롤 연신에 의한 PBT 시트의 미세구조적 특성

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Fine structural characteristics of Poly(butylene terephthalate) sheets prepared from roll-drawing

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1. Introduction

Poly(butylene terephthalate)(PBT) is an important engineering polyester. It crystallizes much more easily and faster than PET. And these crystallization properties determine its use as an injection molding resin. Although it is more extensive than PET, its crystallization can be controlled much more easily during processing. General electric (Schenectady, NY) is the main producer of PBT films. Its production capacity was 3-5million pounds per year in 1987. PBT film is mainly used for electrical/electronic applications, because it is flame retardant and has a high dielectric strength.

While there are many methods by which orientation can be produced in synthetic polymers, but they fall into two groups. In one group the orientation is introduced after the polymer has first solidified in an unoriented state or a state of low orientation, a simple example of this being the drawing(stretching) of a cast film. In the other group the orientation is achieved by solidification form a fluid state in which the molecules are sometimes partially aligned. Further orientation is then often produced by subsequent drawing.

Drawing can be done in essentially three different ways : (a) A single piece of material, in the form of a fiber or sheet, is drawn in a tensile test machine[1-2]. This process is often used for experiemetal studies. (b) As a continuous process : a continuous filament[3-4] or sheet passes through two sets of rolls. The stretching rolls rotate at a higher speed than the feed rolls and the ratio of the speeds controls the draw ratio. In the commercial drawing fibers, the neck is localized by a heat roller over which drawing takes place and the fibers may be heat set by passing over a heated plate before being wound up. (c) Die drawing : In this process the sample is pulled, not pushed, through the die. The important difference here is that the type of stress applied is quite different.

The roll drawing process in solid phase[5] promises to become the lowest cost approach for the production of ordered plastics and has the virtue of being applicable to most commercial thermoplastic resins. Of course, solid phase processing is a well-known process in the packaging industry where it has been used extensively for the mass production of rigid containers and bottles for many years.

In this presentation an attempt has been made to adapt the rolling process to the economical production of high modulus PBT sheet. We describe a study of the formation of PBT sheets prepared from T-die extruder and of the application of the uniaxial roll-drawing process with various winding speed. Fine structure of PBT sheets investigated by the molecular orientation, crystal structure, thermal properties, etc.

2. Experimental

2.1. Sample preparation

PBT chips was a Duranex® obtained from Polyplastics Co., Ltd. The chips had an intrinsic viscosity(IV) of 1.14dl/g. PBT sheets were extruded from T-die using a single extruder (LABOPLASTOMILL, Toyoseiki Co.), after the pellets were dried at 130℃. Each zone temperatures(C1, C2 and C3) of extruder were set at 240, 250, and 255℃. The die temperature was controlled at 255℃. The screw rotation speed was fixed at 40rpm. PBT sheets were winded by a take-up roller whose temperature was controlled at 50℃ and speed at 1m/min. Oriented PBT sheets were prepared with various winding roll speed at 3.6, 4.8 and 6.0 m/min.

2.2. Characterization

Dielectric measurements at microwave frequencies were carried out by means of a microwave molecular orientation analyzer(MOA-3020A, New Oji Paper Co.,Ltd.). Information about the orientation in the sheet plane could be obtained.

Wide angle X-ray diffraction(WAXD, Rigaku Denki Co., Ltd) experiments were carried out by using a Ni-filterd Cu-Kα radiation (40kV,20mA). Intensities were measured by a scintillation counter and pulse height analyzer.

The dynamic-mechanical behavior of the sheets was analyzed in a sinusoidal oscillation using a non resonant forced-vibration type viscoelastometer(Rheovibron, Model DDV-25FP, Orientec Co.). Measurements were performed at a heating rate of 3℃/min between -150℃ and 220℃ and at frequencies of 1 Hz.

The thermal behaviors of PBT sheets were investigated using differential scanning calorimetry. DSC carried out over the temperature range 30℃ to 300℃ with a Seiko DDD 220C at a heating rate of 10℃/min. The sample weight was 5mg.

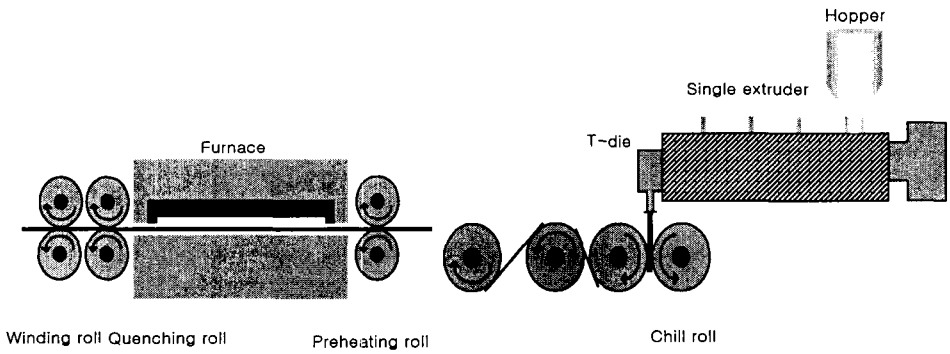
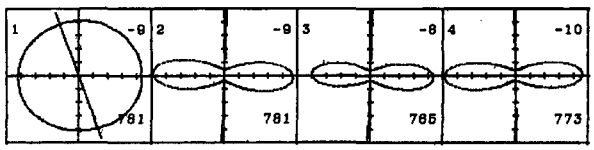


Figure 1. The Scheme of T-die extruder and roll drawing machine

3. Results and Discussion

Figure 2 presents MOA orientation patterns of PBT sheets with various winding speed. The orientation pattern, which corresponds to the orientation distribution of molecules in the film plane, was detected from the angular dependence of the transmitted microwave intensity. For un-drawn sample, the patterns were nearly spherical. For drawn samples, they became elliptical, with the long axes along transverse direction of orientation. Uniaxially stretched samples clearly showed orientation along the stretched direction at high draw ratio.



(a) Original (b) 3.6m/min (c) 4.8m/min (d) 6.0m/min

Figure 2. MOA patterns of PBT sheets with various winding speed.

Figure 3 shows the effect of winding speed on the WAXD profiles of PBT sheets. The reflection peaks observed at 2θ = 17.2° and 23.25° are assigned to the (010) and (100) reflections, respectively, of α-crystal, and those at 2θ =16.8° and 22.40° are ascribed to the (010) and (100) reflections of β-crystal. As winding speed is the higher, the intensities of the reflection of (010) increased.

In **Figure 4**, the E′ and tan δ of PBT sheets at various winding speed are presented. The DMA curves showed the temperature dependence of the dynamic modulus E′, the loss modulus E", and the loss factor, tan δ. They offer a means of characterizing the crystallization and orientation effects in the sheets over a wide temperature range. **Table 1** shows the E′ and Tg of stretched PBT sheets measured by DMA. As winding speed is the higher, the peak of tan δ value decreased and Tg increased. The change of intensity of tan δ with increasing winding speed means that the thermal motion of amorphous chains was restricted by chain orientation or orientation induced crystallization. For E", a small increased observed as the winding speed increased.

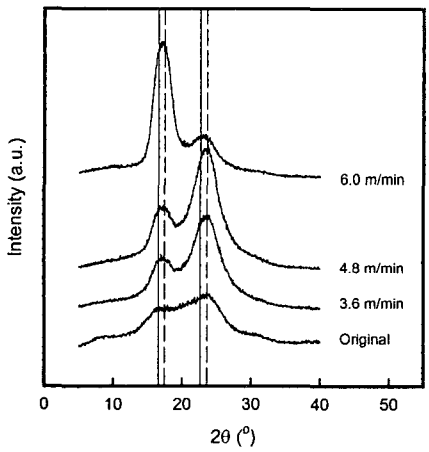


Figure 3. WAXD equatorial patterns of PBT sheets with various winding speed.

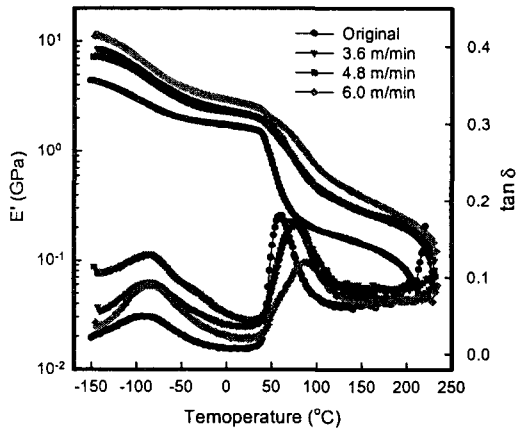


Figure 4. Comparison of E′ and tan δ for PBT sheet with various winding speed.

Table 1. Comparisons of the dynamics mechanical behaviors of PBT sheets at various winding speed

Winding speed (m/min)	Peak value of tan δ	Tg (℃)		E′ (GPa)	
		tan δ	E"	- 145 ℃	25 ℃
Original	0.1087	59.3	49.6	4.22	1.61
3.6	0.1722	69.8	61.8	8.50	2.2
4.8	0.1701	73.8	62.1	7.33	2.13
6.0	0.1198	87.5	76.4	11.10	2.67

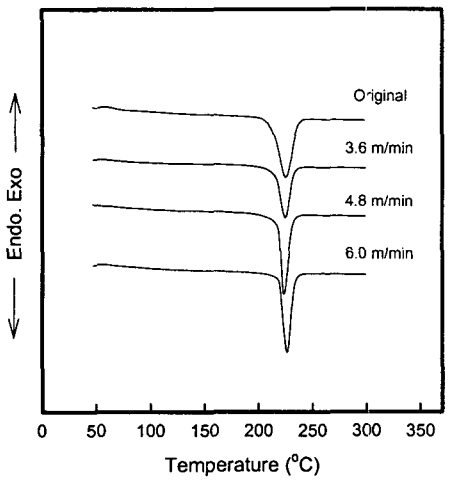


Figure 4. DSC thermograms of PBT sheet with various winding speed.

Table 2. T_m and X_c of PBT sheets with various winding speed

Winding speed (m/min)	T_m (℃)	ΔH (J/g)	X_c * (%)
Original	222.5	-	-
3.6	223.2	48.374	34.41
4.8	225.2	53.616	37.75
6.0	225.9	62.542	44.04

$$* X_{c(\%)} = \Delta \frac{H_s}{\Delta H_{100}} X100 \ , \ \Delta H_{100}=142J/g$$

According to Rong and Williams[6], the α relaxation represents the Tg, while the β relaxation at ca. -50℃ is assigned to restricted rotation around the ester or methylene links or to a cooperative wagging and rocking motion of the phenylene rings.

Figure 5 shows the DSC thermograms of PBT sheets with various winding speed. The endothermic melting peak is sharpened and shifted to higher temperature with increasing the winding speed. In the case of original PBT sheet, the other peaks beside T_m peak cannot be observed. The melting temperature is slightly changed with increasing the winding speed.

4. References

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