

IMPROVEMENT OF POLYPROPYLENE BIAXIAL STRECHABILITY BY CRYSTALLIZATION CONTROLL

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Abstract

The low modulus polypropylene (LMPP) is a low tacticity polypropylene (PP). Recently, it was found that the stretchability of polypropylene (PP) is improved by blending a small amount of LMPP. Generally, the stretching methods which can produce biaxial stretching PP films are the simultaneous biaxial stretching and the sequential biaxial stretching. But there are a few researches that reported the relationship between dynamic in a stretching process and physical properties. The purpose of this research is to investigate the effect of blending LMPP, which has different characteristic of resin such as tacticity and a molecular weight, on PP and to study the mechanism of the structure formation in a biaxial stretching process.

The blending LMPP to PP reduces the spherulite size and increases the thickness of amorphous phase in the lamella without changing the thickness of crystal phase. As a result, reducing the crystallinity and improving the stretchability and the thickness uniformity of PP were achieved.

Keywords: low modulus PP, biaxial stretching, tacticity, crystallinity, stretchable temperature width

1. Introduction

Polypropylene (PP) is widely used for the biaxially oriented film using sequentially biaxial oriented process (Fig.1) and the supply capacity in 2013 reached 10 million tons/year. This film is mainly used in the field of food package and industrial usage because of high clarity, heat resistance and chemical resistance.

In recent year, according to the increasement of the demand, high prodction speed and ultra thin film such as capacitor film have been required.

In case of high speed production,as the high stress is applied during the biaxially oriented process, the film break and the problem of uneven film thickness occur.

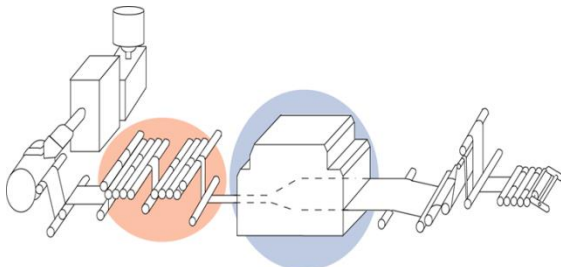


Fig.1 Sequential biaxial stretching by tenter method

Low tacticity polypropylene (LMPP) ¹⁾ has low crystallinity, low melt temperature and low density.

Our previous research reported that the addition of LMPP to PP which reduced the size of spherulites and decreased the yield value of Stress-S expected the better stretchability from the results of uniaxial stretching ^{2), 3)}.

The purpose of this research is to improve the stretchability of PP and to investigate the mechanism

of stretchability in terms of both S-S curve and super structure when a small amount of LMPP is blended to PP.

2. Experiment

2.1 Samples

The samples which were used are listed in Table 1. Isotactic polypropylene was BOPP grade A produced by Prime Polymer. L1, L2 and L3 are LMPP grades and L1 is standard grade of LMPP and L2 is lower tacticity than L1 and L3 is higher molecular weight than L1. Iso-polypropylenes A blended with 5 wt% of LMPP, namely L1, L2 and L3 were formed 500 μ m sheets of A/L1, A/L2 and A/L3 respectively under the resin temperature 250°C and chill roll temperature 30°C. The samples were cut in 58mmx 58mm square size. The previous research showed that as 5 wt % LMPP blended to PP had the best stretchability, 5 wt % blended various samples were prepared.

Table1 Characteristics of resins

Sample	MFR (g/10min)	Mw $\times 10^5$ (g/mol)	Tm (°C)
A	3	3.8	161
L1	60	1.3	70
L2	60	1.3	60
L3	7	2.3	70

2.2 Experimental equipment

The biaxial stretcher SDR-527K which was designed by our group and made by Etoh Corporation was used. The schematic view of this equipment is shown in Fig.2. Various data could be obtained at the same time such as stress strain curve (S-S), refractive index in

three directions and light scattering data. The stretching conditions are shown in Table 2.

Table 2 Stretching conditions

Stretching mode	Sequential biaxial stretching
Stretching speed	10mm/s
Stretching ratio	MD5times×TD7times
Stretching temp.	159°C
Preheating time	7min

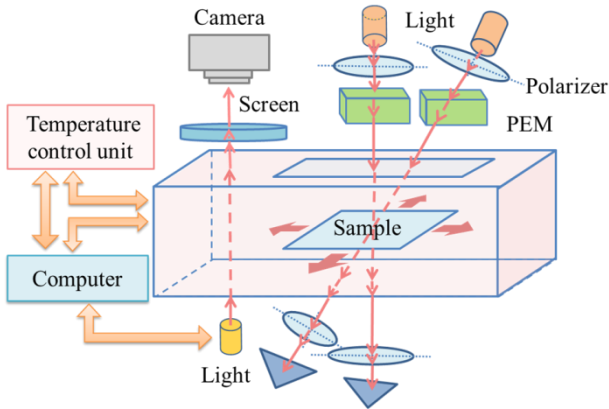


Fig.2 Schematic diagram of biaxial stretching machine

2.3 Stress- Strain Curve during the Stretching

Fig.3 shows an image pattern of stress- strain curve during the sequentially biaxial stretching. As the tenter process is usually used in the TD stretching and the final thickness uniformity is considered to be determined in TD stretching, TD stretching was focused.

From the previous research, good and not good stretchable patterns are shown in Fig.3. The stress pattern which has a high yield point at the initial stretching stage and then reducing stress shows undesired film thickness uniformity.

On the contrary, the stress pattern which has a low yield point at the initial stretching stage and then increasing stress shows good film thickness uniformity. The reduction of yield value is important to obtain good thickness uniformity²⁾

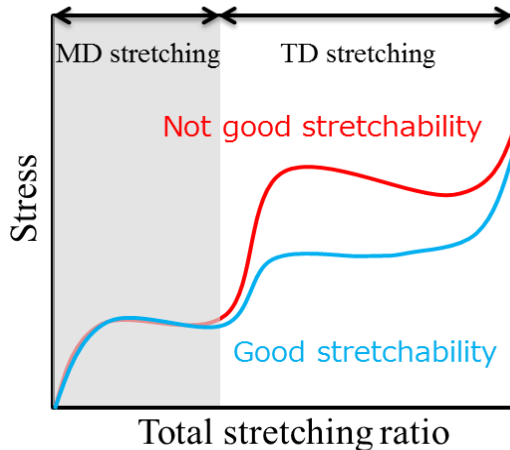


Fig.3 Models of Stress-Total stretching ratio curves in TD

3. Results and Discussion

3.1 Stress- strain Curve

Fig.4 shows stress- total stretching ratio (MD stretching ratio x TD stretching ratio) curves for various samples. Sample A has high yield value and after this point passes, the stress decreases. This means the necking deformation during the stretching process occurs and is undesirable for thickness uniformity.

The A/L1 and A/L2 which have about 40% lower yield values than PP A show stress hardening. Although A/L3 shows almost same yield value as PP A, the stress of A/L3 increases rapidly in the field of the high stretching ratio. L3 is high molecular weight LMPP and has molecular entanglement in the amorphous phase during the stretching process.

From these results, it is expected that LMPP blended samples create better film thickness uniformity than PP A sample and furthermore film break during the stretching process can be reduced.

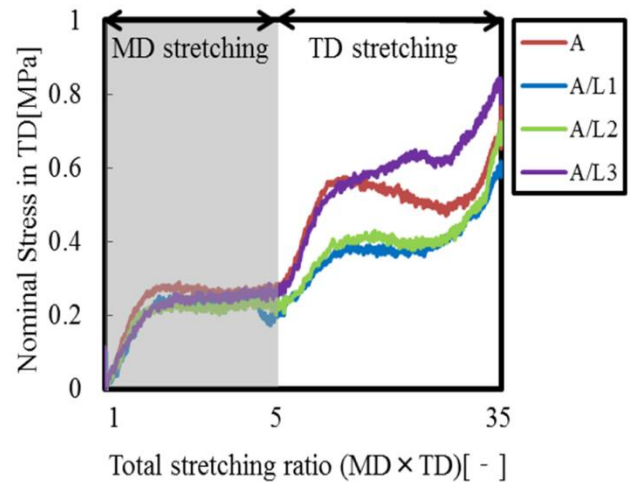


Fig.4 Nominal Stress-Total stretching ratio curves in TD

3.2 Film Thickness Uniformity of Biaxially oriented film

Table 3 shows the yield value σ_{yield} , maximum stress σ_{max} , stress build up ratio $\sigma_{max}/\sigma_{yield}$ and standard deviation σ_t when the samples are stretched in TD at stretching temperature 159 °C. The thickness uniformity was measured at 60 points, 1 cm interval by Toyo Seiki Thickness Meter B-1. Fig.5 shows that the relationship between stress build up ratio $\sigma_{max}/\sigma_{yield}$ and thickness uniformity. This result shows good correlation and the increasing the stress build up ratio $\sigma_{max}/\sigma_{yield}$ has a potential of improving thickness uniformity.

The reduction of yield value increases stress build up ratio $\sigma_{max}/\sigma_{yield}$ and reduces the necking deformation. It makes uniform stretching and reduces standard deviation of film thickness.

Table 3 shows the data of the stretching properties of PP samples in TD (159°C)

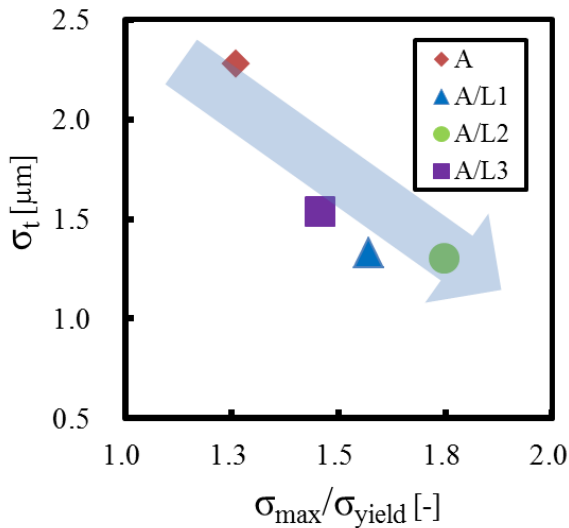


Fig.5 σ_t vs $\sigma_{\max}/\sigma_{\text{yield}}$

3.3 Relationship between stretchable temperature window width and film thickness uniformity

The stretchable temperature window width was defined as the stretchable temperature range. Fig.6 shows the relationship between the stretchable temperature window width and the standard deviation of film thickness uniformity.

The stretchable temperature range of PP A is 158~163°C (6°C) and the ones of A/L1, A/L2 and A/L3 which have lower stretchable temperature windows are 156~163°C (8°C).

As the blending LMPP to PP increases lower melting components and decreases crystallization speed during the stretching process, the stretching at a lower temperature is possible.

As a result, A/L1 and A/L2 improved the film thickness uniformity and the standard deviation is about half at 159 °C, compared with PP A. A/L3 also improved thickness uniformity, but it is not so good as A/L1 and A/L2. A/L3 which has high molecular component shows molecular chain entanglement and strain hardening, but does not show the reduction of yield value at the initial stretching stage and stress build up ratio does not become large.

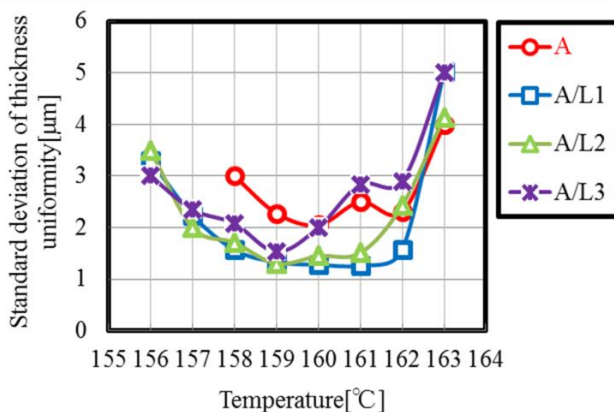


Fig.6 Standard deviation of thickness uniformity-temperature

Table3 Stretching properties of PP samples in TD(159°C)

Sample	σ_{yield} [MPa]	σ_{max} [MPa]	$\sigma_{\text{max}}/\sigma_{\text{yield}}$ [-]	σ_t [μm]
A	0.57	0.72	1.26	2.28
A/L1	0.35	0.55	1.57	1.33
A/L2	0.40	0.70	1.75	1.30
A/L3	0.56	0.83	1.46	1.53

3.4 Light Scattering (LS)

The spherulite size of sheet sample was measured by the light scattering. The existence of spherulites in a sheet makes the stretchability worsen³⁾. He-Ne laser (wave length $\lambda=632.8\text{nm}$) was used as a light source and the polarizer and the analyzer were mutually set perpendicularly and Hv pattern was observed.

Hv patterns measured by the light scattering are shown in Fig.7. The radius of spherulite size U_{max} was calculated by Eq.(1).

$$U_{\text{max}} = 4.09 / \{ (4 \pi / \lambda) \sin(\theta_{\text{SALS,max}}/2) \} \quad (1)$$

$\theta_{\text{SALS,max}}$: Maximum scattering angle showing maximum value 45 degree to polarizing direction

Table 4 shows the spherulite size of various samples. As Hv scattering pattern of sample A has small, the spherulite size is large and reaches about 10.5 μm . On the contrary, Hv scattering pattern of samples A/L1 and A/L2 are large and the spherulite size is reduced and about half, compared with PP A. As the crystallization speed of LMPP is much slower than PP, it is considered that the blending of LMPP to PP reduces the crystallization speed and the growth speed of spherulite. As the spherulite size of A/L3 is almost same as PP A, the blending effect of L3 is weak.

Table4 Spherulite sizes of PP samples

Sample	Spherulite sizes [μm]
A	10.5
A/L1	5.0
A/L2	4.7
A/L3	10.4

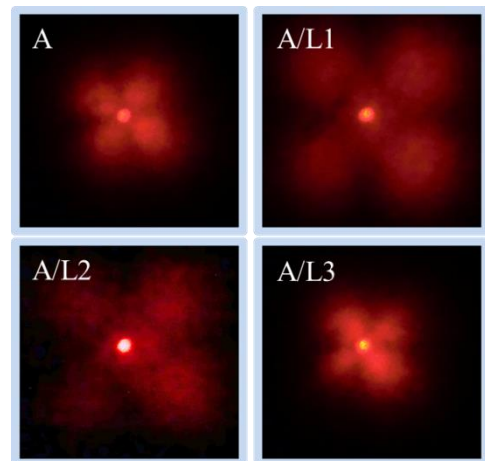


Fig.7 Light scattering images of PP samples

3.5 Differential Scanning Calorimetry (DSC)

The enthalpy of fusion ΔH and the melting temperature were measured by DSC-7 produced by Perkin Elmer. Fig.8 shows DSC curves.

The blending LMPP to PP A reduces ΔH by about 4%. The melting temperature of LMPP blends which keeps constant is the same as PP A.

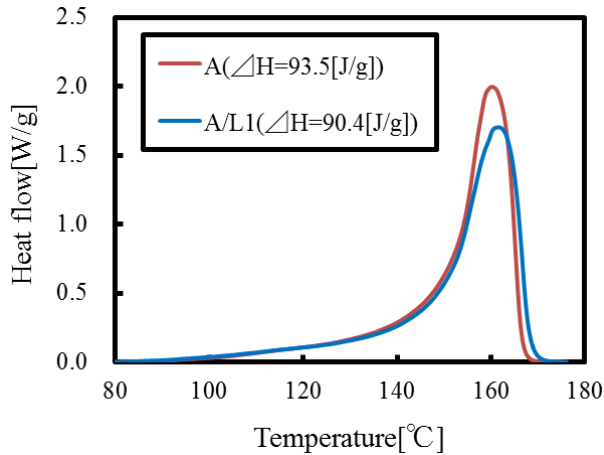


Fig.8 DSC curves on 2nd heat

3.6 Small Angle X-ray Scattering (SAXS)

The long period L was measured for 30 minutes using Rigaku X-ray SAXS at voltage 50kV, Ampere 280mA, CuK α ($\lambda=1.5418\text{\AA}$) and calculated by the maximum value of scattering pattern $2\theta_{\max}$ and Bragg equation Eq.(2).

$$2L\sin \theta_{\max} = \lambda \quad (2)$$

Fig.9 shows the relationship between the relative intensity and the scattering angle $2\theta_{\max}$. From these results, the scattering peak of A/L1 and A/L2 are shifted to the small angle side. It means the long period increases, but A/L3 shows a little shift.

From the long period and ΔH obtained by DSC, the thickness of crystal phase was obtained. Table5 shows the long period, the thickness of crystal phase and amorphous phase. The increase of LMPP blend samples' long period is caused by penetrating LMPP into amorphous phase, not crystal phase. LMPP reduces the crystallinity of blend samples.

Fig.10 shows that the superstructure is changed by blending LMPP into PP.

Table5 Higher-order structures of PP samples

Sample	Long period [μm]	Crystalline phase [nm]	Amorphous phase [nm]
A	12.6	5.6	7.0
A/L1	13.9	6.0	7.9
A/L2	13.4	5.8	7.6
A/L3	13.0	5.6	7.4

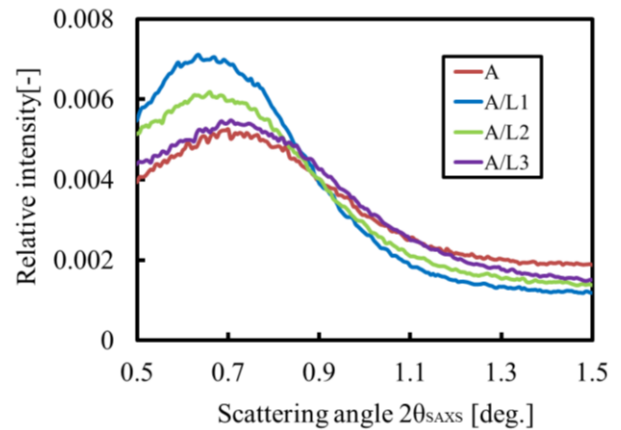


Fig.9 Relative intensity vs scattering angle 2θ

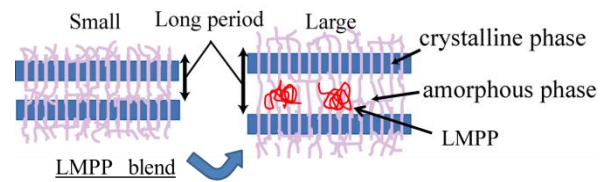


Fig.10 High order structure model by LMPP blend

4. Conclusions

Blending LMPP into PP was investigated in order to improve the biaxial stretchability of PP.

LMPP blends reduced the yield values during the stretching process and increased the stress build up ratio. As a result, they improved film thickness uniformity of biaxially stretched film and reduced film break during the production line. Furthermore, as the stretchable temperature window was widened to low temperature side, the thickness uniformity was improved in the wide stretchable temperature.

The blending LMPP to PP reduces the spherulite size and increases the thickness of amorphous phase in the lamella without changing the thickness of crystal phase, namely melting temperature.

As a result, reducing crystallinity and improving the stretchability and the film thickness uniformity of PP were achieved.

References

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