STUDY OF ADHESION PROPERTIES OF DIRECT 3D PRINTING OF POLY(LACTIC ACID) ON COTTON FIBERS

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Abstract – The aim of this work was focused on the direct 3D printing of poly(lactic acid) (PLA) on a cotton textile substrate and the study of the printing parameters that modify their adhesion. PLA samples were printed by using Fused Deposition Modelling technique (bed and nozzle temperatures of 60 and 210 °C, respectively) and two filling printing directions (45° and 180°). PLA and cotton textile substrate were characterized by FTIR, XRD, DSC and TGA. In addition, adhesion was studied by peeling tests. Peeling tests revealed that samples printed with a filling direction of 45° presented a maximum adhesion force and separation energies twice higher than samples printed at 180º. These results could be attributed to a better surface connection between PLA and cotton fibers.

Keywords: *poly(lactic acid) (PLA), cotton fibers, PLA characterization, 3D printing, peeling test.*

Introduction

During last decades, 3D printing has become in an innovative technology in several areas, such as biotechnology, medical devices, and fashion industry, among others. In this sense, the combination of direct 3D printing over textile materials is useful to obtain rigid objects with embedded flexibility as well as soft materials with additional functionality [1-5]. Raw textile materials have a wide range of mechanical properties: they are flexible and may be stretchable, they can be easily folded, twisted or deformed, and tensile strength can be high. On the other hand, 3D printing creates rigid objects which can benefit from the flexibility, stretch ability, and aesthetic qualities found in many textiles [3, 5]. One of the most important aspects to take into account for this kind of application is the adhesion mechanics between printed polymeric objects and the textile surface. In this sense, different breakdown patterns of textile-polymer connection can occur during peeling tests. For example, delamination can occur by polymer-textile separation or by separation between the layers of the polymer print. In addition, it is also important to measure other mechanical properties such as strain strength [2, 3, 6].

Poly(lactic acid), PLA, is a semi-crystalline biodegradable polymer that has an excellent thermoplastic behavior and good processability. PLA has a glass temperature (T_g) at around ~55 °C and a melting temperature range (T_m) between 168-172 °C. In addition, it has as high strain strength and elastic modulus. Therefore, it is in several applications fields such as food packaging, containers, lamination films, and filaments, among others. Mofokeng et al. [8] reported that linear polyesters as PLA have a better adhesion with natural fibers, exhibiting a high quality of printing and good flexural strength [7-10].
In this work, the direct 3D printing of PLA probes on cotton substrate by Fused Deposition Modeling (FDM) technique was studied. PLA filament was chemically characterized by Fourier Transform Infrared Spectroscopy (FTIR-ATR) and X-Ray Diffraction (XRD), while cotton substrate was studied by FTIR-ATR. The thermal transitions of PLA filaments were determined by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). Finally, through peeling tests, the adhesion forces between polymer probes and cotton fibers was evaluated.

Experimental

Materials and methods: Commercial cotton textile and PLA filament (Rojo 3D) with a diameter of 1.75 mm and transparent color were used as received. PLA specimens, with and without textile, were printed on a Pía-Hnos 3D Printer by FDM technique by using the Repetier-Host 0.95F software package and "SketchUp-Maker" free license program. The printing parameters employed are listed as follows: impression nozzle 0.5 mm, layer thickness 0.2 mm, top and bottom solid layer 0 mm and perimeter layer 1 mm, base temperature of 60 °C, nozzle temperature of 210 °C, printing speed 60 mm s-1, and 100% internal filling for two printing directions (45° and 180°).

Fourier transforms infrared spectroscopy (FTIR-ATR). PLA and cotton fibers spectra were essayed on a Nicolet® iS5 spectrometer, equipped with an attenuated total reflectance accessory (iD5-ATR7). Samples were recorded at 4 cm^{-1} resolution, over the 3,500 – 550 cm^{-1} range by using an accumulation of 16 scans. A zinc selenide (ZnSe) internal reflection crystal was used for ATR measurements.

X-ray diffraction (XRD). Crystal structure identification of PLA was determined by XRD. Patterns were obtained in an X-ray diffractometer Philips PW1710 (Philips, Holland), provided with a tube, a copper anode, and a detector operating at 45 kV and 30 mA within 2θ from 5 to 25º.

Differential Scanning Calorimetry (DSC). Thermal transitions of PLA filaments were studied in a Perkin-Elmer® Calorimeter. Samples (10 mg) were measured under nitrogen atmosphere. First heating was performed from -90 to 210 ºC at 10 ºC min^{-1}. Then, samples were kept at 210 ºC during 5 min in order to avoid the influence of the previous thermal history. After cooling at 10 $Cmin^{-1}$, they were heated again from -90 to 210 ºC at 10 º$Cmin^{-1}$. From this second heating process, T_g and T_m were determined.

Thermogravimetric Analysis (TGA). The thermal stability of PLA was analyzed by using Discovery TA Instruments TGA5500® equipment and an oscillatory temperature program. Tests were carried out under nitrogen atmosphere, with a flow rate of 25 mL min^{-1} and 2 °C min^{-1} heating rate, in the 30 - 800 °C range. Mass curves as a function of temperature were registered.

Peeling tests. Adhesion essays were performed according to DIN 53530 by using a Texture Analyzer model TA-XT2i (Stable Micro System) testing device, equipped with a 25 kg load cell. Specimenns of 12.5 mm x 100 mm x 0.3 mm were tested. Two different configurations were studied by printing PLA on the textile surface (woven cotton fabric) at 45° and 180° filling directions. Samples were tested at a constant tensile speed of 5 mm s^{-1}, at room temperature, in order to determine the maximum adhesion forces and separation energies, respectively.

Results and Discussion

Figure 1a shows the FTIR-ATR of PLA and cotton fibers, respectively. FTIR-ATR spectra exhibited the typical absorption bands of these materials, in accordance with those reported by literature [8, 11]. In this sense, PLA absorption bands were detected at 2,993 and 2,853 cm^{-1} (symmetric and asymmetric vibrations of the C-H bond of the CH_3 groups); at 1,750 and 1,180 cm^{-1} (carbonyl and C-O-C stretching peaks, respectively). The band at 1,450 cm^{-1} is attributed to C-H stretching vibration in methyl groups; the band at 1,381 and 1,362 cm^{-1} to the symmetric and asymmetric vibrations of -CH- bending; and the band at 1,080 cm^{-1} corresponds to carbonyl C=O and -OH groups. Finally, two peaks at 868 and 752 cm^{-1} are assigned to the C-C stretching vibration. Cotton substrate shows a typical cellulose-based material spectrum. Between 3,400 and 3,100 cm^{-1} a band associated to O-H cellulose vibration is observed [12]. Besides, the angular deformation of C-H groups at 1,329 cm^{-1} and the angular deformation of C-O bonds of primary alcohols at 1,104 cm^{-1} are also detected. Finally, at 898 cm^{-1}, the glycosidic bonds between glucose units can be observed. Figure 1b shows the X-ray diffraction pattern of PLA., Three peaks associated to orthorhombic semi-crystalline structure of PLA are detected at 2Θ = 16.8°, 19.2° and 22.4° which correspond to the crystalline planes (110/200), (203) and (015), respectively [7].

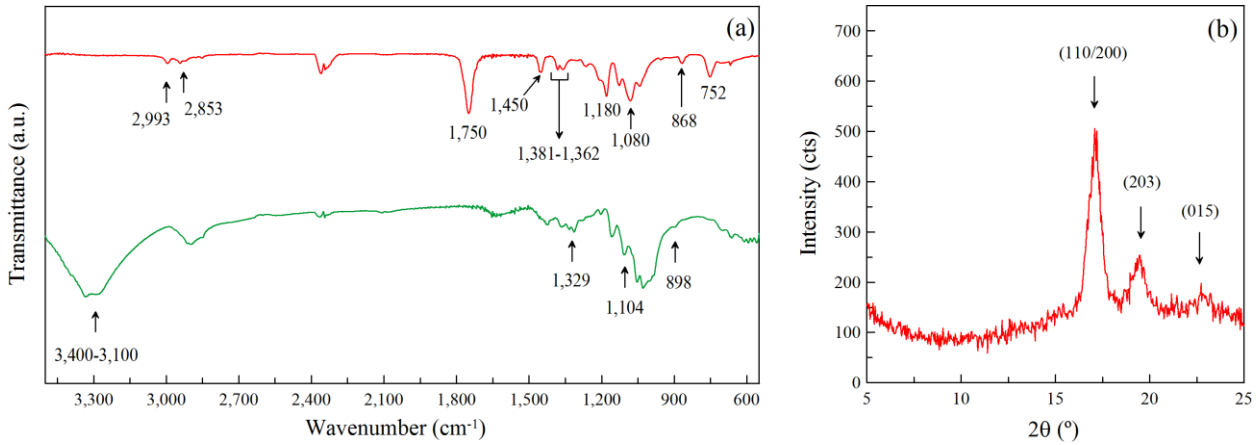

Figure 1. (a): FTIR-ATR spectrum of PLA (red) and cotton textile fibers (green). (b): XRD diffractogram of PLA.

Figure 2 shows the results obtained in the thermal characterization of PLA. By DSC measurements, T_{gPLA} and T_{mPLA} temperatures were determined. The values obtained (close to 65 and 175 ºC, respectively) agree with those reported by literature for commercial PLA [9]. Figure 2b displays the weight mass loss vs temperature and the first derivative curve for PLA filament. As it can be seen, the decomposition of PLA started at 320 °C and is completed at 359 °C. 98% of weight loss was recorded for PLA decomposition. The first derivative dW/dT curve of PLA shows a single peak at 375 °C [13].

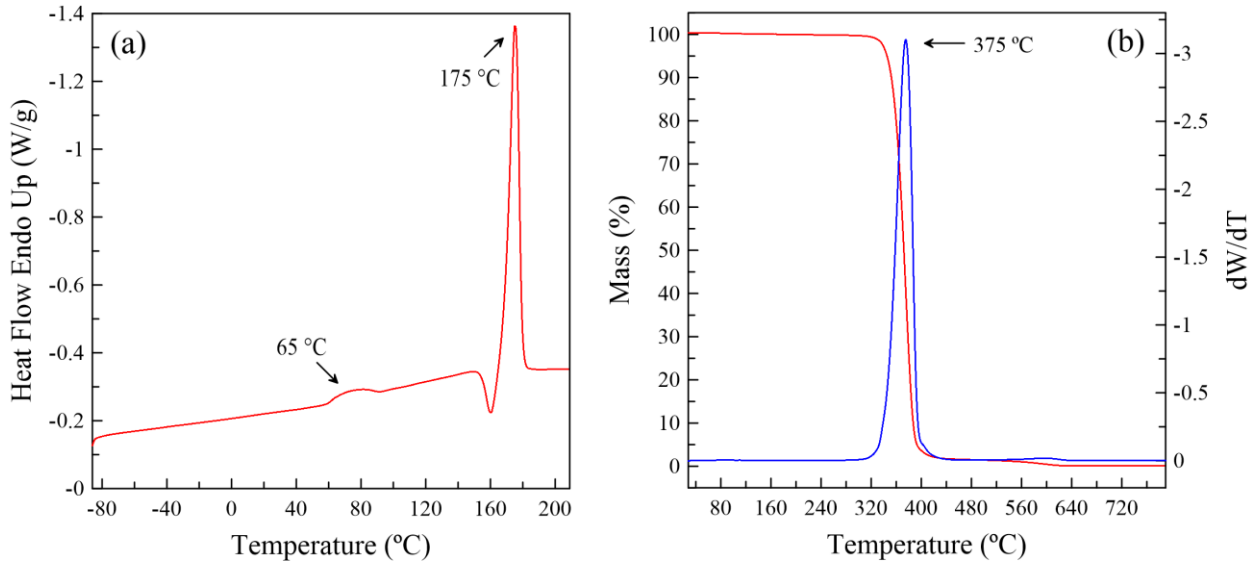

Figure 2. Thermal characterization of PLA, (a): DSC thermogram and (b): TGA curve (red) and first derivative dW/dT curve (blue).

Regarding adhesion tests, force-displacement curves were obtained for PLA and cotton textile fibers in the filling directions of 45° and 180° (Figure 3). At 45°, a significant increased adhesion was found when compared to 180°. The maximum adhesion force and the energy of separation values for these samples are 15.24 ± 3.49 N and 1,954.25 ± 445.52 N mm, while for a filling direction of 180° these values are 6.52 ± 1.09 N, and 1,034.3 ± 196.63 N mm, respectively. The difference could be explained by considering a better-crisscrossed surface connection between the fibers. Fafenrot et al. [3] reported similar results during the study of mechanical properties of composites from textiles and three-dimensional printed materials. Thus, different filling directions resulted in a change of the maximum adhesion force but not in its slope, and a change in the energy that causes adhesive failure and separation between PLA and the textile substrate. It is important to note that the values of maximum adhesion force and energy of separation (obtained from the area under the curve in Figure 3) are an average of several tests performed under the same experimental conditions and parameters.

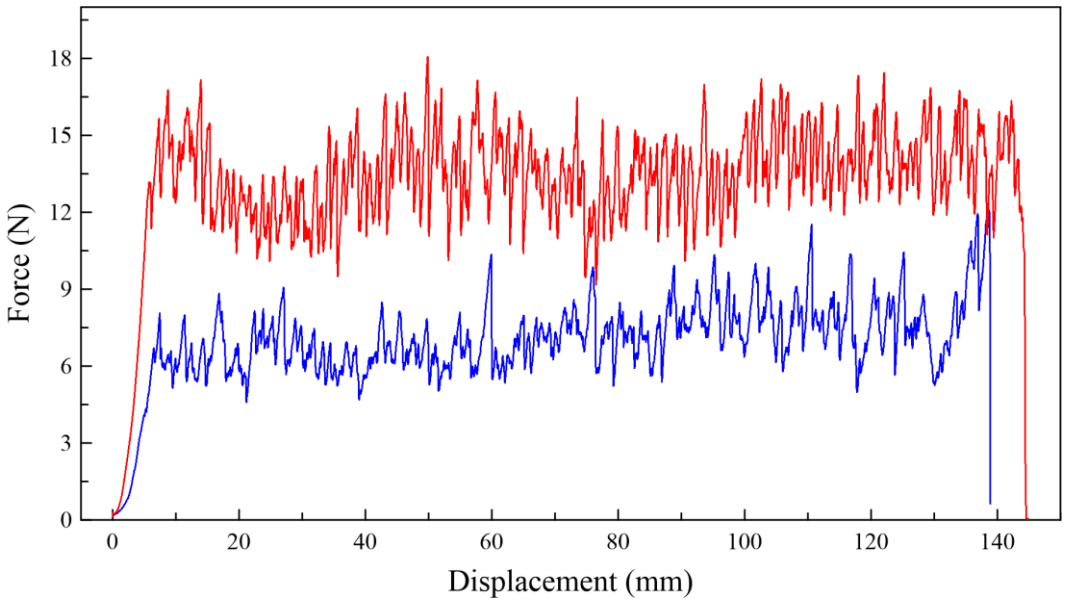

Figure 3. Force-displacement curve from adhesion tests from printing PLA on woven cotton fabric in the filling directions of 45° (red) and 180° (blue).

Conclusions

PLA filaments were characterized by complementary techniques (FTIR, XRD, DSC and TGA) The influence of different filling directions on adhesion tests between a printed probe of PLA and cotton fibers were analyzed. Maximum adhesion force and energy of separation values were obtained for a filling direction of 45°. This result can be explained by taking into account a better-crisscrossed surface connection between PLA and fibers. Values were approximately twice as large for the filling direction of 45° when compared to samples printed at 180°.

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