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Novel nanofibrillated cellulose/chitosan nanoparticles nanocomposites films and their use for paper coating

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ABSTRACT

Novel nanocomposites films were prepared from TEMPO-oxidized nanofibrillated cellulose isolated from rice straw, chitosan nanoparticles (CHNP), and glycerol by solution casting. The percentage of chitosan nanoparticles ranged from 2.5 to 20% while a fixed ratio of glycerol (25%) was added. The effect of chitosan nanoparticles on porosity, tensile strength properties, water vapor permeability, grease-proof, and antimicrobial properties was studied. The results showed that addition of chitosan nanoparticles can improve tensile strength properties, reduce porosity, and impart NFC antimicrobial properties against Gram-positive bacteria (*Staphylococcus aureus*), Gram-negative bacteria (*Escherichia coli*), and yeast (*Saccharomyces cervisiae*). CHNP did not affect WVP or grease-proof properties of NFC films.

The mixture containing CNF and 10% CHNP was used for paper coating and the effect of coating on tensile strength, porosity, water vapor permeability, water absorption, and grease-proof properties of paper sheets was studied. The results showed coating of paper sheets with thin film of NFC or NFC/CHNP can improve tensile strength properties, decrease porosity and water absorption, and increase grease-proof properties of paper sheets but did not affect their WVP. Presence of CHNP in the coating mixture resulted in higher tensile strength properties of coated paper sheets than in case of using NFC alone but no noticeable differences were found regarding porosity, WVP, grease proof, and water absorption of paper sheets coated with NFC or NFC/CHNP under the conditions used.

1. Introduction

The development of polymeric materials, based on renewable resources has become increasingly important in recent years due to the inevitable rising prices of petroleum-based materials and environmental concerns. Nowadays, most materials used in the packaging industry are produced from fossil fuels (Vieira et al., 2011). Therefore, the utilization of renewable resources is of great significance for sustainable development. Many bio-based polymers from renewable resources such as cellulose, starch, chitin and chitosan have been studied for application in packaging (De Azeredo, 2009). Cellulose and chitosan are the most abundant natural polymers. They have close chemical structure. The former consists of D-anhydroglucose units joined together by 1,4-β-glycosidic linkages (Klemm et al., 2005) while the later consists of glucosamine and *N*-acetyl glucosamine units joint by 1,4-β-glycosidic linkages (Pillai et al., 2009). Recently, cellulose and chitosan nanomaterials have been in the spot light of research in different areas. Nanofibrillated cellulose (NFC) is an interesting nanomaterial with unique physicomechanical properties such as high tensile strength properties, low density, oxygen barrier properties, transparency, ability for chemical modification, biodegradability and biocompatibility. Different technologies have been used for isolation of NFC from different resources; these technologies are based on mechanical, enzymatic/mechanical, or chemical/mechanical actions on cellulose fibers (Abdul Khalil et al., 2014; Kalia et al., 2014; Zhang et al., 2013). The ability of NFC to form films with good mechanical properties, air and oxygen barrier, and transparency is another advantage since no dissolution and precipitation of cellulose are necessary for making films (Fukuzumi et al., 2009). NFC has been used in different areas such as reinforcing elements in nanocomposites, coating for paper products, tissue engineering, and drug delivery systems (Kolakovic et al., 2012; Abdul Khalil et al., 2014; Kalia et al., 2014; Jorfi and

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Foster, 2015; Hassan et al., 2015). But cellulose lacks resistance to attack by some microorganisms due to its polysaccharide nature and absence of functional groups having antimicrobial activity. On the other hand, chitosan nanoparticles have unique physicochemical properties compared to bulk chitosan such as larger surface area, i.e., higher surface charge density (gives more cationic sites) and higher affinity to bacteria cells due to their ability to tightly adsorbed onto their surface to disrupt the membrane and kill them (Avadi et al., 2004; Qi et al., 2004; Zhang et al., 2010; Romainor et al., 2014). Chitosan nanoparticles are prepared by different methods from chitosan solutions such as emulsion-droplet coalescence (Tokumitsu et al., 1999), emulsion solvent diffusion (El-Shabouri, 2002), reverse micellar method (Mitra et al., 2001), ionic gelation, polyelectrolyte complexation (Calvo et al., 1997; Sarmento et al., 2006) and desolvation (Tian and Groves, 1999). Chitsoan nanoparticles have many potential applications in different areas (Singh and Mishra, 2015; Cheaburu-Yilmaz et al., 2015) such as drug delivery systems (Duttagupta et al., 2015), heavy metal ion removal (Trujillo-Reyes et al., 2014) and as antimicrobial and oxygen barrier material in nanocomposites (Radulescu et al., 2015).

Due to interesting and complementary properties of both chitosan and cellulose, they have been used together in composites. For preparation of these composites, chitosan is first dissolved in an appropriate solvent such dilute acetic acid then mixed with cellulose or cellulose solution and the mixture is casted and dried. The formed chitosan composites is water sensitive and contain residual acetic acid unless alkali treated to convert the quaternary chitosan to its original non-protonated form. On the other hand, the use of chitosan nanoparticles, which are water insoluble, could have positively charged surface, and highly suspended in aqueous medium with cellulose can impart the later antimicrobial properties without the use of acid for dissolving chitosan. For these reasons, chitosan nanoparticles were used with cellulose to impart it antimicrobial properties. For example, chitosan nanoparticles were coated onto surface of oxidized cellulose fibers to prepare antimicrobial cellulosic materials (Sauperl et al., 2015). The study also proved stronger adhesion of the positively charged chitosan nanoparticles to the surface of oxidized cellulose fibers than non-oxidized fibers. In a similar study, paper sheets made from untreated fibers were impregnated with chitosan nanoparticles and chitosan solution (Fithriyah and Erdawati, 2014). The results showed higher impregnation of paper sheets when chitosan nanoparticles were used than in case of using chitosan solution. The strong adhesion of chitosan nanoparticles was utilized in another study for doping of cellulose film prepared by casting cellulose from NaOH/Urea/thiourea solvent system containing chitosan nanoparticles (Romainor et al., 2014). The doped films showed good antimicrobial properties against *Escherichia coli* bacteria (~85% maximum inhibition). Chitosan nanoparticles were also used with some cellulose derivatives to improve mainly their antimicrobial properties. For example, carboxymethyl cellulose films containing chitosan nanoparticles were prepared to prepare edible film with antimicrobial properties (De Moura et al., 2011). Improvement of thermal and mechanical properties was observed in films containing chitosan nanoparticles in addition to the imparted antimicrobial properties. However, the composite films are still highly sensitive to water due to solubility of carboxymethyl cellulose in water. The incorporation of chitosan nanoparticles into hydroxypropyl methyl cellulose to prepare antimicrobial films was studied. Improvement of mechanical properties of cellulose films was also reported (De Moura et al., 2009).

Since NFC is not antimicrobial material, the use of nanoparticles to impart it that property is one of the active areas of research to widen the applications of NFC. Different nanoparticles such as silver (Martins et al., 2012; Xiong et al., 2013), zinc oxide (Martins et al., 2013), and titanium dioxide (Missoum et al., 2014) have been added with NFC to impart it antimicrobial properties. However, for the best of our knowledge, the use of chitosan nanoparticles with nanofibrillated cellulose to prepare films with antimicrobial properties has not been studied so far.

The current work is focused on the development of new and natural nanostructured films of NFC and chitosan nanoparticles. The properties of glycerol-plasticized NFC/chitosan nanoparicles films regarding their tensile strength, water vapor permeability, porosity, grease proof, and antimicrobial properties were investigated. In addition, use of NFC/chitosan nanoparticles mixture for coating of paper sheets and effect of coating on tensile strength, water vapor permeability, porosity, and grease proof properties were briefly studied.

2. Experimental

2.1. Materials

Rice straw pulp was obtained by pulping of rice straw with 15% aqueous sodium hydroxide solution at 150 °C for two hours. After washing the pulp to remove excess chemicals, it was bleached using sodium chlorite/acetic acid mixture (Wise et al., 1946). Chemical composition of the bleached pulp was determined according to the standard methods (Browning, 1967) and was: Klason lignin 1.46%, alpha-holocellulose 69.7%, hemicelluloses 19.7%, and ash content 10.6%.

Chitosan was a low molecular weight grade and used as received (75–85% deacetylated; Brookfield viscosity 20–300 cP, 1 wt.% in 1% acetic acid at 25 °C). Analytical grade sodium tripolyphosphate, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), sodium hypochlorite, ethanol, and glacial acetic acid were used as received.

2.2. Preparation and characterization of chitosan nanoparticles

Chitosan nanoparticles (CHNP) were prepared according to the previously published method via ionic gelation where chitosan dissolved in acetic acid (2% chitosan solution in 2% acetic acid) was precipitated by slow addition of 0.01 wt.% sodium tripolyphosphate solution (Dounighi et al., 2012). The obtained nanoparticles were characterized using high-resolution transmission electron microscopy (JEM-2100 transmission electron microscope, JEOL, Japan). Particle size distribution and the zeta potential of chitosan nanoparticles were determined using Zetasizer Nano-ZS90 (Malvern Instruments). The analysis was performed at a scattering angle of 90 at a temperature of 25 °C using samples diluted with de-ionized distilled water.

2.3. Preparation and characterization of nanofibrillated cellulose (NFC)

Nanofibrillated cellulose was prepared from bleached rice straw pulp according to the previously published methods (Saito et al., 2007). Rice straw pulp (3 g) was dispersed in distilled water (400 ml) with TEMPO (0.048 g, 0.3 mmol) and sodium bromide (0.48 g, 4.8 mmol). Then 30 ml of sodium hypochlorite solution was then added with stirring and the pH was adjusted to 10. At the end of reaction the pH is adjusted to 7 and the product was centrifuged at 5000 rpm. The product was further purified by repeated adding water, dispersion, and centrifugation. Finally the product was purified by dialysis against de-ionized water.

To obtain nanofibrillated cellulose (NFC), the oxidized pulp was disintegrated by a high-shear homogenizer (CAT Unidrive 1000) at 10000 rpm using pulp suspensions of 2%.

The prepared nanofibrillated cellulose was characterized regarding its carboxylic groups' content of oxidized fibers according to TAPPI Test Method T237cm-98 and found to be 0.31 mmol/g.