International Journal of Engineering and Technical Research (IJETR)
ISSN: 2321-0869 (O) 2454-4698 (P), Volume-7, Issue-3, March 2017

Ultrasound Effect on Cellulose Decomposition in Solution and Hydrogels

Huixin Jiang, Takaomi Kobayashi

***Abstract*— Effect of ultrasound (US) on cellulose decomposition was studied in the solution and hydrogels, when the US with different frequencies and powers were exposed to the cellulose having different molecular weight. Gel permeation chromatography (GPC) results showed that higher US frequency and power were much more effective to depolymerize cellulose. The cellulose in looser network hydrogel and lower cellulose concentration solution were easier to be depolymerized by US irradiation. The effect of US exposure was more effective on the cellulose with lower molecular weight in both hydrogel and solution configuration. Moreover, the results also showed that US could depolymerize the cellulose more effectively in solution than hydrogel.**

***Index Terms*— Cellulose, Depolymerization, Molecular weight, Ultrasound.**

I. INTRODUCTION

Cellulose is one of the abundant biomass in the earth and treated as a resource to generate biofuel [1] and other materials [2]. In general, cellulose consisted of glucose repeated unit is converted into glucose and then used as feedstock to produce biofuels and bio-based products. Therefore, depolymerization of high molecular weight cellulose into low molecular weight cellulose turns to be a key step and attractive in research [3]. In order to depolymerize cellulose, physical, chemical, physiochemical, and biological pretreatment technologies have been developed [4]. These methods include acidic hydrolysis [5], enzymatic hydrolysis [6], hydrolysis in supercritical water [7], microwave [8], ultrasound [9] and so on. However, these methods suffer from disadvantages of using acid [5] and high temperature [10]. Therefore, a simple and effective method to depolymerize cellulose is needed.

Ultrasound (US) is treated as a green technique and could accelerate chemical and physical processes [11]. US has also been used to depolymerize synthetic polymers [12] and biopolymers [13] into lower molecular weight fragments. These studies also proved that less chemical nature of the polymer changed and just simply reduced its molecular weight by US exposure. Moreover, the US was applied in the degradation of cellulose [14]. Aliyu *et al*. investigated the degradation of cellulose materials with enzymatic support [15]. Besides, the US mediated enzymatic hydrolysis of cellulose and carboxymethyl cellulose were also investigated, and showed that US is useful in accelerating the enzyme catalyzed saccharification of cellulose [16]. Zhang *et al*. reported the depolymerization of cellulose by the combination of US and Fenton reagent [9]. While, in these studies, enzymes and other additional reagents or functionalized cellulose are used. The US effect on the bulk cellulose without additional reagents has not been revealed yet.

It's well known that highly crystalized structure of bulk cellulose results in the difficulty in its depolymerization [17]. Through reducing the crystallinity of bulk cellulose may be a good way to assistant the depolymerization of cellulose. As reported in our prior studies [18], cellulose hydrogel was prepared from *N, N*-dimethylacetamide/lithium chloride (DMAc/LiCl) solution, suggesting that the dissolution decreased the crystallinity of cellulose. Recently, our report showed that US technology for drug releasing from cellulose hydrogels has advantages in controlling the medicine release under the US exposure. Especially in lower US frequencies of 23 and 43 kHz, the drug release was effective without damage of the cellulose hydrogel matrix by US exposure [19]. However, the US effect on the hydrogel wasn't clearly known at that time.

Cellulose hydrogels possess a three dimensional network structure, which have served as an excellent biocompatible material [20]. The stability of cellulose hydrogel under US exposure is also an important factor for its application. Therefore, the investigation of US effect on the cellulose hydrogel is very important topic. The present work investigated US effect on depolymerization of bulk cellulose in solution and hydrogel without additional reagents at different frequencies and output powers of US. Evidence showed that the US exposure could depolymerize cellulose in both the solution and hydrogel form.

II. MATERIALS AND EXPERIMENTS

A. Materials

Samples of cellulose for defatted cotton and sugarcane bagasse cellulose are listed in Table 1. Defatted cotton was purchased from Kawamoto Corporation (Osaka, Japan). Cellulose purified from sugar cane bagasse [20] was obtained from a local sugar factory (Okinawa, Japan). *N, N*-dimethylacetamide (DMAc) was purchased from TCI Co. Ltd. (Japan). Lithium chloride (LiCl), potassium hydroxide (KOH), sulfuric acid (H_2SO4), sodium hypochlorite (NaOCl), sodium hydroxide (NaOH), and ethanol (C_2H_5OH) were products of Nacalai Tesque Inc. (Japan). Before using, DMAc was dried with KOH at room temperature for 5 days and LiCl was dried in vacuum at 80 °C for 24 h.

Huixin Jiang, Department of Materials Science and Technology, Nagaoka University of Technology, Nagaoka, Japan, Tel.: +81 8067638321,
Takaomi Kobayashi, Department of Materials Science and Technology, Nagaoka University of Technology, Nagaoka, Japan, Tel.: +81 258479326,

Table 1. Cellulose contents and pre-treatments of different cellulose hydrogels and solutions.

Sample	Configuration	Sources	Cellulose content (wt%)	NaOCl-treatment	Shear viscosity (cP)	G' at 0.01 % strain (Pa)
CH1	Hydrogel	Defatted cotton	0.5	-	-	22300
CH2	Hydrogel	Defatted cotton	1	-	-	65300
CH3	Hydrogel	Defatted cotton	2	-	-	73900
CH4	Hydrogel	Sugar cane bagasse	0.5	40 °C	-	9800
CH5	Hydrogel	Sugar cane bagasse	0.5	50 °C	-	8310
CS1	Solution	Defatted cotton	0.5	-	340	-
CS2	Solution	Defatted cotton	1	-	4527	-
CS3	Solution	Defatted cotton	2	-	43899	-
CS4	Solution	Sugar cane bagasse	0.5	40 °C	55	-
CS5	Solution	Sugar cane bagasse	0.5	50 °C	22	-

B. Preparation of cellulose hydrogels

Each cellulose was firstly dissolved in DMAc and then converted to their hydrogels. The preparation of cotton solution was followed with the reported methods [21, 22]. Briefly, cotton was suspended in 300 mL of distilled water and stirred overnight. Then, water was removed with glass filter under vacuum, and ethanol (300 mL) was added to the swelled cotton. The mixture was stirred at room temperature for 24 h. Afterwards, ethanol was removed and 300 mL of DMAc was added. After 24 h stirring, the DMAc was removed and replaced with DMAc/LiCl solution containing 6 wt% LiCl. The mixture was stirred at room temperature for 14 days until a viscous and transparent solution was obtained. The cotton cellulose solutions with different cellulose concentration of 0.5, 1.0, and 2.0 wt% were prepared to use for each cellulose hydrogel by phase inversion process [19]. In the gelation, 7 g of the cotton cellulose solution was poured into a glass tray (10 cm diameter) and kept in a container filled with 15 mL of ethanol at room temperature for 24 h. The resulting film was washed by abundant distilled water to remove the remained DMAc. The hydrogels made from 0.5, 1.0, and 2.0 wt% cellulose in the solution were marked as CH1, CH2, and CH3, respectively (Table 1). The resultant solutions containing 0.5, 1.0, and 2.0 wt% of cotton cellulose were denoted as CS1, CS2, and CS3, respectively, (Table 1). The cellulose purified from sugar cane bagasse and the related hydrogels were reported in our prior report [18]. The sugar cane bagasse was stirred in 300 mL of 4 vol% sulfuric acid solution for 1.5 h at 90 °C after well washed by 80 °C of hot water. Then, it was stirred in 300 mL of 10 wt% NaOH aqueous solution for 12 h at 90 °C. Afterwards, the sugar cane bagasse was treated with 10 vol% NaOCl for 3 h at 40 °C or 50 °C. The resultant cellulose had different molecular weight, when the treatment condition of NaOCl was changed, especially for the temperature. After each treatment step was finished, the treated bagasse was well washed with abundant distilled water until neutral pH. At last, the bleached bagasse was dried in a vacuum oven at room temperature for 24 h. The preparation procedure of sugar cane bagasse hydrogels was almost same with that of cotton cellulose hydrogels. Briefly, the treated sugar cane bagasse was prepared by 0.5 wt% concentratioin in DMAc/LiCl solution for each cellulose, which was treated at 40 and 50 °C. In Table 1, CH4, CH5, CS4, and CS5 were for cellulose obtained at 40 and 50 °C, respectively.

C. Ultrasound exposure to cellulose hydrogel and solution

Cellulose hydrogel and solution were used in the following US exposure experiment. Fig. 1 shows the experimental setup of US exposure on cellulose hydrogel. Before US exposure, the hydrogel matrix (d = 4.6 cm, h = 0.1 cm) was cut into 4 pieces and put into a cylindrical glass vessel (4 cm diameter, 12 cm height) with 30 mL distilled water. Then, the vessel was immersed in US water bath (8.5 × 13.5 × 13 cm^3). The depolymerization behavior of cellulose hydrogel was studied in a sonoreactor device (HSR-305R, Honda electrics Co. Ltd. Japan), when the different US frequencies of 43, 141, and 500 kHz was exposed at 26 °C. The US powers were controlled in the range of 10, 30, 50, and 75 W with a wave factory (WF1943B multifunction synthesizer, NF, Japan). For cellulose solution, similar size of the cylindrical vessel was used. Briefly, 8 mL of cellulose solution was added into the vessel and then exposed to US in the water bath at 26 °C.

D. Characterization of the cellulose hydrogel and solution

For their celluloses, GPC was performed to measure their molecular weight according to reported method [20]. The GPC determination was carried out before and after US exposure for each cellulose in DMAc/LiCl solution. The GPC system was equipped with a refractive index (RI) detector (RID-10A, Shimadzu), online degasser (DGU-20A, Shimadzu, Japan), high-pressure pump (LC-20AD, Shimadzu), manual injector (7725i, Rheodyne), GPC column (KD-806M, Shodex) and a chromatpac integrator (CR8A, Shimadzu). The column temperature and the RI detector cell were kept at 50 °C and 40 °C, respectively. As the eluent, 1

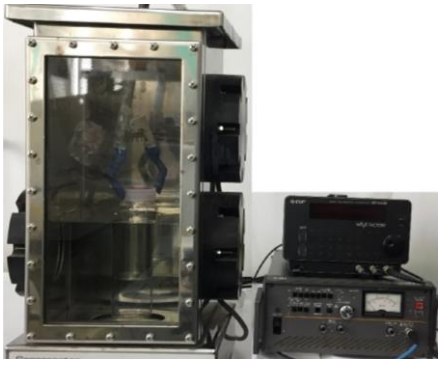

Fig. 1. Experimental setup of US exposure on cellulose hydrogel.

wt% of cellulose in DMAc/LiCl solution was used for the GPC system. Narrow distribution polystyrene standards were used as the weight average molecular weight (Mw) calibration. Before the GPC measurement, the cellulose hydrogel with or without US exposure were stirred in distilled water for 24 h, and then were stirred with pure ethanol for 24 h. Afterwards, DMAc replaced the ethanol and stirred for 24 h. After that, the hydrogels (0.08 g) were dissolved in 10 mL DMAc having 8 wt% LiCl. The sample solutions were diluted with DMAc adjust to be 0.1 wt% cellulose concentration in DMAc/LiCl eluent. Before injection to the GPC, sample solution (100 µL volume) was filtered by using a PTFE disposable membrane filter (DISMIC-25HP, Toyo Roshi Kaisha) with 0.45 µm pore size.

The shear viscosity of cellulose solution (CS) with and without US exposure was tested using a rheometer (Physica MCR 301, Anton Paar with PP25-cone, Φ= 25 mm) with 0.1 1/s shear rate at room temperature. The shear viscosity of cellulose solution was measured immediately after the pre-determined US exposure. By using the similar rheometer, viscoelasticity of hydrogels was measured at a constant frequency of 1 Hz. The strain sweep measurement was immediately carried out after the hydrogel was irradiated by US. The strain was changed in the range of 0.01-3 % for storage modulus.

The X-ray diffraction (XRD) patterns of celluloses and the resultant hydrogels were determined with CuKα radiation (λ = 1.5418) at 40 kV and 30 mA in the range of 10°- 40° by X-ray diffractometer (Smart Lab, Rigaku, Japan). Before the measurements, the samples were dried in vacuum at room temperature.

In the present study as seen in Table 1, three kinds of cellulose were used for hydrogels and their solutions. Fig. 2 shows the pictures of cellulose solutions and the hydrogels. It could be seen that all the solutions and hydrogels were transparent like that the cotton cellulose solution (Fig. 2(a)) and the related hydrogel (Fig. 2(d)) were colorless. However, the sugar cane cellulose solution (Fig. 2(b)) and the corresponding hydrogel (Fig. 2(e)) were yellowish, while the solution (Fig. 2(c)) and hydrogel (Fig. 2(f)) prepared from NaOCl solution at 50 °C showed less yellow.

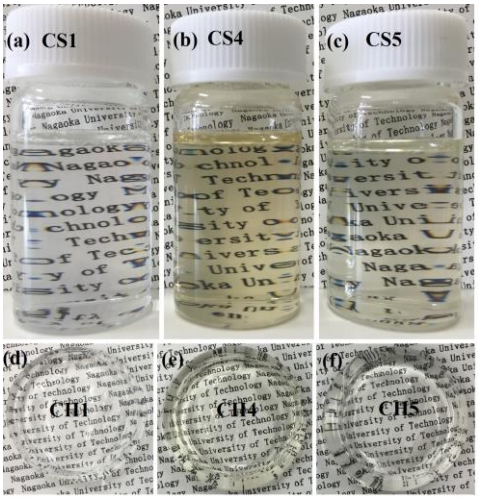

Fig. 2. Pictures of cellulose solutions and hydrogels for defatted cotton (a, d) and sugar cane cellulose pre-treatement with NaOCl at 40 °C (b, e) and 50 °C (c, f).

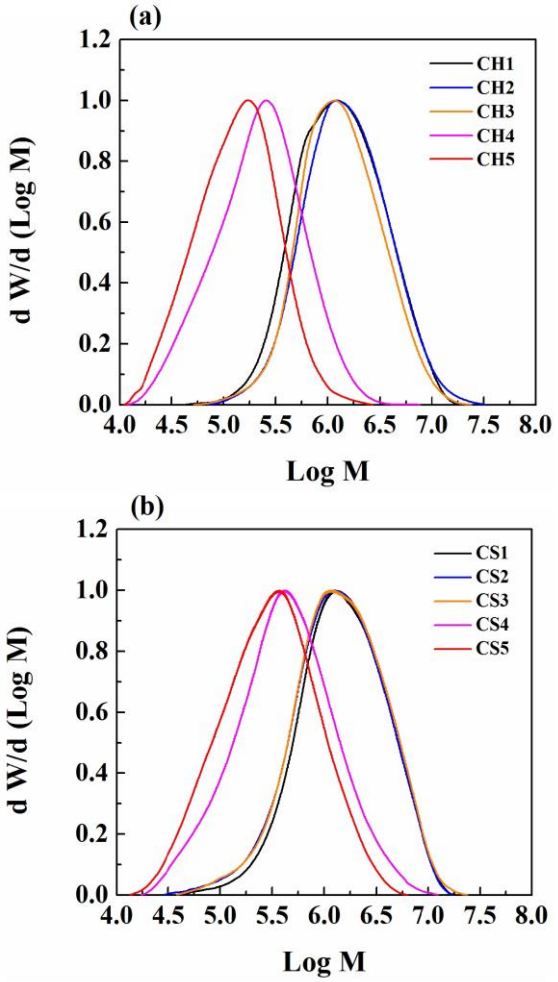

Fig. 3. Chromatogram for molecular weight distributions of different cellulose hydrogels (a) and solutions (b).

Fig. 3 shows GPC profiles for the Mw of CH1-CH5 and CS1-CS5. In the sugar cane cellulose, the Mw of CH4 and CS4 were much higher than CH5 and CS5, since the cellulose degradation was occurred by the NaOCl treatment at higher temperature [18].

III. Results and Discussion

A. US effect of US frequency on the depolymerization of cellulose in hydrogel and solution configuration

The depolymerization behaviors were studied under US exposure. The US condition was different in the frequency and output US power with the exposure time. Fig. 4 shows the GPC profiles of CH1 and CS1 before and after 500 kHz US exposure at 75 W for 0.5-4 h. Here, the US was exposed to different sample configuration of hydrogel in water (Fig. 4(a), CH1) and DMAc/LiCl solution (Fig. 4(b), CS1). The CH1 hydrogel was seen that the value of the peak top of the chromatograph was shifted toward lower molecular weight side, when the US exposure time was increased. Table 2 includes Mw, number average molecular weight (Mn), and Mw/Mn for cellulose hydrogel and the solution, which were measured before or after 500 kHz US for 4 h. The values of Mw of CH1 decreased from 20.2×10^5 to 10.0×10^5 after the US exposure for 4 h. It was noted that each sample decreased the molecular weight, as the 500 kHz US was exposed. In comparison with cellulose solution (CS1), similar change

Table 2. Molecular weight of different hydrogels and solutions before and after 75 W US exposure at 500 kHz for 4 h.

Sample	Before			After		
	Mw[a] ($\times 10^5$)	Mn[b] ($\times 10^5$)	Mw/Mn	Mw[a] ($\times 10^5$)	Mn[b] ($\times 10^5$)	Mw/Mn
CH1	20.2	8.7	2.3	10.0	5.5	1.7
CH2	22.9	10.1	2.2	15.1	7.7	1.9
CH3	19.9	9.5	2.0	17.6	8.6	2.0
CH4	7.8	1.7	4.5	3.3	1.3	2.4
CH5	4.7	1.6	2.9	1.9	0.9	2.1
CS1	22.5	9.3	2.4	8.6	4.2	2.0
CS2	21.4	8.0	2.6	11.1	5.0	2.2
CS3	22.2	8.3	2.6	13.9	6.9	1.9
CS4	7.4	2.3	3.1	2.5	1.5	1.6
CS5	5.0	1.7	2.9	1.4	0.8	1.8

[a] Weight average molecular weight
[b] Number average molecular weight

was observed as shown in Fig. 4(b). It could be seen that with the increase of US exposure time, the peak shifted towards lower molecular weight region. As seen in Table 2, after 4 h exposure, the Mw decreased from 22.5 × 10^5 to 8.6 × 10^5. This indicated that the US exposure decreased the molecular weight by effective depolymerization of cellulose. It is interesting to see the comparison between hydrogel and the DMAc/LiCl solution. The decline tendency in the solution was higher than the hydrogel.

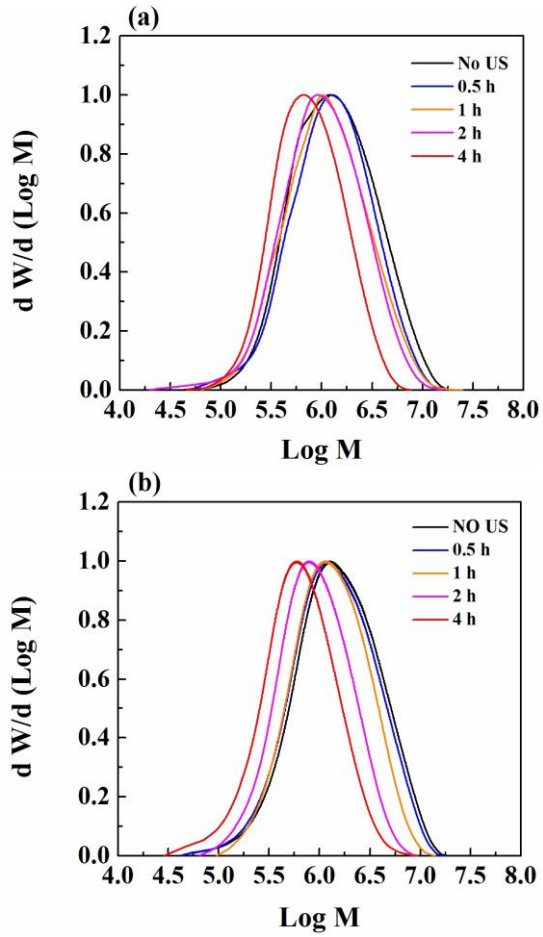

Fig. 4. Chromatogram for molecular weight distributions of CH1 (a) and CS1 (b) before and after 75 W US exposure at 500 kHz for different time.

To fully understand the depolymerization behavior of cellulose in the configuration of hydrogel and solution, the US exposure was carried out at different frequency. Different US frequencies of 43, 141, and 500 kHz were operated with 75 W for CH1 and CS1. Fig. 5(a) shows plots of molecular weight ratio (Mw(t)/Mw(0)) *vs* US exposure time. The solid

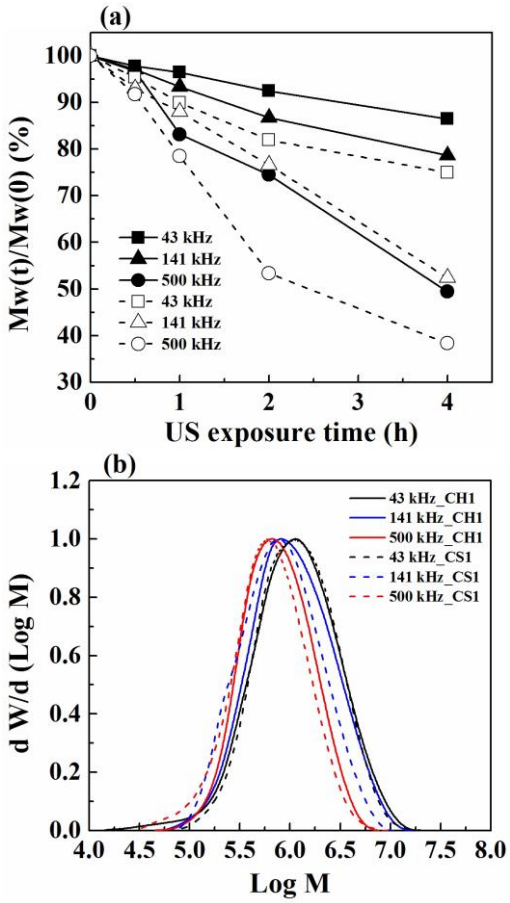

Fig. 5. (a) Molecular weight ratio (Mw(t)/Mw(0)) of CH1 (solid line) and CS1 (dash line) under 75 W US exposure at different frequencies for 0 - 4 h. Mw(t) is average molecular weight of the sample irradiated by US exposure for t h, Mw(0) is average molecular weight of the sample without US irradiation. (b) Chromatogram for molecular weight distributions of CH1 and CS1 after 75 W US exposure for 4 h.

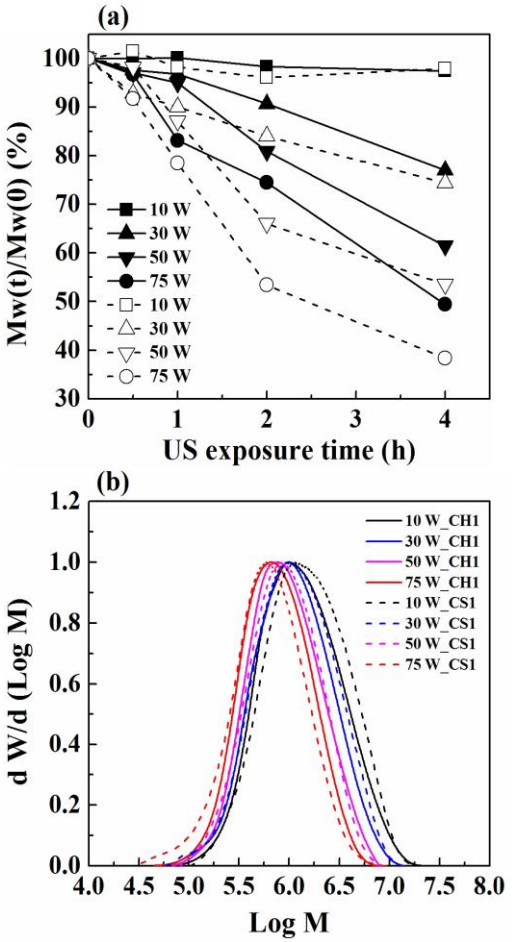

Fig. 6. (a)Molecular weight ratio (Mw(t)/Mw(0)) of CH1 (solid line) and CS1 (dash line) under US exposure at 500 kHz for 0 - 4 h. Mw(t) is average molecular weight of the sample irradiated by US exposure for t h, Mw(0) is average molecular weight of the sample without US irradiation. (b) Chromatogram for molecular weight distributions of CH1 and CS1 after 500 kHz US exposure for 4 h.

line represents the cellulose hydrogel (CH1) and the dash line refers to the cellulose solution (CS1). Here, Mw(t) and Mw(0) refer the average molecular weight after the US exposure for t h and without US exposure, respectively. In their plots, it could be seen that for three frequencies, the Mw(t)/Mw(0) values of CH1 and CS1 decreased with the increasing of the US exposure time, suggesting depolymerization of each cellulose. It is noted that the hydrogel configuration was less in the depolymerization of the cellulose than the solution one. For the hydrogels, their Mw(t)/Mw(0) values decreased to 86 %, 78 %, and 49 % for 43, 141, and 500 kHz after the US exposure, respectively. In contrast, the cellulose solution showed that the Mw(t)/Mw(0) values deceased to 75 %, 52 %, and 38 % for 43, 141, and 500 kHz, respectively. As a result, in the both hydrogel and solution configuration, the 500 kHz was effective to depolymerize cellulose. Fig. 5(b) shows the GPC profiles for the CH1 and CS1 after 75 W US exposure at different frequencies for 4 h. It could be seen that the value of the peak top of the chromatograph shifted to the lower molecular weight side when the frequency was increased, which indicated that the 500 kHz was more effective to depolymerize the cellulose. In addition, the peak of cellulose in solution configuration tended to move to the lower molecular weight side than the hydrogel configuration.

Fig. 6(a) shows the Mw(t)/Mw(0) values of cellulose hydrogel and solution under 500 kHz US exposure with different powers of 10-75 W and their GPC profiles at 4 h exposure. It could be seen that the values of the Mw(t)/Mw(0) decreased at 30, 50, and 75 W. However, the 10 W case was very less in the change of the molecular weight distribution. It could be seen from Fig. 6(b) that the value of peak top turned to shift to lower molecular weight side when the sample was irradiated by US at higher power.

As reported in our prior study [19], cellulose hydrogel with different cellulose contents showed different structure and affected their drug release efficiency. Thus, the cellulose hydrogel contains different cellulose contents might affect their depolymerization behavior under US exposure. The prior study [19] also revealed that cellulose hydrogel with higher cellulose content possessed a denser structure as compared with the cellulose hydrogel with lower cellulose content. Fig. 7(a) shows that the value of Mw(t)/Mw(0) in hydrogel and solution decreased, when the US exposure time increased. However, the decline tendency was observed significantly in looser cellulose in hydrogel and lower concentration in solution. For CH1, CH2, and CH3, the value of the Mw(t)/Mw(0) decreased to 49 %, 65 %, and 88 % after

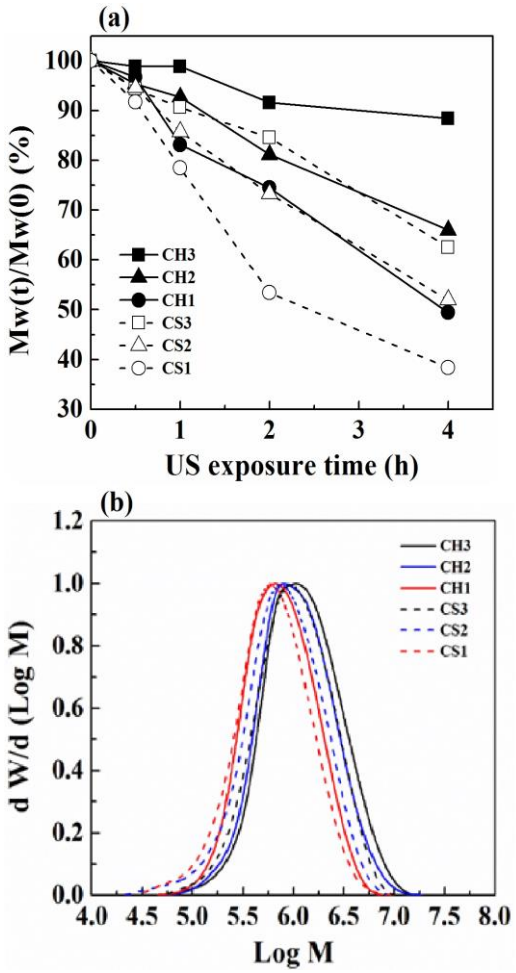

Fig. 7. (a) Molecular weight ratio (Mw(t)/Mw(0)) of CH1, CH2 and CH3 under 75 W US exposure at 500 kHz for 0 - 4 h. Mw(t) is the average molecular weight of the sample irradiated by US exposure for t h, Mw(0) is the average molecular weight of the sample without US irradiation. (b) Chromatogram for molecular weight distributions of samples after 75 W US exposure at 500 kHz for 4 h.

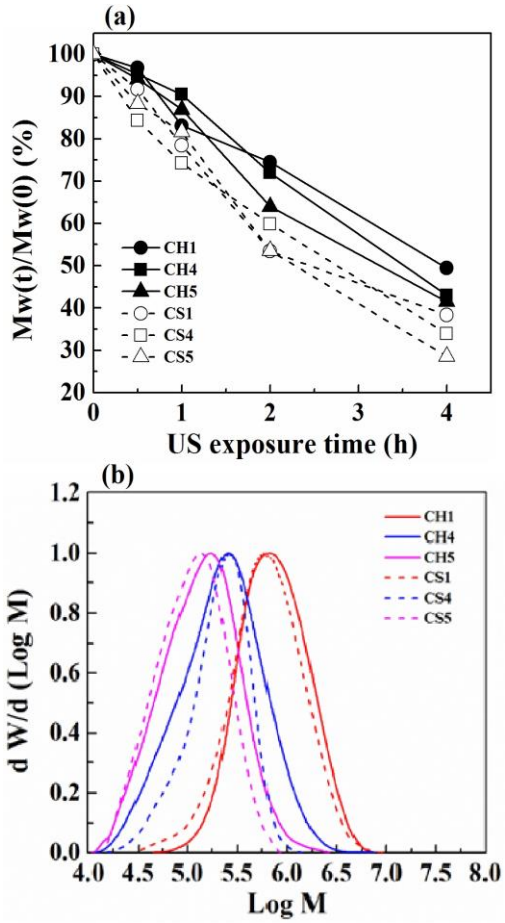

Fig. 8. (a) Molecular weight ratio (Mw(t)/Mw(0)) of CH1, CH4, CH5 (solid) and the responding solution (dash) under 75 W US exposure at 500 kHz. Mw(t) is average molecular weight of the sample irradiated by US exposure for t h, Mw(0) is average molecular weight of the sample without US irradiation. (b) Chromatogram for molecular weight distributions of samples after US exposure for 4 h.

the US exposure, respectively. This suggested that the hydrogel with loose networking of the cellulose segments was more sensitive to the US effect. The dense structure made it difficult in cellulose depolymerization under the US exposure. As well as CH1-CH3, the similarity of the cellulose solution was observed, depending upon their cellulose concentration. In case of high concentration, molecular weight had a lower change, but, the change was higher than that of the hydrogel configuration. Fig. 7(b) shows the GPC profiles for the samples after US exposure for 4 h. It could be seen that the value of the top peak shifted to the lower molecular weight side when the cellulose hydrogel was looser. In addition, the value of the top peak tended to be at the lower molecular weight side when the cellulose was in the solution configuration.

B. US effect on different molecular weight of cellulose in the depolymerization

Molecular weight of cellulose in similar configuration was investigated for the depolymerization of cellulose. Fig. 8(a) shows plots of Mw(t)/Mw(0) at US exposure time for CH1, CH4, and CH5. Similarly, the 500 kHz US was exposed at 75 W for 0- 4h. As shown in Table 2, CH1, CH4, and CH5 had different molecular weights with Mw = 20.2×10^5, 7.8×10^5, and 4.7×10^5, respectively. In results of Fig. 8(a), it could be seen that hydrogel depolymerization was similar tendency in CH1, CH4, and CH5. If anything, somewhat CH1 had a less depolymerization. The same results were seen in the solution configuration. This suggested that cellulose hydrogel with lower molecular weight might be easier to be depolymerized in the vibration that was driven by the US. Fig. 8(b) shows the GPC profiles of the samples irradiated by US for 4 h. It could be seen that the value of the top peak shifted to the lower molecular weight side for the lower molecular weight sample. In addition, the value of the top peak moved to the lower molecular weight side in the solution configuration compared with the hydrogel configuration.

C. US effect on cellulose properties

As mentioned, 500 kHz US at 75 W was effective for the cellulose depolymerization relative to other frequencies of 43 kHz and 141 kHz at the same US power. Therefore, it is very interesting to analyze the cellulose properties after the US was exposed. Firstly, shear viscosity of the cellulose solution (CS1) before and after US exposure was measured for each frequency of US. Fig. 9(a) shows shear viscosity of the cellulose-DMAc/LiCl solution (CS1). The shear viscosity decreased with the increase of US exposure time. Among them, the 500 kHz US decreased the shear viscosity much higher than the others. It was noted that the change of shear viscosity is consistent with change of molecular weight. Therefore, Fig. 9(b) plots the value of Mw against the US exposure time at different frequency. It could be seen that the Mw of all the samples was decreased as increased the US

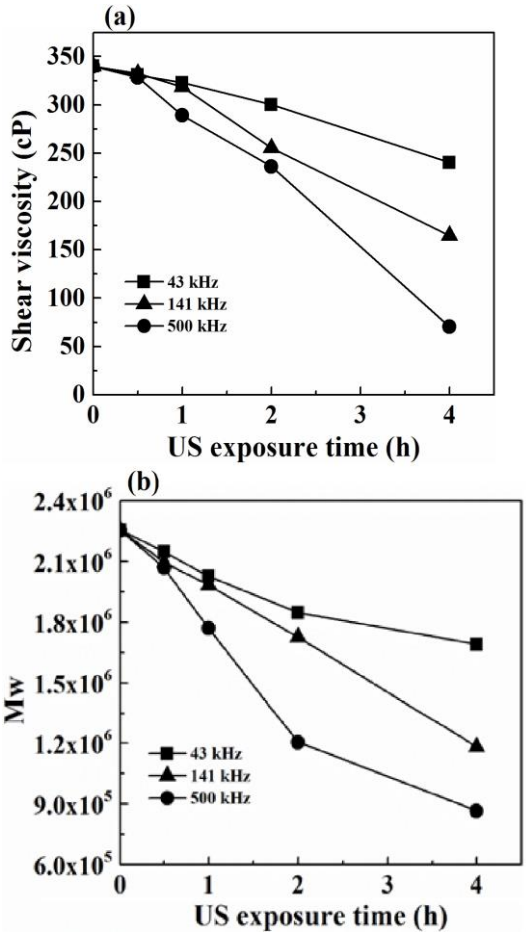

Fig. 9. Shear viscosity (a) and weight average molecular weight (b) of CS1 under 75 W US exposure at different frequencies for 0 - 4 h.

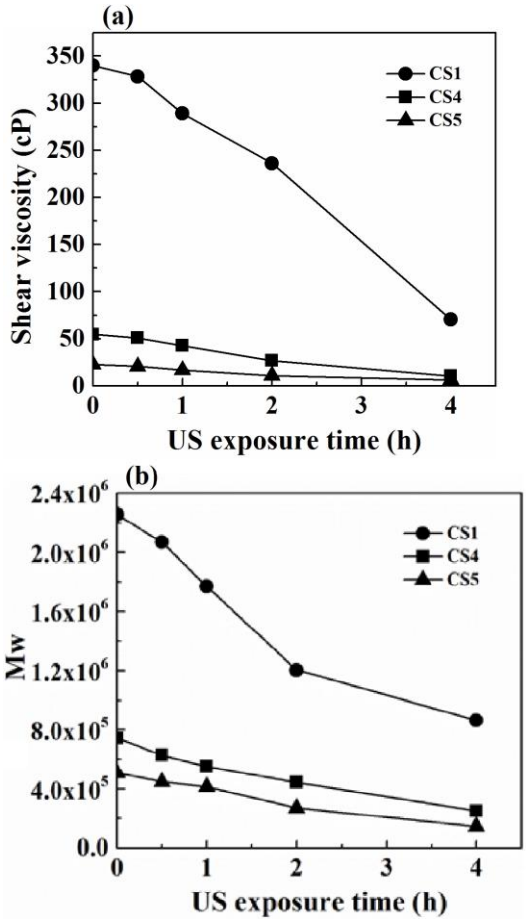

Fig. 10. Shear viscosity (a) and weight average molecular weight (b) of CS1, CS4, CS5 under 75 W US exposure at 500 kHz for 0 - 4 h.

exposure time. In addition, the decrease of Mw was more significantly at the higher frequency. It could confirm that US exposure could depolymerize cellulose effectively.

Fig. 10(a) shows the shear viscosity of cellulose solutions with different molecular weight under US exposure for 0-4 h. It could be seen that the shear viscosity decreased as increased the US exposure time. The shear viscosity of CS1, CS4, and CS5 was 340, 55, and 22 cP before US exposure. However, the shear viscosity decrease to 70, 10, and 6 cP after 75 W US exposure at 500 kHz for 4 h. The US exposure

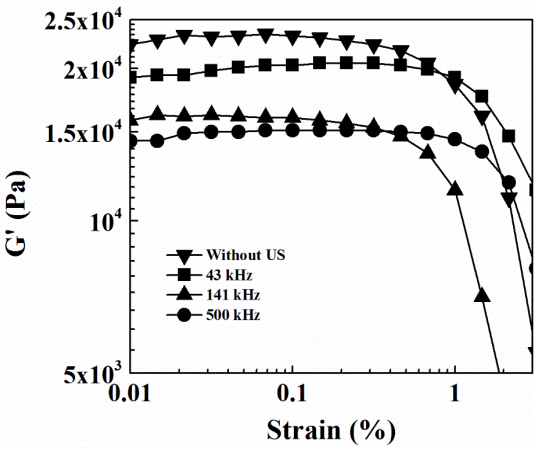

Fig. 11. Strain sweep measurements of CH1 before and after 75 W US exposure at different frequencies for 4 h. G': storage modulus.

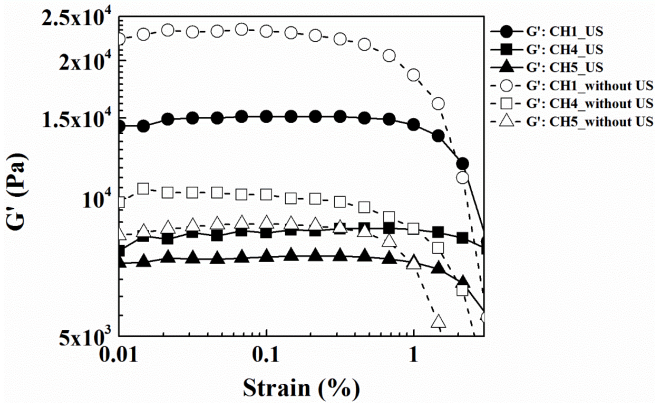

Fig. 12. Strain sweep measurements of CH1, CH4, CH5 before and after 75 W US exposure at 500 kHz for 4 h. G': storage modulus.

decreased the shear viscosity of all the cellulose solutions effectively. Fig. 10(b) shows similar tendency as Fig. 10(a) when the US exposure was driven. The Mw of CS1, CS4, and CS5 decreased as increased the US exposure time. The Mw of CS1, CS4, and CS5 was decreased from 22.5×10^5, 7.4×10^5, and 5.0×10^5 to 8.6×10^5, 2.5×10^5, and 1.4×10^5 after US exposure for 4 h. It indicated that US depolymerized all the cellulose in the solution configuration effectively.

Fig. 11 shows viscoelasticity of CH1 hydrogel before and after the US exposure at 75 W for 4 h. It was shown that the value of G' at 0.01 % strain of CH1 without US exposure was 2.2×10^4 Pa, indicating characteristic viscoelasticity. Moreover, the value of G' decreased after US exposure, which indicated that the hydrogel became softer after US exposure. This may be caused by the depolymerization of cellulose including that the gel network was broken by the US, the intermolecular interactions of cellulose segments [19] and the entanglements [23, 24]. In addition, after the 500 kHz US was exposed, the G' turned to be the smallest, which also indicated that the 500 kHz decreased the molecular weight most effectively.

Fig. 12 shows the viscoelasticity of cellulose hydrogels with different molecular weight before or after the 75 W US exposure at 500 kHz for 4 h. The G' at 0.01% strain of CH1, CH4, and CH5 was 2.2×10^4, 9.8×10^3, and 8.3×10^3 Pa, respectively. All the hydrogels had high storage ability, indicating characteristic viscoelasticity. Moreover, the G' at 0.01% strain was decreased with the decreased cellulose molecular weight, which indicated that the hydrogel with lower cellulose molecular weight was softer. In addition, the G' at 0.01% strain of all the samples were decreased significantly, which indicated that the gel network was broken by the US exposure.

Fig. 13 shows the XRD patterns of cotton cellulose, sugar cane bagasse cellulose and hydrogels before and after US exposure. For cotton and sugar cane cellulose, typical crystalline lattice of cellulose I with peaks at 22.6° and amorphous cellulose at 16.1° were observed [25]. In the cases of the cellulose hydrogel (Fig. 13(a)), significant change in the diffraction pattern was observed as compared with cotton cellulose. One broad peak at around 20°, which belonged to the crystalline of cellulose II, were observed. The same change in the XRD pattern was seen for cotton and sugar

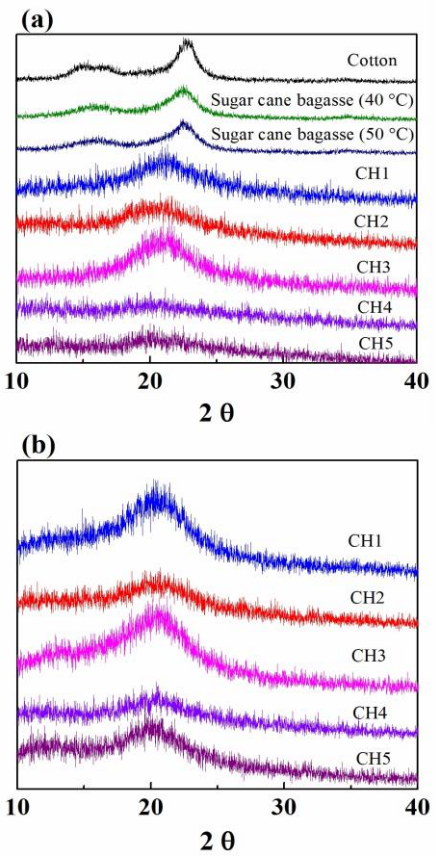

Fig. 13. X-ray diffraction patterns of cellulose and hydrogels before (a) and after (b) 75 W US exposure at 500 kHz for 4 h.

cane bagasse. These results suggested that cellulose I was transformed to cellulose II during the phase inversion process. Similar results for the sugar cane bagasse and cellulose hydrogel regenerated from sugar cane bagasse were obtained in our prior study [18]. The change indicated that the crystalline structure from bulk cellulose disappeared in the hydrogels. From the XRD results as seen in Fig. 13(b), it could be seen that after US exposure the diffraction pattern of the hydrogel kept the same at about 20°.

IV. Conclusion

In the present study, the US effect on the depolymerization of cellulose was described. The comparison was made in the hydrogel and solution configuration. The effect of US frequencies and US powers was examined to hydrogel with dense or loose network and different molecular weights. It was found hydrogel form was less than the solution in the depolymerization. The higher US frequency and power were much more effective to depolymerize cellulose. Moreover, looser hydrogel and lower cellulose concentration solution showed higher depolymerization. These results indicated that US can depolymerize cellulose effectively.

References

[1] T.E. Amidon, C.D. Wood, A.M. Shupe, Y. Wang, M. Graves, S. Liu, Biorefinery: Conversion of woody biomass to chemicals, energy and materials, Journal of Biobased Materials and Bioenergy, 2 (2008) 100-120.

[2] N. Petersen, P. Gatenholm, Bacterial cellulose-based materials and medical devices: current state and perspectives, Applied Microbiology and Biotechnology, 91 (2011) 1277-1286.

[3] R. Rinaldi, R. Palkovits, F. Schüth, Depolymerization of cellulose using solid catalysts in ionic liquids, Angewandte Chemie International Edition, 47 (2008) 8047-8050.

[4] M.J. Bussemaker, D. Zhang, Effect of ultrasound on lignocellulosic biomass as a pretreatment for biorefinery and biofuel applications, Industrial & Engineering Chemistry Research, 52 (2013) 3563-3580.

[5] S. Miller, R. Hester, Concentrated acid conversion of pine softwood to sugars. Part I: Use of a twin-screw reactor for hydrolysis pretreatment, Chemical Engineering Communications, 194 (2007) 85-102.

[6] S.I. Mussatto, G. Dragone, M. Fernandes, A.M. Milagres, I.C. Roberto, The effect of agitation speed, enzyme loading and substrate concentration on enzymatic hydrolysis of cellulose from brewer's spent grain, Cellulose, 15 (2008) 711-721.

[7] S. Kumar, R.B. Gupta, Hydrolysis of microcrystalline cellulose in subcritical and supercritical water in a continuous flow reactor, Industrial & Engineering Chemistry Research, 47 (2008) 9321-9329.

[8] J. Fan, M. De Bruyn, V.L. Budarin, M.J. Gronnow, P.S. Shuttleworth, S. Breeden, D.J. Macquarrie, J.H. Clark, Direct microwave-assisted hydrothermal depolymerization of cellulose, Journal of the American Chemical Society, 135 (2013) 11728-11731.

[9] M.-F. Zhang, Y.-H. Qin, J.-Y. Ma, L. Yang, Z.-K. Wu, T.-L. Wang, W.-G. Wang, C.-W. Wang, Depolymerization of microcrystalline cellulose by the combination of ultrasound and Fenton reagent, Ultrasonics Sonochemistry, 31 (2016) 404-408.

[10] A.T.W.M. Hendriks, G. Zeeman, Pretreatments to enhance the digestibility of lignocellulosic biomass, Bioresource Technology, 100 (2009) 10-18.

[11] K.S. Suslick, Y. Didenko, M.M. Fang, T. Hyeon, K.J. Kolbeck, W.B. McNamara, M.M. Mdleleni, M. Wong, Acoustic cavitation and its chemical consequences, Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences, 357 (1999) 335-353.

[12] A. Grönroos, P. Pirkonen, J. Heikkinen, J. Ihalainen, H. Mursunen, H. Sekki, Ultrasonic depolymerization of aqueous polyvinyl alcohol, Ultrasonics Sonochemistry, 8 (2001) 259-264.

[13] S.C. Szu, G. Zon, R. Schneerson, J.B. Robbins, Ultrasonic irradiation of bacterial polysaccharides. Characterization of the depolymerized products and some applications of the process, Carbohydrate research, 152 (1986) 7-20.

[14] P.B. Subhedar, P.R. Gogate, Intensification of enzymatic hydrolysis of lignocellulose using ultrasound for efficient bioethanol production: A review, Industrial & Engineering Chemistry Research, 52 (2013) 11816-11828.

[15] M. Aliyu, M.J. Hepher, Effects of ultrasound energy on degradation of cellulose material, Ultrasonics Sonochemistry, 7 (2000) 265-268.

[16] A.Z. Sulaiman, A. Ajit, Y. Chisti, Ultrasound mediated enzymatic hydrolysis of cellulose and carboxymethyl cellulose, Biotechnology Progress, 29 (2013) 1448-1457.

[17] C.P. Azubuike, H. Rodríguez, A.O. Okhamafe, R.D. Rogers, Physicochemical properties of maize cob cellulose powders reconstituted from ionic liquid solution, Cellulose, 19 (2012) 425-433.

[18] K. Nakasone, T. Kobayashi, Effect of pre-treatment of sugarcane bagasse on the cellulose solution and application for the cellulose hydrogel films, Polymers for Advanced Technologies, 27 (2016) 973-980.

[19] H. Jiang, K. Tovar-Carrillo, T. Kobayashi, Ultrasound stimulated release of mimosa medicine from cellulose hydrogel matrix, Ultrasonics Sonochemistry, 32 (2016) 398-406.

[20] K. Nakasone, S. Ikematsu, T. Kobayashi, Biocompatibility evaluation of cellulose hydrogel film regenerated from sugar cane bagasse waste and its in vivo behavior in mice, Industrial & Engineering Chemistry Research, 55 (2016) 30-37.

[21] A. Striegel, Theory and applications of DMAc/LiCl in the analysis of polysaccharides, Carbohydrate Polymers, 34 (1997) 267-274.

[22] K.L. Tovar-Carrillo, K. Nakasone, S. Sugita, M. Tagaya, T. Kobayashi, Effects of sodium hypochlorite on Agave tequilana Weber bagasse fibers used to elaborate cyto and biocompatible hydrogel films, Materials Science and Engineering: C, 42 (2014) 808-815.

[23] K.L. Tovar-Carrillo, S.S. Sueyoshi, M. Tagaya, T. Kobayashi, Fibroblast compatibility on scaffold hydrogels prepared from Agave tequilana weber bagasse for tissue regeneration, Industrial & Engineering Chemistry Research, 52 (2013) 11607-11613.

[24] T. Kobayashi, Fabrication of cellulose hydrogels and characterization of their biocompatible films, Studies in Natural Products Chemistry, 45 (2015).

[25] T. Nishino, I. Matsuda, K. Hirao, All-cellulose composite, Macromolecules, 37 (2004) 7683-7687.