



Synthesis of kenaf cellulose carbamate using microwave irradiation for preparation of cellulose membrane



Sinyee Gan, Sarani Zakaria*, Chin Hua Chia, Hatika Kaco, Farah Nadia Mohammad Padzil

School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

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ABSTRACT

Cellulose carbamate (CCs) was produced from kenaf core pulp (KCP) using microwave reactor-assisted method. The effects of urea concentration and reaction time on the formation of nitrogen content in CCs were investigated. The CCs' solubility in LiOH/urea system was determined and its membranes were characterized. As the urea content and reaction time increased, the nitrogen content in CCs increased which enhanced the CCs' solubility. The formation of CCs was confirmed by Fourier transform infrared spectroscopy (FT-IR) and nitrogen content analysis. The CCs' morphology was examined using Scanning electron microscopy (SEM). The cellulose II and crystallinity index of the membranes were confirmed by X-ray diffraction (XRD). The pore size of the membrane displayed upward trend with respect to the urea content observed under Field emission scanning electron microscope (FESEM). This investigation provides a simple and efficient procedure of CCs determination which is useful in producing environmental friendly regenerated CCs.

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1. Introduction

In 1838, cellulose was found in the plant tissue and was used to produce a constant fibrous material. Since then, cellulose is generally accepted as a polymer consisting of D-anhydroglucose units bonded with α -1,4-glycosidic. Kenaf is a species of plant with scientific name *Hibiscus cannabinus* and considered as one of the most important commercially fibre sources which has world production at approximately 970,000 tones (Eichhorn et al., 2001). Kenaf fibres are proven to be a better option than wood fibres in producing textiles, paper, pressed wood materials and so on. Cellulosic kenaf fibre are renewable and recyclable thus assisting indirectly in the production of ethanol fuel additives and butanol (Ooi, Rambo, & Hurtado, 2011). Kenaf core consists of around 46.1% cellulose, 29.7% hemicellulose and 22.1% lignin (Ashori, Harun, Raverty, & Yusoff, 2006).

Several methods have been employed in synthesizing CCs and have been reported in many literatures. CCs is a combination of cellulose esters and carbamate acids which is unknown to occur in a free state. This compound can be attained through heating up a combination of both cellulose and urea at a temperature roughly 140 °C (Iller, Stupinska, & Starostka, 2007). In conventional methods, CCs are produced from the reaction of urea in alkaline solutions and organic solvents such as toluene and xylene with or without the presence of catalyst. However, this conventional process requires

a long reaction time, high temperature, catalysts and organic solvents. Nowadays, an alternative path to obtain CCs is through the mixing of cellulose with ammonia solution that contains urea. This alternative has limitations in technical applications because of the strict conditions imposed and highly involved of chemicals (Vo, Siroka, Manian, & Bechtold, 2010; Yin & Shen, 2007). The CCs is considered as an environmentally friendly material which could also serve as a potential alternative to petroleum based polymers since it can be renewed and biodegradable, while having natural compatibility properties and soluble in conventional solvents (Yin & Shen, 2007). The CCs have many applications due to its property which can be dissolved with ease in the organic solvents (Mormann & Michel, 2002).

Microwave heating is believed to be significantly accelerating the solubility of cellulose and its solution properties in the ionic liquid constitution. Zhu et al. (2006) stated that solutions containing up to 25 wt% cellulose content can be prepared in the ionic liquid under microwave heating. Microwave irradiation has been used to accelerate organic reactions with the ionic liquid as cellulose solvents, thus reducing reaction period from hours to minutes (Wang, Cao, Li, & Tang, 2011). Microwave-enhanced chemistry is based on the efficiency of the interaction between molecules in a reaction mixture beamed upon by generated electromagnetic wave. Microwave initiates rapidly an intense heating of polar molecules such as water. Therefore, the use of water is advantageous in microwave chemistry and expedited the overall process with greater energy efficiency. The process primarily relies on the specific polarity of molecules. Since water is polar, it has high potential to absorb microwaves and convert them into heat energy,

* Corresponding author. Tel.: +60 389213261; fax: +60 389213777.

E-mail addresses: sarani.zakaria@yahoo.com, sarani@ukm.my (S. Zakaria).

consequently accelerating the reaction in an aqueous medium compared to results obtained using conventional heating. This contrast can be construed by two key mechanisms which are the polarization and the ionic conduction of water molecules. Irradiation of a reaction mixture in an aqueous medium by microwave results in the dipole reorientation of water molecules and reactants in the electric field (Vivek & Rajender, 2010). Finding the optimal reaction conditions to scale up the synthesis method on CCs' formation is compelling; thus the objectives of this paper are to investigate the effects of urea content on the formation of CCs using microwave reactor and the effects of its resulting nitrogen content on the solubility and crystallinity index of the regenerated CCs membranes.

2. Materials and methods

2.1. Materials

Raw kenaf core was supplied by the Malaysian Agricultural Research and Development Institute (MARDI). The analytical grade of lithium hydroxide monohydrate (LiOH·H₂O), urea and 98.8% sulfuric acid were purchased from Sigma Aldrich. Urea and other reagents used in this study were of analytical grade and were used without further purification. The raw kenaf core was soda pulped in Forest Research Institute Malaysia (FRIM) in a digester with 25% NaOH concentration at 170 °C for 2½ h. The KCP was bleached using four stages bleaching method (DEED) where process D composed of 1.7% sodium chlorite at 80 °C for 4 h and process C is an alkaline treatment on KCP with 4–6% NaOH solution at 80 °C for 3 h. After every single stage performed, the sample was washed until neutral to remove the bleaching chemicals and dissolved lignin from the sample prior to entering the next stage. Then, the sample was dried at 105 °C for 24 h.

2.2. Viscosity measurement and molecular weight calculation for KCP

The viscosity of the average molecular weight (M_n) of KCP was determined in cadoxen solution at temperature 25 °C using an Ubbelohde viscometer tube capillary. The bleached KCP was dissolved in cadoxen solution at a concentration of 3×10^{-3} g/mL and diluted for five times to achieve concentration range from 1×10^{-3} to 3×10^{-3} g/mL. Intrinsic viscosities $[\eta]$ of cellulose dissolved in cadoxen solution were measured at 25 °C using the Ubbelohde viscometer tube capillary. Kraemer Eq. (1) and Huggins Eq. (2) were used to estimate the value $[\eta]$ value obtained by extrapolating the graph to zero concentration (c). It was then further used to calculate the specific viscosity (η_{sp}/c) using Eqs. (1) and (2).

$$\frac{\eta_{sp}}{c} = [\eta] + k'_k [\eta]^2 c \quad (1)$$

$$\ln \frac{\eta_{sp}}{c} = [\eta] + k'_H [\eta]^2 c \quad (2)$$

where k'_k is a constant for a given polymer at a given temperature in a given solvent in the Kraemer equation, while k'_H is a constant for a given polymer at a given temperature in a given solvent in the Huggins equation and η_{sp}/c is the specific viscosity of the cellulose.

2.3. Preparation of CCs

In a typical reaction procedure, every 10 g of KCP was milled and immersed into an urea aqueous solution containing 2 g/6 g/10 g of urea in 200 ml H₂O separately. Therefore, the weight percentage for urea content were 0.9 wt%, 2.8 wt% and 4.5 wt% in each KCP/urea aqueous solution and later were referred as K/U-0.9 wt%, K/U-2.8 wt% and K/U-4.5 wt% respectively. Each mixture was stirred

at an ambient temperature for 30 min and placed in the desiccators that connected to a vacuum pump giving rise to a vacuum condition for 30 min. The vacuum pump was then turned off and allowed atmosphere forces the urea aqueous solution to penetrate into KCP for 30 min. The mixture was later poured into a reaction flask and was heated in a microwave reactor at the power set at 380 W for different reaction time which was 10 min, 20 min and 30 min. The microwave reactor is a multimodal microwave apparatus (Electrolux-EMM1908S) that has been equipped with a condenser to prolong the microwave irradiation. Therefore, the CCs K/U-0.9 wt%, K/U-2.8 wt% and K/U-4.5 wt% with different urea content were formed at different reaction time. In each case, whenever the reaction time reached, the mixture in the reaction flask was immersed instantly in an ice bath to stop the reaction. The obtained kenaf CCs were washed with deionized water using both vortex shaker and centrifuged to remove the excessive urea. The kenaf CCs were then vacuum-dried at 80 °C for 12 h.

2.4. Preparation of cellulose membranes from KCP and CCs

A LiOH/urea aqueous solution with the weight ratio 4.6:15 was prepared and frozen at 13 °C for 6 h. The 3 wt% of each raw KCP and kenaf CCs (K/U-0.9 wt%, K/U-2.8 wt% and K/U-4.5 wt%) which was produced in 10 min reaction time were dissolved using rapid dissolution method. The cellulose samples were dissolved in the LiOH/urea aqueous solutions and the cellulose solutions were stirred vigorously for 5 min. Upon stirring, a transparent cellulose solution is obtained in a dissolution of KCP and slightly yellow transparent cellulose solution is obtained which is caused by the dissolution of kenaf CCs (K/U-0.9 wt%, K/U-2.8 wt% and K/U-4.5 wt%). The cellulose solution and undissolved cellulose were separated using centrifugation method. Only soluble cellulose solution was used to form cellulose membrane. The cellulose membranes were formed by casting each soluble KCP solution and soluble kenaf CCs solutions (K/U-0.9 wt%, K/U-2.8 wt% and K/U-4.5 wt%) on a glass plate and immersed in diluted sulfuric acid bath until the membrane coagulate. All of membranes were then immersed and washed in deionized water bath for three days to eliminate the residue of unreacted LiOH and urea. A portion of the membrane samples were freeze dried for 48 h and stored in desiccators for further characterization. The undissolved cellulose solution were cleaned and dried in a vacuum oven at temperature 80 °C for 12 h to determine the percentage of solubility of each kenaf sample.

2.5. Characterizations

The samples were characterized by FT-IR to observe the functional groups in the CCs (Perkin Elmer Spectrum 400 FT-IR). The nitrogen content of CCs was examined using Kjeldahl method conducted at UNIPPEC Sdn. Bhd. The morphology of KCP, bathed-in-urea KCP and CCs has been analyzed under a scanning electron microscopy (SEM, Supra 55 VP Zeiss). The morphology and pore size of regenerated cellulose membranes were measured using the scanning electron microscope (Zeiss/Supra 55VP). Phase and crystallinity index for both raw KCP and regenerated cellulose membranes were characterized using X-ray diffraction (Bruker Axs D8 Advance).

3. Results and discussion

3.1. Characterization of KCP

Fig. 1 shows the plot of intrinsic viscosity $[\eta]$ against cellulose concentration $[c]$ for the KCP. The intercept of each straight line determines the intrinsic viscosity of the KCP which is 486 (mL g⁻¹). Molecular weight (M_w) of the KCP can be calculated from

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