Mechanical and Barrier Properties of Cellulose Nanocrystals Reinforced Chitosan Nanocomposites

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Abstract

Strong study efforts have been concentrated on the application of natural fillers as reinforcing materials for polymer composites, because these fillers are renewable, sustainable and possess low rough nature than mechanically robust nano-sized fillers (Pandey et al., 2001). Cellulose nanocrystals (CNCs) with one dimension in the nano-scale range have great potential as reinforcements in polymer hosts because of their promising mechanical properties with very good strength and stiffness (Cao et al., 2007; Azizi et al., 2013). In the recent years, cellulose nanocrystals have merited considerable attention as potential nano-sized filler in blending with diverse polymers. Cellulose nanocrystals are characteristically rod shaped monocrystals, 2 to 20 nm in diameter and from tens to hundreds of nanometers in length, and extracted after acid hydrolysis of different natural cellulose fibers for example cotton, cellulose fibers from lignocellulosic materials, and marine animal tunicate (Habibi et al., 2010). Cellulose nanocrystals as a reinforcing phase have some advantages over other types of nano-sized fillers, for instance high aspect ratio, large surface area, low density, outstanding mechanical properties, renewability, and bio-compatibility (Xu et al., 2013).

Chitosan (CS) is a heteropolysaccharide achieved from the alkaline deacetylation of chitin which is the most plentiful polysaccharide after cellulose on earth (Ravi Kumar et al., 2000). Chitosan is biocompatible, biodegradable, non-toxic, hydrophilic, and anti-bacterial, thus, it is broadly used in water treatment, agriculture, fabric and textiles, cosmetics, nutritional enhancement and food processing (Sashiwa et al., 2004). The enhanced physical and chemical properties of chitosan are valuable. In this article, CNCs extracted from the acid hydrolysis of cotton were incorporated into CS host to develop the mechanical and oxygen barrier properties of CS/CNCs bio-nanocomposite films.

Preparation of Bionanocomposite

Chitosan solution was prepared by dissolving 2 g of CS powder in 100 ml of acetic acid solution (1%, v/v), under magnetic stirring at 80◦C for 15 min and subsequently cooled. The glycerol plasticizer (25% wt on CS solid base) was then added to the CS solution while stirring for 20 min at 60◦C. Nanocomposite samples were fabricated by dispersing different amounts of CNCs (0 wt%, 1 wt%, 3 wt% or 5 wt%) in 100 ml of distilled water for 1 h at room temperature. The obtained suspension was added to the CS solution, stirred for 1 h at room temperature and then sonicated for 30 min at 25◦C in a bath type ultrasound sonicator. The suspensions were then poured into glass plates and dried at 25◦C for three days, until the solvent was completely evaporated and a self-standing film was achieved.

Morphology of the CS/CNCs Nanocomposite

The polymer nanocomposites were prepared with different CNCs filler loading level (0 wt%, wt%, 1 wt%, 3 wt%, 5 wt%) in CS matrices. Figure 1 shows the rod-like cellulose nanocrystals were well dispersed into the polymer matrix when the low concentrations of CNCs were used. On the other hand, with the increase of CNCs contents into CS hosts, their distribution became poor and most of the cellulose nanocrystals were agglomerated by hydrogen-bonded free hydroxyl groups.

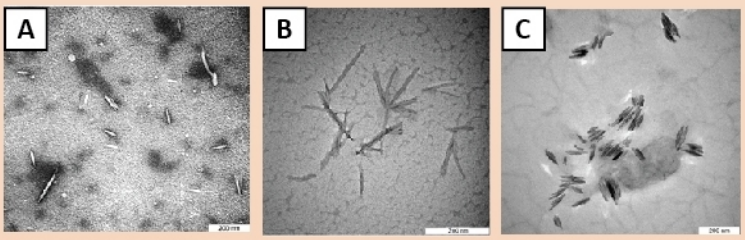

Fig. 1. TEM images of CS/CNCs nanocomposites with 0.1 wt% (A), 3.0 wt% (B), and 5.0 wt% (C) CNCs contents.

Tensile Properties

Table 1 shows the effects of CNCs contents on the tensile properties of the CS/CNCs nanocomposite. Tensile values display that the addition of CNCs enabled to promote the tensile strength (Ts) and modulus (Tm) of the films. The maximum values were achieved when 1.0 wt% of CNCs were dispersed in the CS matrix. The nanocomposite showed ~ 87% and 63% tensile strength and modulus enhancements, respectively than that of the original polymer. This improvement is owing to the creation of a network structure originated from the filler-matrix interactions in nanocomposites, which promotes hard portion crystallinity, declines molecular mobility and increases rigidity (Rueda et al., 2013). Furthermore, the incorporation of cellulose nanocrystals from 0 wt% to 5.0 wt% decreased the elongation at break (Eb) of CS nanocomposites films with the highest reduction at 1.0 wt% loading level. This phenomenon can be explained by the fact that the stiff filler network structure, responsible for the enforcing effect, was formed perfectly as the CNCs level was 1.0 wt% which powerfully restricted the chain mobility of the matrix and therefore considerably declined elongation at break (Azeredo et al., 2010).

Table 1. Tensile data of CS and its CNCs nanocomposites.

Sample	Ts(MPa)	Tm(MPa)	Eb(mm)
CS/CNCs (0 w%)	35.1 ± 1.6	295 ± 21	12.2 ± 0.4
CS/CNCs (1 w%)	66.2 ± 1.4	480 ± 25	6.4 ± 0.5
CS/CNCs (3 w%)	57.4 ± 1.0	432 ± 39	9.5 ± 0.4
CS/CNCs (5 w%)	51.2 ± 1.3	401 ± 26	8.9 ± 0.8

Oxygen Transmission Rate

Figure 2 shows the oxygen transmission rate (OTR) of the pure chitosan film is reduced in the CS nanocomposites, and most considerably declined i.e by ~66%, in the 1.0 wt% CS/CNCs sample. These results propose that the addition of CNCs make a tortuous path for the diffusion of oxygen molecules. When the low contents of CNCs were used, the CNCs were well dispersed as shown in the TEM results, thus yielding a more efficient barrier outcome (Fortunatia et al., 2012). Consequently, a proper affinity between the polymer and the surface of the CNCs can be recommended. A weak affinity would lead to the presence of holes that allow the oxygen molecules to penetrate faster through the film. The OTR is not decreased further with a higher content of CNCs. This can be because of accumulation of the CNCs. The agglomeration seen beyond 1.0 wt% level may provide channels, or holes, in the film that allow more rapid permeation (Paralikar et al., 2008).

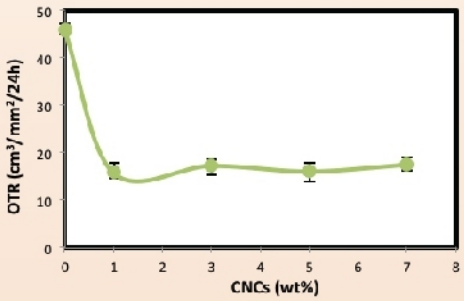

Fig. 2. Effect of CNCs addition on OTR property of CS films.

Conclusions

Chitosan nanocomposites were prepared by casting a mixture of chitosan and cellulose nanocrystals. Incorporation of cellulose nanocrystals into chitosan resulted in obtaining composites with enhanced tensile and modulus strength and decreased elongation at break. Use of cellulose nanocrystals with hydrophilic polymer matrix such as chitosan declines its resistance to oxygen permeation.

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