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Regenerated cellulose/halloysite nanotube nanocomposite films prepared with an ionic liquid

Mohammad Soheilmoghaddam [a], Mat Uzir Wahit [b],*, Shaya Mahmoudian [c], Nurbaiti Abdul Hanid [a]

[a] Department of Polymer Engineering, Faculty of Chemical Engineering, Universiti Teknologi Malaysia (UTM), Johor, Malaysia
[b] Center for Composites, Universiti Teknologi Malaysia (UTM), 81310 Skudai, Johor, Malaysia
[c] Department of Textile Engineering, Kashan Branch, Islamic Azad University, Kashan, Iran

HIGHLIGHTS

- The RC/HNT nanocomposite films were prepared via ionic liquid, BMIMCl.
- XRD diffraction patterns and FESEM revealed well dispersed HNT in cellulose matrix.
- The nanocomposite films exhibited excellent mechanical properties.
- Moisture absorption and diffusion coefficient of RC reduced by HNT incorporation.
- Addition of HNT enhanced thermal stability and activation energy of the RC.

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ABSTRACT

Regenerated cellulose/halloysite nanotube (RC/HNT) nanocomposite films were successfully prepared in ionic liquid, 1-butyl-3-methylimidazolium chloride (BMIMCl) using solution casting method. The structural, morphological, thermal and mechanical properties of RC/HNT nanocomposites were investigated. X-ray diffraction analysis revealed a cellulose II crystalline structure and well dispersed HNT in RC/HNT nanocomposite films. At 6 wt.% HNT film, tensile strength and Young's modulus of RC films improved by 55.3% and 100%, respectively. Moisture absorption by the nanocomposites in an environment with 75% constant relative humidity was reduced by the addition of HNT to the RC. The presence of HNT enhanced the thermal stability and char yield of RC. The significant reinforcing effects of HNTs demonstrated that there is a possible interface interaction between cellulose and HNT which yielded better thermal and mechanical properties of the nanocomposite films as compared to pure RC.

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1. Introduction

Biopolymers from renewable resources have gained significant attention over the past decade. Due to their biodegradability, biopolymers are ideally positioned to reduce the over-exploitation of our limited fossil recourses [1]. Cellulose is the most abundant naturally occurring linear polymer in nature, which consists of β 1–4 glucopyranose units, exhibiting many unique properties and an applicability to a variety of uses such as paper, textiles, membranes, artificial fibers and the food industry [2].

However, the development and utilization of cellulose is an ongoing challenge as this natural polymer does not melt and is not soluble in usual solvents which have been attributed to formation of strong inter- and intra-hydrogen bonds and its partially crystalline structure. Moreover, serious environmental problems and the complicated processing procedures of classical viscose technologies for cellulose regeneration require considerable efforts. These efforts are still being scrutinized in order to find easier methods to get around these complex procedures [3,4].

Over the years, several solvent systems for the preparation of regenerated cellulose materials have been developed. Due to environmental concerns, N-methylmorpholine-N-oxide (NMMO)/water has emerged as the most commercially desirable process. However, the NMMO/water process still has some environmental issues to contend with including several adverse side reactions, the formation of undesired byproducts and expensive solvent recovery. These issues need to be overcome prior to efficient and environmentally-friendly production of regenerated cellulose [5,6].

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* Corresponding author. Tel.: +60 7 553 5909; fax: +60 7 553 6165.
E-mail address: mat.uzir@cheme.utm.my (M.U. Wahit).

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Recently, room temperature ionic liquids (ILs), which exhibit a series of unique properties such as chemical and thermal stability, non-flammability, negligible vapor pressure and recyclability, have emerged as 'green' solvents for cellulose regeneration. This class of environmentally friendly cellulose solvents have became an attractive alternative to conventional viscose technologies in the preparation of the regenerated cellulose materials [7–9]. In 2002, Swatloski et al. [9] were the first to report that ionic liquid 1-butyl-3 methylimidazolium chloride (BMIMCl) has good dissolving capability for cellulose, disclosing a new cellulose dissolution and processing method. Since then, a number of ILs dissolving cellulose have been found [4,10–12].

Over the past few decades, the incorporation of nanofiller (nano-sized filler) into a polymer matrix has drawn much attention, mainly due to its potential to increase the polymer's properties. Over the past few years, several studies have been conducted in which different nanofillers have been incorporated in a regenerated cellulose (RC) matrix to enhance thermal and physical properties. These include graphite oxide [13], carbon nanotube [14–16], nano-carbon black [17,18], nanohydroxyapatite [19,20] and nanoclay [3,5,21,22]. Recently, halloysite nanotubes (HNTs) have attracted interest as nanoparticles for polymers. HNT is a significant member of the kaolin group of clay minerals, with a chemical composition of $Al_2Si_2O_5(OH)_4$.nH2O, where $n = 0$ and 2, for dehydrated form halloysite (7 Å d_{001} spacing) and hydrated mineral halloysite (10 Å d_{001} spacing) respectively [23,24]. Halloysite nanotubes have a highly unusual meso/macroscopic structure, which results in the formation of an appropriate hollow nanotubular geometry [25]. In addition, its typical dimensions are on the nanoscale [23]. The surface of HNT is made of siloxane and few hydroxyl groups which presents the potential for hydrogen bond formation between HNT and polymer matrix [26,27]. The combination of siloxane surface, tubular geometry and also the higher stiffness of the HNT nanotubes can promote excellent nano reinforcement for polymer nanocomposites [28].

The main objective of the present study is to prepare an environmentally friendly RC/HNT nanocomposites by incorporating it into a cellulose matrix using an ionic liquid, BMIMCl, as solvent. To the best of our knowledge, this type of study has not been reported in the open literature. The morphology of RC and RC/HNT nanocomposite films was characterized by X-ray diffraction. Thermal stability, water absorption and mechanical properties of the films were also studied.

2. Experimental

2.1. Materials

Microcrystalline cellulose, a commercial reagent from Sigma with an 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 ≥95% was supplied by Sigma Aldrich. The inorganic filler, Halloysite nanotube (HNT) clay, was purchased from Aldrich. The HNT tube dimension was 30 nm × 0.25–4 μm.

2.2. Preparation of nanocomposite films

Cellulose/HNT nanocomposite films were prepared according to the following procedure; dried (3 h at 70 °C) cellulose was dissolved in ionic liquid BMIMCl with magnetic stirring for 4 h at 85 °C. Meanwhile HNT nanoclays were dispersed in BMIMCl using a sonicator (Model FB15053, Fisher Scientific Co., Germany) for 1 h followed by stirring for 4 h at 85 °C. Two solutions were mixed and stirred for 24 h at 85 °C to get a homogenous cellulose/HNT/ionic liquid solution with a cellulose concentration of 6 wt.%. After degassing the solution in vacuum oven, it was cast on a glass plate with a thickness of about 0.03 mm and immediately immersed into a distilled water bath at room temperature for 24 h in order to remove BMIMCL from the films, since BMIMCL is completely miscible with water in any ratio. The obtained nanocomposite films were washed with running water and dried in a vacuum oven at 45 °C for 3 h. All the dried films were stored in a moisture controlled desiccators until tested. The RC/HNT nanocomposites films prepared by different HNT contents (2, 4, 6 and 8 wt.%) were coded as RC/HNT-2, RC/HNT-4, RC/HNT-6 and RC/HNT-8, respectively.

2.3. Characterization

X-ray diffractometry (XRD) was performed on a Rigaku Miniflex II X-ray diffractometer with Cu-Ka radiation. The X-ray diffraction patterns were recorded with a step size of 0.05° and scanning speed of $0.02^\circ\ \mathrm{min}^{-1}$ from $2\theta = 2–70°$. The X-ray beam wavelength is 0.15147 nm.

The average crystalline size was determined by Scherrer's equation [29]

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

where D is the average crystallite size, β the corrected full width of the peak at half of the maximum intensity, FWHM (in radians), λ the wavelength of X-ray radiation (1.540562 Å), K is a constant related to the crystallite shape and is 0.84 for cellulose.

The peak widths, expressed in radians are inversely proportional to the average crystallite size, D. Based on Scherrer's equation [29] the RC nanocomposite films' average crystallite size was determined upon using $(1\,\bar{1}\,0)$ and (1 1 0)/(0 2 0) peaks from the XRD pattern to compare the products with each other. The β parameter was corrected using the following equation:

$$\beta = \sqrt{\beta_{\mathrm{exp}}^2 + \beta_{\mathrm{inst}}^2} \tag{2}$$

where β_{exp} corresponds to the experimentally determined full width at half of the maximum intensity, FWHM, of the peak while the β_{inst} is the instrumental broadening contribution.

The degree of crystallinity for RC and their nanocomposites was determined by means of the X-ray empirical method using Segal's equation [30].

Tensile testing was performed on an LRX Tensile Testing Machine (Lloyd, USA) according to ASTM D882-10 with crosshead speed of $10\ \mathrm{mm\ min}^{-1}$. A gauge length of 25 mm was used. The specimens were cut into strips of 60 mm × 13 mm × 0.03 mm. All measurements were performed at 23 °C with relative humidity of 60%. The samples were kept at 23 °C for 40 h before the test and experiments were repeated with 5 specimens of each formulation and the average values were reported.

Moisture absorption was conducted when the samples (60 mm × 13 mm × 0.03 mm) were dried until constant weight in an oven at 85 °C for 24 h, to remove the moisture before moisture absorption test. These samples were weighed immediately after removed from the oven. The samples were kept in a 75% constant relative humidity environment generated in a hermetic glass container with aqueous saturated NaCl solutions (ASTM E 104-02) at 25 °C. The moisture content (w%) was calculated as follows:

$$w = \frac{w_t - w_0}{w_0} \tag{3}$$

where w_t is the wet weight of films at each time and w_0 is the initial weight of dry films.

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