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Full Length Article

Development of polyvinyl alcohol/chitosan bio-nanocomposite films reinforced with cellulose nanocrystals isolated from rice straw

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ABSTRACT

Eco-friendly bio-nanocomposite films based on polyvinyl alcohol/chitosan (PVA/CS), reinforced with cellulose nanocrystals (CNC) were prepared by solution casting method. The CNC was successfully isolated from agriculture waste; rice straw (RS) by acid hydrolysis method and characterized with respect to their morphology, size, and thermal stability. The isolated CNC exhibited a rod-like structure with particle size around 15 nm in diameter. Subsequently, the PVA/CS films reinforced with various concentrations (1, 3, and 5 wt%) of CNC were assessed for their morphological features, thermal and mechanical properties. It was noted that the addition of RS-CNC increased the tensile strength (98.15 MPa) and thermal stability of the PVA/CS films. The bio-nanocomposites sustained similar transparency level of the PVA/CS blend film suggesting that the CNC were dispersed at the nanoscale range. The PVA/CS/CNC bio-nanocomposite film also exhibited good antifungal and antibacterial activity. Therefore, the present study suggests that the eco-friendly bio-nanocomposite film have great potential in food packaging applications.

1. Introduction

In past few decades, we have seen a great improvement in the quality of life resulting from the innovation and development of more sustainable products. Efforts have been taken to develop sustainable composite materials for a variety of industrial application owing to its renewability, biodegradability, low cost and non-petroleum based source [1]. To meet this increasing trend, there is a need to exploit resources that are sustainable and renewable. In this regard, polysaccharides such as chitin and cellulose are important since these two are the most abundant natural polymer.

Chitin is a linear polysaccharide comprised of 1,4-N-acetylglucosamine. Due to the large crystalline configuration and hydrogen bonding among carbonyl, hydroxyl and acetamide groups, chitin is not soluble in common solvents. Chitosan (CS) is extracted by N-deacetylation of chitin, and it mainly consists of glucosamine and N-acetylglucosamine units [2]. Chitosan is biocompatible, biodegradable, and is derived from plentiful and low-cost biomass [3]. Also, it has a good antimicrobial property that makes chitosan-based composites valuable in the packaging field. However, the poor mechanical and thermal properties, dissolution in highly acidic solution and low surface area, limit the application of CS in the packaging industry. Therefore, it is important to blend CS with another mechanically stronger and hydrophilic material such as poly (vinyl alcohol) [PVA] and nanocellulose. Blending of CS with other polymers is an important way to obtain high-performance materials. It is expected that the combination of PVA with CS might have substantial effects on the biological activities of films, taking into account the good biological performance of CS [4]. Poly (vinyl alcohol) is a non-toxic, water-soluble synthetic polymer, biodegradable, environmental friendly and is chemically stable. To further enhance the mechanical and barrier properties of PVA it is combined with other polymers or fillers in order to use it in the packaging industry [5]. Numerous researchers have emphasized the usefulness of cellulose fibers in improving the mechanical properties of PVA and CS based materials. Bonilla et al. [6] studied the blending of PVA with CS in various concentrations to obtain biodegradable films, and the results showed that the addition of CS significantly decreased the film deformability and concurrently increased the film rigidity, as well as providing the antimicrobial activity. Similarly, Luzi et al. [7] reported that the PVA, CS film reinforced with CNC extracted from *Actinidia deliciosa*

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pruning waste combined with carvacrol were able to modify the mechanical properties of the film. Previous reports suggest that the addition of CNC to PVA [8] and CS [9] significantly improved the mechanical properties of the film.

Cellulose is one of the most abundant natural biopolymers in the world, which is renewable and biodegradable. Mechanical and chemical treatments of the native cellulose yield a more useful class of materials, nanocelluloses such as nanocrystals and nanofibers. The cellulose nanocrystals (CNC) have gained great interest primarily in the field of nanotechnology due to its high mechanical strength, aspect ratio, environmental benefits, thermal, barrier properties and low cost [10]. Much effort has been committed to the use of CNC's as reinforcing agent in polymeric matrices. CNC consists of highly crystalline rod-like particles with a high specific area with diameters ranging from 1 to 100 nm and the length from ten to hundreds of nm [11]. Additionally, CNC possess abundant hydroxyl groups on their surfaces, making them hydrophilic nanomaterials, which may facilitate their dispersions within water-soluble polymer matrices [12]. Cellulose nanocrystals are obtained from many sources such as cotton, wood, tunicate, etc., Recently, various studies have been performed for the isolation of cellulose nanocrystals (CNC) from various agricultural residue such as grain straw [13], wheat straw [14], sugarcane bagasse [15], kenaf [16], waste cotton [17], Kiwi pruning wastes [7], and rice straw [18]. The lignocellulosic resources obtained from agricultural wastes are of great importance because of their abundance, low price, renewability, and biodegradability [19]. Rice straw (RS) is one such agricultural waste having great potential for the use as renewable cellulosic resources. Rice straw is a major by-product of cereal crop, which is the largest agricultural waste and is usually burned or used as animal feed and bedding material [20]. The relatively high cellulose content of RS makes it an attractive material for use in the preparation of biocomposites, which can effectively minimize the environmental contamination, saving the limited forest and petroleum resources, and thereby promoting the added value of RS. Only a few studies have been reported on the extraction and characterization of CNC from RS and the utilization of CNC as reinforcing fillers in the polymeric blend [13,18].

In this investigation, CNC from RS was used for the first time, as reinforcing filler in PVA and CS based blend. It would be interesting to study the formation of polymer blend films using the unique properties of CS, PVA, and CNC. Previously, Fortunati et al. [21] reported that the PVA_CS nanocomposites reinforced with CNC extracted from barley straw and husk as fillers modified the optical properties as well as thermal and mechanical properties of the film. Furthermore, it exhibited better antimicrobial properties against both bacteria and fungi. Therefore, the present study aimed to isolate the CNC from RS and to evaluate the reinforcing effects of various CNC concentrations on the PVA/CS film properties.

2. Materials and methods

2.1. Materials

Rice straw was collected from a local farm in Vellore, Tamil Nadu, India. Dialysis membrane and culture media (Hi-media, India), and glacial acetic acid (99.9%) [RANKEM, Mumbai, India] were used. PVA and sodium chlorite (80%) was purchased from Loba Chemie, Mumbai, India. Chitosan, polyethylene glycol, sodium hydroxide pellets (97.0%) and sulfuric acid (97.0%) were procured from SRL, Mumbai, India.

2.1.1. Cultures

The bacterial cultures *Staphylococcus aureus* (ATCC 29213), *Escherichia coli* (ATCC 25922) and *Pseudomonas aeruginosa* (ATCC 27853) were procured from American Type Culture Collection (ATCC). *Streptococcus mutans* (MTCC 497) were purchased from Microbial Type Culture Collection (MTCC). Fungal cultures such as *Colletotrichum gloeosporioides* and *Lasiodiplodia theobromae* used in this study were previously isolated from mango fruit samples [22].

2.2. Extraction of cellulose nanocrystals from rice straw

Cellulose nanocrystals (CNC) were extracted from RS by acid hydrolysis method [23]. Initially, the RS were treated with 4% sodium hydroxide for 3 h under constant stirring at 80 °C to remove hemicellulose, pectin, and residual starch. Afterwards, delignification was attained by bleaching the fibers with 1.7% w/v sodium chlorite and acetic acid buffer at 80 °C for 4 h, this process was repeated thrice. Further, the bleached fibers were filtered, rinsed with distilled water until the residues were neutralized, and was air dried [24]. The CNC was prepared by sulfuric acid hydrolysis (65 wt%) of resultant cellulose at 55 °C for 45 min under constant mechanical stirring. Subsequently, the suspension was diluted using ice-cold distilled water and centrifuged at 10,000 rpm for 10 min to remove the excess sulfuric acid. The aqueous CNC suspension was dialyzed against distilled water using a cellulose membrane until a constant pH was attained. The suspension was then sonicated for 15 min, using a probe ultrasound (Sonics Vibra Cell Ultrasonic), and stored in a refrigerator until further use. The sonication treatment was carried out in an ice water bath to avoid overheating. Also, a specified amount of the CNC suspension was freeze-dried (Lyodel) and stored for further analysis.

2.3. Characterization of raw RS, bleached RS and extracted CNC

The surface morphology of the raw and bleached RS fibers was analyzed using an FEI Quanta FEG 200-High Resolution Field Emission Scanning Electron Microscope (FESEM) at a magnification of 400x, under an accelerating voltage of 10 kV. The samples were spluttered with gold after mounting onto an aluminum stub by double side faced tape.

The CNC morphology was assessed using a Transmission electron microscope (TEM) [Tecnai F12 JEOL-JEM 2100]. The diluted CNC suspension was dropped on a Cu grid covered with a thin carbon film. The negative staining of nanocrystals using 2 wt% uranyl acetate solution was performed to enhance the contrast. The samples were air dried at room temperature and used for TEM analysis.

The zeta potential of CNC was analyzed using Zeta sizer-Nano ZS90 (Malvern Instruments, United Kingdom).

FTIR spectra of the CNC were conducted using an Agilent cary 660 with transmittance mode from 600 to 4000 cm^{-1} at a resolution of 8 cm^{-1}. The CNC was analyzed by means of KBr discs prepared by using lyophilized CNC and dust of KBr.

X-ray diffraction (XRD) patterns of raw RS, bleached RS fibers, and CNC were studied using an X-ray diffractometer (PANalytical X'pert Pro), at operating conditions of 40 kV and 40 mA, equipped with a monochromatic CuKα radiation source (λ = 1.54 nm). The analysis was performed in the step scan mode with a 2θ angle over the range of 10–50°. The crystallinity index (CrI) was measured using the equation given below

$$\text{Crystallinity Index} = \frac{I_{200} - I_{am}}{I_{200}} \quad (1)$$

where I_{200} is the maximum intensity of the diffraction peak (200 peak) at 2θ = 22.7°, and I_{am} is the minimum intensity corresponding to the amorphous structure which was located at 2θ = 19°.

Finally, the thermal stability of the untreated raw RS, bleached RS fibers, and CNC was analyzed with Perkin Elmer thermogravimetric analyzer (TGA 7), UK. Each sample was heated from 30 °C to 700 °C at a rate of 10 °C min^{-1} in a nitrogen atmosphere.

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