

Physico-Mechanical Properties of Kenaf Pulp Cellulose Membrane Cross-linked with Glyoxal

(Sifat Fiziko-Mekanik Membran Selulosa daripada Pulpa Kenaf yang Ditaut-silang dengan Glioksal)

ANIS SYUHADA MOHD SAIDI, SARANI ZAKARIA*, CHIN HUA CHIA, SHARIFAH NABIHAH SYED JAAFAR & FARAH NADIA MOHAMMAD PADZIL

ABSTRACT

Cellulose was extracted from kenaf core pulp (KCP) by a series of bleaching processes (D) and alkali treatment (E) in the sequence of (DEED) and pretreated with acid hydrolysis in room temperature for 6 hours. The pretreated and non-treated cellulose were dissolved in lithium hydroxide/urea (LiOH/urea) and subsequently used to produce cellulose membrane cross linked with various percentages of glyoxal from 2.5 to 20%. The effects of acid hydrolysis pretreatment on solubility, crystallinity and morphology were investigated. The acid hydrolysis pretreatment leads to higher solubility of the cellulose solution. The formation of cellulose II and crystallinity index of the cellulose membrane were examined by X-ray diffraction (XRD). Cellulose membrane without acid hydrolysis pretreatment cross linked with higher percentage of glyoxal has higher tensile strength compared with the treated cellulose.

Keywords: Acid hydrolysis; aldehyde; cross linked; kenaf core pulp

ABSTRAK

Selulosa diekstrak daripada pulpa teras kenaf menerusi satu siri proses pelunturan (D) dan rawatan alkali (E) mengikut urutan (DEED). Kemudian, selulosa tersebut melalui pra-rawatan hidrolisis asid pada suhu bilik selama 6 jam. Selulosa yang melalui proses rawatan dan tanpa rawatan dilarutkan di dalam larutan litium hidroksida/urea (LiOH/urea) dan digunakan untuk penghasilan membran. Membran tersebut ditaut-silang dengan peratus glioksal yang berbeza iaitu 2.5 hingga 20%. Kesan pra-rawatan hidrolisis asid terhadap keterlarutan, kehabluran dan morfologi dikaji. Pembentukan selulosa II dan indeks kehabluran membran selulosa dikenal pasti dengan menggunakan pembelauan sinar-X (XRD). Membran selulosa tanpa pra-rawatan hidrolisis asid ditaut-silang dengan peratus glioksal yang lebih tinggi mempunyai kekuatan regangan yang lebih tinggi berbanding dengan membran selulosa tanpa pra-rawatan.

Kata kunci: Aldehida; hidrolisis asid; pulpa teras kenaf; taut-silang

INTRODUCTION

Lignocellulosic materials are abundantly found on earth and refer to plant materials which consist of cellulose, hemicelluloses and lignin (Klemm et al. 2005). Kenaf (*Hibiscus cannabinus* L.) is an agricultural plant which originates from Malvaceae family. Kenaf grows very fast as it can reach 12 to 14 feet of height in just four to five months period. Kenaf bast fibre is commonly used in pulp, papers and textiles industries. In Malaysia, kenaf has become an alternative plantation in textile manufacturing, biocomposites, source for animal food and fuel materials (Shi et al. 2011).

Cellulose is a biopolymer material and has renewable and biodegradable properties. Cellulose consists of β -1,4 bonding attached with D-glucopyranosyl units and three hydroxyl groups to form intermolecular and intramolecular hydrogen (Jin et al. 2006). Cellulose is insoluble in most solvents and does not melt until thermal degradation (Li et al. 2011).

In cellulose dissolution process, there are many types of solvents commonly used such as N_2O_4 /

N,N-dimethylformamide (DMF), SO_2 /amine, Me_2SO /paraformaldehyde (PF), N,N-dimethylacetamide/LiCl (DMAc/LiCl), N-methyl-morpholina-N-oxide (NMMO) and NaSCN/KSCN/LiSCN/water. However these solvents are toxic, volatile and high in cost (Jin et al. 2006).

LiOH/urea has been identified as a good solvent to dissolve lower molecular weight cellulose of the average reading below 1.2×10^5 . Dissolution process by using LiOH/urea is fast, environmental friendly and cost saving. Plus, cellulose can be dissolved at lower temperature compared to other solvents which require higher temperature for dissolution process (Luo & Zhang 2010). Formation of hydrates in aqueous solution occur due to Li^+ , OH^- ions and urea as hydrates that break the cellulose chain bonding forming hydrogen bonding in lower temperature to produce stable complex solution between LiOH, water cluster and cellulose. Inclusion complex (IC) channel hosted by urea trap cellulose macromolecules in the LiOH/urea solution and creates well distribution from cellulose. Low temperature, -12 to 5°C is crucial in exchanging hydrogen bonding between cellulose and small molecules

that enable macromolecules dissolution in aqueous solution (Jin et al. 2006). Rapid cellulose dissolution occurs and in fact only few seconds are required as the existence of Weissenberg effect occurs within 30 s. Weissenberg effect describes the phenomenon when a spinning rod is inserted into a solution of liquid polymer and the solution is drawn towards the rod and rises up around it (Cai & Zhang 2005).

Cross linking reaction enables prepared materials produced to have better aspects in terms of mechanical, thermal, and physio-chemistry properties. There are three types of cross linking reactions normally take place; covalent cross linking, ionic bonding, and physical cross linking (Tillet et al. 2010).

The effect of different percentages of glyoxal on the strength of the membranes is studied. Besides that, the acid hydrolysis effect on the formation and properties of membrane produced after cross linking agent is used were investigated.

MATERIALS AND METHODS

Raw kenaf core was supplied by the Malaysian Agricultural Research and Development Institute (MARDI). The 98.0% analytical grade of lithium hydroxide monohydrate (LiOH. H₂O) and sulfuric acid were purchased from Sigma Aldrich while urea and sodium chlorite (NaClO₂) was obtained from R & M Chemicals. Cadoxen solvent preparation which comprises of ethylene diamine and cadmium oxide for molecular weight purpose was also purchased from Sigma Aldrich.

PULPING AND BLEACHING PROCESS

The raw kenaf core underwent soda pulping process in a digester with 25% NaOH concentration at 170°C for 150 min at Forest Research Institute Malaysia (FRIM). The KCP was bleached at various stages (DEED) where stage D and E are the acidic and alkali treatment, respectively, to remove lignin and hemicelluloses. Buffer solution was prepared during the D stage which consists of 27 g NaOH, 75 mL of acetic acid, distilled water and 1.7% of NaClO₂ solution at 80°C for 4 h. Step E involved the preparation of 4-6% of NaOH solution at 80°C for 3 h. After all of the stages were completed, the KCP was washed with distilled water until it neutralized before dried at 105°C for 24 h.

PREPARATION OF ACID HYDROLYSIS PRETREATMENT ON KENAF CORE PULP

Bleached KCP (BKCP) of 3 g and 60 g of 10% sulfuric acid were weighed with the ratio of KCP to sulfuric acid 1:20. The BKCP was added into the sulfuric acid solution and the mixture was stirred continuously by using mechanical stirrer for 6 h at room temperature. The 6 h treatment was chosen as it possesses the highest solubility compared to 2 h and 4 h treatment after tested and it is the optimum hydrolysis time for acid hydrolysis to occur. Then, the treated KCP was washed with distilled water until it neutralized. Next, the treated KCP (A6) was dried at 105°C

for 24 h. The 6 h treated sample is referred as A6 while KCP without acid hydrolysis pretreatment is referred as BKCP.

MOLECULAR WEIGHT CALCULATION FOR KENAF SAMPLES

Average molecular weight (M_w) of BKCP and A6 samples were carried out by using viscometer measurement. Each sample was dissolved in 3×10^{-3} g/mL concentration of cadoxen solution and diluted for five times to obtain concentration ranging from 1 to 3×10^{-3} g/mL. Cellulose solution dissolved in cadoxen is put into Ubbelohde viscometer capillary tube at 25°C and average time was recorded. Intrinsic viscosities (η) of each sample are determined by Kraemer and Huggins equation. The graph is extrapolated to zero concentration and the intersection between the Kraemer and Huggins line gave the reading of the estimated value of (η). The specific viscosity (η_{sp}) and relative viscosity (η_r) are calculated using the following:

Kraemer equation:

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

Huggins equation:

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

where c is concentration, k'_k is a constant for a given polymer at a given temperature in a given solvent in the Kraemer equation and k'_H is a constant for a given polymer in a given solvent in the Huggins equation. The reduced viscosity is referred as $\frac{\eta_{sp}}{c}$ and the inherent viscosity of the cellulose is labeled as $\frac{\eta_r}{c}$.

CELLULOSE MEMBRANE PREPARATION

Solvent consisting of 4.6 wt. % LiOH:15 wt. % urea was prepared and stored in a freezer until it reached -13°C. 3 wt. % of cellulose was weighed and subsequently dissolved in the solvent by using mechanical stirrer for 5 min to form a heterogeneous mixture in which the insoluble and soluble cellulose were formed in the slightly transparent yellowish solution. Cellulose solution produced was then centrifuged at 8000 rpm for 5 min at 5°C to separate the dissolved and undissolved cellulose.

Soluble cellulose was used to form cellulose membrane. Each soluble BKCP and A6 solutions were casted on glass plate to form membrane and immersed in 2.5, 5, 10 and 20% of glyoxal solution. Glyoxal solution was measured by using weight to volume ratio. For instance 250 g of glyoxal was measured in 250 mL of distilled water (DW) for 20% concentration. Membrane without cross linking agent was prepared by immersing the membrane in distilled water. The thicknesses of membranes recorded were in the range of 0.273-0.294 mm. All of the membranes were then immersed and washed with DW for three days to remove the alkali and urea excess. The treated cellulose membranes (AM) cross

linked with 2.5, 5, 10 and 20% of glyoxal were referred as AM-2.5, AM-5, AM-10 and AM-20 whereas the untreated samples (M) crosslinked with different percentage of glyoxal were referred as M-2.5, M-5, M-10 and M-20. The samples without cross linking agent are labeled as AM (6 h-treated membrane) and M (untreated membrane). All of the samples were then freeze-dried for 48 h for further characterizations.

CHARACTERIZATION

SOLUBILITY TEST

The insoluble cellulose formed after centrifugation step carried out were collected and crushed into smaller form and immersed in distilled water. The mixture was washed with excess distilled water until it neutralized. Then the sample was dried in oven at 80°C for 12 h before weighted to determine the solubility for A6 and BKCP. The solubility is calculated according to the following:

$$S = \frac{W_o - W}{W_o} \times 100\%, \quad (3)$$

where S is solubility degree, W_o refers as original weight of cellulose and W is the weight of insoluble cellulose (Gan et al. 2014a).

X-RAY DIFFRACTION

Membrane with 6 h acid hydrolysis pretreatment (AM) and membranes underwent acid hydrolysis cross linked with 2.5, 5, 10 and 20 % glyoxal (AM-2.5, AM-5, AM-10 and AM-20) were freeze-dried for three days after liquid nitrogen was applied. Then, the samples were cut into smaller pieces for XRD testing. The samples were distributed equally on the circle sample holder and the machine was run at 2 θ degree.

FIELD EMISSION SCANNING ELECTRON MICROSCOPY (FESEM)

Membrane with and without acid hydrolysis pretreatment (AM and M, respectively) and membranes cross linked with different percentage of glyoxal (AM-2.5, AM-5, AM-10, AM-20, M-2.5, M-5, M-10 and M-20) were slightly cut and coated with gold before cross section of samples were observed under FESEM.

TENSILE TEST

All of the samples (AM, AM-2.5, AM-5, AM-10, AM-20, M, M-2.5, M-5, M-10 and M-20) were air-dried overnight. All the samples were cut into 10 \times 1 cm dimensions of length and width before tested.

RESULTS AND DISCUSSION

CHARACTERIZATION OF KENAF CORE PULP (KCP) AND ACID HYDROLYSIS PRETREATMENT

The value of intrinsic viscosity (η) of KCP is determined by the point of intersection in the graph of intrinsic viscosity against cellulose concentration (c) as illustrated in Figure 1. Viscosity-average molecular weight (M_η) of KCP was determined based on the Mark-Houwink equation as stated in (4) and value of degree of polymerization is expressed in (5).

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

$$(\eta) = 1.75 (DP)^{0.69}. \quad (5)$$

The computed values of (η), M_η and DP of BKCP and A6 samples with acid hydrolysis pretreatment are displayed in Table 1. At 6 h reaction time of acid hydrolysis leads to decreasing trend for both M_η and DP readings. A6 sample

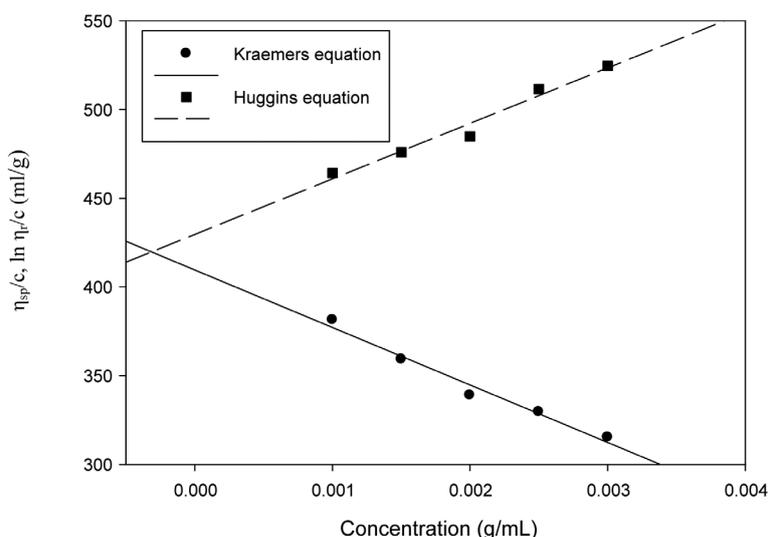


FIGURE 1. Graph of intrinsic viscosity (η) against concentration of cellulose (c)

has lower reading of M_n and DP when compared to BKCP without acid hydrolysis pretreatment. The pretreatment can cut down the M_n by 41.3% of cellulose from 2.095 to 1.23×10^5 in 6 h and therefore it is proven that acid hydrolysis is able to reduce the M_n of cellulose.

DISSOLUTION OF BLEACHED KENAF CORE PULP (BKCP) AND ACID HYDROLYSIS PRETREATMENT (TKCP)

The solubility of BKCP and A6 are determined according to (3). The average solubility percentage of 3 wt. % of cellulose for each sample was taken and the results are shown in Table 1.

The β -1,4-glycosidic bonds of a cellulose chain molecules are split by the addition of water molecules when cellulose is hydrolyzed in the acidic medium. In acid hydrolysis, protonation of glycosidic bond occur. Rapid formation of an intermediate complex between the glucosidic oxygen and a proton is followed by the slow splitting of glucosidic bonds induced by the addition of water molecules. This addition yields fragments or shorter chain lengths of cellulose and reduce its molecular weight (Fan et al. 1987). From the result obtained, it is clear that kenaf cellulose with acid hydrolysis pretreatment has higher solubility than BKCP without pretreatment. Long reaction time of treatment increases the average solubility of cellulose. This is due to cellulose with lower form less packed network and easier for cellulose to be dissolved in urea-alkaline system. The solvent molecules containing Li^+

with relatively small ionic radii and high charge densities enable it to easily penetrate cellulose and expand it to the higher swollen and dissolution state since the intra and inter-molecular hydrogen bonding between the cellulose molecules have been destroyed (Cai & Zhang 2005; Gan et al. 2014b). The solubility of BKCP has increased up to 9.5% and it is therefore true that the solubility of cellulose has been improved by acid hydrolysis pretreatment.

X-RAY DIFFRACTION OF KENAF MEMBRANE

The formation of cellulose I into regenerated cellulose or also known as cellulose II is confirmed by XRD testing as illustrated in Figure 2. The diffraction pattern of BKCP shows a sharp peak at 22.5° and a wide peak between 14.8° and 16.3° which resemble typical cellulose I structure. After regeneration and dissolution process took place, the peaks are shifted to $2\theta = 12^\circ$, 20.1° and 21.5° which describe cellulose II crystalline allomorph (Jin et al. 2006; Yang 2006). This explains why the crystallinity index (CrI) for BKCP is higher than AM (membrane with acid hydrolysis pretreatment) in Table 2.

Membrane cross linked with higher percentage of glyoxal has lower CrI than the one with lower percentage of crosslinker. The results illustrate that disturbance of the crystalline area of cellulose occur when cross linking were carried out as the inter and intra hydrogen bond of cellulose were destroyed (Gan et al. 2014a; Kaco et al. 2014). The H^+ from the cellulose break the double bond of $-OH$ group

TABLE 1. Reading of (η), M_n , DP and solubility of bleached kenaf core pulp (BKCP) and kenaf pulp with 6h acid hydrolysis pretreatment (A6)

| Sample | (η) (mL/g) | M_n | DP | Solubility (%) |
|--------|-------------------|---------------------|---------|----------------|
| BKCP | 427.26 | 2.095×10^5 | 2885.98 | 72.85 |
| A6 | 285.05 | 1.23×10^5 | 1605.53 | 82.34 |

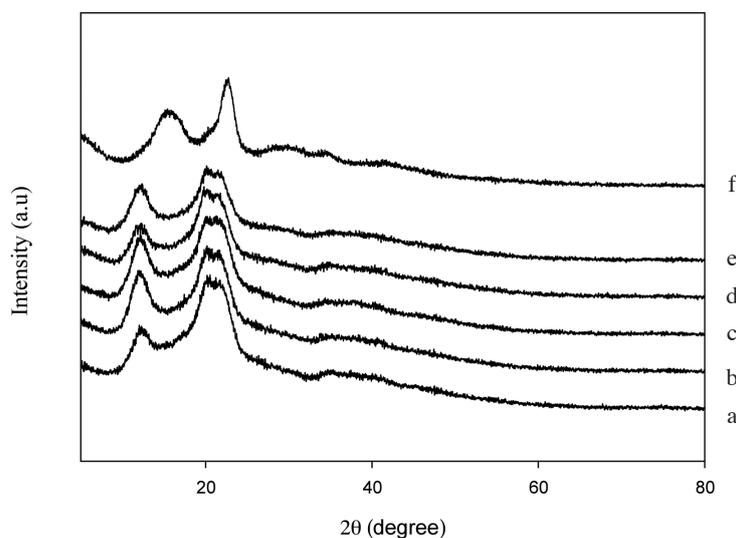


FIGURE 2. XRD graph of kenaf samples from (a) AM (b) AM-2.5 (c) AM-5 (d) AM-10 (e) AM-20 and (f) BKCP

TABLE 2. Crystallinity index for different types of cellulose membranes with pretreatment (AM) crosslinked with different percentages of glyoxal

| Sample | Crystallinity index (%) |
|--------|-------------------------|
| BKCP | 62.73 |
| AM | 53.42 |
| AM-2.5 | 47.48 |
| AM-5 | 45.79 |
| AM-10 | 44.12 |
| AM-20 | 42.97 |

from the glyoxal and water is removed to achieve stable acetal structure (Rojas et al. 2011). Thus, higher percentage of glyoxal leads to more hydrogen bonds to be destroyed and explains the lower reading of CrI value.

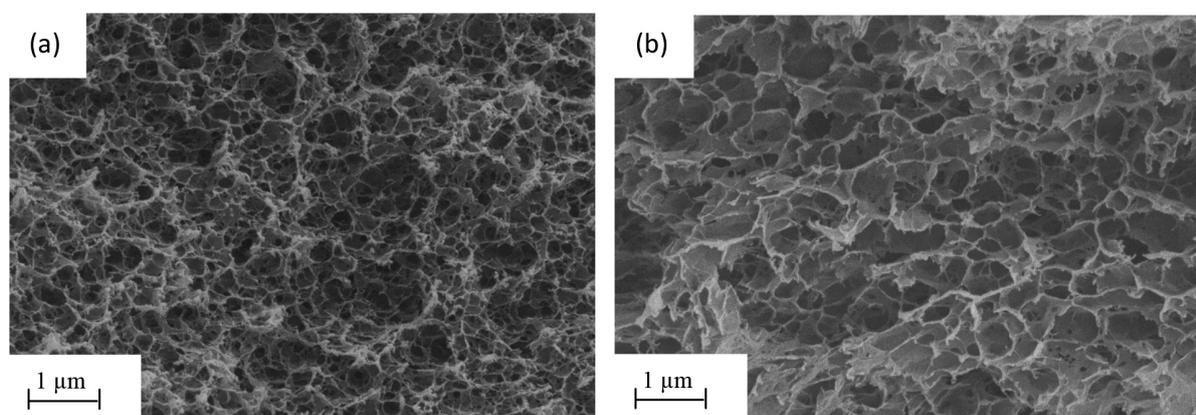
SURFACE MORPHOLOGY OF KENAF CELLULOSE MEMBRANE

FESEM micrographs of cellulose membranes' cross section are shown in Figure 3. The cellulose membranes cross linked with different percentages of glyoxal are colourless and transparent physically with measured thickness in the range of 0.27- 0.28 mm. The surface structure and pore size are observed under FESEM to see the effect of different percentages of cross linking agent on the membranes. As the glyoxal percentage increase, the pore size decrease for both membranes with acid hydrolysis pretreatment and without the treatment. Membrane with 20% of glyoxal has smaller pore size and more packed cellulose arrangements compared to membranes with lower percentage of glyoxal. Aggregation of cellulose chain is lower on samples with less composition of cross linking agent and hence causes the microstructure of cellulose membrane to be less packed (Chang et al. 2010). In addition, membrane without acid hydrolysis treatment cross linked with higher percentage of glyoxal has better packed arrangement and smaller pore size than membrane which undergone pretreatment. This result suggested that reduction in of the cellulose after acid

hydrolysis pretreatment caused the pore to be bigger in size. The protonation of the glycosidic bond resulted in shorter chain lengths of cellulose (Fan et al. 1987). Hence, it caused the cellulose distribution to be distant from the other cellulose structure which leads to bigger pore size.

TENSILE STRENGTH OF KENAF CELLULOSE MEMBRANE

Tensile test was carried out to identify the difference in mechanical properties of cellulose membranes with and without acid hydrolysis pretreatment after cross linked with glyoxal. Figure 4 illustrates the tensile strength for each of the sample. There is a positive correlation between the increasing aldehyde percentage and strength of the cellulose membranes. This is due to the higher steric hindrance effect resulted from higher percentage of glyoxal. Thus, the brittleness on cellulose membranes is lower and gives higher strength (Rojas & Azevedo 2011). The samples without acid hydrolysis pretreatment have higher tensile strength compared with the treated samples. The samples without acid hydrolysis pretreatment have higher and tend to have packed microstructure arrangement due to longer chain of cellulose arrangement and closer cellulose distributions which lead to higher strength. There is less hydrogen bond broken in the samples without acid hydrolysis pretreatment making the samples more firm.



(continue)

Continued (FIGURE 3)

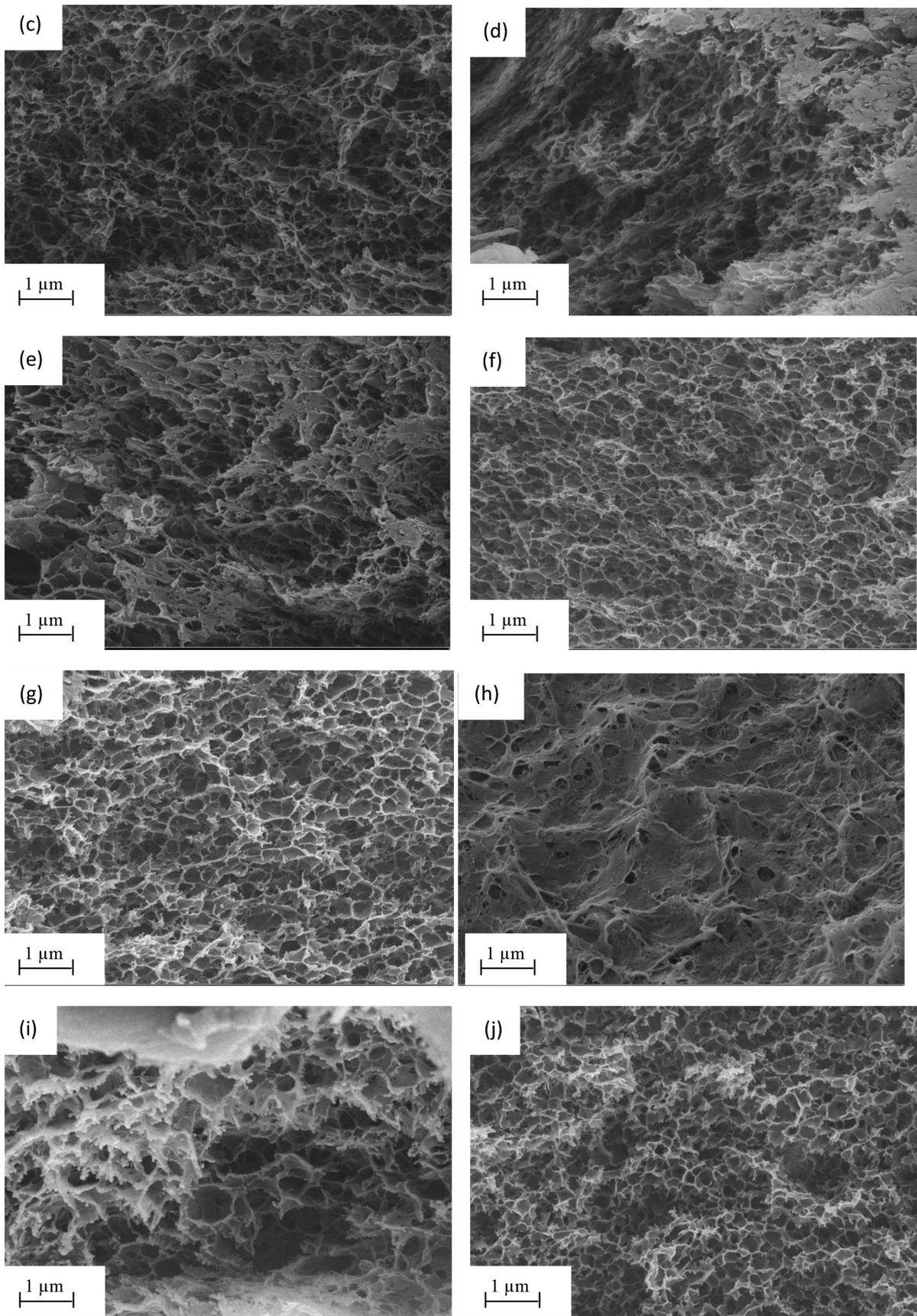


FIGURE 3. FESEM micrograph of (a)AM-2.5 (b) M-2.5 (c) AM-5 (d) M-5 (e) AM-10 (f) M-10 (g) AM-20 (h) M-20 and (i) AM (j) M

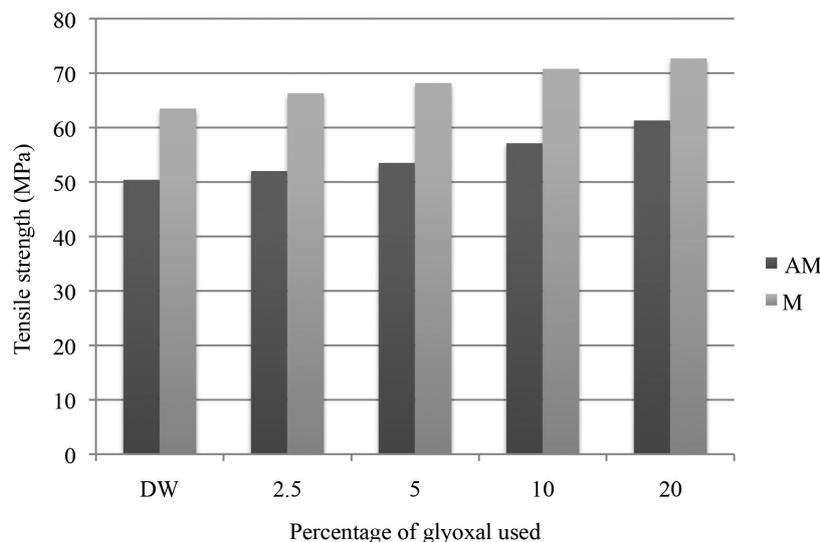


FIGURE 4. Tensile strength for cellulose membranes with pretreatment (AM) and without pretreatment (M) cross linked with different percentages of glyoxal and distilled water (DW) as control

CONCLUSION

The degree of crystallinity and of cellulose are affected by acid hydrolysis pretreatment and resulted into solubility improvement and changes in morphology of regenerated cellulose membranes. Cross linking agent improves the mechanical strength of cellulose membranes and gives better packed arrangement on the microstructure arrangement of the membranes. Cellulose membranes without acid hydrolysis pretreatment cross linked with aldehyde have better properties in terms of tensile strength but lower in solubility while membranes with pretreatment possesses better solubility but lower in strength.

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REFERENCES

- Cai, J. & Zhang, L. 2005. Rapid dissolution of cellulose in LiOH/Urea and NaOH/Urea aqueous solutions. *Macromolecular Bioscience* 5: 539-548.
- Chang, C., Lue, A. & Zhang, L. 2008. Effects of crosslinking methods on structure and properties of cellulose/PVA hydrogels. *Macromolecular Journals* 209: 1266-1273.
- Fan, L-T., Gharpuray, M.M. & Lee, Y-H. 1987. Cellulose hydrolysis. *Biotechnology Monographs* 3: 121-148.
- Gan, S., Zakaria, S., Chia, C.H. & Padzil, F.N.M. 2014a. Effect of hydrothermal pretreatment on solubility and formation of kenaf cellulose membrane and hydrogel. *Carbohydrate Polymers* 115(0): 62-68.
- Gan, S., Zakaria, S., Chia, C.H., Kaco, H. & Padzil, F.N.M. 2014b. Synthesis of kenaf cellulose carbamate using microwave irradiation for preparation of cellulose membrane. *Carbohydrate Polymers* 106(0): 160-165.
- Jin, H., Zha, C. & Gu, L. 2006. Direct dissolution of cellulose in NaOH/thiourea/urea aqueous solution. *Carbohydrate Research* 342(6): 851-858.
- Kaco, H., Zakaria, S., Razali, N.F., Chia, C.H., Zhang, L. & Jani, S.M. 2014. Properties of cellulose hydrogel from kenaf core prepared via pre-cooled dissolving method. *Sains Malaysiana* 43(8): 1221-1229.
- Klemm, D., Heublein, B., Fink, H-P. & Bohn, A. 2005. Cellulose: Fascinating biopolymer and sustainable raw material. *Angewandte Chemie International Edition* 44(22): 3358-3393.
- Li, R., Zhang, L. & Xu, M. 2011. Novel regenerated cellulose films prepared by coagulating with water: Structure and properties. *Carbohydrate Polymers* 87(1): 95-100.
- Luo, X. & Zhang, L. 2010. New solvents and functional materials prepared from cellulose solutions in alkali/urea aqueous system. *Food Research International* 52(1): 387-400.
- Rojas, J. & Azevedo, E. 2011. Functionalization and crosslinking of microcrystalline cellulose in aqueous media: A safe and economic approach. *International Journal of Pharmaceutical Sciences Review and Research* 8(1): 28-36.
- Shi, J., Shi, S.Q., Barnes, H.M., Horstemeyer, M., Wang, J. & El-Barbary, M.H. 2011. Kenaf bast fibers-Part I: Hermetical alkali digestion. *International Journal of Polymer Science* 2011: Article ID 212047.
- Tillet, G., Boutiven, B. & Ameduri, B. 2010. Chemical reactions of polymer crosslinking and post-crosslinking at room and medium temperature. *Progress in Polymer Science* 36(2): 191-217.
- Yang, C-C. 2006. Synthesis and characterization of the cross-linked PVA/TiO₂ composite polymer membrane for alkaline DMFC, *Journal of Membrane Science* 288(1-2): 51-60.

Bioresources and Biorefinery Laboratory
School of Applied Physics, Faculty of Science and Technology
Universiti Kebangsaan Malaysia
43600 Bangi, Selangor Darul Ehsan
Malaysia

*Corresponding author; email: szakaria@ukm.edu.my

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