



Effect of hydrothermal pretreatment on solubility and formation of kenaf cellulose membrane and hydrogel



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ARTICLE INFO

Article history:

Received 26 May 2014

Received in revised form 10 August 2014

Accepted 15 August 2014

Available online 3 September 2014

Keywords:

Alkaline aqueous solution

Urea

Autoclave

Rapid dissolution

Regenerated cellulose

ABSTRACT

The hydrothermal pretreatment on kenaf core pulp (KCP) was carried out using an autoclave heated in a oil bath at 140 °C for 0.5/1/3/5 h. The hydrothermal pretreated kenaf (HPK) was dissolved in a LiOH/urea aqueous solution and subsequently used to produce cellulose membrane and hydrogel. The effects of hydrothermal pretreatment time on solubility, viscosity, crystallinity and morphology of the cellulose membrane and hydrogel were investigated. The hydrothermal pretreatment leads to higher cellulose solubility and higher viscosity of the cellulose solution. The formation of cellulose II and crystallinity index of the cellulose membrane and hydrogel were examined by X-ray diffraction (XRD). The pore size of the cellulose membrane and hydrogel displayed an upward trend with respect to the hydrothermal pretreatment period observed under a field emission scanning electron microscope (FESEM). This finding provides an efficient procedure to improve the solubility, viscosity and properties of regenerated cellulose products.

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1. Introduction

Lignocellulosic materials (LCMs) are the most abundant renewable biomass and mainly composed of cellulose, hemicellulose and lignin. The annual production of LCMs was roughly 200 billion metric tonnes worldwide in 2007 and has great potential as cheap and renewable feedstock for different applications. Cellulose is the most abundant biopolymer that can be obtained from numerous LCMs resources and there is a clear opportunity to develop commercial processes that could generate products that are needed at very high volumes and low selling price (Ruiz, Rodríguez-Jasso, Fernandes, Vicente, & Teixeira, 2013). Cellulose is generally accepted as a polymer consisting of D-anhydroglucose units linked by the α -1,4-glycosidic bonds (Eichhorn et al., 2001).

Malaysia is well-endowed with rich and renewable natural tropical forest resources. Cellulose based polymer can be used to reduce the use of the limited fossil resources in Malaysia with its environmental friendly properties and have been used for industrial applications. However, cellulose application is limited because it cannot be formed easily into a desired shape and it cannot be dissolved in a cheaper and more common solvent. Cellulose contains specific structure that tends to arrange of the polymer chains into tightly packed, highly crystalline structures that are water

insoluble and resistant to depolymerization (Carpita & Gibeaut, 1993). Solubility of cellulose is also an issue since its solubility varies with its molecular weight and is limited (El-Wakil & Hassan, 2008; Vo, Široká, Manian, & Bechtold, 2010). Therefore, the aim of the pretreatment is to disrupt the lignin seal and dislocate the crystalline structure of cellulose (Mosier et al., 2005).

Due to the robustness of LCMs, the pretreatment on cellulose is needed in order to change its structure and chemical composition. The pretreatment technologies are usually classified into physical, chemical, physicochemical, and biological. The physical pretreatment includes breakdown of biomass size and degree of crystallinity by milling or grinding. The physical pretreatments will affect the final particle size and reduce the crystallinity of the lignocellulosic material. The pretreatment process that involved liquid water under high temperature and pressure are referred as autohydrolysis, hydrothermal treatment, hot compressed water (HCW), hydrothermolysis, liquid hot water (LHW), aquasolve process, aqueous processing and pressure-cooking in water (Ruiz et al., 2013).

Hydrothermal pretreatment affects the re-localization of lignin on the surface of cellulose. Hence, after pretreatment on cellulose, the accessibility to cellulose structure is improved due to the physical changes in cellulose such as increase in pore size and accessible area. The hydrothermal pretreatment is a process that does not require the addition and recovery of any chemicals but water and it only causes limited equipment corrosion problems. The hydrothermal processing is considered as a simple and cost-effective

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pretreatment. At subcritical region (100–374 °C), the ionization constant (K_w) of water increases with temperature. However, the dielectric constant value, ionization constant (K_w) and ionic product of water drop drastically when exceeding its critical point (374 °C). Furthermore, the hydronium ions are formed from organic acids, mainly acetic acid from acetyl groups and uronic acid (Ruiz et al., 2013).

In urea–alkaline dissolution method, urea hydrates which are placed on the surface of the soda hydrate-bonded cellulose networks are used to prevent cellulose from forming aggregation, and this method leads to a good cellulose dissolution (Cai et al., 2008; Kaco et al., 2014). In the urea alkaline system, soda with urea or thiourea mixture using different weight ratios in water can be used to dissolve up to 5 wt.% of cellulose at temperature as low as –12 °C. In fact, only few seconds is required since the Weissenberg effect occurs within 30 s. This fact indicates that it might be the fastest dissolution methods (Cai et al., 2008; Luo & Zhang, 2013).

Hydrothermal method has been applied for pretreatment of LCMs since several decades ago, especially in pulp industries. Taherzadeh and Karimi (2008) discussed about the hydrothermal pretreatment was used to enhance the bio-digestibility of the waste for ethanol and biogas production and enhanced the accessibility of the enzymes to the materials. The hydrothermal pretreatment has been widely investigated in several LCMs such as sunflower stalks (Ruiz, Cara, Manzanares, Ballesteros, & Castro, 2008), poplar, eucalyptus, wheat straw, brassica carinata, sweet sorghum bagasse (Ballesteros, Oliva, Negro, Manzanares, & Ballesteros, 2004) and corn stover (Mosier, Hendrickson, Ho, Sedlak, & Ladisch, 2005) at range of temperature from 180 °C to 230 °C. These published reports were focused on enzymatic hydrolysis yield and xylose recovery for improving biogas production.

In spite of these studies, very little reports have been found in the literature on the solubility and properties of regenerated cellulose products. The main aim of this pretreatment is to increase accessible surface area, to decrystallize cellulose, and to remove hemicelluloses and lignin. In order to find a method to improve the cellulose solubility so as to decrease the undissolved cellulose, the objective of this work is to investigate the effects of hydrothermal pretreatment on the solubility and viscosity of the cellulose solution produced. The morphology, crystallinity index and properties of the regenerated cellulose produced from the cellulose solution are also investigated.

2. Materials and methods

2.1. Materials

Raw kenaf core was supplied by the Malaysian Agricultural Research and Development Institute (MARDI). The 98.0% analytical grade of lithium hydroxide monohydrate (LiOH·H₂O), epichlorohydrin (ECH) and 98.8% sulfuric acid were obtained from Sigma Aldrich. The sodium hydroxide and urea were obtained from R & M Chemicals. The sodium chlorite with purity 80% were obtained from Acros Organics. All the chemicals were used without further purification. The raw kenaf core was soda pulped at 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 is composed of 1.7% sodium chlorite at 80 °C for 4 h and process E is an alkaline treatment on KCP with 4–6% NaOH solution at 80 °C for 3 h. After every single stage is performed, the sample was washed until sample becomes neutral to remove the bleaching chemicals and to dissolve lignin from the sample prior to entering the next stage. The bleached KCP was then dried at 105 °C for 24 h.

2.2. Preparation of hydrothermal pretreatment Kenaf core pulp

The bleached KCP which had undergone hydrothermal pretreatment was produced by using an autoclave immersed in hot oil bath. The amount of urea and cellulose used to prepare HPK were in the ratio of 1:1. The urea was added into an autoclave to improve the solubility of cellulose in rapid dissolution method. The hydrated urea and KCP were stirred at a room temperature for 30 min to produce a homogeneous mixture. The autoclaves were filled with KCP/urea mixtures and closed tightly before immersed in oil bath at temperature 140 °C for 0.5 h, 1 h, 3 h and 5 h. These HPK samples prepared at different reaction time are referred as HPK-0.5h, HPK-1h, HPK-3h, HPK-5h accordingly. The HPK were then washed with distilled water several times with the aid of vortex shaker and centrifuged to remove the residue of urea remained on the HPK then dried in a vacuum oven at 80 °C for 12 h.

2.3. Viscosity measurement and molecular weight calculation for kenaf samples

Average molecular weight (M_n) of bleached KCP and HPK samples were determined via viscometer measurement of the cadoxen solution. Each KCP and HPK samples was dissolved in the cadoxen solution at a concentration of 3×10^{-3} g/mL and diluted for five times to achieve concentration ranging 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 equation (Eq. (1)) and Huggins equation (Eq. (2)) were used to estimate the $[\eta]$ value obtained by extrapolating the graph to zero concentration (c). It was then further used to calculate the specific viscosity (η_{sp}) and relative viscosity (η_r) using Eqs. (1) and (2).

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

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

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, η_{sp}/c is the reduced viscosity and $\ln \eta_r/c$ is the inherent viscosity of the cellulose.

2.4. Preparation of cellulose membrane

A LiOH/urea aqueous solution at the weight ratio 4.6 wt.% LiOH:15 wt.% urea:80.4 wt.% H₂O, was prepared and cooled at –13 °C for 6 h. This mixture is henceforth referred as alkaline aqueous solution. Firstly, 3 wt.% of each KCP and HPK samples was dissolved in alkaline aqueous solution at –13 °C using rapid dissolution method. The slight yellow transparent cellulose solution was then stirred vigorously for 5 min to form a heterogeneous mixture. The dissolved and undissolved cellulose solutions were separated using centrifuge. However, only soluble cellulose solution was used for viscosity testing and to form cellulose membrane. The cellulose membrane was formed by casting each soluble KCP solution and soluble HPK solutions on the glass plate and the thickness of membranes were in the range of 0.287–0.295 mm. All the kenaf membranes were then immersed and cleaned in deionized water bath for three days. The cellulose membrane that was formed from KCP is referred as kenaf core pulp membrane (KCPM), and the hydrothermal pretreatment kenaf membrane (HPKM) samples prepared at different pretreatment reaction time are referred as HPKM-0.5h, HPKM-1h, HPKM-3h and HPKM-5h. A subset of membrane samples were freeze dried for 48 h for further characterizations. The LiOH and urea residue in undissolved celluloses were

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