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Transparent bionanocomposite films based on chitosan and TEMPO-oxidized cellulose nanofibers with enhanced mechanical and barrier properties

Bhawna Soni[a], El Barbary Hassan[a,*], M. Wes Schilling[b], Barakat Mahmoud[b,c]

[a] *Department of Sustainable Bioproducts, Mississippi State University, Box 9820, Mississippi State, MS 39762, USA*
[b] *Department of Food Science, Nutrition & Health Promotion, Mississippi State University, Box 9805, MS 39567, USA*
[c] *Department of Food Science, Nutrition & Health Promotion and Coastal Research & Extension Center, Mississippi State University, 3411 Frederic St., Pascagoula, MS 39567, USA*

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ABSTRACT

The development of biobased active films for use in food packaging is increasing due to low cost, environmental appeal, renewability and availability. The objective of this research was to develop an effective and complete green approach for the production of bionanocomposite films with enhanced mechanical and barrier properties. This was accomplished by incorporating TEMPO-oxidized cellulose nanofibers (2,2,6,6-tetramethylpiperidine-1-oxyl radical) into a chitosan matrix. An aqueous suspension of chitosan (100–75 wt%), sorbitol (25 wt%) and TEMPO-oxidized cellulose nanofibers (TEMPO-CNFs, 0–25 wt%) were cast in an oven at 40 °C for 2–4 days. Films were preconditioned at 25 °C and 50% RH for characterization. The surface morphology of the films was revealed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The thermal properties and crystal structure of the films were evaluated by thermogravimetric analysis (TGA-DTG) and X-ray diffraction (XRD). Incorporation of TEMPO-CNFs enhanced the mechanical strength of the films due to the high aspect ratio (3–20 nm width, and 10–100 nm length) of TEMPO-CNFs and strong interactions with the chitosan matrix. Oxygen and water vapor transmission rates for films that are prepared with chitosan and TEMPO-CNFs (15–25 wt%) were significantly reduced. Furthermore, these bionanocomposite films had good thermal stability. Use of TEMPO-CNFs in this method makes it possible to produce bionanocomposite films that are flexible, transparent, and thus have potential in food packaging applications.

1. Introduction

Since the 1980s, plastic debris has accumulated on the earth due to the production and use plastic packaging that is not biodegradable (Thompson, Moore, vom Saal & Swan, 2009). This has contributed to environmental issues caused by non-biodegradable waste materials and the depletion of natural resources. Approximately more than 300 million tons of plastic are produced throughout the world (Thompson et al., 2009). Packaging is the largest single market of plastics. In addition plastic disposal contributes to growing landfills and enhanced greenhouse effects when plastics are burned (Rhim & Ng, 2007). With the growing consumer demand for high quality food products and concern for limited natural resources, researchers have investigated the use of biobased materials that are environmentally friendly, biodegradable, renewable, and abundant in nature. These biobased materials are being investigated for their feasibility to replace petrochemical based packaging such as, polyolefins and polyesters with a variety of renewable biopolymers. Polysaccharides (Krochta & Mulder-Johnston, 1997), proteins (Cuq, Gontard & Guilbert, 1998), lipids (Gennadios, Ghorpade, Weller & Hanna, 1996), and their composites (Bourtoom, 2008) can be used to produce biodegradable packaging that can maintain product quality and reduce waste disposal problems. Water vapor and oxygen permeability, mechanical strength, transparency, and flexibility are important properties for packaging films. Therefore, film formation requires the use of at least one component that is capable of forming a structural matrix with a sufficient cohesiveness. The degree of cohesion of the polymer matrix affects film properties such as density, permeability and porosity, brittleness and flexibility (Rhim & Ng, 2007). Previous research has evaluated chitosan (Martínez-Camacho et al., 2010), starch (Ghanbarzadeh, Almasi & Entezami, 2011), hemicel-

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* Corresponding author.
E-mail address: e.hassan@msstate.edu (E.B. Hassan).

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lulose (Hansen & Plackett, 2008), xylan (Saxena, Elder & Ragauskas, 2011), cellulose (Wu et al., 2016), and their derivatives for film forming properties.

Chitosan is a natural polycationic, deacetylated derivative of chitin, which is found in the crustacean's shell, insect's cuticle and cell wall of fungi. It is a linear polysaccharide consisting of (1,4)-linked 2-amino-deoxy-β-D-glucan, which is the second most abundant polysaccharide found in nature after cellulose (Dutta, Dutta & Tripathi, 2004). Chitosan exhibits unique physicochemical properties including biocompatibility, non-toxicity, biodegradability, excellent film forming ability and strong antimicrobial and antifungal activities (Darmadji & Izumimoto, 1994; Jo, Lee, Lee & Byun, 2001). Chitosan has been evaluated for its applicability in biotechnology, pharmaceutics, biomedicine, packaging, wastewater treatment, cosmetics, and food science among others (Belgacem & Gandini, 2008). Chitosan has been used to produce active biodegradable films to extend the shelf-life of food and prevent contamination. Chitosan may be more advantageous than other biomolecule based active films due to its antimicrobial activity and ability to chelate bivalent minerals (Chen, Zheng, Wang, Lee & Park, 2002). However, despite the numerous advantages and unique properties of chitosan, its films are poor barriers to gas and water vapor and have poor mechanical properties, which restricts its use in packaging applications. Therefore, several strategies have been used to improve the mechanical and barrier properties of chitosan films, including blending chitosan with polyvinyl alcohol (Li, Chen & Wang, 2015), poly *N*-vinyl pyrrolidone (Sakurai, Maegawa & Takahashi, 2000), polyethylene glycol (Kiuchi, Kai & Inoue, 2008), polyethylene oxide (Amiji, 1995), starch (Bourtoom & Chinnan, 2008), collagen (Sionkowska, Wisniewski, Skopinska, Kennedy & Wess, 2004), cellulose (Dehnad, Mirzaei, Emam-Djomeh, Jafari & Dadashi, 2014; Fernandes et al., 2009; Fernandes, Freire, Silvestre, Pascoal Neto & Gandini, 2011; Shih, Shieh & Twu, 2009), carboxymethyl cellulose (Dayarian, Zamani, Moheb & Masoomi, 2014) sulfonated cellulose fibers (Li, Chen & Wang, 2015), hydroxypropylmethylcellulose (Sebti, Chollet, Degraeve, Noel & Peyrol, 2007), and cellulose acetate (Abou-Zeid, Waly, Kandile, Rushdy, El-Sheikh & Ibrahim, 2011). Polymer blending is the most effective method to create biobased films with desirable properties.

The formulation of composite films from the utilization of green materials contributes to a more sustainable society. Chitosan-cellulose combinations are compatible due to structural similarity, which results in fibers with the physicochemical properties of chitosan and the mechanical properties of cellulose fibers (Twu, Huang, Chang & Wang, 2003; Wu et al., 2004; Yin, Luo, Chen & Khutoryanskiy, 2006). Cellulose is used to produce potential reinforcing bionanomaterials called cellulose nanofibers (Soni, Hassan & Mahmoud, 2015). Cellulose nanofibers (CNFs) have been researched for their use in biodegradable packaging due to their renewable, low cost, low density, and nonabrasive nature. This allows them to formulate bio-based nanocomposites with easy process ability. All these important characteristics of CNFs have made it an attractive candidate for nanomaterial research fields. More recently, cellulose of hardwood pulp (Shih, Shieh & Twu, 2009) and nanocellulose (Dehnad, Mirzaei, Emam-Djomeh, Jafari & Dadashi, 2014) have been incorporated into chitosan matrices to produce bionanocomposite films. Similarly, cellulose nanowhiskers (CNWs) and cellulose nanocrystals (CNCs) have been reinforced into chitosan biopolymers to produce green nanocomposite films, with improved thermal, mechanical and oxygen barrier properties (de Mesquita, Donnici & Pereira, 2010; El Miri et al., 2015; Li, Chen & Wang, 2015). However, in these research projects, water vapor permeability and transparency of the films was not evaluated. Furthermore, bacterial cellulose (Fernandes et al., 2009) incorporated into chitosan matrix have shown reasonable thermal, and mechanical properties but have not shown any concern about moisture permeability and oxygen barrier quality. Polysaccharides are generally good oxygen barriers because hydrogen bonds contribute to excellent packing of the material and thus a low permeability. Water vapor and oxygen resistivity are fundamental requirement for new packaging materials since water molecules contribute microbial growth and influence the shelf life of the packaged products at different water activities and temperatures. Oxygen promotes degradation mechanisms in food such as corrosive phenomena, oxidations, and great modification of organoleptic properties (Russo, Simon & Incarnato, 2006). The tensile strength is an important factor in the film forming processes since brittle films are more likely to fracture. Thus testing tensile strength is a good way to measure how strong a material will be under certain conditions. In a long run, it is necessary to ensure a safe, high quality material and avoiding the major liabilities associated with providing non-compliant products. These actions will keep the end consumer satisfied and dramatically reduce the chance of failure of the packaging.

Recently, completely individualized cellulose nanofibers have been extracted from cotton stalks (Soni, Hassan & Mahmoud, 2015) by 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation under moderate aqueous condition (Saito, Kimura, Nishiyama & Isogai, 2007). This oxidation process coupled with ultrasonication selectively converts primary alcohols to aldehyde and carboxylate groups (Soni, Hassan & Mahmoud, 2015). The width and length of TEMPO —CNFs was ranging from 3 to 15 nm and 10–100 nm of range. This was the first time to develop uniform nano-sized fibers, which are not only small in diameter but also small in length with more than 90% yield from cotton stalks (Soni, Hassan & Mahmoud, 2015). However, to the best of our knowledge, there are no studies about the blending of TEMPO-oxidized cellulose nanofibers and chitosan for producing bionanocomposite films with enhanced comprehensive performance for packaging applications. Hydrogen bonds and electrostatic attraction between the negatively charged carboxylate groups ($-COO^-$) and the positively charged ammonium groups ($-NH_3{}^+$) of chitosan are the driving force for the best combination of both the polymers (Scheme 1). Therefore, these strong bonds ensure the high compatibility between both TEMPO-CNFs and the chitosan biopolymers.

The aim of this research is to describe a fully green approach for the preparation of transparent and high performance bionanocomposite films based on chitosan matrices with TEMPO-oxidized cellulose nanofibers as reinforcing agents. Extensive characterization of the chitosan/TEMPO-CNFs films revealed the unique properties of these films.

2. Experimental

2.1. Materials

Chitosan (DDA ∼ 72%) was synthesized from Mississippi gulf brown shrimp (penaeus aztucus) exoskeletons, which were obtained from the Mississippi Gulf Coast in Biloxi, MS. Cellulose was isolated from cotton stalks by alkaline-acid pretreatment and used for the preparation of nanocellulose by the TEMPO-mediated oxidation method (Soni, Hassan & Mahmoud, 2015). Morphological (FE—SEM, AFM), structural (FTIR), and thermal analysis (TGA-DTG) of TEMPO-CNFs were investigated in our previous work (Soni, Hassan & Mahmoud, 2015). All chemicals used in this study were purchased from commercial resources and used as received without further purification. The following chemicals were purchased from Fisher Scientific, USA: ethanol (95%), glacial acetic acid, calcium sulfate, calcium nitrate, magnesium nitrate hexahydrate, potassium sulfate, sorbitol, and TEMPO