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# Structure and Properties of Biodegradable Polymers: Rolling Effect in Poly (butylene succinate) Sheets

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## SUMMARY

Sheets made from poly (butylene succinate) (PBS) were prepared by extrusion. They have been studied under uniaxial drawing as a function of the draw condition. Changes in molecular orientation and crystallinity were investigated using the criteria of differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), tensile testing, sonic modulus, X-ray diffraction, density, birefringence and measurements of % Haze. Rolling improved the thermo-mechanical and dynamic properties of extruded sheets as a result of changes in molecular orientation and crystallinity.

## INTRODUCTION

The increased consumption of plastics has resulted in increased waste, and the effects of this waste on the environment can no longer be neglected<sup>1</sup>. Hopes have therefore increased for developing biodegradable polymers such as poly (butylene succinate) – (PBS) and certain polymers blends<sup>2, 3, 4</sup> can be degraded by microorganisms in soil and water, without polluting the environment.

This study addresses the improvement of the properties of biodegradable aliphatic polyester films by altering the molecular chain orientation. Some aliphatic polyesters are biodegradable under microbial attack and unique applications are expected. These materials have somewhat low melting temperatures and low mechanical properties compared with aromatic polyesters<sup>5</sup>, for example, poly(hexano-6-lactone)PCL is an aliphatic polyester that is a relatively stable synthetic polymer under usual conditions and is biodegradable under microbial attack<sup>6</sup>.

In this study, the rolling of aliphatic polyester has been carried out, and the effects of the resulting stretching and the molecular orientation of films on the fine structure are examined.

Materials were characterized for their thermal properties using Differential Scanning Calorimetry (DSC), with orientation measurements by X-ray diffraction, birefringence, dynamic mechanical properties using the non-resonant forced vibration method, tensile testing, and measurement of sonic velocity and density.

## EXPERIMENTAL

### Materials

PBS samples were obtained and characterized as mentioned in the previous paper<sup>7</sup> and the patent<sup>8</sup>. The product was compared with commercial PBS – Bionelle 1000 (Showa Kobunshi LTD., Japan, Mn:  $5.52e^4$ , Mw:  $1.13e^5$ )

### Sheet processing

Sheets of PBS were obtained from pellets using a single-screw extruder (LABO PLASTOMILL, Toyoseiki Co) with a T-die (50 mm in width and 0.6 mm in clearance) at 60 rpm in screw rotation. Take-up speed was 2 m/min, and mass out-put was 49 g/min. The temperature of the chill roller was 50°C. The extrusion temperature profile in the barrel zones was set from hopper to die at 100, 135, 140 and 140°C. The last temperature was 140 °C. PBS pellets were dried overnight under vacuum at 80°C, and then, placed in a dry oven prior to use.

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### **Uniaxial stretching and rolling**

A polymer rolling mill machine, designed by one of the authors (K.N.) was equipped with an apparatus for applying tension forces to the sheets during the rolling, in order to produce a uniaxial molecular orientation in the samples. Rollers with 120 mm diameter and 150 mm length were used. They were heated with an internal cartridge heater at 60°C. PBS sheets were drawn to various draw ratios (from 0 to 4.1) at a constant draw rate of 1 rpm. The draw ratio ( $\lambda$ ) was defined as the ratio of length after (L) to length before ( $L_0$ ) rolling. L was determined from the displacement ink marks on the surfaces of the sheets.

### **Characterization**

Differential scanning calorimetry (DSC) was performed on a thermoanalyser (Thermo plus DSC 8230, Rigaku, Co.). All experiments were carried out under a constant flow of dry nitrogen. Samples weights ranged from 10-15 mg and heating rate was 20°C/min. A DSC thermogram served to obtain the melting temperature ( $T_m$ ) and melting enthalpy ( $\Delta H$ ).

Density measurements were made using a saturated solution of sodium bromide in a density gradient column at 25°C in accordance with a Japanese standard method JIS K 7112.

The Haze percentage (%) of the rolled samples was obtained, using a Digital Haze Computer, SUGA Test Instruments HGM-2DP. The test was conducted at room temperature.

Sonic velocity modulus was evaluated using a sonic propagation method at room temperature with a pulse propagation meter Rheovibron DDV-5-B (Orientec Co.). Pulse frequency was 10 KHz and pulse propagation distance between sending and receiving the sonic pulse was 250-300 mm. In some cases, it was 100-150 mm. The sonic modulus ( $E_s$ ) was calculated from the sonic velocity "c" and density "ρ" by use of the relation  $E_s = C^2\rho$ . The value of "c" was obtained from the propagation time vs. sample length line.

In the tensile tests, we used an UTM-111-10T Orientec Co, Ltd. tensile testing machine. Stress-strain curves were obtained and Young's modulus and tensile strength were determined. A load cell of 20 kg was used with an average sample thickness from 0.5 to 0.1 mm, average sample width 6.0 mm, gauge length 35.0 mm, a crosshead speed of 10 mm/min, and a

range of 100 % strain at 25 °C. An oven was used to increase the temperature in the range from 40 to 80°C.

Dynamic mechanical thermal analyses were carried out using a non-resonant forced vibration type apparatus (Rheovibron DDV-II-EA, Orientec Co). Measurements were made at a heating rate of 2°C/min in the temperature range from -150 to 150°C. The glass transition temperature,  $T_g$ , was defined as the maximum temperature of  $\tan \delta$  at a frequency of 1 Hz.

The shrinkage of the rolled samples was measured by a non-resonant force vibration type of apparatus, the Rheovibron DDV-II-EP (Orientec Co., LTD.), in the temperature range from 25 to 150°C, a heating rate of 2°C/min and the distance between jaws of 60 mm. The percentage shrinkage was based on the difference between L and  $L_0$ , the final and initial distance respectively.

X-ray diffraction analysis was carried out by wide-angle X-ray diffraction. Diagrams of samples were recorded using  $CuK\alpha$  radiation with a RAD-C instrument (Rigaku Denki Co). The X-ray generator was operated at 40 KV and 35 mA for 40 minutes. WAXD photographs were taken using a flat film. WAXD equatorial and meridian scan intensity profiles were obtained.

An OLIMPUS BX50 apparatus was used to obtain a birefringence ( $\Delta n$ ) index.

## **RESULTS AND DISCUSSION**

### **Rolling Conditions**

First measures were made using PBS samples with a draw ratio of 1, i.e. unrolled samples. They were characterized by tensile testing at different temperatures. Figure 1 shows the strain – stress curve for these samples. Deformation resistance decreased when the temperature was increased during the tensile test. All samples showed the same deformation behaviors. They had a high elongation at break. Figure 2 shows the Young's modulus obtained from as-extruded PBS samples. The modulus decreased when the tensile test temperature was increased. Therefore, a temperature of 60°C was used to obtain roller samples with different draw ratios.

The PBS sheets were treated in the polymer rolling machine to induce uniaxial molecular orientation. The draw ratios were 1.1, 1.3, 2.6, 3.5, 3.9, 4.0 and 4.1.

Figure 1 Stress-strain curves of as-extruded PBS sheets measured at five different temperatures, 25, 40, 60, 70 and 80°C (from top to the bottom)

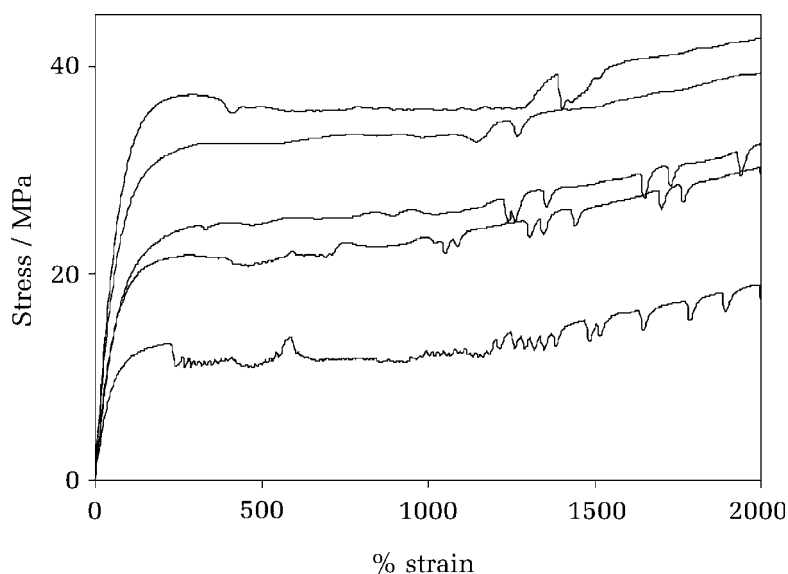
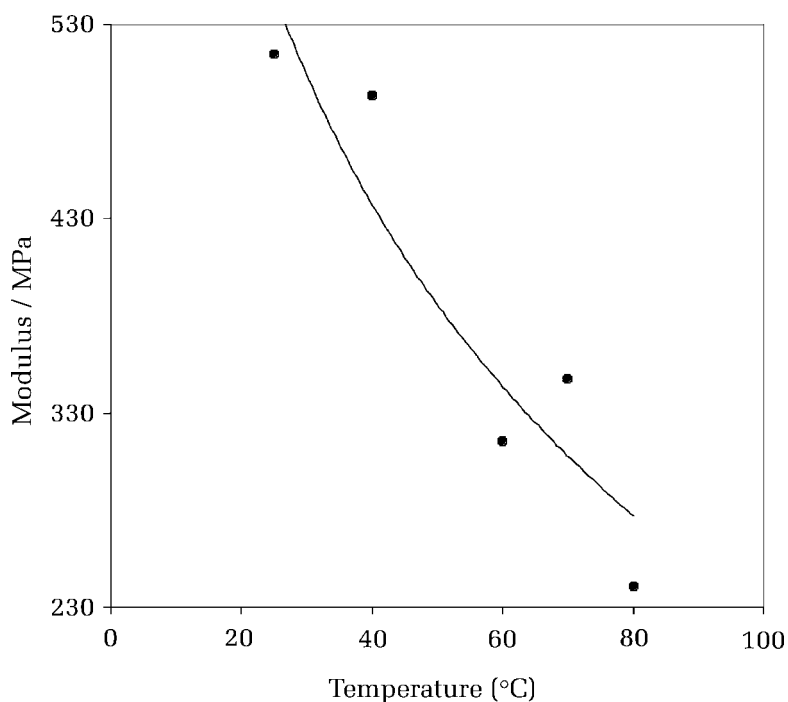


Figure 2 Young's modulus of as-extruded PBS sheets measured at five different temperatures, 25, 40, 60, 70 and 80°C



### Tensile Test

Figure 3 shows the stress-strain curves of rolled PBS sheets. In this case, roller treatment increased the tensile strength, modulus and yield stress but lowered the elongation at break. All the changes are related to molecular orientation and crystallinity.

### X-ray Diffraction

A qualitative trend can be seen in the X-ray diffraction results obtained from rolled samples. Figure 4 shows flat – film patterns for the as-extruded state after drawing. Debye rings indicate an isotropic material, highly oriented as the draw ratio increased. Also,

Figure 3 Stress-strain curves of rolled PBS sheets of draw ratios 1, 1.1, 1.3, 2.6, 3.5, 3.9, 4.0 and 4.1 (from bottom to top)

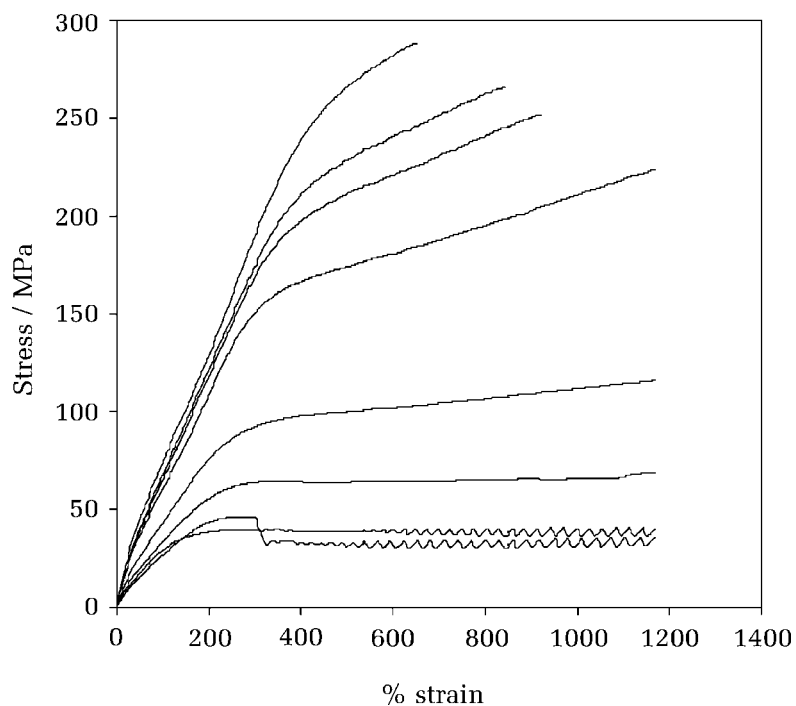
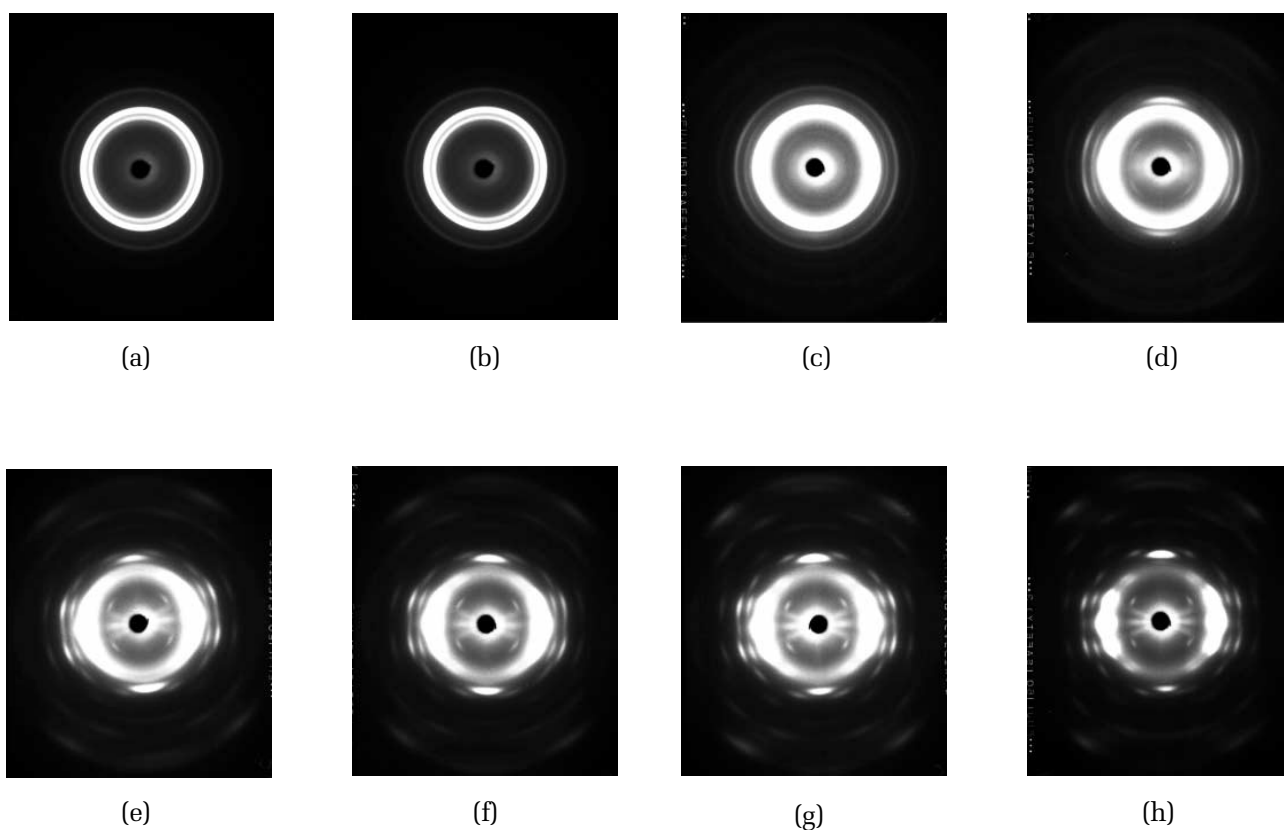


Figure 4 WAXD patterns of PBS sheets at various draw ratios. (A) as extruded,  $\lambda = 1$ , (B)  $\lambda = 1.1$ , (C)  $\lambda = 1.3$ , (D)  $\lambda = 2.6$ , (E)  $\lambda = 3.5$ , (F)  $\lambda = 3.9$ , (G)  $\lambda = 4.0$ , (H)  $\lambda = 4.1$ . Drawing direction is vertical



there is evidence of increased crystallinity as showed in Figures 5 and 6. Using WAXD equatorial and meridian scan intensity profiles of PBS sheets of different draw ratios (Figures 5 and 6) it is possible to observe how the profiles are different at high draw ratios. On the other hand, at low draw ratio, the profiles are similar. Therefore, the rolling process produces a molecular reorientation in the polymer matrix and hence an increase in crystallinity.

### Density

According to density analyses shows in Figure 7, is increased when the draw ratio is increased in response to the changes in molecular reorientation and crystallinity mentioned above.

### Differential Scanning Calorimetry

In differential scanning calorimetry (DSC), two kinds of transition can be observed (Figure 8) after the drawing process. It is suggested that the low endotherm corresponds to the melting of the original crystallites and the high endotherms to the melting of the recrystallized ones. Consequently, in the heating scan of PBS, two kinds of morphologically different crystallites as well as the process of melting and

recrystallization becomes evident. In some cases, the shapes of the peaks were remarkably affected by rolling. Figure 9 shows the relationship between melting temperature, melting enthalpy and draw ratio. Samples with high draw ratio showed a higher  $T_m$  than those with a low draw ratio. The enthalpy transition was hardly changed when the draw ratio was increased. Therefore, both trends imply an increase in the crystallinity as a result of molecular orientation induced by rolling.

### Measurements of % Haze

Rolled sheets were white at low draw ratio, but if it is increased, they became transparent. Percentage Haze in Figure 10 implies that rolling decreased the scattering of visible light and therefore, improved the transparency as a result of reorientation of the spherulitic structure to give oriented lamellae. This implies molecular reorientation as a result of rolling.

### Birefringence

Figure 11 relates to the birefringence ( $\Delta n$ ) analysis. To obtain  $D_n$  values, it is necessary for the sample to be transparent, as in PBS samples with high draw ratios. In this case, when PBS was rolled, with a high degree

**Figure 5** WAXD equatorial scan intensity profiles of PBS sheets at various draw ratios. The draw ratios are: (A) as extruded,  $\lambda = 1$ , (B)  $\lambda = 1.1$ , (C)  $\lambda = 1.3$ , (D)  $\lambda = 2.6$ , (E)  $\lambda = 3.5$ , (F)  $\lambda = 3.9$ , (G)  $\lambda = 4.0$ , (H)  $\lambda = 4.1$ , from bottom to top

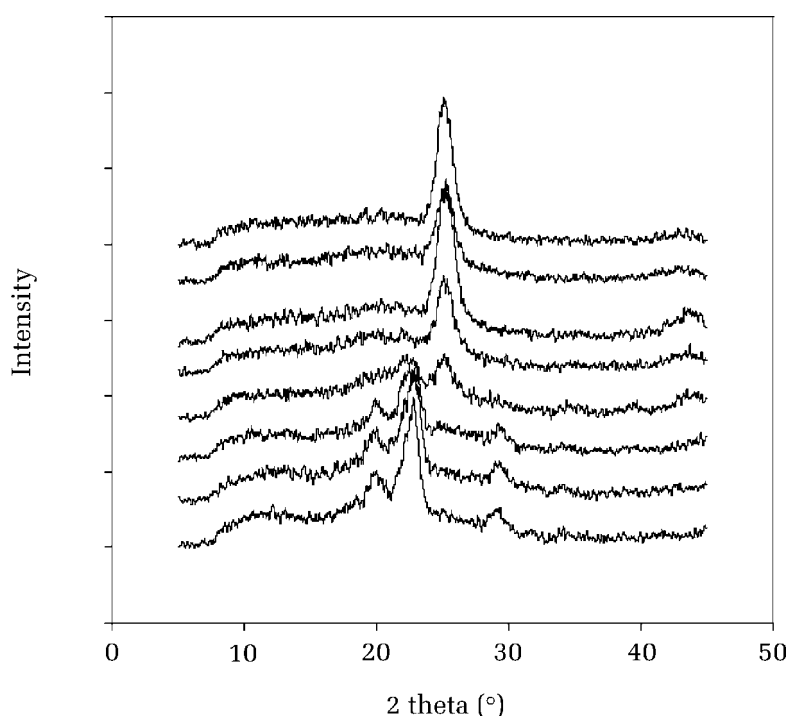


Figure 6 WAXD meridian scan intensity profiles of PBS sheets at various draw ratios. The draw ratios are: (A) as extruded,  $\lambda = 1$ , (B)  $\lambda = 1.1$ , (C)  $\lambda = 1.3$ , (D)  $\lambda = 2.6$ , (E)  $\lambda = 3.5$ , (F)  $\lambda = 3.9$ , (G)  $\lambda = 4.0$ , (H)  $\lambda = 4.1$ , from the bottom to top

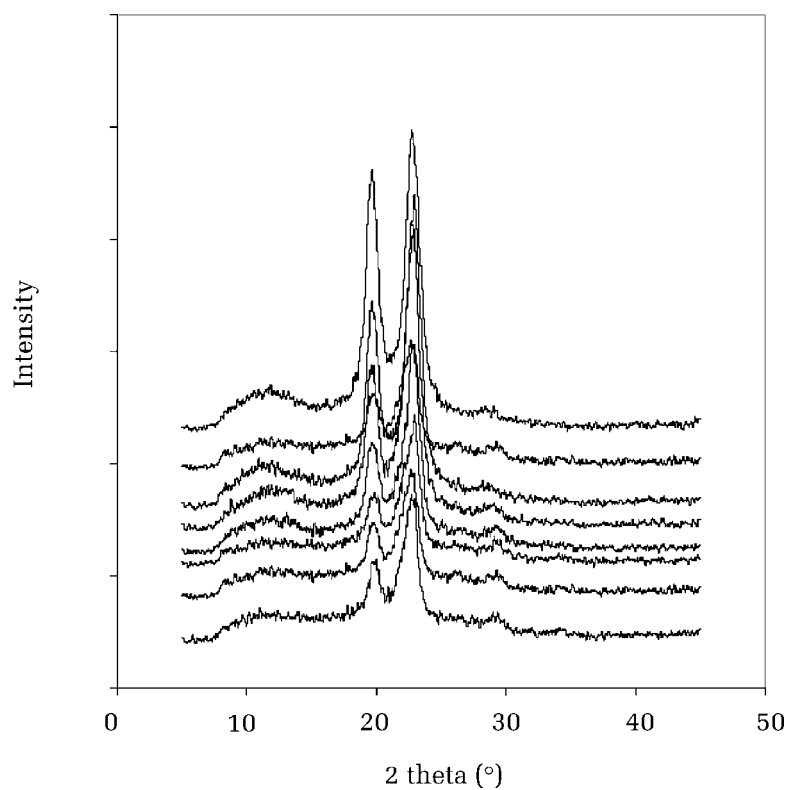
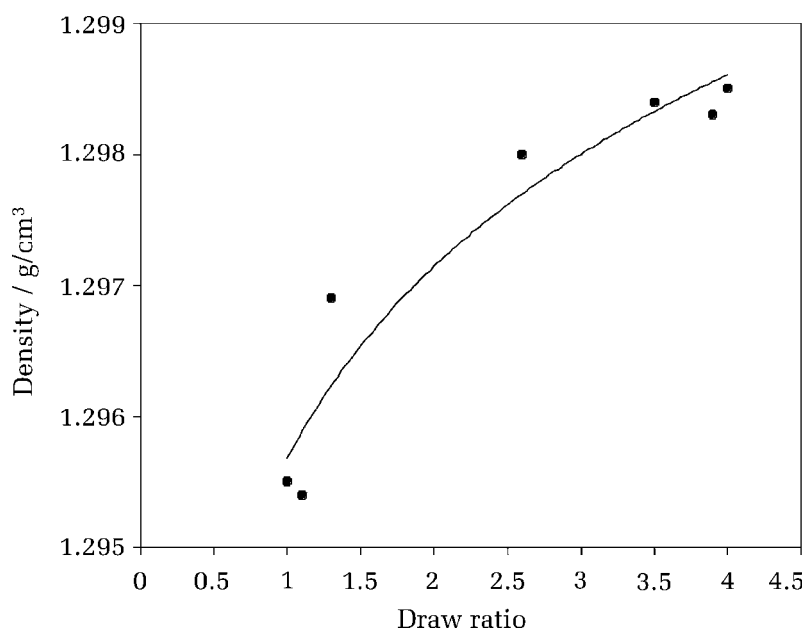
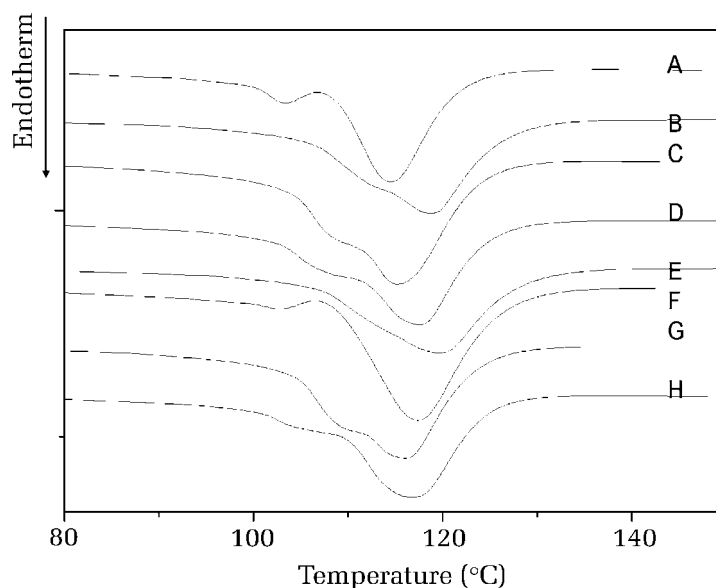


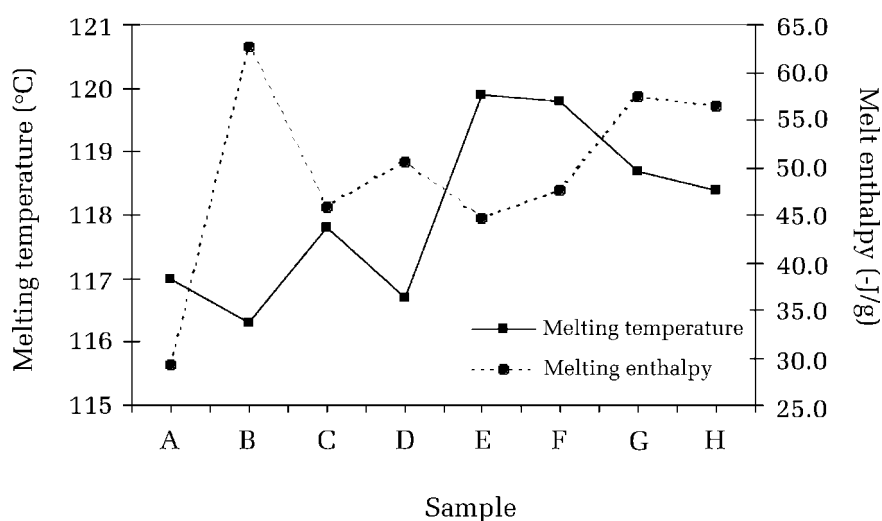
Figure 7 Density of PBS rolled samples, 25°C



**Figure 8** DSC thermograms of rolled PBS samples at various draw ratios: (A) as extruded,  $\lambda = 1$ , (B)  $\lambda = 1.1$ , (C)  $\lambda = 1.3$ , (D)  $\lambda = 2.6$ , (E)  $\lambda = 3.5$ , (F)  $\lambda = 3.9$ , (G)  $\lambda = 4.0$ , (H)  $\lambda = 4.1$ , from top to bottom



**Figure 9** Transition temperatures and transition enthalpy for rolled samples at various draw ratios: (A) as extruded,  $\lambda = 1$ , (B)  $\lambda = 1.1$ , (C)  $\lambda = 1.3$ , (D)  $\lambda = 2.6$ , (E)  $\lambda = 3.5$ , (F)  $\lambda = 3.9$ , (G)  $\lambda = 4.0$  and (H)  $\lambda = 4.1$



of molecular orientation, and was observed under crossed polars, the light was split up into two rays that vibrate along the two principal directions of the anisotropic crystal lattice. The general trends suggest that  $\Delta n$  is increased when the draw ratio is increased.

### DMA Measurements

They were made in order to study dynamic mechanical behaviour at different temperatures. A non-resonant

forced vibration method was used. Figure 12 shows the temperature dependence of the storage modulus,  $E'$ , of PBS rolled samples at various draw ratios using a frequency of 1 Hz. There was an increase in  $E'$  when the draw ratio was increased, too. Figure 13 shows the relationship between  $\tan \delta$  and temperature, at a frequency of 1 Hz, and Figure 14 shows the direct relation between  $T_g$  and draw ratio. Subsequently, glass transition temperature was enhanced by this treatment. So, it seems that changes

Figure 10 Percentage Haze in PBS sheets as a function of draw ratio

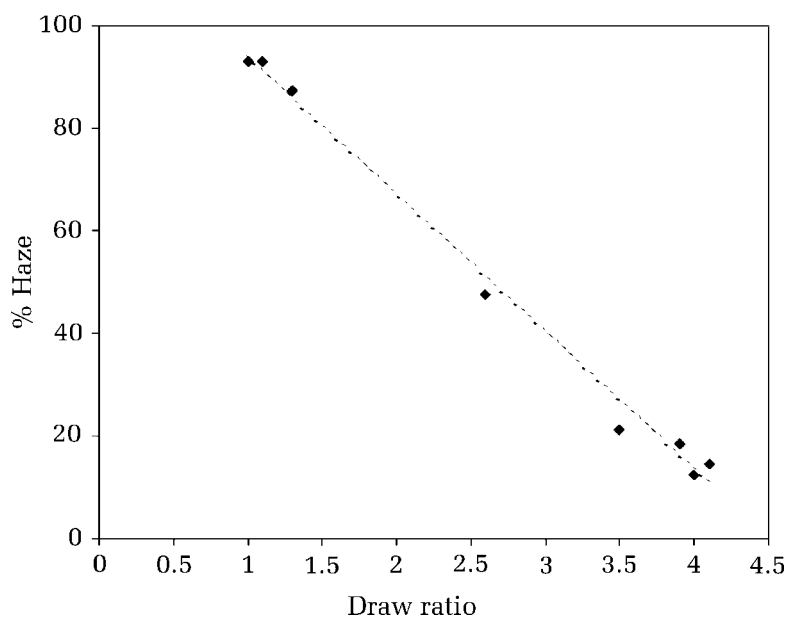


Figure 11 Percentage shrinkage of PBS rolled samples as a function of draw ratio

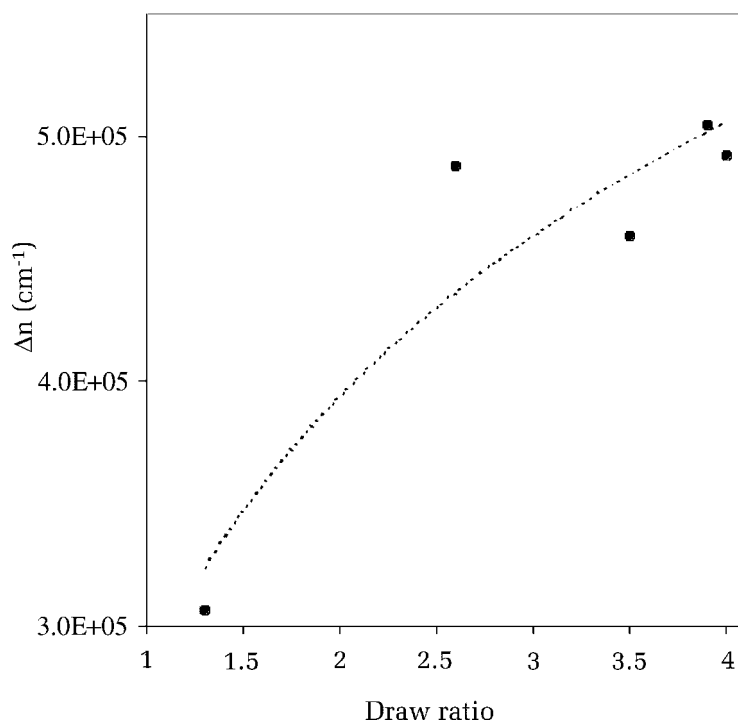




Figure 12 Temperature dependence of dynamic storage modulus  $E'$  in PBS rolled samples at various draws ratios. (Frequency = 1 Hz)

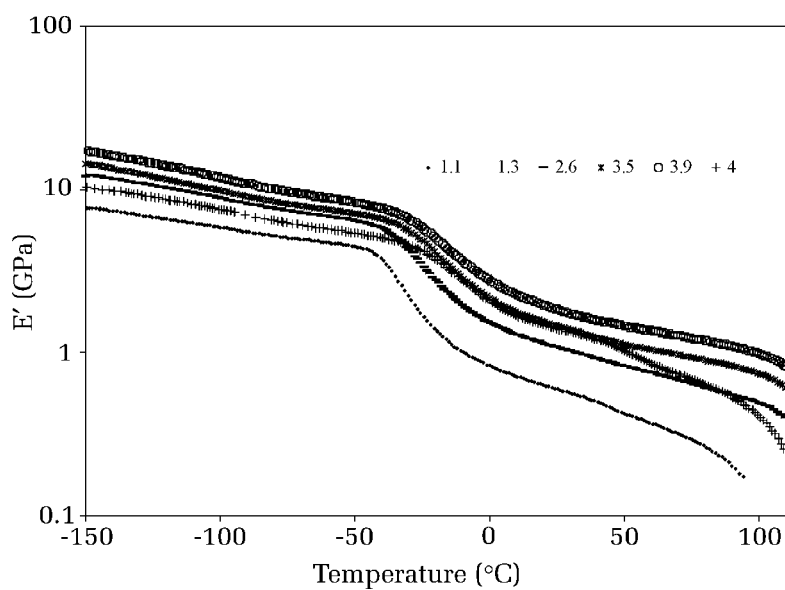
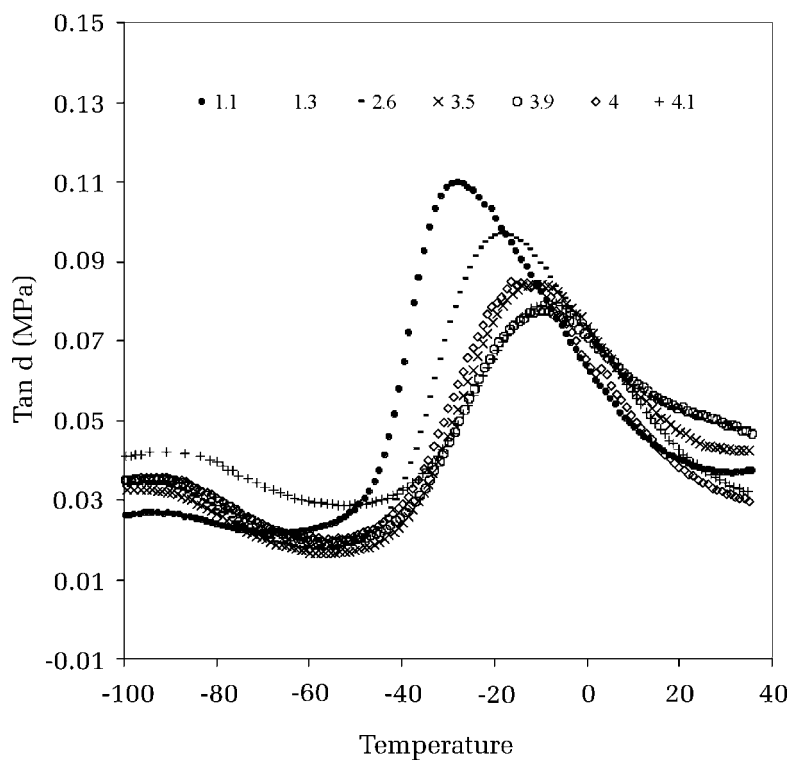


Figure 13 Relationship between  $\tan \delta$  and temperature at 1 Hz, for rolled samples at various draw ratios



in crystallinity of PBS rolled samples can affect the  $T_g$ . In general, it was demonstrated that rolling improves the dynamic mechanical properties.

The shrinkage of PBS sheets was measured using a DMA. A non-resonant forced vibration method was used to determine the internal stresses locked in the

film material at different temperatures, as a result of rolling (Figure 15). This percentage was low when the draw ratio was high. But, when the draw ratio was low, a plot of percentage shrinkage is dramatically raised. It is a consequence of molecular orientation induced by rolling.

Figure 14 Temperature dependence of glass transition temperature ( $T_g$ ) and draw ratio for rolled and unrolled samples

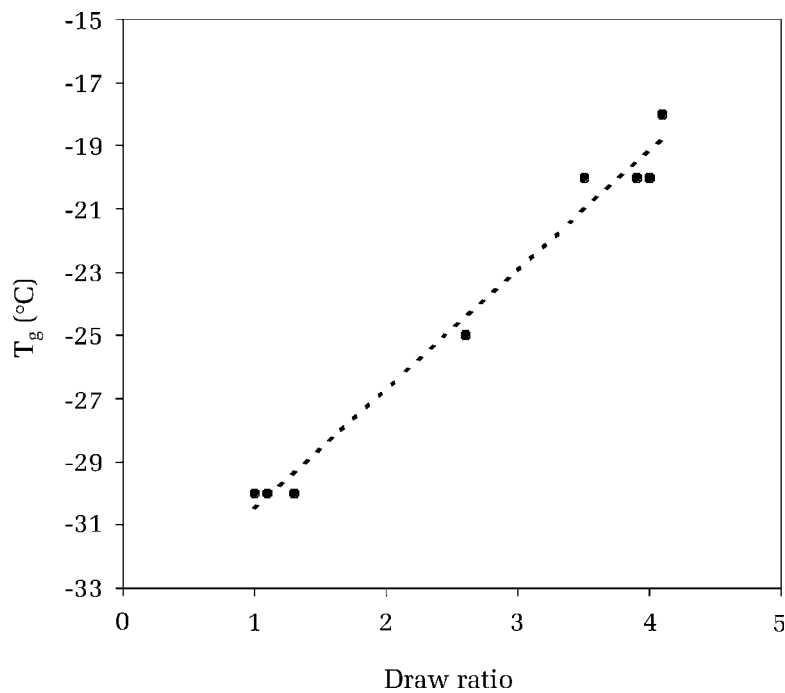


Figure 15 Percentage shrinkage of rolled PBS sheets as a function of temperature at various draw ratios

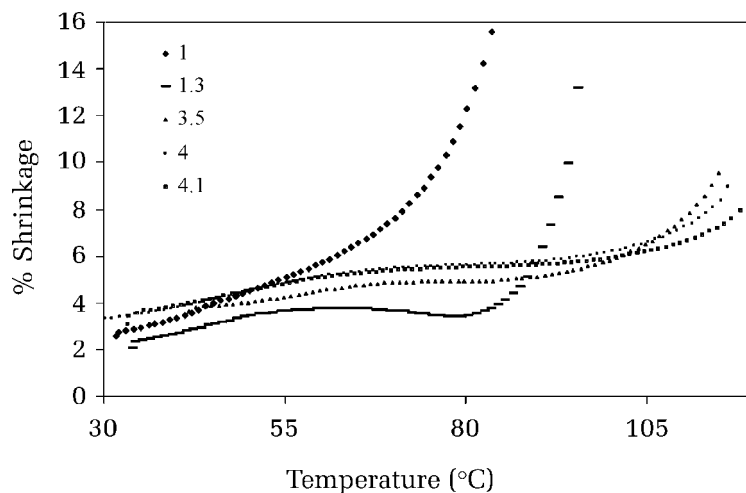
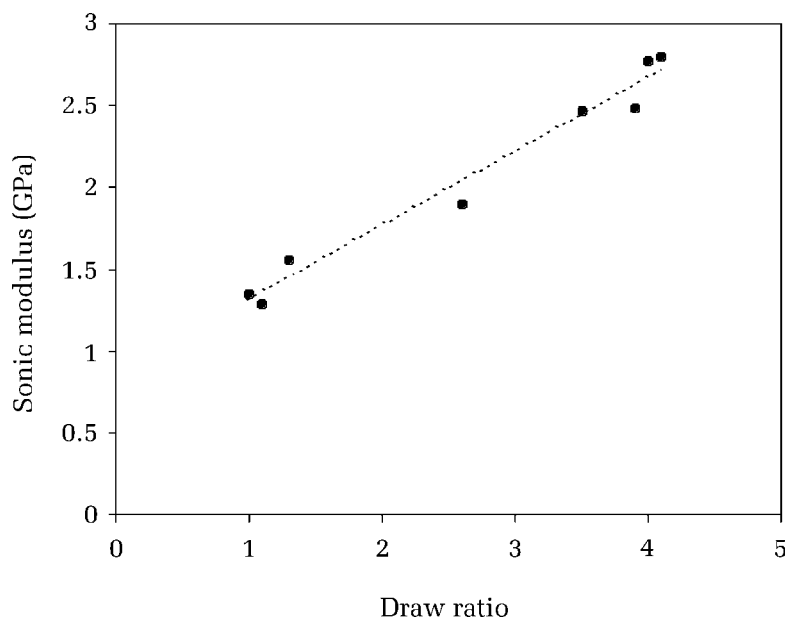


Figure 16 Sonic modulus measurements for rolled and unrolled samples



### Sonic Modulus Measurements

Sonic modulus is shown in Figure 16. It is possible to observe how sonic modulus increases with draw ratio. It is the result of the polymeric structure influence on the acoustic waves, i.e. crystallinity degree. It is consistent with birefringence and X-rays results, shown above.

### CONCLUSIONS

PBS rolled sheets with various draw ratios were obtained using a polymer rolling mill machine. It was concluded that rolling can improve the thermo-mechanical and dynamics properties of PBS sheets extruded. This is because during the draw processing, molecular orientation and crystallinity were increased. Therefore, rolling can be used to improve and control the physical properties of PBS sheets.

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