



PLLA-CELLULOSE NANOCRYSTALS NANOCOMPOSITE PREPARED BY *IN SITU* POLYMERIZATION

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Abstract: This work reports the preparation and characterization of a PLLA-cellulose nanocrystals nanocomposite obtained by in situ polymerization. The nanocomposite was prepared by ring opening polymerization of the lactide dimer in the presence of cellulose nanocrystals (CNCs) and the as-obtained materials was characterized using FTIR, DSC, XRD and TGA measurements. The incorporation of cellulose nanocrystals in PLLA using this method improved the thermal stability and increased the crystallinity of PLLA. These results indicate that the incorporation of CNCs by in situ polymerization improve thermal properties and has potential to improve also mechanical properties of this biodegradable polymer.

Keywords: PLLA, cellulose nanocrystals, bionanocomposites.

Introduction

Bio-based nanocomposites are a relatively new class of materials which have attracted significant attention during the last decade mainly due to ecological and climatic factors. The concept of a bio-based nanocomposite can be stated as a biodegradable or a natural polymer matrix with nanofillers incorporated within them. These materials represent an alternative to the production of new materials which can be used in different areas such as medical, pharmaceutical and packaging [1, 2].

Among biodegradable polymers, the family of polylactides has recently received a great deal of investigation. A polylactide can be obtained from a ring opening polymerization of the lactide dimer, producing poly(lactic acid), PLLA. The resulting plastic can be easily processed by conventional processing techniques and presents mechanical properties that are intermediate between the polyolefins and other biopolymers. However, PLLA can not be used for load bearing applications due to its relatively low mechanical strength. In this way, the preparation of bio-based nanocomposites through the incorporation of nanofillers appears as an alternative to reach some desired properties in the final product.



Cellulose nanocrystals (CNCs) are highly crystalline rod-like nanostructures obtained from a controlled acid hydrolysis of cellulose. The CNCs dispersions obtained using sulfuric acid are stable due to the grafting of sulfate ester groups on the surface of the whiskers, which stabilize the aqueous whisker suspensions by electrostatic repulsion [3,4]. The average CNCs dimensions are 100-250 nm in length and 5-15 nm in diameter for acid-hydrolyzed nanowhiskers obtained from a majority of cellulose fibers. Besides their high aspect ratios, the advantages of using CNCs for the design of new bio-based nanocomposites include their renewability, low density and high specific mechanical properties [3-5].

There are some examples of PLLA/CNCs nanocomposites reported in the literature, using mainly the simple solvent casting method [6] or extrusion [7]. With the aim to obtain a better dispersion of the CNCs in the PLA matrix, we described in this work preliminary results related to an in-situ polymerization of PLLA in the presence of CNCs. The obtained materials were characterized using FTIR, DSC, XRD and TGA measurements. The method used here is different from those described in the literature and can be used as a potential method to achieve well-dispersed CNCs in polylactides.

Experimental

Cellulose Nanowhisker Preparation

Sulfuric acid hydrolysis of eucalyptus wood pulp was performed as described in the literature with minor modifications [3-5]. Briefly, 10.0 g of cellulose wood pulp was added to 160.0 mL of 64 wt% sulfuric acid under strong mechanical stirring. Hydrolysis was performed at 50 °C for about 50 minutes. After hydrolysis, the dispersion was diluted 2-fold in water, and the suspensions were washed using repeated centrifuge cycles. The last washing was conducted using dialysis against deionized water until the dispersion reached pH ~ 6. Afterward, the dispersions were ultrasonicated for about 5 minutes and finally filtered using a 20- μ m pore size filter.

Incorporation of CNCs by in situ Polymerization

The PLLA/CNC nanocomposite was obtained by ring opening polymerization of the lactide dimer in the presence of cellulose nanocrystals using stannous octoate (Sn(Oct)) as catalyst. The



monomer/ catalyst ratio was 5000.

Results and Discussion

Using TEM images (not shown here), the length and diameter of the CNCs were characterized as being 145 ± 25 nm and 6 ± 1.5 nm, respectively.

FTIR analysis was used to evaluate the chemical compositions of the obtained system and the results of the neat CNC, PLLA and PLLA/CNCs are shown in Fig. 1.

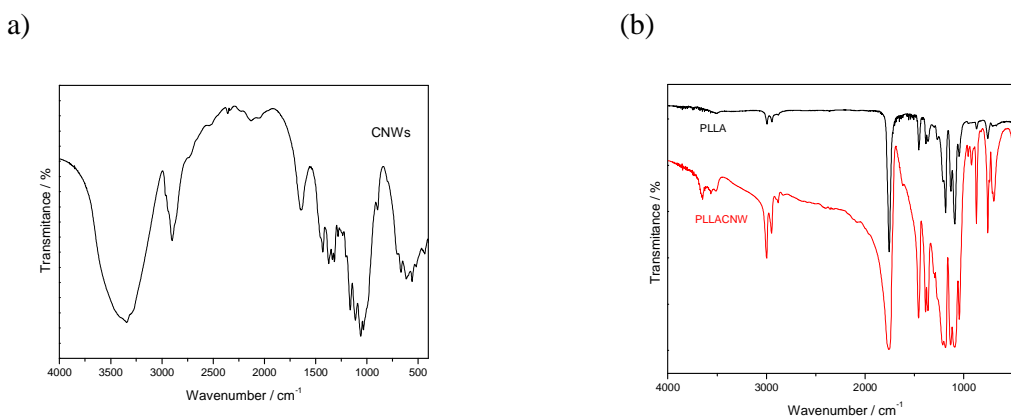


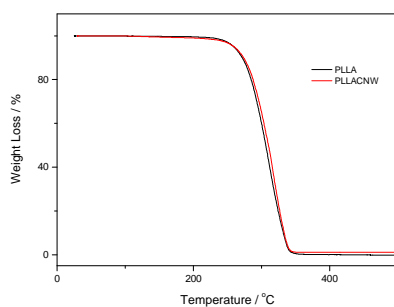
Figure 1. FTIR spectra of (a) CNCs; (b) PLLA e PLLA/CNC.

In the CNCs, the band at 3340 cm^{-1} is attributed to the O-H stretching vibration. The bands at 2893 and 1431 cm^{-1} are characteristic of C-H stretching and bending of $-\text{CH}_2$ groups, respectively, whereas the peaks at 1160 and 1070 cm^{-1} are attributed to the saccharide structure. For the PLLA the main bands are located in: 1756 cm^{-1} corresponds to the C=O stretching, in 1265 cm^{-1} from stretching C-O-C group and in 2994 e 2943 cm^{-1} corresponds to the $-\text{CH}-$ stretching vibration. After in situ incorporation of the CNCs, new absorption bands appears in the spectrum of the PLLA: one band is in the region of $3650\text{--}3500\text{ cm}^{-1}$ belonging to the hydroxyl group of the CNCs; another band at 2885 cm^{-1} is attributed to the C-H stretching of the CNCs and also at 920 cm^{-1} , associated to the out of plane C-H deformation of the nanocrystals.

In order to evaluate the thermal stability of the material synthesized in presence of the CNCs, the neat PLLA and PLLA/CNC were analyzed by Thermogravimetric Analysis. The curves are shown in Fig. 2 and the results are summarized in the Table 1.



(a)



(b)

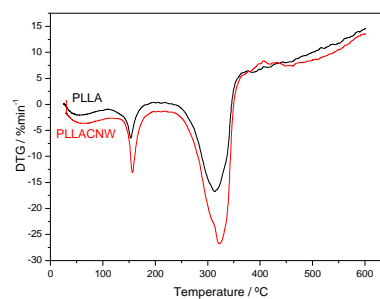


Figure 2. TG curves (a) and DTG curves (b) of pure PLLA and PLLACNW.

Table 1. TGA data (heating rate of $20^{\circ}\text{C min}^{-1}$) of PLLA and PLLA/CNC.

	$T_{\text{begin1}} / ^{\circ}\text{C}$	$T_{\text{end1}} / ^{\circ}\text{C}$	$T_{\text{max1}} / ^{\circ}\text{C}$	$T_{\text{max2}} / ^{\circ}\text{C}$	$T_{\text{begin2}} / ^{\circ}\text{C}$	$T_{\text{end2}} / ^{\circ}\text{C}$
PLLA	106	180	153	313	212	376
PLLACNW	131	199	156	323	232	405

T_{begin} - temperature of the beginning of mass loss; T_{end} - temperature of the end of mass loss; T_{max} - temperature of maximum mass loss; 1 and 2 refer to first and second stage of weight loss, respectively.

PLLA and PLLA/CNCs show two stages of weight loss (Fig. 2b). In both materials, the first is related to the loss of the solvent used in the process of precipitation of the material. The second one is the degradation of matrix PLLA. Thermal decomposition of polylactide involves one stage above 300°C . This event is due to depolymerization catalyzed by tin due to the presence of tin catalyst residue in the PLLA sample. With the presence of the CNC, this event occurred at higher temperatures, revealing that the incorporation of cellulose nanocrystals in PLLA improves the thermal stability of this biopolymer, increasing its maximum temperature of mass loss by approximately 10°C .

The thermal behavior of PLLA and the PLLA/CNC material were also evaluated by DSC. DSC curves are shown in Fig. 3 and the results are summarized in Table 2.

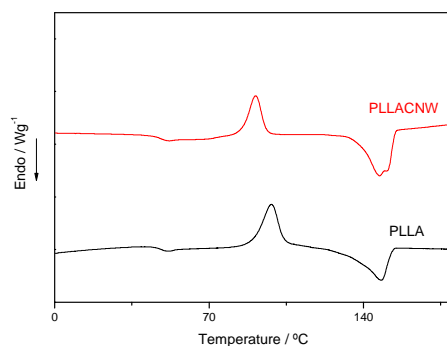


Figure 3. DSC curves of the neat PLLA and PLLA/CNC.

Table 2. Thermal Characteristics of PLLA and PLLA/CNCs.

	$\Delta H_c / Jg^{-1}$	$T_c / ^\circ C$	$\Delta H_m / Jg^{-1}$	$T_m / ^\circ C$	$T_g / ^\circ C$	crystallinity / %
PLLA	-43.4	98.0	36.2	148	46.5	40.0
PLLA/CNC	-28.0	91.0	55.6	147	46.6	60.0

DSC results showed that the T_g values remain almost unmodified for the composite in relation to the neat PLLA. On the other hand, the crystallization peak (around $98^\circ C$) of the composites decreased compared to the neat PLLA. It is an indication that CNC tend to aid the crystallization of the polymer.

XRD patterns of the neat PLLA and the PLLA/CNC are shown in Fig. 4.

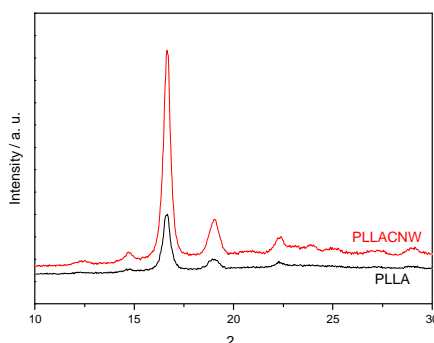


Figure 4. XRD pattern TG curves of pure PLLA and PLLA/CNC.

These results revealed an increase in crystallinity of the composite in about 30% compared



to the neat PLA polymer. XRD results showed an increase in the crystallinity of PLLA with the incorporation of CNCs. The increase in crystallinity with the addition of CNC can be explained by the assumption that the CNC act as efficient nucleating agents for this polymer.

Conclusion

PLLA/CNCs nanocomposite was prepared through in situ method by ring opening polymerization of the lactide dimer in the presence of the cellulose nanocrystals.

The incorporation of cellulose nanocrystals in PLLA using this method improved the thermal stability of this biopolymer, increasing its maximum temperature of mass loss. Moreover, XRD and DSC results showed an increase in the crystallinity of PLLA with the incorporation of CNCs. The increase in crystallinity with the addition of CNC can be explained by the assumption that the CNC act as efficient nucleating agents for this polymer. As the increased degree of crystallinity can improve tensile modulus and strength of the materials, these results indicate that the incorporation of CNCs by in situ polymerization in the PLA polymer has potential to improve thermal and mechanical properties of this polymer. Additional TEM of the PLLA/CNC composites and tensile tests are under investigation.

Acknowledgements

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