Carbohydrate Polymers 106 (2014) 160–165

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

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

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ARTICLE INFO

Article history:
Received 5 November 2013
Received in revised form 16 January 2014
Accepted 22 January 2014
Available online 7 February 2014

Keywords:
Alkaline aqueous solution
Urea
Rapid dissolution
Nitrogen content
Cellulose membrane

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 form 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.

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,

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http://dx.doi.org/10.1016/j.carbpol.2014.01.076

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 ($LiOH{\cdot}H_2O$), 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_η) 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 [η] 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 [η] 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 H_2O 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 UNIPEC 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 [η] 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 (Mw) of the KCP can be calculated from

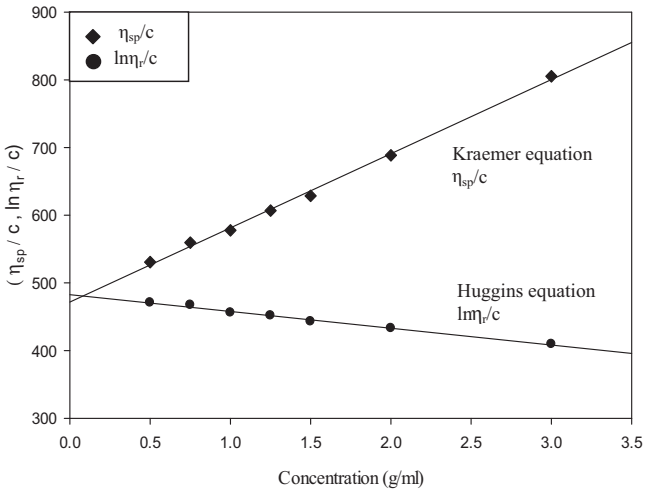

Fig. 1. Intrinsic viscosity of KCP versus cellulose concentration in cadoxen solution at 25 °C.

the Mark–Houwink equation as expressed in Eq. (3). Meanwhile its degree of polymerization (DP) can be determined using [η] as described in Eq. (4). The computed values of both viscosity-average molecular weight (M_η) and degree of polymerization (DP) for the raw KCP are 2.45×10^5 and 3416.86 respectively.

$$[\eta] = 3.85 \times 10^{-2}(\mathrm{Mw})^{0.76} \quad (3)$$

$$[\eta] = 1.75(\mathrm{DP})^{0.69} \quad (4)$$

3.2. FT-IR spectra of KCP and CCs

Fig. 2 displays the FT-IR spectra of (a) KCP and (b) K/U-4.5 wt% CCs with 10 min reaction time. Both KCP's and CCs' spectra exhibit a transmittance peak at 2904.19 cm^{-1} due to the stretching of N-H functional group in urea. Spectrum of the raw KCP shows the transmittance peaks at wavelength 1641 cm^{-1}. Compared to that of KCP, CCs' spectrum shows two distinct transmittance peaks at wavelengths 1665.86 cm^{-1} and 1626.12 cm^{-1}, which is assigned to the stretching vibration of the carbonyl (C=O) in the base of

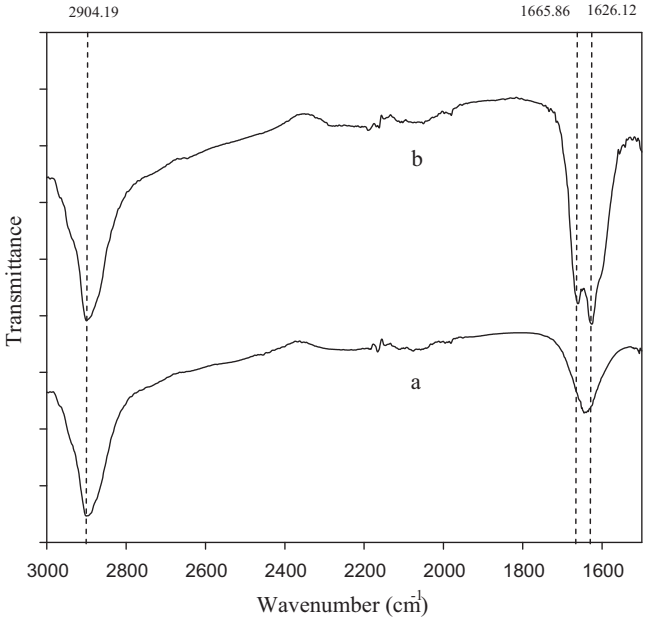

Fig. 2. FT-IR spectra of kenaf samples from (a) KCP and (b) K/U-4.5 wt% CCs.

Table 1
Nitrogen content in each cellulose sample.

Sample	Nitrogen (wt%)
KCP	0.3
K/U-0.9 wt% in 10 min	1.0
K/U-0.9 wt% in 20 min	1.3
K/U-2.8 wt% in 10 min	2.6
K/U-2.8 wt% in 20 min	2.1
K/U-4.5 wt% in 10 min	3.8
K/U-4.5 wt% in 20 min	5.6
K/U-4.5 wt% in 30 min	5.7

urethane (Nada, Kamem, & El-Sakhawy, 2000). From the previous study, these two peaks indicated the formation of CCs from cellulose and urea as described in Eq. (5) (Turunen et al., 1983).

$$\text{Cell-OH} + \text{HNCO} \longrightarrow \text{Cell-O-C-NH}_2 + \text{NH}_3 \quad (5)$$

Therefore, an efficient formation of CCs via the microwave reactor process has been demonstrated qualitatively in this study.

3.3. Effects of urea content and reaction time on nitrogen content of CCs

Table 1 exhibits the percentages of nitrogen content in KCP and kenaf CCs formed from varied urea contents and at different reaction time (10 min, 20 min and 30 min). The weight percentage (wt%) of nitrogen in KCP is 0.3 wt%. The wt% of nitrogen in kenaf CCs with same reaction time is increasing as the urea content contributed to the CCs formation increases from 0.9 wt% to 4.5 wt%. Hence an increase in urea content indicating the formation of CCs will lead to an increase in their nitrogen content. Guo, Zhou, Wang, Zhang, & Lin (2010) found that the urea content in the mixture forming the CCs should be around 30 wt% to 40 wt% to minimize the cost of material. However, synthesizing CCs assisted by microwave reactor within a polar medium, the minimum requirement of urea content is only from 0.9 wt%.

For sample K/U-4.5 wt% CCs, as the microwave reaction time increases from 10 min to 30 min, the nitrogen content of CCs increases from 3.8 wt% to 5.7 wt%. Hence, the reaction time is another factor which will contribute to the amount of urea content in the products.

3.4. Morphology of KCP and CCs

Fig. 3 shows the SEM micrographs of the (a) raw KCP, (b) KCP in urea solution and (c) K/U-4.5 wt% CCs that was produced under microwave reactor with 10 min reaction time. Morphology of cellulose fibre can be observed under SEM. Raw KCP as shown in Fig. 3(a) exhibits a smooth and compact surface which does not have any external fibrillation or formation of fibrils. In Fig. 3(b), the fibre structure has changed visibly as it was immersed in urea solution. The observed relative density of cellulose was reduced which helps the urea to penetrate into the fibres and reacts with cellulose easily. Fig. 3(c) presents SEM micrographs of CCs with 3.8 wt% nitrogen content. It can be seen that the fibres swelled significantly and the surfaces of CCs become loosed. These properties and changes in the morphology and structure of cellulose fibres might give rise to high diffusion and good swelling properties which is substantially important in chemical reaction, solubility and spinnability of CCs.

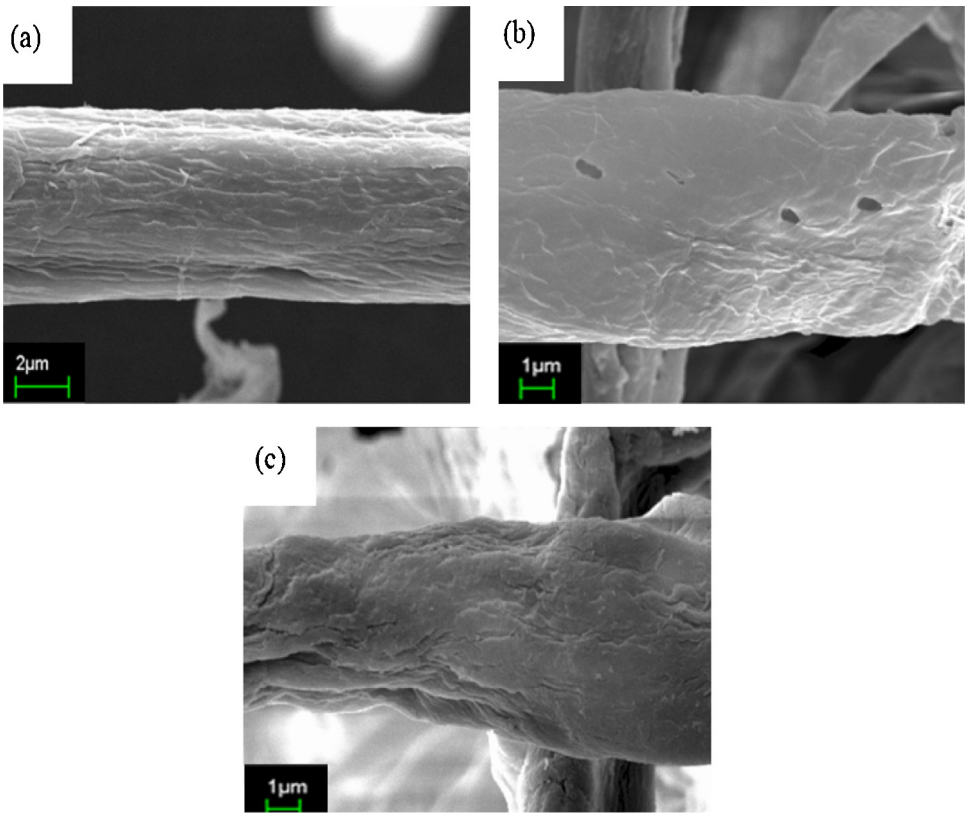

Fig. 3. SEM photographs of (a) KCP, (b) KCP in urea solution and (c) K/U-4.5 wt% CCs.

3.5. Solubility of KCP and CCs in alkaline aqueous solution

The solubility of 3 wt% KCP and 3 wt% kenaf CCs (K/U-0.9 wt%, K/U-2.8 wt% and K/U-4.5 wt% with reaction time 10 min) in the LiOH/Urea aqueous solution were calculated according to Eq. (6).

$$S\,(\%) = \frac{W_o - W}{W_o} \times 100 \tag{6}$$

where S is the degree of dissolution for cellulose, W is the weight of undissolved cellulose residue and W_o is the original weight of the cellulose. Table 2 presents the percentage of solubility for each sample immersed in the LiOH/Urea aqueous solution. It can be seen that the K/U-4.5 wt% has the highest solubility among all the CCs samples which is 94.3%. Noted also that the solubility of K/U-0.9 wt% CCs does not differ much from the solubility of raw KCP. Thus, the synthesized K/U-4.5 wt% CCs with 10 min reaction time could improve the cellulose solubility by as high as 9.6% in the urea alkaline aqueous solution. The CCs produced from higher wt% of urea in microwave reactor have been verified contain higher nitrogen wt% than those prepared at lower concentration of urea. Based on Table 2, it can be concluded that the CCs synthesized at higher urea concentration will have higher nitrogen content contributing to higher solubility in the LiOH/urea aqueous solution.

Table 2
Solubility (%) of cellulose samples in LiOH/Urea aqueous solution.

Sample	Average solubility (%)
KCP	84.7
K/U-0.9 wt%	85.8
K/U-2.8 wt%	91.5
K/U-4.5 wt%	94.3

3.6. Morphology of regenerated cellulose membranes from KCP and CCs

Fig. 4 presents four FESEM micrographs of regenerated kenaf membranes from KCP and CCs produced in 10 min reaction time such as K/C-0.9 wt%, K/C-2.8 wt% and K/C-4.5 wt%. The morphology and pore size of the regenerated cellulose membranes can be observed under FESEM. The regenerated kenaf membrane from KCP in Fig. 4(a) displays a wavy and disordered image, which might be due to the reducing of cellulose crystallinity after dissolution in urea-alkaline aqueous system. There are few curve-structured nanoparticles appear to form thicker bundles of aggregates which known to have a general tendency to aggregate in parallel with one another (Marchessault, Morehead & Walter, 1959). Fig. 4 (b), (c), and (d) are the regenerated CCs membranes formed from different percentage of urea composition. From these figures, as the percentage of urea used to produce CCs increased, the pore size of its regenerated cellulose membrane also increased. The nitrogen content during the formation of CCs and its solubility might have affected the morphology of its regenerated cellulose membrane, since the increase in urea content will enhance the substitution of nitrogen within CCs molecule. The pore size of the regenerated CCs membranes lies in a range between 100.5 nm and 725.8 nm as shown in the pictures with the scale 1 μm.

3.7. XRD patterns and crystallinity index of regenerated cellulose membranes from KCP and CCs

Fig. 5 reveals the XRD patterns of (a) raw KCP, (b) regenerated KCP membranes and regenerated CCs membranes of (c) K/U-0.9 wt%, (d) K/U-2.8 wt% and (e) K/U-4.5 wt% at 10 min reaction time. The diffraction pattern of KCP native cellulose is identical with that of typical cellulose I structure, with a sharp peak at the angle 22.2° and a wide peak between angles 14.7° and 16.3°

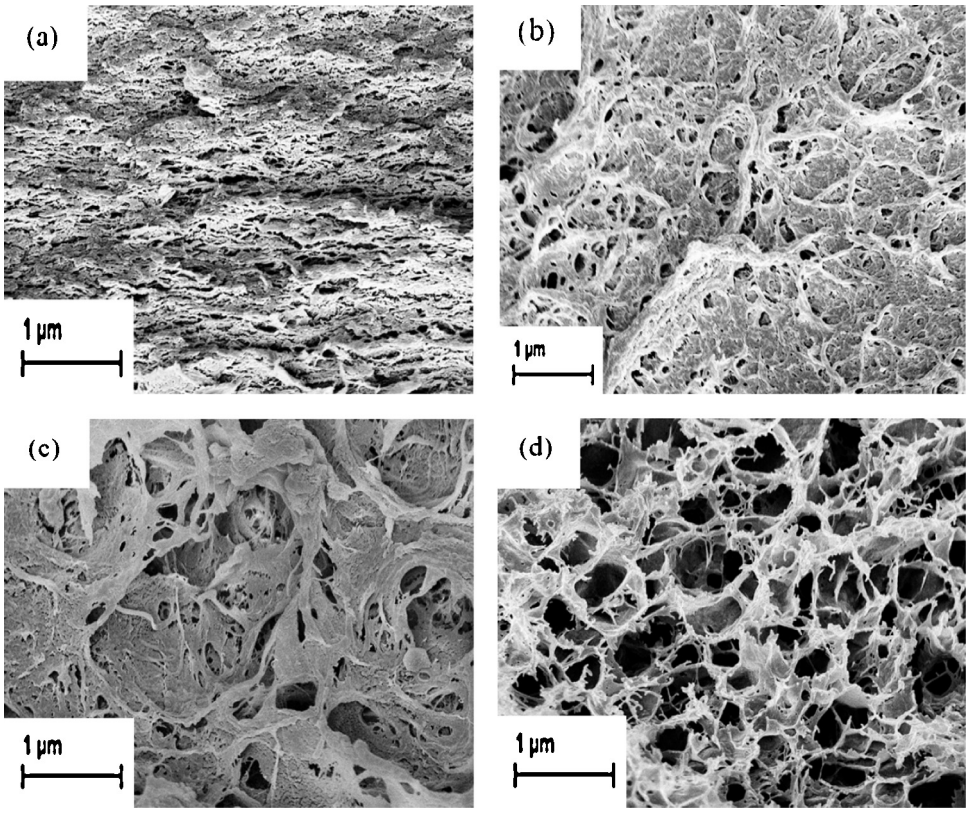

Fig. 4. FESEM photographs of regenerated kenaf membrane samples (a) KCP, (b) K/C-0.9 wt%, (c) K/C-2.8 wt% and (d) K/C-4.5 wt%.

(Liu et al., 2011). The sharp 2θ peaks at the angles approximately 12.2°, 19.8° and 20.9° signify the formation of cellulose II in all regenerated cellulose membranes.

Table 3 shows the crystallinity index of raw KCP, the regenerated KCP membrane and regenerated CCs membrane. The regenerated kenaf membrane samples were formed from the dissolution of 3 wt% KCP and 3 wt% CCs (K/U-0.9 wt%, K/U-2.8 wt% and K/U-4.5 wt% with 10 min reaction time) respectively. The crystallinity index (%) of raw KCP is higher than that of all other regenerated kenaf membranes as reported previously (Jin, Zha, & Gu, 2007). A downward trend is observed between the crystallinity index of CCs membrane and the percentage of urea content supplied in the formation of CCs. This observation might be related to the resulting nitrogen content and the solubility trend among CCs samples. Hence, the urea content supplying the formation of CCs is negative correlated with the crystallinity index of the regenerated CCs membrane.

Table 3
Crystallinity index of KCP and the regenerated kenaf membranes.

Sample	Crystallinity index (%)
KCP	32.32
Regenerated KCP	24.45
Regenerated K/U-0.9 wt%	29.24
Regenerated K/U-2.8 wt%	22.27
Regenerated K/U-4.5 wt%	19.47

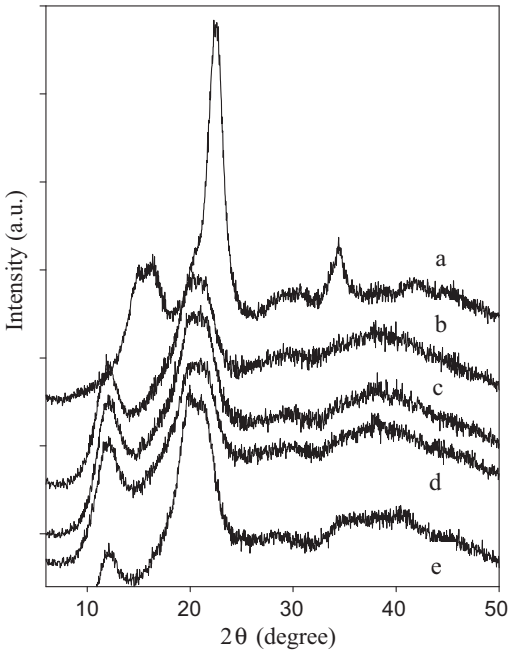

Fig. 5. XRD patterns of kenaf samples from (a) KCP, (b) Regenerated K/U-4.5 wt%, (c) Regenerated K/U-2.8 wt%, (d) Regenerated K/U-0.9 wt% and (e) Regenerated KCP.

4. Conclusion

The kenaf CCs were synthesized efficiently from the KCP/urea mixture assisted by microwave reactor in a polar medium under catalyst-free conditions. This is considered as a simple, efficient and convenient method to synthesize the CCs from native cellulose. Only a 10 min reaction time and urea content as low as 0.9 wt% are needed to produce CCs in the microwave reactor. The formation of CCs from KCP has been verified based on the FT-IR spectra and by the nitrogen content test. The SEM showed higher pore is observed on the membranes produced at higher urea concentration. The urea and the resulting nitrogen content in cellulose/urea aqueous mixtures were found to enhance CCs' solubility in the aqueous alkaline solution. The XRD indicated that the higher urea content in the

formation of CCs', the lower the crystallinity index of the CCs membrane. Both urea content and solubility of CCs were discovered to have the corresponding effect on crystallinity index and morphology of the regenerated CCs membrane. The urea content supplying the formation of CCs can be optimized in minimizing the cost of materials.

Acknowledgements

The authors thank Universiti Kebangsaan Malaysia for the financial support via the research Project Grants LRGS/TD/2012/USM-UKM/PT/04, ERGS/1/2012/STG05/UKM/01/4 and the Ministry of Higher Education Malaysia for MyBrain15-MyMaster Scholarship. The authors are also thankful to the Centre for Research and Instrumentation Management (CRIM) at UKM for providing the FTIR, XRD and FESEM testing.

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