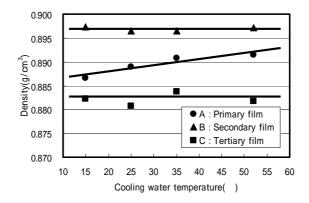Fig 1. Schematic drawing of the double bubble tubular film process

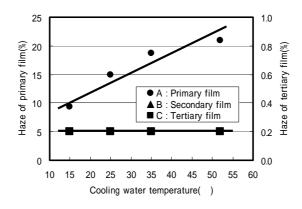Fig 2. Relationship between cooling water temperature and density of films at each process

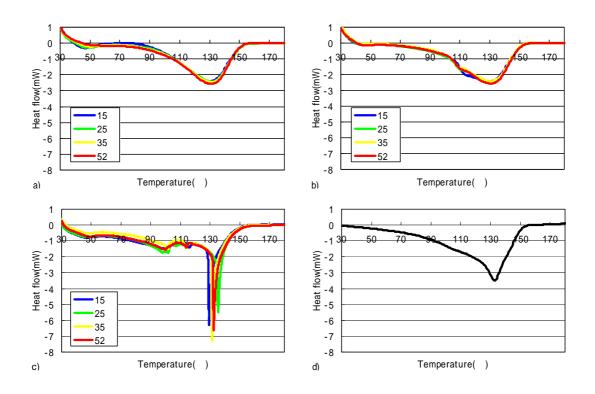Fig 3. Relationship between cooling water temperature and haze of films at each process

Fig 4. DSC data of films at each process and raw material
a) 1st run of primary film, b) 1st run of secondary film, c) 1st run of tertiary film, d) 2nd run of r-PP's raw material
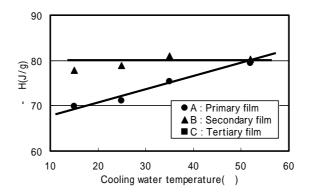

Fig 5. The ΔH change of films at each process

Cooling water temperature( )	15	25	35	52
A : Primary film				
Spherulite size(μm)	0.81	1.01	1.39	1.81
B : Secondary film				
Spherulite size(μm)	0.85	1.04	1.44	1.97
C : Tertiary film				
Spherulite size(μm)	-	-	-	-

Fig 6. The photos and the spherulite size of films at each process by lightscattering

Fig 7. X-ray analysis data of films at each process or under various cooling water temperature
a) crystallinity change by WAXS, b) long-period change by SAXS, c) SAXS of primary films, d)
SAXS of secondary films, e) SAXS of tertiary films

cooling water temperature( )	primary film	secondary film	tertiary film
15			
52			

Fig 8. The schematic drawing of superstructure difference and change

Fig 9. Relationship between the stretch ratio and the stretching force during stretching of primary films in laboratory stretching machine
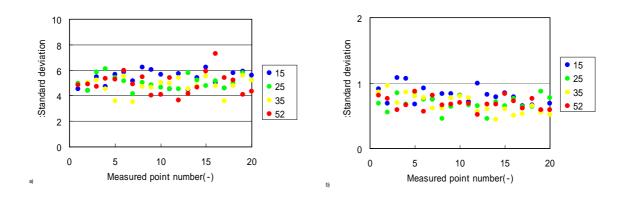

Fig 10. Thickness uniformity of films at each process under various cooling water temperature for the double bubble tubular machine
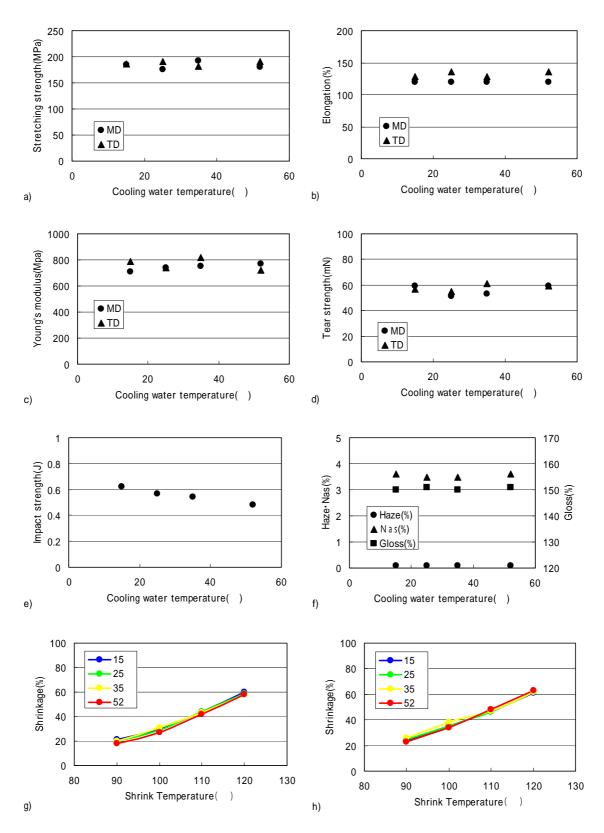a) primary films, b) tertiary films

Fig 11. The properties of tertiary films under various cooling water temperature on double bubble tubular machine

a) stretching stress, b) elongation, c) young's modulus, d) tear strength, e) impact strength, f) optic, g) MD shrinkage, h) TD shrinkage
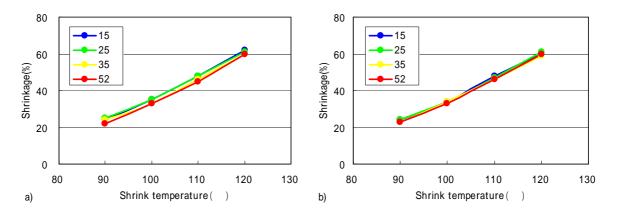
Fig 12. The shrinkage of tertiary films under various cooling water temperature stretched by laboratory stretch machine(stretched at 90)