ROLL AND TENSILE DRAWING OF PET: EFFECT OF PROCESS CONDITIONS ON STRUCTURE AND PROPERTIES

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Abstract

Orientation of polyethylene terephthalate sheets, both amorphous and crystalline, was carried out in this study by means of roll-drawing using a series of four rolling stations and tensile drawing. Drawing temperatures from 80 - 200°C and drawing rates from 5 to 50 cm/min were used. Orientation was measured using both birefringence and FTIR spectroscopy. Crystallinity was observed to increase with draw ratio and crystallization temperature decreased. Birefringence increased continuously with draw ratio and depended on draw rate. For semicrystalline rolled samples, some biaxial birefringence was observed. Under tension and for a constant draw ratio, the developed birefringence decreased for amorphous samples over long periods of time while it remained mainly constant for crystalline ones. The relaxation of unconstrained samples was monitored: the amorphous ones relaxed completely in about 2 min. whereas the crystalline ones kept their orientation. Increasing tension on the sheet during rolling increased draw ratio. Lowering temperature below T_g hindered relaxation and increasing drawing speed increased orientation for the same draw ratio. Finally, the modulus of drawn PET increased linearly with draw ratio.

Introduction

Properties of polymeric materials can be enhanced significantly through orientation processes either in the solid state, in the rubbery state or from the melt. On the other hand, replacement of some conventional structural materials has led material scientists and engineers to look at new processes to enhance the properties of some of the existing ones. Very interesting properties can be obtained for oriented polymers, including the mechanical, impact, optical and barrier properties.

Solid state deformation of polyolefins has been studied more extensively than that of engineering or speciality resins (1-4). Using polyesters or polyamides will allow the use of oriented materials at temperatures beyond 100°C. In the case of polyesters, the most studied polymer is poly(ethylene terephthalate) (PET) because of its wide use in fibers, films and bottles. We recently investigated the orientation of this polymer using solid state roll-drawing from the semi-crystalline state (5-6) as well as tensile drawing of amorphous films (7-10). However, the use of continuous solid state deformation processes to produce thick oriented transparent PET sheets was not investigated. I this case, questions such as the evolution of orientation and relaxation as well as the behavior of the polymer under different deformation modes and process conditions remain to be studied.

From the orientation characterization point of view, many techniques have been developed: optical birefringence, infrared spectroscopy (IR), X-ray diffraction and ultrasonic measurements (1-6) have been developed. Other techniques such as Raman and NMR spectroscopy have also been used. Of these techniques, birefringence, IR spectroscopy and ultrasonic measurements are the most promising ones for on-line use (7-10). In this study, we will investigate also the on-line use of a birefringence technique developed in this laboratory for the monitoring of orientation development and relaxation in PET. The processes of interest are roll-drawing and tensile-drawing. The process parameters to be studied are tension, temperature and deformation speed.

Experimental Procedure

The material used in this study was an extrusion grade PET without any nucleating agent (Selar PT 7086 from DuPont) having an intrinsic viscosity of 1. Its molecular characteristics as determined by GPC were M_n = 28,800 and M_w = 54,600. For roll-drawing experiments, amorphous sheets of PET 3 mm thick by 10 cm wide were extruded from previously dried material. These sheets were then roll-drawn at low temperatures (amorphous PET) or high temperatures (crystalline PET). For tensile-drawing, 0.5 mm thick sheets were prepared, after drying PET, by compression molding at 280°C followed by quenching into ice water.

The roll-drawing experiments were carried out using a complete pilot plant line described elsewhere (5-6). The amorphous sheet was first preheated to the desired temperature between 80 and 200 °C, then fed to the first rolls. The rolling speed ranged from 20 to 60 cm/min. The gap between the rolls was varied to obtain different draw ratios and tension was applied to the sheet by the subsequent rolls. Draw ratios λ from 1 to 4.4 were thus obtained. Birefringence and video-camera monitoring after the second pair of rolls was performed for some tests. Strips were then cut from the oriented sheet for the orientation and mechanical testing.

Tensile drawing was performed mainly at a temperature of 80°C in the environmental chamber of an Instron tensile machine. Both stress and birefringence were monitored during orientation development and relaxation. The drawing speeds varied from 1 to 64 cm/min.

The crystallinity of the different samples with different λ was determined from DSC measurements. The crystallinity was calculated as the ratio of the enthalpy measured under the melting peak of the material to that of the corresponding fully crystalline material. The enthalpy of melting of completely crystalline materials was taken as 140 J/g for PET (11).

Birefringence measurements were performed using an technique developed in-house that enables the measurement of absolute biaxial birefringences for transparent samples. It is based on a multiwavelength light source, a photodiode array and in-house data acquisition and analysis software. This technique is described in more detail elsewhere in this conference (12). For opaque samples, measurement of birefringence were performed using an Abbe refractometer. Infrared dichroism measurements were made on a Nicolet 170SX FT-IR spectrometer at a resolution of 4 cm^{-1} in the specular (external) reflection mode at a low angle of incidence. Spectra were measured at two orthogonal polarizations (parallel and perpendicular to the draw direction) without changing the sample position. The Kramers-Kronig transformation was performed with the commercial software Spectra Calc^{TM} from Galactic Industries Corporation, using the Maclaurin's series algorithm to perform the integration. The details of the calculations of the dichroic ratio and band assignments were published elsewhere (7-10).

Mechanical properties of the oriented materials were measured at room temperature. The samples were tested on an Instron tensile tester using a jaw speed of 5 cm/min. The results obtained were expressed in terms of tensile modulus and strength in both the longitudinal and transverse directions. Measurements of flexural modulus using dynamic mechanical testing (DMTA) at 1 Hz and room temperatures were also performed.

Results

The crystallinity results as a function of λ are shown in Figure 1 for amorphous samples roll-drawn at 80°C. The roll-drawing speed was about 20 cm/min. Crystallinity increases in a fashion similar to that observed for uniaxially drawn samples (8-10, 13). The stress-induced crystallinity onset occurs between λ values of 1.5 and 2. Similar results were obtained for amorphous tensile drawn material and are not shown here for the sake of brevity. For crystalline roll-drawn PET (at 200°C), the initial crystallinity was about 30% and increased to about 45% for a λ of 5.

The results obtained for birefringence for the different samples are presented in figures 2 to 4. In Figure 2, birefringence was monitored during the tensile drawing of PET sheet at 80°C and 2 cm/min. It increases linearly with λ up to λ of 2.5, then the slope becomes steeper above this draw ratio, due to the onset of stress induced crystallization. This effect was even more pronounced for higher drawing speeds. Figure 3 shows a similar increase in the birefringence developed in roll-drawn amorphous PET. No slope change was observed in this case, this is probably due to greater scatter in the data compared to that in figure 2. In these two cases, no biaxial orientation was observed. For the roll-drawn crystalline PET, shown in Figure 4, birefringence also increases with λ. This increases seems however less pronounced than that observed for the amorphous case. This may be due to the intrinsic birefringences of the amorphous and crystalline phases which were estimated to be 0.275 and 0.220 respectively. It is to be noted that in the case of crystalline PET, some biaxial orientation was obtained as can be seen in figure 4.

As orientation develops, usually at temperatures above the glass transition (Tg), some relaxation can occur under tension and also after the tensioning stage. This relaxation is dependent on the process conditions, such as drawing speed and temperature. In order to evaluate this relaxation, birefringence measurements were performed on-line on sheets under tension, drawn to different λ at 80°C. Dichroic ratio measurements were performed following free relaxation at 70-80°C. The results are shown in Figures 5 and 6 for a λ of 2 and

Figures 7 and 8 for λ between 3 and 4. For λ = 2, relaxation of birefringence is linear with log(t) under tension and some orientation is still present up to times of 1000 s. Under free relaxation conditions, it is observed that the dichroic ratio relaxes almost completely (to the initial isotropic value of 1.00) in about 120 s. This sample is mainly amorphous as already mentioned above. For λ of 3 or above (3.5 and 4 were also studied), negligible relaxation was observed in samples undergoing free or constrained relaxation. In fact, apart from a slight decrease in the birefringence of the constrained samples (λ of 3.5) over short times (particularly those drawn at higher rates), no relaxation was observed. For free relaxed samples, no decrease in dichoroic ratio was observed over periods of time of 10 min.

As discussed above, the process conditions have a large effect on the structure of drawn PET, either crystalline or amorphous. This will be illustrated here in three examples. Figure 9 shows the effect of tension on the final λ of roll-drawn crystalline PET where a λ of 5 was applied at the second set of rolls. With no tension applied to the sample λ relaxes to a value of 2.5 but by increasing the tension the relaxation is reduced. Figure 10 shows that as soon as the temperature of PET drops below its Tg, almost no relaxation can be observed for amorphous samples. Finally, Figure 11, shows that for the same λ, increasing the deformation speed increases the degree of orientation developed.

Mechanical properties of the different samples were measured in tension in the static mode and in flexion in the dynamic mode. The results in tension (both longitudinal and transverse) and in flexion (longitudinal only) for roll-drawn crystalline PET are presented in Figure 12 for the modulus. For the longitudinal direction, a large linear increase of the modulus as a function of λ is observed as is expected. In the transverse direction, a slight increase is also observed in accordance with the biaxial birefringence noted above for these samples.

Conclusion

Upon deformation of PET by tension or roll-drawing, crystallinity increased with λ. Orientation also increased and depended on temperature, λ, draw rate, nature of the polymer (amorphous or crystalline) and deformation mode (tension or roll-drawing). Relaxation under tension and free relaxation occurred in amorphous samples only. Increasing tension on the sheet during rolling increased λ, lowering polymer temperature below Tg hindered relaxation and increasing drawing speed increased orientation for the same λ. Finally, the modulus of drawn PET increased linearly with λ.

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Key Words: Polyethylene terephthalate, Orientation, Birefringence, Relaxation. Mechanical Properties.

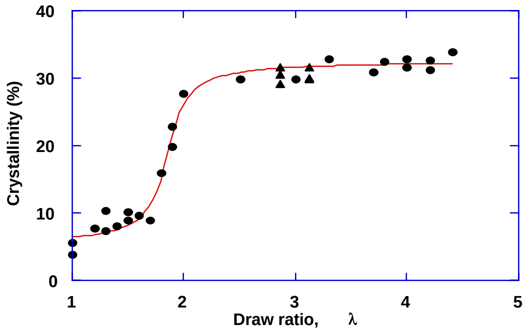

Figure 1: Crystallinity as a function of draw ratio of amorphous PET rolled at 80°C and about 20 cm/min from DSC.

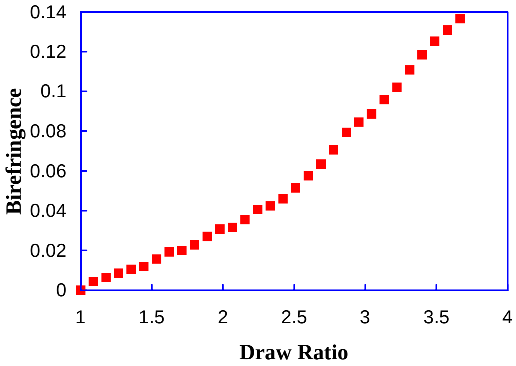

Figure 2: Orientation development by monitoring birefringence during tensile drawing at 80°C and 2 cm/min.

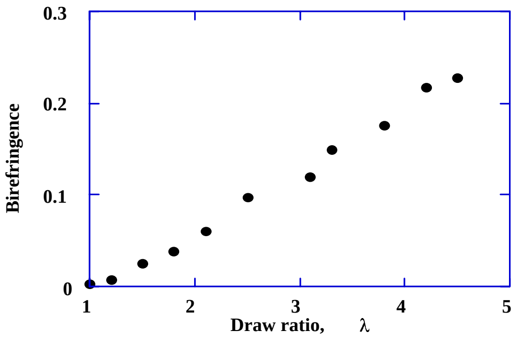

Figure 3: Birefringence as a function of draw ratio for amorphous PET roll-drawn at 80°C and about 20 cm/min.

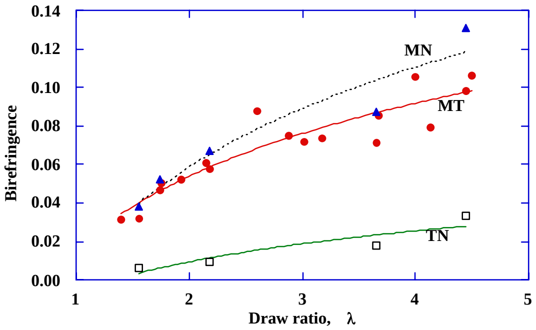

Figure 4: Birefringence as a function of draw ratio for crystalline PET roll-drawn at 200°C and about 50 cm/min. (MN=machine-normal, MT=machine-transverse and TN=transverse-normal)

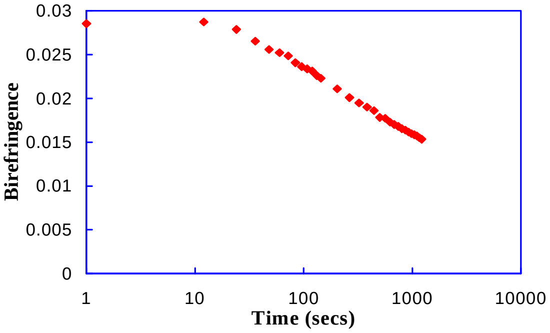

Figure 5: PET orientation relaxation after drawing to a draw ratio of 2 at 80°C under tension.

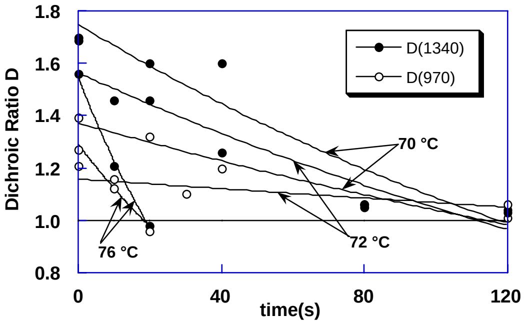

Figure 6: Variation of dichroic ratios with time at 70, 72 and 76°C for PET film with λ = 2 following free relaxation.

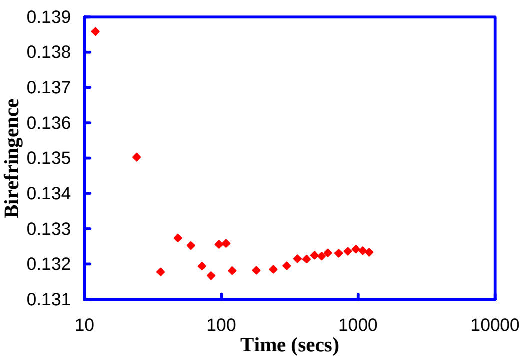

Figure 7: Relaxation of birefringence of PET Film tensile drawn to a draw ratio of 3.5 at 80°C and held under tension.

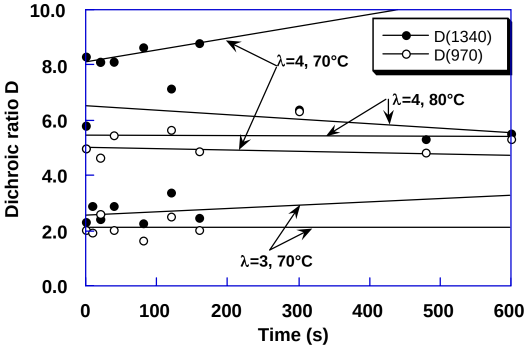

Figure 8: Variation of dichroic ratios with time at 70°C for PET film with λ = 3 and 4. and at 80°C for λ = 4 following free relaxation.

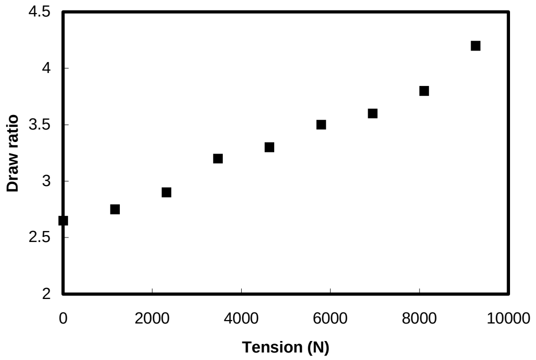

Figure 9: Measured draw ratio as a function of tension at the last rolls station for rolled crystalline PET at 200 °C and 50 cm/min.

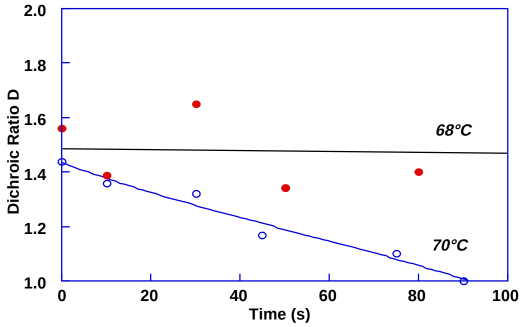

Figure 10: Variation of dichroic ratio of peak at 970 cm^{-1} for films with λ = 2, at 68°C and 70°C following free relaxation.

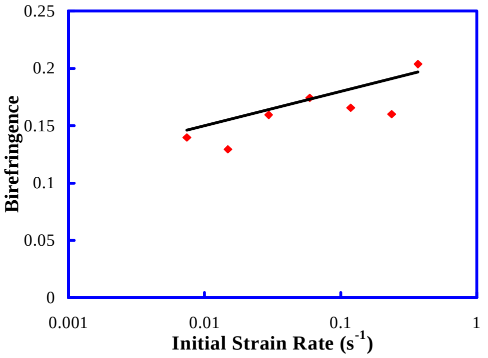

Figure 11: Effect of tensile drawing speed at 80°C on the developed birefringence at a draw ratio of 3.5.

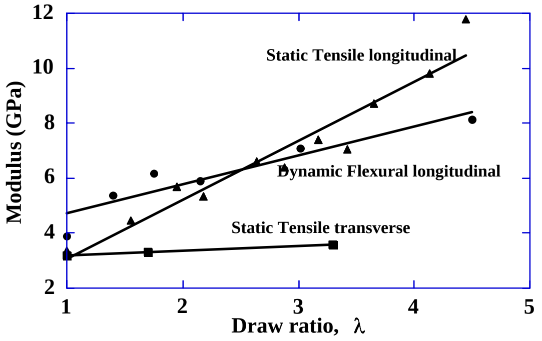

Figure 12: Modulus obtained for roll-drawn crystalline PET as a function of draw ratio measured in the indicated direction and deformation mode.