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CHARACTERIZATION OF ORIENTATION AND STRUCTURE IN ROLL-DRAWN POLYMERS USING BIREFRINGENCE AND FTIR SPECTROSCOPY

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INTRODUCTION

Oriented polymers can have very interesting properties from the mechanical, impact, optical and barrier points of view. In fact, the first developments in highly oriented polymers were performed on fibers in the 70's, with the most familiar ones such as Kevlar (aromatic polyamide) and Spectra (polyethylene) fibers having tensile modulus and strength in the vicinity of 200 GPa and 3 GPa respectively. Both types of fibers are presently used in composites. Extension of orientation processes to larger parts such as sheets, rods, pipes and other shapes is possible, even though the range of mechanical properties will be lower than for fibers. The range of properties that can be achieved is comparable to fiber reinforced composites, with the advantage of avoiding the fiber matrix adhesion problem. In addition, oriented polymers show the advantage of easy recyclability over composites, particularly thermoset-based ones.

Substantial efforts have been directed toward orientation of semi-crystalline polymers such as polyolefins, polyesters and polyamides (Ward, 1975; 1985). In the past, much effort has been directed toward solid state deformation (extrusion, rolling and drawing) of polyolefins (SPE RETEC, 1987; Ward 1985; Zachariades and Porter, 1983, 1988). Although there are still many aspects that are not well understood, such as relaxation, interface contribution, biaxial orientation and prediction and modeling, extending these techniques to engineering and specialty polymers as well as polymer blends will open up many opportunities. In fact, due to the low melting temperature of polyolefins, their practical use as oriented materials is limited. Hence, particular focus has to be directed towards polymers such as polyoxymethylene, polyesters, polyamides and polyketones because of their higher melting temperatures. This will push up the useful range for the oriented parts to temperatures well beyond 100°C.

Although PET, PA and PEEK do not show an α crystallization transition, orientation of these materials can lead to very high mechanical properties (Zachariades and Porter, 1983, 1988). PET has a high melting point, T_m (250°C) and chemical resistance, which makes this polymer very interesting for structural applications. Similarly, polyamides (PA) are characterized by high toughness, chemical resistance, high drawability, a wide range of melting points

(medium to high T_m), and a low friction coefficient. They are well suited for a wide range of engineering applications. However, development of applications based on oriented PA parts (apart from fibers) is still lacking. On the other hand, poly(etheretherketone) (PEEK), a wholly aromatic polymer, has attracted the attention of many researchers because of its excellent mechanical and thermal properties ($T_g=145^\circ\text{C}$ and $T_m=334^\circ\text{C}$). Despite its high melting point, PEEK can be melt-processed into films and fibers by conventional methods. Many attempts have been made to orient PEEK using stretching techniques such as drawing in an oven, die drawing (Richardson et al., 1985), zone-drawing (Kunugi, Hayakawa and Mizushima, 1990) and solid state extrusion (Lee, Lefebvre and Porter, 1988; Lee and Porter, 1991; Kaito and Nakayama, 1994).

In all the cases mentioned above, the contribution of the different phases to the overall orientation and structure as measured by different techniques was not often determined. Determination of the molecular orientation and structure is of critical importance in understanding the properties and structure of oriented materials. Many techniques such as infrared (IR) spectroscopy, optical birefringence and x-ray diffraction (Ajji et al, 1995, 1996) have been developed for the characterization of orientation and structure in polymers.

On the other hand, in terms of performance, Berg et al. (1989) and D.C. Sun et al. (1990) studied the 3-D structure-property relationships in rolltruded polymers. They measured the three dimensional mechanical properties of several rolltruded polymers. These included iPP, PVDF and propylene/ethylene block copolymers. They found that mechanical strength is enhanced triaxially for all these materials upon rolltrusion. Materials stiffness also exhibited 3-D improvement, depending on the polymer type and processing conditions. These new results were discussed in regard to some structural models in the literature. They found that mechanical property enhancement not only occurs in the principal draw direction, but also in the transverse directions. A variety of observations were made during tensile and compressive tests. Deformation bands, anisotropic yielding and ductile to brittle behavior were observed. These results were presented along with a morphological model that has been developed to account for the behavior of the unique triaxially oriented polymers, but no structural evolution determination was performed.

Higashida et al. (1991) studied the mechanical properties of uniaxially and biaxially rolled PE and PP sheets. They found that the tensile strength of the rolled PP sheet, initially elongated by 5.0 in the L-direction and then elongated by 1.5 in the C-direction, reached almost 100 MPa, and the value was three times as large as that of the stock in all directions in the plane. This combination of the first rolling elongation of 5.0 and second rolling elongation of 1.5 was the condition to get substantially the same rolling elongation in both L and C-directions because the uniaxially rolled sheets become thicker by shrinking when reheated for biaxial rolling and the substantial second rolling elongation is larger than 1.5. The tendency of molecular orientation corresponds with the tensile strength characteristics of uniaxially and biaxially rolled sheets. The degree of crystallinity of the rolled sheets decreases with increasing rolling elongation.

Chen et al. (1994) studied the properties of oriented PP laminates. They found that the longitudinal strength and modulus of the oriented PP (OPP) increases with an increase in

draw ratio; however, the transverse properties remain relatively unchanged. In this study, multidirectional OPP laminates (with (0)₂, (0/90)_s and (0/±45)_s lay-ups) were made to obtain sheet materials with improved properties in more than one direction in the plane. A hot-plate welding technique was used to produce these translucent and recyclable laminates. The in-plane properties of the laminates were successfully predicted with classical laminate theory (CLT), which is commonly used to predict the properties of fiber reinforced materials. These laminates can be quasi-isotropic and were found to have improved modulus (up to 6 GPa for (0/90)_s laminates) and strength (up to 150 MPa for (0/90)_s laminates) as well as exceptionally good impact toughness.

Fourier transform infrared spectroscopy coupled with photoacoustic detection (PA-FTIR) has been shown to be a powerful technique to investigate quantitative structural changes in solid materials (Quintanilla et al. 1993). For PET, the results indicated that the structural characteristics of the thermally treated samples are related to the fabrication process. Two different strata in the plates were distinguished: a skin layer and the core. The correlation between the apparent degree of crystallinity of the surface obtained by DSC and the percentage of trans conformer obtained by PA-FTIR allowed the latter parameter to be separated into crystalline and amorphous trans conformer and to follow its evolution with the annealing process. Amorphous trans conformer vanishes at the primary isomerisation (100 °C) while crystalline trans conformation shows an approximately linear increase at the expense of the gauche conformation.

Reflection techniques have also been used to characterize orientation. For PET, polarized internal reflectance spectroscopy has been used to evaluate molecular orientation and crystallinity at the surface of films (Lofgren and Jabarin, 1994). Measurements were made on samples stretched in both uniaxial and biaxial modes. All bands of interest were normalized with respect to a reference band near 1410 cm⁻¹, resulting from phenylene ring vibrations. Normalization was performed in order to overcome problems with sample contact and effective thickness. Results obtained using bands representing trans and gauche rotational conformers, occurring at 1340 cm⁻¹ and 1370 cm⁻¹ respectively, have been correlated with density and birefringence data. The polarized internal reflectance spectroscopy technique was well suited for investigations of polymer orientation and crystallinity since it avoids limitations related to sample thickness and clarity imposed by polarized transmission IR spectroscopy. Parameters such as orientation function, attenuation indices, dichroic ratios and structural factors have been determined from data collected in each of the three spatial directions. Results were found to be in agreement with corresponding density, birefringence, and refractive index data.

However, this technique has limitations: the quality of the sample-prism contact and difficulty of making on-line measurements. A technique based on specular reflection can help to overcome these limitations and yield very useful information on orientation and structure of oriented PET (Cole et al., 1994; Guèvremont et al., 1995). In particular, it was shown that a quantitative treatment of the specular reflection spectra obtained for uniaxially drawn PET films is possible. Corrections for surface inhomogeneities and an overall orientation function based on trans conformers were calculated. The results have been correlated with mechanical modulus and crystallinity values (Guèvremont et al., 1995).

Few, if any, studies have dealt with orientation of PET, PA and PEEK drawn by solid state deformation processes in the semi-crystalline state. In the present study, we will investigate the orientational behavior and structure of different semi-crystalline polymers (HDPE, PA-6, PET and PEEK). Crystallinity was determined by differential scanning calorimetry and orientation by FT-IR and birefringence. The results will be discussed in terms of the contribution of the different phases.

EXPERIMENTAL PROCEDURE

For the roll-drawing experiments, the materials used were all extrusion grade PET, PA-6, PA-11 and PEEK. Some of their characteristics are presented in Table 1. The PET resin had an intrinsic viscosity (IV) value of 1.0, M_w of 57×10^3 and M_w/M_n of 1.9. The PA-6 had a melt index of 18. The PET and PEEK resins were dried at 120°C , for at least 24 hours, prior to extrusion, whereas PA's were extruded directly from the sealed bags. For all polymers, flat profiles (approximately 1 cm thick and 10 cm wide) were prepared first by extrusion, then stored for later use in roll-drawing. For high density polyethylene (HDPE), flat profiles 12 mm thick and 10 cm wide were purchased or extruded in our laboratory and used as received for the rolling tests. Two different HDPE's were used.

Table 1: Some characteristics of the polymers used.

Polymer	Density (g/cm^3)	T_g ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	Isotropic modulus (GPa)	Crystal modulus (GPa)
HDPE	0.95	-120	130	0.4-2	300
PET	1.39	70	255	3.2	108
PA-6	1.13	50	220	2.8	165
PEEK	1.32	150	335	3.6	≈ 60

The roll-drawing assembly consisted of a series of 4 oil-heated stations preceded and followed by controlled temperature tunnels. A sketch showing one rolling station is shown in Fig. 1. PET roll-drawing was performed at 200°C , PA-6 at 160°C , PEEK at 250°C and HDPE at 110°C . Profile speed, rolls speed, tension at the last station, draw ratio and temperatures were monitored during the roll-drawing process. The draw ratio in the length direction was determined by measuring the distance between two ink marks before and after the process (after complete cooling of the samples below the glass transition temperature).

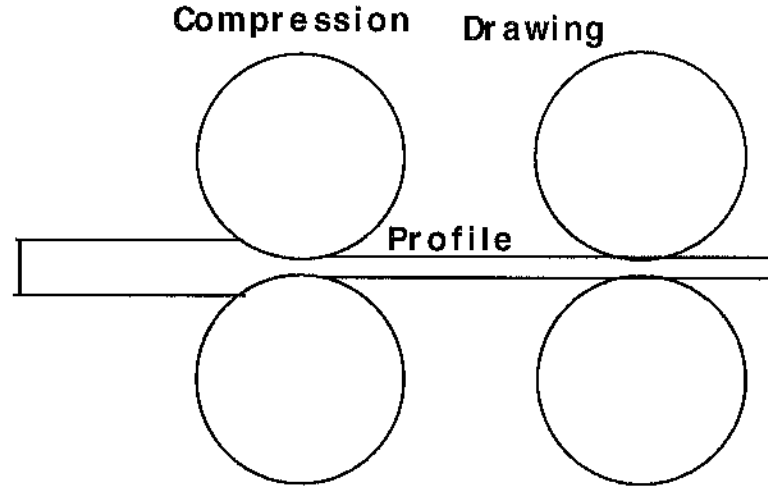


Figure 1: Sketch of the rolls with tension on the profile.

The crystallinity of the samples having different draw ratios was determined from DSC measurements. The crystallinity was calculated as the ratio of the enthalpy measured under the melting peak of the oriented material to that of the corresponding fully crystalline material. The enthalpy of melting of completely crystalline materials was taken as 280 J/g for PE, 140 J/g for PET, 230 J/g for PA-6 and 130 J/g for PEEK (Wunderlich, 1978; Bassigny et al., 1993; Séguéla, 1993). For PET, density measurements were also performed to determine the crystalline fraction and the results compared to those obtained using DSC. The crystalline and amorphous densities used were 1.445 and 1.336 respectively. The crystallinity was calculated using equation 1:

$$\chi_c = \frac{d - d_a}{d_c - d_a} \quad \text{Eq. 1}$$

Birefringence measurements were made at room temperature using a refractometer in combination with a polarizer to measure the refractive index of the samples in different directions. The contact liquid used was 1-bromonaphthalene, having a refractive index of about 1.63 (well above that of PET). The light source used was a sodium light having a wavelength of 0.5896 μm . The second moment of the orientation function f , was calculated from birefringence results (Δn) according to equation 2:

$$f = \frac{3\langle \cos^2(\theta) \rangle - 1}{2} = \frac{\Delta n}{\Delta n_{\max}} \quad \text{Eq. 2}$$

$$\Delta n_{\max} = \chi \Delta n_c^o + (1 - \chi) \Delta n_a^o$$

where θ is the average angle between the chain axis and the draw direction, χ is the crystalline fraction, Δn_c° and Δn_a° are the absolute birefringences for crystalline and amorphous phases respectively.

Infrared dichroism measurements were made on a Nicolet 170SX FT-IR spectrometer at a resolution of 4 cm^{-1} in the reflection mode using a low-angle (11°) specular reflection accessory from Spectra-Tech Inc. Each spectrum was the result of an accumulation of 128 scans. A front-surface gold mirror was used as reference. Drawn samples were mounted with the draw direction perpendicular to the plane of incidence. The beam was polarized by means of a wire-grid polarizer (ZnSe substrate) from Spectra-Tech. 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™ from Galactic Industries Corporation, using their Maclaurin's series algorithm to perform the integration. The details of the calculations of the dichroic ratio and band assignments are published elsewhere (Cole et al., 1994; Guèvremont et al., 1995). The second moment of the orientation function was calculated according to the equation:

$$f = \frac{D-1}{D+2} \frac{2}{3\cos^2 \alpha - 1} \quad \text{Eq. 3}$$

where D is the dichroic ratio (ratio of the parallel to the perpendicular absorbances) of a vibration corresponding to a transition moment making an angle α with the chain axis.

RESULTS AND DISCUSSION

The most important factor in solid state orientation of polymers is the maximum achievable draw ratio, λ_m . In general, the higher the draw ratio λ , the better will be the mechanical properties of the oriented material. Generally, λ values in the range of 4 were obtained for the engineering resins, and around 10 for HDPE. In some cases, a larger λ was achieved at some point in the process. However, the temperature being maintained above T_g of the material, some relaxation occurs (up to 0.5 decrease in λ).

POLYETHYLENE

Crystallinity results for both HDPE's used are presented in Figure 2. First, at low deformation ratios, a decrease in crystallinity is observed, up to a draw ratio of 3 to 6 (depending on the HDPE); this is followed by a constant increase in crystallinity for higher draw ratios. This behavior can be explained by the deformation process imposed on the polymer. Starting from a spherulitic structure for the crystalline phase, the first stages of deformation will involve slight deformation of the spherulites followed by their destruction to make place for the fibrillar structure which will be the final structure of the polymer at high deformation ratios.

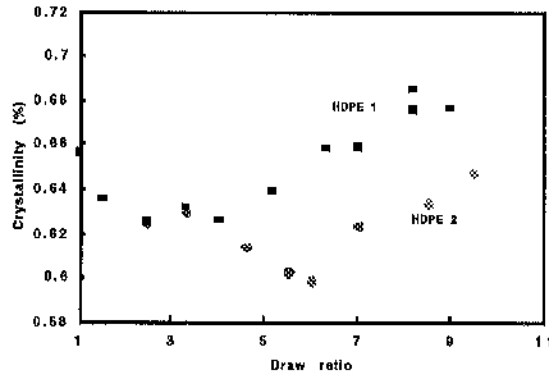


Figure 2: Crystallinity of PE from DSC as a function of draw ratio.

The results obtained for birefringence between the machine and transverse directions (Δn_{MT}) are shown in Figure 3. A constant increase as a function of draw ratio is observed, except for the last draw ratio, for which a decrease is observed that cannot be explained at this stage. The second moment of the orientation function f was determined using a value of 0.063 for the intrinsic birefringence (Pietralla, 1982). The results are presented in Figure 4 together with those obtained from FTIR for the vibrations of 1460-1473 ($\alpha=79^\circ$) and 720-730 cm^{-1} ($\alpha=90^\circ$). Different results are obtained for f . This can be explained by the different contributions involved in each case. For birefringence, an overall contribution from both the crystalline and amorphous phases are obtained. From FTIR, the result will depend on the contribution of each phase to the vibration considered. We can readily conclude that the contribution of the crystalline phase in the FTIR results is larger than the weight average of this phase, and that the 1460-1473 vibration region is more sensitive to the crystalline phase than the 720-730 region.

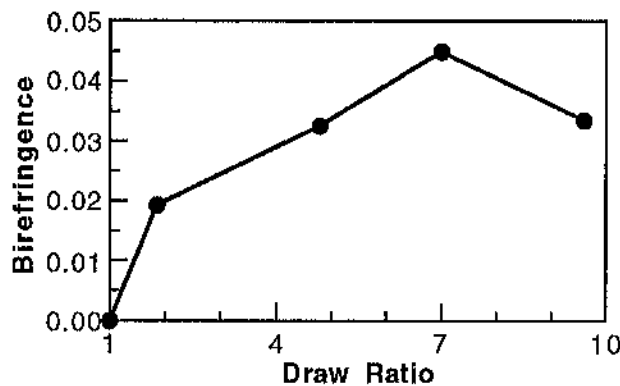


Figure 3: Birefringence vs draw ratio for PE-1

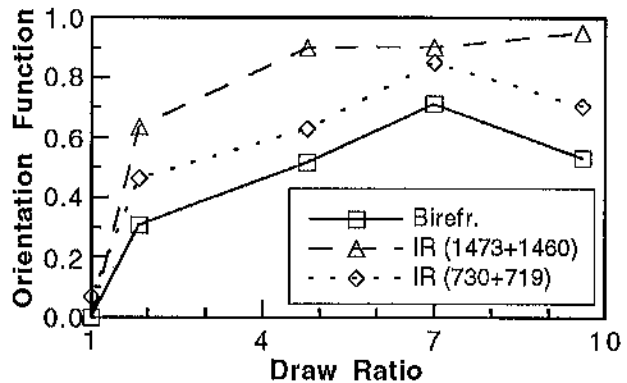


Figure 4: Orientation function obtained from birefringence and FTIR for PE-1.

POLYAMIDE-6 (NYLON-6)

Polyamide 6 (PA-6) is a semi-crystalline polymer having two main crystalline forms α and γ . The crystallinity results obtained from calorimetric measurements are presented in Figure 5. A constant increase in crystallinity with draw ratio is observed, with no indication of an initial decrease such as that observed for PE. Similarly as indicated for PE, the vibration located at 1198 cm^{-1} , characteristic of the CONH group (Grzegorz, 1977), can be followed on the isotropic spectrum. The evolution of its height with draw ratio is shown in Figure 6. An increase is also observed with draw ratio, which indicates that a correlation between the height of this peak and crystallinity can be obtained.

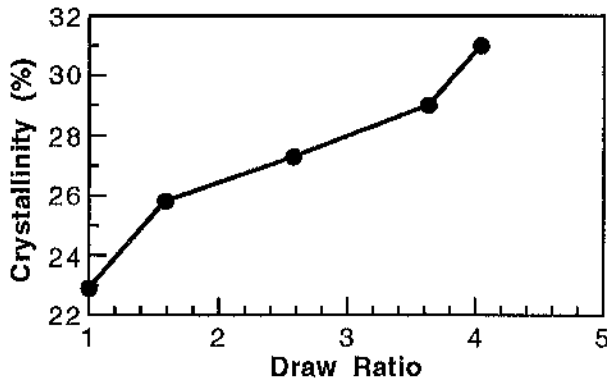


Figure 5: Crystallinity of PA-6 vs draw ratio.

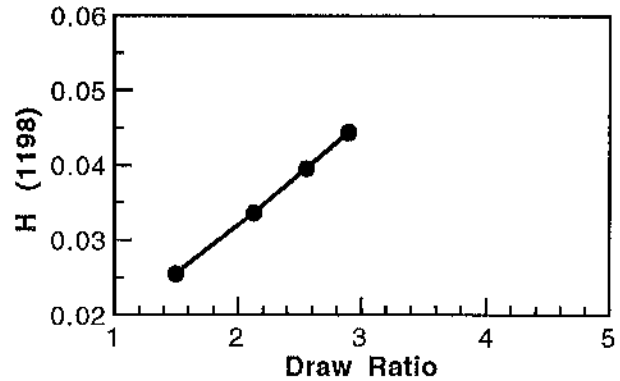


Figure 6: 1198 peak height vs draw ratio.

The results obtained for birefringence between the machine and transverse directions (Δn_{MT}) are shown in Figure 7. A regular increase as a function of draw ratio is observed. The second moment of the orientation function f was determined using a value of 0.067 for the intrinsic birefringence (Owen, 1973). The results are presented in Figure 8 together with those obtained from FTIR for the vibrations of 3298 cm^{-1} (N-H stretch, $\alpha = 90^\circ$) and 1644 cm^{-1} (C=O stretch, $\alpha = 90^\circ$). All the results fall on the same curve within experimental error. It was not possible to evaluate the crystalline phase orientation from the 1198 vibration because the angle of the transition moment with the chain axis is not known. The evolution of the ratio $(D-1)/(D+2)$ for this vibration as a function of draw ratio (not reported here) indicated a decrease between a draw ratio of 2.5 and 3.6. This is due to the conversion of helicoidal γ crystalline form to the more stable planar α form (Grzegorz, 1977). Similar behavior has been observed using X-ray diffraction on drawn PA-6 (Moffatt, 1996).

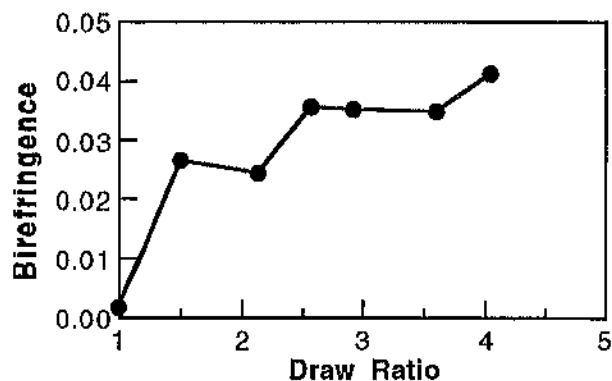


Figure 7: Birefringence vs draw ratio for PA-6

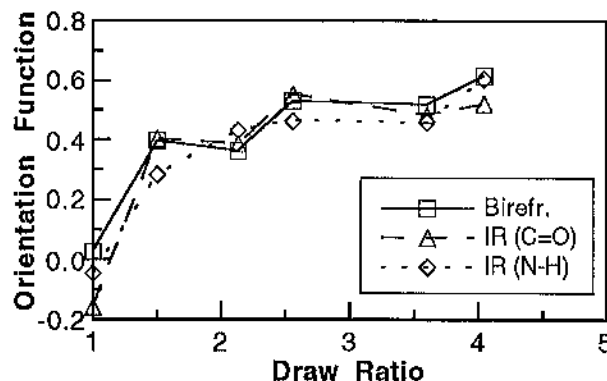


Figure 8: Orientation function obtained from birefringence and FTIR for PA-6.

POLYETHYLENE TEREPHTHALATE

Crystallinity results are presented in Figure 9 as a function of draw ratio. It can be seen that an increase in draw ratio induces an increase in crystallinity, but considerable scatter in the results is observed. Two reasons can explain this scatter. First, the samples came from different rolling trials, possibly causing the samples to have different thermal histories. Secondly, crystallinity may depend on position in the profile. In fact, for a profile drawn to a draw ratio of 2.55, variations in crystallinity of about 4% were observed across the thickness. Because of the type of deformation, variations in the degree of orientation across the thickness of the oriented PET profiles are to be expected. Since crystallinity depends on orientation, variations in crystallinity are also probable for these samples. In order to ascertain the precision of the technique itself, repeatability tests were performed on two amorphous PET films heated above the melting temperature, then cooled to room temperature. The results showed an average variability of 2.5%. They show clearly that the technique gives reproducible results for samples having the same thermal history, thereby confirming that the scatter in Figure 9 corresponds to real differences caused by different thermo-mechanical histories.

Crystallinity results using density measurements are also presented in Figure 9. The crystalline and amorphous densities used first were 1.445 and 1.336 respectively. The trend observed in the evolution of crystallinity with draw ratio is similar to that obtained from enthalpy measurements, but are shifted towards higher values for crystallinity. It has already been mentioned in the literature that the crystalline density of PET may change with the thermomechanical history of the material. Values between 1.455 and 1.515 have been reported (Lapersonne et al., 1992; Northolt and Stuu, 1978). If a value of 1.480 is used for the crystalline density, both crystallinity values from density and enthalpy measurements overlap as can be seen on Figure 9. In the rest of the paper, the values of crystallinity used are those obtained from thermal measurements.

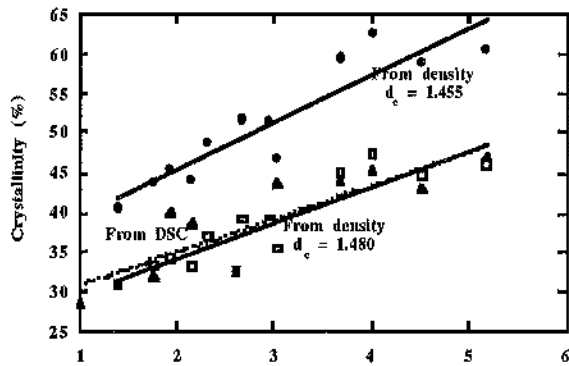


Figure 9: Crystallinity of PET obtained by DSC and density.

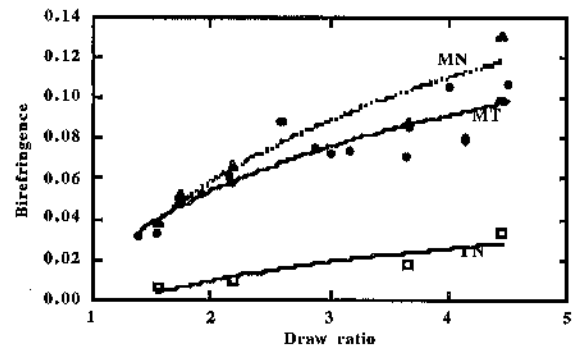


Figure 10: Birefringence of PET in the different directions.

The results of birefringence measurements are presented in Figure 10 in terms of the differences Δn_{MT} between the machine and transverse directions, Δn_{MN} between the machine and normal directions and Δn_{TN} between the transverse and normal directions. It can be seen that a slight biaxial orientation is present in the rolled samples. The corresponding results for the second moment of the orientation function f are presented on Figure 11. For the crystalline intrinsic birefringence, we used a value of 0.22. For the amorphous one, two values were used. In Figure 11, we present the results obtained using a value of 0.275 (T. Sun et al., 1986; Dumbelton, 1968) and in Figure 12, we compare the results obtained for f in the machine-transverse direction using values of 0.275 and 0.24 for the amorphous intrinsic birefringence (Yazdanian et al., 1985; Brody, 1983). About 10% difference is observed between the two curves obtained. Comparison with the results obtained with other techniques will allow us to better assess the value of the intrinsic birefringence of the amorphous phase.

The second moment of the orientation distribution was also determined from Infrared dichroism measurements by the specular reflection technique as already mentioned above and explained in detail elsewhere (Cole et al., 1994; Guèvremont et al., 1995; Aji et al., 1995; 1996). Figures 13 and 14 show the conformers fraction and orientation function obtained by the specular reflection technique as a function of draw ratio λ for the trans conformers. The results clearly indicate an alignment of the chains' trans segments along the direction of draw for all draw ratios. For the gauche conformers, negligible orientation was observed for all draw ratios. Since this conformation is present only in the amorphous phase, this indicates that the amorphous phase is not significantly oriented. In Figure 14, we present also the contribution of the trans conformers to the overall orientation, which is equal to the overall orientation since the gauche conformers orientation is negligible as already mentioned. The results thus obtained for the overall orientation are slightly higher than those obtained by birefringence. This may be due to the intrinsic birefringence values used for the calculations of the orientation function from birefringence results.

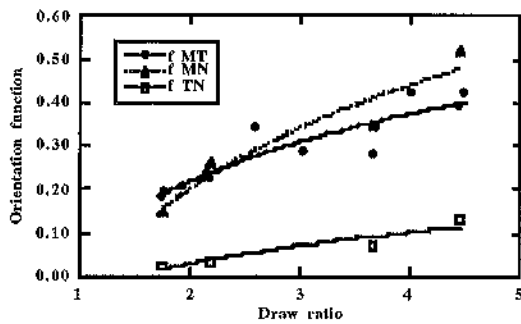


Figure 11: Orientation functions from birefringence in the three different directions, as a function of draw ratio.

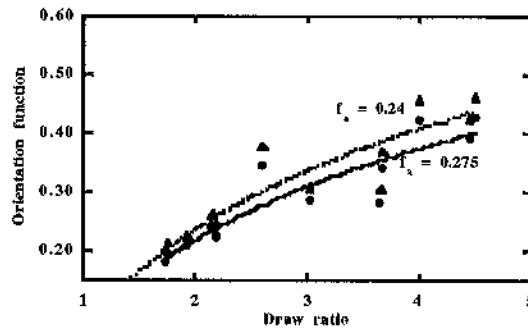


Figure 12: Orientation function in the MT direction using different values for the amorphous intrinsic birefringence.

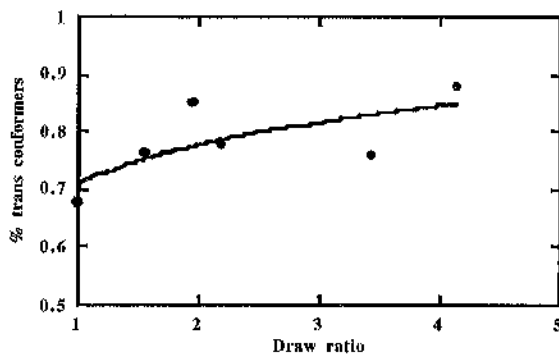


Figure 13: Conformers evolution with draw ratio.

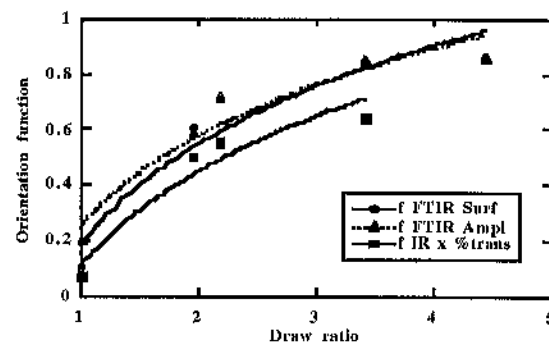


Figure 14: Orientation function from FTIR measurements.

POLY ETHER ETHER KETONE

Crystallinity results obtained by DSC for PEEK are shown in Figure 15. First, at low deformation ratios, a decrease in crystallinity is observed, as already seen for HDPE, but at lower draw ratios (around 1.6). This is followed by a regular increase in crystallinity for higher draw ratios. This behavior can be explained by the deformation process imposed to the polymer. Starting from a spherulitic structure for the crystalline phase, the first stages of deformation will involve slight deformation of the spherulites followed by their destruction to make place for the fibrillar structure which will be the final structure of the polymer at high deformation ratios.

From the isotropic spectrum as indicated above, and by following the 1312 and 1284 cm^{-1} vibrations, which are characteristic of the crystalline phase (Lovinger, 1985), one can also follow the evolution of crystallinity using FTIR. The results, in terms of the ratio of absorbances at 1312 and 1284 cm^{-1} , are presented in Figure 16. A similar dependency as for crystallinity obtained by calorimetric measurements is observed, including the initial decrease at low draw ratios.

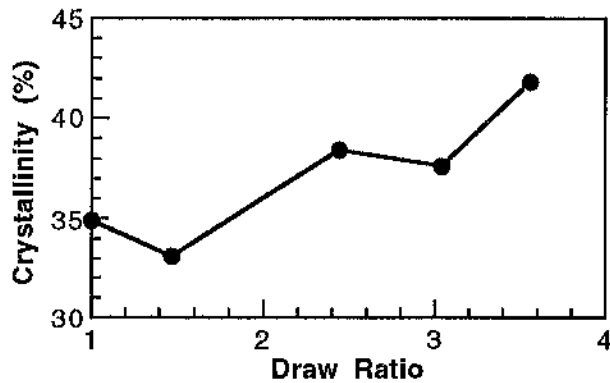


Figure 15: Crystallinity of PEEK from DSC, as a function of draw ratio.

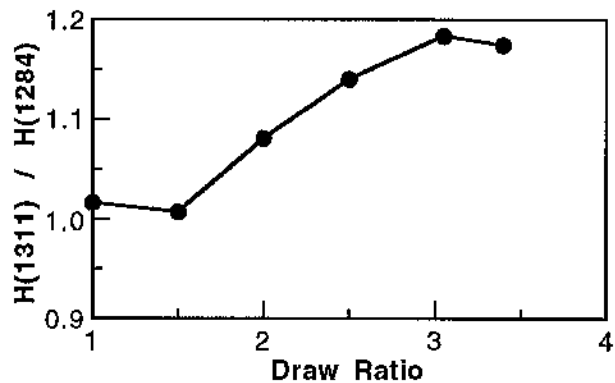


Figure 16: 1311 and 1284 absorbance ratio vs draw ratio for PEEK.

It was not possible to study the birefringence of our oriented samples because of their high refractive indexes. In fact, for non oriented PEEK, we measured a refractive index of 1.676 (using a contact liquid having a refractive index of 1.749, namely diiodomethane), but we were not able to measure it for the oriented samples.

The second moment of the orientation distribution, f , was thus determined using Infrared dichroism measurements only. The results obtained for f , calculated for the vibration of the carbonyl group at 1648 cm^{-1} ($\alpha = 90^\circ$) are presented in Figure 17. A regular increase of the orientation function as a function of draw ratio is observed. The contributions of the different phases could not be resolved at this stage. The vibrations at 1599 , 1492 cm^{-1} characteristic of the phenyl ring and at 1190 cm^{-1} characteristic of the diphenyl ether group (Nguyen and Ishida, 1986) also present dichroism, but the angle of their transition moment with the chain axis was not known and therefore could not be used for the calculation of f . Based on the values of f obtained using the 1648 cm^{-1} vibration, the transition moment angles of the 1599 , 1492 and 1190 cm^{-1} vibrations were estimated to be 37° , 28° and 31° respectively.

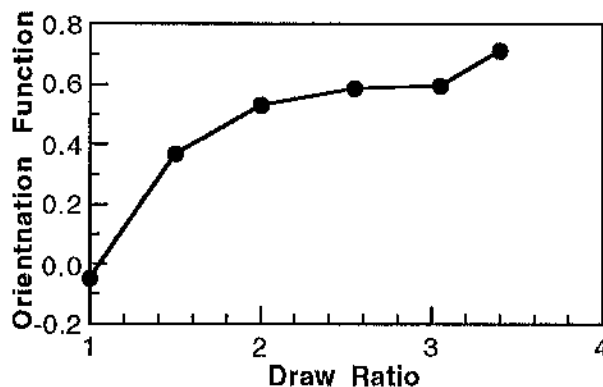


Figure 17: Orientation function of PEEK as a function of draw ratio, obtained from FTIR results using the carbonyl vibration at 1648 cm^{-1} .

Tests were also carried out on different locations on the surface of the profiles as well as across its thickness and showed no significant variations in the orientation function.

CONCLUSION

The results presented here indicate that the second moment of the orientation function for different thermoplastics can be readily determined from front surface specular reflection technique and compares favorably with that obtained from birefringence measurements. FTIR measurements can allow also for the determination of the crystalline fraction for most of the polymers studied. For PET, one has to be careful about the values to be used for the crystalline and amorphous densities and intrinsic birefringences. They may depend on the thermomechanical history of this polymer.

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