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Synthesis of Liquid Hot Water Cotton Linter to Prepare Cellulose Membrane using NaOH/Urea or LiOH/Urea

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The liquid hot water (LHW) pretreatment on cotton linter (CL) was carried out using an autoclave heated in a hot oil bath. The LHW pretreated CL (LCL) was dissolved in NaOH/urea and LiOH/urea aqueous solutions and subsequently used to produce cellulose membrane. The effects of LHW pretreatment, amount of cellulose, and type of alkaline solvent on properties of cellulose solution and cellulose membrane were studied. The formation of cellulose II and crystallinity index (CrI) on the cellulose membranes were confirmed by X-ray diffraction (XRD). The morphology of cellulose membranes were observed by field emission scanning electron microscopy (FESEM). The LHW pretreatment resulted in higher cellulose solubility, higher cellulose solution viscosity, and improved properties of regenerated cellulose products compared to non-treated cellulose. Results also revealed that the amount of cellulose used affected the solubility and viscosity of the cellulose solution and the higher dissolving power of the LiOH/urea system as compared to the NaOH/urea system. In fact, higher solubility and viscosity properties are key factors in many cellulose applications such as membranes, fibers, hydrogels, and other regenerated cellulose products.

INTRODUCTION

Malaysia is a country well-endowed with abundant, renewable natural tropical forests and agricultural resources. Cellulose-based polymers offer a promising source of raw material for industrial applications due to environmentally friendly properties and the limitation of fossil resources in Malaysia. However, cellulose application is limited because of the difficultly in casting it into a desired shape, and it cannot be dissolved in the most common solvents. The cellulose dissolution problem is related to the solubility that varies with its molecular weight (Cai and Zhang 2005; Agbor *et al.* 2011; Kaco *et al.* 2014). Hence, pretreatment has been conducted for the purpose of disrupting the lignin seal and dislocating the cellulosic crystalline structure (Carpita and Gibeaut 1993).

Lignocellulosic biomass can be referred to as a heterogeneous complex of carbohydrate polymers, *i.e.*, cellulose, hemicellulose, and a non-carbohydrate component (lignin) (Gan *et al.* 2014). The cellulose molecular structure is similar to starch, which is a polymer of glucose. However, unlike starch, cellulose is water-insoluble. It has highly crystalline structures that are tightly packed with well-ordered polymer chains, causing it to resist depolymerization. Hemicellulose is a branched polymer of glucose or xylose, substituted with arabinose, xylose, galactose, fructose, mannose, glucose, or glucuronic

acid depending on the species (Zhu *et al.* 2011). Hemicelluloses are bonded to cellulose microfibrils *via* hydrogen bonding, and thus form a network that provides a structural backbone to the plant cell wall (Liu *et al.* 2010). The recalcitrance of lignocellulosic biomass to hydrolysis can be attributed to the crystallinity of cellulose, the amount of accessible surface area, the protection of cellulose by lignin, the heterogeneous character of biomass components, and cellulose sheathing by hemicellulose (Carpita and Gibeaut 1993).

Pretreatment technologies are usually classified into four groups: physical, chemical, physicochemical, and biological. The physical pretreatment can either be a milling or grinding process that involves the breakdown of biomass size and reduction on the degree of crystallinity of lignocellulosic material. Meanwhile, the pretreatment process that involves liquid water under high temperature and pressure is referred to in various terms, such as autohydrolysis, hydrothermal treatment, hot compressed water (HCW), hydrothermolysis, LHW, aquasolve processing, aqueous processing, and pressure-cooking in water (Liu *et al.* 2011). The LHW pretreatment involves the addition of water at elevated temperatures and high pressures. This will promote the disintegration and separation of the lignocellulosic matrix. Additionally, LHW is a promising method due to its environmentally friendly features and enhancement of cellulosic digestibility. The main advantages of the LHW process are the use of lower temperatures and that the formation of degradation products can be minimized. During biomass hydrolysis, hot water cleaves hemiacetal linkages and liberates acids, which facilitates the breakage of ether linkages in biomass (Marchessault *et al.* 1959; Yu *et al.* 2015). Since the cost of the solvent is minimal, it can also be an advantage for large scale application.

In the urea-alkaline dissolution method, urea hydrates are placed on the surface of soda hydrate-bonded cellulose networks. This prevents cellulose from forming aggregations, and leads to good cellulose dissolution. Only a few seconds are required for the chemical reaction to occur; this quick timing is due to the Weissenberg effect occurring within 30 s. The Weissenberg effect is seen in clastic liquids during rotary stirring (Mosier *et al.* 2005). The LHW pretreatment has the ability to increase accessible surface area and decrystallize cellulose. In order to improve the cellulose solubility and decrease the undissolved cellulose in the urea-alkaline system, the objectives of this work are to investigate the effects of LHW pretreatment and cellulose content on the solubility, viscosity, morphology, and crystallinity degree of the regenerated cellulose membrane.

EXPERIMENTAL

Materials

Raw CL (average viscosity molecular weight (M_η) 9 x 10^4) was purchased from Hubei Chemical Fiber (Xiangfan, China). Analytical grade sodium hydroxide (NaOH), lithium hydroxide monohydrate (LiOH·H_2O), urea, and 98.8% sulfuric acid were purchased from Sigma Aldrich (USA). All the raw materials were used without further purification.

Methods

Preparation of liquid hot water cotton linter (LCL)

The content of urea and cellulose, at a ratio of 1:1, was used to prepare the LCL. The urea addition is used to enhance the cellulose solubility in the rapid dissolution

method. The urea and CL with 20 mL of distilled water were stirred for 30 min at room temperature (25 °C) to form a homogeneous mixture. The autoclave was filled with the hydrated urea/CL mixtures and then closed tightly before being immersed in an oil bath at a temperature of 140 °C for 3 h. The LCL was taken out from the autoclave and washed several times with distilled water with the aid of a vortex shaker, followed by centrifudgation in order to eliminate the urea residue remaining on the LCL. The LCL was dried in a vacuum oven at 80 °C for 12 h.

Viscosity measurement and molecular weight calculation for LCL

The M_η value of LCL was measured at 25 °C using an Ubbelohde capillary tube viscometer in a cadoxen solution. The LCL was dissolved in the cadoxen solution at a concentration of 3×10^{-3} g/mL, and diluted five times to achieve a concentration range of 1.5×10^{-3} to 3×10^{-3} g/mL. The intrinsic viscosities $[\eta]$ of cellulose dissolved in cadoxen solution were determined. The Kraemer equation (Eq. 1) and Huggins equation (Eq. 2) were used to calculate the $[\eta]$ value obtained by extrapolating the graph to zero concentration (*c*) (Gan *et al.* 2015). By using Eqs. 1 and 2, the specific viscosity (η_{sp}) and relative viscosity (η_r) were then computed,

$$\eta_{sp}/c = [\eta] + k_K`[\eta]^2 c \qquad\qquad (1)$$

$$\ln\eta_r/c = [\eta] + k_H`[\eta]^2 c \qquad\qquad (2)$$

where $k_K`$ is a constant for a given polymer at a given temperature in a given solvent in the Kraemer equation, $k_H`$ 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 η_r/c is the inherent viscosity of the cellulose.

Preparation of cellulose membrane from CL and LCL

Two types of urea-alkaline solutions at different ratios were used: NaOH/urea, and LiOH/urea systems. For the NaOH/urea system, the weight ratio for the NaOH/urea aqueous solution was 7 wt% NaOH, 12 wt% urea, and 81 wt% H_2O; whereas the LiOH/urea aqueous solution had a weight ratio of 4.6 wt% LiOH, 15 wt% urea, and 80.4 wt% H_2O. Both the urea-alkaline solutions were prepared and pre-cooled at -13 °C for 6 h. Firstly, 4, 5, 6, and 7 wt% of each CL and LCL samples were immersed immediately in the pre-cooled solvent using a rapid dissolution method. The slight yellow transparent cellulose solution was vigorously stirred for 5 min to produce a heterogeneous mixture. For the cellulose dissolution in both NaOH/urea and LiOH/urea solvent, the cellulose solutions prepared from 4, 5, 6, and 7 wt% CL were referred as CL4, CL5, CL6, and CL7, respectively. Meanwhile, the cellulose solutions formed from different contents of LCL were labelled as LCL4, LCL5, LCL6, and LCL7. The dissolved and undissolved cellulose solutions were separated using centrifugation. The cellulose solution was used to study the viscosity and formation of the cellulose membrane. The cellulose membrane was fabricated by casting each cellulose solution on a glass plate. The cellulose membrane was then immersed and cleaned in a deionized water bath for 3 d. The CL membranes were formed from different pure CL content, and were named as follows: CLM4, CLM5, CLM6, and CLM7. The membrane samples prepared at different LCL content were labeled as follows: LCLM4, LCLM5, LCLM6, and LCLM7. A subset of membrane sample was freeze-dried for 48 h for further characterizations. The NaOH,

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LiOH, and urea residues from undissolved cellulose were washed using deionized water, dried in a vacuum oven at 80 °C for 12 h, and weighed to determine the solubility of each CL and LCL samples.

Characterizations

A viscometer (Brookfield DV Prime I, USA) was used to determine the viscosity (centipoise (cP)) of the cellulose solutions. Phase and CrI of CL and cellulose membrane (CLM, LCLM) were characterized by X-ray diffraction (XRD) (Bruker Axs D8 Advance, Germany). The XRD was performed using radiation of Cu Kα = 1.5458 Å at a diffraction angle (2θ) range of 5 to 60° (Kaco *et al.* 2014). The CrI of the samples was determined by means of Eq. 3,

$$CrI\ (\%) = A_{Cystal}/A_{Total} \times 100 \tag{3}$$

where $A_{Crystal}$ is the sum of the areas under the crystalline diffraction peaks and A_{Total} represents the total area under the diffraction curve between $2\theta = 5$ to 60°. The morphology and pore size of cellulose membranes were measured using a Zeiss/Supra 55VP field emission scanning electron microscope (FESEM, Germany).

RESULTS AND DISCUSSION

Characterization of Cellulose Samples

Figure 1 displays intrinsic viscosity [η] against cellulose concentration [c] for the LCL. The intrinsic viscosity of the LCL was determined by the intercept of each straight line, which was 137.40 (mLg^{-1}).
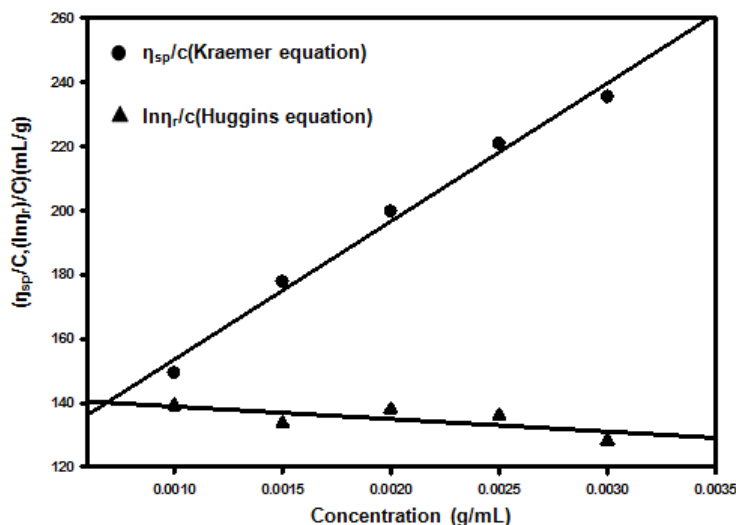
Fig. 1. Intrinsic viscosity (η) against cellulose concentration (c) for the LCL

As described in the Mark-Houwink equation (Eq. 4), M_η of the LCL can be calculated, by using [η] as expressed in Eq. (5), and the degree of polymerization (DP) can be found (Gan *et al.* 2015):

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

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

The calculated values of M_η and DP for the LCL were 4.71×10^4 and 558, respectively.

Dissolution of CL and LCL

The solubilities of both CL and LCL in the NaOH/urea and LiOH/urea aqueous solution were calculated using Eq. 6,

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

where S is solubility of cellulose, and W and W_o are the weight of undissolved cellulose residue and the initial weight of the cellulose, respectively (Gan *et al.* 2014).

Table 1 describes the solubility percentages of 4, 5, 6, and 7 wt% of CL and LCL in NaOH/urea and LiOH/urea aqueous solutions. It can be noted that the LCL samples had higher solubility than the dissolution of CL samples in the rapid dissolution method in both urea alkaline solution. Hence, this finding demonstrates that LHW improved the solubility of cellulose in urea alkaline solution due to lower M_η as compared to CL. The LiOH/urea aqueous dissolving solution provides higher solubility rather than NaOH/urea aqueous dissolving solution. This can be ascribed to the smaller size of the LiOH molecules that can easily access cellulose for effective dissolution purposes compared to the larger NaOH molecules. The cellulose dissolution solvent that consists of the Li^+ ion had a small ionic radius and higher charge density which allowed for easier penetration into the cellulose as compared to the Na^+ ions to be imbibed on the cellulose chain (Luo and Zhang 2013). Therefore, cellulose had a higher dissolving power in the LiOH/urea aqueous solution.

Table 1. Solubility of CL and LCL in NaOH/urea and LiOH/urea Aqueous Solutions

Sample	Solubility (%)	
	NaOH/urea	LiOH/urea
CL-4	85.62	88.99
LCL-4	91.31	94.19
CL-5	80.78	85.95
LCL-5	87.12	93.06
CL-6	70.93	76.92
LCL-6	74.23	78.49
CL-7	68.51	70.23
LCL-7	69.65	75.38

On the other hand, the solubility of both CL and LCL decreased with increased CL and LCL content dissolved in the NaOH/urea and LiOH/urea solvent. This is attributed to the limited capacity of urea-alkaline solution in dissolving cellulose and that the solubility mainly relies on low temperatures (Gan *et al.* 2014; Kaco *et al.* 2014) and

properties of the chosen cellulose in the rapid dissolution method, especially its M_η. The cellulose dissolution was a dynamic process between the solvent molecules and macromolecules of cellulose in urea-alkaline aqueous solution. Thus, when the maximum dissolution capacity of urea-alkaline solution is attained, the excessive cellulose added will be undissolved, causing the dissolubility of cellulose to be decreased.

Viscosity of Cellulose Solutions

From the viscosity readings in Table 2, the LCL solutions from all wt% of cellulose were more viscous as compared to the CL solution in both NaOH/urea and LiOH/urea solution. This is due to the cellulose percentage solubility in urea-alkaline system being proportional to the viscosity of cellulose solution. Cellulose samples with lower M_η had higher solubility; therefore, the cellulose content dissolved in cellulose solution was higher, which resulted in higher viscosity. The LHW pretreatment reduced the M_η and dislocated the crystalline region of cellulose, which subsequently affected the solubility and viscosity of cellulose samples. For both CL and LCL samples, as the amount of cellulose added in NaOH/urea or LiOH/urea solution was increased, the viscosity increased. The cellulose solution of LiOH/urea possessed higher viscosity than the cellulose solution of NaOH/urea solvent in all cellulose samples. This is because the cellulose dissolution solvent that consist Li^+ ions have relatively small ionic radius and higher charge density than Na^+ ions. The Li^+ ions can more easily penetrate into cellulose compared to Na^+ ions to be imbibed on the cellulose chain, giving rise to an inclusion complex that is relatively stable in cellulose dissolution (Luo and Zhang 2013). Hence, the solubility of cellulose in LiOH/urea is higher than NaOH/urea solution, which resulted in higher viscosity for cellulose dissolved in LiOH/urea solution.

Table 2. Viscosity of CL, and LCL in NaOH/urea, and LiOH/urea Aqueous Solutions

Sample	Viscosity (cP)	
	NaOH/urea	LiOH/urea
CL4	1519	1620
LCL4	2218	2347
CL5	2899	3047
LCL5	5602	5717
CL6	9986	10466
LCL6	18724	19316
CL7	39015	41691
LCL7	45914	46310

X-ray Diffraction of CL Membrane

Figure 2 shows the diffractogram of CL pulp, LCL pulp, CLM, and LCLM formed using LiOH/urea solvent; this demonstrates the transformation of cellulose I to cellulose II in the formation of cellulose membrane. The diffraction pattern of CL pulp and LCL pulp display the typical cellulose I structure, with a sharp peak at 22.2° and a broad peak between 14.7 and 16.3°, as reported previously (Ruiz *et al.* 2013). Upon dissolution and regeneration, the characteristic peaks for all LCLM membranes were shifted at $2\theta = 12.2$, 19.8, and 20.9°, which corresponded to the cellulose II crystalline

allomorph (Gan *et al.* 2015). The XRD patterns for all the membrane samples formed using NaOH/urea solvent (not shown) exhibited the same behavior as membrane samples formed using LiOH/urea solvent, as shown in Fig. 2.
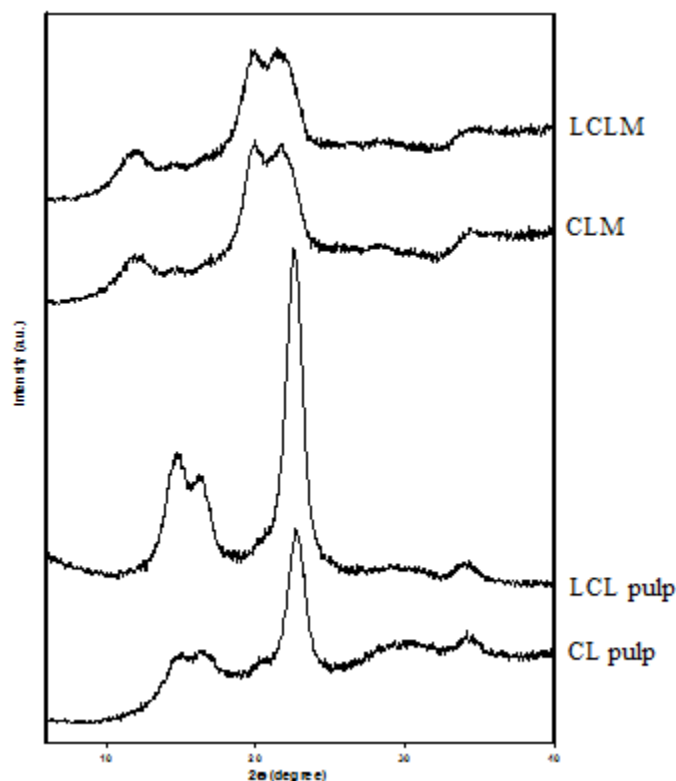

Fig. 2. Diffractogram of CL pulp, CLM, and LCLM in LiOH solvent

Table 3 describes the CrI of CLM and LCLM prepared from different cellulose content using NaOH/urea and LiOH/urea aqueous solutions. The CrI for LCLM samples were lower than the CLM samples prepared for both solvents. The cellulose content supplied for the formation of CLM and LCLM was negatively correlated to the CrI of the regenerated cellulose membrane.
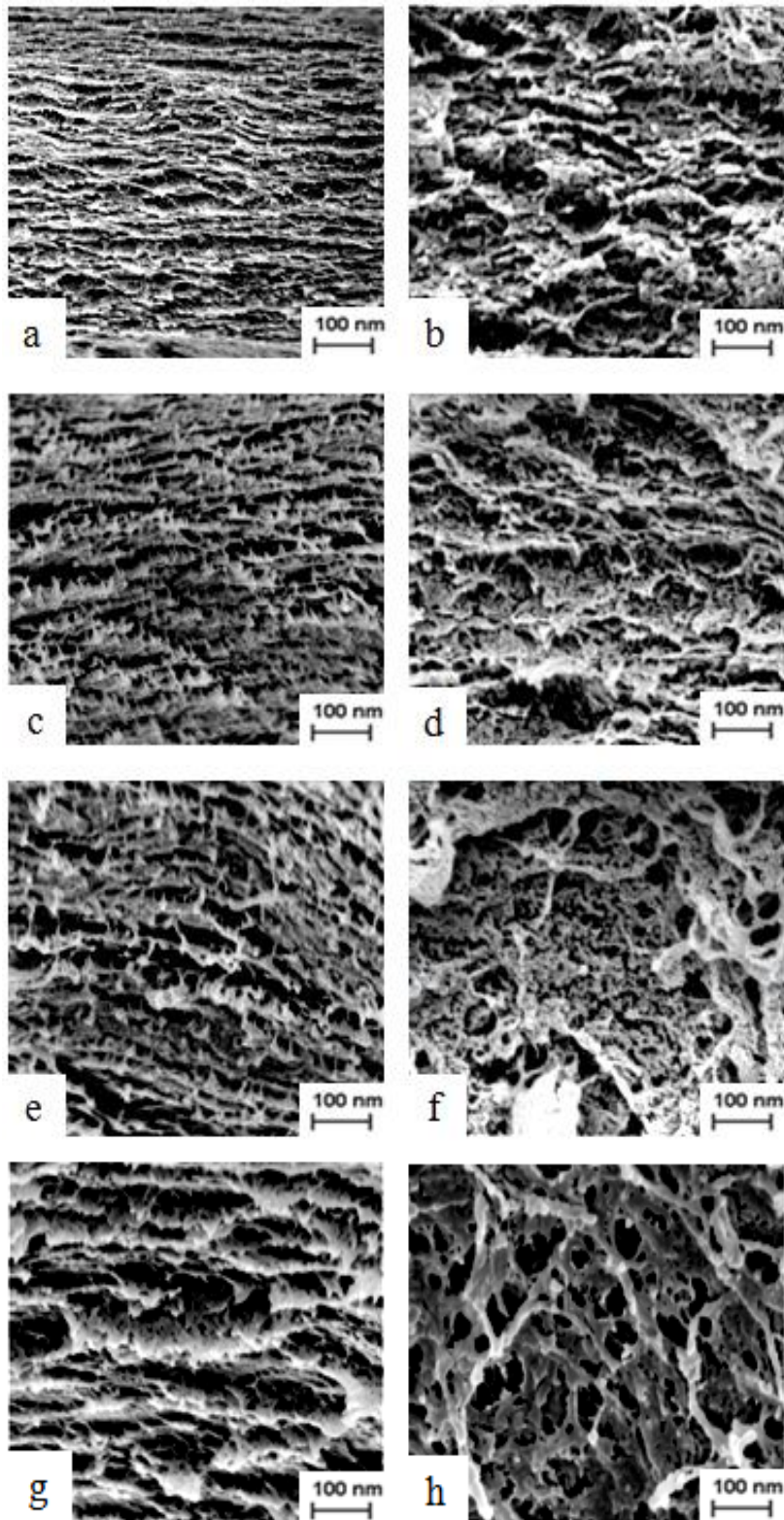
Table 3. The CrI of CLM and LCLM

Sample	CrI (%)	
	NaOH/urea	LiOH/urea
CLM4	32.45	28.26
LCLM4	25.75	23.93
CLM5	36.66	32.52
LCLM5	29.98	27.75
CLM6	38.44	34.62
LCLM6	34.22	32.96
CLM7	43.84	36.31
LCLM7	39.71	34.77
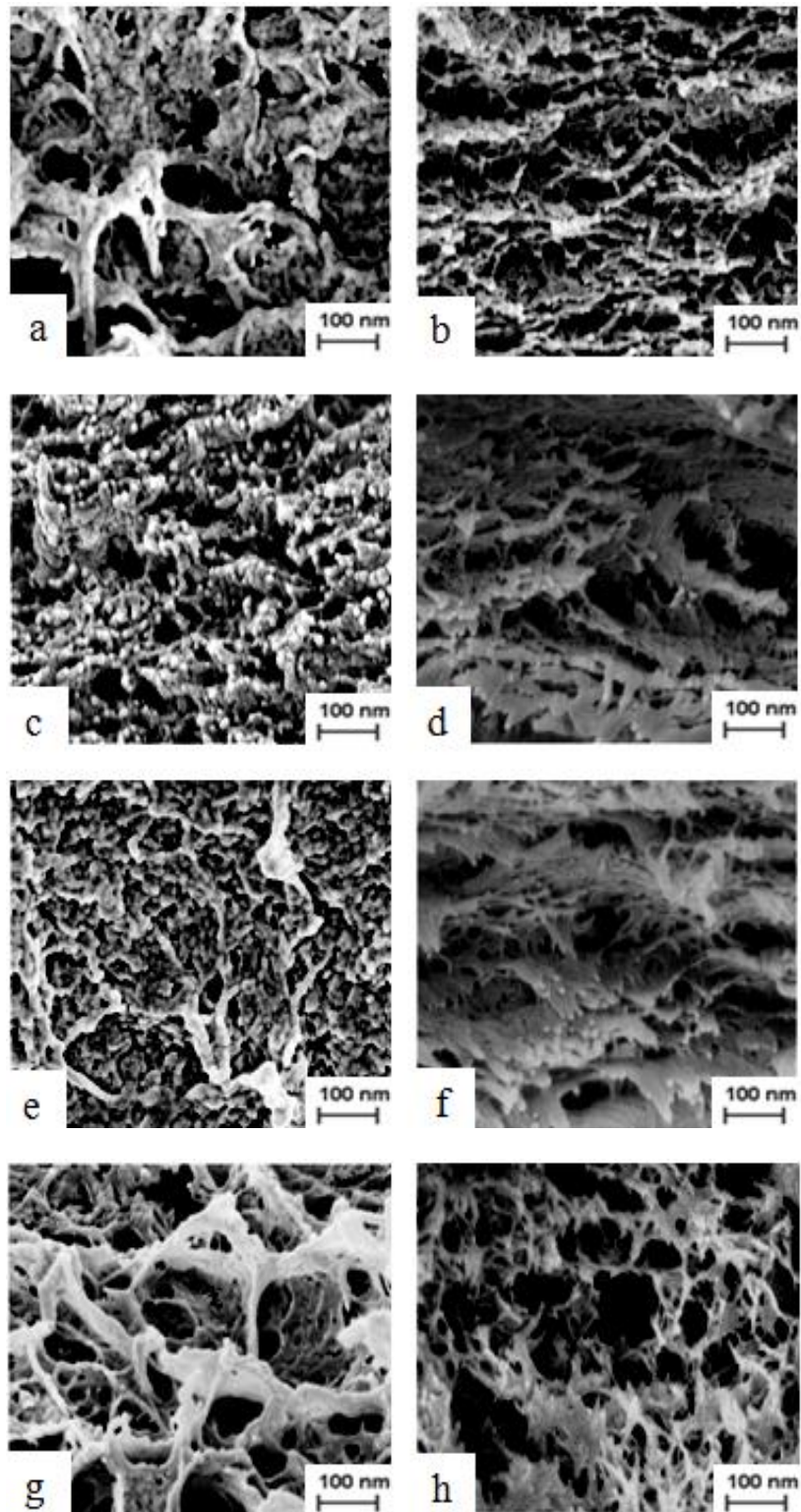
Fig. 3. FESEM micrographs of (a) CLM4, (b) LCLM4, (c) CLM5, (d) LCLM5, (e) CLM6, (f) LCLM6, (g) CLM7, and (h) LCLM7, which are membranes produced from NaOH/urea

Fig. 4. FESEM micrographs of (a) CLM4, (b) LCLM4, (c) CLM5, (d) LCLM5, (e) CLM6, (f) LCLM6, (g) CLM7, and (h) LCLM7 are membranes produced from LiOH/urea

The cellulose samples dissolved in LiOH/urea solvent had lower CrI than the cellulose samples dissolved in NaOH/urea. This is because the CrI of cellulose membranes was correlated with the solubility of cellulose samples, in which sample with higher solubility possessed greater accessible area, thus affecting the CrI of cellulose membrane. In LHW process, the water is most likely to enter the amorphous region of cellulose and then cause further damage to the regularity of the cellulose structure. These results portray that the LHW process, cellulose content, and type of alkaline solvent resulted in the disturbance of the cellulose structure (Brodeur *et al.* 2011).

Morphology of Regenerated Cellulose Membrane

Figure 3 depicts the FESEM micrographs of CLM and LCLM formed from 4, 5, 6, and 7 wt% cellulose content in NaOH/urea solvent. Figure 4 shows the FESEM micrographs of CLM and LCLM formed from 4, 5, 6, and 7 wt% cellulose content in LiOH/urea solvent (Gan *et al.* 2015). Based on the size measurements provided by the FESEM software, the pore size of all cellulose membranes was between 15.2 and 145.1 nm. The micrographs of membrane samples formed using NaOH/urea solvent (Fig. 3) illustrate a more porous structure than those formed with LiOH/urea solvent (Fig. 4). This is probably due to the fact that the solubility of cellulose samples in NaOH/urea is lower than LiOH/urea solvent. Hence, less of the cellulose sample dissolved in NaOH/urea solvent, which resulted in lower cellulose content and higher porosity in the cellulose membranes. The pore distributions appear better for the membrane samples in the NaOH/urea solvent. Interestingly, unlike in NaOH/urea solvent, the micrographs of the CLM samples in LiOH/urea solvent display a wavy, disordered, and partly fused image, which might be due to the reduction of cellulose crystallinity (Gan *et al.* 2014). From the observations in Figs. 3b, 3d, 3f, and 3h and Figs. 4b, 4d, 4f, and 4h, LCLM samples show that the curve-structured appears to form thicker bundles of aggregates. Similar observations were previously reported in which cellulose in aqueous suspension is known to have a general tendency to aggregate in parallel with each other (Wright *et al.* 1987). The agglomeration in cellulose membranes may be due to the surface ionic charge of the cellulose (Vo *et al.* 2010). However, there was no substantial difference in morphology of the cellulose membrane as the amount cellulose used to dissolve increases. This might be because of the urea-alkaline solvents such as NaOH/urea and LiOH/urea can only dissolve up to a certain amount of cellulose as it achieves maximum capacity.

CONCLUSIONS

1. The LHW pretreatment reduced the M_η and CrI of cellulose, which led to the enhancement of solubility, viscosity, and properties of the regenerated cellulose membrane. This implies that LHW pretreatment using an autoclave and oil bath improved the cellulose solubility up to 94.19 % in comparison with untreated CL.

2. The cellulose dissolved in the LiOH/urea aqueous solution had a higher solubility compared to that in the NaOH/urea aqueous solution.

3. As the cellulose content dissolved in urea-alkaline solvent increased from 4 to 7 wt%, its percentage of solubility decreased. This is because the urea-alkaline solution had limited capacity in dissolving a certain amount of cellulose. Therefore, when it attains the maximum capacity, the further addition of cellulose content will cause the decreasing of the cellulose solubility percentage.

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