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Structural and thermal properties of silk fibroin films obtained from cocoon and waste silk fibers as raw materials

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Abstract

This study compares the structural and thermal properties of silk fibroin (SF) films obtained from different raw materials: silk coccons (SC) and silk fibrous wastes (SW). Samples were processed by solution casting (SFC and SFW), and casting with a subsequent water annealing treatment (WA-SFC and WA-SFW). The presence of crystalline (silk I and silk II) and amorphous structures was evaluated using X-ray diffraction (XRD) and Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy. Thermal properties of SF films were studied by DSC measurements. Accordingly, to FTIR and XRD results, the presence of silk I structure is greater in SFW that in SFC. Differences in enthalpy of crystallization peaks in DSC curves reveals that SFC presents a higher content of amorphous structures than SFW. The analysis also point that water annealing treatment induces conformational changes in secondary structures of SF films. It can be concluded that the presence of crystalline structures in SF films varies with the raw material and water annealing treatment. This fact represents a progress in the development of processing alternatives to control SF materials structure and properties.

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Keywords: silk fibroin; fibrous wastes; protein secondary structure, water vapor annealing.

1. Introduction

As well as silkworm cocoons (SC), silk fibrous wastes (SW) can be used as a raw material to obtained silk fibroin (SF). SW count for 20 to 30% of the total raw silk being processed [1], it is composed of waste from cocoons, reeling and threads, and presents a higher fibroin content (~91%) than that found in silk cocoons (~68%). This

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waste is a low cost raw material, representing an opportunity to produce new SF materials, based on proteins with high added value. Some studies have been reported that thermal processes in silk fiber textile processing can affect the structure of fibrous wastes and therefore the properties of SF extracted from them [2].

The structural conformation of SF materials refers to its relative content of secondary structures. It has been reported that conformational structure of this protein be controlled by modulating its hydration state during processing or in the application of post-treatments [3]. In this way, it has been possible to develop materials from this protein that exhibit a differentiated behavior in terms of biodegradability, mechanical strength and other specific properties [4]. Some of secondary structures obtained in regenerated SF materials include crystalline and amorphous structures. Crystalline structures include a dominant conformation of β-turns (silk I), and an insoluble structure formed by folded β-sheets (silk II). Meanwhile, α-helices, random coils and turns are understood as amorphous and less stable SF structures [5].

The aim of this study was to explore the role of raw materials and water annealing treatment in structural and thermal properties of SF films, oriented to biomedical and other applications.

2. Methodology

SF solutions were prepared using silk fibrous wastes and silk cocoons, which were degummed with 0.5% w/v Na_2CO_3 aqueous solution. The fibers were dissolved in 9.3 M LiBr solution at 60 °C [6]. The obtained SF suspensions were dialyzed and purified, reached aqueous solutions of 3.8% w/v approximately, for both samples. SF films were prepared by casting and evaporation process, using an environmental chamber for 20 h at 22 °C, 38% RH (SFC and SFW). Once dried, one set of each kind of dry films was placed in a vacuum oven for 12 h, in saturated water vapor environment, in order to induce SF crystallization by water annealing treatment (WA-SFC and WA-SFW) [6].

The structure of SF films was analyzed by Fourier Transform Infrared-Attenuated Total Reflection Spectroscopy (FTIR-ATR) using an IR Affinity-1S spectrophotometer (Shimadzu), equipped with an ATR (SPECAC). For each measurement, 64 scans with a resolution of 4 cm^{-1} were coded in the range of 400 to 4000 cm^{-1}. To determine the relative content of the secondary structures presents in each sample, the spectral region corresponding to the Amide I was normalized and baseline corrected, and then fit to 13 Gaussian curves. Associated bands to each type of secondary structure were then added to obtain its relative content in SF films [7].

X-ray diffraction experiments were performed using a PANalytical EMPYREAN diffractometer, to study the crystalline structure of the silk films. Ni-filtered Cu-Kα radiation (λ = 1.540598 Å) was used as X-ray source at 30 KV and 20 mA. All scans were performed in the range of 5-50° at a speed of 2 min^{-1}, with a step size of 0.6.

Thermal properties of the SF films were measured in a TA Instrument Q2000 DSC under a dry nitrogen gas flow of 50 ml min^{-1}. The samples were heated at 10 °C min^{-1} from 30 to 320 °C.

3. Results

Structural changes, attributable to different raw materials and water annealing treatment, were initially studied by qualitative analysis of IR spectra analysis in the region within 1700-1500 cm^{-1} (Fig. 1). This region has been commonly used for the analysis of different secondary structures of silk fibroin and it is assigned to absorption of the peptide backbones of the Amide I (1700-1600 cm^{-1}) and the Amide II (1600-1500 cm^{-1}), which are the two major bands in the protein IR region [7,8]. For SF films produced by casting, SFW sample showed a shoulder at 1652 cm^{-1}, corresponding to silk I. Furthermore, characteristic peaks of silk I (1652 cm^{-1} and 1539 cm^{-1}) and silk II (1622 cm^{-1} and 1515 cm^{-1}) were observed in WA-SFC and WA-SFW. The results indicate that water annealing treatment induces conformational transition in SF films.