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Biaxial Orientation Characterization On-line and Off-line and Structure Properties Correlations in Films

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Summary: In this paper, biaxial orientation characterization techniques are briefly reviewed. Results obtained using birefringence and Fourier Transform Infrared Spectroscopy (FTIR) techniques are presented for different applications: On-line monitoring of birefringence for an amorphous polymer (polystyrene); On-line and off-line determination of orientation (birefringence) of polyethylene terephthalate (PET) and finally off-line measurement of orientation on polyethylene (LDPE) films using FTIR. Some typical morphologies of blown LDPE films are reported and discussed. Finally, correlations between orientation on one hand and shrinkage and tear strength on the other are attempted.

Introduction

Orientation in polymers is known to enhance certain properties such as mechanical, optical, barrier, etc. This orientation in polymers can be induced by several processes such as film blowing, film tentering (biaxial sheet orientation), blow moulding etc. In order to evaluate and optimise polymer properties and process conditions it is thus of great importance to be able to know the orientational states developed in the polymer. Several techniques can be used for measurement of orientation in polymers. These techniques include birefringence, spectroscopy (Fourier transform infrared spectra, Raman, fluorescence, NMR, ...), X-ray scattering (XRS), ultrasonic techniques, etc. Among these, birefringence and FTIR are the simplest. From birefringence measurements, the biaxial 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). 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 infrared spectroscopic technique is based on the absorption of

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radiation at different frequencies that correspond to the vibrations of specific groups in the molecule. Each vibration possesses a transition moment that has a specific direction with respect to the chain axis. By measuring the absorption with the electric field vector of the radiation polarized in different directions (for example, M, T, and N), it is possible to quantify the orientation in terms of the Herman's orientation function. For thin films, since it is not possible to measure the spectrum in the normal direction, the tilted technique can be used.

Experimental

On-line birefringence measurements were made on a polystyrene (PS) biaxial orientation commercial line (BOPS). The measurements were made using a bouble incidence multiwave length beam as briefly described below. On-line birefringence measurements were also carried out on uniaxially stretched PET. The PET used was an extrusion grade obtained from Dupont (Selar PT 7086), its molecular characteristics determined by GPC were Mn = 28,800 and Mw=54,600. Sheets made of thin PET were unixailly drawn at different stain rates at 80°C. Measurments of birefringence were taken both upon orientation development during stretching as well as during constrained relaxation after stopping the deformation. Finally, for the blown film experiments, Novapol LF-Y819-A LDPE film resin with density of 0.92 g/cc and melt flow index of 0.75 g/10min from Nova Chemicals was used. LDPE films were prepared by extrusion blowing process, two blow-up ratio (BUR) of 1.6 and 2.5 were used, and three drow-down ratio at each BUR. The effect of frost-line height was also checked.

The technique used for birefringence measurements was a multiwave length polarized white light technique, which allows one to measure the absolute biaxial orientation in biaxially oriented films, sheets and shapes [1]. The absolute values of birefringence along the machine, transverse, and normal direction were measured by an incident multi-wavelength double beam and photodiode array assembly, combined with an in-house developed software. Detailed description of the technique can be found in previous publications [1,2].

The spectroscopic FTIR measurements allowed the determination of IR dichroism on films in transmission with the use of the tilted film technique [3]. The M and T spectra are first measured in the usual way with the film perpendicular to the IR beam. M and T spectrum (S_M and S_T) can be easily obtained by using a planarly polarized beam with the electric vector in the desired direction. For example, specimen were put perpenticular to the FTIR beam with the machine direction vertically and transverse direction horizontally, and the measurements were performed with the polarization in the M and T direction, respectively. This allows the determination of S_M and S_T. The normal spectrum was obtained using the tilted method [3,4], i.e. the films were tilted by 45°. The result is a mixture of the M and N spectra (or T and N, depending on the axis of tilt), from which the N spectrum can be obtained using the following expression [4]:

$$S_N = \frac{\cos\beta}{\sin^2\beta}(S_{TN} - S_T\cos\beta) \qquad (1)$$

where

$$\sin\beta = \frac{\sin 45°}{n} \qquad (2)$$

and

$$S_{TN} = \frac{(S_T\cos^2\beta + S_N\sin^2\beta)}{\cos\beta} \qquad (3)$$

and n is refractive index of the polymer. Because of the refraction, the beam passes through the sample at an angle β, as defined in Eq.(2).

The isotropic spectrum was calculated by : $S_0 = 1/3\,(S_M + S_T + S_N)$ (4)

Measurements were carried out on a Nicolet 170SX FTIR at a resolution of 4 and 2 cm^{-1} with an accumulation of 128 scans. Polarization of the beam was done by a zinc selenide wire grid polarizer from Spectra-Tech. The spectra were recorded with the plane of polarization parallel and perpendicular to the draw direction with tilted angle 0° and 45°, respectively.

Measurements using birefringence technique were made on-line on biaxially oriented polystyrene sheet and during uniaxial drawing and relaxation of polyethylene terephthalate. FTIR and birefringence were used to characterize biaxial orientation of blown polyethylene films. The lamellar morphology of LDPE blown films was observed using a Jeol JSM-6100 scanning electron microscope and atomic force microscope. LDPE films were etched in a 0.7% solution of potassium permanganate in a mixture of equal volumes of orthophosphoric and sulphuric acid. Both sides of the LDPE films were examined with marked machine direction.

Results and Discussion

BOPS Orientation Monitoring

Figure 1 shows a typical result obtained after one hour of monitoring of a biaxially oriented PS sheet. It shows the birefringence values measured in both MD and TD directions. The significant scatter in the data observed is due to the fact that the set-up was fixed on the process line in which significant vibrations are present. Mounting on an independent stand would significantly reduce it. It was shown that the calculated stress in both MD and TD is in good agreement with the measured value (indicated by the horizontal line in the figure). Correlations between shrinkage and orientation wre also studied and showed a linear correlation (not shown here).

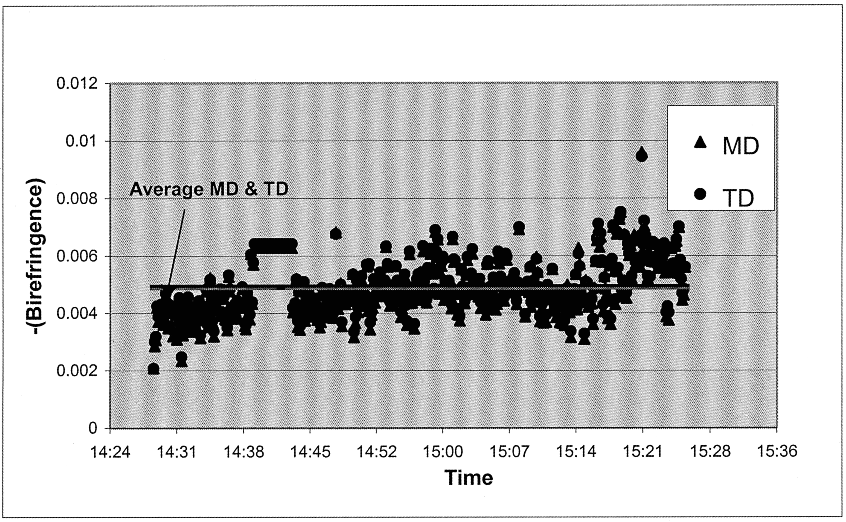

Figure 1. On-line birefringence measurements of PS sheet

PET Orientation and Relaxation Monitoring

Fig. 2 shows the results obtained for the online birefringence measurements during drawing of amorphous PET at 80°C to a draw ratio of λ=3.5. For all the strain rates, the birefringence increased with draw ratio. There was an increase in the slope for draw ratios above 2.0, which is probably due to the onset of strain-induced crystallization.

Constrained relaxation at λ=2.0 in Fig. 3(a) showed that for all the drawing rates, the birefringence decreased almost linearly with the logarithm of time. That can be misled using a single relaxation time. This was probably due to the low level of strain induced crystallization at λ=2.0. The curves were more complicated when the samples were crystalline (Fig. 3(b)) due to the strain-induced crystallization. An initial decrease attributed to relaxation in the amorphous phase is shown followed by a plateau, indicating the level of orientation of the crystalline phase. Birefringence monitors the orientation and relaxation very well.

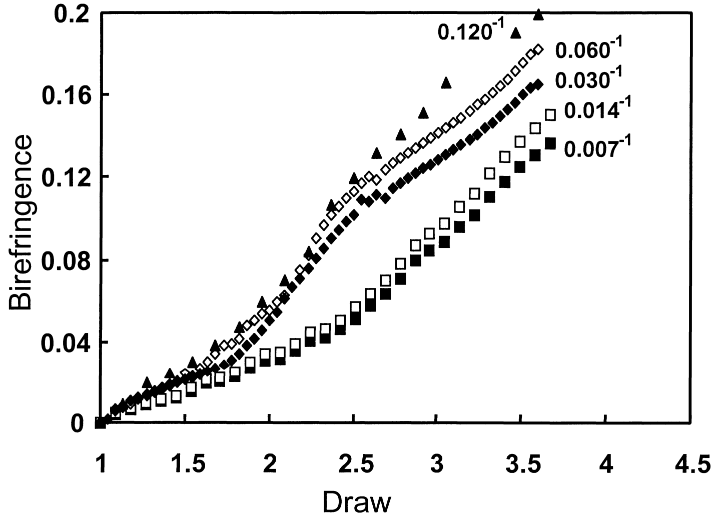

Figure 2. Online birefringence measurements of amorphous PET with different strain rates at 80°C

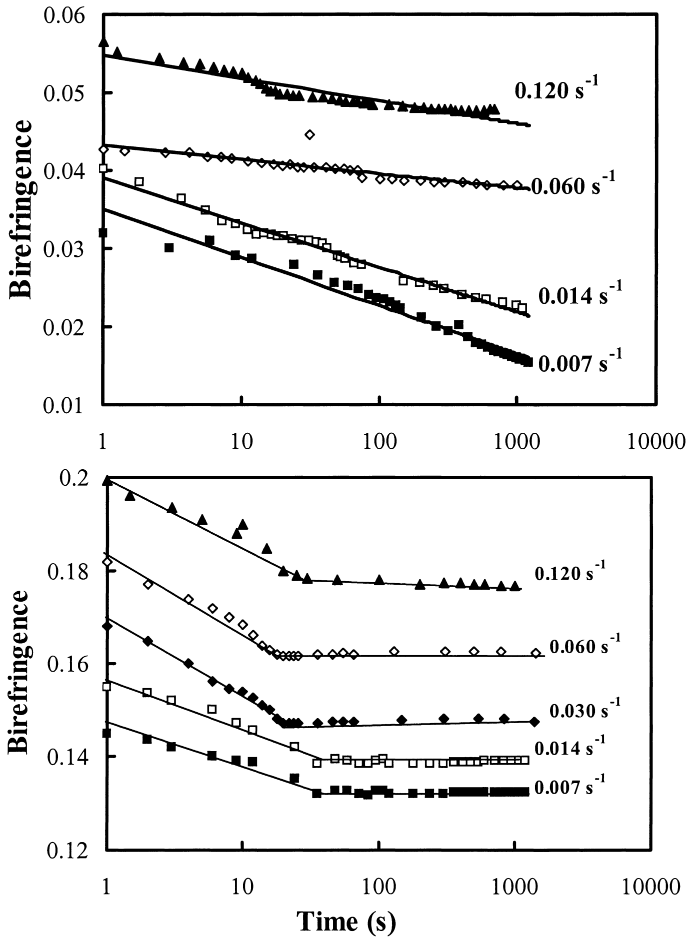

Figure 3. Constrained relaxation of PET at draw ratio (a) upper, $\lambda=2.0$ (b) bottom, $\lambda=3.5$

LDPE Blown Films

For blown films, the overall orientation is low, however, a relative strong orientation was observed for the a and b axes of the crystalline phase rather than for the molecular chain direction. This is due to the fact that the oriented crystalline lamellae are formed from the oriented melt under stress through a row nucleation mechanism, resulting in a tendency for the crystalline a- axes to orient towards the machine direction and b-axes towards to normal or transverse directions. A typical absorption spectra (machine, transverse, normal and isotropic) in the region 710-740 cm^{-1} are given in Fig. 4. The peak at 730 cm^{-1} whose transition moment is parallel to the crystalline a-axis [4], is strong in M spectra, indicating the crystalline a-axes are preferentially oriented towards the machine direction. The peak at 720 cm^{-1} whose transition moment is parallel to the crystalline b-axis, is weak in the machine direction and strong in the transverse-normal plane. Deconvolution of the spectra indicated that, below the two narrow peaks of crystalline a- and b-axis is the abroad peak at 722 cm^{-1} arising from the contribution of the amorphous phase.

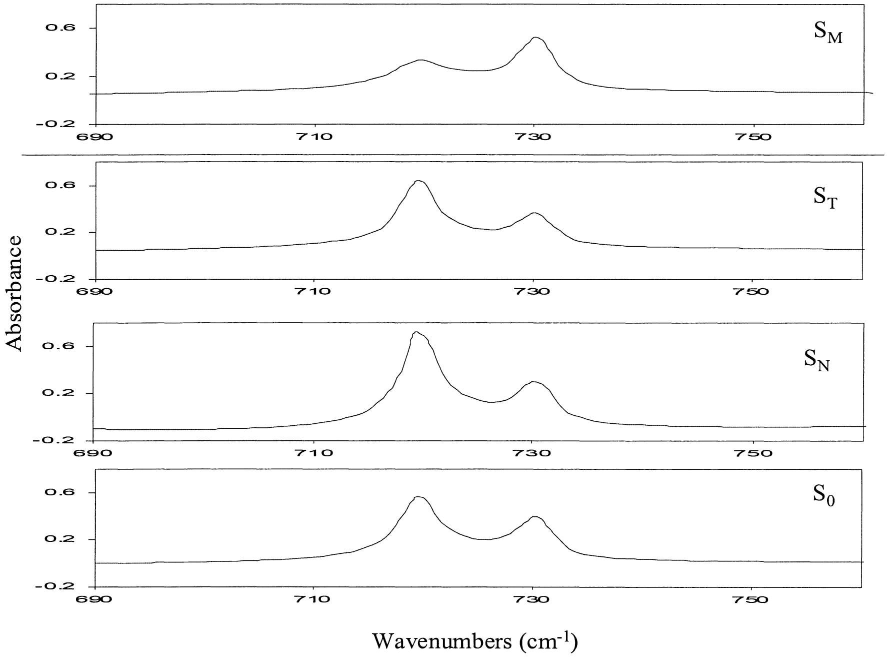

Figure 4. CH_2 rocking band of LDPE blown film with BUR = 1.6 and DDR =17.5

The orientation results of the LDPE films is represented using the triangle plot with the three apices corresponding to perfect orientation in MD, TD and ND and the centre correpsonding to isotropic state. These are shown in Fig. 5, with the numbers indicating DDRs. The crystalline a-axis uniaxially oriented toward MD, the crystalline b-axis located in the TD-ND plane, and c-axis did not show a clear trend but oriented along MD at high DDR.

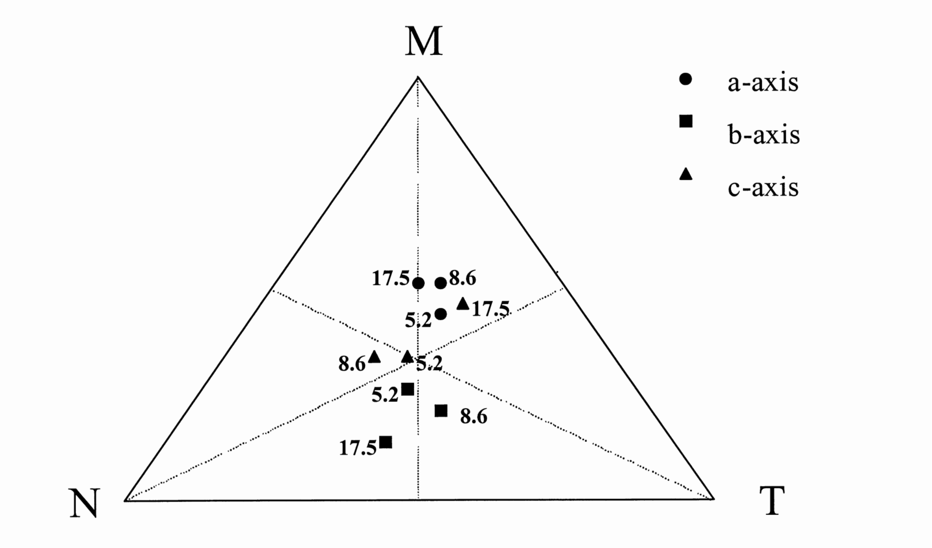

Figure 5. Triangle plot of LDPE blown films at BUR = 1.6

Because the film surface acts as a nucleation site, crystal growth takes place along the b axis direction. Similar results have been obtained by X- ray diffraction [5]. Morphological observations also reveals significant effect of processing conditions on crystalline morphology as shown on Figure 6. Blown films have a unique morphology that results from the large elongational flow in the melt and the interaction between BUR, DDR and cooling conditions. Lamellae with uniform thickness can be observed in a(1) and allign randomly along the MD and TD, no so called row nucleated morphology is observed. As the DDR increased, the a-axis orientation increased and the lamellae were more perpendicular to MD, and a perfect nucleated row structure was distinctly found at high DDR, as can be seen in Fig. 6a(2). These stacked lamellae were aligned parallel to MD. These columns rows have a uniform width of about 0.5 μm in each row.

The morphology patterns for BUR = 2.6 with two DDRs are shown in b(1) and b(2). The lamellae were found to be not aligned uniformly along MD or TD but curl and interconnect. No row strucutre was observable because of the low lamellar orientation. In b(2), DDR = 6.8, both a-axis orientation along MD and b-axis orientation in the plane normal to MD increased, the row nucleation was formed but with a tilted angle toward

TD due to the interaction of the stress along TD and MD. As DDR increased, a more perfect row structure was observed due to the prepondenance of the stress in MD.

The dependence of lamellar structure on the frost-line height is depicted in c(1) and c(2). Crystallization from the stressed LDPE melt did not produce the familiar randomly nucleated spherulitic crystal stucture, instead, an oriented lamellar or row-nucleated structure was observed at low frost-line height. As the frost-line height was increased, more relaxation time was available for the oriented lamellae, thus partially or compeltely destroyed the formed orientation. The crystallization style changed from the lamellar growth with a preference to the oriented direction, to the more familiar three dimensional spherulitic growth style. This morphology change has significant influence on the physical properties, such as the optical properties or mechanical performance.

The crystalline morphology was also studied by AFM, shown in Fig.7. Again row nucleated structure was observed, from which the lamellea dimension and thickness can be determined. It should be noted that this row nucleated structure can only be formed at specific conditions, different physical properties can be targeted by controlling the level of the row nucleated structure.

Correlations between some properties (tear resistance and shrinkage) and orientation is investigated (Figure 8 (a), (b), (c) and (d)). The correlation shown in Fig. 8(a) is in agreement with what would be expected, i.e., a higher a-axis orientation along MD or a higher b-axis orientation in the TD, a higher degree of row nucleated structure of LDPE, yields a higher TD tear resistance. Birefringence was also observed to show an acceptable correlation with tear resistance. Good correlation between birefringence and orientation functions with shrinkage was found in Fig. 8(c) and (d).

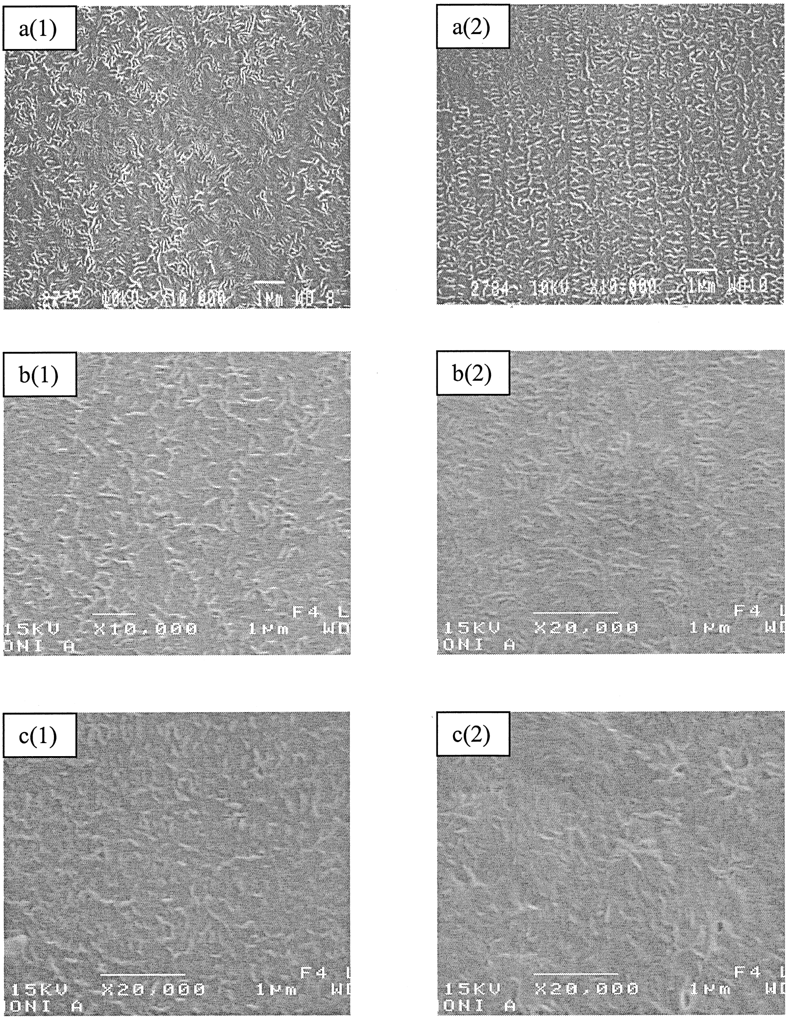

Figure 6.The dependence of lamellae alignment of LDPE layer on processing conditions:
a(1) DDR = 5.2 at BUR = 1.6;   a(2) DDR= 17.5 at BUR= 1.6
b(1) DDR= 2.7 at BUR = 2.5;   b(2) DDR= 5.4 at BUR = 2.5
c(1) frost-line height = 20 cm;   c(2) frost-line height = 120 cm

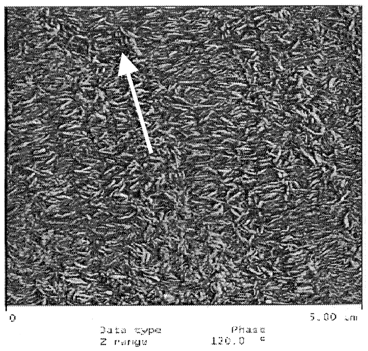

Figure 7. AFM picture of LDPE blown film with BUR = 1.6, DDR = 17.5

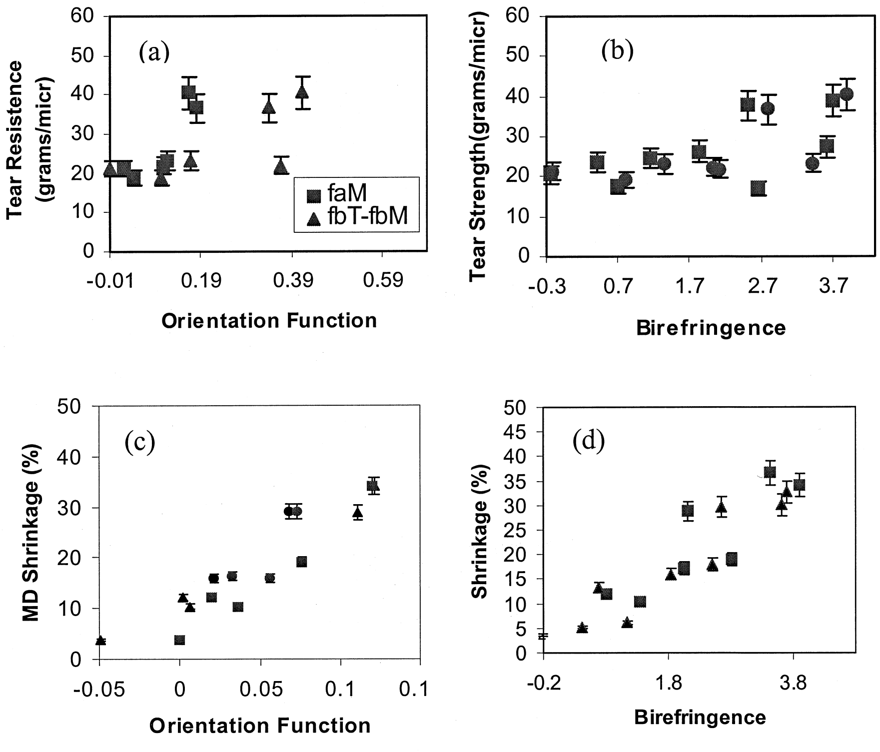

Figure 8. Correlation of tear resistance and shrinkage with birefringence and orientation function

Conclusions

(1) For the amorphous biaxially oriented PS, on-line birefringence measurement monitors very well the orientation, which is consistent with calculated stress.

(2) For PET stretching, birefringence measurements are used not only successfully for on-line monitoring of orientation but also for the studies of relaxation and strain-induced crystallization.

(3) For blown LDPE films, birefringence gives a measure of the overall orientation, and FTIR provides the orientation for both crystalline and amorphous phases. A more detailed study on LDPE blown films showed that some physical properties correlated well with orientation and crystalline morphology.

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