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A TECHNIQUE FOR ONLINE BIAXIAL BIREFRINGENCE MEASUREMENTS AND ITS APPLICATION*

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ABSTRACT: In this study, we discuss the applications of a birefringence technique for online or off-line quantitative measurement of biaxial orientation in transparent films, sheets, bottles, etc. Absolute values of biaxial birefringence are measured in two directions using a technique based on an incident multiwavelength double beam and photodiode array assemblies, combined with in-house developed software. Both machine and transverse direction birefringences (relative to the normal direction) were measured simultaneously. Film and sheet of different thicknesses can be tested and birefringence values from 0.0005 to 0.25 can be measured. The results reported here are on the use of this technique for online birefringence measurements in two different cases: orientation and relaxation of birefringence during and after deformation of polyethylene terephthalate sheet; and online biaxial orientation of polystyrene sheet monitoring in an industrial process plant.

KEY WORDS: polyethylene terephthalate film, polystyrene film, biaxial orientation, online, off-line, birefringence.

INTRODUCTION

ORIENTATION IN POLYMERS is known to enhance some properties such as mechanical, optical, barrier, etc. In most polymer processing operations, it is thus often desirable to induce orientation in the material, except in some specific cases, where any anisotropy in

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the material should be avoided (such as compact discs). This orientation in polymers can be induced by several processes, such as film blowing, film tentering (biaxial sheet orientation), blow molding, thermoforming, compression, rolling and drawing. In order to evaluate and optimize polymer properties and process conditions, it is of great importance to be able to know the orientational states developed in the polymer.

Several techniques can be used for off-line measurement of orientation in polymers. These techniques include birefringence, spectroscopy (FTIR, Raman, fluorescence, NMR, etc.), X-ray scattering (XRS), ultrasonic techniques, etc. Among these, birefringence (that is the anisotropy in refractive indices of the material) is the simplest. The orientation within the material can be described by the refractive index ellipsoid (indicatrix), which is defined by the refractive indices n_M, n_T, and n_N in the three axial directions (machine, transverse, and normal, respectively), which originate from the different polarizabilities in the three directions as a result of molecular chain alignment.

Birefringence is the difference between the different refractive indices: $\Delta n_{MT} = n_M - n_T$, $\Delta n_{MN} = n_M - n_N$, and $\Delta n_{TN} = n_T - n_N$. The techniques most widely used for its measurement include refractometry, monochromatic polarized light retardation [1,2], and multiwavelength polarized light retardation [3–5], and some qualitative techniques (fringes and light scattering). Refractometry is limited by several factors: use of contact liquid is not appropriate in many cases, it is a reflection technique, and it is tedious and cannot be applied for online monitoring. Monochromatic polarized light techniques are suitable for low orientations (low retardation), which are encountered in some cases, but are useless for moderately or highly oriented – films, sheets, or shapes and for relatively thick films. This technique was used for biaxial orientation measurements [6,7] in polymers with low degrees of orientation, mostly in the molten state. The multiwavelength technique, on the other hand, has been limited to uniaxial orientation and monolayer materials.

To overcome the limitations described above, particularly for moderate to highly biaxially oriented or thick samples, we developed the multiwavelength polarized light technique to measure the absolute biaxial orientation in biaxially oriented films, sheets, and shapes by directing at least two beams at different angles in order to measure the biaxial birefringence for transparent or translucent materials. One light source, that is bifurcated to yield two incidence beams, two array detectors and data acquisition and analysis software that take into account the effect of wavelength and the change of material optical properties with wavelength were used. The wavelength range used is from 400 to 800 nm [8,9]. For multilayer materials, provided they are significantly optically different, the authors exploited the difference in birefringence dependence on wavelength (optical dispersion) to discriminate the contributions of different layers [8].

Technique and Background

The technique is sketched on Figure 1. A multiwavelength light source is directed using a bifurcated fiber. At the end of the optical fiber, a collimating lens and rotating polarizer are fixed and the light beam directed at two different incident angles to the sample to be measured. After the sample, and directed to the light path, a set of polarizers and focusing beam lenses collect the light into two optical fibers which take the light to two photo diode array detectors. The detectors are connected to a computer for data acquisition and analysis. Data is acquired in the form of intensity or transmittance as a function of wavelength at different time intervals. With both polarizers oriented in the same position and the sample having a plane XY perpendicular to light path, for example the machine–transverse plane, the governing equation for the light intensity can be written as:

$$I \propto \cos^2\left\{\frac{\pi \Delta n_0 d}{\lambda} f(\lambda)\right\}$$

where I is the light intensity, Δn_0 is a birefringence constant, d the thickness of the sample, λ the wavelength (we will call the term $\Delta n_0 d$ retardation and note it Γ_0) and $f(\lambda)$ the variation of birefringence

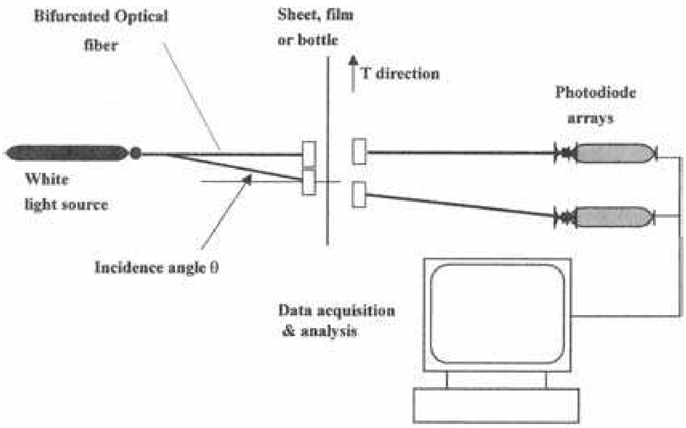

Figure 1. Sketch of the setup used for measurements.

with wavelength, which depends on the material (optical dispersion). The birefringence in the XY plane for a wavelength λ_0 (in most cases $\lambda_0 = 589.6\,\text{nm}$, corresponding to the sodium light) can thus be determined as:

$$\Delta n_{XY}(\lambda_0) = \Delta n_0 f(\lambda_0)$$

For the $f(\lambda)$ function, different dependencies have been proposed, but the simplest and most convenient form used here is:

$$f(\lambda) = \alpha + \frac{\beta}{\lambda^2} + \frac{\delta}{\lambda^4} + \frac{\gamma}{\lambda^6} + \cdots$$

In most cases the first three terms are sufficient for calculations. The α, β, δ, and γ constants depend on the material. For a multilayer material, containing two or more significantly optically different materials, that is the dependencies of their refractive indices (or birefringences) as a function of wavelength are significantly different, there will be $f_1(\lambda)$, $f_2(\lambda)$, etc. which are associated with retardation in the corresponding materials. The cosine argument becomes:

$$\frac{\pi d}{\lambda}\left[\Delta n_{01} f_1(\lambda) + \Delta n_{02} f_2(\lambda) + \cdots\right]$$

Since the functions f_1, f_2, are known, the regressions can be made on the different Δn_{0i}. The same equations apply in the case of oblique incidence. The retardation obtained in this case will depend on the incidence angle. The different birefringences can then be obtained from measurements at two angles. Let us assume Γ_1 the retardation obtained for an angle θ_1 and Γ_2 that for θ_2. The angles θ_1 and θ_2 (between 0 and 90°) are the angles between the normal to the MT plane and the incident light beam, by rotating the MT plane around the M direction. Calculations lead to the following equations for the birefringences:

$$\Delta n_{TN} = \frac{n}{d(\sin^2\theta_2 - \sin^2\theta_1)}\left[\Gamma_2\left(n^2 - \sin^2\theta_2\right)^{1/2} - \Gamma_1\left(n^2 - \sin^2\theta_1\right)^{1/2}\right]$$

$$\Delta n_{MT} = \frac{\Gamma_1}{nd}\left(n^2 - \sin^2\theta_1\right)^{1/2} + \frac{\sin^2\theta_1}{n^2}\Delta n_{TN}$$

$$\Delta_{n_{MN}} = \Delta n_{MT} + \Delta n_{TN}$$

where n designates the average refractive index. Since in the intensity equation the sine or cosine functions are squared, it is not possible to know the sign of the birefringence by a single measurement. However, through the comparison of the retardation values at two different angles, this sign can be determined by evaluating the sign of the derivative of Γ as a function of θ, which is incorporated in the software used for calculation of birefringences.

Illustration of the Technique on Two Films Off-line

Biaxially Oriented Polypropylene Film (BOPP)

Figure 2 shows the results obtained for four superimposed PP films (total thickness of 80 μm) obtained by the biaxial orientation process. The figure shows both the experimental and regression results at two angles. The best parameters found by regression yielded the following values for the different birefringences at a wavelength of 589 nm using the equations above: $\Delta n_{MT} = -0.0012$, $\Delta n_{MN} = +0.0067$, and $\Delta n_{TN} = +0.0191$. The average refractive index of 1.490 was used for the calculations. It can be concluded that this film is highly oriented in the transverse direction and moderately oriented in the machine direction.

Biaxially Oriented Polyethylene Terephthalate Film (BOPET)

Figure 3 shows the results obtained for a PET film (thickness of 90 μm) obtained by the biaxial orientation process. The figure shows both the experimental and the regression results at three angles (the third angle was used to confirm the values). The best parameters found

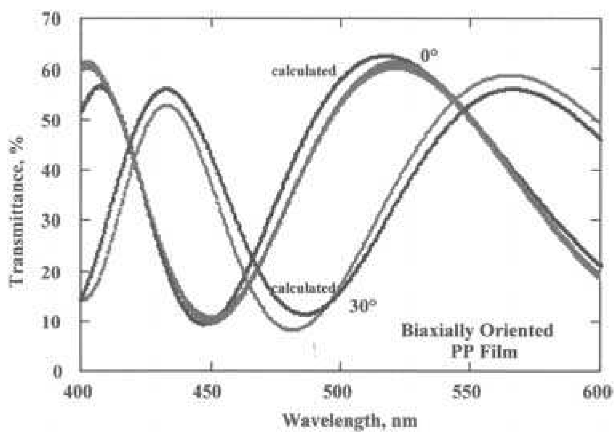

Figure 2. Experimental and calculated results for biaxially oriented PP film (80 μm thick).

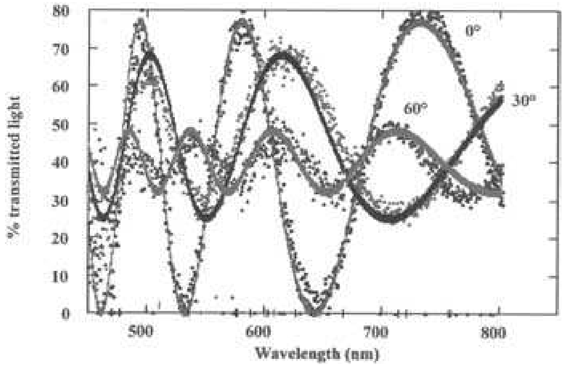

Figure 3. Experimental and calculated results for biaxially oriented PET film (90 μm thick).

by regression yielded the following values for the different birefringences at a wavelength of 589 nm using the equations above: $\Delta n_{MT} = +0.0322$, $\Delta n_{MN} = +0.1203$, and $\Delta n_{TN} = +0.0881$. The average refractive index of 1.640 was taken for the calculations. It can be concluded that this film is highly oriented in both the machine and the transverse directions with a lower orientation in the transverse one.

Illustration of the Technique for Online Monitoring

PET Orientation and Relaxation

Measurements using the birefringence technique were made during uniaxial drawing and relaxation of polyethylene terephthalate. Figure 4 shows the results obtained for the online birefringence measurements during drawing of amorphous PET at 80°C to a draw ratio of $\lambda = 3.5$. For all the strain rates, the birefringence increased with draw ratio. Two different sets of curves can be depicted from Figure 4. One at low stretch-rates (0.007 and 0.014 s^{-1}) and the other for higher stretch rates. For the curves at low stretch-rates, the evolution of birefringence is rather smooth with a slight change of slope around a draw ratio of 2. This may be indicative of the start of stress-induced crystallization and formation of few crystallites. For the higher rates, however, a steep change in the slope of birefringence around a draw ratio of 1.5–2 is obvious, indicating the formation of many crystallites. Another change in slope is observed around a draw ratio of 2.5, which may be indicative of the end of stress-induced crystallization and start of impingement of crystallites.

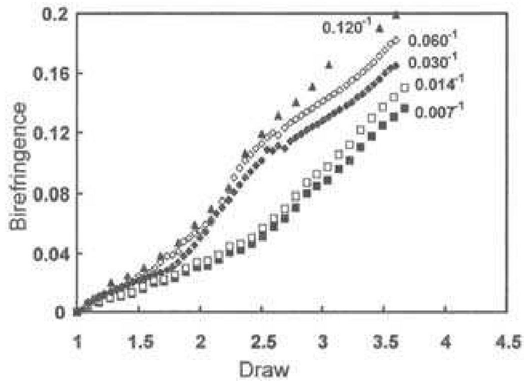

Figure 4. Online birefringence measurements of amorphous PET with different strain rates at 80°C.

Constrained stress and birefringence relaxation experiments were carried out on two different PET samples drawn to draw ratios of 2 and 3.5. For the draw ratio $\lambda = 2.0$, shown in Figure 5(a), it is observed that for all the drawing rates, the birefringence decreased almost linearly with the logarithm of time. That can be modeled using a single relaxation time Maxwell model. This was probably due to the low level of strain-induced crystallization at $\lambda = 2.0$, and continuous relaxation of the amorphous phase orientation. For the draw ratio of $\lambda = 3.5$, the curves are more complicated as shown in Figure 5(b). In this case, as discussed above, we have a region where stress-induced crystallization has clearly occurred. An initial decrease of birefringence is observed, and is attributed to the relaxation of the amorphous phase. It is followed by a plateau due to the orientation of the crystalline phase, the level of this plateau is indicative of the amount of crystalline phase present as a result of the stretching at the different rates. Finally, it can be concluded that this online birefringence monitoring technique gives valuable insights into the development of orientation and during relaxation of polymers.

BOPS Orientation Process Online Monitoring

Measurements using the developed birefringence technique were made online on biaxially oriented polystyrene sheets. Figure 6 shows a typical result obtained after seven hours of monitoring a biaxially oriented polystyrene sheet in the static mode in the laboratory. It shows the birefringence values measured in both MD and TD directions. No significant scatter in the data is observed.

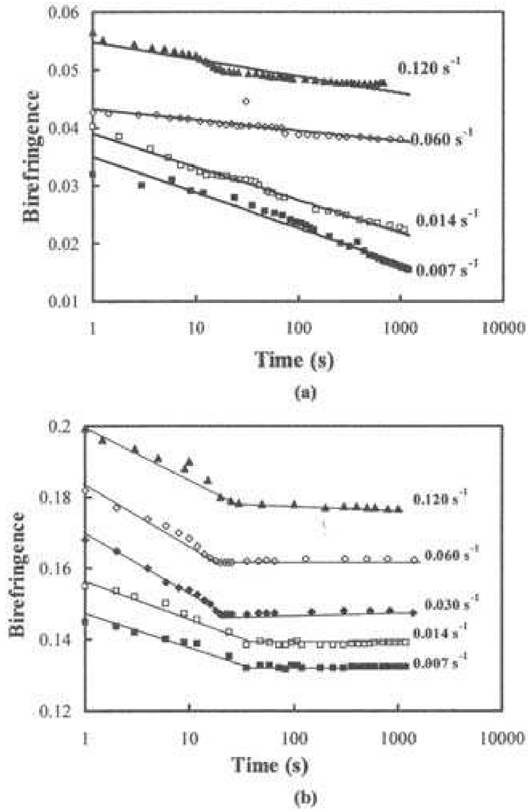

Figure 5. Constrained relaxation of PET at draw ratio: (a) $\lambda = 2.0$ and (b) $\lambda = 3.5$.

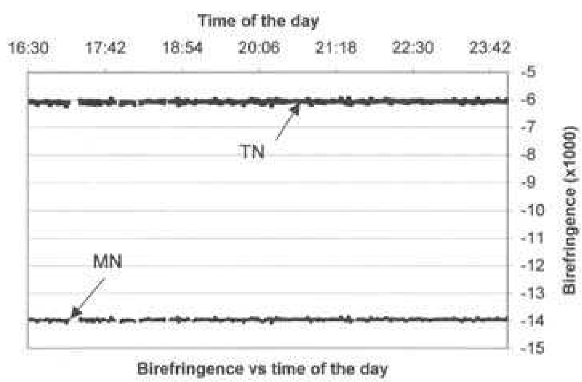

Figure 6. Online birefringence measurements of BOPS sheet in a fixed position in the laboratory.

Subsequent tests were carried out on a tentering line for the production of BOPS. The thickness of the final sheet produced that day was 7.25 mils (nominal). The results obtained for optical retardation, birefringence, and shrink stress are presented in Figures 7–10. In all cases, a significant scatter in the data was observed and, on an average, was about 10%. A part of this scatter is due to thickness variation, which is about 5% on an average. The other source of variations is from fluctuations in the incidence angles due to vibrations of the support used to fix the system or from sheet vibrations or both. Fluctuations in the angle of 2° may cause up to 5% fluctuations in the

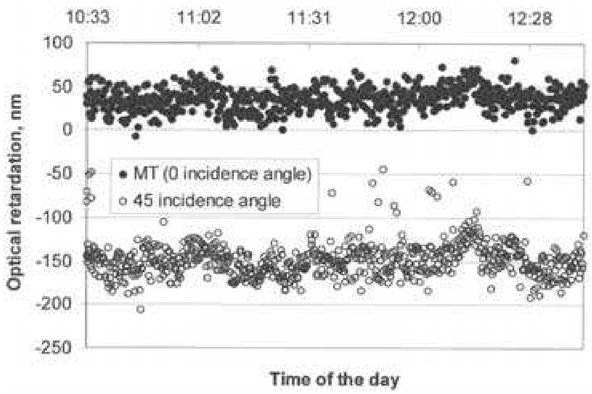

Figure 7. Online optical retardation measurements of a BOPS moving sheet in a production plant.

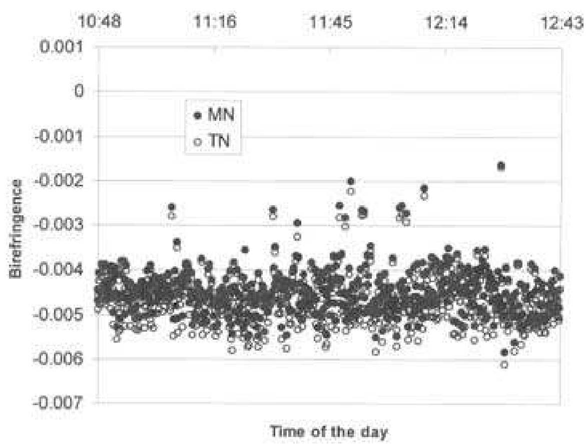

Figure 8. Online birefringence measurements of a BOPS moving sheet in a production plant.

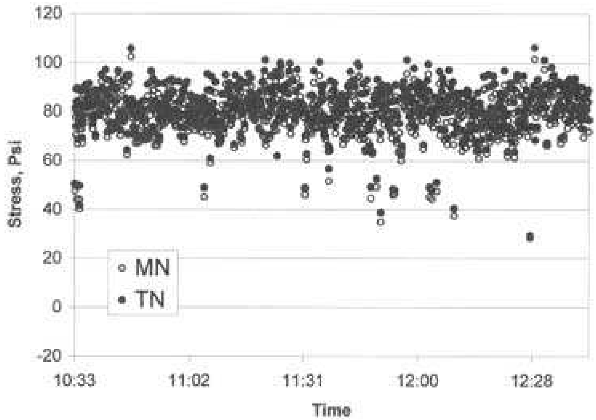

Figure 9. Shrink stress calculated from online optical birefringence measurements for a BOPS moving sheet in a production plant.

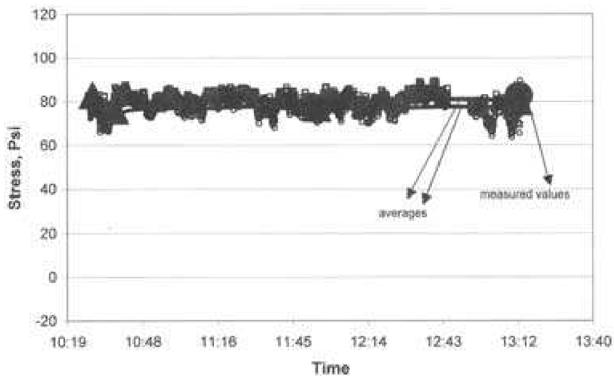

Figure 10. Shrink stress for a BOPS sheet in a production plant: calculated from online birefringence measurements, cumulative averages, and lab-measured values.

measured values. All these are in addition to possible sheet orientation variations caused by temperature, speed, etc. Hence, the seemingly significant fluctuations are mostly due to the way the system is fixed and in not including thickness in real time (which can be easily incorporated). In Figures 9 and 10, the shrink stress in both MD and TD was determined from birefringence using the stress–optical law (using a stress–optical coefficient of $8.325 \times 10^{-9}\,\mathrm{Pa}^{-1}$). In Figure 10, the lines show results obtained on stress calculated from birefringence including the averaged value over time (or cumulative average) and that measured on strips cut from the sheet at three different times. A very good agreement between all these values is clearly seen.

CONCLUSIONS

A technique for the measurement of absolute biaxial birefringence of films and sheets based on oblique incidence of a polarized multi-wavelength beam was presented. It can also be used for multilayer materials, as long as the transparency and the difference in optical dispersion are sufficient enough. It is shown that precise values can be obtained for biaxial birefringence and that the technique can be used for monitoring the orientation and relaxation processes as well as to control the quality of oriented articles and online monitoring of orientation processes.

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