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Effects of heat treatment on chitosan nanocomposite film reinforced with nanocrystalline cellulose and tannic acid

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ABSTRACT

This article presents an analysis of the influence of heat treatment on chitosan nanocomposite film. A series of samples comprising: pure chitosan film, chitosan film embedded with nanocrystalline cellulose (NCC), chitosan film crosslinked with tannic acid and chitosan film with a blend of NCC and tannic acid were heat treated using a convection oven. Fourier-transform-infrared spectroscopy (FTIR) and X-ray diffraction test (XRD) shows the changes in chemical interaction of the heat treated films. The heat treated films show significant improvements in moisture absorption. Tensile strength and Young's Modulus were increased up to 7 MPa and 259 MPa, respectively when the samples were subjected to heat treatment. For the NCC particles, a transmission electron microscope (TEM) was used to inspect the structural properties of cellulose particle in suspension form.

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1. Introduction

In recent years, biopolymer based films have gained much interest in the scientific community and industry for their potential to replace conventional non-biodegradable materials for structures and packaging material (Sousa & Gonçalves, 2015). Naturally available materials, such as: polysaccharides, proteins and lipids are being studied extensively for this purpose. However, among these materials, polysaccharides are of particular interest due to their availability and excellent film forming capability (Kanmani & Rhim, 2014). However, in present form, polysaccharides possess poor mechanical and barrier properties. Therefore, biopolymer based materials have not been widely used in industry, when compared to conventional plastic films (Tunç & Duman, 2011). One of the most common means to solve this problem is by introducing nano-sized materials, such as: silk fibroin (Sionkowska, Płanecka, Lewandowska, & Michalska, 2014), chitin (Ma, Qin, Li, Zhao, & He, 2014), and cellulose (Azeredo et al., 2010) to the polysaccharide matrix. Besides these nano-fillers, polysaccharides can also be crosslinked by ferullic and tannic acid (Cao, Fu, & He, 2007), genipin (Muzzarelli, 2009) and citric acid (Reddy & Yang, 2010). These modifications offer promising methods of enhancing the properties of polysaccharide-based films. However, there is a limitation on the amount of additives that can be added before negative aggregation effects occur. Studies shows that filler materials (e.g. nanocrystalline cellulose NCC) have an optimum loading to achieve the desired mechanical properties, beyond which a degradation of these properties occurs (Li, Zhou, & Zhang, 2009). Another method to change polymers properties, besides the filler loading and crosslinking processes already discussed, is by heat treatment. Previous articles by (Kim, Weller, Hanna, & Gennadios, 2002; Liu, Tellez-Garay, & Castell-Perez, 2004) have reported improvements in mechanical and barrier properties by exposing samples to high temperatures. Heat treatment disrupts the hydrogen bonds between polymer chains. This promotes a more open structure, which allows intra- and intermolecular crosslinking interactions, as describe by Kim et al. (2002).

This article describes research to produce a high performance wing membrane for a biomimetic micro air vehicle (BMAV) that closely resembles dragonfly wing material. Dragonfly wings are mostly composed of chitin shell and protein structures (Sun & Bhushan, 2012). Since chitin is insoluble in most of organic solvents, we desire to utilize chitosan (*N*-deacetylated derivative of chitin) as the membrane material for our BMAV. Chitosan has excellent film forming properties that are suitable for membrane applications. However, its poor mechanical properties led us to produce two different high performance nanocomposite chitosan films. The first film has chitin whiskers and tannic acid used as a

crosslinker (Rubentheren, Ward, Chee, & Tang, 2015a), while the second film has nanocrystalline cellulose and tannic acid additives (Rubentheren, Ward, Chee, & Nair, 2015b). Interesting results were observed in these articles, showing the interaction of both chemical and physical reinforcement in the chitosan film.

The objective of this work is to study the heat effects on the chitosan film reinforced with NCC and tannic acid (the second film). Very few (or no) publications have reported heat treatment studies of NCC blended with chitosan and tannic acid. Therefore, this article presents new results on the chemical interaction and changes in mechanical and barrier properties of these films.

2. Materials and methods

2.1. Materials

Chitosan powder (with minimum deacetylation degree of 75%) was purchased from Sigma-Aldrich. Microcrystalline cellulose (MCC), glacial acetic acid (grade AR), Sulfuric acid (96–98% grade AR) and tannic acid were purchased from Friendemann Schmidt. Other agents were provided by Fisher Scientific and used as received.

2.2. Preparation of nanocrystalline cellulose

NCC was prepared by using acid hydrolysis method. Initially 10.2 g of MCC was added into distilled water and stirred under an ice bath. This is to avoid a sudden temperature spike from an exothermic reaction caused by ion interaction between concentrated sulfuric acid and water. Once the solution temperature has cooled down, concentrated sulfuric acid was added (drop-by-drop) until the desired acid concentration of 63.5 wt% was reached. The suspension was then stirred constantly with a magnetic stirrer at 45 °C for 130 min. After acid hydrolysis, the slurry solution was subjected to centrifugation at 6000 RPM for 10 min. Upon completion, the sulfuric acid was removed from the container and distilled water was added to dilute it. This process was repeated 3 times. Next, the NCC slurry was carefully collected and transferred into a dialysis bag (molecular-weight cutoff of 14,000 Da). The NCC slurry was dialyzed for 24 h under running water and then under distilled water to bring the pH to a neutral state. NCC was then treated with ultrasonic bath for 10 min to disperse the solution. Then 5 drops of chloroform was added to prevent bacterial/fungus growth. Finally, the suspension was refrigerated in an air tight container at 6 °C with a final concentration of 4.6 wt% of NCC.

2.3. Preparation of chitosan nanocomposite

Chitosan solution was prepared by adding 2 wt% of chitosan powder into 2% (v/v) of acetic acid under constant stirring at 50 °C for 90 min. The solution was then cooled to room temperature. NCC was slowly added into the chitosan solution under rigorous stirring for 60 min. The mass ratio of NCC to chitosan was kept at 10:90. For the crosslinking process, 20 mg of tannic acid was incorporated into both the chitosan and chitosan/NCC solutions and stirred for another 60 min. The mixed suspensions were then cast into petri dishes and left overnight in a dry cabinet to remove excess bubbles. A convection oven was used to evaporate the solution at 40 °C for 48 h to obtain a dry composite film.

2.4. Heat treatment of chitosan nanocomposite

Dried films were then subjected to heat treatment. Essentially, film samples of pure chitosan, chitosan crosslinked with tannic acid, chitosan/NCC nanocomposite, and chitosan/NCC crosslinked with tannic nanocomposite were heat treated at 180 °C for 30 min in a

convection oven. Samples were then recovered and stored in dry cabinet prior to characterization.

The film nomenclature used in this article is: C for chitosan film, CX for chitosan film crosslinked with tannic acid, CN for chitosan/NCC nanocomposite and CNX for chitosan/NCC crosslinked with tannic acid. For films subjected to heat treatment, the letter "H" has been assigned at the end of their labels.

2.5. Material characterization

2.5.1. Morphological studies of NCC particle by transmission electron microscope (TEM)

The size and morphological studies of NNC were carried out using a Zeis EFTEM Libra 120 transmission electron microscope (TEM). The stored NCC particles were treated with an ultrasonic bath for 15 min to disperse the particles. Then three drops were collected from the NCC container and diluted with distilled water until a semi-opaque solution was obtained. Next the solution was dropped in a carbon-coated copper grid as reported by Kaboorani et al. (2012). It was then stored in dry cabinet for 48 h, before viewing.

2.5.2. Fourier-transform-infrared spectroscopy (FTIR)

The Fourier transform infrared spectroscopy of the films was recorded using a Perkin Elmer Spectrum 400 FT-IR/FT-FIR spectrometer. A wavelength range of $4000\,\text{cm}^{-1}$ to $400\,\text{cm}^{-1}$ was used for 32 scans of each sample at a resolution of $4\,\text{cm}^{-1}$.

2.5.3. X-Ray diffraction (XRD)

The film samples were analyzed using a X-ray diffractometer (Panalytical Empryean) equipped with Cu-$K\alpha$ radiation source ($k = 1.54060\,\text{Å}$) operating at 40 kV and 40 mA (at room temperature). The relative intensity was recorded in the scattering range of (2θ) 5–80° with a step size of 0.1.

2.5.4. Mechanical properties

Mechanical properties for all treated and untreated film samples were obtained using a universal testing machine (Shimadzu AGS-X series) with 500 N load cell. The crosshead speed was set to 1 mm/min. The composite films were cut in a rectangular shape (50 mm by 8.5 mm). The tensile strength and elongation-at-break were calculated according to the ASTM D882-02 method. At least three samples were tested for each film.

2.5.5. Water uptake test

All film samples were cut into 15×12 mm pieces. Then all samples were weighed to the nearest 0.0001 g in a dry state after heating in a convection oven at 105 °C for 1.5 h. Water uptake was measured by immersing the dried film pieces in 75 ml of distilled water for 1 h at 25 °C. The samples were then recovered and dried with filter paper to remove excess surface water and weighed again. The average value of water uptake was calculated using the following equation:

$$\%\text{water uptake} = \left[\frac{(W_s - W_i)}{W_i} \times 100 \right] \tag{1}$$

where W_s is the weight of the swollen sample and W_i is the weight of the sample after heating it in a convection oven for re-drying purpose.

2.5.6. Statistical analysis

All data were subjected to one-way analysis variance (ANOVA) and Fisher's Least Significant Difference LSD mean comparison. The correlation between the results were analyzed using SPSS statistical software (SPSS 22). All statistical analysis and calculations were performed at a confidence level of 95%.