Characterization of the Polylactic acid stretched uniaxial and annealed by Raman spectrometry and Differential scanning calorimetry

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Abstract. In this work, we have been interested in the characterization of the effect of heat treatment and mechanical treatment on the crystallinity of a polylactic acid (PLA) film by two techniques, DSC and Raman spectroscopy. The results obtained by the DSC for the stretched film shows the appearance of a broad peak of crystallization around 120 °C, a rise in melting peak in a significant way, which shows that the uniaxial stretching has increased the crystallinity of the PLA, whereas for the annealed film appearance of a double melting peak. The result obtained by Raman spectroscopy show a new peaks appears at 922 cm⁻¹ and 540 cm⁻¹ after stretching and annealed process, indicating crystallization process.

1 Introduction

The characterization of materials by the Raman technique is based on the measurement of the vibrational states of the molecules or crystals. The use of this technique for the characterization of polymers is of great interest, given the amount of information can be collected such as the chemical composition of the macromolecules of the polymer including the identification of basic unit, the chemical structure, the interactions intra- or intermolecular, chain conformation, crystallinity and orientation of macromolecules. This technique is non-destructive, fast and will require minimal preparation of the sample [1, 2]. On the other hand the Differential scanning calorimeters (DSC) becomes a standard tool in polymer science. This technique takes a particular place among other methods. Additionally to its universal and simple process, the advantage of DSC compared to other calorimetric techniques lies in the broad dynamic range regarding heating and cooling rates, it is an effective analytical tool for characterizing the physical properties of a polymer. It is used to determinate crystallization, melting, enthalpy, entropy changes, and characterization of the glass transition [3].

Poly lactic acid (PLA) is analiphatic polyester, which is biodegradability and biocompatibility; it is derived mainly from agricultural biopolymer resources such as corn and sugarcane [4]. The process technology such as annealing or stretching increases the rate of crystallinity of the PLA [5]. This treatment has an improvement of the mechanical properties. The aim of this work is to study the effect of thermal and mechanical treatments on the structure of PLA and crystallinity using optical and thermal techniques.
2 Experimental

2.1 Material
The polylactic acid (PLA) used in the experimental was supplied by NatureWorks for our laboratory in film form. Figure 1 presents the chemical composition of polylactic acid (PLA) with its different chemical bonds. Chemical composition between two hooks presents the repeated unit of PLA.

![Chemical composition of polylactic acid (PLA).](image)

2.2 Preparation of the annealed sample
The PLA film is cut into pieces and encapsulated in aluminium cup and saddle with a press. Afterward, the sample is put in the oven at 95 °C during 4 hours.

2.3 Instrumentation
The Raman spectroscopy was made using a LabRAM HR Evolution micro-spectrometer (HORIBA). For recording spectra, we used an exciting wavelength (λ = 633 nm) that is provided by a helium-neon laser. All peaks were obtained using an x50 lens.

Differential Scanning Calorimetry (DSC) analysis gives for each sample a thermogram reflecting the variation of heat flux as a function of temperature. The device used for this analysis is a micro calorimeter DSC-7, the system is initially calibrated in temperature and heat output using high-purity Indium and Zinc sample. The baseline is determined with the capsule without sample at the same heating rate as for the analyzed samples. The weight of each sample is 8±0.5 mg. The thermal experiments were performed by heating the samples from 25 to 200°C. The value of the specific fusion enthalpy ΔHf was determined from the area under the peak of the melting curves and the reference enthalpy ΔHf° at 100% crystalline (ΔHf° = 93.1 j/g for the PLA). The degree of crystallinity is given by the following equation:

\[
\text{Crystallinity [%]} = \frac{\Delta H_f - \Delta H_c}{\Delta H_f^0} \times 100
\]

2.4 Mechanical test
The PLA specimens was prepared according to the ASTM D-882, this norm is used to test thinner plastic sheets. It was carried out on specimen 0.39 mm thick and room temperature of 35°C (summer period), with relative humidity of about 50%. The tensile test was performed on an MLS machine with a load capacity of 100KN. The speed of this tensile was 10 mm/min and five specimens were tested, in order to a good reproducitvity of results.
3 Results and discussions

3.1 Raman analysis

The Raman spectra of three PLA films with different states; unstretched film, film undergoes uniaxial stretching and annealed film are shown in figure 3. The Raman active modes obtained for the three spectra are typical of those associated with PLA [6], the observed wavenumbers are given in Table 1, and assignments of vibrational wavenumbers are proposed by comparison with work on other compounds with a helical structure such as polypropylene and poly(α-L-alanine) [8;6]. The Raman bands observed at 3002 cm\(^{-1}\), 2949 cm\(^{-1}\) were assigned to stretching asymmetric and symmetric modes of CH\(_3\), stretching mode of CH bonds was observed at 2882 cm\(^{-1}\) [7]. The symmetric and asymmetric deformation modes of the CH\(_3\) group which were observed at 1386 cm\(^{-1}\) and 1454 cm\(^{-1}\) respectively [10]. The typical carbonyl stretching (C = O) was centred at 1766 cm\(^{-1}\) [8]. In addition, the 1091 cm\(^{-1}\) and 740 cm\(^{-1}\) bands can be assigned to the COC and C = O stretching modes respectively [9-11].

Two other bands appeared around 1130 cm\(^{-1}\) and 1045 cm\(^{-1}\) are assigned to the \(\nu(CH3)\) symmetric rocking and \(\nu C-CH3\) stretching, respectively.

The C—COO stretching of the repeated unit is responsible a very strong Raman band at 873 cm\(^{-1}\) and has been assigned to both semi-crystalline and amorphous states [10]. Another to 713 cm\(^{-1}\) which shows the out-of-plane deformation of the C = O double bond [12]. The weak bands located at 922 cm\(^{-1}\) and 540 cm\(^{-1}\) was observed only in the Raman spectra of stretched film and annealed film are attributed to the swing mode of the CH\(_3\) group and the deformation mode of C-C, and to the $\delta_1$ C-CH\(_3\)+\(\delta\)CCO respectively. The Raman bands 922 cm\(^{-1}\) and 540 cm\(^{-1}\) were associated with crystalline phase corresponding to a helical conformation (α form) by analogy with poly(α-L-alanine)[6].

![Figure 2. Geometry of the tensile test specimen used in this study according to ASTM D882.](image-url)
Figure 3. Raman spectra of PLA, stretched PLA and annealed PLA.

Table 1. Wavenumbers (cm\(^{-1}\)) and Vibrational Assignments of Raman Spectra of the PLA, PLA stretched and annealed PLA in the 4000–400 cm\(^{-1}\) Region

| Wavenumber (cm\(^{-1}\)) | Assignments          |
|--------------------------|-----------------------|
| 3002                     | \(\nu_{as}\) CH\(_3\) |
| 2949                     | \(\nu_s\) CH\(_3\)   |
| 2882                     | \(\nu\) CH            |
| 1766                     | \(\nu\) (C=O)         |
| 1454                     | \(\delta_{as}\) CH\(_3\) |
| 1392                     | \(\delta_s\) CH\(_3\) |
| 1301                     | \(\delta_s\) CH      |
| 1129                     | \(\tau_{as}\) CH\(_3\) |
| 1043                     | \(\nu\) C-CH\(_3\)   |
| 922                      | \(r\text{CH}_3\) + \(\nu\text{CC}\) |
| 873                      | \(\nu\) C- COO        |
| 740                      | \(\delta\) C=O        |
| 713                      | \(\gamma\) C=O        |
| 540                      | \(\delta_1\) C-CH\(_3\) + \(\delta\) CCO |
3.2 DSC analysis

Figure 4 shows the DSC thermograms superposition of three PLA films with different states; unstretched film, film undergoes uniaxial stretching and annealed film. From the results obtained by DSC for unstretched PLA, a clear glass transition at a temperature around 64 °C, a very low melting peak is shown at 154 °C. This result shows the PLA has an amorphous state. After stretching uniaxial, the film exhibits a broad peak of crystallization around 120 °C, and an increase melting peak in a significant way, which shows that the uniaxial stretching has increased the crystallinity. After uniaxial stretching, the movement of the chains is restricted, which can increase the glass transition temperature, which also reflects the rearrangement of macromolecular chains. Knowing that, endothermic melting peak \( T_f \) gives information on the morphology as well as information on the type of crystallization present in the polymer.

The appearance of lower and higher melting peaks at 145 °C and 154 °C respectively for annealed PLA are shown in Figure 4; that can be explained by the existence of two different crystal morphologies [13].

![Figure 4. Superposition DSC thermograms of PLA, stretched PLA and annealed PLA.](image-url)
4 Conclusion
The effect of uni-axial stretching and rubber annealed on the microstructure of PLA was studied by Raman spectroscopy, which allowed us to identify the chemical bonds of the characteristic bands, and to see the influence of uni-axial stretching and rubber annealed on the chemical bonds. Functional groups through the variation of their frequency and intensity and the appearance of new frequencies in the stretched and annealed polymer, this result is verified by scanning differential calorimetry (DSC) indicating the influence of mechanical and thermal treatment on the microstructure of PLA, change of the latter from an amorphous state to semi-crystalline state.

References
[1] Urban Marek W 1996 Attenuated Total Reflectance Spectroscopy of Polymers Theory and Practice. Polymer Surfaces and Interfaces Series Journal of the American Chemical Society 119(45) p 11136
[2] Fontaine N H, Furtak T E 1998 Variable-angle internal-reflection Raman spectroscopy for depth-resolved vibrational characterization of polymer thin films Phys. Rev. B 57 pp 3807-3810
[3] Schick C 2009 Differential scanning calorimetry (DSC) of semicrystalline polymers Anal Bioanal Chem 395 pp 1589-1611
[4] Armentanoun I, Bitinis N, Fortunati E, Mattioli S, Rescignano N, Verdejo R, Lopez-Manchado M A, Kenny J M 2013 PLA multifunctional nanostructure materials for packaging and tissue engineering Progress in Polymer Science 38 pp 1720-1747
[5] Ruijie Xu, Jiayi Xie and Caihong Lei 2017 Influence of melt-draw ratio on the crystalline behaviour of a polylactic acid cast film with a chi structure The Royal Society of Chemistry 7 pp 39914–39921
[6] Kister G, Cassanas G, Vert M, Pauvert B, Terol A 1995 Vibrational analysis of poly( l-lactic acid) J Raman Spectroscopy 11 pp 26-307
[7] Wu Jyh-Horng, Ming-Shien Yen, Wu-Chien-Pang, Chia-Hao Li, Kuo C 2013 Effect of Biaxial Stretching on Thermal Properties, Shrinkage and mechanical properties of Poly (Lactic Acid) Films J. of Polymers and the Environment 21 pp 303-311
[8] Kister G, Cassanas G, Green M 1998 Effects of morphology, conformation, and configuration on IR and Raman spectra of various poly (lactic) acids Polymer 39 pp 267-273
[9] Auras R, Harte B, Selk S 2004 An overview of polylactides as packaging materials Macromol. Biosci. 4 pp 835-864
[10] Herrera K V, Misiu A, Vogt C 2015 Preparation, and characterization of poly (lactic acid) / poly (methyl methacrylate) tablets compressed for application in quantitative analysis by Raman spectroscopy J. Raman Spectrosc. 46 pp 273-279
[11] Arrieta M P, López J, López D, Kenny J M, Peponi L 2015 Development of flexible materials based on plasticized electrostatic mixtures PLA-PHB: structural, thermal, mechanical and disintegration properties Euro. Polym. J. 73 pp 433-446
[12] Sudha Muttavarapu R 2015 Characterization of Cold Drawn Poly L Lactic Acid by Raman Spectroscopy and Raman Hyperspectral Imaging Master of Science in Chemistry for the Department of Chemistry, CLEVELAND STATE UNIVERSITY, May
[13] Radjabian M, Kish M H, Mohammadi N 2010 Characterization of Poly(lactic acid) Multifilament Yarns. I. The Structure and Thermal Behavior Journal of Applied Polymer Science 117 pp 1516-1525