

Characterization of Molecular Orientation in Injection–Stretch–Blow-Molded Poly(ethylene terephthalate) Bottles by Means of External Reflection Infrared Spectroscopy

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ABSTRACT: The molecular orientation at the outer surface of injection–stretch–blow-molded bottles made from poly(ethylene terephthalate) was characterized and quantified by means of front-surface reflection infrared spectroscopy based on a method developed previously. Results were obtained for two different bottle shapes (cylindrical and rectangular) molded at different injection mold temperatures (16, 38, and 60°C). For the cylindrical bottles, the preferred molecular chain orientation was found to be in the axial direction, with the Hermans orientation function near 0.3 for all three mold temperatures. For the less symmetrical rectangular bottles, a significant difference was observed between the large and small faces. For the large face, the orientation was mainly in the hoop direction; the

Hermans orientation function was in the range of 0.3–0.5 and was essentially the same at all mold temperatures and positions along the bottle height. For the small face, on the other hand, the preferred orientation changed from the hoop direction near the bottom to the axial direction near the top, and the variation was more pronounced at lower mold temperatures. The utility of the front-surface reflection technique was clearly demonstrated. It was also applied, with the use of an infrared microscope, to examine the orientation gradient across the wall thickness. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1319–1327, 2007

Key words: infrared spectroscopy; injection molding; orientation; polyesters

INTRODUCTION

Injection–stretch–blow molding is a widely used process for producing hollow plastic products such as bottles of different sizes and shapes from thermoplastic polymers such as poly(ethylene terephthalate) (PET). The first step of this two-stage process involves injection molding around a core pin to produce a closed-end hollow preform with closely controlled wall thickness and a high-quality neck finish. In the second step, the hot preform is transferred to a blow-molding station, at which it is stretched and inflated under pressure inside a cooler mold. The injection and inflation processes induce molecular orientation in the polymer. When the outside surface of the inflated preform comes in contact with and conforms to the cooler mold cavity, this orientation is frozen in and is conserved when the part is removed from the mold. The end properties of these molded products (e.g., the me-

chanical performance, optical clarity, permeability to oxygen or carbon dioxide, and distortion after hot filling) depend to a large extent on their morphology (i.e., the state of orientation and crystallinity).^{1–5} For example, it has been noted that orientation reduces gas permeability.^{6,7} On the other hand, the distortion of the bottles after hot filling is related to the relaxation of the oriented polymer molecules. One way of alleviating this problem is to increase the crystallinity of the polymer during processing.⁸ It is clear that if plastics are to compete successfully with glass, all the aforementioned properties must be optimized, and this means that it is important to characterize the morphology and to understand how it varies as a function of the processing conditions. Information can be obtained by means of various techniques, including birefringence, X-ray diffraction, heat-shrinkage measurements, differential scanning calorimetry, and infrared (IR) and Raman spectroscopy. IR spectroscopy has the advantage of being relatively easy to apply while at the same time giving rather detailed information. In recent years, we have developed the use of the external front-surface reflection IR technique for characterizing the orientation in industrial polymer samples^{9,10}

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and have demonstrated its application to injection-molded products.¹¹ In this work, we show how it can be applied to obtain useful and interesting information on the biaxial orientation in injection-blow-molded bottles made from PET.

EXPERIMENTAL

Materials and processing

Injection-blow-molded bottles with two different shapes were made out of PET 9921 from Eastman Chemical Co. (Kingsport, TN). The typical properties of this product were an intrinsic viscosity of 0.8, a density of 1.33 g/cm³, a heat deflection temperature of 69°C at 0.45 MPa, a melting point of 240°C, and a tensile modulus of 2400 MPa. The bottles were molded on an Aoki Technical Laboratory (Minamijo, Japan) model SB III-100H-15 injection-blow-molding machine with a 35-mm screw diameter and a single cavity mold. The shapes and dimensions of the two bottle types, along with the corresponding preforms, are illustrated in Figures 1 and 2. The type I bottles were cylindrical, whereas the type II bottles possessed a rectangular cross section. The processing conditions were as follows: the injection barrel temperature was 275°C; the residence time of the preform at room temperature

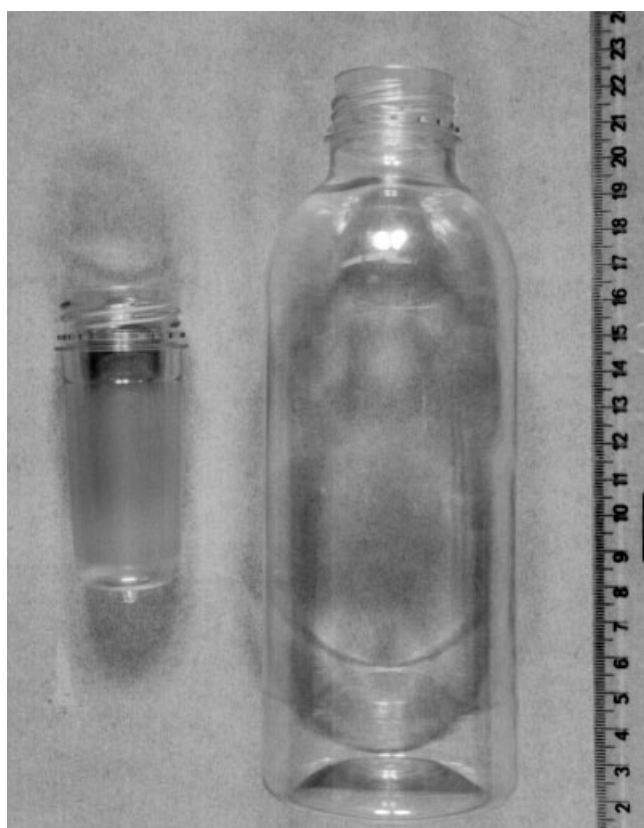


Figure 1 Illustration of the type I bottle produced in this work. The ruler is graduated in centimeters.

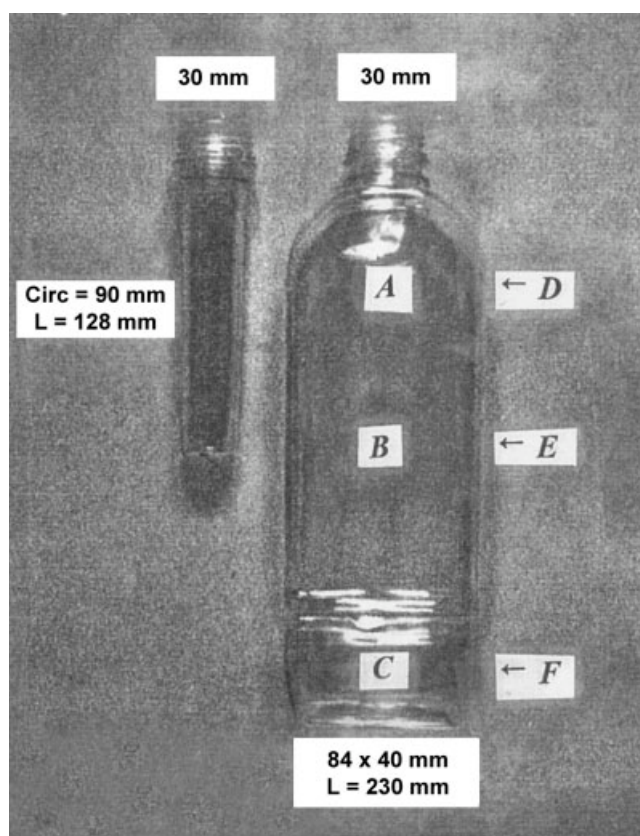


Figure 2 Illustration of the type II bottle produced in this work.

before the inflation step was 2 s; the blowing pressure was applied in two steps, initially at 0.52 MPa (75 psi) and then at 1.72 MPa (250 psi); and the cooling time in the mold was 4 s. Three different injection mold temperatures were used: 16, 38, and 60°C.

Molecular orientation

For the purpose of describing the molecular orientation, the machine direction (MD) is defined as the axial or longitudinal axis of the bottle, the transverse direction (TD) is defined as the hoop or circumferential direction, and the normal direction (ND) is defined as the wall thickness direction.

The molecular orientation in the bottles was characterized by means of front-surface external reflection IR spectroscopy according to the procedures described in our earlier publications.⁹⁻¹¹ Each spectrum measured was the result of an accumulation of 128 scans recorded at a resolution of 4 cm⁻¹; the beam was polarized with a Spectra-Tech zinc selenide wire-grid polarizer from Thermo Fisher Scientific Inc. (Waltham, MA) and a front-surface gold mirror was used as a reference. For the study of the external surface orientation as a function of the mold temperature, spectra was measured on a Nicolet 170SX Fourier transform spectrometer Thermo Fisher Sci-

tific Inc. equipped with a liquid-nitrogen-cooled mercury–cadmium–telluride (MCT) detector. The reflection accessory was a Spectra-Tech model 134 horizontal specular reflection accessory with an angle of incidence of 11°. To ensure that the spectrum involved mainly Fresnel-type reflections from the measured surface, the rear surface was sanded to eliminate any reflection therefrom. For the study of the orientation variation across the wall thickness, spectra were measured on a Nicolet Magna 860 instrument coupled to a Spectra-Tech IR Advantage microscope equipped with a narrow-range MCT detector. The sample was mounted in Struers Epofix (Cleveland, OH) epoxy resin (room-temperature cure with a cylindrical mold with a 3-cm diameter) to expose the TN plane and then polished to a finish of 0.05 μm .⁹ Spectra were then measured at different points across the thickness direction with a spot size of 40 $\mu\text{m} \times 40 \mu\text{m}$ and polarization in the TD and ND.

RESULTS AND DISCUSSION

Theoretical concepts for the determination of the orientation of the polymer chains

The definition and characterization of molecular orientation have been described in detail elsewhere,¹² but a brief summary is included here to aid in understanding the results. First, it is necessary to define an orthogonal coordinate axis system fixed in the sample, typically the machine–transverse–normal system already mentioned. Then, a coordinate axis system—*a*–*b*–*c*—is defined for a polymer chain. It is convenient to define the *c* direction as the polymer chain direction, whereas the choice of *a* or *b* will depend on the molecular structure. The orientation of a given molecule with respect to the sample geometry can be precisely defined by the three Euler angles— θ , ϕ , and ψ —made between the two coordinate systems. The molecules will be found in a distribution of orientations, and the probability of finding a molecule at the specific angles θ , ϕ , and ψ can be expressed as the sum of generalized Legendre functions [$Z_{lmn}(\cos \theta)$]:

$$N(\theta, \phi, \psi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \sum_{n=-l}^{+l} P_{lmn} Z_{lmn}(\cos \theta) e^{-im\phi} e^{-in\psi} \quad (1)$$

where P_{lmn} is the coefficient that defines a particular orientation distribution. To fully define the distribution would require the knowledge of all the coefficients, but IR spectroscopy is limited to determining only the four second-order coefficients: P_{200} , P_{220} , P_{202} , and P_{222} . However, this usually gives a sufficiently good indication of the orientation.

In this work, it is assumed that there is cylindrical symmetry with respect to the polymer chains; in

other words, only the chain axis orientation is important, and there is no preferential orientation with respect to molecular axes *a* and *b* perpendicular to the chain. This is often found to be the case in polymer studies. Under these circumstances, P_{202} and P_{222} are equal to zero, so only P_{200} and P_{220} need to be determined. Together, they quantify the overall biaxial orientation of the polymer chains. Alternatively, it can be defined in terms of the well-known Hermans orientation functions, which are related to the coefficients as follows:

$$f_{cM} = \frac{1}{2}(3\langle \cos^2 \theta_{cM} \rangle - 1) = P_{200} \quad (2a)$$

$$f_{cT} = \frac{1}{2}(3\langle \cos^2 \theta_{cT} \rangle - 1) = -\frac{1}{2}P_{200} + 3P_{220} \quad (2b)$$

$$f_{cN} = \frac{1}{2}(3\langle \cos^2 \theta_{cN} \rangle - 1) = -\frac{1}{2}P_{200} - 3P_{220} \quad (2c)$$

where θ_{cJ} is the angle between polymer chain axis *c* and sample direction *J* (i.e., MD, TD, or ND) and the angle brackets indicate an average over all the chains. For perfect alignment of the chains along the *J* direction, f_{cJ} is 1, and for perfect alignment perpendicular to the *J* direction, f_{cJ} is -0.5 . To characterize the biaxial orientation, it is necessary to determine only two of the three quantities (f_{cM} , f_{cT} , and f_{cN}) because the third can be calculated from the relationship $f_{cM} + f_{cT} + f_{cN} = 0$. If the orientation is uniaxial in the MD, then f_{cM} (or P_{200}) alone is sufficient because $f_{cT} = f_{cN}$ and $P_{220} = 0$.

The IR spectrum contains various peaks corresponding to different vibrational modes of the polymer molecule. Each vibrational mode possesses a transition moment that makes an angle α with respect to the chain axis of the polymer molecule. Under these circumstances, if the IR spectrum is measured with polarization of the electric field vector along a particular direction *J* of the sample (*J* = MD, TD, or ND), the absorbance intensity of a given peak in the spectrum will be

$$A_J = A_0\{1 + (3 \cos^2 \alpha - 1)f_{cJ}\} \quad (3)$$

where α is the transition moment angle of the peak and A_0 is the intensity that the peak would have if the sample were unoriented. IR spectra are usually measured in transmission on thin films or in attenuated total reflection on the surface of thicker samples. In such cases, the peak height or area can be used as a measure of absorbance in eq. (3). External reflection, on the other hand, gives spectra in which the peaks are distorted by effects related to the variation of the refractive index. Figure 3 shows examples of external reflection spectra measured with polarization in the MD and TD on the surface of

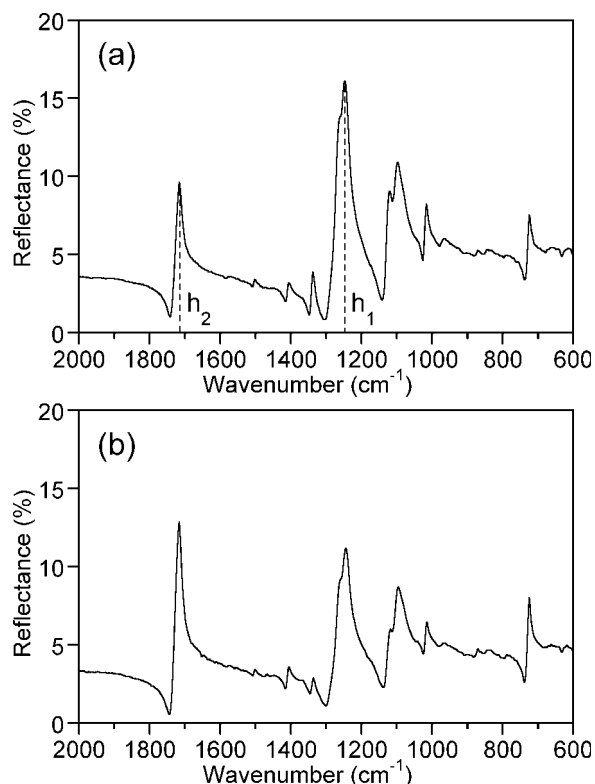


Figure 3 Typical front-surface reflection spectra obtained from the outer surface of a type I bottle with polarization in (a) the longitudinal direction (MD) and (b) the hoop direction (TD).

type I PET bottles studied in this work. The difference in the orientation between the two directions is evident from the difference in the relative peak intensities in the two spectra, especially for the peaks at 1243 and 1717 cm^{-1} . These spectra resemble the ones that we obtained previously by external reflection for a set of thick PET films.¹⁰ In that work, we converted the reflectance spectra to absorbance-like spectra by means of the Kramers–Kronig transformation,¹³ and we then applied the usual procedures to characterize the orientation. We then showed that for PET it is possible to determine the orientation directly from the reflection spectrum by taking the ratio R of the maximum reflectance values of the two peaks at 1243 and 1717 cm^{-1} , which corresponds to h_1/h_2 in Figure 3(a). These two peaks possess different transition moment angles and therefore exhibit different dichroic behaviors. There is an excellent correlation between R and the orientation function determined by the more rigorous but more laborious Kramers–Kronig treatment. The ratio involves only the raw reflectance values at the peak maxima, and no baseline correction or peak fitting is required. Furthermore, taking the ratio of two peaks in the same spectrum minimizes any error that might arise from the fact that the overall reflection intensity can be affected by the surface quality and sample posi-

tioning. The equation relating the reflectance ratio to the chain orientation function is as follows:¹⁰

$$f_{cJ} = \frac{R_J - 1.12}{0.657 + 0.528R_J} \quad (4)$$

where R_J is the ratio of the heights of the reflectance peaks at 1243 and 1717 cm^{-1} in a spectrum measured with polarization in sample direction J and f_{cJ} is the chain orientation function with respect to that direction. Thus, for example, in this work reflection spectra were measured on the surfaces of the PET bottles with polarization along both the MD and TD, and the approach just described was used to calculate f_{cM} and f_{cT} ; f_{cN} was then calculated from the relationship $f_{cM} + f_{cT} + f_{cN} = 0$. This characterizes the biaxial orientation of the samples, and if desired, the coefficients P_{200} and P_{220} can be calculated by means of eq. (2).

Effect of the mold temperature

For type I (round) bottles, spectra were measured at mid-height for bottles molded at 16, 38, and 60°C. The chain orientation is plotted on a triangular graph in Figure 4. Each apex of the triangle represents perfect orientation ($f = 1$, $\theta = 0^\circ$) parallel to one particular direction (MD, TD, or ND, as indicated). For a given point, orientation function f with respect to a given direction is related to the location of the point along the median corresponding to that direction and can vary from 1 at the apex to 0 (random orientation) at the center to -0.5 (perfect perpendicular orientation, $\theta = 90^\circ$) at the side opposite to the apex. For perfect orientation in the MD, the point would be located at the machine apex, and

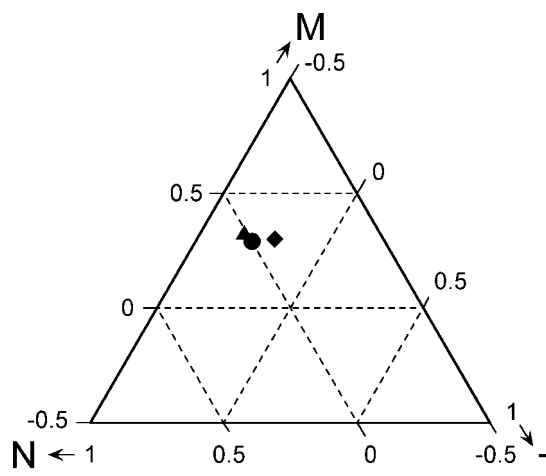


Figure 4 Orientation functions measured on the outer surface of a type I bottle for different mold temperatures: (▲) 16, (●) 38, and (◆) 60°C.

for perfect orientation in the TD, it would be located at the transverse apex. For perfect equibiaxial orientation, it would be at the midpoint of the machine–transverse side of the triangle. Thus, if we take the 60°C point in Figure 4 as an example, the orientation functions are as follows: $f_{cM} = +0.30$, $f_{cT} = -0.21$, and $f_{cN} = -0.09$.

Figure 4 shows that generally the molecular chains are oriented most strongly toward the MD (axial), with the orientation function f_{cM} near 0.3. This is not surprising, given that a simple estimation of the draw ratios, based on initial (preform) and final (bottle) dimensions, gives a higher value for the axial direction (2.5) than for the hoop direction (2.1). The orientation does not seem to be very sensitive to the mold temperature. An unexpected feature, however, is the fact that the points tend to lie more toward the normal apex than toward the transverse apex; that is, f_{cT} is lower (more negative) than f_{cN} . In the usual situation for biaxial orientation in the machine–transverse plane, the polymer chains align preferentially in the plane and therefore perpendicular to the thickness direction, so that as a result f_{cN} is the lowest (most negative) of the three functions. In this case, the chains appear on average to be less aligned along the hoop direction than along the thickness direction. Further work would be required to determine whether this effect is real or simply the result of a certain degree of experimental error. (One possible source, for example, might be the slight curvature of the sample.) The overall process is rather complex, given that it involves both injection and blowing, so unexpected behavior could occur. It could be related, for example, to thermally induced orientation, as described by Isayev,¹⁴ or to specific directional crystallization effects occurring at the surface.

For the much less symmetrical type II bottles, spectra were measured at six different points (A–F), as shown in Figure 2. These correspond to three different heights on both the large and small faces of the bottle. The orientation results are given in Table I and represented graphically in Figure 5. As shown in Figure 6, the blowing is a two-stage process, with the first stage characterized mainly by axial stretching and the second mainly by circumferential stretching. For the type II bottles, the estimated draw ratio for the axial direction, based on initial and final dimensions, is 1.8. For the circumferential or hoop direction, the overall calculated draw ratio is 2.8, but if we (rather crudely) assume that each face originates from one quarter of the initial circumference, then the calculated draw ratios are 1.8 for the small face and 3.8 for the large face. Thus, for the large face, the estimated circumferential draw ratio is higher than the axial draw ratio, and the preferred orientation would be expected to be in the hoop direction rather than in the axial

TABLE I
Orientation Results for Type II Bottles

Point	Mold temperature (°C)	f_{cM}	f_{cT}	f_{cN}	P_{200}	P_{220}
A	16	-0.16	+0.38	-0.22	-0.16	+0.100
	38	-0.27	+0.34	-0.07	-0.27	+0.068
	60	-0.34	+0.43	-0.09	-0.34	+0.087
B	16	-0.16	+0.44	-0.28	-0.16	+0.120
	38	-0.38	+0.47	-0.09	-0.38	+0.093
	60	-0.37	+0.48	-0.11	-0.37	+0.098
C	16	-0.30	+0.40	-0.10	-0.30	+0.083
	38	-0.25	+0.38	-0.13	-0.25	+0.085
	60	-0.40	+0.52	-0.12	-0.40	+0.107
D	16	+0.36	-0.10	-0.26	+0.36	+0.027
	38	+0.24	-0.04	-0.20	+0.24	+0.027
	60	+0.20	-0.06	-0.14	+0.20	+0.013
E	16	+0.11	+0.12	-0.23	+0.11	+0.058
	38	+0.02	+0.05	-0.07	+0.02	+0.020
	60	0.00	+0.07	-0.07	0.00	+0.023
F	16	-0.14	+0.32	-0.18	-0.14	+0.083
	38	0.00	+0.10	-0.10	0.00	+0.033
	60	+0.05	+0.01	-0.06	+0.05	+0.012

direction as it was for type I bottles. This is indeed the case for the larger face, as can be seen for points A, B, and C in Figure 5 and Table I. Furthermore, the estimated draw ratio of 3.8 is higher than the critical value of around 2.2–2.5 required to generate shear-induced crystallization and inhibit molecular relaxation during the cooling phase.^{8,15} Thus, the points generally tend toward the transverse apex, with f_{cT} lying between 0.3 and 0.5, whereas the values of f_{cM} and f_{cN} are negative. As was observed for the type I bottles, for some points the value of f_{cN} is not the lowest of the three, and this suggests a certain preference of the chains for the thickness direction. For the smaller face of the type II bottles, the estimated draw ratio of 1.8 in the hoop direction is smaller than the axial draw ratio, so the preferred orientation would be expected to be in the axial direction. This is the case for point D near the top of the bottle, but for point E near the middle, the orientation is close to equibiaxial and rather weak, and for point F near the bottom, the chains align along the circumferential direction, as on the larger face. This variation appears to be a result of the complex geometry of the bottle and the two-stage drawing process. Relaxation may also play a greater role because the estimated hoop draw ratio of 1.8 for the smaller face is lower than the critical value for shear-induced crystallization. In this respect, it is also interesting to note that the orientation at points D, E, and F decreases in magnitude as the injection mold temperature increases, probably as a result of slower cooling and therefore greater relaxation. Consequently, the variation in orientation among all considered points is greatest at the lowest mold temperature of 16°C. To better show this variation,

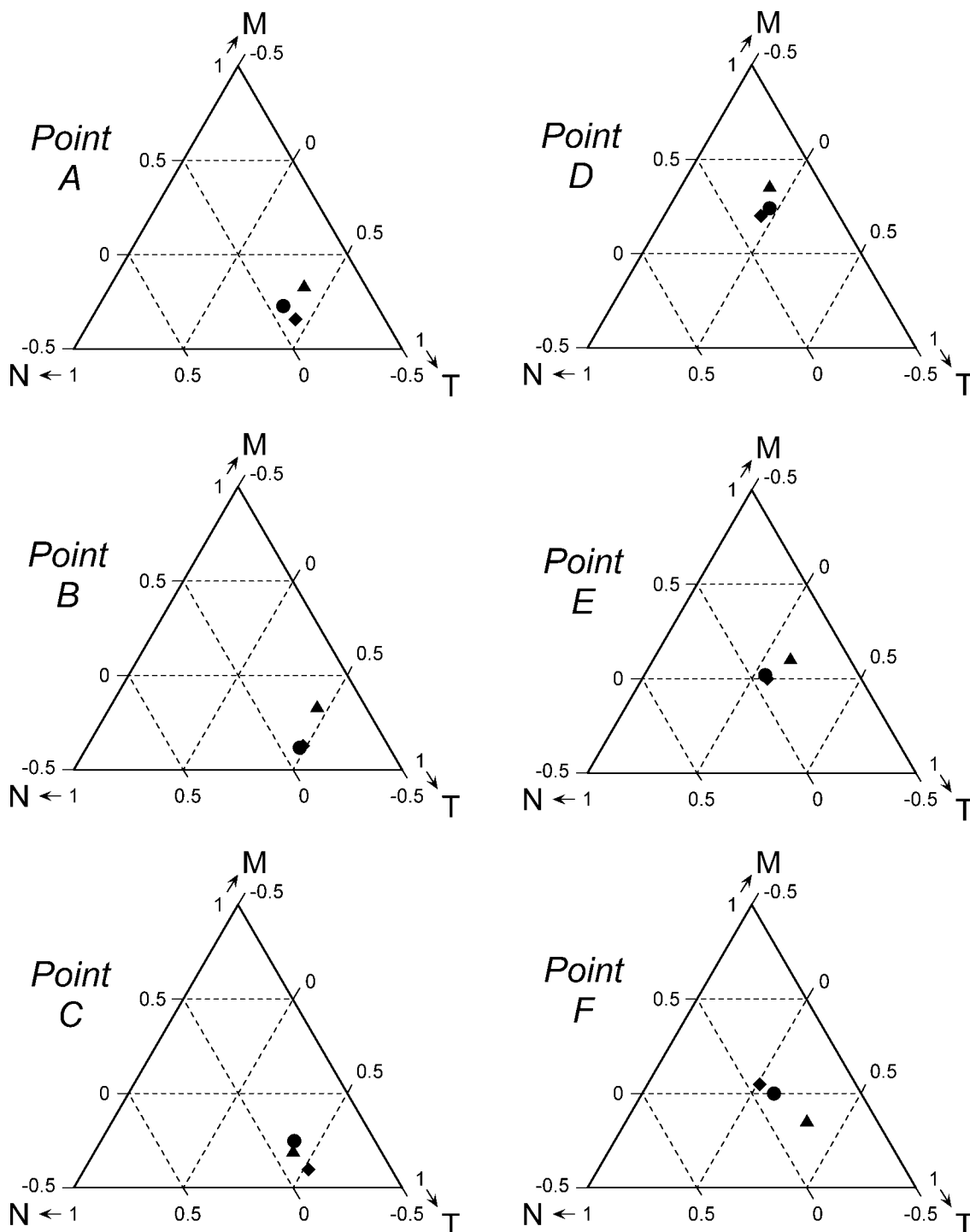


Figure 5 Orientation functions measured at different points on the surface for type II bottles produced at different mold temperatures: (▲) 16, (●) 38, and (◆) 60°C.

Figure 7 compares the orientation for the six different points at a mold temperature of 16°C.

Variation of the orientation across the thickness

Figure 8 shows the external reflection spectra measured with the IR microscope across the thickness of a type I bottle, with polarization corresponding to

the TD and ND. In this case, the spectra measured in the two directions resemble each other more closely than the machine and transverse surface spectra of Figure 3, although they are not identical. These results show that the orientation is mainly uniaxial in the MD, with little difference between the TD and ND. The orientation functions calculated by means of eq. (4) are plotted in Figure 9. The

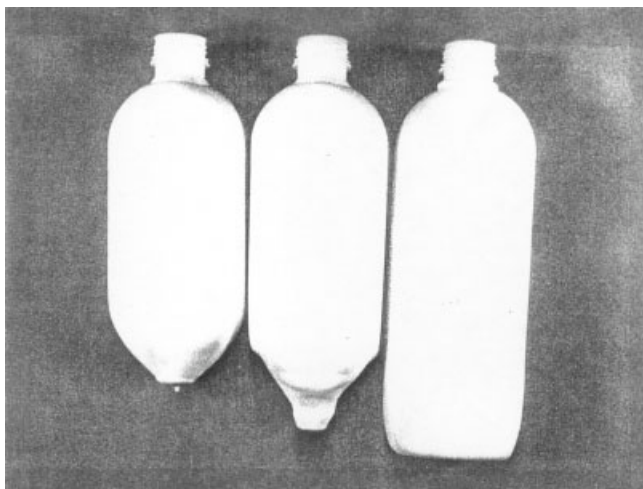


Figure 6 Stages in the blowing of type II bottles. The photograph shows polyethylene bottles, but the behavior is similar to that of PET.

points are clustered together, and there is no clear evidence of a trend with respect to a gradient across the thickness. Generally, the orientation is close to uniaxial in the longitudinal direction with f_{cM} around 0.4. The points measured across the thickness show the same unexpected effect observed for the point corresponding to the outer surface, namely, $f_{cT} < f_{cN}$, even though on the surface the measurements were made in the MD and TD, whereas across the thickness they were made in the TD and ND.

A close examination of the spectra in Figure 8 reveals an interesting feature. The out-of-plane benzene ring C—H band near 727 cm^{-1} has its transition moment normal to the ring and therefore perpendicular to the polymer chain, like the carbonyl band near 1717 cm^{-1} . Thus, they would be expected

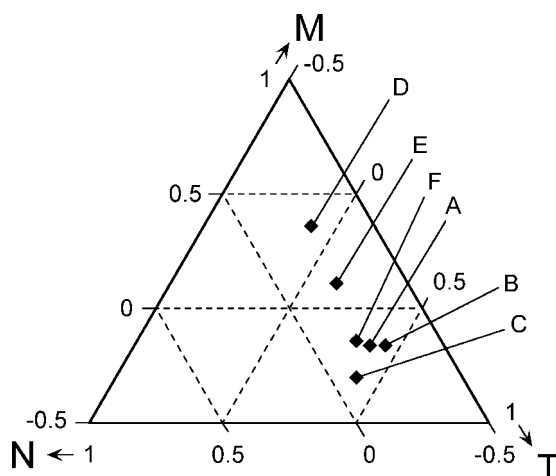


Figure 7 Orientation functions measured at different points on the surface for a type II bottle produced at a mold temperature of 16°C .

to show similar dichroic behavior. However, although the carbonyl peak is consistently weaker in the ND spectrum than in the TD spectrum, the reverse is clearly the case for the benzene ring peak. This indicates that the benzene rings are preferentially aligned with their normals in the thickness direction; that is, the ring planes lie in the plane of the sample. Such alignment has been observed previously in PET films under certain circumstances.^{16,17} Its presence means that the assumption of cylindrical symmetry with respect to the polymer chains, used in developing eq. (4), may not be perfectly valid, and the intensities of the carbonyl peak could be

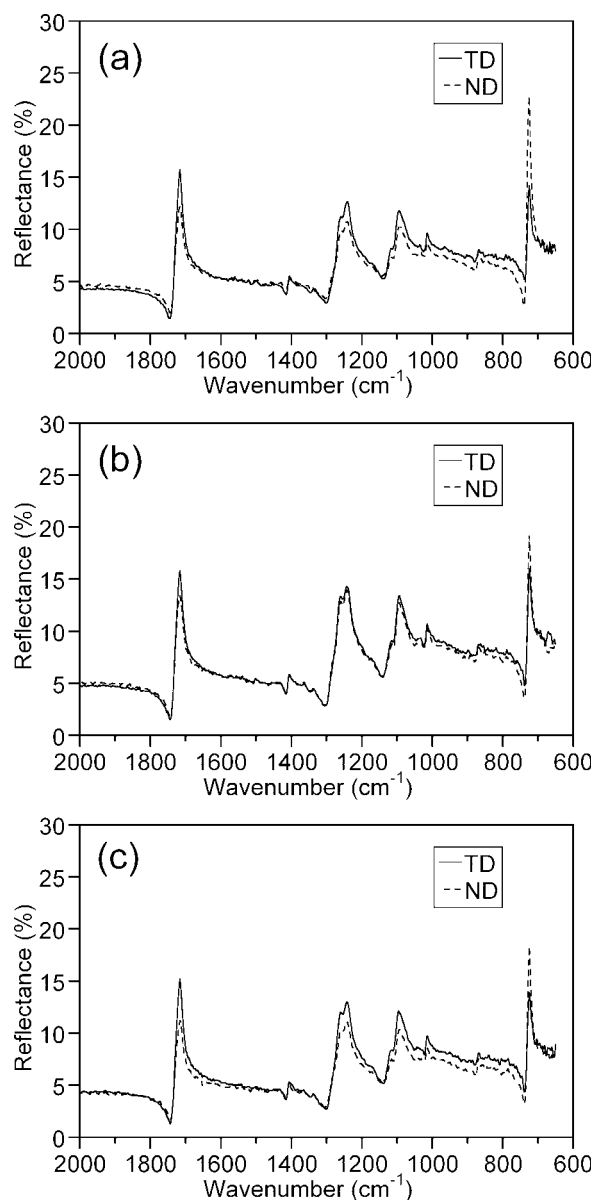


Figure 8 IR external reflectance spectra measured with polarization in the TD and ND at different distances from the outer surface on the cross section of the wall of a type I bottle obtained at a mold temperature of 60°C : (a) 80, (b) 160, and (c) 240 μm .

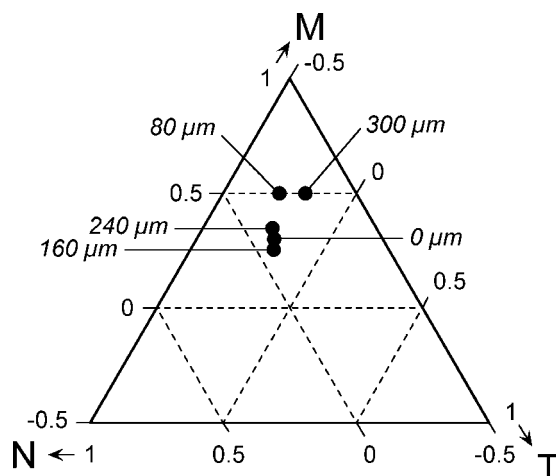


Figure 9 Variation of the orientation across the wall thickness from the outer surface (0 μm) to the inner surface (300 μm) for a type I bottle obtained at a mold temperature of 60°C.

affected. This may introduce some degree of error into the calculated orientation values. It is not expected to be large, but it could be enough to account for the unexpected effect in which f_{cN} is not the lowest of the three orientation functions. Further work is required to clarify this. However, the main conclusions concerning the surface orientation in the bottles and its variation in type II bottles should not be significantly affected. (It may be noted that non-cylindrical symmetry means that P_{202} and P_{222} are not necessarily zero.)

The results obtained across the thickness for the type I bottle contrast with those reported earlier for a type II bottle near the center of the larger face; the spectra were measured on the MT plane at different depths after the removal of material by polishing.¹⁰ In that case, although the clearly preferred orientation in the hoop direction was maintained across the wall thickness, the orientation with respect to the axial direction appeared to diminish from the outer surface to the inner surface.

Apparently, the final molecular orientation in PET bottles depends to a large extent on the different morphological characteristics at each layer across the thickness of the injected preform. According to our previous work,¹¹ the morphology is characterized by a high degree of molecular orientation and a high degree of shear-induced crystallinity at the subskin layer of the injected part. The core and the skin layer of that part were found, however, to be basically amorphous with a low degree of orientation. By increasing the injection mold temperature, we found that the maximum of the molecular orientation is shifted to the skin layer with an increase in the crystallinity at all layers of the injected part. The relationship between such complex morphological char-

acteristics and the buildup of the molecular orientation at each layer across the thickness of the blown bottles is a subject that warrants further investigation, and the experimental approach that we have developed and applied in this study will serve as a useful technique for this purpose. Future studies of interest could involve, for example, X-ray diffraction measurements to correlate with the IR results and measurements near the corners of the bottle in areas of high stress concentration.

CONCLUSIONS

It has been clearly shown that the front-surface reflection IR spectroscopy technique previously developed^{9,10} and applied to injection-molded parts¹¹ can also be successfully applied to injection-stretch-blow-molded bottles. PET bottles with two different shapes molded at three different temperatures were successfully characterized. For cylindrical bottles, the molecular chains show a definite preferred orientation ($f \sim 0.3$) in the axial (longitudinal) direction, as expected from the estimated draw ratios for this geometry. The orientation does not vary much with the mold temperature or axial position. For bottles with rectangular cross sections, the orientation in the larger faces is mainly in the hoop direction ($f \sim 0.3$ to 0.5), and this agrees with the estimated draw ratios. It is not very sensitive to the mold temperature. However, in the smaller (side) faces, the orientation varies from the hoop direction at the bottom to the axial direction at the top, with the variation being more pronounced at lower mold temperatures. The technique was also applied to characterize the variation in the orientation across the wall thickness. An apparent effect by which the orientation function in the thickness direction is not the lowest of the three, as would be expected for biaxial orientation in the machine-transverse plane, was detected and is difficult to explain, but it warrants further investigation. There is evidence of alignment of the benzene rings in the plane of the sample, which can complicate the analysis.

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