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Properties of Cellulose Hydrogel from Kenaf Core Prepared via Pre-cooled Dissolving Method

(Sifat Selulosa Hidrogel daripada Teras Kenaf Menggunakan Kaedah Pra-penyejukan)

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ABSTRACT

Hydrogels were produced from cellulose derived from kenaf core powder with weight average molecular weight of cellulose was 1.68 × 10^5 and was dissolved in NaOH/urea solvent at -13°C. To obtain the optimal dissolving parameters, different percentage of NaOH, urea and kenaf core cellulose was used to study the degree of dissolution and formation of hydrogel. From the results obtained, it was found that the ratio of 6% NaOH/4% urea and 2% cellulose produced a good hydrogel. UV-Vis spectroscopy and XRD analysis were performed to analyze the transparency and crystallinity index of the cellulose solution and hydrogel, respectively. It showed that the hydrogel with the highest degree of solubility gave highest transparency due to the reduction of cellulose crystallinity as a result of the dissolution process. XRD analysis results showed the crystallinity of cellulose from kenaf core decreased by 70% after dissolution and hydrogel formation. Samples with 4% urea possess highest water content of 73% and decreased with increasing urea content.

Keywords: Crystallinity; dissolution; hydrogel; kenaf core; transparency

ABSTRAK

Hidrogel telah berjaya dihasilkan daripada selulosa serbuk teras kenaf dengan didapati purata berat molekul selulosanya adalah 1.68 × 10^5. Selulosa ini kemudiannya dilarutkan dalam pelarut NaOH/urea pada suhu -13°C. Bagi mendapatkan parameter yang optimum, peratus NaOH, urea dan berat selulosa divariasikan. Hasilnya didapati bahawa nisbah 6% NaOH/4% urea dan 2% selulosa dapat menghasilkan hidrogel yang paling baik. Analisis spektroskopi UV-Vis dan XRD dijalankan untuk menganalisis ketelusan dan index kehabluran larutan selulosa dan hidrogel yang terhasil. Hidrogel dengan peratus kelarutan yang paling tinggi mempunyai ketelusan yang paling baik. Ini adalah disebabkan oleh peratus kehabluran selulosa semakin berkurang disebabkan oleh hasil proses pelarutan yang dilakukan. Analisis XRD menunjukkan selulosa daripada teras kenaf mengalami pengurangan daripada segi kehabluran sebanyak 70% selepas proses pelarutan dan pembentukan hidrogel. Sampel dengan kandungan urea sebanyak 4% menunjukkan peratus kandungan air yang paling tinggi iaitu 73% dan menurun dengan peningkatan kandungan urea.

Kata kunci: Hidrogel; kehabluran; kelarutan; ketelusan; teras kenaf

INTRODUCTION

Hydrogel consists of three-dimensional hydrophilic polymer network which can absorb high amount of water, saline and other solution due to its high degree of hydrophilicity. The network of hydrogel can be obtained via physical cross-linking (ionic or hydrogen bond) or chemically-cross linking by covalent bonding (Chang et al. 2010a). Due to the unique properties of hydrogel such as permeability, biocompatibility, biodegradability and nontoxicity, it has been extensively used in various industries, including food, contact lenses, biomedical, tissue engineering, water treatment, agriculture and personal care products (Kimura et al. 2011).

Hydrogel can be produced using various method such as graft copolymerization (Bardajee et al. 2008), radical copolymerization, cross-linking and ionizing radiation (Khoylou & Naimian 2009). These methods were mostly used for synthetic polymers because of the formation of complex system in the gel transition during the hydrogel formation. However, synthetic polymer is harmful to the environment due to less biocompatibility and more toxic effect on this polymer (Chang et al. 2010b). Therefore, the formation of hydrogel using pre-cooled technique from natural resources is preferred since its chemical and physical cross-linking were easier and more environmental friendly (Kimura et al. 2011).

Plant cellulose is one of the most important and abundantly available renewable resources on the Earth. It possesses many attractive properties such as biocompatibility, biodegradability, thermal and chemical stability. Yearly, about 10^{11} to 10^{12} tonnes of cellulose is produced from natural resources (Zhang et al. 2010) and it is increasing from time to time due to the increasing demand on environmentally friendly and biocompatible products from consumer. Plant cellulose can be obtained from many types of natural resources such as cotton linter

(Luo & Zhang 2010), wheat straw (Jimenez et al. 1996) and kenaf and oil palm empty fruit bunch (Zakaria et al. 2014).

Kenaf (*Hibiscus cannabinus L.*) is one of the important industrial crops cultivated in Malaysia under a program monitored by Lembaga Kenaf Tembakau Negara under Ministry of Plantation Industries and Commodities. Kenaf is one type of herbaceous dicotyledonous plant which grows very fast, i.e., to reach 4-5 m in only 5 months. Recently, various studies have been reported in utilizing kenaf for different applications which can be attributed to the advantages of kenaf such as renewable resources, cheaper and fast growing rate and annually available. Kenaf's stem can be separated into two components, i.e., outer bast (25-40%) and inner core (60-75%) which possess different properties. Kenaf bast consists of long fibres, which are suitable for pulp and paper production and woven/nonwoven mats. The major component of kenaf core consists of short fibres which have limited applications (Kuroda et al. 2005).

Cellulose is insoluble in common solvents owing to its strong inter and intra molecular hydrogen bonds between the hydroxyl groups (Jin et al. 2007). Previously, there are several methods which have been developed to dissolve cellulose, for example N-methylmorpholine-N-Oxide-water (NMMO/H_2O) was used to dissolve cellulose for the preparation of Lyocell fibres. However, such solvent produces considerable amounts of byproducts (Chen et al. 2006). Solvents such as lithium chloride and dimethylacetamide (Li/DMA), LiCl/N,N-dimethylacetamide (DMAc), cuaxam, cuen and cadoxen were also used to dissolve cellulose. These solvents possess several disadvantages, including volatility, toxicity due to release of harmful gaseous (H_2S and CS_2) and high cost (Jin et al. 2007). Therefore, a new and environmentally friendly solvent has been developed by Zhang et al. (2010) to replace the previous systems, i.e., solvent containing NaOH and urea. This solvent can dissolve cellulose at low temperature (–12 - –13°C). Various types of products can be produced by using this cellulose solvent such as hydrogel, regenerated films and membranes and microbeads (Jin et al. 2007).

In the present study, cellulose from kenaf core was used to produce cellulose hydrogel. The effect of kenaf cellulose on the new dissolving system using NaOH/urea was investigated. The formation and properties of cellulose hydrogel produced using epichlorohydrin agent was studied.

Materials and Methods

Kenaf core (KC) powder was supplied by the Malaysian Agricultural Research and Development Institute (MARDI). The fibres were dried at 105°C for 24 h and stored in a desiccator before used. The analytical grade sodium hydroxide (NaOH), urea and epichlorohydrin were purchased from Sigma Aldrich. Ethylene diamine and cadmium oxide used to prepare Cadoxen solvent for cellulose dissolution for molecular weight determination also purchased from Sigma Aldrich.

Bleaching Process of Kenaf Core

Bleaching process was conducted to extract the cellulose from kenaf core powder. The process followed seven stages of bleaching sequences (DEDEDED) where D and E are the bleaching process to remove the lignin where D and E are acidic and alkaline treatment respectively. During the D stage, buffer solution was prepared which consists of 27 g of NaOH, 75 mL of acetic acid and distilled water. Then, 1.7% of sodium chlorite solution was prepared. The ratio of buffer solution: sodium chlorite solution: distilled water is 1:1:1. For E stage, 2% of NaOH solution was prepared and the ratio between the KC to the solution was 1:20 by weight (wt. %). Both D and E stages conducted at 80°C for 2 h in water bath. After completing the bleaching process, the KC powder was washed with excess distilled water to neutralize and dried at 105°C for 24 h before use.

Lignin Content Determination

Lignin content of the KC powder was determined according to the TAPPI standard T222 om-06. The carbohydrates in the KC powder sample were hydrolyzed with 72% sulfuric acid at low temperature for 2 h and solubilized by boiling for 4 h. The acid insoluble lignin was filtered off, dried, weighed and the dried lignin calculated.

Viscosity Measurement and Molecular Weight Calculation

Intrinsic viscosities [η] of the solution was obtained by dissolving kenaf core cellulose in cadoxen and measured at 25°C using an Ubbelohde capillary viscometer followed the method reported in the literature (Cai et al. 2006). The KC sample was dissolved in cadoxen solution at a concentration of 2×10^{-3} g/mL and diluted for five times to achieve concentration ranging from 1.0×10^{-5} to 4×10^{-3} g/mL.

Pre-Cooling Dissolution of KC Powder

The effects of different parameters, including NaOH/urea ratio and weight of KC powder, on the degree of dissolution were investigated. The cellulose solution prepared with different ratio of NaOH/urea/KC powder is summarized in Table 1. KC powder was added into an aqueous mixture of NaOH/urea. The mixture was pre-cooled to –13°C in a freezer. The mixture was thawed and vigorously stirring for 10 min to obtain the transparent solution and was subjected to centrifugation at 10000 rpm for 10 min for degassing and excluding the undissolved cellulose fraction. The undissolved cellulose was washed with excess of water. The degree of dissolution was calculated according to the equation:

$$S_a = \frac{W_1}{W_1 + W_2}, \quad (1)$$

TABLE 1. Sample code for different ratio of NaOH/urea/KC powder

Sample code	NaOH (%)	Urea (%)	KC powder (g)
CN2	2	4	2
CN4	4	4	2
CN6	6	4	2
CN8	8	4	2
CN10	10	4	2
CU2	6	2	2
CU4	6	4	2
CU6	6	6	2
CU8	6	8	2
CU10	6	10	2
CF0.5	6	4	0.5
CF1.0	6	4	1.0
CF1.5	6	4	1.5
CF2.0	6	4	2.0
CF4.0	6	4	4.0

where S_a represent the solubility of KC cellulose fibre, W_1 is weight of dissolved cellulose and W_2 is weight of original cellulose.

FORMATION OF HYDROGEL

The cellulose solution obtained in the previous section was used to produce hydrogel using epichlorohydrin (ECH), as crosslinking agent. The mixture of the cellulose solution and ECH was stirred for 3 h to produce hydrogel at room temperature. The hydrogel obtained was washed with deionized water to remove excess NaOH and urea and oven dried before further characterizations.

CHARACTERIZATION

X-Ray Diffraction (XRD) X-ray diffraction analysis (XRD) was performed on KC powder and KC hydrogel by using radiation of Cu Kα = 1.5458 Å at diffraction angle (2θ) range of 5-60°. The crystallinity index of the samples was determined following the equation:

$$\text{CrI}\ (\%) = A_{\text{Cystal}}/A_{\text{Total}} \times 100, \quad (2)$$

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 2θ = 5° – 60°.

Swelling Studies The produced KC hydrogels were immersed in distilled water at 25°C for 24 h. The sample weight was measured and the swelling ratio (SR) was calculated according to the following equation:

$$\text{SR}\ (\%) = \frac{W_s - W_d}{W_d} \times 100, \quad (3)$$

where W_d and W_s are the weights of dried and swollen hydrogel, respectively.

RESULTS AND DISCUSSION

LIGNIN CONTENT

Table 2 shows the decrease of lignin content in the KC powder after each step of bleaching. The effects of bleaching and alkaline treatment show that after four times bleaching and three times of alkaline treatment, the lignin content in the samples calculated is 0.3% and the bleaching process has removed almost all impurities during the production of pure cellulose. This is due to the residual of non carbohydrate constituents especially lignin are removed (Popp et al. 2011) and at the same time some impurities such as inorganic materials and waxes are removed during the process.

MARK–HOUWINK EQUATION

Specific viscosity and relative viscosity with different concentration of cellulose obtained from the dilution process are shown in Table 3. These values followed Huggins (specific viscosity) and Kraemer (relative viscosity) equations and the intrinsic viscosity of KC was determined by double extrapolation to zero concentration of Huggins and Kraemer equations,

$$\eta_{sp}/c = [\eta] + k_H'[\eta]^2 c, \quad (4)$$

$$ln(\eta_{rel})/c = [\eta] + k_K'[\eta]^2 c, \quad (5)$$

where [η], η_{sp} and η_{rel} are the intrinsic, specific and relative viscosities, respectively; k_H and k_K are Huggins and Kraemer coefficients and c is cellulose concentration (Alves et al. 2010; Cai & Zhang 2005).

Figure 1 shows the plot of specific viscosity and relative viscosity against cellulose concentration for the KC sample dissolved in cadoxen solution at 25°C. The intercept of each straight line determined the intrinsic

TABLE 2. Lignin content for every of bleaching steps

Steps	Lignin Content (%)
Raw KC powder	23.8
D	19.8
D-E-D	8.9
D-E-D-E-D	1.4
D-E-D-E-D-E-D	0.3

TABLE 3. Experimental result of reduced viscosity and specific viscosity at different concentration of cellulose dissolved in cadoxen solution at 25°C

Concentration 1×10^{-3} (g/mL)	Relative viscosity $1 \times 10^{2} (\ln \eta_r/c)$	Specific viscosity $1 \times 10^{2} (\eta_{sp}/c)$
2.0	3.28	4.64
1.5	3.33	4.32
1.0	3.43	4.10
0.5	3.52	3.85

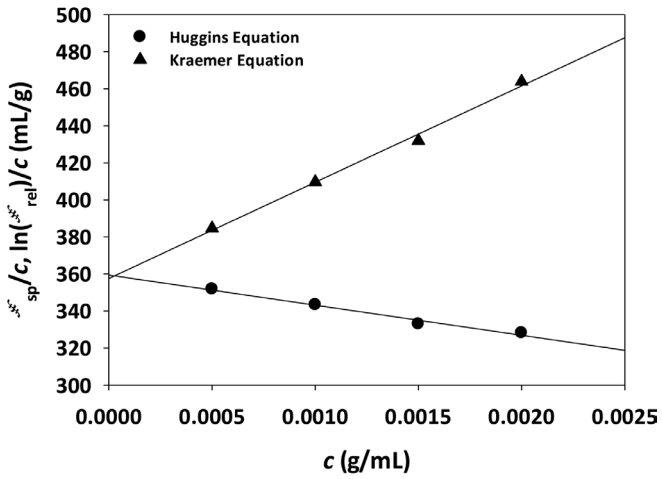

FIGURE 1. Intrinsic viscosity against concentration of cellulose in cadoxen solution at 25°C

viscosity [η] of the cellulose samples where [η] is a direct measure of the flow behavior of macromolecules and an indirect measure of their size and shape. The value of Mη obtained from Mark-Houwink which is represented by a straight line as follows:

$$[\eta] = 3.85 \times 10^{-2} M\eta^{0.76} \text{ (mL/g)}. \quad (6)$$

From the intercept in Figure 1, the value of intrinsic viscosity was determined to be 360.6 mL/g. Therefore according to the equation 6, the viscosity average molecular weight of kenaf core cellulose determined as 1.68×10^{5}.

DEGREE OF DISSOLUTION OF KC CELLULOSE

Effects of Urea on the Solubility and Hydrogel Formation

The percentage of urea in the aqueous NaOH solvent plays an important role in the solubility of cellulose and also the formation of hydrogel by adding in the cross-linking agent. Table 4 shows that only the samples CU4, CU6 and CU8 were successfully formed into hydrogel, while higher than 8% urea and lower than 4% urea unable to form the hydrogel, respectively. These results also presented that solubility of cellulose also can effect of the formability of hydrogel which is > 50% solubility are unable to form the hydrogel. Undissolved cellulose is required during cross-linking for the hydrogel where it can be the reasons of hydrogel

formation. In this system, urea function as hydrogen bonds donor and receptor between the solvent molecules and prevents the re-association of cellulose molecules leading to molecular dissolution of cellulose by breaking the intermolecular hydrogen bonds (Zhang et al 2000). However, in this case, urea between 4-8% tends to form hydrogel due to lower solubility of cellulose. This is due to the higher molecular weight at the beginning of dissolution which induced viscosity increased and leads to the gelling formation by sterically hindered for further dissolution. Therefore the crystalline part of cellulose is difficult to be accessed by chemicals. At higher concentration of urea which is 10% leading to reduce the molecular weight and covalent bond breaking of cellulose which reduced the viscosity of solution. Hence, the cellulose solution is difficult to form hydrogel (Zhang et al. 2000).

Figure 2 shows the photograph of the cellulose hydrogel formed at different urea percentages of 4, 6 and 8% (CU4, CU6 and CU8). From the figure, it can be seen that the transparency of hydrogel CU4 is higher than CU6 and CU8 due to the amount of urea percentages used. This result can be clearly proven from Figure 3 where the transmittance of ultraviolet and visible light for CU4 is the highest followed by CU6 and CU8 measured in the wavelength range between 200-700 nm. The highest solubility of CU4 plays an important role for the transparency effects. Increase the solubility lead to the decrease of crystalline region in the cellulose which resulted increase the light transparency of hydrogel (Chang et al. 2010a). Therefore, from these results, we can summarised that optimizing the percentages of urea is necessary to form the hydrogel due to the solubility of cellulose. The optimum amount of urea suggested is 4% with moderate solubility, higher transparency and lower chemical consumption.

Effects of NaOH on the Solubility and Hydrogel Formation The effects of NaOH percentages on cellulose dissolution and the hydrogel formation were evaluated by comparing the solubility of cellulose in 2, 4, 6, 8 and 10% NaOH in aqueous solution. NaOH is acts to break the inter and intra hydrogen bonds between the cellulose molecules and destroy the long range order of cellulose crystal to form cellulose molecular solution by swell and activate the cellulose. Table 5 presents the solubility of cellulose on the different amount of NaOH. The result showed that solubility of cellulose is increased from 2 to 6% of NaOH and decreased the solubility for > 6% of NaOH. CN6 give the highest solubility of 50.9%. The size of NaOH-water hydrates depend on the concentration of NaOH in the solution. At lower concentration of NaOH (CN2 and CN4) the hydrodynamic diameters of NaOH-water hydrates was too large to penetrate into the crystalline region of

TABLE 4. Comparison of the urea percentages on the solubility and hydrogel formation

Sample	Solubility (%)	Remarks
CU2	57.3	Does not form hydrogel
CU4	50.9	Formed hydrogel
CU6	46.9	Formed hydrogel
CU8	50.3	Formed hydrogel
CU10	55.6	Does not form hydrogel

FIGURE 2. Photographs of the cellulose hydrogels (a) CU4, (b) CU6 and (c) CU8

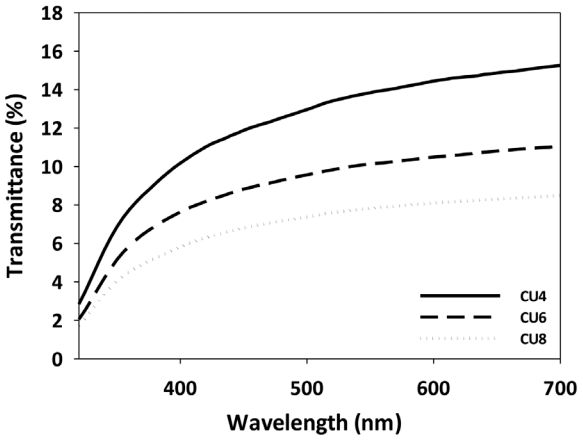

FIGURE 3. Transparency of cellulose hydrogels prepared with different urea percentages

TABLE 5. Comparison of the NaOH percentages on the solubility and hydrogel formation

Sample	Solubility (%)	Remarks
CN2	18.6	Does not form hydrogel
CN4	21.3	Does not form hydrogel
CN6	50.9	Formed hydrogel
CN8	48.0	Does not form hydrogel
CN10	28.3	Does not form hydrogel

cellulose. This is due to the cellulose crystalline chains are very densely packed with the crystallite diameter of only 10 nm and inter-sheet distance of about 10 Å. Lower concentration of NaOH is not enough to dissolved cellulose as well (Zhang et al. 2010).

However, if the NaOH concentration (CN8 and CN10) is too high, the hydration of alkali ion also is not enough to break the hydrogen bonding. Thus, the solubility of the cellulose is lower. From the reaction during the hydrogel formation, only CN6 sample formed hydrogel. This indicates that hydrogel formed if the solubility of cellulose was about 50% and less than that, the hydrogel will not formed. Therefore from the results of comparison between the NaOH concentrations, the optimum condition of NaOH concentration found is 6% NaOH (Figure 4).

Effects of Cellulose Weight on the Solubility and Hydrogel Formation Table 6 summarize the solubility of cellulose in 6% NaOH/4% urea aqueous solution with the different cellulose weight of 0.5, 1.0, 1.5, 2.0 and 4.0 in sample CF0.5, CF1.0, CF1.5, CF2.0 and CF4.0. With the increase of cellulose weight, the solubility decreased. Cellulose which dissolved in NaOH/urea aqueous could be chemically cross-linked by ECH and physically cross-linked by formation of hydrogen bonding and chain entanglements of hydrogel.

CHARACTERIZATION OF HYDROGEL

X-RAY DIFFRACTION (XRD)

Figure 5 shows the XRD patterns of KC powder and KC hydrogel. The diffraction peaks at $2\theta = 14.8^{o}$, 16.5^{o} and 22.6^{o} for (1 -1 0), (1 1 0) and (2 0 0) planes are characteristic for cellulose I crystal and $2\theta = 12.1^{o}$, 19.8^{o} and 22.6^{o} are characteristic for cellulose II (Luo & Zhang 2010). Kenaf core powder exhibits cellulose I peaks while kenaf core hydrogel exhibit cellulose II peaks. However the decreased of crystallinity for kenaf core powder after hydrogel formation by crosslinking with ECH demonstrated that during the dissolution the crystal structure of cellulose I become amorphous state where the inter and intra hydrogen bond of cellulose destroyed during dissolution in aqueous alkali solution leading to the loss of crystallinity and destruction of crystalline structure of cellulose I (Ding et al. 2012). This can proved that the crystallinity index for kenaf core powder is 64.8% and decreased to 19.3% after the dissolution and crosslinking to form kenaf core hydrogel.

WATER SWELLING

Figure 6 shows the percentage of swelling ratio in the hydrogel against urea percentage. The higher the swelling

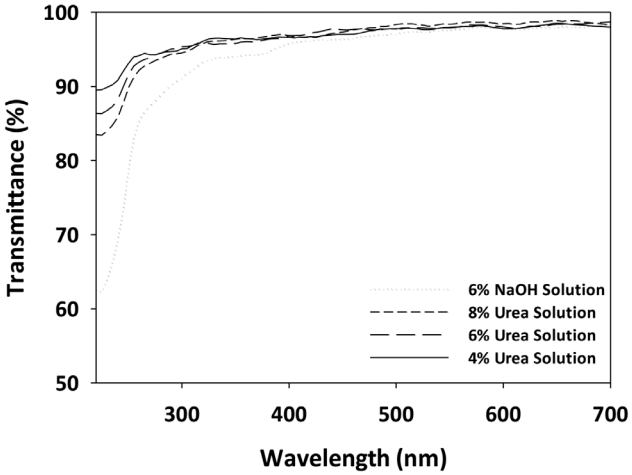

FIGURE 4. Transparency of 6% NaOH solution with different percentage of urea solution

TABLE 6. Comparison of the cellulose weight on the solubility and hydrogel formation

Sample	Solubility (%)	Remarks
CF0.5	67.2	Does not formed hydrogel
CF1.0	63.4	Does not formed hydrogel
CF1.5	55.7	Does not formed hydrogel
CF2.0	50.9	Formed hydrogel
CF4.0	–	Does not dissolved

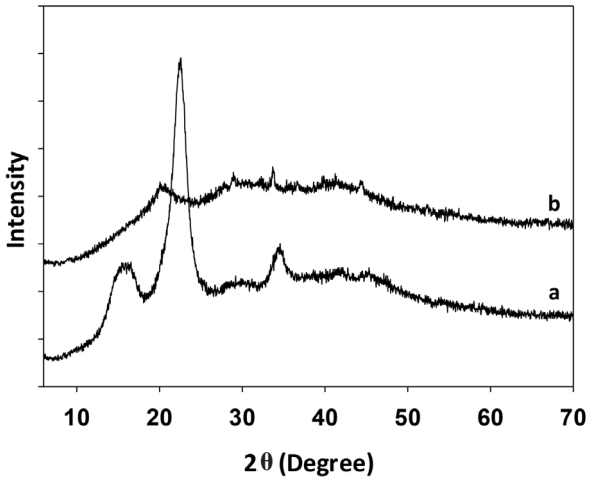

FIGURE 5. XRD patterns of (a) kenaf core cellulose and (b) kenaf core hydrogel

ratio the lower the urea percent used. Hydrogel with 4% urea shows highest swelling ratio compared to hydrogel with 6% and 8% urea. This is due to the chemical cross-links by ECH that occurred during the hydrogel formation. However, physical cross-links also occur in the hydrogel where the degree of cross-links is one of the important factors for determining the rate of diffusion of water in the hydrogel. With the increase of cellulose concentration by 8% urea, cross-links in the hydrogel further amplified by the presence of more clutter chain hydrogen bonds and cellulose. Tangle of cellulose chains through hydrogen bonding can occur easily in solution with higher urea

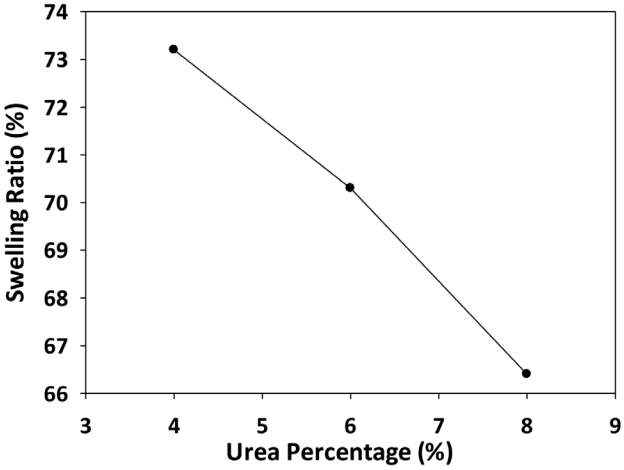

FIGURE 6. Swelling ratio of hydrogel against urea percentage

concentrations. Therefore it caused a decrease in water diffusion in hydrogel (Chang et al. 2010a).

CONCLUSION

In summary, hydrogels have been successfully synthesized using cellulose derived from kenaf core powder dissolved in NaOH/urea aqueous solutions by using ECH as cross-linker via pre-cooled method. The optimum concentration of NaOH, urea and KC weight is 6, 4 and 2%, respectively, which give hydrogel the highest transparency. With the increase of the solution concentration, the light transparency and equilibrium swelling ratio of the hydrogels decreased. At high alkali concentration (10%), increase in urea percentages will block the solubility of cellulose. However, a lower percentage of NaOH is not sufficient to dissolve cellulose. Thus the optimum concentration of NaOH used is 6%. Crystallinity of cellulose decreased from 64.8 to 19.3% after cross-linked with ECH and formed hydrogel.

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