



Synthesis of hydrogel from sugarcane bagasse extracted cellulose for swelling properties study

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ABSTRACT

Insolubility of cellulose in common solvent had been a challenge in generating cellulose hydrogels. In the present work, hydrogels from sugarcane bagasse extracted cellulose and modify with synthetic polymer, poly (vinyl alcohol) (PVA) and cross-linker, glutaraldehyde (GA) was synthesized. Cellulose was isolated from sugarcane bagasse via pre-treatment with 4 vol% sulphuric acid (H_2SO_4) and 10 wt% sodium hydroxide (NaOH) solution. The cellulose extracted was dissolved in $ZnCl_2/CaCl_2$ solution at 65 °C to fabricate self-standing cellulose hydrogel without cross-linker. Another cellulose hydrogel was generated and immersed into 5 wt% GA solution to cross-link the cellulose chains. To improve the stability and swelling properties of cellulose, PVA was introduced into the hydrogel by using GA to cross-link cellulose chains with PVA chains. The resulting hydrogels were characterized with Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy and solid state ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy for structural determination. Three self-standing cellulose-based hydrogels, including regenerated cellulose (RC), GA cross-linked cellulose (C-GA), followed by PVA and GA cross-linked cellulose (C-GA-PVA) were successfully generated from $ZnCl_2/CaCl_2$ dissolution system and each hydrogel possessed different physical aspects. The occurrence of chemical cross-linking reaction between cellulose, GA and PVA was further evidenced by the data analyzed from ATR-FTIR and NMR spectra. The swelling degree of hydrogels generally increase after the addition of PVA and GA into cellulose suspension, showing 52 % (RC), 80 % (C-GA) and 135 % (C-GA-PVA). C-GA-PVA possessed the best swelling capability and potential for possible application as water reservoir in agriculture.

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1. Introduction

Sugarcane bagasse is the waste generated by sugar manufacturers after the extraction of sugarcane juice. Accumulation of large quantities of sugarcane bagasse as agriculture waste affords a complex waste problem, as only a few commercial uses were initiated for those massive quantities of wastes [1]. Sugarcane bagasse is made up of about 40–50 % of cellulose, 25 % of hemicellulose, mainly constitutes of glucose, galactose, xylose, arabinose and mannose, 25 % of lignin and small portion of mineral, wax and other compounds [2]. The cementing matrix of hemicellulose and lignin diminish the accessibility to cellulose fibres and cause difficulty in cellulose isolation process. In order to isolate cellulose effectively and maximize the performance of extracted cellulose,

lignin and hemicellulose must be removed [3]. Two-stage chemical pre-treatments, in which the combination of alkaline pre-treatment and acid pre-treatment have been reported to exhibit high efficiency in the removal of hemicellulose and lignin contents [4]. Cellulose is the most abundant natural polymer, which is non-toxic, biodegradable, biocompatible, renewable and low cost. It is a linear chain consists of β -1,4-linked anhydro-D-glucose units, in which each unit is twisted 180° spirally with respect to its neighboring unit, and exhibits a degree of polymerization ranging from several hundreds to over ten thousand. Furthermore, hydroxyl groups are found abundantly on the cellulose molecular chains. Due to this characteristic, cellulose can be modified easily to produce improved and effective cellulose-based materials through physical or chemical cross-linking [5]. Hydrogel is polymeric material which made up of three-dimensional network structure and hydrophilic polymer chains, that is capable to swell, absorb and retain a huge proportion of water, saline or physiological solutions

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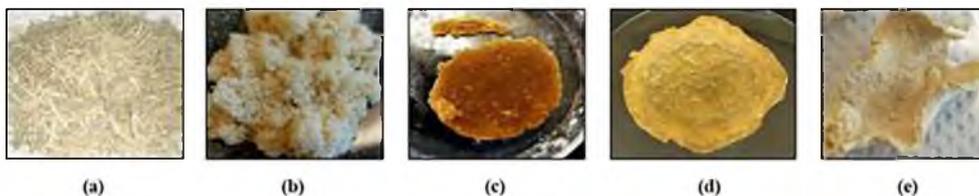
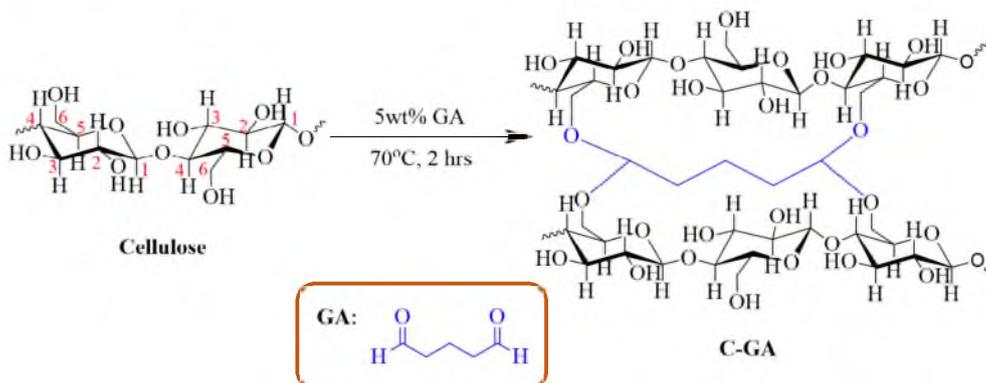


Fig. 1. Physical images of the samples used and modified, (a) untreated sugarcane bagasse, (b) extracted cellulose, (c) regenerated cellulose (RC), (d) cellulose-glutaraldehyde (C-GA) and (e) cellulose-glutaraldehyde-poly(vinyl alcohol) (C-GA-PVA) hydrogels.



Scheme 1. Cross-linking reaction between cellulose and GA to produce cellulose-glutaraldehyde (C-GA) hydrogel.

within its structure [6]. The ability of cellulose to swell in water is influenced by numerous factors, including crystallinity, amorphous regions, pore volume and total surface area. Cellulose hydrogels possessed major drawbacks such as moisture absorption, quality variations, low thermal stability, and poor compatibility with the hydrophobic polymer matrix [7]. Glutaraldehyde (GA) consists of di-functional group C=O within its structure and is commonly utilized as cross-linker for cellulose to give resiliency and dimensional stability as they are capable of forming a three-dimensional hydrophilic network via covalent linkage to different cellulose molecules [8]. Addition of synthetic polymers into cellulose hydrogel have been developed for different objectives, such as transparency, mechanical properties and swelling behaviour. Poly(vinyl alcohol) (PVA) is the largest synthetic polymer which is water soluble and biodegradable. As PVA possesses the compatible structure and hydrophilic properties due to the presence of hydroxyl group, it is widely employed in improving the mechanical strength of films in industrial.

In this study, cellulose extracted sugarcane bagasse was synthesized and modified with synthetic polymer, PVA and cross-linked with GA. Acid and alkali pre-treatment were used to isolate cellulose from sugarcane bagasse and regeneration of cellulose hydrogels from $\text{CaCl}_2/\text{ZnCl}_2$ solvent system was studied. The reaction product was characterised using ATR-FTIR and NMR spectroscopy to confirm the modifications was successful. A preliminary test on swelling properties of each hydrogel was studied for 48 h by using tea-bag method to observe the effect of cellulose modification. This study can further assist the material characteristic as to be apply in environmental applications.

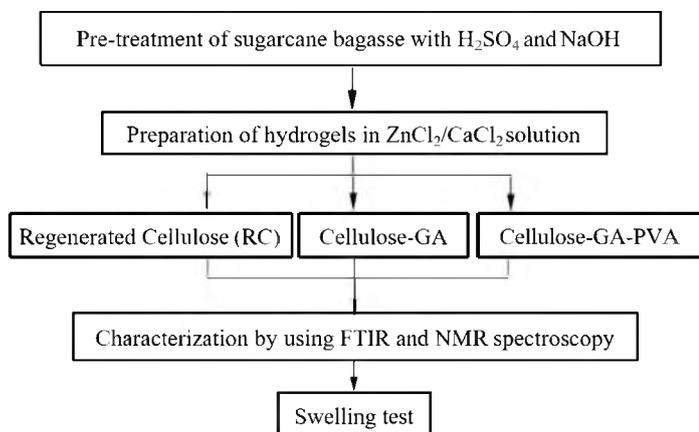
2. Experimental

2.1. Isolation of cellulose from sugarcane bagasse

First, 10 g of sugarcane bagasse was added into 300 mL of 4 vol% H_2SO_4 aqueous solution at 90 °C, and stirred for 1.5 h [9]. Then, the acid treated sugarcane bagasse was filtered and washed with excess deionized water until neutral pH was achieved. The resulting sugarcane bagasse was stirred in 300 mL of 10 wt% NaOH aqueous solution at 90 °C for 12 h. By using excess deionized water, the remaining fibres were washed until neutral pH was achieved. Subsequently, the fibres were filtered and dried in vacuum oven at room temperature over-night.

2.2. Preparation of regenerated cellulose (RC) hydrogels

For the preparation of regenerated cellulose (RC) hydrogel, 9.87 g of ZnCl_2 and 0.2 g CaCl_2 were dissolved in 3.63 g of distilled water at 65 °C for 15 min [10]. Meanwhile, 0.45 g of pre-treated cellulose fiber was mixed with 1.05 g of deionized water to produce cellulose suspension. After that, $\text{ZnCl}_2/\text{CaCl}_2$ solution was poured into the cellulose suspension and stirred for 45 min. The resulting solution was then casted over a glass plate. Subsequently, the glass plate was fully immersed into 500 mL of ethanol (EtOH) for 30 min to separate the hydrogel from the plate. The resulting



cellulose hydrogel was fixed on a metallic frame and dried at 25 °C. The collected RC hydrogel was used for all synthesis here after.

2.3. Preparation of cellulose-PVA hydrogels

A piece of RC hydrogel was immersed into 5 wt% GA solution at 70 °C for 2 h, subsequently dried at 25 °C and labelled as C-GA hydrogel. After that, the same procedure as of RC hydrogel was repeated, except for the addition of PVA solution (0.015 g of PVA was dissolved in deionized water at 90 °C for 1 h) into the cellulose suspension in advance. The resulting C-PVA hydrogel was further soaked into 5 wt% GA solution at 70 °C for 2 h and dried at 25 °C to impart C-GA-PVA hydrogel.

2.4. Characterization of cellulose-PVA hydrogels

Sugarcane bagasse, cellulose, RC, C-GA and C-GA-PVA hydrogels were characterized by using Perkin-Elmer TM 400 ATR-FTIR Spectrometer and Bruker Avance II NMR spectrometer.

2.5. Swelling test

First, 0.01 g of the dry hydrogel powder was weighed by using analytical balance and the weight was recorded as initial dry weight (W_0) [11]. Then, the hydrogel powder was placed into a tea-bag and the tea-bag was immersed into 100 mL distilled water for a prescribed period of time t . After that, the tea-bag was removed from water, placed on a filter paper and gently wiped with another filter paper to remove excessive fluid and weakly bound liquid. The tea-bag was then weighed and recorded as W_2 . The weight of tea-bag was recorded at time $t = 1, 2, 3, 4, 5, 6, 24$ and 48 h. The procedure was repeated for an empty tea bag, and the weight of the tea bag was recorded as W_1 . The swelling degree

of hydrogels at time t was calculated by applying the following equation:

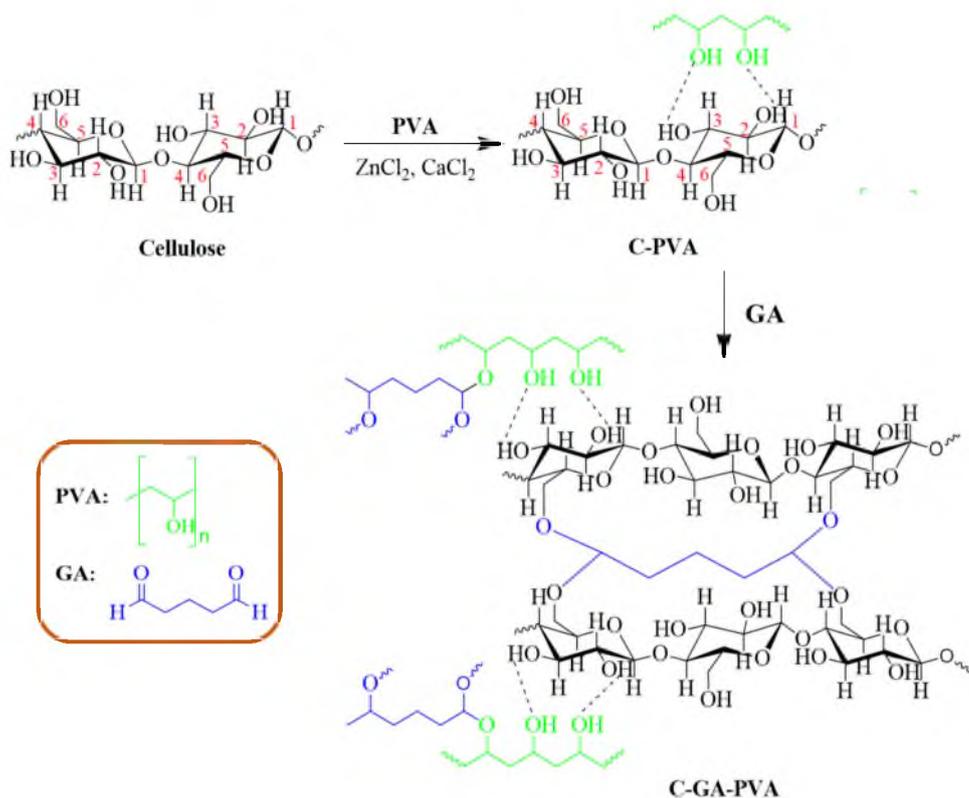
$$\text{Swelling degree} = \frac{(W_2 - W_1 - W_0)}{W_0} \times 100\%$$

3. Results and discussion

Fig. 1 showed the physical images of (a) untreated sugarcane bagasse, (b) extracted cellulose, (c) regenerated cellulose (RC), (d) cellulose-glutaraldehyde (C-GA) and (e) cellulose-glutaraldehyde-poly(vinyl alcohol) (C-GA-PVA) hydrogels. The images serves as preliminary observation for the modification done on the cellulose in every steps. The RC hydrogel obtained from extracted cellulose from sugarcane bagasse was 1.73 g in light brown colour product 1(c). Scheme 1 demonstrated the cross-linking reaction between cellulose and GA via the formation of acetals. Chemical cross-linking of cellulose hydrogel with GA (cross-linker) gave 2.40 g self-standing translucent light yellow colour membrane 1 (d). Scheme 2 illustrated the reaction of cellulose and PVA in the presence of GA (cross-linker) which gave 0.43 g of yellowish-white colour product 1(e). It is clearly observed that physical changes happened when GA and PVA was added to cellulose as backbone of the material.

3.1. Structure of cellulose extracted from sugarcane bagasse

For the molecular level observations, ATR-FTIR and ^{13}C NMR were applied to confirm the reaction of each steps. Fig. 2 is the ATR-FTIR spectra recorded for untreated sugarcane bagasse and extracted cellulose. Spectrum 2(a) of sugarcane bagasse possessed a strong and broad absorption band centred at 3344.32 cm^{-1} , corresponded to hydrogen-bonded O–H stretching vibrations. The absorption band at 2899.34 cm^{-1} was attributed to the elongation of aromatic sp^3 -hybridised C–H bonds of lignin. Furthermore, the absorption band recorded at 1731.95 cm^{-1} was associated with



Scheme 2. Reaction of cellulose, GA and PVA to produce cellulose-glutaraldehyde-poly(vinyl alcohol) (C-GA-PVA) hydrogel.

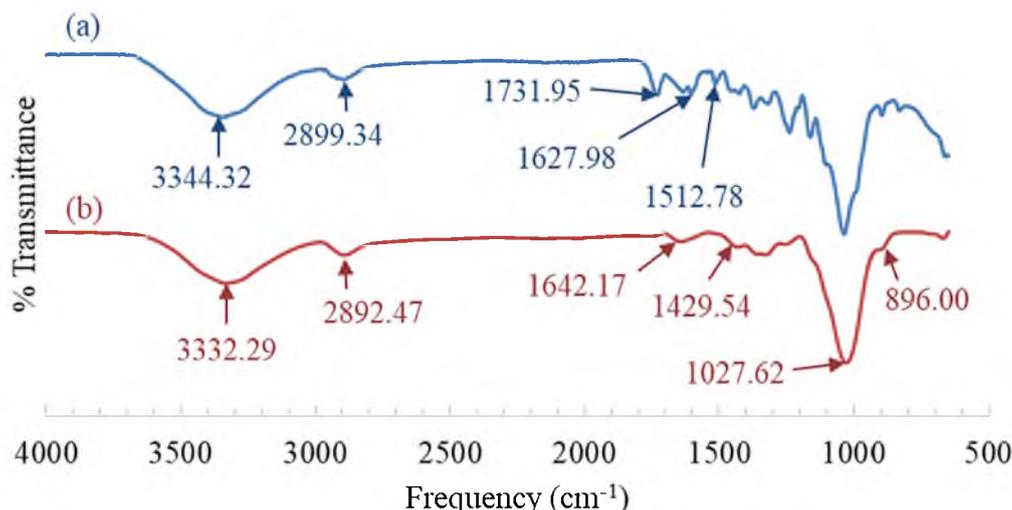


Fig. 2. ATR-FTIR spectra of (a) untreated sugarcane bagasse and (b) extracted cellulose.

the C=O group of hemicellulose and lignin. Another two bands recorded at 1627.98 cm^{-1} and 1512.78 cm^{-1} were attributed to the C=C bond of the lignin aromatic ring. Spectrum 2(b) demonstrated all major absorption bands associated with cellulose. Obviously, a strong and broad absorption band centred at 3332.29 cm^{-1} was corresponded to hydrogen-bonded O–H stretching vibrations. Another absorption band at 2892.47 cm^{-1} , related to sp^3 - hybridised C–H stretching vibration was also observed. Moreover, a weak absorption band at 1642.17 cm^{-1} , corresponded to O–H bending vibrations was observed. A strong absorption band at 1027.62 cm^{-1} , indicated the C–O–C pyranose ring skeletal vibration. Another characteristic feature for cellulose was the weak absorption band at 896.00 cm^{-1} , arising from β -glycosidic linkages between the glucose units in cellulose. The absorption band appeared at 1429.54 cm^{-1} was attributed to the CH_2 bending vibration. In comparison, it was clearly to be observed that the pre-treatment techniques eliminated most of the lignin polymers and hemicellulose due to the disappearance of their corresponded infrared absorption bands at 1731.95 cm^{-1} (acetyl group),

1627.98 cm^{-1} and 1512.78 cm^{-1} (aromatic C=C) [12] in spectrum 2(b).

Fig. 3 revealed the ^{13}C NMR spectra recorded for both untreated sugarcane bagasse and extracted cellulose. Both spectra recorded the most intense signals in the region of 50 ppm to 120 ppm, mostly originated from the cellulose carbons, but also contributed by the carbon from hemicellulose and lignin. According to spectrum 3(a) of untreated sugarcane bagasse, the chemical shift at 20.56 ppm was associated with the hemicellulose carbon only whereas at 55.21 ppm, it was corresponded to the aryl methoxy groups in lignin. Nevertheless, the absence of the aforementioned chemical shift in spectrum 3(b) of extracted cellulose gave evidence to the almost complete removal of hemicellulose and lignin after the pre-treatment with H_2SO_4 and NaOH . In comparison, an improvement of the spectral resolution in the region of 50 ppm to 120 ppm was clearly observed, as a result of the removal of hemicellulose signals within this region after the pre-treatment [13]. In spectrum 3(b), the chemical shift related to cellulose carbon were observed at 61.69 ppm and 83.56 ppm, predominated

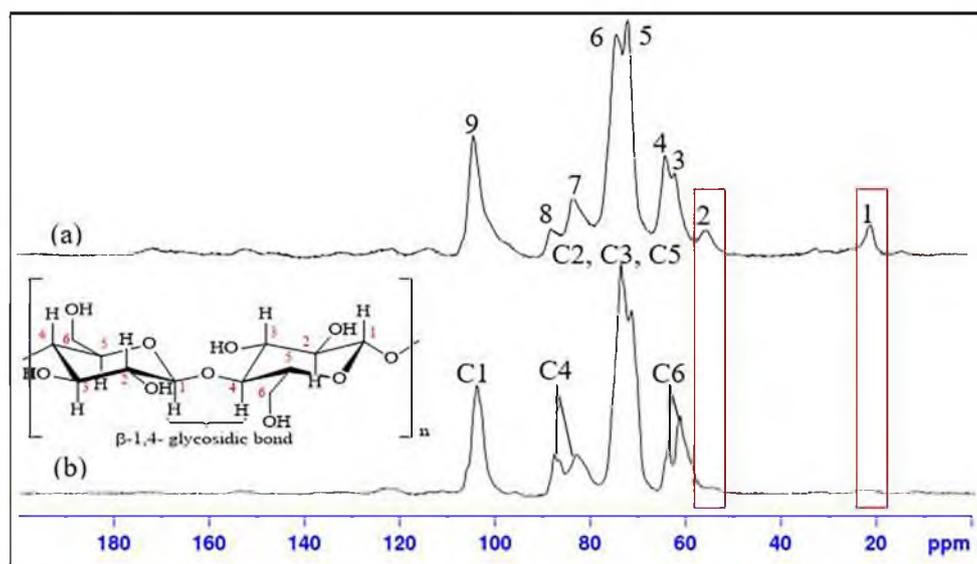


Fig. 3. Solid state ^{13}C NMR spectra for (a) untreated sugarcane bagasse (b) extracted cellulose.

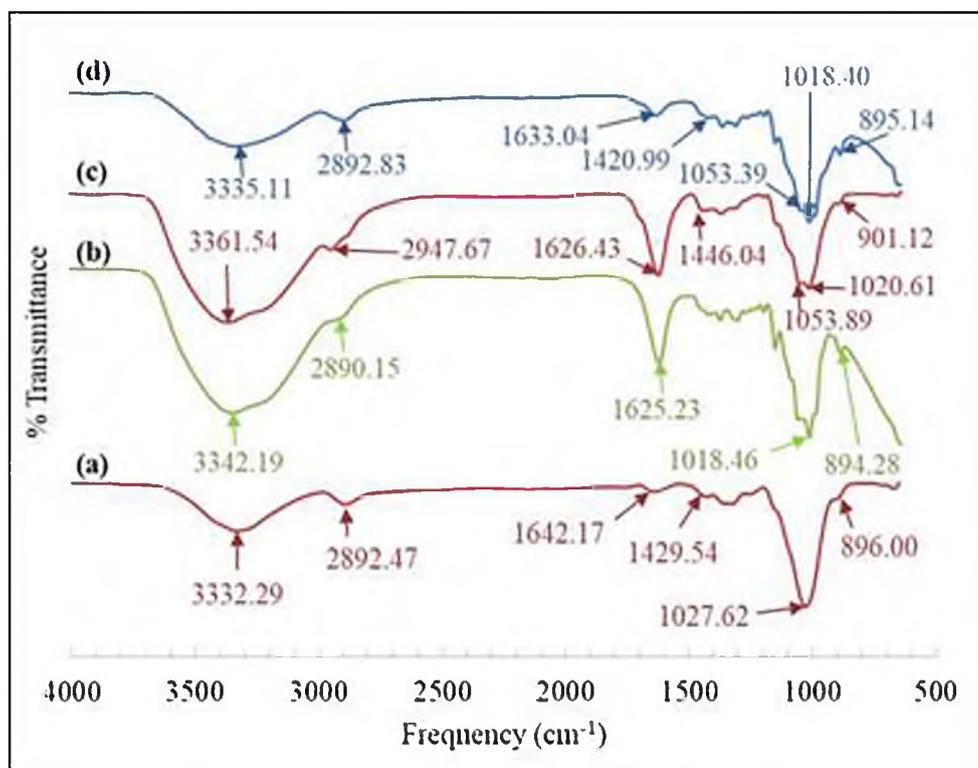


Fig. 4. ATR-FTIR spectra of (a) extracted cellulose, (b) regenerated cellulose (RC), (c) cellulose-glutaraldehyde (C-GA) and (d) cellulose-glutaraldehyde-poly (vinyl alcohol) (C-GA-PVA) hydrogels.

by C6 and C4 respectively from amorphous cellulose, 64.18 ppm and 88.11 ppm, attributed to C6 and C4 respectively in crystalline cellulose.

3.2. Preparation of regeneration cellulose modified PVA hydrogels

Solution of ZnCl_2 was capable to penetrate into the cellulose chains in which Zn^{2+} and Cl^- ions broke the strong hydrogen bond formed between the hydroxyl groups and led to the dissolution of cellulose. CaCl_2 can effectively reduce the degrading effect of cellulose dissolved in ZnCl_2 solution due to the increase in viscosity of the solution. Fig. 4 exhibited the ATR-FTIR spectra of RC, C-GA hydrogel and C-GA-PVA hydrogels. Spectrum 4(a) of RC hydrogel showed no significant difference from that of the extracted cellulose as no new characteristic absorption band were observed, suggesting that no chemical changes taken place in the regenerated cellulose. However, some differences in the absorption frequency and intensity of the band for certain functional group in extracted cellulose and the regenerated cellulose were observed. The absorption band of hydrogen-bonded O-H stretching vibrations in regenerated cellulose (3342.19 cm^{-1}) was shifted to higher frequency and was more intense than that of extracted cellulose (3332.29 cm^{-1}). Intermolecular hydrogen bonding in cellulose weakened the O-H bond, thereby shifted the band to lower frequency. Hence, indicates that there are less hydrogen bonding interaction reformed on regenerated cellulose [14]. A weak absorption band was recorded at 2890.15 cm^{-1} , related to sp^3 -hybridised C-H stretching vibration in regenerated cellulose, which was slightly lower than that in extracted cellulose, showing 2892.47 cm^{-1} . A medium absorption band at 1625.23 cm^{-1} , associated with the O-H bending vibrations, may attributed to the hydroxyl group in regenerated cellulose and the chemically absorbed water. Moreover, the strong absorption band at 1018.46 cm^{-1} was corresponded to C-O-C pyranose ring skeletal

vibration in regenerated cellulose. Another weak absorption band attributed to β -glycosidic linkages between the glucose units in regenerated cellulose was recorded at 894.28 cm^{-1} .

Spectrum 4(b) of C-GA hydrogel revealed a strong and broad absorption band centered at 3361.54 cm^{-1} , associated with O-H stretching vibration and a weak absorption band at 2947.67 cm^{-1} , was corresponded to sp^3 -hybridised C-H stretching vibration. Furthermore, a medium absorption band was recorded at 1626.43 cm^{-1} , related to O-H bending vibrations. Two strong absorption bands were observed at 1053.89 cm^{-1} and 1020.61 cm^{-1} , indicates the C-O stretching vibration, attributed to the C-O-C and C-OH in the pyranose ring, also the O-C-O linkage between GA and cellulose. A weak absorption band was recorded at 901.12 cm^{-1} , due to the β -glycosidic linkages between the glucose units in cellulose. In comparison with spectrum 4(a), a slight decrease in intensity for the hydrogen-bonded O-H stretching vibration (3361.54 cm^{-1}) and O-H bending vibrations (1626.43 cm^{-1}) for C-GA may due to the reduction of hydroxyl group after cross-linking reaction to form acetal. During the cross-linking reaction, the aldehyde groups of GA and hydroxyl groups of cellulose were consumed. Thus, the cross-linked regenerated cellulose may have less hydroxyl group as compared to regenerated cellulose with no cross-linkers. The reduction of hydroxyl absorbance indicated successful cross-linking reaction to form C-GA hydrogel via acetal linkage.

As compared to the spectra 4(a) and 4(b), spectrum 4(c) of C-GA-PVA hydrogel showed a drastic decrease in the band intensity for the hydrogen-bonded O-H stretching vibration (3335.11 cm^{-1}) and O-H bending vibrations (1633.04 cm^{-1}). The decline in intensity for O-H band may due to the reaction of PVA with GA, and cellulose with GA, which consumed aldehyde group from GA and hydroxyl group from PVA and cellulose to form acetal bridges. It was observed that the absorption frequency for O-H stretching vibration decrease significantly. The decline in fre-

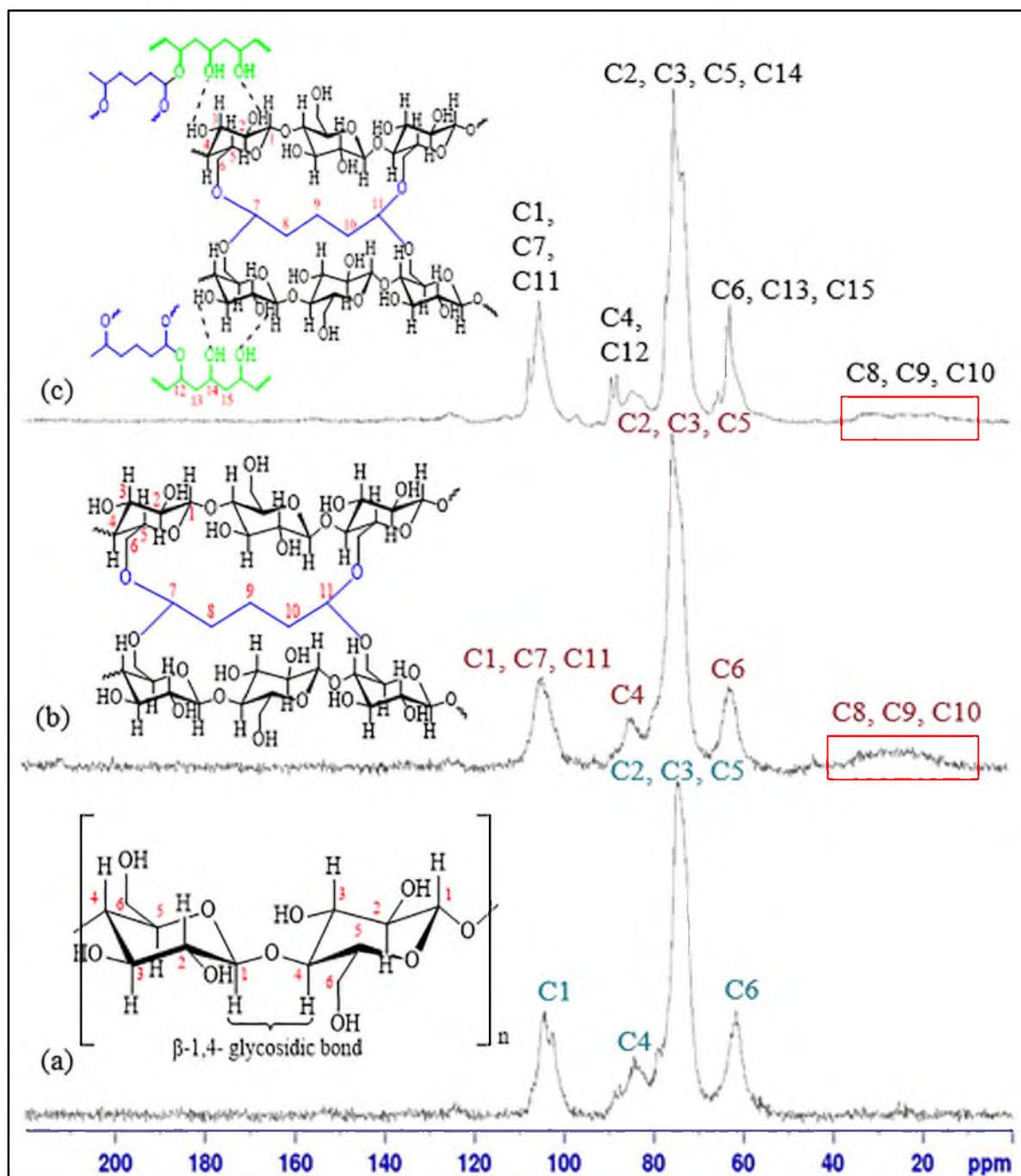


Fig. 5. Solid state ^{13}C NMR spectra of (a) regenerated cellulose (RC), (b) cellulose-glutaraldehyde (C-GA) and (c) cellulose-glutaraldehyde-poly (vinyl alcohol) (C-GA-PVA) hydrogels.

quency confirmed the presence of hydrogen bond between cellulose and PVA, which can be explained by the increase in the intermolecular hydrogen bonding attributed to the interaction of PVA with cellulose. Moreover, a weak absorption band at 1420.99 cm^{-1} , corresponded to the $-\text{CH}_2$ bending vibration experienced a decline in intensity. This band was also designated as the “crystallinity” absorption band in cellulose, therefore a decrease in its intensity indicated reduction in the degree of crystallinity of the hydrogel. A slight increase in intensity for β -glycosidic linkages (895.14 cm^{-1}), also known as an “amorphous” absorption band, reflects extend of the amorphous region in cellulose [15]. The absence of characteristic absorption bands for aldehyde,

including $\text{C}=\text{O}$ band at $1720\text{--}1750\text{ cm}^{-1}$ and doublet for $\text{C}-\text{H}$ stretching at 2850 cm^{-1} and 2750 cm^{-1} , suggested that excess GA had been eliminated after rinsing with distilled water.

Fig. 5 illustrated ^{13}C NMR spectra recorded for RC, C-GA and C-GA-PVA hydrogels. Spectrum 5(a) of RC hydrogel revealed the characteristic chemical shifts of carbon in cellulose, including 56.15 ppm and 61.54 ppm (C6 carbon), 74.69 ppm (C2, C3 and C5 carbon), 83.91 ppm , 84.31 ppm and 87.52 ppm (C4 carbon), 104.18 ppm and 104.57 ppm (C1 carbon). These data indicated that cellulose hydrogel was successfully regenerated in CaCl_2 and ZnCl_2 solution with no changes in the bonding of the structure.

Table 1

Physical appearance for regenerated cellulose (RC), cellulose-glutaraldehyde (C-GA), cellulose-glutaraldehyde-poly(vinyl alcohol) (C-GA-PVA), and poly(vinyl alcohol) (PVA) in dry state and swollen state at 48 h.

Types of hydrogels	Dry state($t = 0$ h)	Swollen state($t = 48$ h)
Regenerated cellulose(RC)	 Swelling degree = 0 %	 Swelling degree = 52 %
Cellulose-glutaraldehyde(C-GA)	 Swelling degree = 0 %	 Swelling degree = 80 %
Cellulose-glutaraldehyde-poly (vinyl alcohol)(C-GA-PVA)	 Swelling degree = 0 %	 Swelling degree = 135 %
Poly(vinyl alcohol)(PVA)	 Swelling degree = 0 %	 Swelling degree = 138 %

Spectrum 5(b) of C-GA hydrogel showed the characteristic peaks for the different carbons present. In the region between 15 ppm and 35 ppm, weak absorption peak for the CH₂ group present in GA was observed. The chemical shifts related to carbon in cellulose was observed at 62.25 ppm (C6 carbon), 74.73 ppm (C2, C3 and C5 carbon), 83.85 ppm (C4 carbon), and 103.80 ppm

(anomeric C1 carbon). The broad peak observed at 103.80 ppm, which was corresponded to the O-C-O bond, also indicated the formation of acetal. Moreover, the absence of signals in the range of 180–220 ppm, where aldehyde function group (C=O) usually resonate, confirmed complete removal of unreacted GA and also the occurrence of cross-linking in cellulose chains [16].

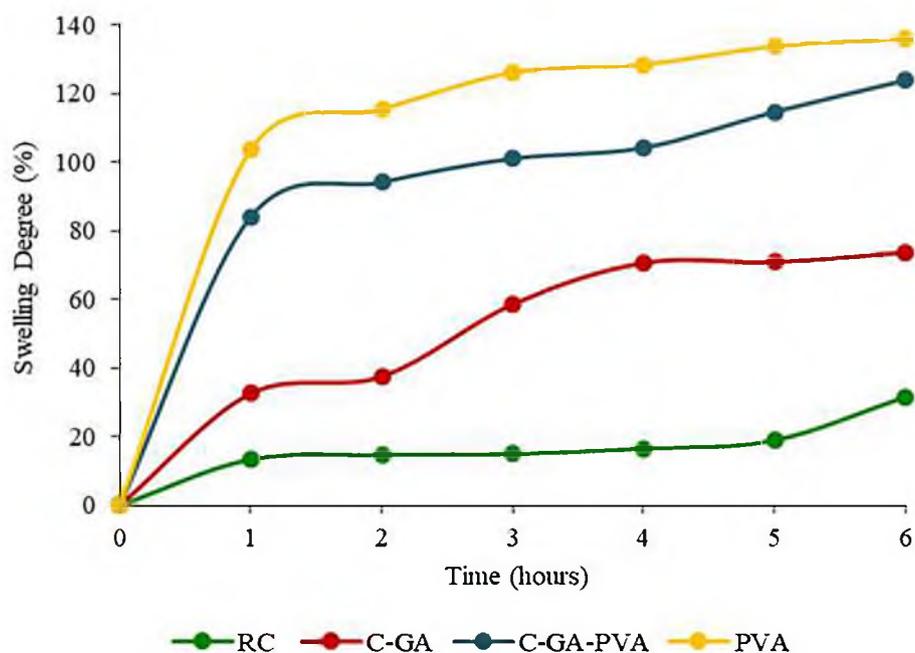


Fig. 6. Graph of swelling degree against time for regenerated cellulose (RC), cellulose-glutaraldehyde (C-GA), cellulose-glutaraldehyde-poly (vinyl alcohol) (C-GA-PVA) and poly (vinyl alcohol) (PVA) at the first 6 h.

Spectrum **5(c)** of C-GA-PVA hydrogel indicated that CH₂ group from GA gave very weak absorption peak in the upfield region of 15–35 ppm. The signals at 62.34 ppm and 63.06 ppm were assigned to C6 carbon in cellulose and CH₂ group from PVA. The four sharp peaks detected at 72.71 ppm, 73.05 ppm, 74.87 ppm and 76.64 ppm were attributed to HC-OH functional group in cellulose and PVA. The chemical shifts of 84.22 ppm, 87.54 ppm and 88.80 ppm were assigned to the C4 carbon in cellulose and the C-O bond in PVA. Finally, C1 carbon in cellulose together with O-C-O bond of acetal appeared at 104.89 ppm and 107.23 ppm as sharp broad peak. No signal related to C=O in GA was observed in the downfield region of 180–220 ppm confirmed the absence of unreacted GA.

3.3. Swelling properties

All samples were dried before grounded and used for swelling tests. **Table 1** showed the physical appearance of RC, C-GA, C-GA-PVA, and PVA hydrogels in dry and swollen state. It was obviously observed that each hydrogel could swell and experienced changes in size in the swollen state at 48 h without dissolving or changing in original shape.

Fig. 6 revealed the graph of swelling degree against time for each hydrogel. In general, different hydrogel swell at different initial rate in the first six hours. Compared to the equilibrium swelling degree at 48 h for RC hydrogel (52 %), C-GA exhibited higher percentage of swelling (80 %) in distilled water. The increase in swelling of GA-cross-linked cellulose hydrogel can be explained by the resulting cellulose hydrogel experienced a reduction in crystallinity after cross-linking reaction occurred and became more amorphous. Amorphous region of cellulose absorbed more water and thus there was an increase in swelling degree of C-GA hydrogel [17].

In comparison with C-GA hydrogel (80 %), C-GA-PVA revealed higher equilibrium swelling degree (135 %) in distilled water at 48 h. The cross-linking reaction between cellulose and PVA in the presence of GA can reduce the availability of hydroxyl groups, which interact with water, due to the formation of hydrogen bonding and lead to the lower swelling degree of the hydrogel. On the other hand, an increase in swelling degree after introducing PVA into cellulose hydrogel was reported [18]. The increase in the porosity of the hydrogels' surface, hydrophilic capability of the PVA and the reduction of PVA crystallinity after the cross-linking reaction between PVA and cellulose can cause an increase in the swelling degree of cellulose hydrogels. These should be further studied to determine the effect of cross-linking reaction on the pore structure and crystallinity of the hydrogels.

As compared to PVA (138 %), C-GA-PVA possessed lower equilibrium swelling degree (135 %) and slower rate of water absorption in distilled water. The decrease in swelling percentage after cross-linking reaction indicated the reformation of strong intermolecular hydrogen bonding between cellulose and PVA, and also the formation of covalent bond between GA with cellulose and PVA. PVA had high water absorption rate and moisture sensitivity which caused the reduction of its mechanical properties. Nevertheless, by cross-linking the PVA chains, water absorption rate can be reduced and lead to more stable structure of hydrogel for swelling without dissolution and degradation.

In the present study, C-GA-PVA hydrogel generated via cross-linking mechanism possessed increase swelling properties as compared to the RC hydrogel without cross-linker. Biodegradable cellulose hydrogel of high swelling capability was desired to be utilized as water reservoir in soil, which could significantly increase the water retention capability of the soil, and allow sustainable water supply to the plants for a prolonged time, without additional watering required. The swelling result of this study suggested that

the obtained C-GA-PVA could be a promising method for optimizing water management in agriculture, especially in the zone facing with severe water scarcity.

4. Conclusion

In conclusion, cellulose (2.84 g, yellowish-white) was successfully isolated from sugarcane bagasse through pre-treatment with H₂SO₄ and NaOH. By comparing ¹³C NMR spectra recorded for sugarcane bagasse and extracted cellulose, the removal of hemicelluloses and lignin from sugarcane bagasse was evidenced by the improve in resolution, the absence of chemical shift at 20.56 ppm and 55.21 ppm and the occurrence of characteristics peak for cellulose in the spectrum of extracted cellulose. Self-standing regenerated cellulose (RC) hydrogel without cross-linker (1.73 g, light brown, opaque) was generated from sugarcane bagasse extracted cellulose in ZnCl₂/CaCl₂ dissolution system. The characteristic peaks for cellulose were observed in ATR-FTIR and ¹³C NMR spectra and the absence of new absorption peaks confirmed that RC hydrogel was successfully synthesized with no chemical changes or degradation of structure taken place. Another two self-standing membrane, including GA cross-linked cellulose (C-GA), followed by PVA and GA cross-linked cellulose (C-GA-PVA) were successfully generated. It was further supported by the data interpreted from ATR-FTIR and ¹³C NMR spectra, which confirmed the formation of acetal in the chemical cross-linking reaction. The equilibrium swelling degree of hydrogel generally increase in the order, RC (52 %), C-GA (80 %) and C-GA-PVA (135 %). C-GA-PVA has the best swelling performance as successful cross-linking between cellulose and PVA led to an increase in porosity and water absorption. The excellent swelling capacity showed potential for the possible use of C-GA-PVA hydrogel as water reservoir in agriculture.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] E.S. Abdel-Halim, Chemical modification of cellulose extracted from sugarcane bagasse: Preparation of hydroxyethyl cellulose, *Arabian J. Chem.* 7 (3) (2014) 362–371.
- [2] A. Manzoor, Z.-U. Khokhar, U. Athar Hussain, S.A. Ahmad, Dilute sulfuric acid: A cheap acid for optimization of bagasse pretreatment, *Cellulose* 10 (2012) 100.
- [3] R.G. Candido, A.R. Gonçalves, Evaluation of two different applications for cellulose isolated from sugarcane bagasse in a biorefinery concept, *Ind. Crops Prod.* 142 (2019) 111616, <https://doi.org/10.1016/j.indcrop.2019.111616>.
- [4] J.W. Lee, J.Y. Kim, H.M. Jang, M.W. Lee, J.M. Park, Sequential dilute acid and alkali pretreatment of corn stover: Sugar recovery efficiency and structural characterization, *Bioresour. Technol.* 182 (2015) 296–301.
- [5] H. Kang, R. Liu, Y. Huang, Cellulose-based gels, *Macromol. Chem. Phys.* 217 (12) (2016) 1322–1334.
- [6] S. Mohammadi-Khoo, P.N. Moghadam, A.R. Fareghi, N. Movagharnezhad, Synthesis of a cellulose-based hydrogel network: Characterization and study of urea fertilizer slow release, *J. Appl. Polym. Sci.* 133 (5) (2016) n/a–n/a.
- [7] S.T. Georgopoulos, P.A. Tarantili, E. Avgerinos, A.G. Andreopoulos, E.G. Koukios, Thermoplastic polymers reinforced with fibrous agricultural residues, *Polym. Degrad. Stab.* 90 (2) (2005) 303–312.
- [8] Y.W. Chen, S.H. Binti Hassan, M. Yahya, H.V. Lee, Novel superabsorbent cellulose-based hydrogels: Present status, synthesis, characterization, and application prospects, *Cellulose-Based Superabsorb. Hydrog.* (2019) 155–195.

- [9] K. Nakasone, T. Kobayashi, Effect of pre-treatment of sugarcane bagasse on the cellulose solution and application for the cellulose hydrogel films, *Polym. Adv. Technol.* 27 (7) (2016) 973–980.
- [10] T. Hou, K. Guo, Z. Wang, X.-F. Zhang, Y.i. Feng, M. He, J. Yao, Glutaraldehyde and polyvinyl alcohol crosslinked cellulose membranes for efficient methyl orange and congo red removal, *Cellulose* 26 (8) (2019) 5065–5074.
- [11] J. Sun, X. Sun, H. Zhao, R. Sun, Isolation and characterization of cellulose from sugarcane bagasse, *Polym. Degrad. Stab.* 84 (2) (2004) 331–339.
- [12] C.A. Rezende, M.A. de Lima, P. Maziero, E.R. deAzevedo, W. Garcia, I. Polikarpov, Chemical and morphological characterization of sugarcane bagasse submitted to a delignification process for enhanced enzymatic digestibility, *Biotechnol. Biofuels* 4 (1) (2011) 54.
- [13] K. Zhang, W. Feng, C. Jin, Protocol efficiently measuring the swelling rate of hydrogels, *MethodsX* 7 (2020) 100779, <https://doi.org/10.1016/j.mex.2019.100779>.
- [14] C.M. Altaner, L.H. Thomas, A.N. Fernandes, M.C. Jarvis, How cellulose stretches: Synergism between covalent and hydrogen bonding, *Biomacromolecules* 15 (3) (2014) 791–798.
- [15] A. Abdulkhani, E. Hojati Marvast, A. Ashori, Y. Hamzeh, A.N. Karimi, Preparation of cellulose/polyvinyl alcohol biocomposite films using 1-n-butyl-3-methylimidazolium chloride, *Int. J. Biol. Macromol.* 62 (2013) 379–386.
- [16] K. Chauhan, J. Kaur, A. Kumari, A. Kumari, G.S. Chauhan, Efficient method of starch functionalization to bis-quaternary structure unit, *Int. J. Biol. Macromol.* 80 (2015) 498–505.
- [17] S.D. Petroudy, Physical and mechanical properties of natural fibers. *Advanced high strength natural fibre composites in construction*, 2017, 10, 59–83.
- [18] T. Abitbol, T. Johnstone, T.M. Quinn, D.G. Gray, Reinforcement with cellulose nanocrystals of poly (vinyl alcohol) hydrogels prepared by cyclic freezing and thawing, *Soft Matter* 7 (6) (2011) 2373–2379.