CELLULOSE CHEMISTRY AND TECHNOLOGY

PHYSICAL PROPERTIES OF REGENERATED KENAF CELLULOSE MEMBRANE: USING H_2SO_4 AS COAGULANT

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Regenerated kenaf cellulose membranes were prepared by dissolving cellulose in a cellulose solvent of sodium hydroxide and urea, followed by coagulating in a sulfuric acid (H_2SO_4) solution. Different coagulant concentrations and coagulation reaction times were applied to study the morphology, physical and mechanical properties of the prepared cellulose membrane. The crystallinity index, surface morphology, mechanical performance and transparency of cellulose membrane were evaluated using X-ray diffraction (XRD), variable pressure scanning electron microscopy (VPSEM), tensile tests and UV-visible spectroscopy (UV-Vis), respectively. The results revealed changes in the pore size of the cellulose membranes, which were correlated with the concentration of sulfuric acid coagulant. However, the pore size of the membranes was not significantly affected by the coagulation time. Cellulose membranes that had been coagulated in lower concentration sulfuric acid with moderate coagulation time showed desirable mechanical properties. Thus, this study reports a favorable reaction time and coagulant concentration to fabricate regenerated cellulose membranes with desired physical properties.

Keywords: kenaf core pulp, rapid dissolution method, NaOH/urea solvent system, coagulation, regenerated cellulose membranes

INTRODUCTION

Malaysia is one of the biggest agriculture producers in the Asian region, as it abounds in various types of natural resources, such as kenaf. Kenaf (*Hibiscus cannabinus* L.) comprises 21.5 wt% hemicellulose, 45-57 wt% cellulose, 8-13 wt% lignin and 3-5 wt% pectin.[1,2] Cellulose is one of the main components in several kinds of natural resources, such as cotton linter,[3] oil palm empty fruit bunch,[4] kenaf,[2] wheat straw,[5] *etc.* It can be renewed, regenerated or derivatized into various cellulose derivatives.[6] Hence, cellulose can be considered as a harmless and biodegradable material that could be used to produce numerous value-added products.

The preparation of a cellulose solution from viscose, cuprammonium and N-methylmorpholine-N-oxide (NMMO) is complicated as several additional steps are required to handle the waste emissions.[7] Hence, a green cellulose solvent, sodium hydroxide (NaOH)/urea aqueous solution, has gradually attracted the researchers' attention. This is because the NaOH/urea cellulose solvent is cheaper and has more environmentally friendly properties, while it can dissolve cellulose in a few minutes, as compared to other common solvents available in the market.[8] In this urea alkaline system, no toxic substance is employed or released throughout the cellulose dissolving process. After the cellulose dissolution process, the cellulose solution can be regenerated into various materials, such as regenerated cellulose fiber, regenerated cellulose membrane,[9] regenerated cellulose hydrogel,[10] regenerated cellulose beads, *etc.*

Nowadays, regenerated cellulose membranes have attracted much research interest, as they possess outstanding mechanical properties, biological compatibility and permeability.[11] Regenerated cellulose membranes have been extensively used in membrane separation[12,13] and gas barrier technologies[14,15] due to their fascinating structure. The properties of regenerated cellulose membranes are closely associated to their structure and morphology, which are mainly controlled by coagulation conditions, coagulant nature and coagulation mechanism.[16] Thus, the types of coagulant and the coagulation conditions are really important in the cellulose industry. Regeneration of cellulose solutions can be performed from several non-solvents, such as sulfuric acid, sodium sulfate,[17] water, ethanol and methanol.[18]

Therefore, the effects of coagulation conditions on the formation of regenerated cellulose membranes are important for their wide applications in the separation technology. It is believed that the study could reveal the possibility to produce regenerated cellulose membranes using a green solvent system. In this study, regenerated cellulose membranes were fabricated from the dissolution of cellulose in the NaOH/urea solvent system, followed by the coagulation of the cellulose solution at several sulfuric acid concentrations and various coagulation times. The effects of coagulant concentration and coagulation time on the structure, morphology and properties of the cellulose membranes were evaluated and discussed.

EXPERIMENTAL

Materials

Kenaf core pulp was supplied by the Forest Research Institute Malaysia (FRIM). 98.0% analytical grade sodium hydroxide (NaOH) and 98.0% sulfuric acid (H_2SO_4) were purchased from R&M Chemicals, whereas urea and sodium chlorite ($NaClO_2$) were obtained from Sigma Aldrich. All the chemicals were used without further purification.

Bleaching process

The kenaf core pulp (KCP) was bleached in a series of stages (DEED), where stages D and E represented acidic and alkaline treatments, respectively.[10] Both treatments were carried out to remove lignin and hemicellulose. The buffer solution for stage D consisted of 27 g sodium hydroxide, 75 mL of acetic acid and distilled water, whereas the $NaClO_2$ solution was prepared at 1.7%. The ratio of the buffer solution to the $NaClO_2$ solution and to water was 1:1:1. The D stage was performed using a solid to solvent ratio of 1:20 at 80 °C for 4 h. Step E involved 4-6% of NaOH solution at 80 °C for 3 h. After completion of the four bleaching stages, the KCP was washed with distilled water and dried in an oven for 24 h at 105 °C.

Fabrication of cellulose membrane

The NaOH/urea solvent was prepared at 7:12:81 (wt%) (NaOH:urea:distilled water) and was stored at -13 °C for 24 h. The cellulose pulp (4 wt%) was added to the NaOH/urea solvent and was stirred extensively to obtain a homogeneous cellulose solution. The cellulose solution was then subjected to centrifugation at 10000 rpm at 5 °C to remove gas bubbles. Subsequently, the dissolved cellulose solution and undissolved cellulose were separated. Then, the cellulose solution was cast on a glass plate and underwent coagulation in 1 L of sulfuric acid solution, as one surface of the cellulose solution contacted the glass slide (bottom side) and the other side was exposed to the coagulant solution (top side) to form the regenerated cellulose membrane. The coagulated cellulose membranes in sulfuric acid with different concentrations (5, 7, 10 and 12 wt%) during 10 min coagulation time were coded as MC5, MC7, MC10 and MC12, respectively. Meanwhile, the cellulose membranes that were coagulated with 5 wt% sulfuric acid solutions during 1, 3, 5 and 10 min were referred to as MT1, MT3, MT5 and MT10, respectively. The cellulose membranes were washed with distilled water and dried on a poly(methyl methacrylate) sheet at room temperature for further characterizations.

Characterization

The surface morphology of the cellulose membrane was characterized *via* a variable pressure scanning electron microscope (VPSEM) (ZEISS EVO MA 10 (UK)). The pore size of the cellulose membrane was measured using the established software – SmartTiff software from Carl Zeiss Microscopy Limited in Cambridge, United Kingdom. The sample was sputter coated with gold prior to the observation under microscope. Phase and crystallinity index (CrI) of the cellulose membranes were characterized by X-ray diffraction (XRD) (BrukerAxs D8 Advance, Germany). The XRD was carried out using the radiation of CuK = 1.5458 Å at a diffraction angle (2Θ) range of 5 to 60^o.[19] The crystallinity index of the cellulose membrane was calculated using the Bruker Advanced X-Ray Solutions software, DIFFRAC^{PLUS} Evaluation (EVA) with the following equation with slight modifications:

$$CI(\%) = \frac{A_{crystal}}{A_{Total}} x100 \qquad (1)$$

where $A_{crystal}$ is the total of the areas under the crystalline diffraction peaks and A_{Total} represents the total area under the diffraction curves at 2Θ between 5 and 50^o.

The transparency of the cellulose membranes was determined by a UV-visible spectrophotometer (UV-Vis) (Jenway 7315) at wavelengths ranging from 200 to 700 nm. The thickness of the regenerated cellulose membrane was around 0.042 mm. The cellulose membrane was placed in a conditioned room with humidity control of 59% for 24 hours before mechanical testing. The tensile property of the cellulose membrane was measured using a tensile machine (GOTECH, model AI-3000) at a speed of 10 mm min^{-1}. The cellulose membrane samples were prepared to the size of 100 mm x 10 mm, and 5 replicate runs were performed for each sample.

RESULTS AND DISCUSSION

Effect of H_2SO_4 coagulant concentration

Phase and CrI

XRD measurement was performed to characterize the crystalline properties of the cellulose membranes. Figure 1 shows the XRD patterns of the cellulose membranes, which were prepared using different coagulant concentrations. All the cellulose membranes were found in the form of cellulose II considering the peaks at 2Θ = 12.1, 19.8 and 22°, as reported in Gan *et al.*,[20] which were consistent with the $(1\bar{1}0)$, (110) and (200) planes, as discussed by Li *et al.*[21] This has proven that all the cellulose membranes have been regenerated and transformed to cellulose II from cellulose I in native cellulose, as discussed by Gan *et al.*[22] From Table 1, it may be noted that the CrI values of the regenerated cellulose membranes were within the range of 34.5 to 44.9%. This has proven that the CrI values of cellulose membranes were negatively correlated to the sulfuric acid concentration used during the coagulation process.

Surface morphology

Figure 2 displays the surface structure of the cellulose membranes that were coagulated during 10 min of coagulation time and with various concentrations of H_2SO_4 coagulant. The homogeneous porosity of the cellulose membranes indicates that the cellulose was completely regenerated in the urea alkaline solvent system, as it was a physical regeneration during the coagulation. Figure 2 shows that the cellulose membrane with a lower coagulant concentration (5 wt%) exhibited a smaller pore size. The pore size of the cellulose membrane increased as the coagulant concentration was higher. This is due to the fact that the higher concentration of coagulant is more likely to facilitate the decomposition of cellulose, which is responsible for an increase in the pore size of the cellulose membranes.[17] This result can be also correlated to the mechanical strength results, as shown in Figure 3a (will be discussed), which revealed a higher tensile strength value for the cellulose membranes coagulated with a lower coagulant concentration.

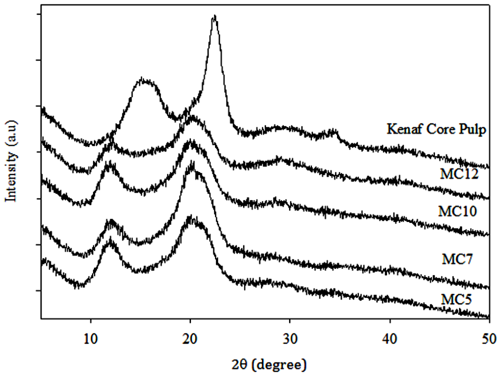

Figure 1: XRD patterns of cellulose membranes obtained at 10 min coagulation time and different H_2SO_4 coagulant concentration

Table 1
CrI of cellulose membranes obtained at 10 min coagulation time and different H_2SO_4 coagulant concentration

Sample	CrI (%)
MC5	43.2 ± 1.2
MC7	43.2 ± 0.8
MC10	44.9 ± 0.9
MC12	34.5 ± 0.6

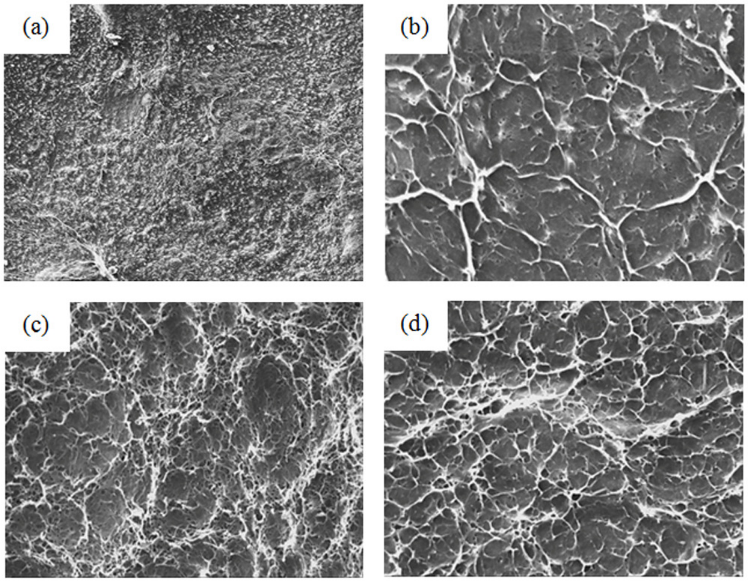

Figure 2: SEM images of (a) MC5, (b) MC7, (c) MC10 and (d) MC12

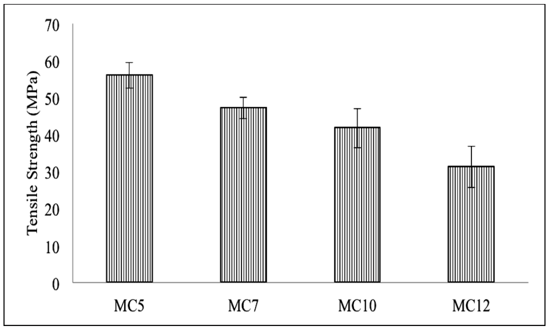

Figure 3: Tensile strength of cellulose membranes coagulated with various concentrations of H_2SO_4

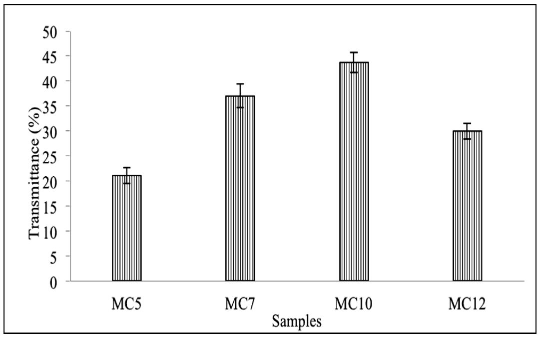

Figure 4: Optical transmittance of cellulose membranes at different coagulant concentrations

Mechanical properties

Figure 3 depicts the dependences of the tensile strength and elongation of the membranes obtained after 10 min of coagulation time with different sulfuric acid concentrations. The cellulose membrane that was coagulated with 5 wt% coagulant exhibited the highest tensile strength. The graph shows that the tensile value of the cellulose membrane decreased with an increase in sulfuric acid coagulant concentration. This indicates that lower coagulant concentration provides a positive effect on the mechanical properties of the cellulose membrane. This can be explained by the fact that the rate of the diffusion process may increase and the diffusion of a non-solvent has an advantage over that of a solvent, which diffuses from the spinning solution in the coagulation bath.[23]

Transparency

Optical transmittance is a support method for estimating the quality of a film material. Figure 4 illustrates the optical transmittance of the cellulose membranes coagulated at different sulfuric acid concentration at a setting time of 10 min. The cellulose membranes that have undergone the coagulation process at 10 wt% sulfuric acid concentration exhibited the highest transmittance (%), as portrayed in Figure 4. This can be explained by the higher concentration of the accelerators, promoting the solvent exchange process, which results in a less rigid structure of the cellulose film. This result can also be related to the SEM results in Figure 2, which shows a significant increase in pore size with increasing sulfuric acid concentration.

Effect of coagulation time

Phase and CrI

Figure 5 presents the XRD diffraction peaks of the cellulose membranes prepared with 5 wt% sulfuric acid concentrations and different coagulation times. The cellulose membrane sample peaks were found at $2\theta = 12.1$, 19.8 and 22°, representing the cellulose II allomorph, as discussed by Gan *et al.*[9] The crystallinity index (CrI) of the cellulose membranes is listed in Table 2. However, the coagulation time of the cellulose membrane had no significant effect on the CrI of the cellulose film.

Surface morphology

Figure 6 shows the SEM image of the cellulose membranes coagulated with 5 wt% sulfuric acid solution at different coagulation times. In the fabrication of the cellulose membrane samples, shorter coagulation times resulted in the formation of cellulose membranes with smaller pore sizes. By increasing the coagulation time, the newly formed cellulose gel sheet gradually released the urea/alkaline solvent, and precipitated out of the cellulose solution due to non-solvent permeation. Finally, a semi-solid cellulose membranes was obtained with a smaller woven mesh network structure.[11] As shown in Figure 6, the pore size of the cellulose membranes slightly varies with the increase in the membrane coagulation time. According to Ruan *et al.*,[24] the large pore size of the cellulose membranes was caused by the incomplete mass transfer between the solution and coagulant, as in the case of MT1.

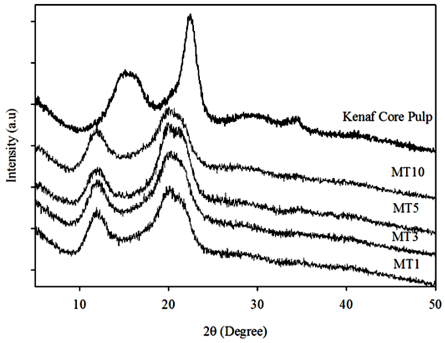

Figure 5: XRD patterns of cellulose membranes obtained at 5 wt% H_2SO_4 concentration and different coagulation times

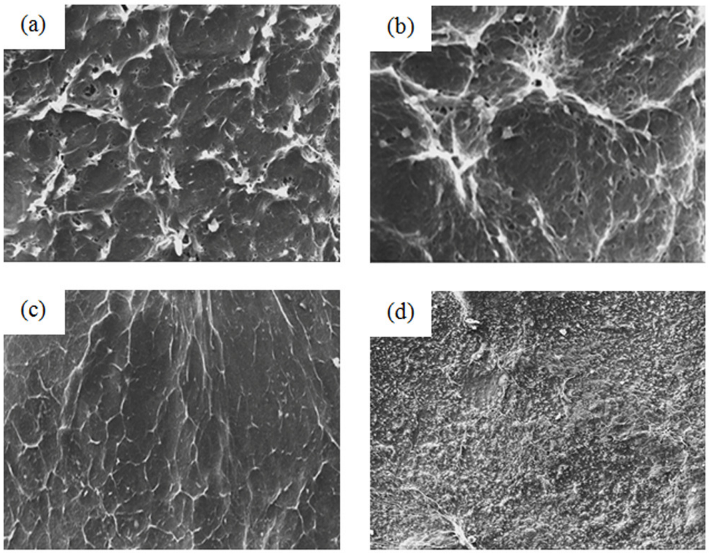

Figure 6: SEM images of the (a) MT1, (b) MT3, (c) MT5 and (c) MT10

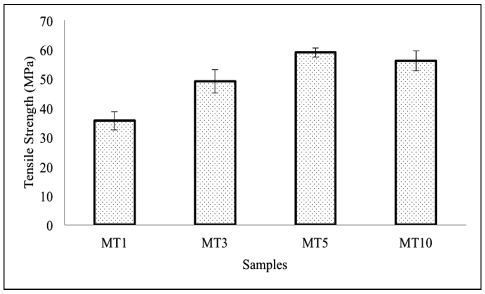

Figure 7: Tensile strength of cellulose membranes coagulated at various coagulation times

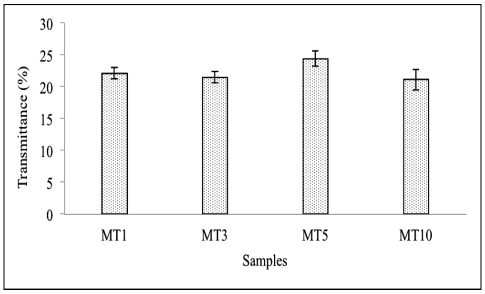

Figure 8: Optical transmittance of cellulose membranes obtained at different coagulation times

Table 2
CrI of cellulose membranes obtained at different coagulation times

Sample	CrI (%)
MT1	51.4 ± 0.8
MT3	51.3 ± 1.3
MT5	54.1 ± 1.4
MT10	43.2 ± 1.2

Mechanical properties

The effect of coagulation time on the mechanical properties of the cellulose membranes is shown in Figure 7. The tensile strength of the cellulose membrane gradually increased as the coagulation time increased up to 5 min. However, the tensile strength value decreased when the coagulation of the cellulose membrane was set for 10 minutes. This may be due to the fact that the cellulose membrane has been completely formed; excessive coagulation time can lead to membrane degradation and affect the strength of the cellulose membrane. It can be explained by the fact that the sulfuric acid in the coagulatation bath could break the cellulose structure and the intermolecular hydrogen bonding within cellulose due to the prolonged time, leading to deterioration of the mechanical properties of the cellulose membrane.[11]

Transparency

Figure 8 displays the optical transmittance of the cellulose membranes coagulated in 5 wt% sulfuric acid within a coagulation time varying from 1 min to 10 min. The cellulose membranes subjected to the coagulation process for 5 minutes showed the highest transmittance (%), as presented in Figure 8. This can be explained by the fact that a longer coagulation time possibly resulted in lower porosity of the cellulose membrane and the stiffer structure of the cellulose membranes brought to lower transparency. This result was supported by the SEM results in Figure 6.

CONCLUSION

All the cellulose membranes prepared by coagulation with different concentrations (5-12 wt%) of the aqueous sulfuric acid solution and different coagulation times (1-10 min) showed uniform microporous structure. The regenerated cellulose membranes displayed the cellulose II crystalline form with relatively low CrI. SEM results revealed the pore size of the membranes varied with the concentration of the sulfuric acid coagulant, whereas it hardly changed with coagulation time. The cellulose membranes that were coagulated with a relatively dilute sulfuric acid solution and shorter coagulation time exhibited good mechanical properties. Therefore, the coagulation concentration plays an important role, affecting the structure, pore size and mechanical properties of regenerated cellulose membranes.

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