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

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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.

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 sorgum 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 ($LiOH{\cdot}H_2O$), 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 immerged 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_η) 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 [η] 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 [η] 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.% H_2O, 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

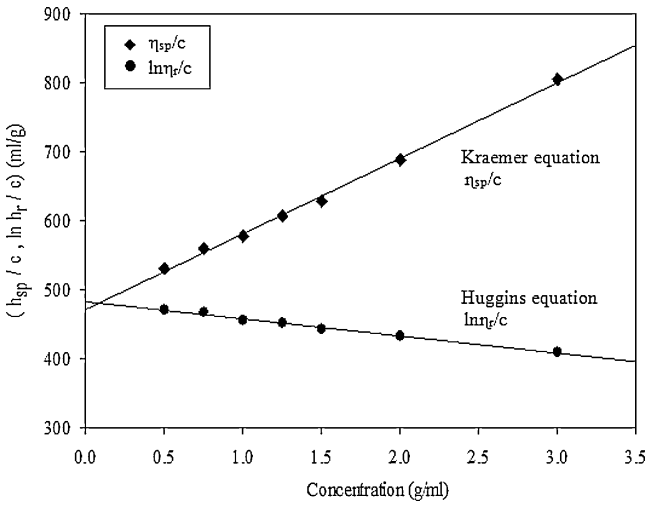

Fig. 1. Plot of intrinsic viscosity [η] against cellulose concentration [c].

washed away by deionized water, dried in vacuum oven at 80 °C for 12 h and weighted to determine the solubility of each kenaf sample.

2.5. Preparation of cellulose hydrogel

The 3 wt.% of cellulose samples (KCP, HPK-0.5h, HPK-1h, HPK-3h and HPK-5h) were dissolved in alkaline aqueous solution. The kenaf cellulose solution was stirred for 5 min to obtain a yellowish transparent cellulose solution. The cellulose solution was subjected to centrifugation at 10,000 rpm for 5 min at 5 °C to remove air bubbles and to separate the dissolved and undissolved cellulose solutions. ECH solution (5%) was then dropped carefully into the soluble cellulose solution for a cross linking process and stirred until the hydrogel was formed. The obtained hydrogels were washed with deionized water to remove the excess LiOH and urea. Hydrogel formed using KCP and HPK are referred to kenaf core pulp hydrogel (KCPH) and hydrothermal pretreatment kenaf hydrogel (HPKH) respectively. HPKH prepared at different pretreatment reaction time are labelled as HPKH-0.5h, HPKH-1h, HPKH-3h and HPKH-5h. A portion of the HPKH sample was freeze dried for 48 h and stored in a desiccator for further characterization. The undissolved cellulose solutions were then cleaned and dried in a vacuum oven at 80 °C for 12 h in order to determine the percentage of cellulose solubility.

2.6. Characterizations

Brookfield viscometer with unit of centipoise (cP) was used to determined the viscosity of soluble cellulose solutions. Phase and crystallinity of KCP, cellulose membrane (KCPM, HPKM) and cellulose hydrogel (KCPH, HPKH) were characterized by X-ray diffraction (Bruker Axs D8 Advance). The morphology and pore size of cellulose membranes and hydrogels were measured using field emission scanning electron microscope (Zeiss/Supra 55VP). In the transparency test, the hydrogels were cut into a thickness of 0.5 cm and the light transmittance through the hydrogels was measured using an UV–vis spectrophotometer at wavelength ranging from 200 to 800 nm. The hydrogels were immersed in distilled water at 25 °C for few days to determine the swelling of hydrogel. The samples' weight was measured and the degree of swelling (DS) was calculated according to the following equation:

$$\mathrm{DS}(\%) = \frac{W_s - W_d}{W_d} \times 100 \quad (3)$$

Table 1
[η], M_η and DP of KCP and HPK samples at different hydrothermal pretreatment reaction time.

Sample	[η] (mL g^{-1})	M_η	DP
KCP	486.0	2.49×10^5	3478.9
HPK-0.5h	462.8	2.34×10^5	3240.9
HPK-1h	419.3	2.05×10^5	2808.9
HPK-3h	316.9	1.42×10^5	1872.0
HPK-5h	264.0	1.12×10^5	1436.6

where W_d and W_s are the weights of hydrogel before and after immersion respectively.

3. Results and discussion

3.1. Characterization of kenaf core pulp (KCP) and hydrothermal pretreatment kenaf (HPK)

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}). Viscosity-average molecular weight (M_η) of the KCP was calculated from the Mark–Houwink equation as expressed in Eq. (4), while its degree of polymerization (DP) was found using [η] as described in Eq. (5).

$$[\eta] = 3.85 \times 10^{-2}(M_\eta)^{0.76} \quad (4)$$

$$[\eta] = 1.75(\mathrm{DP})^{0.69} \quad (5)$$

The computed values of both viscosity-average molecular weight (M_η) and degree of polymerization (DP) for the KCP are 2.49×10^5 and 3478.9 respectively.

Table 1 shows the [η], M_η and DP of KCP and HPK samples that undergone hydrothermal pretreatment using different

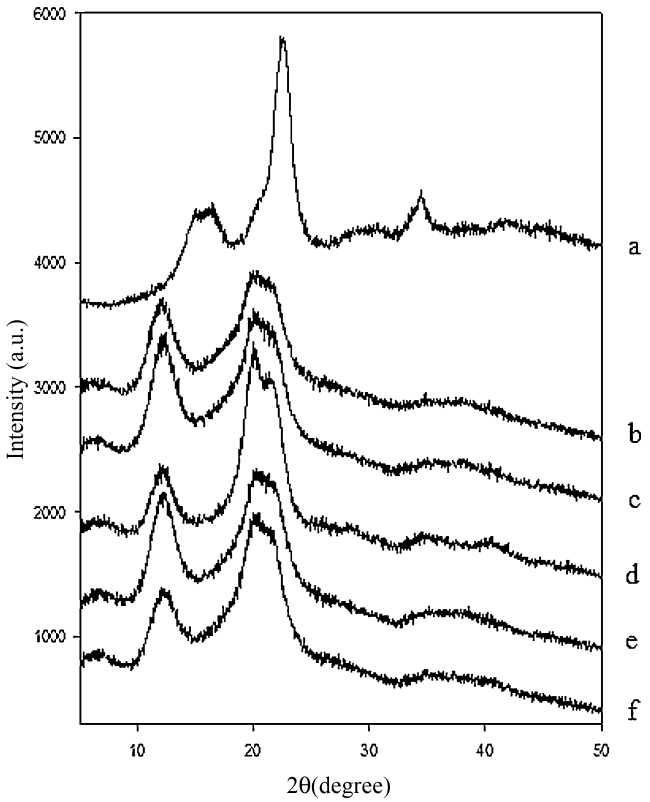

Fig. 2. XRD patterns of kenaf samples from (a) KCP, (b) KCPM, (c) HPKM-0.5h, (d) HPKM-1h, (e) HPKM-3h, (f) HPKM-5h.

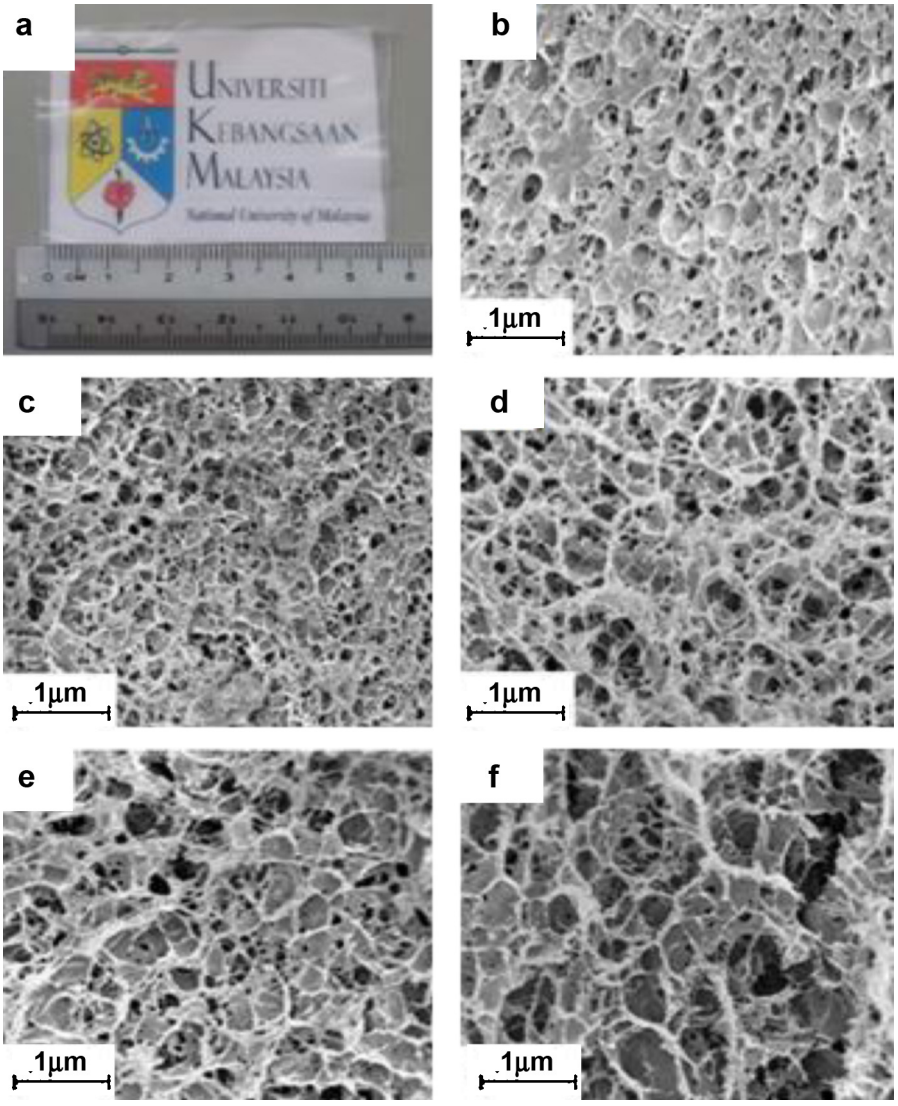

Fig. 3. Physical appearance of (a) cellulose membrane and FESEM photographs of cellulose membrane samples (a) KCPM, (b) HPKM-0.5h, (c) HPKM-1h, (d) HPKM-3h, (e) HPKM-5h.

reaction time. The value of M_η and DP are obtained from the [η] and these values are positively correlated with the value of [η]. The M_η of HPK samples displayed a downward trend with respect to the hydrothermal pretreatment time. Upon hydrothermal pretreatment, the M_η of KCP (2.49×10^5) can be reduced to as low as to 1.12×10^5 in 5 h hydrothermal pretreatment with significant reduction up to 1.37×10^5. The HPK samples have lower M_η compare to KCP, therefore, the hydrothermal pretreatment on cellulose is proven to be capable of reducing the M_η of cellulose. This is because of once water reaches high temperatures (150–230 °C), the H-bonding begins weakening, allowing autoionization of water into acidic hydronium ions (H_3O^+) that act as catalysts and basic hydroxide ions (OH^-). The hydronium ions will hydrolyze the cellulose and causes the reduction of its M_η, hence, hydrothermal pretreatment results in cell's structures penetration, cellulose hydration and hemicelluloses depolymerization (Ruiz et al., 2013).

Table 2
Degree of crystallinity of kenaf membranes.

Sample	Crystallinity index (%)
KCP	63.1
KCPM	54.3
HPKM-0.5h	50.4
HPKM-1h	44.8
HPKM-3h	44.7
HPKM-5h	40.7

3.2. Dissolution of kenaf core pulp (KCP) and hydrothermal pretreatment kenaf (HPK)

The solubility of KCP and HPK in the alkaline aqueous solution was calculated according to Eq. (1).

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

where S is solubility of cellulose, W is the weight of undissolved cellulose residue and W_o is the original weight of the cellulose (Gan, Zakaria, Chia, Kaco, & Padzil, 2014). The average solubility percentage of 3 wt.% cellulose samples is as following order; HPK-5h (95.7%) > HPK-3h (95.5%) > HPK-1h (93.5%) > HPK-0.5h (89.75%) > KCP (84.4%). It is found that the HPK that had been treated from different reaction time have higher solubility compared to dissolution of KCP. As the reaction time of hydrothermal pretreatment on cellulose increases, the average solubility

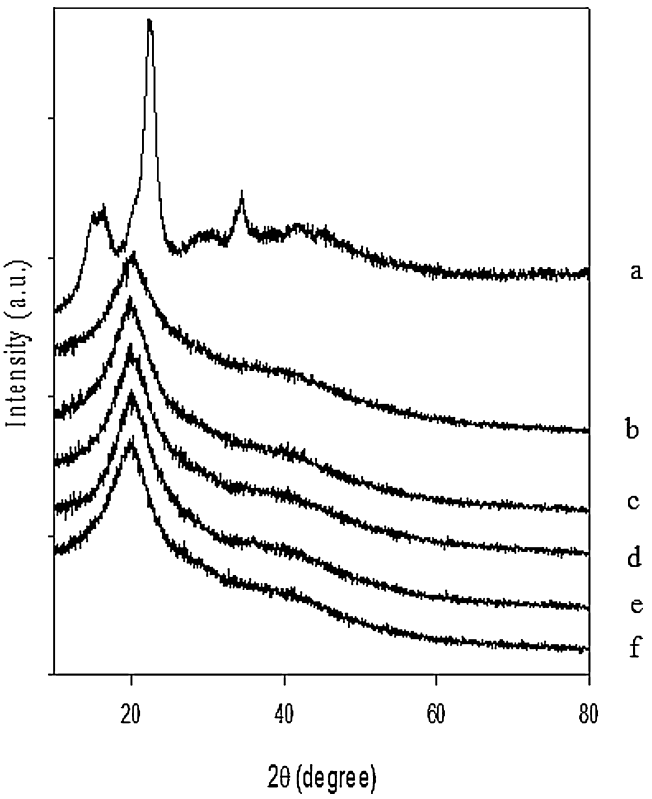

Fig. 4. XRD patterns of kenaf samples from (a) KCP, (b) KCPH, (c) HPKH-0.5h, (d) HPKH-1h, (e) HPKH-3h, (f) HPKH-5h

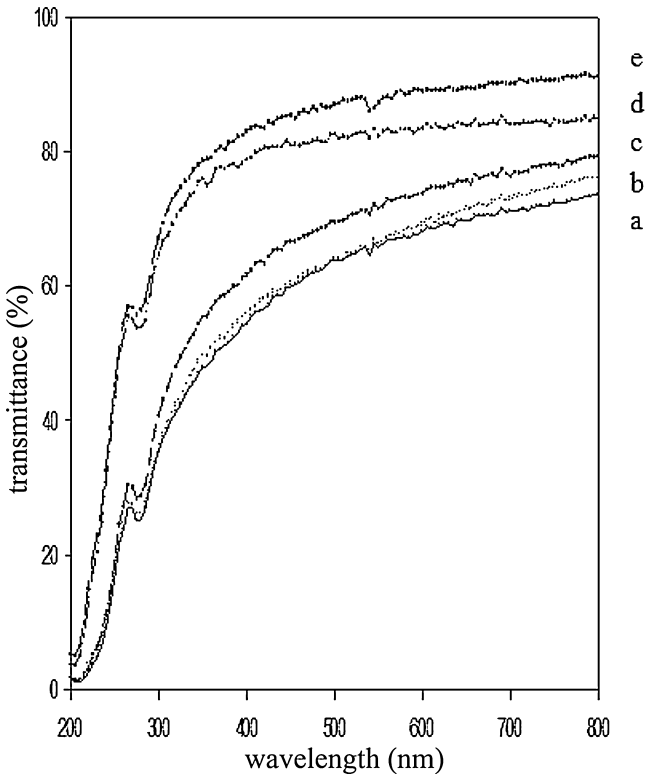

Fig. 5. Transparency of cellulose hydrogel prepared from (a) KCPH, (b) HPKH-0.5h, (c) HPKH-1h, (d) HPKH-3h, (e) HPKH-5h.

of cellulose increases. Cellulose sample with higher M_η forms a more packed network, which is more difficult to be dissolved in urea–alkaline system. This suggests that the inter-molecular hydrogen bonding between the cellulose molecules have been destroyed and is easier penetrate into cellulose chain expanding to the higher swollen and dissolution state (Cai & Zhang, 2005). The hydrothermal pretreatment improves the solubility of KCP as high as 11.3%. There is only 0.2% little difference between the solubility of 3 h and 5 h HPK. Reaction time of 3 h for hydrothermal pretreatment on cellulose is sufficient to obtain optimum solubility of cellulose up to 95.5%. Hence, the finding has proven that hydrothermal pretreatment has enhanced the solubility of cellulose in aqueous alkaline solution.

3.3. Viscosity of cellulose solutions

The viscosity (cP) of both kenaf solutions and HPK solutions were measured by viscometer. The increasing trend of average viscosity measurement of soluble cellulose solutions is as following; KCP (1749 cP) < HPK-0.5h (1767 cP) < HPK-1h (1790 cP) < HPK-3h (1790 cP) < HPK-5h (1990 cP). The value of M_η, average solubility and average viscosity of the samples are correlated with each other. From the readings, all HPK solutions are more viscous than KCP solution, and for HPK samples, the viscosity of cellulose solutions increases as the hydrothermal pretreatment time on cellulose increases. This is because of the solubility of the cellulose samples in alkaline aqueous solution is positively correlated with the viscosity of cellulose solutions. The cellulose samples with lower M_η will obtain higher solubility, therefore, the cellulose content in cellulose solution is higher which resulted in higher viscosity in cellulose solution. The hydrothermal pretreatment will reduce the M_η and dislocate the crystalline region of cellulose which affects solubility and viscosity of cellulose samples. The hydrothermal pretreatment on cellulose have produced cellulose solutions with higher viscosity.

3.4. X-ray diffraction of kenaf membrane

XRD testing was used to confirm the transformation of cellulose I to cellulose II during the formation of cellulose membrane as shown in Fig. 2. The diffraction pattern of KCP shows typical cellulose I structure, with a sharp peak at 22.2° and a wide peak between 14.7° and 16.3° (Liu et al., 2011). Upon dissolution and regeneration process, the characteristic peaks are shifted to $2\theta = 12.2°$, 19.8° and 20.9° which are attributed to the cellulose II crystalline allomorph (Gan et al., 2014). The results illustrate the transformation of the crystal structure of KCP from cellulose I to cellulose II. Table 2 displays the degree of crystallinity of (a) KCP (b) KCPM (c) HPKM-0.5h (d) HPKM-1h (e) HPKM-3h and (f) HPKM-5h in XRD diffractogram. The degree of crystallinity of regenerated cellulose membrane produced from both KCP and HPK are in the range between 40.7% and 54.3%. The degree of crystallinity for all HPKM are apparently lower than KCPM that never undergone any hydrothermal treatment. The results portray that the hydrothermal pretreatment process has resulted in the disturbance of the crystalline area of cellulose.

3.5. Morphology of kenaf membrane

Fig. 3 shows (a) physical appearance of cellulose membrane and the FESEM micrographs of (b) KCPM (c) HPKM-0.5h (d) HPKM-1h (e) HPKM-3h and (f) HPKM-5h. In Fig. 3(a), the cellulose membrane is colourless and transparent film with thickness less than 0.3 mm. The morphology and pore size of KCPM and HPKM are observed under FESEM. Pore size of each HPKM samples are bigger than KCPM. As the reaction time of hydrothermal pretreatment on cellulose increases from 0.5 h to 5 h,

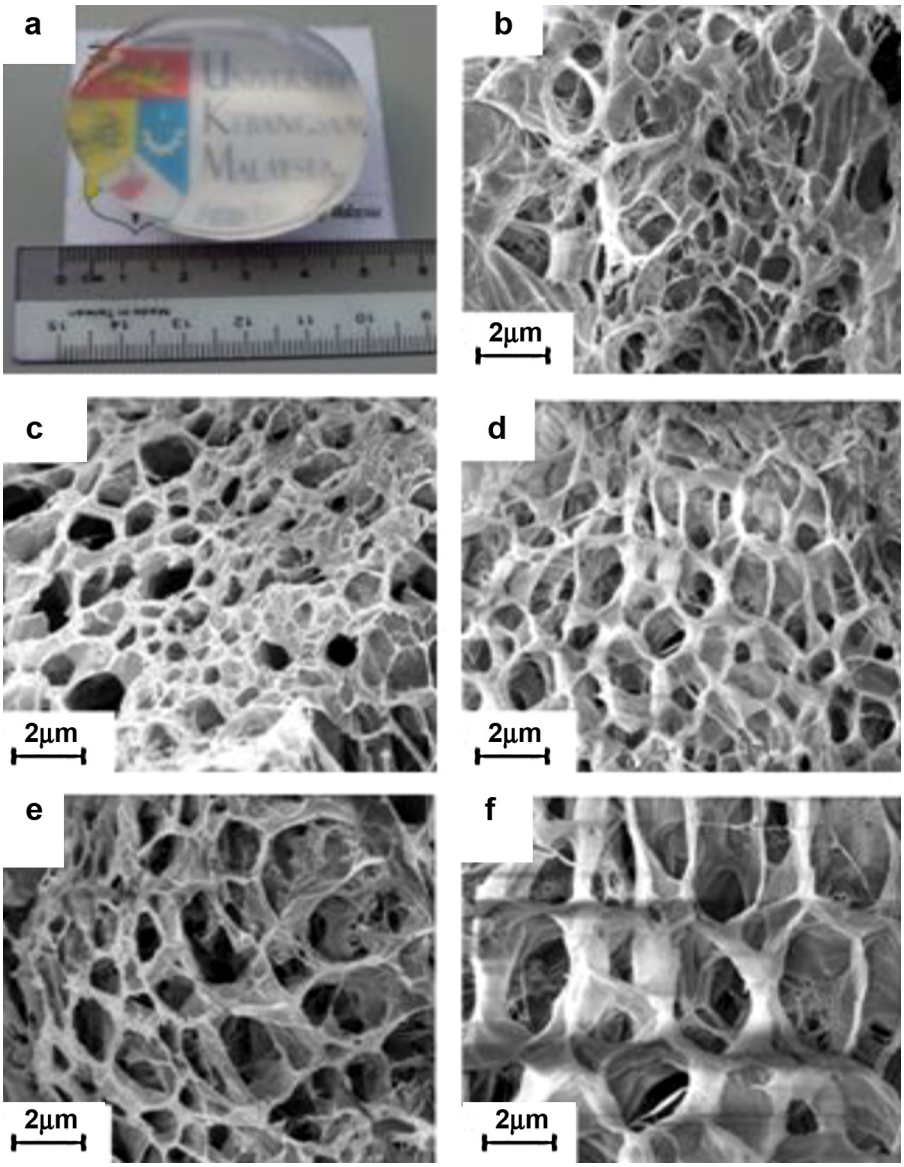

Fig. 6. Physical appearance of (a) cellulose hydrogel and FESEM photographs of cellulose hydrogel samples, (b) KCPH, (b) HPKH-0.5h, (c) HPKH-1h, (d) HPKH-3h, (e) HPKH-5h.

the pore size of the cellulose membrane grows gradually. This is due to the M_η of the cellulose samples decrease after hydrothermal pretreatment which resulted in a less pack network in HPK samples. Therefore, the morphology of cellulose samples with lower M_η contribute in bigger pore size of cellulose membrane. The cellulose membrane technologies have been widely applied in drug delivery, optical media, biomembrane, separation, water treatment, adsorption and package (Qiu & Hu, 2013).

3.6. X-ray diffraction of kenaf hydrogel

Fig. 4 shows the XRD diffraction patterns of (a) KCP, (b) KCPH, (c) HPKH-0.5h, (d) HPKH-1h, (e) HPKH-3h and (f) HPKH-5 h. The diffraction peaks at $2\theta = 14.9^\circ, 16.3^\circ, 22.6^\circ$ and 34.5° can be assigned to cellulose crystal planes of $(1\ \bar{1}\ 0)$, $(1\,1\,0)$, $(2\,0\,0)$ and $(0\,0\,4)$, respectively (Lu & Hsieh, 2012). The crystallinity index of cellulose hydrogel cannot be obtained because the cross linking of cellulose with ECH has occurred in cellulose hydrogel. Fig. 4 exhibits the shifted peak from cellulose I to cellulose II and proves the formation of cellulose II in cellulose hydrogel samples.

3.7. Transparency of kenaf hydrogel

The transparency of (a) KCPH, (b) HPKH-0.5h, (c) HPKH-1h, (d) HPKH-3h and (e) HPKH-5h are shown in Fig. 5. The light transmittance through KCP and HPK hydrogels were measured by using an UV–vis spectrophotometer. The transmittances of ultraviolet and visible light of cellulose hydrogels were measured in the wavelength range between 200 and 800 nm. The transmittance of the HPK hydrogels increased gradually as the reaction time of hydrothermal pretreatment on KCP increases. The HPKH-5h sample that undergone longest reaction time exhibits the highest transmittance (%) compared to other HPKH samples. This is because hydrothermal pretreatment reduces the M_η of KCP and disrupts the crystalline region of KCP which affects the cross linking of cellulose in hydrogel structure. Cellulose with higher M_η forms a more packed network in the cellulose hydrogel , therefore, its transmittance decreases. The transmittance is mainly dependent on the amount of light to transmit through the cellulose hydrogel structure, hence, transmittance decreases when the light has difficulty to transmit through the hydrogel sample (Chang, Lue, & Zhang, 2008). The hydrothermal pretreatment has

affected the M_η of KCP, which affects the transparency of HPKH samples that have been formed.

3.8. Swelling studies

The degree of swelling (DS) of KCPH, HPKH-0.5h, HPKH-1h, HPKH-3h and HPKH-5h are 144.69%, 146.03%, 159.90%, 193.87% and 207.50% respectively. It can be seen that the kenaf hydrogel formed from HPK with longer reaction time exhibits higher DS than KCPH formed from untreated kenaf. The FESEM pictures show that HPK with longer hydrothermal pretreatment reaction time produces KCPH with bigger pore size (Fig. 6). The swelling mechanism is mainly due to the diffusion of water which fills the pores in kenaf hydrogel. Diffusion of water fill in HPKH-5h is faster than HPKH-3h, HPKH-1h, HPKH-0.5h and KCPH which might be due to pore size of hydrogels, since HPKH-5h has lowest M_η and has the least packed structure (Ganji, Vasheghani-Farahani, & Vasheghani-Farahani, 2010). As seen in Fig. 6, the porosity of HPKH-5h is bigger and therefore water can penetrate into the structure more easily and approaches equilibrium after a certain period of time.

3.9. Morphology of regenerated kenaf hydrogel

Fig. 6(a) depicts physical appearance of cellulose hydrogel. In comparison to cellulose membrane in Fig. 3(a), the cellulose hydrogel, as shown in Fig. 6(a), is transparent, short cylinder and soft gel like. Hydrogel technologies have been extensively employed in a number of industrial applications such as hygienic products, drug delivery systems, cool dewatering, sealing, pharmaceuticals, food additives, separation of biomolecules or cells, tissue engineering and biomedical applications (Ahmed, 2013).

The FESEM images of the cross section of the cellulose hydrogel samples are shown in Fig. 6(b) KCPH, (c) HPKH-0.5h, (d) HPKH-1h, (e) HPKH-3h and (f) HPKH-5h. All hydrogel samples possess macroporous structure with bigger average pore size as the reaction time of hydrothermal on cellulose increase. After hydrothermal pretreatment, the M_η of cellulose decreased and formed a less pack network, thus, this might causes the pore size of formed kenaf hydrogel to become bigger. This suggests that more water can be retained in the hydrogel at longer hydrothermal pretreatment reaction time, leading to increase in the pores size.

4. Conclusion

The hydrothermal pretreatment results in several effects including hemicelluloses depolymerization (oligomers, monomers), alteration or degradation of lignin and increase availability of cellulose. The reaction time of hydrothermal pretreatment affects the M_η and degree of crystallinity of cellulose which results in improvement of solubility, viscosity and morphology of regeneration cellulose products. Hence, the hydrothermal pretreatment decrease the waste of undissolved cellulose and improve properties of regenerated cellulose products. This implies that HPK can promote the cellulose solubility up to 95.7% using hydrothermal pretreatment with autoclave and oil bath compare to untreated KCP. This process is useful in reducing the M_η of cellulose, so as to produce environmental friendly regenerated cellulose products.

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