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Biodegradable superabsorbent hydrogels derived from cellulose by esterification crosslinking with 1,2,3,4-butanetetracarboxylic dianhydride

Hiroyuki Kono*, Sayaka Fujita

Department of Science and Engineering for Materials, Tomakomai National College of Technology, Nishikioka 443, Tomakomai, Hokkaido 059 1275, Japan

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ABSTRACT

Superabsorbent hydrogels were prepared from native celluloses dissolved in lithium chloride and *N*-methyl-2-pyrrolidinone (LiCl/NMP) by esterification crosslinking with 1,2,3,4-butanetetracarboxylic dianhydride (BTCA). Subsequent conversion of the unreacted carboxyl groups to sodium carboxylates by the addition of aqueous NaOH was performed to enhance the water affinity of the gels. The absorbency of the products was strongly dependent on the amount of BTCA that was esterified to cellulose, and the highest absorbency was observed for the hydrogel composed of approximately 0.25 molecules of BTCA per anhydroglucose unit (AGU) of cellulose. Furthermore, it was confirmed that the absorbency was enhanced as the average degree of polymerization (DP) of the starting cellulose increased. The use of cotton cellulose with a high DP of about 2400 produced a hydrogel with an absorbency of 720 times its dry weight, which exceeded the absorbency of commercial crosslinked sodium polyacrylate superabsorbent hydrogel (SPA). The hydrogels exhibited good biodegradability, with a maximum degradation of 95% within 7 days using cellulase.

1. Introduction

Superabsorbent hydrogels are crosslinked hydrophilic polymers that are capable of absorbing large amounts of water, as much as 100–500 times their own weight. These crosslinked polymers are widely used in many applications such as paper diapers, sanitary napkins, and as soil additives in agriculture (Buchholz, 1998; Buchholz & Peppas, 1994). The most widely used commercially available superabsorbent hydrogel is crosslinked sodium polyacrylate (SPA), which is synthesized by the copolymerization of acrylic acid with various monomers. A major drawback of SPA is that it is non-biodegradable (Buchholz, 1998). Because many of the applications of SPA fall within the category of disposable goods, widespread use of this polymer may lead to environmental pollution. The development of biodegradable superabsorbent polymers as substitutes for SPA is thus necessary.

Because of the increasing focus on environmental problems associated with synthetic polymers, there is an emerging tendency toward the use of naturally occurring polymers instead of synthetic ones. Among these natural polymers, cellulose, which is composed of β-(1→4)-D-glucopyranose repeating units and forms fibrous structures with high crystallinity (Updegraff, 1969), is a prime candidate as a starting material for biodegradable superabsorbent polymers because it is the most abundant biopolymer on earth. Among the biodegradable cellulose derivatives, sodium carboxymethylcellulose (CMC) is a representative water-soluble polymer in which sodium carboxylate groups are substituted onto the AGU of the cellulose chain via an ether linkage. The biodegradation speed of CMC can be easily regulated by controlling the degree of substitution (DS), because the biodegradability of CMC generally decreases as its DS increases (Hamacher & Sahm, 1985; Sieger, Kroon, Batelaan, & van Ginkel, 1995; Wirick, 1968). Therefore, a vast number of reports on methods of preparing biodegradable superabsorbent hydrogels from CMC have emerged (Matsumoto & Zenkoh, 1992; Qiu et al., 2007; Reza & Nicoll, 2010; Wach, Mitomo, Nagasawa, & Yoshii, 2003). However, most of these methods have never been put to practical use because of associated issues regarding cost, scaling up for production and ecological safety of the products, among other concerns.

Recently, biodegradable superabsorbent hydrogels have been prepared from unmodified cellulose by the reaction with succinic anhydride in the presence of 4-dimethylaminopyridine (DMAP), as an esterification catalyst, in a mixture of either LiCl/NMP or tetrabutylammonium fluoride/dimethylsulfoxide (Yoshimura, Matsuo, & Fujioka, 2006). In this reaction, succinic anhydride serves to initiate both the crosslinking of cellulose by the formation of the diester as well as the formation of succinylated cellulose by grafting. Following neutralization with NaOH, the carboxyl group generated by the graft reaction is converted to sodium carboxylate, which enhances the affinity to water, and consequently, the product is

* Corresponding author. Tel.: +81 144 67 8036; fax: +81 144 67 8036.
E-mail address: kono@sem.tomakomai-ct.ac.jp (H. Kono).

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capable of absorbing water. This simplified procedure for converting biodegradable polymers into hydrogels was also applicable to other polysaccharides such as chitin (Yoshimura, Uchikoshi, Yoshiura, & Fujioka, 2005) and starch (Yoshimura, Yoshimura, Seki, & Fujioka, 2006). However, the maximal absorbency of the products obtained by this method was less than or comparable to that of commercially available SPA. Absorbency and absorption speed were considered to be positively correlated to the amount of sodium carboxylate, in the case of SPA. Therefore, increasing the degree of grafting of succinic anhydride onto cellulose is expected to improve the absorbency of the hydrogel, even though increased grafting of cellulose generally leads to diminished biodegradability (Glasser, McCartney, & Samaranayake, 1994; Park, Liang, Mohanty, Misra, & Drzal, 2004).

In this study, the attention is focused on BTCA as a crosslinker in the preparation of superabsorbent polymers from cellulose. BTCA has two acid anhydrides in its structure, each of which reacts readily with certain functional groups such as isocyanate and hydroxyl to undergo crosslinking (Fukukawa and Ueda, 2008). In the reaction of cellulose with BTCA, two free carboxylate groups were formed with simultaneous crosslinking of cellulose chains; hence, the absorbency of the product is expected to be enhanced in comparison with that of the succinylated cellulose hydrogel. This article describes a detailed study of the synthesis of superabsorbent hydrogels from cellulose and BTCA under various conditions. In addition, the water absorption behavior and biodegradability of the products were also investigated to reveal the formation of an excellent, superabsorbent, biodegradable polymer, which is also described herein.

2. Experimental

2.1. Materials

High-purity hardwood pulp with a DP of 800 (Sulfate HJ, from Rayonier), Avicel PH-101 (microcrystalline cellulose powder with DP of 225, Sigma–Aldrich), and purified cotton and purified ramie (DP of 2400 and 1600, respectively, kindly provided by Prof. J. Hayashi, Hokkaido University, Japan) were used as cellulose sources. BTCA and cross-linked SPA superabsorbent polymers were kindly supplied by Shin Nippon Rika Co., Ltd., Japan, and Sundaiya Polymer Co., Ltd., Japan, respectively. CMC with DP of 505 and DS of 0.72 was purchased from Junsei Chemicals Co., Japan. *Trichoderma viride* cellulase ONOZUKA R-10 was purchased from Yakult Pharmaceutical Industry Co., Japan. All other reagents used in this study were analytical grade, purchased from Wako Chemicals Co., Japan.

2.2. Preparation of superabsorbent hydrogels

Superabsorbent hydrogels were prepared from cellulose according to the scheme presented in Fig. 1. The procedure for the preparation of the hydrogel from cellulose pulp with the BTCA feed ratio of 2.5 in Table 1 was as follows. The high-purity hardwood cellulose pulp (1.0 g, 6.2 mmol of AGU) was completely dissolved in a 300 mL Erlenmeyer flask containing LiCl/NMP (5 g of LiCl and 95 g of NMP) under stirring with teflon impeller at 500 rpm of the rotation at 25 °C for 2 days. 1.14 g of DMAP (9.3 mmol) was added to the mixture. After complete dissolution of DMAP, 3.07 g of BTCA (15.5 mmol), which corresponds to 2.5 times the molar feed ratio to the AGU, was added to the mixture. Esterification was allowed to proceed with stirring with the teflon impeller (500 rpm) at room temperature for 24 h, after which the reaction mixture was poured into a mixture of methanol (800 g) and water (200 g) with stirring to precipitate the product, and then the product was neutralized to pH 7.0 with 10% (w/v) aqueous NaOH by use of pH electrode. The precipitate was filtered by use of a glass filter, and was then purified twice by re-precipitation with methanol and water. The purified product was dried under reduced pressure, finally cut with a mixer, and screened through a 16 mesh sieve to obtain a white granular product. Hydrogels from the cellulose sources listed in Table 1 were prepared according to a procedure similar to that described above by changing the molar feed ratio of BTCA or by changing cellulose source. The amount of cellulose was fixed to 1.0 g for the preparation of the all hydrogels.

2.3. Structural analysis

Structure analysis of the hydrogels was carried out with a Fourier transform infrared (FTIR) spectrophotometer (FT/IR-8300, Shimadzu) and solid-state NMR (Bruker Avance II 300 with 4 mm dual-tuned MAS probe, 75 MHz for ^{13}C nucleus and 300 MHz for ^{1}H nucleus). FTIR spectra were obtained after grinding the sample into a powder and mixing with KBr powder. The powder mixture was compressed into a transparent disk and scanned from 4000 to 400 cm^{-1} using the average of 32 scans, with a resolution with 4 cm^{-1}. ^{13}C NMR spectra were recorded with dipolar-decoupling at a MAS frequency of 4000 Hz. ^{13}C-excitation pulse with the flip angle of 30°, date acquisition time, and repetition time were set to 1.5 μs, 20 ms, and 30 s, respectively. During the data acquisition period, TPPM proton decoupling (Bennett, Rienstra, Auger, Lakshmi, & Griffin, 1995) was applied with a ^{1}H field strength of 72 kHz. Chemical shifts were calibrated based on the carbonyl carbon resonance of glycine at 176.03 ppm, used as an external reference. The obtained NMR data were transferred to a Windows PC for line fitting. Lineshape analysis of the NMR spectra was performed using the Nuts software (Arcon NMR Co.), and nonlinear least-squares methods were engaged for line fitting with the previously described Lorentzian function (Kono, Erata, & Takai, 2003; Kono, Numata, Erata, & Takai, 2004; Kono, Yunoki, Fujiwara, Erata, & Takai, 2002). Ester content in the product was determined by a titration method (Tanghe, Genung, & Mench, 1963). The procedure was as follows: 100–250 mg of product was weighed accurately and placed in a 200 mL flask and the mixture was stirred for 10 h at room temperature. 30 mL of 0.1 mol/L NaOH was then added, and the mixture was heated at 50 °C for 3 h for hydrolysis of ester linkages between BTCA and cellulose. The mixture was cooled to room temperature, and the NaOH consumed for ester hydrolysis was determined by the back-titration with aqueous 0.1 mol/L HCl using phenolphthalein as an indicator for the titration. Total ester linkages in 1 g of each product (E), which was in mmol/g were determined by this procedure.

2.4. Determination of the water absorbency

The water absorbency of the products was determined according to the tea-bag method of the Japan Industrial Standard, JIS K7223 (Yoshimura et al., 2006a). A nylon teabag with dimensions of 100 mm × 200 mm was prepared from a nylon sheet with a pore size of 255 mesh, using a heat sealer. 200 mg of the superabsorbent hydrogel sample was placed into the teabag. The teabag was then immersed in water at 25 °C. After a prescribed time, the teabag was removed from the water, and excess water was drained for 10 min. The weight of the teabag including the swollen hydrogels (W_h) was measured, and the water absorbency was calculated using the following equation:

$$\text{Water absorbency} = \frac{W_h - W_b - W_p}{W_p}$$

where W_b is the weight of the blank teabag after water treatment, and W_p is the weight of the dried superabsorbent hydrogel. Absorbency measurements were taken for five samples of each

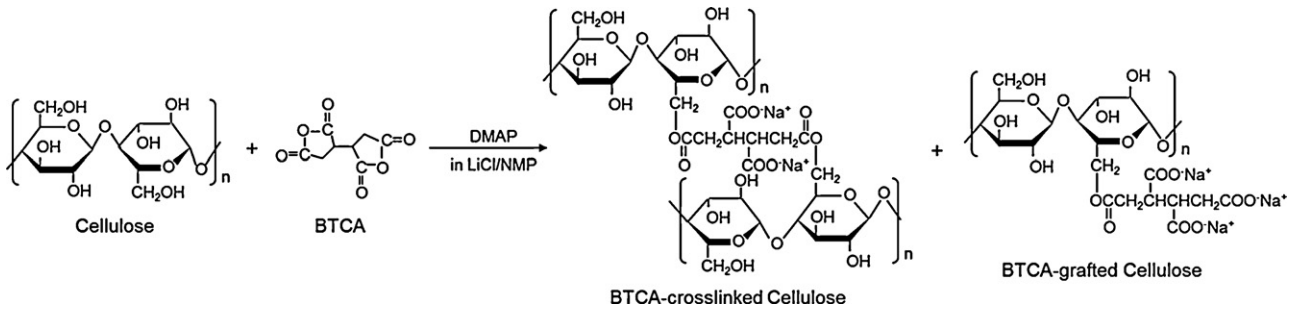

Fig. 1. Reaction of 1,2,3,4-butanetetracarboxylic dianhydride (BTCA) and cellulose in LiCl/NMP. Esterification crosslinking and grafting occur simultaneously.

product, and the average of the five values was plotted against the absorbency time.

2.5. Biodegradability test using cellulase

Before performing the biodegradability test, *T. viride* cellulase ONOZUKA R-10 was purified according to the following method at 4 °C. The cellulase powder (10 g) was dissolved in 250 mL of 50 mM acetate buffer, pH 5.0. 180 g of ground-powdered $(NH_4)_2SO_4$ was added to the solution to give 90% saturation. The precipitate formed was collected by centrifugation, desalted by ultrafiltration using a Q0100 filter (Advantec Co. Ltd., Japan), and then lyophilized (Kono, Walchili, Fujiwara, Erata, & Takai, 1999). The obtained cellulase powder was used for the biodegradation of the hydrogels. The protein mass of cellulase was determined by use of the Bio-Rad protein assay kit (Bio-Rad Co.) with bovine serum albumin as the standard (Zor & Selinger, 1996). Cellulase activity was measured using CMC as a substrate. A total of 10 mL of the reaction mixture containing 9 mL of 1% (w/v) CMC in 50 mM sodium acetate buffer, pH 5.0, and 10 mg of the purified cellulase dissolved in 1 mL of the same buffer solution was incubated at 40 °C. After 30 min, the amount of reducing sugars in the mixture was measured by the method of Miller, Blum, Glennon, and Burton (1960). One unit of cellulase activity was defined as the amount of enzyme liberating 1 μmol of reducing sugar per min.

The hydrogel biodegradability test was carried out according to the following procedure. 100 mg of hydrogel sample was sufficiently soaked in the 19 mL of 50 mM acetate buffer for 2 days. Cellulase dissolved in 1 mL of the same buffer solution was added to the suspension to give a cellulase concentration of 0.20 U/mL. The mixture was incubated at 40 °C. After a prescribed period, an aliquot (0.5 mL) was withdrawn from the mixture, and the amount of reducing sugars in the aliquot was determined by the method described above. The biodegradability of the superabsorbent hydrogels was determined using the following equation:

$$\text{Biodegradability}\ \ (\%) = \frac{(M_s - M_b) \times 100}{M_s}$$

where M_s is the molar mass of AGU in the superabsorbent hydrogel before the cellulase digestion, and M_b is the molar mass of the reducing sugars liberated by the cellulase.

3. Results and discussion

3.1. Structure of cellulose hydrogel

As shown in Fig. 1, preparation of superabsorbent hydrogels from cellulose was performed in the homogeneous reaction system containing DMAP as an esterification catalyst. The reaction mixture became increasingly viscous soon after adding BTCA as a crosslinker, and the morphology of mixture gradually changed from solution to gel about 30–60 min after starting the reaction. Esterification was allowed to proceed with stirring at room temperature for 24 h, and then the reaction product was poured in to the mixture of methanol and water. Subsequent conversion of the unreacted carboxyl groups to sodium carboxylates in the product by the addition of aqueous NaOH was performed to enhance the water affinity. Finally, the product was purified twice by re-precipitation with methanol and water, dried under reduced pressure, cut with a mixer, and then screened through a 16 mesh sieve to obtain a white granular product.

Following the crosslinking esterification reaction of purified cellulose pulp with BTCA, the obtained product showed several new absorption bands in the FTIR spectrum, in addition to the original peaks from pure cellulose itself, as shown in Fig. 2. The new absorption band at 1716 cm^{-1} was assigned to the C=O stretching vibration of the ester group, and the absorption appearing at

Table 1
Reaction conditions and results of the esterification crosslinking of cellulose with BTCA in LiCl/NMP.

Cellulose source	BTCA feed ratio	E^a (mmol/g)	$n_{COONa}/n_{ester}{}^b$	$C_{CR}{}^c$ (%)	$C_{GR}{}^d$ (%)	$n_{BTCA}{}^e$	Absorbency^f (g/g)
Pulp	0.5	0.715	1.16	85	15	0.069	25
	1.0	1.10	1.18	83	17	0.11	182
	2.5	2.05	1.25	78	22	0.26	308
	5.0	2.82	1.27	76	24	0.43	129
	7.5	2.89	1.32	72	28	0.47	107
Avicel	2.5	1.93	1.18	83	17	0.23	46
Ramie	2.5	1.90	1.26	77	23	0.24	440
Cotton	2.5	2.02	1.23	79	21	0.25	720

[a] Total ester linkages in 1 g of each product, obtained from the result of the titration method.
[b] Molar ratio of sodium carboxylate to ester, which was determined by the lineshape analysis of the ^{13}C NMR spectrum of each product.
[c] Molar percentages of the crosslinked BTCA molecules in total esterified BTCA in each product.
[d] Molar percentages of the grafted BTCA molecules in total esterified BTCA in each product.
[e] Number of BTCA molecules per AGU.
[f] Absorbency of each product after 6 days.

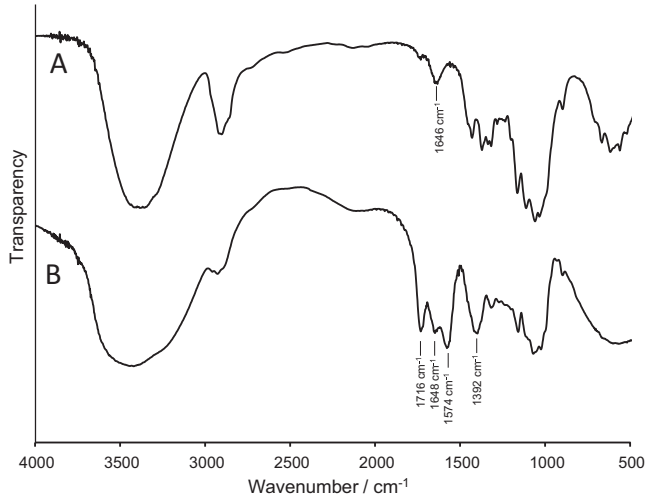

Fig. 2. FTIR spectra of pure cellulose pulp (A) and the hydrogel produced from BTCA crosslinking with cellulose pulp, prepared at a BTCA molar feed ratio of 2.5 (B).

1578 cm^{-1} was assigned to the C=O asymmetric stretching vibration of the sodium carboxylate group (Lia et al., 2009). The low intensity, broad band at 1648 cm^{-1} arises from the bending vibration of residual water molecules in the sample (Fukuzumi, Saito, Okita, & Isogai, 2010). Formation of the sodium carboxylate group in the products was also confirmed by the typical absorption at 1392 cm^{-1}, arising from the carbonyl symmetric stretching vibration (Lia et al., 2009). The IR analysis indicates that the hydroxyl group of cellulose may have esterified with BTCA, resulting in the formation of carboxylate anions as well as crosslinking between the cellulose chains.

Solid-state ^{13}C NMR spectra of the product and pure cellulose are shown in Fig. 3. Compared with the spectrum of pure cellulose, four new resonance lines were observed in the spectrum of the product. The lines at 46 ppm and 40 ppm proved the existence of CH_2 and CH groups of BTCA in the product, respectively, and the peak at 54 ppm was attributed to the unsubstituted C6 carbon of the AGU of cellulose (Kono, Erata, & Takai, 2002; Kono et al., 2004). The remaining resonance line observed in the region of 186–168 ppm was assigned to carbonyl carbons. Lineshape analysis of the spectra resolved the carbonyl carbon resonance into two Lorentzian lines with peaks at 181 ppm and 176 ppm, which could be assigned to carbonyl carbons of the ester group and those of sodium carboxylate, respectively, because the carboxylate carbons are more shielded than the ester carbons (Moghimi et al., 2002). The molar ratio of sodium carboxylate groups to the ester linkages formed in the product (n_{COONa}/n_{ester}) was represented as an area ratio of the two lines at 181 ppm and 176 ppm. The values of n_{COONa}/n_{ester} ratio are summarized in Table 1.

For the elucidation of the structural features of each hydrogel product, the number of BTCA molecules per AGU of cellulose (n_{BTCA}) and the molar percentages of crosslinked BTCA and grafted BTCA (C_{CR} and C_{GR}, respectively) were determined by the results obtained from solid ^{13}C NMR and the titration method for the estimation of total amount of ester contents, which was is as follows. In 1 g of the product, it was supposed that there was X mmol of crosslinked BTCA and Y mmol of grafted BTCA. As shown in Fig. 1, one diester and two sodium carboxylate groups are formed during crosslinking of BTCA and cellulose, whereas the graft reaction resulted in the formation of one ester and three sodium carboxylate groups. Therefore, the following simultaneous equations could be expressed as:

$$2X + Y = E \quad (1)$$

$$2X + 3Y = \frac{E \times n_{COONa}}{n_{ester}} \quad (2)$$

where the abbreviation E, which was in mmol/g product, was the total ester linkages in 1 g of the product. In addition, the E value is given by the contribution of both crosslinked BTCA, $2X$, and grafted BTCA, Y, which could be obtained from the result of the titration method. The total sodium carboxylate groups in 1 g of the product was given by the contribution of the crosslinked BTCA, $2X$, and grafted BTCA, $3Y$, which could be determined by multiplying the E by the n_{COONa}/n_{ester} in the solid NMR. By solving simultaneous Eqs. (1) and (2) simultaneously, X and Y were given by

$$X = \frac{E \times (3 - n_{COONa}/n_{ester})}{4}$$

$$Y = \frac{E \times (n_{COONa}/n_{ester} - 1)}{2}.$$

As shown in Fig. 1, the average molecular weight of the product is increased by 242 g/mol when one BTCA molecule crosslinks to hydroxyl group of cellulose per AGU. Similarly, grafting of one BTCA molecule per AGU increases the average molecular weight of the product by 282 g/mol. Therefore, because the number of AGU in 1 g of the product was given by $(1\,g - 242X/1000 - 282Y/1000)/162$, the n_{BTCA} value in the hydrogel sample could be determined by the following equation:

$$n_{BTCA} = \frac{X + Y}{(1\,g - 242X/1000 - 282Y/1000)/162}.$$

In addition, C_{CR} and C_{GR} were given by

$$C_{CR}\ (\%) = \frac{X \times 100}{X + Y}$$

$$C_{GR}\ (\%) = \frac{Y \times 100}{X + Y}.$$

Table 1 summarizes the structural parameters of the hydrogels from each cellulose starting material. Based on the data presented in this table, the n_{BTCA} values increased drastically as the feed ratio of BTCA increased, whereas the C_{CR}/C_{GR} values increased only marginally. This indicated that the molar ratio of grafted polymer to crosslinked polymer was nearly independent of the BTCA feed ratio. In addition, the C_{CR} and n_{BTCA} values of the samples prepared from cotton, pulp, ramie, and Avicel celluloses at the same BTCA feed ratio of 2.5 showed little variation, with values of approximately 77–83% and 0.23–0.26, respectively. The data indicate that the species of cellulose used as the starting material had little influence on the C_{CR}/C_{GR} and n_{BTCA}.

3.2. Water absorbency

White granular products prepared from the crosslinking esterification reaction of cellulose and BTCA absorbed water readily upon soaking, with concomitant alteration of their morphologies to form transparent hydrogels. Fig. 4 shows the time dependence of water absorbency of the hydrogel samples synthesized from cellulose pulp in which the BTCA feed to AGU of cellulose ratio was varied. The absorbency of SPA is also presented as a dotted line in this figure for comparison. The maximum absorbency of each sample was reached within 24 h, and very little change in the absorbency was observed beyond 24 h. The absorbency of each sample after 6 days is shown in Table 1. Comparison of the absorbencies of the pulp hydrogels shows that the absorbency of the pulp hydrogels increased with increasing BTCA feed ratio up to 2.5, and that the highest water absorbency of 308 g/g was obtained at a BTCA feed ratio of 2.5, which was still much lower than that of SPA (ca.

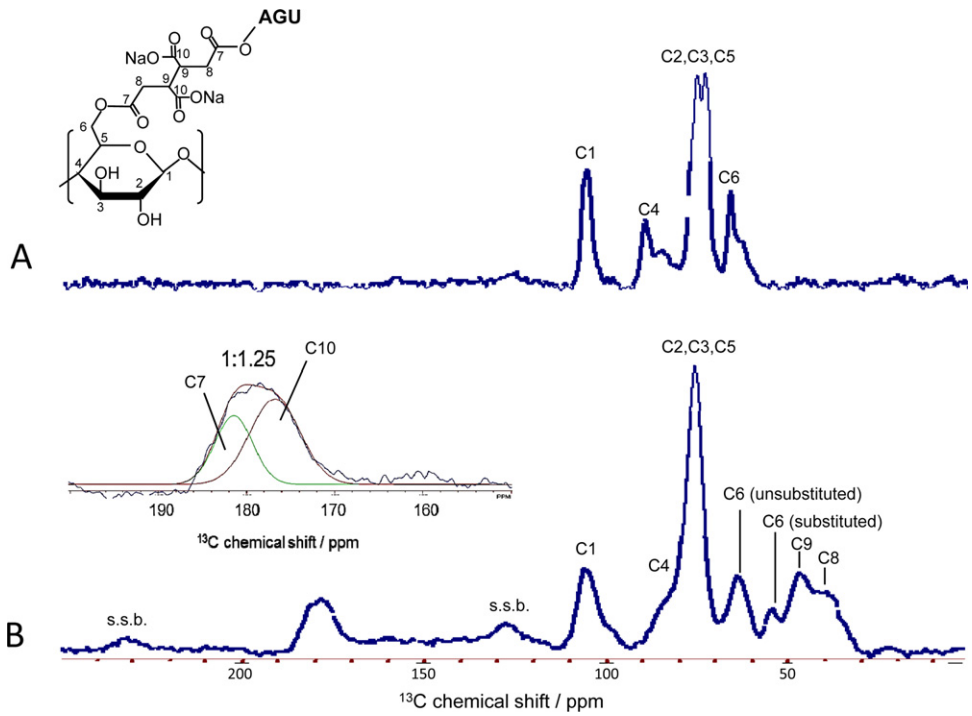

Fig. 3. Solid-state ^{13}C NMR spectra of pure cellulose pulp (A) and the hydrogel produced from BTCA crosslinking with cellulose pulp, prepared at the BTCA molar feed ratio of 2.5 (B). Expanded spectra of the carboxyl carbon region of the hydrogel product and individual fit lines determined by the lineshape analysis are shown in this figure. The abbreviation "s.s.b." indicates spinning sideband of the carbonyl carbon resonances.

470 g/g). The optimum n_{BTCA} was revealed to be ca. 0.26. In addition, the absorbency of the samples prepared at the feed ratio of 5 and 7.5 was drastically decreased, suggesting that swelling of the hydrogel samples was suppressed due to high crosslink density.

Next, effect of the starting cellulose sources on the absorbency of the hydrogels were investigated by use of Avicel, ramie, and cotton celluloses. Hydrogel samples was prepared from these cellulose sources at the BTCA feed ratio of 0.5–7.5, and then absorbency of the resultant samples were determined. As a result, the highest absorbency was observed in the samples prepared at the feed ratio of 2.5 in any of cellulose sources (data not shown). The time dependence of water absorbency of the hydrogels synthesized from Avicel, ramie, and cotton at the BTCA feed ratio of 2.5 is shown in Fig. 5. The samples obtained from Avicel and ramie reached their respective saturated water absorbencies of 40 g/g^{-1} and 450 g/g^{-1} within 24 h, which was similar to the absorbency behavior of the hydrogel obtained from pulp. On the other hand, the cotton-based hydrogel, which had a significantly higher absorbency than the other products, required about 3 days to reach its maximum absorbency of 720 g/g^{-1}. The relationship between the absorbency after 6 days and the average DP of the starting cellulose material is summarized in Table 1. These data suggested that the absorbency of the products was increased with increasing DP of the starting cellulose. In addition to this, as described above, the optimum feed ratio was observed to be 2.5 in any cellulose sources. Because the structural data corresponding to C_{CR}, C_{GR}, and n_{BTCA} were not significantly different for the products prepared form the various materials at a BTCA feed ratio of 2.5, it was postulated that the difference in the absorbency of the products could be, therefore, mainly controlled by the average DP of the starting cellulose. As a consequence, the average molecular weight of the products

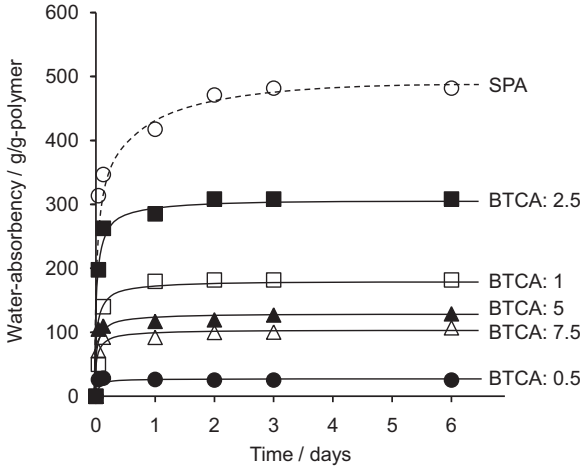

Fig. 4. Absorbency of hydrogel products prepared from cellulose pulp. Dotted line shows the absorbency of SPA for comparison.

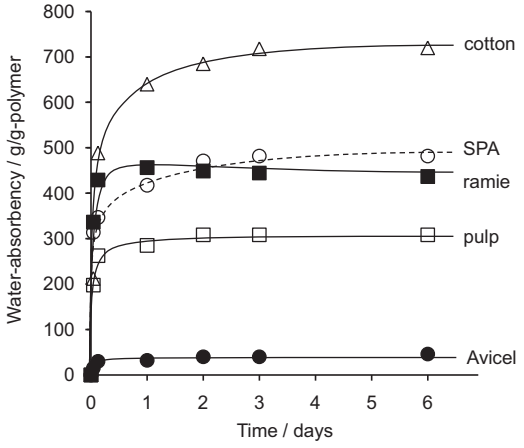

Fig. 5. Absorbency of hydrogel products prepared from Avicel, pulp, ramie, and cotton. Dotted line shows the absorbency of SPA for comparison.

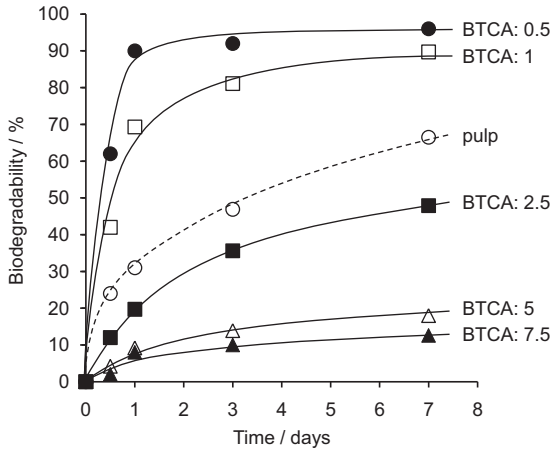

Fig. 6. Enzymatic degradation of hydrogel products prepared from pulp. The dotted line indicates the degradation of unmodified cellulose pulp for comparison.

was expected increase if cellulose with high DP was used for the crosslinking esterification. In the case of high molecular weight products, it was deemed that the internal volume for retaining water molecules per unit mass was higher than that of products with a lower molecular weight, which resulted in the increase of the absorbency. On the other hand, the molecular surface area per unit mass was expected to decrease with an increase in the molecular weight of the hydrogel. It was, therefore, found that the product prepared from cotton required a lot of time to reach its maximum absorbency although this product exhibited the highest absorbency of all the samples tested in this study.

3.3. Biodegradability

Enzymatic degradation of the samples prepared from pulp was performed at 40 °C using cellulase. The time dependence of degradation is shown in Fig. 6. The dotted line in this figure represents the degradation of unmodified cellulose pulp. After 7 days of incubation with cellulase, 64% of the cellulose pulp degraded under the conditions employed. The hydrogel products were also biodegradable, and the degradation speed decreased with increasing BTCA feed ratio due to a higher n_{BTCA} of the structure. In particular, the products obtained at the BTCA feed ratios of 0.5 and 1 exhibited 95% and 87% degradability, respectively, which were much higher than the degradability of cellulose pulp. Cellulose has a highly crystalline hydrogen-bonded structure, and only the fiber surfaces were enzymatically degraded (Eriksson et al., 2005; Hoshino, Shiroishi, Amano, Nomura, & Kanda, 1997). On the other hand, the interchain distances were increased in the hydrogel products when the product was soaked in water, and cellulase could easily make contact with the interior cellulose chain as well as the surface chains, which resulted in enhanced biodegradability. In the case of the products prepared at the BTCA feed ratios of 5 and 7.5, the biodegradability declined to 15% and 11%, respectively, because of the high n_{BTCA}.

4. Conclusion

Novel biodegradable superabsorbent hydrogels were prepared from cellulose via simple esterification crosslinking of BTCA under mild conditions. Simultaneous crosslinking and grafting of BTCA occurred by the formation of diester and monoester linkages. The BTCA feed to cellulose ratio strongly influenced n_{BTCA}, and a feed ratio of 2.5 produced optimal absorbency. The absorbency of the products also depended on the DP of the starting cellulose, and celluloses with high DP, such as cotton, were preferable as the starting material. At a BTCA feed ratio of 2.5, the maximum absorbency of the cotton-based hydrogel was ca. 720 g/g-polymer, which exceeded the absorbency of SPA. In addition, the hydrogel products exhibited good biodegradability. The products are therefore expected to be applicable for biomedical and agricultural use and should be viable alternatives to SPA.

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