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Hydroxypropyl cellulose/rice straw oxidized cellulose nanocrystals nanocomposites and their use in paper coating

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ABSTRACT

A series of hydroxypropyl cellulose (HPC)/oxidized cellulose nanocrystals (OXCNC) nanocomposites films was prepared via casting and evaporation. OXCNC was used in ratios from 2.5 to 20% in HPC matrix. The prepared nanocomposites films were evaluated using scanning electron microscopy (SEM), X-ray diffraction (XRD), dynamic mechanical thermal analysis (DMTA), tensile strength properties (TS) and water vapor permeability (WVP). Significant increase in the crystallinity and tensile strength accompanied by an increase in WVP of HPC films occurred as a result of adding OXCNC. HPC/10% OXCNC film was found to possess the maximum tensile strength properties and that composition was chosen for coating bagasse paper sheets. Coating of paper sheets increased TS, WVP and decreased porosity of the paper sheets. The slight increase in WVP of the films and the coated paper sheets was attributed to the hydrophilic nature of OXCNC.

1. Introduction

The increasing interest in alternative and durable packaging materials research over the last few years is due to the concern of environmental safety of synthetic packaging and coating materials as well as consumer demands for high quality and long shelf life products. Different renewable biopolymers – processed by different methods – have been used for packaging applications (Khan et al., 2014). Cellulose-based materials are considered the most common renewable bio-based packaging materials e.g., paper and paperboard. Due to its hydrophilicity and porosity, paper loses its physical and mechanical properties because of water absorption from the environment or from the packaged materials, especially in case of food packaging. Coating with polyolefins, aluminum foil and plastics improve the barrier properties to water vapor, oxygen and aroma but on the other hand, the obtained material loses its biodegradability and recyclability due to the addition of synthetic polymer layers. Biopolymers can be considered as a promising alternative to synthetic polymers. Recently, the use of nanotechnology to develop biopolymer composites with addition of nanofillers (derived from natural resources) has opened new possibilities for improving their mechanical and barrier properties (Bilbao-Sainz et al., 2011).

A new class of cellulosic composites has been developed where the critical problems of reinforcement and matrix interfacial adhesion can be overcome by using cellulosic derivatives as the matrix and cellulosic fibers as reinforcing agent (Huber et al., 2012; Nishino et al., 2004; Soykeabkaew et al., 2008).

The nano-scaled celluloses, with high strength and stiffness, are suitable candidates to become promising reinforcing elements for the preparation of composite materials (Tee et al., 2013). Comparing to the neat polymers, CNC containing composites has higher tensile strength properties (higher tensile strength and modulus) due to this rod-like structure, high crystallinity, and stiffness. CNC can align and orient along matrix axis improving mechanical performance (Chen et al., 2011).

Rice straw is a common agricultural residue in many countries in the world. Rice straw fibers have similar properties to hardwood fibers such as short fiber length, hemicelluloses that consist mainly of pentoses (mainly xylose and arabinose sugars), and lignin which consists mainly of syringyl–guaiacyl units. Rice straw fibers have diameters from 5 to 14 μm with lengths from 0.65 to 3.48 mm (Hans and Rowell, 1997; Hassan et al., 2012). Rice straw fibers are characterized also by the presence of high amount of silica (~15% of fiber weight). Due to high silica content in rice straw, its use in papermaking is not widely practiced. After pulping and bleaching of rice straw, silica remains in the pulp in significant amounts

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causing deterioration of strength properties of paper products. In addition, silica in the black liquor left from the alkaline pulping process causes problems during concentration of the liquor to be used as fuel. In many countries, burning of rice straw leads to serious environmental problems (Hassan, 2015).

Many studies have been conducted dealing with nanocellulose derived from rice straw as a source for cellulose fibers. Isolation of cellulosic nanomaterials from rice straw and their use in novel bionanocompsites having the potential to be used in different applications have been recently studied (Hassan, 2015).

HPC is an important thermoplastic, water-soluble and temperature-sensitive cellulose ether, which can be processed by virtually all fabrication methods used for plastics. HPC finds wide applications in the construction, medicine, food, daily chemical industry, and "smart" materials fields (Qiu and Hu, 2013). Moreover, HPC films are characterized by excellent flexibility, low T_g at high humidity and being a barrier to oil and fat.

Few studies dealt with improving properties of HPC by incorporation of nanocellulose. For example, incorporation of CNC into HPC matrix using a mixing/evaporation technique was carried out by Ma et al. (2014). The prepared cellulosic nanocomposite membranes showed significant increase in the tensile strength and Young's modulus at 5 wt% content of CNC when compared to neat HPC. The use of carboxymethylated nanofibrillated cellulose powder and TEMPO oxidized nanofibrillated cellulose as reinforcing fillers with HPC were also reported (Eyholzer et al., 2010; Johnson et al., 2009). The use of TEMPO-oxidized nanofibrillated cellulose in HPC nancomposites showed strong fibril-matrix interactions, as evidenced by remarkable storage modulus retention at high temperatures and a suppression of matrix glass transition at 5 wt% nanocellulose loadings (Johnson et al., 2009). Oxidation by TEMPO converts the cellulose primary C6 hydroxyls on the CNC surfaces into the more polar carboxylic groups. Nanocomposite films based on HPC matrix and fibrillated oxidized celluloses were found to have superior mechanical properties when compared to those prepared non-modified CNC and MFC. The improvement in mechanical properties could be attributed to the higher H-bonding groups, dipole-dipole interaction, and Van der Waals forces between HPC and oxidized nanocelluloses.

The current work aims to investigate using of oxidized CNC (OXCNC) isolated from rice straw as reinforcing elements to improve tensile strength properties of HPC and decrease its water vapor permeability, and use HPC/OXCNC mixture as a coating for paper sheets made from bagasse pulp.

2. Experimental

2.1. Materials

HPC of molecular substitution (MS) 3.4–4.4 propylene oxide groups per anhydroglucose unit, DS 2.9 and average molecular weight (Mw) of 100,000 g/mol was used. Sodium bromide, sodium hypochlorite solution and 2, 2, 6, 6- tetramethyl-1- piperidinyloxy (TEMPO) were purchased from Sigma Aldrich and used as received. All other reagents were of analytical grade.

Bleached kraft bagasse pulp was kindly supplied by Qena Company for Pulp and Paper, Qena, Egypt. The chemical composition of bagasse pulp was: α −cellulose 70.6%, pentosans 26.8%, ash 0.82% and degree of polymerization (number of glucose units in cellulose chain) 1174.

Rice straw pulp was obtained by pulping of rice straw with 15% aqueous sodium hydroxide solution at 150 °C. 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: Klason lignin 1.46%, α −cellulose 69.7%, pentosan 19.7%, and ash content 10.6%.

2.2. Preparation of CNC and OXCNC from rice straw

CNC were prepared from the bleached rice straw pulp using 64% sulfuric acid for 45 minutes at 45 °C (Hassan et al., 2014). The obtained suspension was purified by repeated centrifugation and washing with water and finally dialyzed against water. The suspension was then treated using ultrasonic processor for 2 minutes to obtain gel-like material.

Oxidized cellulose nanocrystals were prepared according to the previously published method (Habibi et al., 2006): 1.94 g (4 mmol of anhydroglucose units) of cellulose were suspended in water (150 ml) containing 30 mg of TEMPO, 195 mmol and 0.6 mg of sodium chlorite (5.7 mmol) at room temperature for 30 min. The TEMPO_mediated oxidation was initiated by slowly adding 14.7 ml of 13% NaClO (20.4 mmol) over 20 min at room temperature under gentle agitation. The reaction pH was monitored using a pH meter and maintained at 10 by incrementally adding 0.5 M NaOH. About 15 ml of methanol was then added to react and quench with the extra oxidant. After adjusting the pH to 7 by adding 0.5 M HCl, the TEMPO_oxidized product was washed with deionized water by centrifugation and further purified by dialysis against deionized water for two days. Carboxylic groups' content of CNC was determined according to TAPPI Test Method T237cm-98 and found to be 0.22 mmol/g.

The obtained nanocrystals were characterized using high-resolution transmission electron microscopy (HR-TEM) (JEM-2100 transmission electron microscope, JEOL, Japan**).**

2.3. Preparation of OXCNC/HPC films

HPC aqueous solution (2 wt.%) was prepared .The aqueous dispersion of OXCNC (1 wt. %) was added to the HPC solution in different ratios ranging from 2.5 to 20% (based on dry weight of HPC) and the mixture was stirred for two hours. The suspension was poured and spread evenly in Teflon dishes of diameter 10 cm and dried at 40 °C for 12 h.

2.4. Characterization of OXCNC/HPC films

Scanning electron microscopy was performed for HPC, HPC/10%OXCNC films using a Jeol JXA 840A system running at 5–10 keV. Before scanning, samples were coated with gold using a sputter coater system (Edwards Sputter Coater, UK). Diffraction patterns were obtained using a Phillips X-ray diffractometer. The diffraction patterns were recorded using Cu-Ka radiation at 40 kV and 25 mA. Tensile tests were carried out with a Lloyd instrument (LR10 K; Lloyd Instruments, Fareham, UK) with a 100-N load cell. The measurements were performed at a crosshead speed of 2 mm/min at 25 °C. The samples were prepared by cutting strips of the films 50 mm long and 10 mm wide. The distance between the jaws was 20 mm. DMTA of the nanocomposites films was carried out with an Anton Paar MCR-301 rheometer (Anton Paar, Graz, Austria) working in tensile mode. The measurements were performed at a constant frequency of 1 Hz and a strain amplitude of 0.08% in the temperature range from 100 to 150 °C with a heating rate of 3 °C/min and a distance between the jaws of 20 mm. Static water vapor permeability (WVP) test was carried out according to the ASTM standard (ASTM E96). Film samples were conditioned at 25 °C and 60% RH for 24 h and then used to hermetically cover cups containing 5 g of anhydrous calcium chloride. The films were hermetically sealed to the wall of cups with Teflon seals and silicone grease. The cups were accurately weighed and then placed inside a desiccator at 25 °C and 60% RH. The cups were weighed at regular