

An Analysis of the Correlation Between Structural Anisotropy and Dimensional Stability for Drawn Poly(lactic acid) Films

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ABSTRACT: The anisotropic structures found in drawn poly(lactic acid) films are strongly correlated to their overall dimensional stability. Several aspects of this relationship can be efficiently characterized by Raman spectroscopy. We determined the degree of orientation in these drawn films by measuring the relative intensity of the polarized and depolarized components and the shift in the relative band positions. The bandwidth and specific band frequency also correlated well with the degree of sample crystallinity. These aspects make the Raman method amenable for the online monitoring of orientation and crystallinity in commercial processes. A molecular understanding of heat setting to reduce film shrinkage is also proposed. Raman data from films that were heat-set while physically constrained suggest that amorphous-phase relaxation does not occur during heat setting. Rather, the level of crystallinity increases substantially, indicating that the cause of low shrinkage in the films was due to crystalline network formation rather than amorphous-phase relaxation. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2497–2505, 2001

Key words: Raman spectroscopy; poly(lactic acid); orientation; biaxial films

INTRODUCTION

Poly(lactic acid), an environmentally degradable polymer, has been used in biomedical applications for over a decade.¹ Because of its ideal combination of attractive physical properties (high modulus, good film-forming properties, good heat-seal characteristics, and barrier to flavor and aroma)

and its competitive cost, it is currently being investigated for a number of commodity applications. In particular, poly(lactic acid) is being evaluated as a film for food packaging applications.² A cast-tenter process most often produces films that have a high degree of orientation and strain-induced crystallinity. Characterization of the orientation, especially the amorphous phase, is necessary because one prominent application for poly(lactic acid) is the use of biaxially oriented films for heat-seal packaging. Shrinkage must be minimized when the film is heat-sealed or the seal will pucker.

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The molecular origin of different shrinkage characteristics obtained for poly(lactic acid) films processed in different ways has not been clearly defined, however. Shrinkage has been shown to be a function of both amorphous-phase orientation and crystallinity for fibers.³ The greater the amorphous-phase orientation is, the greater the stresses are that are causing it to retract at elevated temperatures and, therefore, the more shrinkage there is. Heat sealing is performed between approximately 100 and 130°C, well below the crystalline melting point of poly(lactic acid) but above the glass-transition temperature (T_g). It has been postulated that the residual stresses frozen in the amorphous phase upon the drawing of the film can only relax when the film is again heated above T_g .⁴

To raise the processing efficiency and quality of the films produced, one must carry out online monitoring when poly(lactic acid) films are drawn. One of the most convenient methods for carrying out such online monitoring is Raman spectroscopy.^{5–8} The utility of such studies on polymerization,⁹ process control,¹⁰ and crystallization¹¹ has been reported previously. The number of vibrational spectroscopic analyses for poly(lactic acid), particularly Raman scattering, is small. The band assignments and effects of crystallinity on the spectra have been discussed.^{12–14} Orientation behavior based on relative intensity measurements of vibrational transitions has not been discussed, however. Usually, X-ray diffraction, in conjunction with birefringence, is used to determine the orientation function in crystalline and amorphous phases of semicrystalline polymers. The vibrational transitions are typically characteristic of short-range conformational order or disorder of chain segments in both crystalline and amorphous regions. 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 used, making the polarized Raman experiment an attractive technique because of its versatility, convenience, rapidity, and ability to conduct online monitoring.

The difficulty in using Raman spectroscopic measurements for morphological characterization is that absolute intensity measurements are nearly impossible to obtain. The measured intensity can be dependent on the volume fraction of a particular chain conformation, degree of crystallinity, segmental orientation, and sampling geometry. To determine the structural transformation

Table I Compositions of the Resins

D (%)	M_n^a	M_w^a	PDI ^a	Lactide (%)
1.8	94,341	202,980	2.15	0.73
4.1	100,385	211,722	2.11	0.17
7.2	96,181	222,177	2.31	0.11
20.2	113,776	283,787	2.49	1.05
1.4	101,400	204,800	2.02	0.13
4.2	115,100	226,200	1.97	0.16

^a The molecular weights were measured relative to polystyrene standards. M_n = number-average molecular weight; M_w = weight-average molecular weight; PDI = polydispersity index.

of poly(lactic acid) from the initial isotropic sample to either uniaxially or biaxially oriented films, one must identify a band for use as an internal standard for normalization. This band should be insensitive to changes in the degree of crystallinity and segmental orientation. For example, infrared spectra were obtained of oriented poly(ethylene terephthalate) films produced by drawing.¹⁵ A band at 1410 cm^{-1} was used as an internal standard to take into account variations in film thickness and other spectral variations. This band was observed to be insensitive to segmental orientation and crystallinity.

In this study, we carried out polarized Raman scattering from various poly(lactic acids) containing different degrees of configurational and conformational disorder. Films of poly(lactic acid) were drawn under various conditions of temperature and draw ratio, and their Raman spectra were observed in the machine direction (MD), transverse direction (TD), and thickness direction. With polarized Raman scattering data, it was possible to characterize the orientational behavior of both the amorphous and crystalline regions. Our results are reported here.

EXPERIMENTAL

The physical characteristics, including the molecular weight and configuration of the poly(lactic acid) samples studied, are listed in Table I. Films of the first four samples in the table were drawn with a TM long stretcher. Biaxially oriented films (1.4 and 4.2% D content) were drawn simultaneously with an Iwamoto film stretcher that was also capable of providing force–displacement curves. A 60-s heat time was used between the loading and drawing of the film. Films were

stretched between 80 and 85°C and at 100%/s. The draw ratios usually ranged from 1×1 to 4×4 and were greater in some cases. If the films were drawn asymmetrically, the larger draw ratio was in the MD. The starting films were nominally 15 mil (381 μm) in thickness.

Raman spectra were obtained with a Kaiser Raman microscope spectrometer with a 785-nm laser (red) as an excitation source. Multimode fibers were used for both excitation (50- μm core) and collection (100- μm core). Polarizing filters were mounted in the probe head, which allowed the sample to be analyzed with linearly polarized light. With such a device, backscattered radiation was collected with polarization parallel along two orthogonal axes: the MD and TD. The 20 \times magnification objective used could provide a spatial resolution of 20 μm . This was convenient for thin poly(lactic acid) film analysis. Spectra were acquired in 2-min blocks, and two of these spectra were coadded. The low-frequency region (100–1850 cm^{-1}) of the spectrum was exported to GRAMS for subsequent plotting and data analysis.

The crystallinity of the samples was also determined with differential scanning calorimetry (DSC) from 0 to 200°C at 10°C/min. The enthalpic change at melting was 93 J/g.¹⁶

RESULTS AND DISCUSSION

Spectral Behaviors of the Bands in the 400- cm^{-1} Region

Figure 1 presents the overall Raman spectra of an unoriented 4.1% D poly(lactic acid) sample. This

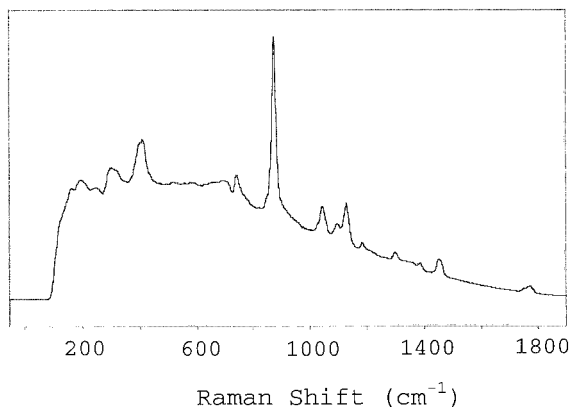


Figure 1 Raman spectrum of a 4.1% D poly(lactic acid) unoriented cast film.

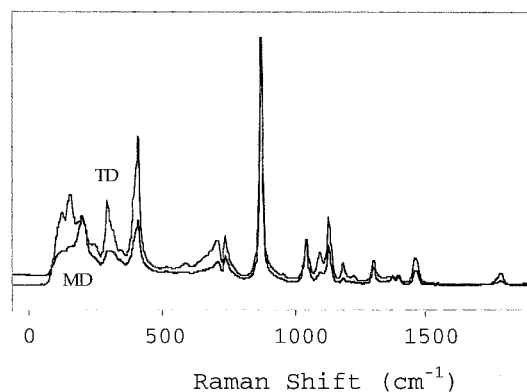


Figure 2 Raman spectrum of a 4.1% D poly(lactic acid) film uniaxially drawn to 4 \times at 80°C.

254- μm (10-mil) cast film shrank less than 5% with a 100°C hot oil shrinkage test. Many intense Raman active features can be observed. When the sample is uniaxially drawn to 4 \times at 80°C, polarized scattering obtained along two directions (MD and TD) is shown (Fig. 2). In this case, polarized and depolarized spectra differ considerably, with the most dramatic differences observed in the 300–400- cm^{-1} region. Of particular interest for this analysis were those bands at 410 and 397 cm^{-1} that were assigned as in-plane bending vibrations along the carbon, carbon, and oxygen backbone.^{13,14,17,18} The band at 873 cm^{-1} was assigned to a stretch of the carbon and carbonyl bond.^{13,14,17,18}

We expect and show later that the degree of crystallinity and segmental orientation in poly(lactic acid) films increase as a function of the draw ratio. A stress-strain curve is given in Figure 3 for a 4.2% D poly(lactic acid) material that was drawn with the Iwamoto film stretcher. The poly(lactic acid) strain hardens above a draw ratio of 3 \times , an effect associated with the crystallization of the polymer. The level of crystallinity increases rapidly with film stretching because strain-induced crystallization is very efficient with poly(lactic acid), even though quiescent (thermal) crystallization is not.³ The observed Raman scattering is sensitive to this change in segmental orientation when films are drawn. The polarized spectra taken with polarization parallel to the incident polarization [along the direction of the uniaxial stretch (MD)] will differ from those taken with polarization perpendicular to the stretch direction (TD), as observed (Fig. 2). In the first case, we have a polarized spectrum; in the second case, we have depolarized scattering.

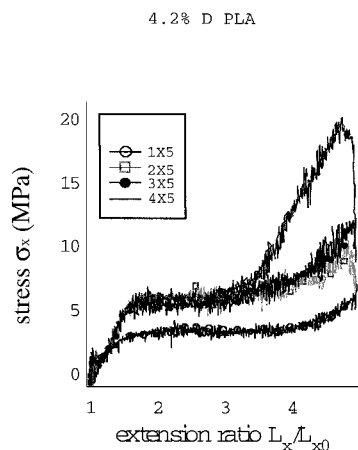


Figure 3 Stress–strain curves for a series of 4.2% D poly(lactic acid) films drawn uniaxially (bottom) and simultaneously biaxially (top three curves) at 80°C.

One of the primary goals of this Raman study is to establish an empirical method to assess the crystallinity increase when films are processed. We intend for this analysis to be based on the frequency, bandwidth, or relative intensity of specific Raman bands observed. The validity of such an analysis must be established beforehand. It is then important to examine samples with the apparent difference in scattered intensity due to orientational difference removed. This can be done in several ways. For example, the polarization of the incident polarization can be scrambled with an appropriate quarter wave plate.¹⁹ A second method is to examine sample films from the edge. Third, it is possible to spin the sample in the beam. The spectra obtained for a film sample spun in the beam are shown in Figure 4. Com-

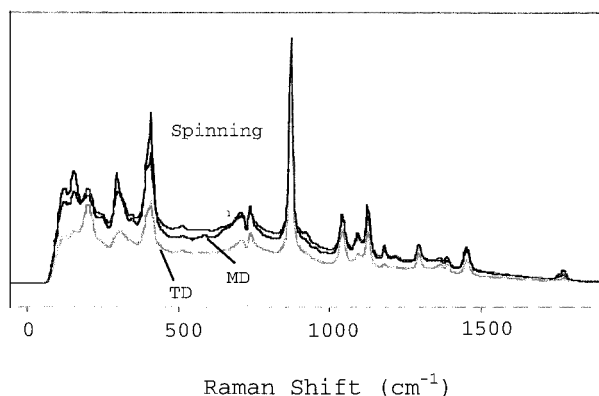


Figure 4 Raman spectra taken by the physical rotation of a 4.1% D poly(lactic acid) film uniaxially drawn to 4× at 80°C spinning and nonspinning (TD and MD).

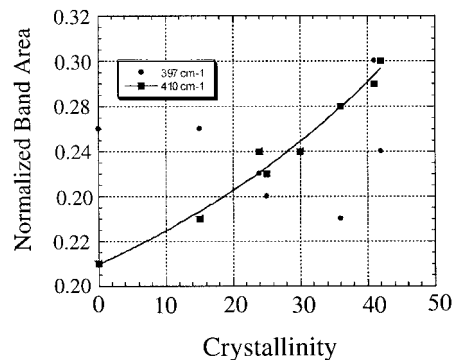


Figure 5 Normalized Raman intensities of 1.4% D poly(lactic acid) versus crystallinity. The samples were spun to remove orientation effects

pared with the other two methods, this technique removes most completely the effects associated with segmental orientation.

It is clear that the bands in the approximately 300 and 400 cm^{-1} are quite complex, containing several components. The low-frequency side of the 300- cm^{-1} band ($\sim 297 \text{ cm}^{-1}$), like the high-frequency side of the 400- cm^{-1} band (the A modes),¹⁸ grows with an increasing draw ratio. When films were drawn to 4×, we found enthalpic changes of 0, 17, and $24 \pm 3 \text{ J/g}$ in the 20, 7.2, and 4.1% D samples, respectively. Therefore, the degree of crystallinity for the two samples increased from 0 to 26% when drawn. The 20% D material did not crystallize. We found that the intensity of the 873- cm^{-1} band was insensitive to sample crystallinity, and it was thus used as an appropriate normalization band. The plot clearly indicates that some bands exhibit sensitivity to changing crystallinity (297- and 410- cm^{-1} bands). Others, such as the one at 315 cm^{-1} , do not. The normalized band intensity for the 315- cm^{-1} band remains nearly constant as a function of crystallinity, suggesting that this band is insensitive to changes in crystallinity or is related to the amorphous phase.

Examples of such changes are shown in Figure 5. In this case, the correlation between band intensity and crystallinity for the 4.1% D sample is shown. The level of crystallinity was determined from thermal measurements to be 6, 29, and 24 J/g for the 2×, 3×, and 4× films, respectively. The spectroscopic data show the same trend of increasing crystallinity when these films are drawn. The bands at 297 and 410 cm^{-1} are strongly affected, whereas those at 315 and 397 cm^{-1} are not. A plot of the 410- and 397- cm^{-1} -band inten-

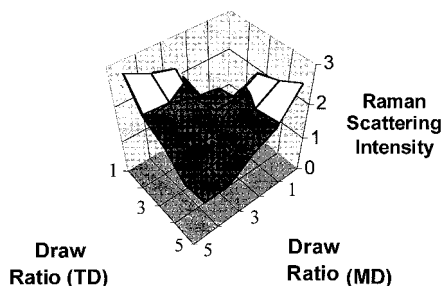


Figure 6 Relative Raman scattered intensities as a function of the draw ratio for 1.4% D poly(lactic acid) simultaneously drawn at 80°C and 100%/s.

sities (normalized to 873 cm^{-1}) versus the sample crystallinity is given in Figure 6. These data lead to the same and consistent conclusion that the 410- cm^{-1} band is due to the molecular structure present in the crystalline phase only, but the lower frequency component is not. Several other bands were also analyzed in this fashion. The band at 410 cm^{-1} was chosen for our analysis because of its high sensitivity to sample crystallinity.

Structural Anisotropy and Characteristic Bands

As shown in Figure 2, the two polarized Raman spectra obtained for the uniaxially drawn film differ considerably. To approximate the degree of orientation in poly(lactic acid) films drawn to different draw ratios, we want to take advantage of the dramatically different scattered intensities. This is especially important when online monitoring is required. Generally speaking, we need a combination of a number of different techniques to obtain a quantitative description of the segmental orientation distribution function.^{20,21} For Raman spectroscopy, even the quantification of the lower moments, P_2 and P_4 , in the distribution function^{22,23} require the analysis of the entire scattering tensor.^{20,21,24,25} Simpler analyses can be carried out, however.²⁶ 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).²⁶ Strictly speaking, we should consider the entire scattering polarizability tensor in the analysis of

Raman intensity. However, if the term along the bond dominates, the relative scattered intensity may then be used quite similarly to the dichroic ratio generally used in infrared absorption spectroscopy.²⁶ The relative scattering intensities are shown in Figure 6.

As mentioned previously, the 400- cm^{-1} region contains multiplets, with crystalline and mainly amorphous components located at 410 and 397 cm^{-1} , respectively. After resolving the bands in both polarized and depolarized spectra, we can then obtain the most probable frequency and relative intensity. The relative scattered intensity for the 410- and 397- cm^{-1} bands increased as a function of the draw ratio from 1 to 4. The frequency of these bands was also observed to change with an increasing draw ratio. The difference between the bands decreased, going from about 17 cm^{-1} in the undrawn samples to about 14 cm^{-1} in the 4 \times drawn films. Both the apparent frequency shift and change in relative scattering for the 1.4, 4.1, 7.2, and 20% D samples are summarized in Table II. The 3–4- cm^{-1} shifts observed are considerably larger than the precision of the measurement, conservatively estimated to be 0.3 cm^{-1} . This means that the measured intensity ratio and the Raman shifts can both be used to assess the degree of film orientation. This is shown in Figure 7 for a poly(lactic acid) containing 1.4% D isomer, drawn at 80°C and 100%/s. The use of the relative Raman shift versus the draw ratio is particularly interesting. This observation allows orientation to be determined for most commercially interesting oriented films, that is, truly biaxially oriented films, with a relatively simple Raman measurement.

These two empirical methods deserve some additional comments. Raman spectra of the 20% D films displayed no intensity difference or frequency change (Table II). This sample did not crystallize and could not be oriented under our experimental conditions. Another article of ours demonstrates that in fact two optically active species exist in this region.^{17,18} The poly(lactic acid) exists in a 3/1 helix structure (sequences of *gt* conformers) in the crystalline phase. Factor group analysis shows there are 25 symmetrical A modes and 26 doubly degenerate E modes. The higher frequency component generally seen at 410 cm^{-1} is an A mode. The E mode exists near the 397- cm^{-1} position. Because of its extremely favorable potential energy, the *gt* sequence is the dominant term in the ensemble of chain conformations, even when long-range order is missing, such as in

Table II Relative Intensity Measured for Polarized and Depolarized Scattered Radiation and Frequency Differences between the Crystalline and Amorphous Components of the 400-cm^{-1} Band versus the Draw Ratio for Uniaxial Poly(lactic acid) Films Drawn at 80°C

	Draw Ratio			
	1	2	3	4
1.4% D poly(lactic acid)				
Intensity ratio crystalline	0.9	1.1	2.2	2.4
Intensity ratio amorphous	1.0	1.0	1.9	2.5
Frequency shift (cm^{-1})	16.5	16.7	13.8	13.4
4.1% D poly(lactic acid)				
Intensity ratio crystalline	1.0	1.0	1.28	2.4
Intensity ratio amorphous	1.0	1.05	1.09	1.9
Frequency shift (cm^{-1})	16.6	16.8	14.3	13.8
7.0% D poly(lactic acid)				
Intensity ratio crystalline	1.0	1.0	2.56	3.00
Intensity ratio amorphous	1.0	1.1	1.75	1.61
Frequency shift (cm^{-1})		17.1	13.7	13.6
20% D poly(lactic acid)				
Intensity ratio crystalline		1.0	1.0	0.9
Intensity ratio amorphous		1.04	1.1	1.04
Frequency shift (cm^{-1})		20	20	19.9

the amorphous (disordered) state. Therefore, polarized and depolarized components remain different even for completely disordered chain conformation distribution. We should emphasize that the band of disordered chains containing all possible chain distributions is centered around the 400-cm^{-1} region as well. For the spectra collected in the MD direction, the A mode is dominant, whereas the E mode is strong in the TD direction. When a sample is drawn, more molecules orient in the MD direction. More A-mode (410-cm^{-1}) and less E-mode (397-cm^{-1}) bands will appear. This explains why the relative scattering intensity increases with the draw ratio for the noncrystallizable sample.

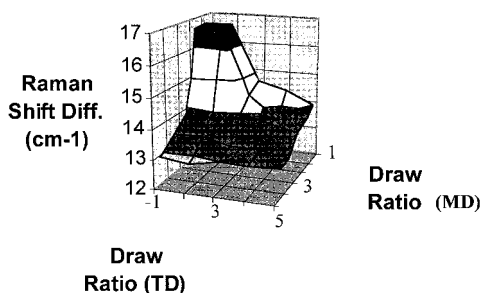


Figure 7 Raman shift difference (cm^{-1}) as a function of the draw ratio for 1.4% D poly(lactic acid) simultaneously drawn at 80°C and $100\%/s$.

For a semicrystalline sample, an amorphous phase always coexists with a crystalline phase. The structure of disordered chains encompasses a broad distribution of chain conformations. In contrast, the chain conformation of the crystalline state is dominated by one state. Therefore, the Raman active modes of the crystalline state are well defined and located at a specific position. For disordered chains, vibrational transitions usually have a broad bandwidth and may not have a specific position. The level of crystallinity increases as poly(lactic acid) is drawn, shifting the ensemble of chain conformations from one based on the relative probability of occurrence²⁷ to one containing only a well-defined crystalline state, resulting in a reduction of the frequency difference between the 410- and 397-cm^{-1} components. Films of poly(lactic acid) containing 1.4 and 4.2% D were drawn under the conditions given previously, and the level of crystallinity was determined by DSC. The line width of the Raman spectra of these samples was strongly dependent on the level of crystallinity, as given in Figure 8.

Characteristics of Biaxial Orientation

As mentioned previously, films were also drawn in the simultaneous biaxial mode with the

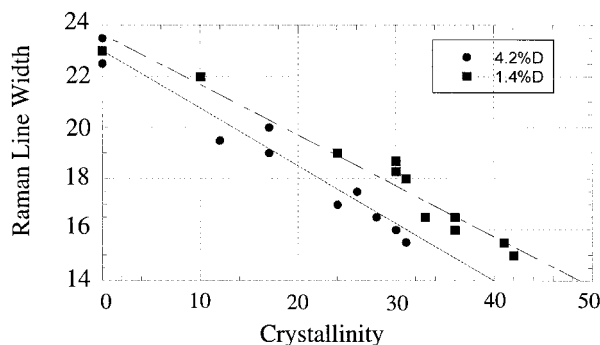


Figure 8 Raman line widths of the 412-cm^{-1} band versus crystallinity for 1.4 and 4.2% D poly(lactic acid) films drawn at 80°C at $100\%/s$.

Iwamoto film stretcher. The draw ratios ranged from 1×1 to 4×4 and were greater in some cases. For biaxially drawn films, the relative scattered intensity and shift in band frequency in the 400-cm^{-1} region were determined and are plotted in Figures 6 (relative scattered intensities) and 7 (Raman shift). As expected, the asymmetry is high when the film is uniaxially drawn and diminishes when it is biaxially drawn. The plot in Figure 6 shows a trough going through the middle (symmetrically drawn films), with maxima at the extremes associated with uniaxially drawn films. For symmetrically biaxially drawn samples, the relative scattering is low because the orientation in the MD and TD is, as expected, mostly the same. Therefore, it is impossible to use Raman scattering intensity ratios to determine orientation for symmetrically drawn biaxial films. However, just because draw ratios along the MD and TD directions are the same, this does not mean that the degree of orientation achieved is identical. Our method provides an empirical way to evaluate the degree of anisotropy in films quickly during processing.

The frequency shift as a function of deformation, shown in Figure 7, can also be correlated to the degree of orientation for uniaxially deformed films and also for symmetrically drawn biaxially deformed films. Because the Raman shift is independent of orientation, it does not suffer from the inability of the Raman technique, employing a polarized electromagnetic wave (a vector quantity) to measure orientation in symmetrically oriented films. It again should also be emphasized that a symmetrically deformed film does not always imply symmetric orientation. Therefore, a plot of the Raman shift versus draw can be used to determine the relative level of orientation for

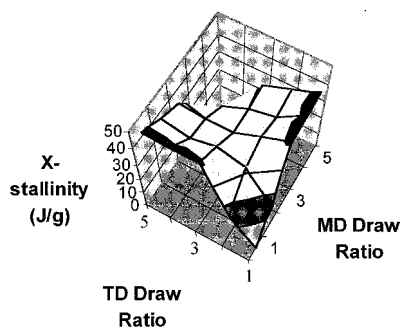


Figure 9 Level of crystallinity as a function of the draw ratio for 1.4% D poly(lactic acid) drawn at 80°C at $100\%/s$.

any type of biaxially drawn film. This observation allows orientation to be determined for most commercially interesting oriented films, that is, biaxially oriented films, with a relatively simple Raman measurement.

Crystallinity and Shrinkage of the Films

The degree of crystallinity produced in poly(lactic acid) films is strongly dependent on the drawing conditions. Figure 9 shows the degree of crystallinity as a function of the drawing conditions at 80°C for 1.4% D poly(lactic acid). The plot shows that the conditions used in uniaxial draws promote higher levels of crystallinity than those of biaxial draws. The same trends are also observed for the 4.2% D sample. Figure 10 shows the shrinkage of the films as a function of the drawing condition. The shrinkage increases as the draw ratio increases, except for uniaxial draws, where it goes through a maximum at a draw ratio of about 2 and then decreases as a crystalline network is established, which reduces shrinkage.³

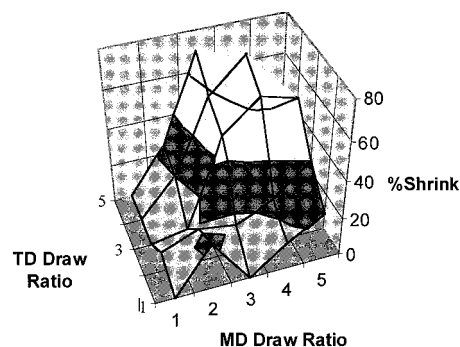


Figure 10 Level of shrinkage as a function of the draw ratio for 1.4% D poly(lactic acid) drawn at 80°C at $100\%/s$.

Table III Raman Band Shifts as a Function of Draw History for 1.4% D Poly(lactic acid)

Draw Conditions	Frequency of 410-cm ⁻¹ Band ^a	Line Width of 410-cm ⁻¹ Band	Frequency of 397-cm ⁻¹ Band ^a
None	413.8	22.5	397.3
2× uniaxial at 80°C	414.2	22.3	397.6
3× uniaxial at 80°C	412.6	13.9	398.8
4× uniaxial at 80°C	412.6	13.8	399.2
5× uniaxial at 80°C	412.4	14	399.5
4 × 4 biaxial at 80°C	412.2	19.4	398.6
4 × 4 biaxial at 85°C	412.4	18.1	398.9
4 × 4 biaxial at 85°C, shrunk	412.0	13.8	397.6

^a The estimated precision of the frequencies is 0.3 cm⁻¹.

This reduction in shrinkage is not as significant for biaxially drawn films.

As described previously, the Raman bands were observed to shift in frequency when poly(lactic acid) was stretched, presumably as a result of a change in the distribution of molecular conformations that occurs when the chains are deformed upon stretching. This orientation of chain segments (stored work) in the film due to stretching will relax when the film is heated above T_g , allowing the film to shrink and release the stored energy. One would expect that the conformational distribution would also relax to a more random state after the film shrinks; therefore, the Raman spectrum of the shrunk film would be expected to be very similar to that of the original, undrawn sample. Table III presents the frequencies of the Raman bands as a function of the draw history for the 1.4% D poly(lactic acid) sample. When the film was drawn to 4 × 4 at 85°C, the two bands, which were previously used to measure the extent of orientation, shifted in frequency as expected. When this sample was heated to 100°C for 20 s, the film shrank by about 50%. The band assigned to the crystalline phase (410 cm⁻¹) increased in intensity and narrowed, suggesting that the level of crystallinity increased. However, it did not change in frequency. The band containing the amorphous phase (397 cm⁻¹) did shift downward in frequency by 1.5 cm⁻¹ to the frequency of the undrawn sample. We postulate that the amorphous-phase conformational distribution did relax back to near its original distribution before drawing, but the crystalline phase did not, as should be. The observations from the Raman spectrum are consistent with this explanation

These films were also heat-set in an alternate fashion, being performed in an apparatus that confined the film such that the film dimension was maintained during heat setting. Films (stretched 4 × 4 at 80°C) that were heat-set at 80°C for 5 s showed 60% shrink (with a 100°C oil bath) subsequent to heat setting, whereas a sample heat-set at 140°C for 5 s possessed 0% shrink after heat setting. The Raman frequencies of these two films were nearly identical, 398.4 and 412.0 cm⁻¹ for the former film and 398.4 and 412.2 cm⁻¹ for the latter. Therefore, it was concluded that when the films were heat-set while constrained, the amorphous phase did not substantially relax. The level of crystallinity rose rapidly, locking in the amorphous-phase orientation, such that it could not relax unless the temperature was sufficiently high to melt this crystalline network. DSC confirmed that the level of crystallinity increased significantly upon heat setting. These observations suggest that low-D poly(lactic acid) will heat-set more easily than high-D samples because it can more efficiently and rapidly establish this crystalline network.

CONCLUSIONS

A Raman technique was employed to characterize structural differences, particularly segmental orientation, in poly(lactic acid) films. A number of spectral parameters were found to be related to the crystallinity of the various deformed films. This development in characterization technique led to better control of the dimensional stability of poly(lactic acid) films.

The method proposed in this study is focused on spectral behaviors of bands around 400 cm^{-1} . Changes were observed in the relative scattering intensity, band shift, and bandwidth. The bands were experimentally determined to be sensitive to the conformational structures. The 410-cm^{-1} band was attributed to the crystalline structure, and the 397-cm^{-1} band was mainly attributed to the amorphous structure. The polarized ratio of the 410-cm^{-1} -band intensities for MD and TD indicates the degree of orientation in both uniaxial and biaxial drawing processes. The band shift of the two bands plays the same role. Correlations between the crystallinity and Raman band widths were also determined, such that the crystallinity in poly(lactic acid) could be measured with an absolute precision of $\pm 5\text{ J/g}$.

Finally, a molecular understanding of heat setting to reduce film shrinkage was proposed. Raman data from the film heat-set while physically constrained suggested that amorphous-phase relaxation did not occur during heat setting. Rather, the level of crystallinity increased substantially, suggesting that the origin of low-shrink films was due to crystalline network formation rather than amorphous-phase relaxation. These observations suggest that low-D isomer poly(lactic acid) compositions will perform best for low-shrinkage applications. The optimal heat-set conditions are those that optimize the rate of crystallinity development.

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