

Development of regenerated cellulose/halloysite nanotube bionanocomposite films with ionic liquid

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ARTICLE INFO

Article history:

Received 17 January 2013

Received in revised form 13 March 2013

Accepted 28 March 2013

Available online 5 April 2013

Keywords:

Regenerated cellulose

Halloysite nanotubes

Ionic liquids

Bio-nanocomposite films

ABSTRACT

In this study, novel nanocomposite films based on regenerated cellulose/halloysite nanotube (RC/HNT) have been prepared using an environmentally friendly ionic liquid 1-butyl-3-methylimidazolium chloride (BMIMCl) through a simple green method. The structural, morphological, thermal and mechanical properties of the RC/HNT nanocomposites were investigated using X-ray diffraction (XRD), Fourier transform infrared (FTIR), field emission scanning electron microscopy (FESEM), thermal analysis and tensile strength measurements. The results obtained revealed interactions between the halloysite nanotubes and regenerated cellulose matrix. The thermal stability and mechanical properties of the nanocomposite films, compared with pure regenerated cellulose film, were significantly improved. When the halloysite nanotube (HNT) loading was only 2 wt.%, the 20% weight loss temperature (T_{20}) increased 20 °C. The Young's modulus increased from 1.8 to 4.1 GPa, while tensile strength increased from 35.30 to 60.50 MPa when 8 wt.% halloysite nanotube (HNT) was incorporated, interestingly without loss of ductility. The nanocomposite films exhibited improved oxygen barrier properties and water absorption resistance compared to regenerated cellulose.

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1. Introduction

In recent years, the development of environmentally friendly materials obtained from renewable resources has attracted enormous attention, spurred on by new sustainable development policies [1–3]. Cellulose is a readily available, naturally occurring biodegradable, and biocompatible linear polysaccharide in which D-glucopyranose rings are connected to one another with β -(1,4)-D-glycosidic links [4,5].

The solvent resistance of cellulose has promoted several researches for its dissolution and modification [6–11]. Consequently, room temperature ionic liquids have been used as 'green' solvents for cellulose regeneration due to their excellent properties such as good chemical and thermal stability, low flammability, low melting point and ease of recycling [12–16]. The confirmation of that ionic liquid 1-butyl-3-methylimidazolium chloride (BMIMCl) as a good solvent for cellulose has opened up a new way of developing a class of cellulose solvent systems [14,17,18].

It is widely accepted that the incorporation of nanofiller into bio-based matrixes to produce nano-biocomposite materials could

be a powerful solution to improve these properties even at low nanofiller content (typically less than 5 wt.%) [19–21]. Due to specific geometrical dimensions, aspect ratios partly affect the final material properties with preservation of the material biodegradability, without eco-toxicity [22,23].

Research on tubular silica based naturally occurring nanoparticles as reinforcing material is still new [24,25]. Halloysite is an aluminosilicate with the chemical composition $\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5(2\text{H}_2\text{O})$. As a kaolinite mineral, halloysite is mined from natural deposits and formed from amorphous allophone by long time weathering [26]. Halloysite nanotube (HNT) exhibits the tubular morphology of rolled layers due to the stress between the silicon dioxide and aluminum oxide sheets [27] (Fig. 1). The particles are 1–15 μm in length with an inner diameter of 10–150 nm [28]. HNTs never intertwine with each other due to their high surface and the unique geometry which indicates their potential to make the hydrogen bonding with polymers and ability to disperse well in the matrix [29].

To the best of our knowledge, detailed study on the characterization of regenerated cellulose/halloysites nanocomposites have not been reported in the literature. In the present work, a simple and environmentally friendly regenerated cellulose/halloysite nanocomposite preparation by direct water coagulation is reported which would lead to lower cost and less pollution. The effect

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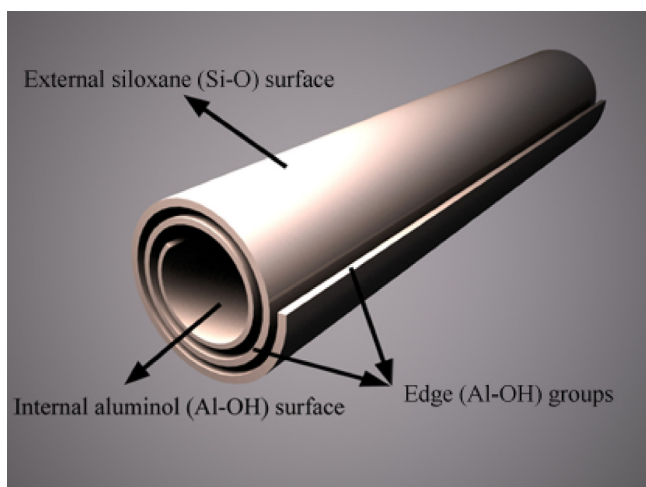


Fig. 1. Schematic structure of a halloysite nanotube (HNT).

of halloysite content on thermal, mechanical and morphological properties of the regenerated cellulose nanocomposite films investigated.

2. Experimental

2.1. Materials

Microcrystalline cellulose, a commercial reagent from Sigma with average powder size of 50 μm , Avicel type with the degree of polymerization of 350 was used. Ionic liquid, 1-butyl-3-methylimidazolium chloride (BMIMCl) with a purity of $\geq 95\%$ was supplied by Sigma Aldrich. Halloysite nanotube (HNT) clay, was purchased from Aldrich. The HNT tube dimension was 30–70 nm \times 1–4 μm .

2.2. Preparation of nanocomposite films

RC and RC/HNT nanocomposite films were prepared according to the following procedure: HNT at 2, 4, 6, and 8 wt.% with respect to cellulose content were dispersed for 90 min in BMIMCl using a sonicator (Model FB15053, Fisher Scientific Co., Germany) before the addition of cellulose powder. In order to dissolve the cellulose in ionic liquid BMIMCl, the mixture was heated at 90 $^{\circ}\text{C}$ for 24 h with constant stirring. The ratio of BMIMCl/cellulose was about 94/6 (wt.%). After degassing the solution in a vacuum oven, it was casted on a glass plate and immersed immediately in a distilled water bath at room temperature for 24 h to remove BMIMCl from the films, since BMIMCl is completely miscible with water in any ratio. The obtained nanocomposite films were washed with water and dried in a vacuum oven at 40 $^{\circ}\text{C}$ for 2 h. The thickness of the RC/HNT films was measured with a digital micrometer and found to be about 30 μm . All the dried films were stored in a moisture controlled desiccator until tested. The RC/HNT nanocomposites films prepared by different HNT contents (2, 4, 6 and 8 wt.% with respect to cellulose content) were coded as RC/HNT-2, RC/HNT-4, RC/HNT-6 and RC/HNT-8, respectively.

2.3. Characterization

Optical transmittance (T_r) of the nanocomposite films was measured with a UV-vis spectroscope (Shimadzu UV-3101PC, Japan) at wave lengths ranging from 400 to 800 nm. The thickness of composites is about 30 μm .

FESEM (field emission scanning electron microscopic) was performed using a JEOL JSM-6701F. The RC and RC/HNT nanocomposite films were frozen in liquid nitrogen, cryo-fractured, and vacuum dried. The fractured surface of the films was coated with gold prior to analysis.

FTIR spectra were recorded by a Perkin-Elmer 180 with resolution of 4 cm^{-1} for 32 scans over a wave number range of 4000–400 cm^{-1} .

X-ray diffraction measurements were performed on XRD diffractometer (Rigaku Miniflex II). Patterns with $\text{CuK}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) at 40 kV and 30 mA were recorded in the region of 2θ from 3 to 70. Peak fitting was performed on Magic software with Gaussian function. The crystallinity χ_c (%) of cellulose composites were estimated by Rabek's method, using the following relationship:

$$\chi_c = \left[\frac{S_c}{S_c + S_a} \right] \times 100 \quad (1)$$

where S_c and S_a are the area of crystal and amorphous diffraction peaks of samples, respectively.

Oxygen permeability rates were measured using a constant-pressure system and a soap bubble flow meter. Permeation tests were carried out at 25 $^{\circ}\text{C}$ with feed gas pressure of 5 bar gauge. The measurement was repeated three times for each sample. Pure gas permeability was calculated using Eq. (2):

$$P = \frac{1}{A\Delta p} \frac{dV}{dt} \quad (2)$$

where P is the permeability, Δp is the pressure difference across films (Pa), A is the effective surface area ($12.5 \times 10^{-4} \text{ m}^2$), l is the thickness of nanocomposites (m), t is the permeation time (s), V is the volume of the gas permeated through the membrane (m^3_{STP}).

Water absorption test was conducted according to ASTM D570-98. The samples (76.2 mm \times 25.4 mm \times 0.03 mm) were dried to a constant weight under vacuum prior to immersion in distilled water at 25 $^{\circ}\text{C}$ for 2 and 24 h. Weight gain of the samples were recorded by removal of the specimens from immersion and weighed. The average value for five samples from every formulation was reported. The % weight gain was determined by Eq. (3).

$$\% \text{weight gain} = \frac{W_w - W_d}{W_d} \times 100 \quad (3)$$

where, W_d and W_w are the weights of samples dry (before immersion) and wet (after immersion) respectively.

Contact angle test was performed using sisal drop method on DropMeter A-100 contact angle system (Maist Vision Inspection and Measurement Co. Ltd.) to characterize the nanocomposite film wetting behavior. The nanocomposite film (70 mm \times 20 mm \times 0.03 mm) was placed on a rectangular glass slide and deionised water droplets were poured on the film surface at 5 different points using a microsyringe.

Thermal analysis of the nanocomposite films was measured using Perkin Elmer TGA 7 (Perkin Elmer Instruments, USA). The temperature ranged from 30 to 900 $^{\circ}\text{C}$ with a heating rate of 10 $^{\circ}\text{C min}^{-1}$ under nitrogen.

The tensile properties were measured on LRX Tensile Testing Machine (Lloyd, USA) according to ASTM D882-10 at a crosshead speed of 10 mm/min at room temperature. The specimen gauge lengths were 30 mm and the specimen widths were 13 mm.

3. Results and discussion

Transparency is a useful criterion for the miscibility of the composite elements. Fig. 2 shows the photographs of RC and RC/HNR-8 films. The films were transparent and the background can be seen

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