# Optimization of physical and mechanical properties for chitosan–nanocellulose biocomposites

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### ARTICLE INFO

### ABSTRACT

Chitosan (CHT) is a biodegradable compound and has excellent performance in forming films; on the other hand, nanocellulose (NCL) crystals have low densities and are less expensive than other nanofillers. A novel and simple method was applied to develop CHT–NCL nanocomposite (NCP) from CHT powder of high molecular weight and NCL particles having two dimensions in nanoscale; a rotor stator and an ultrasound device were used to separate different nanolayers from each other and facilitate their dispersion into polymer matrix. The optimized NCP indicated superior mechanical properties compared with some synthetic films; approximate values of 47% elongation-at-break, 245 MPa tensile strength and 4430 MPa Young's modulus were achieved. Water vapour permeability (WVP) value of the NCP was at optimal level of $0.23 \times 10^{-11}$ (g/m s Pa) which was much less than the most biofilms' WVP values. FESEM analyses revealed that high concentrations of CHT and NCL composed inter-connected structures justifying high elongation capability of CHT–NCL NCP.

## 1. Introduction

Chitosan (CHT), the cationic (1–4)-2-amino-2-deoxy-β-D-glucan, is industrially produced in various quality grades from chitin, the second most abundant polysaccharide in nature (Muzzarelli et al., 2012; Muzzarelli, 2012; Tome et al., 2013). CHT is a non-toxic and biodegradable compound and has excellent performance in forming films (Hardy, Hubert, Macquarrie, & Wilson, 2004). Molecular weight of CHT deeply affects the permeability, mechanical and thermal properties of the obtained film (Butler, Vergano, Testin, Bunn, & Wiles, 1996). CHT films have moderate water vapour permeabilities and exhibit good barrier properties against oxygen permeation (Rudrapatnam & Farooqahrned, 2003).

Cellulose, as the most abundant polymer in the environment, regards as one of the most important elements in the plant structures and guarantees the integrity of cellular structure (Righi et al., 2011). Different cellulose derivations with various applications could be obtained by physicochemical treatments on cellulose; since the aim of treatment application is grinding the long chains of cellulose polymers, hydrolysis process is applied on cellulose

microfibrils and then chemical compounds and impurities are removed by washing and residuals are treated by spray drying process (Dadashi, 2011). Obtained crystals have low densities, high elongation moduli and tensile strengths (Klemm, Heublein, & Fink, 2005); besides, they have high biodegradability rates and are less expensive than other nanofillers (Hansson et al., 2013). This highlights their suitability to be applied as nano-reinforcer materials in biodegradable packaging.

Nanocomposites (NCPs) are novel polymer matrices which have been incorporated by nanoparticles (NPs) having at least one dimension in nanoscale (Petersson & Oksman, 2006). Cellulosic nanocomposites are usually used to achieve excellent strength properties (Mikkonen et al., 2011). Dadashi (2011) evaluated the effect of three different levels of the current nanocellulose (NCL) (3, 5 and 7%) on poly lactic acid matrix. Since NCL, as a polysaccharide and hydrophilic compound, is in fibrous state and its dimensions are greater than counterparts of other NPs, it was recommended to be used as a reinforcement constituent in such a way that it won't change the matrix context. They suggested the level of 3% NCL to obtain less water vapour permeability rates and higher tensile moduli for final films. Khan et al. (2012) reported that incorporation of even 1% (w/w) NCL with 5–10 nm width could significantly increase tensile modulus of CHT film, which was equal to 43% increase compared with control CHT film. Of course, when

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**Table 1**
RSM Box–Behnken experimental design for independent variables.

| Std. No. of treatment | CHT level (%w/0.6v) | NCL level (%w/w$_{CHT}$) | GLY level (%v/w$_{CHT}$) |
|---|---|---|---|
| 1 | 1.00 | 0 | 60 |
| 2 | 1.30 | 0 | 60 |
| 3 | 1.00 | 2 | 60 |
| 4 | 1.30 | 2 | 60 |
| 5 | 1.00 | 1 | 30 |
| 6 | 1.30 | 1 | 30 |
| 7 | 1.00 | 1 | 90 |
| 8 | 1.30 | 1 | 90 |
| 9 | 1.15 | 0 | 30 |
| 10 | 1.15 | 2 | 30 |
| 11 | 1.15 | 0 | 90 |
| 12 | 1.15 | 2 | 90 |
| 13 | 1.15 | 1 | 60 |
| 14 | 1.15 | 1 | 60 |
| 15 | 1.15 | 1 | 60 |

5% NPs was incorporated, tensile strength, tensile modulus and elongation at break reached a plateau; incorporation the higher levels of NCL couldn't improve mentioned parameters, attributed to potential aggregation of NCL particles above the threshold point. Hassan, Hassan, and Oksman (2011) reported that improvement of tensile strength for CHT–NCL NCPs was significant with the incorporation of just 2.5% NCL having 7–24 nm diameters, which was attributed to the formation of percolated/interconnected network of cellulose NPs within CHT matrix. In general, previously prepared chitosan–nanocellulose composites did not show appropriate water vapour permeability or mechanical strength rates to substitute common synthetic polymers. The aim of this research was to apply different types of raw materials to warrant better homogeneity for incorporated NCL particles into CHT matrix in order to improve final diverse properties of nanocomposites. Also, our objective was to obtain the optimized amount considering all factors including the raw material consumption and the properties of final NCPs in order to replace synthetic polymers frequently used in the packaging industry.

## 2. Material and methods

### 2.1. Materials

CHT powder, having molecular weight of 600–800 kDa, and cellulose NPs, with 20–50 nm diameters, were purchased from Acros Organics Co., Belgium and Asahi Kasei Corp., Japan, respectively. Absolute acetic acid and glycerol (GLY), sodium chloride, calcium chloride and magnesium nitrate were prepared from Merck Co., Germany.

### 2.2. Film preparation

Certain amounts of CHT powder (Table 1) were dissolved in 40 mL aqueous solution (1%, v/v) of glacial acetic acid; stirring was conducted at 50 °C and 250 rpm by a heater-stirrer (CB162, Stuart®, UK) for 2 h. In parallel, certain amounts of cellulose NPs (Table 1) were added to 20 mL distilled water and dispersed at the same conditions as CHT for 2 h. Then, the solution was homogenized with a rotor stator (IKA®T25 digital, Ultra-Turrax®, Germany) at 8000 rpm for 15 min and an ultrasound device (TI-H-10, Elma®, Germany) at 35 kHz and 100% power without heating for 30 min. Deaeration was conducted in a thermostat vacuum oven (Croydon, Townson & Mercer Ltd., UK) at 600 mmHg for 1 h without heating. The solutions were casted on the center of glass plates which had 100 cm$^2$ surface areas and were inside the oven at 37 °C; the required time for film forming was 48 h. The dried films were removed from the

plates and placed inside the oven for two further days to evaporate residual solvents completely and finally were placed in hermetic packaging plastics (18 cm × 14 cm; Pollyetilen Co., Iran).

### 2.3. Physical properties of NCPs

#### 2.3.1. Thickness

Thickness of different films was determined by a digital micrometer (Mitutoyo Company, Japan) to the nearest 0.001 mm. For each sample, 8 random positions around the film were measured and mean value was used for determination of physical and mechanical properties.

#### 2.3.2. Transparency

This was determined by a lux-meter device (Testo 540 pocket sized, UK). For this purpose, its light sensor was located under the light source and the number of received luxes from the source was recorded. Then, in the stable conditions, the samples were placed under the light sensor and received luxes were recorded and reported in terms of the percent and on the basis of two obtained values (Dadashi, Mousavi, Emam, Jomeh, & Oromiehie, 2012). Rates of light illustration were measured from four different directions of the films and mean values were reported.

#### 2.3.3. Moisture content

To carry out this analysis, empty capsules were located in the oven at 110 °C for 1 h to reach the constant weight. Film samples were cut into 3 cm × 1 cm pieces; then, they were placed into the capsules and weighed and finally, the capsules were placed in the oven at 110 °C to reach the constant weight (Ghasemlou, Khaksar, Mardani, Shahnia, & Rashedi, 2013). After cooling in the desiccators, the whole films and capsules were weighed to obtain the dry sample weights. Moisture contents of the films were calculated on the basis of wet weight as follows:

$$MC_{Wb} = \left( \frac{\text{Wet sample weight} - \text{Dry sample weight}}{\text{Wet sample weight}} \times 100 \right)$$

#### 2.3.4. Solubility in water

The dried films were then immersed in 50 mL of distilled water for 12 h at 25 °C (Ghasemlou, Khodaiyan, Oromiehie, & Yarmand, 2011). Next, the films were taken out from the water by blotting with filter papers previously dried and weighed to remove the surface adsorbed water. Remaining pieces of films were dried at 110 °C to constant weight (Final dry weight). Solubility in water (WS) was calculated by using the following equation:

$$WS = \left( \frac{\text{Initial dry weight} - \text{Final dry weight}}{\text{Initial dry weight}} \times 100 \right)$$

#### 2.3.5. Color

The values were determined by a chromameter (Minolta CR 300 Series, Minolta Camera Co., Ltd., Japan). Measurements were performed by placing the NCP films over the standard white paper: $L^* = 93.49$, $a^* = -0.25$ and $b^* = -0.09$. The CIELab scale was used, $L^*$ (white = 100 and black = 0) and chromaticity parameters of $a^*$ (red = 60 to green = −60) and $b^*$ (yellow = 60 to blue = −60) were measured. For each film, 3 different points were selected (Ojagh, Rezaei, Razavi, & Hosseini, 2010).

#### 2.3.6. Water vapor permeability (WVP)

The WVP test was conducted gravimetrically using ASTM procedure E96-95 (1995). At first, the measurement cells filled with anhydrous calcium chloride desiccant to create a 0% RH storage condition and the surfaces of cells were covered with the films and sealed with molten paraffin. To maintain a 75% RH gradient across