Determination of Density and Birefringence of Poly(ethylene terephthalate) Fibers Using Raman Microscopy

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ABSTRACT: Multiple regression analysis has been used to calibrate polarized Raman spectra of poly(ethylene terephthalate) fibers in terms of density and birefringence. The calibration spans PET fibers having a wide range of density and birefringence values. The calibration required the Raman spectrum in only one polarization direction, that is, with the polarization directions of the incident and scattered light parallel to each other and to the fiber axis. The peak at 631 cm⁻¹, which has been used previously as an internal standard band, could be used for the prediction of density, but not for the prediction of birefringence. The peak at 702 cm⁻¹ was found to be a good internal standard band for both density and birefringence. Density could be predicted with a standard error of prediction of 0.003 g/cc using only the ratio of the intensity of the band at 996 cm⁻¹ to that of 702 cm⁻¹ and the full width at half maximum of the 1725-cm⁻¹ band. Birefringence was predicted with a standard error of 0.01 using the ratios of the intensities of the bands at 996 and 1616 cm⁻¹ to that of the 702-cm⁻¹ band. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 943–952, 1999

Key words: polyester; Raman; density; birefringence; fiber

INTRODUCTION

The utility of a polymer in a particular application depends on its properties, which in turn, are dictated by its morphology. The two most important aspects of polymer morphology are the extent of crystallization and the level of molecular orientation. A variety of techniques are available for the morphological characterization of polymers, including X-ray diffraction, NMR spectroscopy, birefringence, calorimetry, density, vibrational spectroscopy, etc. Crystallinity of fibers is most frequently estimated using density or X-ray diffraction and orientation using birefringence. With the development of specialty fibers such as bicom-

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ponent fibers, fibers having noncircular cross-sections, melt-blown fibers, crimped fibers, etc., it has become difficult to use the conventional techniques for density and orientation measurements. Raman microscopy, on the other hand, is simple to use on such fibers, and requires virtually no sample preparation. It also offers remote sampling and microsampling capabilities, and has the advantage of being insensitive to water, so that samples immersed in water can also be studied.

The vibrational spectrum of PET has been a subject of extensive investigation.^{1–3} Many attempts have been made to study the changes accompanying crystallization of PET using vibrational spectroscopy. Differences in Raman as well as IR spectra were observed with the development of orientation and crystallinity. Purvis, Bower, and Ward⁴ were the first to show that polarized Raman spectra of PET could be used to

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determine the second- and fourth-order Legendre polynomials, which in turn, were correlated with optical birefringence. McGraw⁵ reported the emergence of a new band at 1100 cm^{-1} with the development of crystallinity, and correlated its intensity, normalized with the 631-cm⁻¹ band intensity, linearly with density. He also found that the bands at 278 and 857 cm^{-1} were sensitive to changes in the crystallinity of the sample. Later, Melveger⁶ found that the intensity of the 1100cm⁻¹ band was influenced by orientation as well as crystallinity. He related the full width at half maximum of the carbonyl band (at 1730 cm^{-1}) to the density. The differences in the Raman spectra between the amorphous and the crystalline samples of PET were explained qualitatively.^{7,8} However, the quantitative approaches to understanding changes in Raman spectra were rarely successful, and often led to ambiguous results. Hence, a need for an understanding at a molecular level to assign the vibrational spectrum was realized. Bahl et al. 9,10 performed a normal coordinate analysis on PET utilizing a force field for a family of chemically and structurally related aromatic polyesters, with and without deuteration.

Bulkin et al.¹¹⁻¹³ studied conformational changes, chain orientation, and crystallinity in PET yarns using Raman spectroscopy. They observed new bands grow with annealing at 73 and 129 cm^{-1} , and a broad low-frequency band centered near 30 cm^{-1} disappear. They looked at internal correlations between different spectroscopic changes to examine whether these changes measure the same molecular phenomena and then derived external correlations to assign the spectroscopic changes to particular events. They noted that the weak band at 1452 cm^{-1} shifts its peak position to 1460 $\rm cm^{-1}$ in the most highly annealed samples. To characterize this change, they used the ratio of intensities at these two wavenumbers. Similar coupled pairs that they reported were 1415/1409, 1279/1259, 996/1019, 795/792, and 282/273. They found linear relationships between the intensity ratios 1096/1117, 1452/1460, and 1415/1409 cm⁻¹ and the half bandwidth of the carbonyl-stretching mode at 1725 cm^{-1} . These correlations led to the assumption that these spectroscopic changes measure the same molecular phenomenon. They denoted these four changes as the "first group." This group was shown to correlate only with conformational changes in the glycol linkage, and although they had a reasonable correlation with density, there were deviations. In the "second group," they analyzed the $631/1289 \text{ cm}^{-1}$, $855/1289 \text{ cm}^{-1}$, the 996/ 1019 cm⁻¹ and the 1172 half-width, all of which are ring modes. They found that their behavior with respect to the 1725 half width was nonlinear, but found them to correlate linearly with the birefringence of the samples. They used the band at 1289 cm⁻¹ as the internal standard. They also reported that the 1610-cm⁻¹ band could also be used as an internal standard, but was not done so because of its large intensity that caused serious round-off errors when used in the denominator due to the nature of the computer programs being used at that time.

In 1985, Adar and Noether¹⁴ recorded polarized Raman spectra, using backscattering from single filaments of spin-oriented and drawn fibers of PET. They used partially oriented yarns (POY) with slowly increasing take-up speeds for their studies to observe the effects of orientation independent of crystallinity. Polarized Raman spectra are denoted using the "Porto" nomenclature, A(bc)D, where A and D represent the propagation directions of the incident and scattered laser beams, respectively, and b and c represent the direction of polarization of the incident and scattered light, respectively. They found that the Raman spectrum of a PET sample with relatively low orientation with the fiber axis parallel $\{Y(ZZ)Y'\}$ and perpendicular $\{Y(XX)Y'\}$ to the laser polarization direction were indistinguishable, whereas for a highly oriented sample, the Raman spectrum in the $\{Y(XX)Y'\}$ direction is significantly lower in intensity than in the $\{Y(ZZ)Y'\}$ direction. For both samples, all bands in the spectrum collected with the analyzer perpendicular to the laser polarization direction $\{Y(ZX)Y'\}$ were reduced in intensity except for the 632 cm^{-1} and the 794 $\rm cm^{-1}$. They monitored the development of orientation in the fibers by looking at the intensity ratios, $I_{\{Y(XX)Y'\}}$: $I_{\{Y(ZZ)Y'\}}$, of various bands. For instance, $I_{\{Y(XX)Y'\}}$: $I_{\{Y(ZZ)Y'\}}$ of the 1616 cm^{-1} band was seen to decrease from 1.1 for the sample with low orientation to 0.1 for the sample having high orientation. The band at 996 cm^{-1} was observed to appear only in the $\{Y(ZZ)Y'\}$ spectrum, showing that this band is highly polarized. They concluded that the Raman peaks measured between 900 and 1220 cm⁻¹ correlated with conformational changes of the polymer and interchain effects rather than amorphous-crystalline differences based on the appearance of these bands in the spectra of spin-oriented amorphous samples. They have reported that the 1725 band actually shows three maxima appearing at 1721, 1725,

and 1731 cm^{-1} . They observed the maxima most clearly in the amorphous sample, whereas in the crystalline sample the main peak at 1725 $\rm cm^{-1}$ was observed, although the other two components were also assumed to be present. They observed a shift of the 1175-cm⁻¹ band to 1182 cm⁻¹ on increasing crystallinity, as reported earlier by Stokr et al.¹⁵ and Ward and Wilding,¹⁶ thus resulting in a broadening of this peak. For highly crystalline samples, the 1175-cm⁻¹ band was seen to split into two bands at 1175 and 1182 cm^{-1} . Thus, the 1182 cm^{-1} band was reported as a true crystallinity band. Finally, they detected the presence of a shoulder at 1080 cm^{-1} that was visible in all spin-oriented samples, but was most clearly seen in a sample drawn at room temperature. Because the difference between drawn and spin-oriented fibers is the concentration of load-bearing, stressed-chain structures in the noncrystalline regions, they suggested that the shoulder at 1080 cm^{-1} could reflect the stressed *trans* glycol units in amorphous regions.

Rodrigues-Cabello et al.¹⁷ monitored structural changes occurring in annealed injection-molded PET samples using Raman spectroscopy. They determined individual *trans* and *gauche* isomer distributions using the bands at 998 cm⁻¹ (associated with *trans* conformation of the ethylene glycol segment), the 886-cm⁻¹ band (associated with the *gauche* conformation of the ethylene glycol segment), and the 795 cm⁻¹ (used as the internal reference band). They related the percentage *trans* content to crystallinity calculated using DSC measurements.

Everall et al.¹⁸ used Fourier Transform Raman (FT Raman) spectroscopy and multivariate data analysis to study density and orientation of PET samples. To compensate for variations in laser intensity and alignment between samples, and to refrain from using an internal standard band, they normalized all spectra to a constant area over the spectral region. They then used Hierarchical Cluster Analysis (HCA) and Principal Components Analysis (PCA) for exploratory analysis to classify their samples and to determine the bands that were most strongly affected by changes occurring in the samples. They determined that the bands at 1730, 1094, 997, and 860 cm⁻¹ were the most important bands for prediction of density. Finally, they used partial leastsquares modeling techniques to calibrate the density of PET samples using the above-mentioned bands and obtained a standard error of prediction of 0.0024 g cm^{-3} for the crossvalidation plot.

In a subsequent study, Everall et al.¹⁹ repeated their study on density calibration using a fibercoupled Raman microprobe and Partial Least-Squares (PLS) technique. They used two approaches for data normalization. In the first approach they fit a few chosen points to a polynomial function for defining the nonlinear baseline arising from the fluorescence background. Then they subtracted the baseline and finally normalized the resultant spectrum to unity. In their second approach, they took the second derivative of the spectrum and subsequently normalized the resultant data. Another pretreatment they used was that of data grouping, by which the number of data points within a spectrum were reduced by dividing the wavenumber axis into blocks containing several points, with each block being assigned the average intensity of its constituent points. They obtained PLS calibration plots with two factors, and a data grouping of eight points with a standard error of prediction close to 0.0023 g cm^{-3} , irrespective of the method used for pretreatment.

As can be seen from the above section, considerable literature is available on the Raman spectra of PET. However, except for Everall et al.,^{18,19} most of the other researchers have correlated different bands of the Raman spectrum of PET to orientation and crystallinity, but these correlations are not adequate to determine the orientation and crystallinity-related parameters from the Raman spectra of PET. Everall et al.^{18,19} have determined good models for determining the density of PET samples from unpolarized Raman spectra, but they have used a purely statistical method that involves many parameters. Moreover, they were not able to predict the birefringence well. Although Raman spectroscopy gives a measure of orientation, birefringence is used more frequently in the industry to monitor orientation.

The aim of this work was to develop correlations for density and birefringence for a set of PET fibers exhibiting a wide range of densities, and birefringence using different bands of the Raman spectra of PET. Multiple regression analysis was used to develop correlations for density as well as birefringence.

EXPERIMENTAL

Three sets of PET yarns spun under different conditions to attain a range of density and birefringence values were used as the training set for this study. The parallel and perpendicular refractive indices of the fibers in the training set were obtained using an Aus Jena Interphako interference microscope. The birefringence and Lorentz density²⁰ were then determined by:

$$\Delta n = n_{\parallel} - n_{\perp} \tag{1}$$

$$n_{\rm iso} = (n_{\parallel} + 2n_{\perp})/3$$
 (2)

$$\rho = 4.0486 \left(\frac{n_{\rm iso}^2 - 1}{n_{\rm iso}^2 + 2} \right) \tag{3}$$

where parallel and perpendicular refer to the fiber axis.

The Raman spectra were collected using a Holoprobe Research 785 Raman Microscope made by Kaiser Optical Systems, Inc. The main components of the system were a 785-nm solid-state laser, a fiber optic probe head, an imaging spectrograph, a charge-coupled device (CCD) camera, and a personal computer. The laser delivered approximately 3 mW of polarized light to the sample.

Individual filaments of PET were mounted on steel washers under slight tension for the collection of Raman spectra. The washer was placed on a mount that could be rotated freely so that the filament could be oriented as desired. Polarized Raman spectra were collected using a backscattering arrangement, as shown in Figure 1. Hence, the propagation directions of the incident and scattered laser beams were along the same axis. The incident laser beam was polarized parallel to the front-to-back axis of the microscope stage, and the fiber axis was oriented along the polarization direction of the incident laser beam or perpendicular to it. Single Raman spectra were recorded using either a 50× or a 10× objective and an integration time of 6 min.

The z-axis in the experimental setup is defined as the macroscopic fiber axis. The y-axis is the direction of propagation (and collection) of the laser beam, and the x-axis is the other orthogonal axis. Because the direction of propagation of the incident and scattered light are fixed, we have used a simplified version of the "Porto" nomenclature, wherein the directions of propagation of the incident and scattered light are omitted. Hence, when the direction of polarization of the incident and scattered light are parallel to the fiber axis, it is called the ZZ spectrum, instead of the {Y(ZZ)Y'} spectrum.

Raman Spectra of the PET fibers were collected in two different configurations: (1) the fiber axis



Figure 1 Schematic representation of the Raman polarization experiment showing the arrangement for the ZZ spectrum. The laser propagates in the Y direction with polarization parallel to the fiber, E_Z , or perpendicular to the fiber axis, E_X . The scattered light is collected with a propagation direction, -Y, and the analyzer is oriented to transmit only light with a polarization parallel to the incident light.

parallel to the laser polarization direction and the analyzer parallel to the polarizer (the ZZ spectrum); (2) the fiber axis perpendicular to the laser polarization direction and the analyzer parallel to the polarizer (the XX spectrum).

Considerable effort was made to collect data at the same point when the fiber axis was parallel and perpendicular to the laser polarization. Some unusual point in the fiber was set as zero, and a known distance was traversed along the fiber before collecting data. When the sample was rotated, the singular point in the fiber was again set as zero, and an equal distance was traversed along the fiber, thus collecting data very near, if not exactly, at the initial point.

Raman spectra were collected from three specimens for each sample for both polarizations and specimen orientation combinations.

All data acquisition was performed using the Kaiser Optical Systems' "HoloGRAMS" software. HoloGRAMS, in combination with GRAMS/386, provided a complete Windows-based spectral acquisition and analysis capability. HoloGRAMS



Figure 2 ZZ and XX spectra of a low-crystallinity, low-orientation sample overlaid and normalized with respect to the 631 cm^{-1} band. The ZZ spectrum has been offset by an arbitrary amount.

was responsible for setup, calibration, and operation of the HoloProbe unit. Spectra acquired by HoloGRAMS was then transferred to the GRAMS/5 software package (Galactic Industries Inc.) for treatment and analysis.

All the Raman spectra were analyzed using the GRAMS/386 or GRAMS/5 software package. Each peak of the Raman spectrum was fit individually for each specimen in both configurations using the curve-fit routine in GRAMS. This routine fit the peaks and gave the area, height, full width at half maximum, position, and the Gaussian and Lorentzian content for each peak. Each peak was fit multiple times to ensure repeatability of the fit. A few of the peaks, such as the 857-cm⁻¹ peak, the 1287-cm⁻¹ peak, etc., which were present as clusters, could not be fit consistently, and were not used in this analysis. For each peak, the peak areas were used as intensity values. However, raw Raman peak intensities could not be used for the final analysis because several procedures such as focusing the sample, the exact point of data acquisition (center of fiber or towards the surface), etc., that affect the Raman spectrum could not be standardized. Hence, the peak intensities were normalized with respect to another band in the spectrum.

The SPSS software package was used to perform linear, multiple regression analysis to develop statistical models relating birefringence and optical density of the fiber to various peak intensity ratios of its Raman spectrum. All three sets of Raman data were incorporated in this analysis.

The results obtained by the regression analysis were then verified by collecting the Raman spec-

tra of a new set of fibers, which consisted of PET fibers prepared by only varying the spinning speeds. Again, three specimens were used from each sample. The relations obtained for birefringence and Lorentz density were employed to predict the properties of these fibers. The results were then compared to the values obtained from interference microscopy.

RESULTS

Qualitative Analysis

The Raman spectra in the ZZ and the XX polarizations were first analyzed qualitatively. The results are exactly as described by Adar and Noether.¹⁴ The ZZ and XX spectra of a low-orientation low-crystallinity sample were almost identical, with only minor differences in their background (Fig. 2). The ZZ and XX spectra of a high orientation, high crystallinity sample, on the other hand, showed significant differences (Fig. 3). The XX spectrum of this sample had much lower intensities compared to the ZZ spectra. An overlay of the ZZ spectra of the low- and highorientation samples, shown in Figure 4, highlights the changes occurring in the Raman spectrum of PET with the development of crystallinity and orientation.

Univariate Analysis

A univariate analysis was performed using the different bands suggested in the literature. The



Figure 3 ZZ and XX spectra of a high-crystallinity, high-orientation sample overlaid and normalized with respect to the 631 cm^{-1} band. The ZZ spectrum has been offset by an arbitrary amount.



Figure 4 ZZ spectra of (a) a low-crystallinity, loworientation sample, and (b) a high-crystallinity, highorientation sample overlaid and normalized with respect to their 631 cm⁻¹ band. The spectrum (b) has been offset by an arbitrary amount.

plots of the full width at half maximum of the carbonyl-stretch band (Fig. 5), as well as the intensity ratio 1096/1117 against density (Fig. 6), showed the general trend as suggested in the literature. However, neither correlation is adequate for determining the density from the Raman spectra. Similarly, the correlation of the 996 and 1616 cm⁻¹ band intensities with birefringence also proved inadequate, as shown in Figures 7 and 8. Hence, it is clear that each of these bands correlates with density and/or orientation, but the correlation is not adequate to determine density and birefringence from the Raman spectrum. A different approach involving two or more of these bands is needed to achieve this goal.



Figure 5 Full width at half maximum of the 1725 cm^{-1} band plotted versus the density and shown with the best straight line fit.



Figure 6 Intensity ratio of 1096 cm^{-1} to 1117 cm^{-1} plotted versus density and shown with the best straight line fit.

Multivariate Analysis

Selection of a Normalizing Band

A normalizing band should be chosen such that it remains constant over the whole sample set. The peak at 631 cm^{-1} was chosen initially, as it had been suggested by McGraw⁵ as a good internal standard band. However, he was looking at changes in Raman spectra with annealing, and hence, was not concerned with orientation. Melveger⁶ and Bulkin et al.¹² later showed that the peak at 631 cm^{-1} changes with orientation, and hence, should not be used as the reference band. Because the present study involves determination of orientation as well as crystallinity, and because the training set contained fibers having varying levels of orientation, it was decided to try a different normalizing band as well to com-



Figure 7 Intensity ratio of 996 to 631 cm^{-1} plotted versus birefringence and shown with the best straight line fit.

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Figure 8 Intensity ratio of 1616 to 631 cm^{-1} plotted versus birefringence and shown with the best straight line fit.

pare results. The only other bands that seem to remain relatively constant are the peaks at 702 and 1117 cm^{-1} . Of these two bands, the 702-cm⁻¹ band is an isolated band, well separated from other bands in the Raman spectrum. Hence, the intensity of this band can be measured fairly accurately. The reproducibility of the peak intensity for this peak would also be higher than for the 1117-cm^{-1} band, which has an overlapping band at 1096 cm⁻¹. Thus, the 702-cm⁻¹ peak was chosen as a second candidate normalizing band.

The other peaks used in the analysis were the 996, 1096, 1117, 1616, and 1730-cm⁻¹ bands in the ZZ direction and the 1096, 1117, and the 1616-cm⁻¹ bands in the XX direction. The peak intensity areas were used for all bands except the 1730-cm⁻¹ band, for which the full width at half maximum was used. The remainder of the peaks were not used, either because they could not be fit reliably for all the samples using the curve-fit routine in GRAMS, for example, 857 and 1182-cm⁻¹ bands, or because of poor a signal-to-noise ratio, for example, 1370, 1415, and 1450 cm⁻¹. Moreover, Bulkin et al.¹² have shown that these peak parameters correlate to other peak parameters that are being used in the analysis.

Multiple Regression Analysis

Multiple regression analysis was performed using the backward approach, with a removal criterion of the probability of F greater than 0.100 or a forward approach with the entry criterion of probability of F less than 0.05. The F-statistic is given by the ratio of the mean square for the model to the mean square for the error. Using the 631-cm⁻¹ peak as the normalizing band, the fits obtained for birefringence were quite complicated [eqs. (4) and (5)]. Also, the fits obtained for the $10 \times$ and $50 \times$ objectives were very different.

$$\begin{split} \Delta n &= -0.170 + 0.0479 * I_{\text{ZZ1616/631}} \\ &+ 0.054 * (I_{\text{ZZ996/631}}/I_{\text{ZZ1096/631}}) \\ &- 0.016 * (I_{\text{XX1616/631}}/I_{\text{ZZ1616/631}}) \\ &+ 0.0627 I_{\text{XX1616/631}} \end{split}$$

 $50 \times objective$

$$\begin{split} \Delta n &= -0.170 + 0.0075 * I_{ZZ1616/631} \\ &+ 0.0981 * (I_{ZZ996/631}/I_{ZZ1096/631}) \\ &+ 0.0055 * (I_{ZZ1096/1117} * I_{ZZ1616/631}) \\ &+ 0.0409 I_{XX1096/1117} \quad (5) \end{split}$$

(4)

where $I_{aa\#\#/@@}$ is the ratio of the intensities of the "##" band to the intensity of the "@@" band in the "aa" orientation, for example, $I_{ZZ1616\ /\ 631}$ is the ratio of the intensity of the 1616-cm $^{-1}$ band to the intensity of the 631-cm $^{-1}$ band in the ZZ spectrum.

In contrast, the fits obtained for birefringence using the 702 cm⁻¹ peak as the normalizing band were much simpler, and the fits for both objectives used the same terms with only slight differences in their coefficients [eqs. (6) and (7)].

 $10 \times objective$

$$\Delta n = 0.001 + 0.0267 * I_{\text{ZZ996/702}} + 0.00047 (I_{\text{ZZ1616/702}})^2 \quad (6)$$

 $50 \times objective$

$$\begin{split} \Delta n &= 0.00266 + 0.0273 * \mathrm{I}_{\mathrm{ZZ996/702}} \\ &+ 0.00059 (\mathrm{I}_{\mathrm{ZZ1616/702}})^2 \quad (7) \end{split}$$



Figure 9 Crossvalidation plot of birefringence using the 702 cm⁻¹ band as the normalizing band. Error bars are one standard error of prediction. The line corresponds to a perfect correlation.

For density, it was found that both the 631 and the 702-cm^{-1} bands performed equally well as normalizing bands. The best correlations obtained for density using the 631 and 702-cm^{-1} peaks as the normalizing bands are given below:

10 imes objective ho = 1.407 + 0.00742

$$* \ I_{ZZ1096/1117} + 0.00293 \ * \ I_{ZZ996/631}$$

$$-0.0028 * FWHM_{ZZ1725}$$
 (8)

 $50 \times \text{objective:}$

 $\rho{=}1.402{+}0.00103$

$$* I_{ZZ1096/1117} + 0.0032 * I_{ZZ996/631}$$

$$-0.0027 * \text{FWHM}_{\text{ZZ1725}}$$
 (9)

and for the 702-cm⁻¹ normalizing band

10 imes objective

 $\rho = 1.402 \pm 0.00177$

$$* I_{ZZ996/702} + 0.0024 * FWHM_{ZZ1725}$$

 $+ 0.00083 * (I_{ZZ996/702})^2$ (10)

50 imes objectiveho = 1.398 + 0.00305

$$I_{\rm ZZ996/702} - 0.0023 * {\rm FWHM}_{\rm ZZ1725}$$

 $+ 0.00072 * (I_{ZZ996/702})^2$ (11)

Thus, the 631-cm⁻¹ band can be used as a reference band for studying crystallinity changes, but not for birefringence, because it depends on orientation. The 702-cm⁻¹ band can be used for studying both orientation and crystallinity changes and, thus, makes a better normalizing band.

The standard error of prediction of birefringence using the 702-cm⁻¹ band as the normalizing peak was 0.01 for the $10 \times$ objective and 0.009 for the $50 \times$ objective. For density, again using 702 as the normalizing peak, the standard error of prediction was 0.003 g/cc for the $10 \times$ objective and 0.0023 g/cc for the $50 \times$ objective. Similar standard errors of prediction for the two parameters were obtained using the 631-cm⁻¹ band as the normalizing band. The crossvalidation plots for density and birefringence using the $50 \times$ objective and 702 band as the normalizing band are shown in Figures 9 and 10.

Verification of the Model

The correlations obtained between the various Raman peak parameters and the two structural parameters, density and birefringence, were finally applied to a new set of eight samples. These



Figure 10 Crossvalidation plot of density using the 702 cm^{-1} band as the normalizing band. Error bars are one standard error of prediction. The line corresponds to a perfect correlation.



Figure 11 Density of the new fiber series as determined from Raman via eq. (11) plotted versus the Lorentz density. Error bars are one standard error of prediction. The line corresponds to a perfect correlation.

samples were not a part of the training set used to build the correlations. These samples were spun at speeds ranging from 2500 to 6000 m/min, and at two different extrusion temperatures. The density and birefringence values of these samples were predicted using the obtained correlations and subsequently verified using interference microscopy. The plot of the density obtained via Raman microscopy and eq. (11) versus the density values obtained via interference microscopy are shown in Figure 11. The agreement between the density predicted by Raman and that measured by interference microscopy is excellent.

The plot of the birefringence obtained via Raman microscopy and eq. (7) versus the birefringence obtained via interference microscopy are shown in Figure 12. Although the agreement is not as good for birefringence as it was for density, the birefringence given by Raman is within two standard errors of prediction of the actual value for all samples and within one standard error of prediction for most of the samples. However, there appears to be a slight offset, 0.007, between the birefringence determined via Raman and that measured by interferometry for this set of samples, as indicated by the dashed line in Figure 12. The slope of the lines are identical, indicating that the correlation between the Raman spectra and the interferometric data is correct to within a small constant, and that the trends are correct. Nevertheless, the birefringence obtained for PET via Raman microscopy is adequate for all but the most exacting work.

CONCLUSIONS

Quantitative correlations between Raman spectroscopy and the birefringence and density have been obtained for PET. The Raman band at 631 cm^{-1} , which has been suggested earlier⁵ as an internal standard band, should not be used for oriented samples because it varies with orientation.^{6,12} The Raman band at 702 cm^{-1} was found to be a good normalizing band, irrespective of orientation. This band was found to be insensitive to the development of crystallinity as well as orientation. This band has not previously been used as a reference band. Its use for normalization of the Raman spectra greatly reduced the complexity of the relations developed as well as the number of peak parameters required.

The density of PET was determined using Raman spectroscopy with a standard error of 0.003 g cm⁻³ for the 10× objective and 0.0023 g cm⁻³ for the 50× objective. The correlations obtained for density [eqs. (10) and (11)] required only the intensity ratio 996/702, the full width at half maximum of the 1725-cm⁻¹ band, and the square of the peak intensity ratio 996/702 cm⁻¹ in the ZZ spectrum. This standard error of prediction is essentially identical to that of Everall, et al.,^{18,19} but the relationships presented herein are much simpler than theirs.

Likewise, the standard error of prediction obtained for birefringence was 0.01. The correlations obtained for birefringence [eqs. (6) and (7)]



Figure 12 Birefringence of the new fiber series as determined from Raman via eq. (7) plotted versus the birefringence measured via interferometry. Error bars are one standard error of prediction. The solid line corresponds to a perfect correlation; the dashed line is the best straight line fit.

used only the intensity ratio 996/702 and the square of the peak intensity ratio 1616/702 cm⁻¹ in the ZZ spectrum. To the best of the authors' knowledge, this is the first time a correlation between the Raman spectra and the birefringence has been made quantitatively for PET.

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