



# Mechanical, thermal and barrier properties of nano-biocomposite based on gluten and carboxylated cellulose nanocrystals



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## ABSTRACT

Bio-based polymers and biocomposites are a relatively new and growing market in light of recent societal concerns including dwindling petroleum reserves, environmental and end-of-life disposal issues. Developing sustainable and environmentally friendly alternatives to current packaging films, such as polyethylene is neither easy nor simple. We report here on our effort to develop a novel nanocomposite-based packaging film comprised of gluten filled with carboxylated cellulose nanocrystals (C.CNCs). We observed the effect of different C.CNC loadings on the mechanical, thermal, sorption and barrier properties of the resulting composite films. The results of differential scanning calorimetry (DSC) indicated that increasing the C.CNC amount from 0 to 10 wt.% showed a minimum at 5 wt.% for the glass transition temperature ( $T_g$ ). The mechanical properties showed that the breaking elongation ( $\epsilon_b$ ) decreased by 26%, but tensile strength (TS) increased (60%) in the presence of C.CNC, with a maximum at 7.5 wt.%. The reinforcing effect of C.CNCs was also confirmed by dynamic mechanical analysis (DMA) where, by adding C.CNC, an increase in storage modulus was detected. As compared to film without C.CNC, the water vapor permeability (WVP) decreased from  $7.74 \times 10^{-11}$  to  $4.96 \times 10^{-11}$  mol/m.s. Pa for the film containing 7.5 wt.% C.CNC; with increasing nanocellulose content, water uptake of the nanocomposites increased but water solubility decreased. These results indicate that the nanocellulose is promising as a reinforcing agent in gluten polymers.

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## 1. Introduction

Most packaging materials are polyethylene, polystyrene or other petroleum-based polymers. They are widely used in different fields due to their low density and unique mechanical and physical properties (Huang and Netravali, 2009). However, most of them are non-biodegradable and in the composite form they are non-recyclable (Kumar et al., 2011). Because of the environmental pollution resulting from these polymers and their dependence on non-sustainable petroleum, attempts have been made to replace some or all of the synthetic plastics with biodegradable and renewable materials in many applications.

Protein is a renewable natural polymer with high quality, in certain cases low price and rapid biodegradability (Mojumdar et al., 2011; Mauricio-Iglesias et al., 2010; Song et al., 2008a,b). Protein-based materials have been explored as potential packaging materials because of their good barrier properties against oxygen (dry conditions) and aromatic compounds (Duval et al., 2013; Ture et al., 2012). However, if they are directly processed into packaging

materials, the results are poor mechanical properties, brittleness, strong water absorption, and susceptibility to corrosion by mold in humid environments. These are the key research issues that must be solved to enable the application of protein materials in packaging. Therefore, research has been performed to modify the properties of proteins by using physical, chemical and biological methods or through the addition of plasticizers and cross-linking agents. Although the performance of protein packaging films has been increased to a certain extent by these methods, some difficulties remain in the commercial production and application of proteins as a packaging material (Ying et al., 2010).

It has been reported that toughening the polymer matrix by using nano-particles is a simple and effective way to make a high-performance protein polymer composite (Ying et al., 2010; Min et al., 2004). Reactive nanoparticles that bond easily with functional groups on the polymer have shown improved mechanical properties and hydrothermal stability. This new generation of composites also offers extra benefits like low density, transparency, good flow, better surface properties and recyclability. It is worth recalling that all these improvements have been obtained at very low filler contents (generally lower than 5%) (Sorrentino et al., 2007).

In this study the effect of carboxylated cellulose nanocrystals (C.CNC) on the mechanical, thermal and barrier properties of a gluten-based nanocomposite has been investigated. Wheat gluten

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(*Triticum aestivum*) is one of the most frequently studied proteins in biodegradable films due to its ready availability as a by-product from the wheat starch industry, and because it has good film-forming properties and is readily polymerisable (Kuktaite et al., 2011; Cho et al., 2010).

Cellulose is a natural linear polysaccharide in which D-glucopyranose rings are connected by  $\beta$ -(1→4)-glycosidic links. The wide availability, renewability and biodegradability, simple hydrolysis process, high intrinsic strength and modulus, high aspect ratio and reactivity of cellulose nanocrystals offer advantages over other traditional nano-fillers (Lu et al., 2008); So current research toward environmentally friendly composites often focuses on the use of cellulose and nanocellulose-based materials (Nishino et al., 2004). In order to obtain a spontaneous and stable dispersion of CNCs in aqueous solution, an oxidation reaction was employed which converts the C<sub>6</sub> hydroxyls of cellulose to carboxyl groups. This then creates a repulsive force between individual CNCs and prevents agglomeration (Salajková, 2012).

## 2. Materials and methods

### 2.1. Materials

Wheat gluten (WG) was donated by Dr Scott Turner of B.C. Williams Bakery Service Inc. (Dallas, Texas, United States, 75235). Sodium hydroxide, sodium azide and hydrochloric acid were obtained from Merck KGaA (Darmstadt, Germany). Avicel PH-101 microcrystalline cellulose (MCC), glycerol and 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) were supplied by Sigma-Aldrich Inc. (St. Louis, MO, USA). Sodium hypochlorite (NaClO), 11%, and sodium bromide (NaBr) were provided by VWR international (West Chester, PA, USA) and EM Industries Inc. (Gibbstown, NJ, USA), respectively.

### 2.2. Methods

#### 2.2.1. CNC preparation

Fifty grams of MCC was combined with 1 L of 2.4 M HCl in a 3 L 3-neck round bottom flask (RBF) equipped with a mixer, reflux condenser, and a glass needle adapter connected to an N<sub>2(g)</sub> source and heated (~100 °C) in an oil bath to reflux for 2 h under a steady stream of N<sub>2(g)</sub>. It was then diluted and allowed to settle. The clear supernatant was removed by siphon without disturbing the pellet. The remaining solution was stirred for about 10 min. The solution was then filtered through 25  $\mu$ m filter paper (Whatman #4) to collect a cellulose cake and the cellulose cake was rinsed with about 500 mL deionized H<sub>2</sub>O from a reverse osmosis unit. Once the pH exceeded 3, the cellulose cake was then mixed in water at about 1% concentration and sonicated to disperse the crystals.

#### 2.2.2. TEMPO-mediated carboxylation of CNC

For TEMPO carboxylation, slight modifications of literature methods were utilized (Paralikar et al., 2008; Habibi et al., 2006). The 1% cellulose suspension (200 mL) was transferred into RBF and slowly stirred with 140 mg of TEMPO (0.896 mmol), 360 mg of NaBr (3.498 mmol) and 10 mL of 11% sodium hypochlorite (NaOCl) with the aim of oxidation and conversion of the surface C<sub>6</sub> primary hydroxyls to carboxylic acids. The reaction mixture was kept at a pH level of 10.2–10.5 for the entire reaction by adding NaOH (55–60 mL) automatically via a pH controller. After reacting for 4–8 h, 30–40 mL of ethanol was added to destroy the residual NaOCl and thereby terminate further oxidation. The mixture was purified by successively diluting with filtered deionized water and

concentrating via diafiltration until a low conductivity (typically 500  $\mu$ S/cm) was reached. The resulting C.CNCs were stored at 4 °C.

#### 2.2.3. C.CNC characterization

**2.2.3.1. Conductometric titration.** The carboxylate content on the surface of the TEMPO-oxidized CNC was determined by a conductometric titration against 0.01 N NaOH. The conductivity of the C.CNC was plotted versus volume of added titrant and carboxyl content (mmol CO<sub>2</sub>H per gram of C.CNC) was calculated from the difference in inflection points between strong acid and strong base lines (reference). The carboxylate content of the C.CNCs was found to be 1.3 mmol/g.

**2.2.3.2. Atomic force microscopy (AFM).** The AFM analysis was performed by Jeremiah Kelley, Oregon State University, using a Dimension 3100 series Scanning Probe Microscope (Veeco Metrology Inc., Santa Barbara, CA) to characterize the dimensions and homogeneity of cellulose nanocrystals. All images were obtained using tapping mode in air at room temperature.

**2.2.3.3. X-ray diffraction (XRD).** An X-ray diffractometer (Bruker D8 Discover) was used to investigate the crystallinity of the produced C.CNC. Samples were analyzed at room temperature within a single goniometer set-up. X-ray Ka radiation was produced from a Cu target with a wavelength of 1.54 Å; Ni was used to filter out L transition radiation. A voltage of 40 kV and current of 18 mA were generated. The angle of incidence was varied from 10° to 35° by step of 0.02° and scanning rate of 6°/min. The crystalline index of cellulose, CrI, was determined based on an empirical method (Flauzino Neto et al., 2013):

$$CrI = \frac{I_{200} - I_{am}}{I_{200}} \times 100 \quad (1)$$

The  $I_{200}$  is the peak intensity at  $2\theta = 22.7^\circ$  and  $I_{am}$  is the peak intensity at  $2\theta$  around  $18^\circ$ .

**2.2.3.4. Fourier transform infrared (FTIR) spectroscopy.** An FTIR, JASCO, 680 plus (Easton, MD 21601 USA), Equipped with a Specac MKII Golden Gate (Kent, England) Attenuated Total Reflection (ATR) platform with diamond crystal was used to characterize the chemical changes of the C.CNC samples. The spectra were acquired in transmission mode and over the 4000–400 cm<sup>-1</sup> wavenumber range. 64 scans at a spectral resolution of 4 cm<sup>-1</sup> were accumulated to achieve an adequate signal-to-noise ratio.

#### 2.2.4. Nanocomposite preparation

The method described by Kayserilioğlu et al. (2003) was followed with slight modification. Water was mixed with surfactant (0.2 wt.%) and glycerol (1.3 wt.%) as plasticizer. Sodium hydroxide solution 0.5 M was carefully added until pH 10.8–11 was obtained. WG (5 wt.%) was dispersed in the solution through a sieve (No. 60) and with magnetic stirring at low speed for 30 min under controlled pH and heated in a water bath at 70 °C for 10 min. After cooling, specific amounts of this dispersion were mixed with a specific amount of the aqueous dispersion of C.CNC at high speed for 15 min. C.CNC loadings in the final composites were 0, 2.5, 5.0, 7.5 and 10.0 wt.% (based on gluten weight) and were denoted as Glu-0, Glu-2.5, Glu-5, Glu-7.5, and Glu-10%, respectively. A certain volume of film-forming solution was poured into a Teflon mold to cast film. Drying was performed at 40 °C until films could be easily removed and they were conditioned in an ASTM room at 20 °C and 60% relative humidity for 72 h.

#### 2.2.5. Nanocomposite characterization

**2.2.5.1. Scanning electron microscopy (SEM).** The fracture surfaces from frozen (liquid nitrogen) samples and surface morphologies

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