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Mechanical and barrier properties of kappa-carrageenan/cellulose nanocrystals bio-nanocomposite films

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Abstract. The aim of this study is to report the effect of the addition of cellulose nanocrystals (CNCs) on the mechanical and barrier properties of Kappa-Carrageenan (KC) bio-nanocomposite films prepared through the solvent casting process. The characterizations of bio-nanocomposite films were carried out in terms of transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), oxygen transmission rate (OTR), and tensile tests. TEM and FESEM results showed that at low loading levels, CNCs were dispersed homogenously in the Kappa-Carrageenan matrix. The tensile strength and modulus in films increased from 45.7 MPa to 108.4 MPa and from 295 MPa to 710 MPa respectively, when CNCs content went from 0 wt% to 3.0 wt%. The oxygen barrier property of Kappa-Carrageenan matrix was best enhanced at 3.0 wt% of CNCs loading. The enhanced properties attained by incorporating CNCs can be beneficial in various applications.

1. Introduction

Last decades, researchers have concentrated their investigations on the processing of nanocomposites to improve physical properties. In the vein of conventional composites, nanocomposites use a matrix where the nano-sized reinforcement materials are dispersed. The reinforcement is generally considered as a nanoparticle with at least one dimension lower than 100 nm. In the meantime, there is a simultaneous and increasing attention in developing application of bio-based products which can decrease the dependence on fossil fuel and shift to a sustainable materials basis [1-2]. This specific condition provides unique bionanocomposites possessing remarkable properties, which have been never found in traditional composites [3]. Hence, the next generation of materials in the future are biodegradable bio-nanocomposites [4].

The nano-sized reinforcements can obtain from various renewable resources depending on their biological origin, e.g., starch, cellulose, chitin [5-6] but main studies are devoted to cellulose fibers as this biopolymer is the most plentiful on earth. Cellulosic fibers are composed of assemblies of microfibrils [7], which form bundles and almost endless rods. Through acid and/or enzymatic hydrolysis, these microfibrils broke down into short crystalline rods or “cellulose micro/nano-crystals.” With a very high modulus of elasticity (138 GPa), and a high specific-surface-area, low



density, low-cost, renewable nature, and recyclability, cellulose nanocrystals have merited substantial consideration for exploring new applications.

Cellulose as “filler” has been mostly used in bio-composites, which in some cases contributes to improve the stiffness but typically embrittles the polymer. The research of cellulosic nanocrystals as a reinforcing material in nanocomposite films was initially reported two decades ago [8]. Since that time significant literatures have been dedicated to nanocrystal cellulose which becomes a topical subject [9-12].

Kappa-carrageenan (KC) is one of the most promising biopolymers; it is composed of a linear chain of sulfated galactans and extracted from certain species of red alga. It exhibits good potential for development as a source of biodegradable films [13]. Though, KC films do not have noble mechanical and oxygen barrier properties, as they are essentially hydrophilic. Consequently, they might not be utilized for extensive applications, particularly in the food industry. Numerous strategies have been reported to overcome these drawbacks, for example blending with natural or synthetic polymers [14], blending with hydrophobic compounds [15] cross-linking [16] and formation of nanocomposite [17, 18]. In a study, the effect of using nanoclay on the properties of KC-based films was investigated [19]. They obtained improved the physical and mechanical properties for KC films. In a similar study, agar/kappa-carrageenan blend nanocomposite films were prepared using different contents of a natural MMT (Cloisite Na⁺), and it was reported that the hydrophilic Cloisite Na⁺ was the great compatible with an agar and kappa-carrageenan polymer matrix [20]. However important improvements in the properties of KC nanocomposite films have been reported in these researches, the films are still not comparable to synthetic plastic films. This specifies that more-efficient approaches or a combination of techniques are required to develop the films' properties to where they can substitute for non-biodegradable plastic films for packaging.

In this study cellulose nanocrystals obtained from acid hydrolysis of cotton cellulose with 50–80 nm in length and a diameter in the range of 5–10 nm were used to improve the mechanical and oxygen barrier properties of Kappa-carrageenan-based films. For these proposes the mechanical properties in terms of tensile strength, tensile modulus and elongation at break and barrier property in term of oxygen transmission rate (OTR) were assessed.

2. Materials and methods

2.1. Materials

All the chemicals were analytical grade and used as received without more purification. Cotton cellulose from filter paper (Q1, Whatman) was supplied by Fisher Scientific (Pittsburgh, PA, USA). Sulfuric acid (95%–98%, reagent grade) was purchased from Scharlau (Barcelona, Spain). Kappa-carrageenan with a 300 000 g mol⁻¹ average molecular weight was obtained from the Malaysian Nuclear Agency.

2.2. Extraction of CNCs

Extraction of the CNCs was carried out according to a previous work [21]. The cellulose powder harvested from one piece of filter paper (2 g) was hydrolyzed with a sulfuric acid solution (20 mL, 64 wt%) at 45 °C for 60 min. The resultant suspension was diluted 10-fold with cold water (4 °C) followed by centrifugation and dialysis until a neutral pH was reached. Finally, the sample was freeze-dried. The final product was cellulose nanocrystals with 50–80 nm in length and a diameter in the range of 5–10 nm.

2.3. Preparation of Nanocomposite

KC solution was prepared by dissolving 2 g of KC powder in 100 mL of distilled water at 82 °C under magnetic, for 30 min and subsequently cooled. The glycerol plasticizer (25 wt % on KC solid base) was then added to the KC solution while stirring for another 30 min. 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 KC 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.

2.4. Characterization

The morphologies of the sample films were studied by using a transmission electron microscope (HITACHI H-700, Japan) with acceleration voltage of 120 kV at room temperature. The ultrathin sections of bio-nanocomposite sample were prepared at −120 °C using a microtome equipped with a diamond knife, and then placed on a copper grid. The surface morphology of the sample films was further examined using a field emission scanning electron microscope (FESEM), (JSM-6360LA Philips), with an acceleration voltage of 5 kV. Before examination the specimens were mounted on a metal stub using carbon tape and then gold-coated under nitrogen atmosphere using a Bal- Tec SCD 005 sputter coater. The tensile properties of the sample films were measured as per ASTM D 638 test methods, using an Instron 4032 Universal Testing Machine. The samples, cut into dumb-bell shapes, employed a steel template and router machine. Seven specimens were tested and the average result of the values of five specimens was taken. Oxygen transmission rate of the sample films were evaluated by using of an oxygen transmission rate test (Labthink BTY-B1, China) instrument. The sample film with a diameter around 30 mm was placed in a cell and oxygen flowed on one side of the films, and the oxygen transmission rate was measured. This is the capacity of molecule gas that transfers through a surface per unit of time. Five specimens were tested and the reported results were average of the values of at least four OTR measurements.

3. Results and discussion

3.1. Morphology of the KC/CNCs bio-nanocomposite films

The polymer nanocomposites were prepared with different CNCs filler loading level (0 wt%, 1.0 wt%, 3.0 wt%, 5.0 wt%) in KC matrices. Figure 1 shows the rod-like cellulose nanocrystals were well dispersed into polymer matrix, when the low concentrations of CNCs were used. The best CNCs distribution was observed at 1.0 and 3.0 wt%, filler loadings. On the other hand, with the increase of CNCs contents (5.0 wt%) into KC hosts, their distribution became poor and most of the cellulose nanocrystals were agglomerated by hydrogen-bonded free hydroxyl groups.

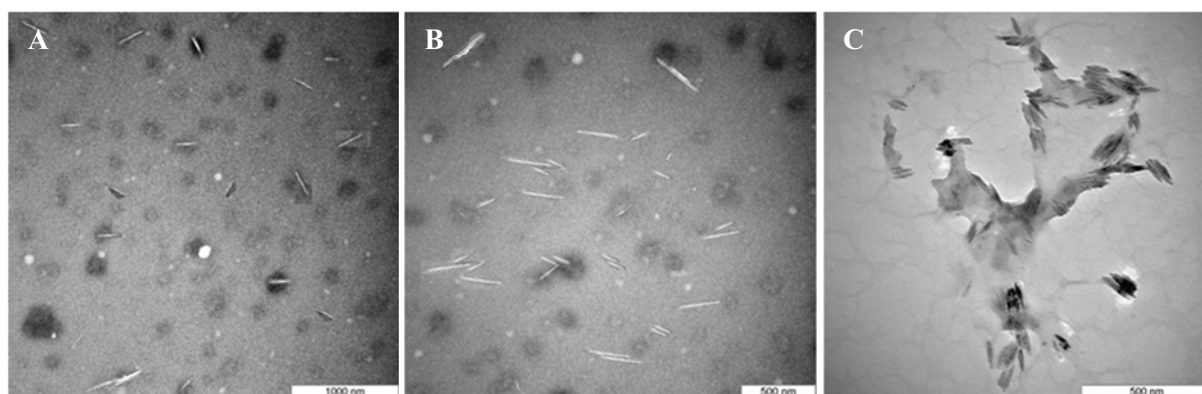


Figure 1. TEM images of KC/CNCs bio-nanocomposite films with 0.1 wt% (A), 3.0 wt% (B), and 5.0 wt% (C) CNCs contents.

3.2. Mechanical properties

Figure 2A and B display the effect of CNC concentration on the mechanical properties of the KC/CNC bio-nanocomposite films. The CNC with the KC matrix as the nano-filler exhibited an important reinforcing effect. As the CNC concentration increased, both the tensile strength and Young's

modulus improved considerably, but the elongation at break of the bio-nanocomposites declined. When the CNC content varied from 0 to 3.0 wt%, the tensile yield strength and Young's modulus enhanced from 295 to 710 MPa, representing a ~140 % enhancement, and the tensile strength increased from 45.7 to 108.4 MPa, indicating a ~137 % increase. This proposes that incorporating CNC into the KC matrix results in powerful interactions between the matrix and the filler, and thus confines the motion of the matrix and enhances rigidity [22]. Furthermore, increased crystallinity, which was donated by CNC, can also promote mechanical properties [23]. Further addition of CNC decreased the tensile modulus and strength, but this still stayed higher than that of the pure KC film. This decline is owing to interparticle interactions, which lead to the creation of weak points in the matrix. Instead, the elongation at break gradually decreased from 0 to 5.0 wt% of filler loading, with maximum decrease at 3.0 wt%. The elongation at breaks decreased from 8.3 to 2.5 wt%, representing a ~70 % reduction. This phenomenon can be described by the fact that the rigid filler network structure was created perfectly when the CNC concentration was 3.0 wt%.

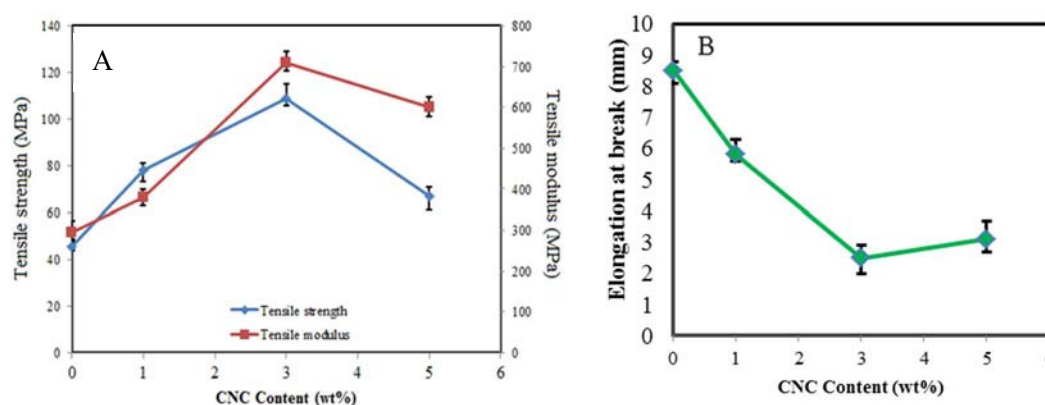


Figure 2. (A) Tensile strength and tensile modulus (B) elongation at break of KC/CNC bio-nanocomposites.

3.3. Oxygen transmission rate

Figure 3 showed the OTR versus percentage of cellulose nanocrystals. From figure 3, it is evidenced that the oxygen permeability is most extremely reduced, i.e. by ~80%, in the 3.0 wt% KC/CNCs compared to the control KC sample. The permeability of the bio-nanocomposite films is always lower than that of pure KC. These results propose that the combined CNCs make tortuous pathway for the diffusion of oxygen molecules.

When the low concentrations of CNCs were incorporated, the CNCs were distributed to a higher degree as revealed in the TEM micrograph, hence yielding a more effective barrier effect [24]. Thus an appropriate interaction between the KC and the surface of the CNCs can be happened. A weak interaction would lead to the being of hollows that permit the oxygen molecules to penetrate faster through the film. The penetrability is not declined more with a higher level of CNCs. This result can be owing to aggregation of the CNCs. The agglomeration observed beyond 3.0 wt% content may provide channels, or pores, in the film that allow further rapid diffusion [25].

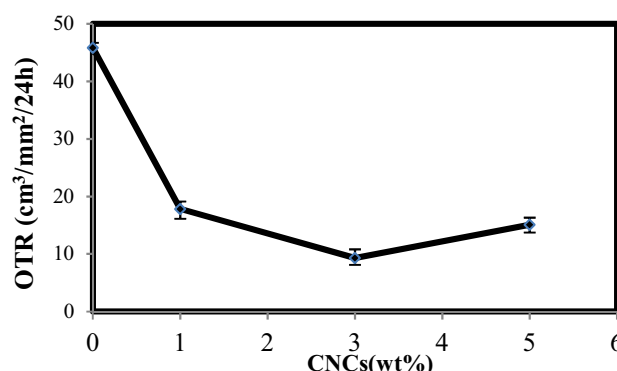


Figure 3. OTR of KC and its CNCs bio-nanocomposite films.

3.4. Surface morphology of KC-based films

The morphological inspection of the upper surfaces of the films was carried out using field emission scanning electron microscopy (FESEM) as is displayed in Figure 4. It is seen that incorporation of CNCs caused alters in the film microstructure. The FESEM micrograph of pure polymer film (Figure 4A) shows KC with some cracks. Adding of 3.0 wt% CNCs affects the microstructure of the KC films definitely (Figure 4B). The homogenous distribution of CNCs at 3.0 wt% content caused an appropriate adhesion between the polymer matrix and the surface of the CNCs and thus generated a smooth and tight surface. In contrast, addition of 5.0 wt% CNCs (Figure 4C) because of accumulation of CNCs and poor interaction between filler and matrix led to increasing density of crack deflection sites and creation of some holes [26]. In conclusion, the FESEM explanations have allowed supporting the measured mechanical and barrier results.

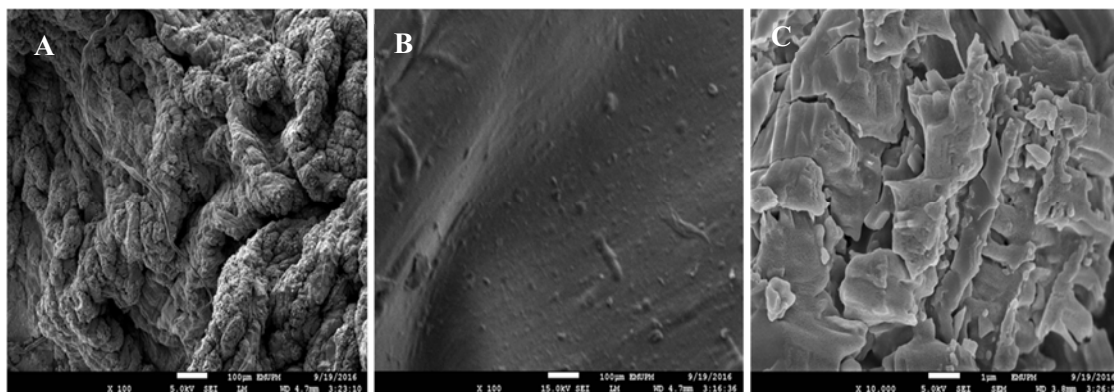


Figure 4. FESEM image of the upper surfaces of (A) KC, (B) KC/CNCs 3.0 wt% and (C) KC/CNCs 5.0 wt% films.

4. Conclusion

The reinforced bio-nanocomposites of KC matrix with cellulose nanocrystals were fabricated and potentiality of cellulose nano-sized filler was assessed on the structure and properties of resulted composites. The observation of TEM-based structures demonstrated that the CNCs were homogeneously distributed at lower filler loading. While compared the control KC film and the KC/CNCs film, the bio-nanocomposite films displayed higher tensile and modulus strength; decreased elongation at break; and reduced oxygen transmission rate. This is owing to the parameters such as the nano-scale size effects of the CNC (high L/D), the high content of cellulose crystalline districts, the well dispersion of CNCs within KC matrix, and the strong interaction between CNC and KC matrix.

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