Using borax as a cross-linking agent in cellulose-based hydrogels

Farin Phoothong¹, Anyaporn Boonmahitthisud²,³* and Supachok Tanpichat⁴,†

¹Program of Petrochemical and Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok, 10330, Thailand
²Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok, 10330, Thailand
³Green Materials for Industrial Application Research Unit, Faculty of Science, Chulalongkorn University, Bangkok, 10330, Thailand
⁴Learning Institute, King Mongkut's University of Technology Thonburi, Bangkok, 10140, Thailand

*anyaporn.b@chula.ac.th and †supachok.tan@kmutt.ac.th

Abstract. In this research, the cellulose-based hydrogels were obtained from the water hyacinth fibers (WHFs) with aids of borax as a chemical cross-linker. The chemical treatment on WHFs, confirmed by Fourier transform infrared (FT-IR) analysis and thermogravimetric analysis (TGA), exhibited the reduction of hemicellulose and lignin. The treated cellulose fibers were dissolved in the mixed solution of NaOH/urea prior to mixing with borax at the cellulose/borax weight ratio of 1/0, 1/0.5 and 1/1 to prepare cellulose-based hydrogels. The effect of borax contents on the properties of cellulose-based hydrogels was investigated. The results showed that the swelling ratio and equilibrium water content of the obtained hydrogels were similar with increasing a borax content.

1. Introduction

Hydrogels, three-dimensional polymeric network materials containing large amounts of water, can be used in a wide range of applications such as agricultural, medical and waste-water treatment [1]. Generally, hydrogels can be derived from synthetic polymers such as poly(acrylic acid), poly(amide-amine), poly(ethylene glycol), and poly(vinyl alcohol) and from natural biomaterials for instance hyaluronate, alginate, starch, gelatin, chitin, chitosan, and cellulose [2]. In order to stabilize hydrogels without any dissolution, the physical or chemical cross-linking should be introduced. Physical cross-linking is usually obtained via a physical process such as chain entanglement, crystallization, and hydrogen bonding while chemical cross-linking is usually obtained via chemical bonding. The main disadvantage of the physical cross-linked hydrogels is the limited stability to long usage; therefore, chemical cross-linking would be suitable in this case [3]. Although synthetic polymer-based hydrogels have advantages over natural-based hydrogels such as adjustable mechanical properties and easy control of chemical compositions, they are non-renewable and non-biocompatible compared with natural-based hydrogels [4]. Recently, cellulose, a renewable resource found in plants such as straw, corncob, bagasse, and water hyacinth, has been widely used to prepare hydrogels due to its favourable properties including hydrophilicity, biodegradability, biocompatibility, nontoxicity, and low cost [2].
In this research, borax was introduced as a cross-linker in order to enhance stability and properties of the hydrogels prepared from water hyacinth fibers (WHFs), and effect of the borax contents on hydrogel properties was investigated.

2. Experimental

2.1. Materials
WHFs were obtained from Phra Nakhon Si Ayutthaya province, Thailand. Ethanol and toluene were purchased from CT Chemical. Hydrochloric acid (HCl) was purchased from JT Baker Chemicals, and sodium hydroxide (NaOH) and sodium hypochlorite (NaClO) were purchased from Loba Chemie. Urea and borax were purchased from Ajax Finechem and Quality Reagent Chemical, respectively. All materials were used as received without further purification.

2.2. Preparation of cellulose hydrogels
Prior to preparation of cellulose hydrogels, WHFs were first treated by chemical method. First, WHFs were dewaxed using a mixture of toluene-ethanol solution (2:1, v/v) at 73 °C for 3 hours. The obtained dewaxed fibers were filtered, washed with deionized (DI) water and then oven-dried at 60 °C for 24 hours. 10 g of these dewaxed fibers were added to 500 ml of 3 vol% of NaClO aqueous solution for 2 hours at 80 °C. After that, alkaline treatment was performed by 1 wt% of NaOH aqueous solution for 2 hours at 60 °C. Next, the second bleaching process was performed using 3 vol% of NaClO aqueous solution for 3 hours at 75 °C. Later, hydrolysis was performed by 5 vol% of HCl solution for 6 hours at 60 °C. The treated cellulose fibers were washed with excess distilled water to neutral and then freeze-dried for 60 hours. The cellulose solution was obtained by dissolving 3 g of the treated cellulose fibers in 100 ml of the mixed solution of 7 wt% of NaOH and 12 wt% of urea [5]. The solution with the cellulose concentration 3 wt% was mixed with borax as a cross-linking agent with three different cellulose/borax weight ratios (1/0, 1/0.5 and 1/1) using a magnetic stirrer at room temperature. Later, the 10 ml of the obtained solution was poured into a Petri dish, and allowed to dry at room temperature for 5 days to form hydrogels.

2.3. Characterization
Functional group analysis of the raw WHFs, treated WHFs and cellulose hydrogels was carried out using Fourier transform infrared spectroscopy (FT-IR) (Nicolet 6700, Thermo Fisher Scientific) over a frequency range of 450 - 4000 cm⁻¹.

Thermal stability of the raw WHFs and treated WHFs was studied by the weight loss from thermal degradation using thermogravimetric analysis (TGA) (TGA/SDTA 851 e, Mettler Toledo). The samples were scanned from 30 to 700 °C at a heating rate of 20 °C min⁻¹ under the nitrogen atmosphere with a flow rate of 40 ml min⁻¹.

The swelling ratio of the hydrogels was investigated at room temperature in DI water by using gravimetric method. The dried hydrogels were swollen in DI water for 24 hours to achieve equilibrium swelling. The weights of the dried hydrogels (Wd) and the swollen hydrogels (Ws) were determined to calculate the swelling ratio.

\[ \text{swelling ratio (\%)} = \left( \frac{W_s - W_d}{W_d} \right) \times 100 \]  

Equilibrium water content (EWC) is the amount of absorbed water in swollen hydrogels calculated by the following equation.

\[ \text{EWC (\%)} = \left( \frac{W_s - W_d}{W_s} \right) \times 100 \]  

3. Results and discussion
Figure 1(a) presents the color change of the WHFs after a series of the chemical treatment from brownish to white fibers. This was due to the reduction of lignin caused by alkaline treatment and
bleaching process. Moreover, the fiber yield after these treatments was 42.7%. Figure 1(b) shows FT-IR spectra of the raw and treated fibers. Both of the raw and treated WHFs reveal the peaks at 3400 and 2923 cm\(^{-1}\), associated with O-H stretching vibration and C-H stretching vibration, respectively. In addition, the peaks located at 1054 and 1101 cm\(^{-1}\), assigned to C-O primary alcohol and C-O secondary alcohol of cellulose are observed from both fibers. Moreover, the reduction in the intensity of the peaks at 1727 and 1519 cm\(^{-1}\), assigned to C=O and C=C aromatic of hemicellulose \([6]\) and at 1245 cm\(^{-1}\), contributed to C-O stretching vibration of hemicellulose and aryl alkyl ether groups in lignin \([7]\) was found from the treated WHFs, compared with the raw fibers. This confirmed the decrease in hemicellulose and lignin contents after the chemical treatments.

Figure 1. (a) Appearance and (b) FT-IR spectra of the raw and treated WHFs.

The Thermogravimetric (TG) curves of the raw and treated WHFs are shown in Figure 2(a). Moreover, Table 1 summarizers the thermal degradation of both fiber materials including onset temperature (T\(_{\text{onset}}\)), endset temperature (T\(_{\text{endset}}\)), maximum degradation temperature (T\(_{\text{max}}\)) of each stage and % char at 700 °C. The T\(_{\text{onset}}\) and T\(_{\text{endset}}\) thermal degradation temperature of the treated WHFs were 326 and 375 °C while the raw fibers presented the T\(_{\text{onset}}\) and T\(_{\text{endset}}\) of 269 and 349 °C, respectively. It can be seen that the thermal degradation temperature of the treated WHFs was higher than that of the raw WHFs, indicating the improvement of the thermal stability due to the removal of the hemicellulose and lignin. Generally, natural fibers present four thermal degradation regions: moisture evaporation, decomposition of hemicellulose and cellulose, degradation of lignin, and formation of pyrolytic char. However, these steps in a TGA curve were overlapped because of the thermal degradation temperature ranges of hemicellulose, cellulose, and lignin. Thus, a derivative thermogram (DTG) curve was used to present the thermal degradation regions, as shown in Figure 2(b). The initial degradation was observed at the range of 41 – 121 °C with T\(_{\text{max},1}\) of 60 °C, attributed to moisture evaporation. The second step was observed at the range of 195 – 387 °C with T\(_{\text{max},2}\) of 319 °C, attributed to the degradation of hemicellulose and cellulose while the third step was the degradation of lignin occurring between 417 – 511 °C with T\(_{\text{max},3}\) of 460 °C. The final step of the degradation happened at the range of 577 – 639 °C with T\(_{\text{max},4}\) of 617 °C, assigned to the formation of carbon \([8]\). On the other hand, the degradation of treated WHFs occurred only two steps. In the first step, moisture was evaporated at the range of 39 – 93 °C with T\(_{\text{max},1}\) of 48 °C and the second step was observed between 220 – 402 °C with T\(_{\text{max},2}\) of 359 °C. The third and fourth steps of the treated WHFs did not find due to a small amount of lignin left in the fibers. Moreover, the raw and treated WHFs presented the residue content at 700 °C of 17.2 and 9.1 wt%, respectively. The higher char content obtained from the raw fibers was due to the formation of pyrolytic char from lignin, hemicellulose, and some inorganic.
Figure 2. (a) TG and (b) DTG thermograms of the raw and treated WHFs.

Table 1. TG and DTG data obtained from the raw and treated WHFs.

| Samples       | $T_{onset}$ (°C) | $T_{endset}$ (°C) | $T_{max,1}$ (°C) | $T_{max,2}$ (°C) | $T_{max,3}$ (°C) | $T_{max,4}$ (°C) | % char at 700 °C |
|---------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| raw WHFs      | 269             | 349             | 60              | 319             | 460             | 617             | 17.2            |
| treated WHFs  | 326             | 375             | 48              | 359             | -               | -               | 9.1             |

Figure 3(a) shows the appearance of the cross-linked cellulose hydrogels at the ratios of cellulose/borax of 1/0, 1/0.5 and 1/1. The cellulose hydrogels were transparent, indicating the good dissolution of cellulose in the NaOH/urea aqueous solution. However, the color of the cellulose hydrogels was light yellow. This might be due to a small amount of lignin remained in the treated WHFs. FT-IR spectra of the cross-linked cellulose hydrogels are presented in Figure 3(b). The cellulose hydrogels exhibited the characteristic absorption peaks at 3400, 2923, 1054, and 1101 cm$^{-1}$, associated with O-H stretching vibration, C-H stretching vibration, C-O primary alcohol, and C-O secondary alcohol, respectively. In addition, the reduction in the peak intensity at 3400 cm$^{-1}$ with increasing a borax content was observed due to the decrease of the hydroxyl groups of cellulose. When borax was introduced into the cellulose hydrogel, the interaction between borax and hydroxyl groups was formed [9]. Moreover, the appearance of the trivial peaks at 1334 and 1278 cm$^{-1}$, assigned with borate (asymmetric stretching relaxation of B-O-C) [10] and vibrations of B-O-C, confirmed the cross-linking reaction between cellulose and borax (Figure 3(c)). Notably, the cross-linked cellulose hydrogels exhibited lower intensity of the peaks at 1334 and 1278 cm$^{-1}$ were compared with others research, due to the low content of borax used in this study [9] [10].

Figure 3. (a) Appearance of cellulose solution and cellulose hydrogels, (b) FT-IR spectra of the cellulose hydrogels, and (c) FT-IR spectra of cellulose hydrogels at 1500–1100 cm$^{-1}$.
The swelling ratio and equilibrium water content (EWC) of the varied cellulose/borax weight ratios of the cross-linked cellulose hydrogels are shown in Table 2. It was observed that the values of the swelling ratio of the cellulose hydrogels did not significantly change when the weight ratio of the borax increased. The swelling ratio of the cross-linked cellulose hydrogels with the ratio of cellulose/borax of 1/0, 1/0.5, and 1/1 was 75.1 ± 1.3, 79.2 ± 1.6, and 83.2 ± 2.6, respectively. The EWC of the cross-linked cellulose hydrogels with the ratio of cellulose/borax of 1/0, 1/0.5, and 1/1 was 89.9 ± 0.9, 90.7 ± 0.4, and 91.0 ± 0.5, respectively. The increase of the borax content did not affect swelling ratio and EWC at the 95% confidence interval. The similar values of these swelling ratio and EWC might be because of the low content of borax and the high hydrophilicity of cellulose interacted with water. The study of the effects of borax on properties of the prepared hydrogels is our future work to deeper understand the mechanism and the role of borax in the cellulose hydrogels.

Table 2. Swelling ratio and equilibrium water content of the cellulose hydrogels

| Weight ratios of cellulose/borax | Swelling ratio (%) | EWC (%) |
|----------------------------------|--------------------|---------|
| 1/0                              | 75.1 ± 1.3<sup>a</sup> | 89.9 ± 0.9<sup>b</sup> |
| 1/0.5                            | 79.2 ± 1.6<sup>a</sup> | 90.7 ± 0.4<sup>b</sup> |
| 1/1                              | 83.2 ± 2.6<sup>a</sup> | 91.0 ± 0.5<sup>b</sup> |

<sup>a,b</sup> The same alphabet means no different statistical meaningful at a 95% confidence interval.

4. Summary
The cross-linked cellulose-based hydrogels derived from WHFs were successfully prepared by chemical cross-linking with borax. The WHFs were firstly treated by the chemical treatment to remove impurities, hemicellulose and lignin. The yield of the treated WHFs was about 42.7%. The FT-IR spectra and TGA could confirm the reduction of hemicellulose and lignin contents in the treated WHFs. The treated cellulose was used to prepare the cellulose hydrogels with various amounts of borax. The appearance of the functional groups between borax and hydroxyl groups of cellulose observed from FT-IR results could confirm the cross-linking in the hydrogels. However, the addition of borax did not affect the swelling content and EWC values of the hydrogels.

Acknowledgments
The authors are grateful to Chulalongkorn University and Faculty of Science, Chulalongkorn University for financial supports.

References
[1] M. R. Guilherme, A. V. Reis, A. T. Paulino, T. A. Moia, L. H. Mattoso, and E. B. Tambourgi: Journal of Applied Polymer Science. Vol. 117 (2010), p. 3146-3154
[2] C. Chang and L. Zhang: Carbohydrate Polymers. Vol. 84 (2011), p. 40-53
[3] V. K. Thakur and M. K. Thakur: Handbook of Polymers for Pharmaceutical Technologies, Processing and Applications. Vol. 2 (2015), p. 95-120
[4] J. Zhu: Biomaterials. Vol. 31 (2010), p. 4639-4656
[5] H. Qi, C. Chang, and L. Zhang: Cellulose. Vol. 15 (2008), p. 779-787
[6] M. Thiripura and A. Ramesh: Carbohydrate Polymers. Vol. 87 (2012), p. 1701-1705
[7] Z. Wang, Z. Yao, J. Zhou, M. He, Q. Jiang, S. Li, Y. Ma, M. Liu, and S. Luo: Biological Macromolecules. Vol. 129 (2018), p. 1081-1089
[8] B. T. N. Thi, L. K. Ong, D. T. N. Thi, and Y. H. Ju: Journal of the Taiwan Institute of Chemical Engineers. Vol. 71 (2017), p. 55-61
[9] H. Bian, L. Jiao, R. Wang, X. Wang, W. Zhu, and H. Dai: European Polymer Journal. Vol. 107 (2018), p. 267-274
[10] M. Lim, H. Kwon, D. Kim, J. Seo, H. Han, and S. B. Khan: Progress in Organic Coatings. Vol. 85 (2015), p. 68-75