Raman Characterization of Orientation in Poly(lactic acid) Films

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SUMMARY: Poly(lactic acid) is a new biopolymer material which is marketed by Cargill Dow Polymers under the tradename Nature Works*. One major application for this material is biaxially oriented films for food packaging because it possesses excellent barrier for flavor constituents, deadfold and heat sealability. Shrinkage must be minimized when the film is heat sealed for these applications and, therefore, characterization of the orientation of the amorphous phase of PLA films is necessary.

Raman spectroscopy methodology has been developed to quantify orientation in PLA films. Bands were assigned to crystalline and amorphous phases of PLA such that orientation in both phases could be monitored. Raman depolarization ratios were used to characterize uniaxial systems but were insufficient for most biaxial draws. A new phenomenon for oriented films involving Raman band shifts was observed in these systems, and was shown to be capable of determining orientation, even for symmetrical biaxially drawn films. The origin of these shifts, as well as their use for the quantification of orientation will be discussed. Further, since the line widths of the bands could be used to quantify crystallinity, both crystallinity and orientation could be determined with one measurement.

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 CCC 1022-1360/00/$ 17.50+.50/0

INTRODUCTION

Poly(lactic acid), an environmentally degradable polymer, has been used in biomedical applications for over a decade[1]. Due to its ideal combination of physical properties (high modulus, good film forming properties, good heat seal characteristics, barrier to flavor and aroma) and competitive cost, it is currently being investigated for a number of commodity applications, including packaging, fibers, coated paper board, and rigids and thermoformed containers. The value attributes that PLA possesses for these applications include heat seal, clarity, gloss, deadfold, excellent food contact attributes and grease resistance for packaging; hand and drape, moisture management, and resilience for fibers; stress crack resistance, ductility (for hinges), clarity, processability, degradable/renewable for thermoformed containers.

PLA films are most often produced commercially by a cast-tenter process giving rise to films with a high degree of orientation and strain-induced crystallinity. Characterization of the orientation, especially the amorphous phase, is necessary because one prominent application for PLA is use of biaxially oriented films for heat seal packaging. Shrinkage must be minimized when the film is heat-sealed or the seal will pucker. Shrinkage has been shown to be a function of both amorphous phase orientation and crystallinity for fibers[2]. The greater the amorphous phase orientation, the greater the stresses causing it to retract at elevated temperatures and, thus, the more shrinkage. Heat sealing is performed between approximately 100 and 130°C, which is above Tg but well below the crystalline melting point of PLA.

Several papers have been published concerning the Infrared and Raman spectra of PLA. The band assignments and effects of crystallinity on the spectra were discussed[3-5, 6]. Orientation behavior based on the relative intensity measurements of vibrational transitions has not been discussed, however, until recently[7]. Generally, bands characteristic of chains in both crystalline and amorphous regions can be found. Therefore, segmental orientation of the entire sample can be determined if bands are well defined. With the current availability of a large variety of lasers, highly polarized excitation sources can be utilized making the polarized Raman experiment an attractive technique because of its versatility, convenience, rapidity and ability to conduct on-line monitoring. The details of the experimental procedure and band assignments are described therein.

In this study, polarized Raman scattering from various poly (lactic acids) containing different degrees of configurational (D-isomer level) and conformational disorder (due to the effects of crystallinity) were obtained. Films of PLA were drawn under various conditions of temperature and draw ratio and their Raman spectra observed in the machine direction (MD), transverse direction (TD) and thickness direction. Based on polarized Raman scattering data, it was possible to characterize the orientational behavior of both the amorphous and crystalline regions.

EXPERIMENTAL

The physical characteristics, including molecular weight and configuration, are listedelsewhere[7]. Films were drawn simultaneously using an Iwamoto film stretcher which is capable of providing force/displacement curves. A 60-sec. heat time was used between loading film and drawing the film. Films were stretched at 80 °C and 100% per second. The draw ratios ranged from 1X1 to 4X4 and greater in some cases. If the films were drawn asymmetrically, the larger draw ratio was in the machine direction. The starting films were nominally 15 mils (381 microns) in thickness.

Raman spectra were obtained with a Kaiser Raman microscope spectrometer using a 785 nm laser (red) as excitation source. Experimental details are provided elsewhere[7].

The crystallinity of the samples was determined using DSC scanning from 0 to 200 °C at 10 °C/minute. We assumed that the enthalpic change at melting is 93 J/g[8].

RESULTS AND DISCUSSION

Drawing PLA films has a dramatic effect on its morphology due to the fact that PLA quiescently crystallizes very slowly (cast films are most often amorphous) but stain-induce crystallizes (SIC) very effectively[7]. Figure 1 gives a force-displacement plot for a 1.4%D PLA film which was uniaxially drawn at 100%/second as a function of temperature. The plot shows that PLA strain-hardens very effectively above a draw ratio of 3.5 at 80°C. This plot defines the processing window for PLA films as being between 75 and 90°C. Below 75°C, the film is too stiff to process and above 90°C, almost no strain hardening is observed. Strain

hardening occurs under these draw rates at a draw ratio of 3.5 to 4. Below this draw ratio, the films possess little crystallinity whereas above this draw ratio, they are quite crystalline.

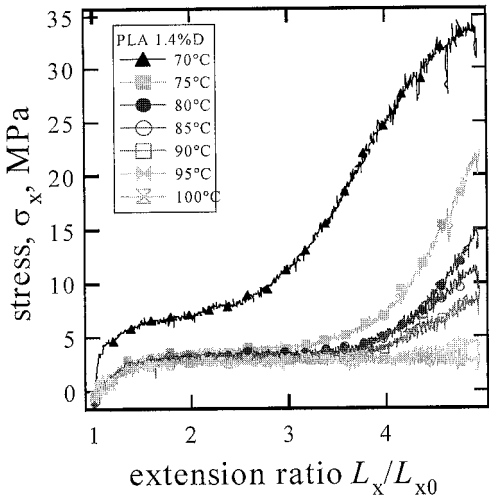

Figure 1 1.4%D PLA Uniaxial draws Vs temperature, 100%/sec

The effect of D-level of the PLA on strain hardening is given in Figure 2. This plot shows that there is a strong dependence of strain hardening on D-level. Above about 4.5%D, PLA does not strain harden significantly under these conditions of temperature and draw rate. This is strong evidence that strain hardening is due primarily to SIC rather than solely on chain entanglements. A plot of the level of crystallinity measured in 1.4% D PLA films, expressed as Joules/gram by DSC, is given in Table 1. Table 2 gives the same data for the 4.2%D PLA material. These data show that the level of crystallinity is less than 20 J/g for draw ratios below 3. Above a draw ratio of 3, the level of SIC grows to nearly 50 J/g.

Table 1 also gives the level of shrinkage as a function of draw ratio for 1.4%D PLA Drawn at 80 C at 100%/Sec. The shrinkage increases with increasing draw ratio for all conditions of draw except for uniaxial draws. The shrinkage actually goes through a local maximum at a draw ratio of 2X and then decreases at higher draws. Above 3X the shrinkage increases again but never to the extent as for biaxial draws. This behavior is not observed for PLA materials that cannot crystallize and it is our belief that it is due to the effect of crystallinity which stiffens the material and inhibits its relaxation (shrinkage)[7].

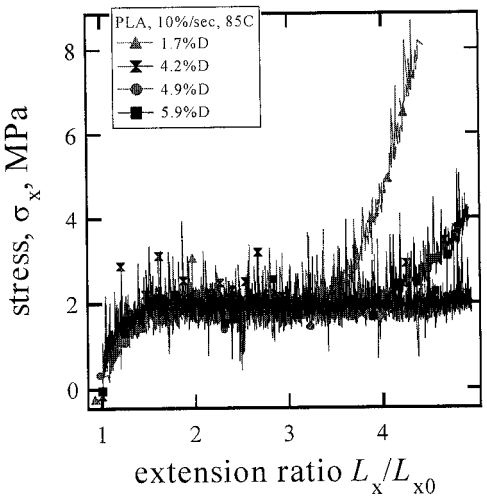

Figure 2 Strain-hardening vs D-level for uniaxial draws at 85°C

Table 1 Shrink, crystallinity (J/g), dichroic ratio and line width (cm^{-1}) of the 410 cm^{-1} band as a function of draw for the 1.4%D PLA films drawn at 80 °C at 100%/sec.

Draw Ratio	Crystallinity (J/g)	Dichroic Ratio	FWHH	Band Shift	% Shrink
1X	0	1.0	22.5		0
2X	15	1.1	22.3	16.6	25
3X	41	2.2	13.9	13.8	0
4X	42	2.4	13.8	13.4	15
5X	42	2.7	14	12.9	5
2X2	32	.9	22	16.6	18
2X3	36	1.8	17.1	14.4	3
2X4	33	2.0	15.4	13.4	20
2X5	36	1.9	15.4	12.8	25
3X3	30	1.1	18.5	13.8	50
3X4	30	1.2	18.2	13.2	58
3X5	31	1.6	18.9	13.6	70
4X4	24	1.1	19.4	13.6	75

Table 2 Shrink, crystallinity (J/g), dichroic ratio and line width (cm^{-1}) of the 410 cm^{-1} band as a function of draw for the 4.1%D PLA films drawn at 80 °C at 100%/sec.

Draw Ratio	Crystallinity (J/g)	Dichroic Ratio	FWHH	Band Shift	%Shrink
1X	0	1.1	23	17.2	0
2X	0	1.1	23	16.8	45
3X	28	2.1	15	13.9	5
4X	31	2.4	15	13.5	18
5X	30	2.9	15	13.2	30
2X2	0	1.0	23	17.1	38
2X3	26	1.7	19	14.1	25
2X4	24	1.6	17	13.8	50
2X5	24	2.2	16	13.2	55
3X3	17	1.2	19	14.2	68
3X4	17	1.2	20	13.7	60
4X4	12	1.0	19	14.0	75

The Raman spectrum of an unoriented 4.1%D PLA is given in Figure 3. This 254 μm (10 mil) cast film shrank less than 5% using a 100°C hot oil shrinkage test. Many intense features are observed in the Raman spectrum whose assignments have been discussed previously[4, 5, 8, 9]. When the sample is uniaxially drawn 4X at 80 °C, the polarized scattering obtained along two directions (MD and TD) is shown in Figure 4. In this case, polarized and depolarized spectra differ considerably with most dramatic differences observed in the 400 and 300 cm^{-1} regions. These differences may be attributed to changes in both segmental orientation and chain conformation. Of particular interest for this analysis were those bands between 415 and 398 cm^{-1} which were assigned to an in plane bending vibration about the carbon, carbon, and oxygen backbone. The band at 873 cm^{-1} was assigned to a stretch of the carbon, carbonyl bond.

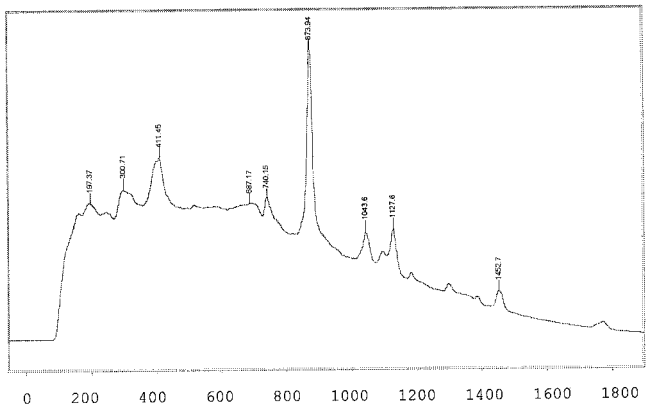

Figure 3 The Raman spectrum of a 4.1%D PLA unoriented cast film

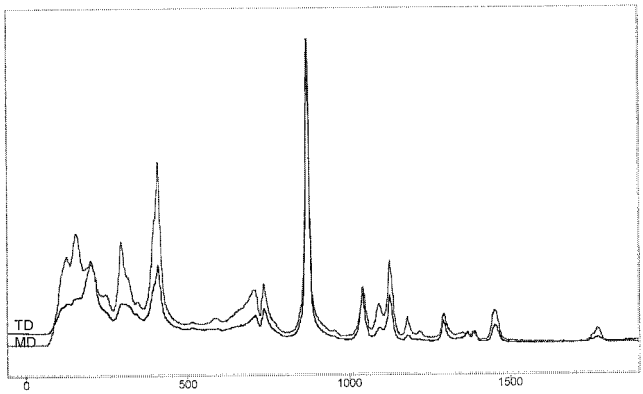

Figure 4 The Raman spectrum of a 4.1%D PLA, uniaxially drawn 4X at 80°C, MD (bottom), TD (middle).

Drawing the films caused two dramatic morphological changes in the sample. The level of crystallinity increased dramatically, as discussed previously, and the material became

oriented. Both effects had significant effects on the Raman spectra[7]. From relative Raman intensity normalized to the 873 cm^{-1} band, it was shown that certain bands changed markedly as a function of drawing to different draw ratios. The bands at 297 and 410 cm^{-1} were strongly affected whereas those at 315 and 397 cm^{-1} were not. Several bands have been analyzed in this fashion. The bands at 397 and 410 cm^{-1} were chosen for this analysis due to their extreme sensitivity to sample crystallinity and orientation with high selectivity and sensitivity. The difficulty in analyzing the spectral changes is decoupling the effects of crystallinity and orientation. One way to decouple the two phenomena is by rotating the sample in the Raman beam fast relative to the acquisition time. Figure 5 gives the Raman spectra of the 4.1%D sample drawn 4X uniaxially at 80°C, taken by rotating the sample in the beam. Thus if the band intensities are plotted as a function of crystallinity for samples rotated in the beam in this fashion to remove the effects of orientation, then the bands that increase in intensity with increasing crystallinity can be unambiguously assigned to the crystalline phase. This plot is given in Figure 6, indicating that the band at 410 cm^{-1} is a crystalline band and that at 397 cm^{-1} is primarily due to amorphous phase contributions. (In fact, recent modeling has shown that the 397 cm^{-1} band has a small contribution from a crystalline E-mode band but is primarily due to an amorphous A-mode band[9].) Thus, these band assignments provide a handle for identifying orientation in both phases.

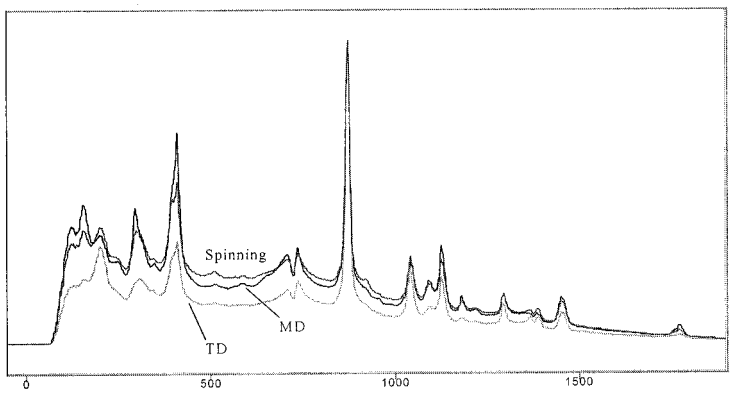

Figure 5 The Raman spectra taken by physically rotating the 4.1%D PLA film, drawn 4X uniaxial at 80 °C, spinning , and non-spinning, TD and MD

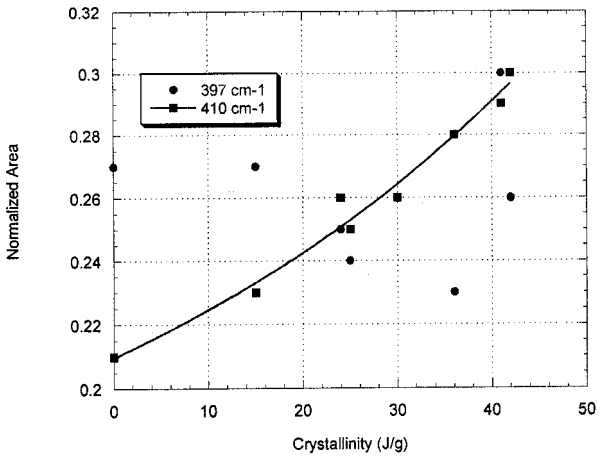

Figure 6 The normalized Raman areas of a 1.4%D PLA versus crystallinity, samples were Spun to remove orientation effects

Effects of Uniaxial Orientation on the Raman Spectrum

Polarized Raman spectra of 4.1%D PLA, 4X uniaxially drawn at 80 °C and obtained with polarization parallel to the MD, TD are shown in Figure 4. The significant differences in band intensities indicate that the spectrum is sensitive to orientation. In order to establish segmental orientation in a quantitative fashion, even lower moments, P_2 and P_4, of the orientation distribution function require detailed analysis by a number of techniques. Simpler analysis can be carried out if the entire scattering tensor is not considered. For the localized skeletal deformation vibrations being considered, a dominant scattering polarizability element may exist. Relative to the polarization of the incident electric field, the scattered intensity may be very strong when a bond is parallel to it. Conversely, the scattered intensity (polarized component) may be much smaller and weaker when a bond is perpendicular to it (depolarized component)[9]. Although, strictly speaking, the entire scattering polarizability tensor should be considered in the analysis of Raman intensity, if the terms along the bonds dominate, the relative scattered intensity may then be used quite similar to the dichroic ratio

generally used in infrared absorption spectroscopy. In our experiments, the convention employed is for the polarization of incident radiation to be along the machine direction.

As mentioned above, the 400 cm^{-1} region contains multiplets with components easily observed at 412 cm^{-1} and 397 cm^{-1}. Using band deconvolution techniques for both polarized and depolarized Raman scattering, it is possible to obtain both the most probable frequency and relative intensity. The relative scattered intensity for the 397 and 410 cm^{-1} bands increases from draw ratios of 1 to 4. The Raman shifts of these bands were also observed to change with draw ratio. The difference between the shifts of the bands decreased markedly, going from about 17 cm^{-1} in the undrawn samples to about 14 cm^{-1} in the 4X drawn films. Both bands changed frequency, the 410 cm^{-1} band decreasing in frequency and the 397 cm^{-1} band increasing in frequency. The spectra of the 4.1%D PLA uniaxial films is given in Figure 7, showing the changes which occur in the region of the spectrum from 450 to 360 cm^{-1} upon drawing. Both the apparent frequency shift and change in relative scattering for the 1.4 and 4.1%D samples are summarized in Tables 1 and 2. The higher frequency component near 410 cm^{-1} and the lower frequency component at 397 cm^{-1} were used to characterize orientation in the crystalline and amorphous component, respectively.

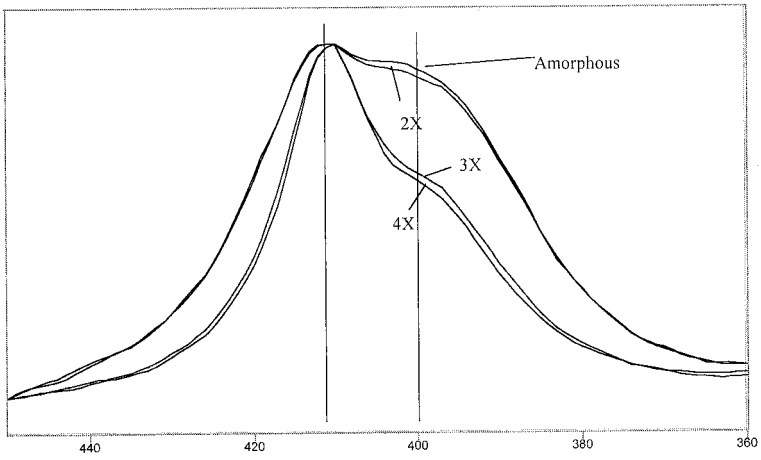

Figure 7 The Raman spectra of 4.1%D uniaxial PLA Film Drawn at 80°C as a Function of Draw Ratio

Effects of Biaxial Orientation on the Raman Spectrum

Films were also drawn in the simultaneous biaxial mode using the Iwamoto film stretcher. The draw ratios ranged from 1X1 to 4X4 and greater in some cases (see Tables 1 and 2). For biaxially drawn films, the relative scattered intensity and shift in band frequency in the 400 cm^{-1} region were determined. Tables 1 and 2 give the relative scattering intensities in the MD/TD (dihroic ratio) for the 1.4 and 4.1%D PLA samples. As expected, the asymmetry is high when the film is uniaxially drawn and diminishes when it is biaxially drawn. When symmetrically biaxially drawn, the relative scattering is low because the orientation in the MD and TD is, as expected, the same. Therefore, it is impossible to use Raman scattering intensity ratios to determine orientation for symmetrically drawn biaxial films. (The same holds true for all spectroscopic measures of dichroic ratio.) The data of Tables 1 and 2 show a minimum in the dichroic ratio for symmetric draws with maxima at the extremes of uniaxial draw. Most commercial applications employ biaxial or even more complex drawing geometries.

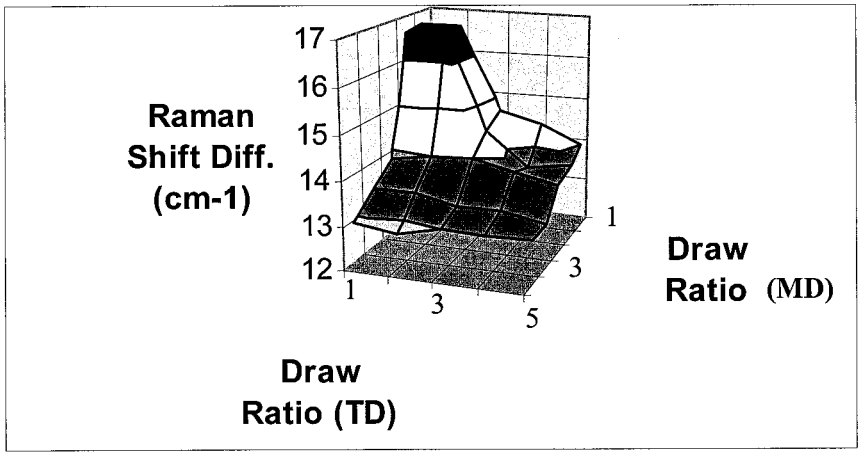

Figure 8 The Raman shift difference (cm^{-1}) as a function of draw ratio for 1.4%D PLA simultaneous draws at 80 °C and 100%/Sec

The frequency shift as a function of deformation, shown in Figure 8, can be correlated to the degree of orientation for uniaxially deformed films and also for symmetrically drawn biaxially deformed films. Since the Raman shift is independent of orientation, it does not suffer from the inability for the Raman technique employing a polarized electromagnetic wave (a vector quantity) to measure orientation in symmetrically oriented films. It should also be emphasized that a symmetrically deformed film does not imply symmetric orientation. Therefore, the plot of Raman shift versus draw can be used to determine the relative level of orientation for any type of biaxially drawn film. This observation allows orientation to be determined for most commercially interesting oriented films, namely biaxially oriented films, using a relatively simple Raman measurement.

For a semicrystalline sample, an amorphous phase always coexists with a crystalline phase. The structure of disordered chains encompasses a broad distribution of chain conformation. In contrast, the chain conformation of the crystalline state is dominated by one state. Therefore, the Raman active mode of the crystalline state is well defined and located at one specific position. For disordered chains, vibrational transitions usually have broad bandwidth and may not have a definite position. For drawn samples, strain-induced crystallization occurs and shifts the ensemble of chain conformations from random to one containing a higher number of well defined crystalline states which thus reduces the relative band position of the crystalline and amorphous components as seen in Figure 8.

It has been demonstrated that 397 and 412 cm^{-1} bands, in fact belong to different vibrational species[9]. The poly(lactic acid) exists in a 3/1 helix structure in the crystalline phase. Factor group analysis shows there are 25 symmetrical A modes and 26 doubly degenerate E modes. The 412 cm^{-1} band is an A mode and the 397 band is an E mode. We should emphasize that disordered chains exist in the 400 cm^{-1} region as well. For the spectra collected in the MD direction, the A mode is dominant while the E mode is dominant in the TD direction. When a sample is drawn, more molecules orient in the MD direction giving rise to more A mode (412 cm^{-1} band) and less E mode (397 cm^{-1}) character. This can explain why the relative scattering intensity increases with drawing ratio.

Films of 1.4 and 4.2%D were drawn under the conditions given above and the level of crystallinity was determined by DSC. The line width of the Raman spectra of these samples was observed to be strongly dependent on the level of crystallinity as given in Figure 9.

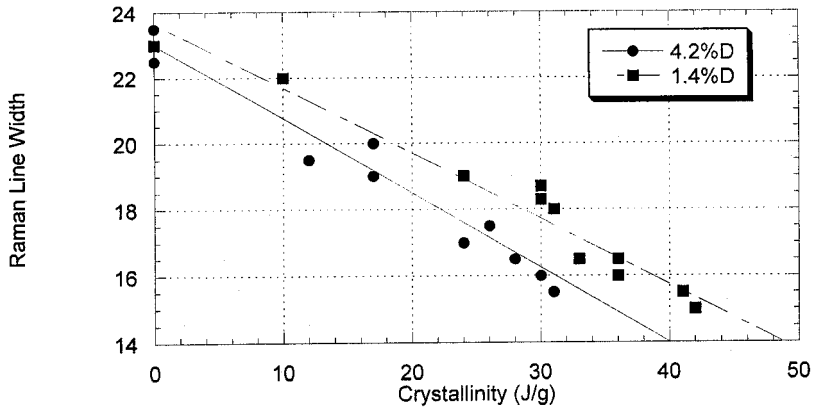

Figure 9 Raman line widths of the 412 cm^{-1} band versus crystallinity for 1.4 and 4.2%D PLA films drawn at 80°C at 100%/Sec

CONCLUSIONS

A Raman method is presented by which the relative orientation of PLA films can be determined. Correlations were developed between draw conditions, Raman dichroism and band shifts. Since correlations between films drawn in this manner and shrinkage are also known, the level of relative orientation and crystallinity can be used to predict film shrinkage. The origin of the Raman shifts will be modeled in a separate work. The expected outcome of these studies is a definition of the transition moment for the vibration and a dependence of the absolute orientation function on the observed frequency shifts. With these parameters, an absolute correlation of the orientation function with Raman band shifts and relative intensity can be defined.

Correlations between crystallinity and the Raman band widths were also determined such that crystallinity in PLA can be measured with a precision of ±5 J/g absolute. Therefore, the crystallinity and orientation can be measured from one spectrum making this technique a good candidate for on-line applications.

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