

# Novel Biodegradable Superabsorbent Hydrogels Derived from Cotton Cellulose and Succinic Anhydride: Synthesis and Characterization

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Received 31 January 2005; accepted 25 April 2005

DOI 10.1002/app.22794

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The synthesis of novel superabsorbent hydrogels was investigated with the reaction of cotton cellulose and succinic anhydride (SA) in the presence of 4-dimethylaminopyridine as an esterification catalyst in a mixture of lithium chloride (LiCl) and *N*-methyl-2-pyrrolidinone (NMP) or in a mixture of tetrabutylammonium fluoride (TBAF) and dimethyl sulfoxide (DMSO), followed by NaOH neutralization. Interestingly, a hydrogel was obtained without any crosslinking agent, and this indicated the partial formation of a diester between the cellulosic hydroxyl group and SA. The products obtained in LiCl/NMP exhibited superior absorbency to those obtained in TBAF/DMSO. The

former absorbed an amount of water about 400 times its dry weight, and this was comparable to a conventional sodium polyacrylate superabsorbent hydrogel. Furthermore, in an aqueous NaCl solution, the absorbency of the product hydrogels was higher than that of the sodium polyacrylate superabsorbent hydrogel. The formed hydrogels biologically degraded almost completely after 25 days, and this showed their excellent biodegradability. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3251–3256, 2006

**Key words:** biodegradable; crosslinking; hydrogels; swelling

## INTRODUCTION

Superabsorbent hydrogels are lightly crosslinked hydrophilic polymers capable of absorbing large amounts of water or saline solutions, as much as 10–1000 times their own weight. Because of these unique characteristics, they have been widely used in various applications such as disposal diapers, sanitary napkins, additives for soil in agriculture, and medicine for drug delivery systems.<sup>1,2</sup> Most commercially available superabsorbent hydrogels are crosslinked sodium polyacrylates with extremely high molecular weights, and they have no biodegradability. Thus, their use may result in environmental pollution because their major applications are in disposable goods. Therefore, biodegradable superabsorbent hydrogels as a substitute for conventional synthetic polymers have been actively studied in recent years.<sup>2</sup>

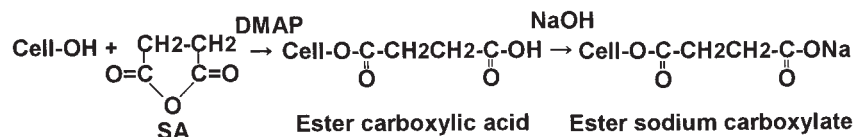
Biodegradable superabsorbent hydrogels include crosslinked poly(amino acid)s such as poly( $\gamma$ -glutamic acid)<sup>3–5</sup> and poly(aspartic acid)<sup>6,7</sup> and crosslinked sodium salt of carboxymethylcellulose (CMC). The crosslinking of CMC has been examined with various methods, such as crosslinking agents<sup>8</sup> and ionizing

irradiation.<sup>9,10</sup> These crosslinking methods include some issues because residual unreacted crosslinking agent may influence the safety of the product, and scaling up ionizing irradiation is rather difficult.

As concerns about environmental problems are increasing today, various naturally occurring polymers should be used instead of synthetic ones. Among them, cellulose exists most abundantly on the earth and is used for various applications. Cotton is one of the most accessible types of cellulose in our daily life and is produced in large amounts every year.<sup>11</sup> One of the typical features of cotton cellulose is its extremely high molecular weight in the cellulosic family, over 1,000,000.<sup>12</sup> Thus, cotton cellulose is a suitable starting material for superabsorbent hydrogels because the extremely high molecular weight of the polymer is one of the indispensable factors for attaining high water absorbency.

The most representative cellulosic derivative containing sodium carboxylate is CMC, which contains it via an ether linkage. The biodegradation speed of CMC has been dependent on its degree of substitution (DS).<sup>13</sup> That is, the extent of biodegradation of CMC (DS = 0.6–1.12) decreases as DS increases. The presence of the carboxymethyl group makes the cellulose molecule resistant to enzymatic attack. This result shows that the derivatization of cellulose should be performed carefully if we intend to obtain a biodegradable product.

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Scheme 1 Synthetic route from cotton cellulose and SA.

In this study, the introduction of sodium carboxylate groups into cotton cellulose was investigated by esterification because esterification proceeds under milder conditions than etherification and ester linkages are more susceptible to hydrolysis and biodegradation than ether linkages. These features are suitable for the design of biodegradable superabsorbent hydrogels. Although we were studying the synthesis of superabsorbent hydrogels by the esterification of cotton cellulose with succinic anhydride (SA), we found that a hydrogel could be obtained without any crosslinker when 4-dimethylaminopyridine (DMAP) was used as an esterification catalyst. This article describes a detailed study of the synthesis of superabsorbent hydrogels under various conditions. New biodegradable superabsorbent hydrogels were successfully obtained from cotton cellulose and SA, and their properties were clarified.

## EXPERIMENTAL

### Materials

Absorbent cotton (Daisan Co., Ltd., Kochi, Japan) as a starting material was commercially available and was used without purification. Cellulose powder (20  $\mu\text{m}$ ; Aldrich Chemical Co., Inc., Milwaukee, WI) as a comparison starting material for hydrogels and as a standard material for biodegradability testing was purchased and used as received. SA and other chemicals were employed as received. A conventional sodium polyacrylate superabsorbent hydrogel (Aqua-Keep SA 60) was kindly supplied by Sumitomo Seika Chemicals Co., Ltd. (Osaka, Japan) CMC (Daicel 2450; DS: 1.15) for the biodegradability testing was a gift from Daicel Chemical Industries, Ltd., Himeji, Japan.

### Preparation of superabsorbent hydrogels

Superabsorbent hydrogels were prepared according to Scheme 1. As an example, the procedure for synthesizing a superabsorbent hydrogel in a mixture of lithium chloride (LiCl) and *N*-methyl-2-pyrrolidinone (NMP) at room temperature is described in detail. Cotton cellulose (0.5 g, 3.1 mmol for the anhydroglucose unit) was pretreated in order with water, methanol, and NMP and was dissolved in a 200-mL Erlenmeyer flask in the LiCl/NMP solvent (8 g of LiCl and 92 g of NMP) with stirring at room temperature for 3

days. DMAP (1.19 g, 9.7 mmol; molar ratio for cellulosic hydroxyl groups = 1.05) was added with stirring. After the dissolution of DMAP, SA (18.6 g, 185 mmol; molar ratio for cellulosic hydroxyl groups = 20) was added to the solution, and the reaction was carried out with stirring at room temperature for 24 h to obtain ester carboxylic acid. The reaction mixture was poured into a large amount of methanol (1 L) with stirring and then neutralized with an aqueous NaOH solution (concentration = 10%; 74.2 g, 185 mmol). After the precipitate was filtered and dried under reduced pressure, the solid was finely cut with a mixer and screened through a 16-mesh sieve to give an off-white, granular product.

The preparation in a mixture of tetrabutylammonium fluoride (TBAF) and dimethyl sulfoxide (DMSO) was carried out in a similar way. The differences were the composition of the solvent (15 g of TBAF and 85 g of DMSO) and skipping the pretreatment procedure.

### Structural analysis

IR spectra of cotton cellulose and the reaction products were recorded on a Jasco FT/IR-410 spectrophotometer (KBr disk; Tokyo, Japan).

The DS of the reaction product was determined by a titration method. All ester linkages were saponified by NaOH, and the amount of remaining excess NaOH was determined by titration with HCl. The procedure in detail was as follows. The sample (0.2 g) was weighed accurately and placed in a 500-mL plastic flask. Distilled water (50 mL) was added to the flask, and the mixture was stirred overnight at room temperature. NaOH (30 mL, 0.1N) was added, and the mixture was heated at 50°C for 3 h. After it was cooled to room temperature, titration was conducted with 0.1N hydrochloric acid with phenolphthalein as an indicator. A molar quantity of the ester linkages was determined, and the concentration of ester linkages per repeated unhydroglucose unit was thus calculated as DS.

### Water absorbency

The water absorbency of the product was measured by the tea-bag method [Japanese Industrial Standard (JIS) K 7223]. A nylon tea bag (200 mm in size and 100 mm in length and width) was prepared by heat seal-

ing, and the superabsorbent hydrogel sample (0.2 g) was charged into it. The tea bag was immersed in water at 25°C. After a 1-h treatment in water, the tea bag was picked up from the water, and excess water was drained for 5 min. The weight of the tea bag and hydrogel ( $W_t$ ) was then measured, and the absorbency was calculated as follows:

$$\text{Absorbency} = (W_t - W_b - W_p) / W_p$$

where  $W_b$  is the weight of the blank tea bag after the water treatment and  $W_p$  is the weight of the dry superabsorbent hydrogel sample. Again, the tea bag was dipped for 2 h and picked up for 5 min to evaluate the absorbency (total treatment time = 3 h). The absorbency after 24 and 48 h was evaluated in the same way.

Furthermore, the absorbency in an aqueous NaCl solution (0.9 and 3.5% concentrations) was investigated similarly. These concentrations corresponded to those of physiological saline and seawater, respectively.

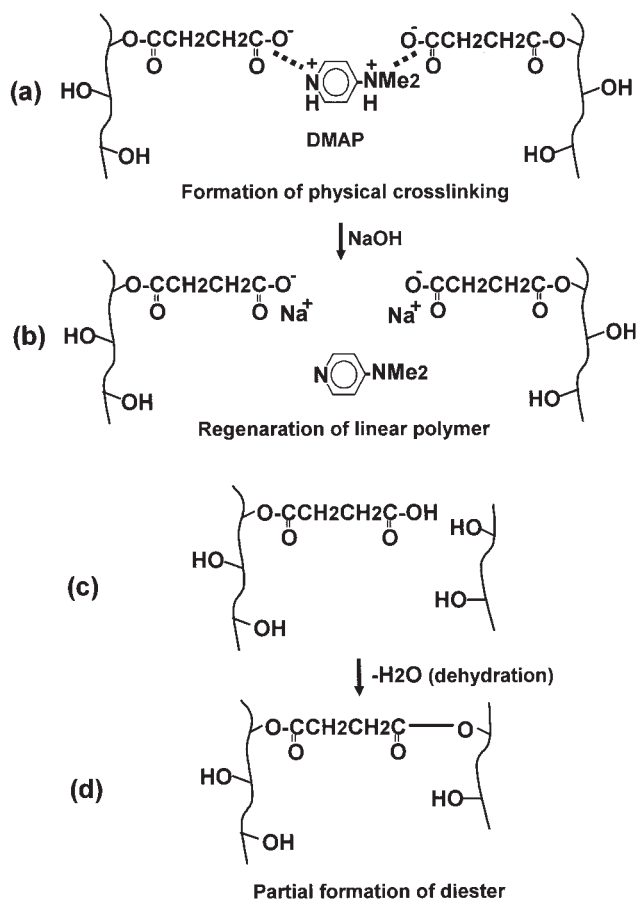
### Biodegradation

The biodegradability of the superabsorbent hydrogel was measured at 25°C for 25 days with reference to JIS K 6950, according to which the sample was placed in activated sludge. The activated sludge was kindly supplied by the Tataragawa sewage-treatment plant (Fukuoka, Japan) and used as received. The biodegradability was evaluated by the monitoring of the biological oxygen demand (BOD) with an OM3001 coulometer from Ohkura Electric Co., Ltd. (Sakado, Japan), which detected the consumption of oxygen during the evaluation.

## RESULTS AND DISCUSSION

### Preparation and structure of the superabsorbent hydrogels

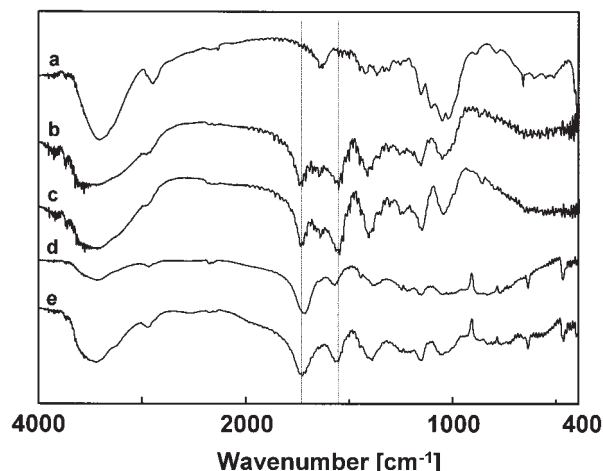
In this study, the introduction of sodium carboxylate into cellulosic hydroxyl groups was investigated by esterification because, in general, esterification proceeds under mild conditions, which can suppress the reduction of the polymer molecular weight during its preparation. During esterification, a reaction between hydroxyl groups and acid anhydride is most commonly achieved and proceeds preferably under nonaqueous conditions because the acid anhydride is subjected to hydrolysis. A mixture of LiCl and *N,N*-dimethylacetamide (DMAc) is a well-known nonaqueous solvent of cellulose.<sup>14</sup> We adopted NMP instead of DMAc because NMP has almost the same chemical properties as DMAc and is somewhat safer than DMAc. Recently, another nonaqueous solvent for



Scheme 2 Presumed reaction scheme of crosslinking.

cellulose, DMSO in combination with TBAF, was reported.<sup>15</sup> The feature of this solvent system is that it can dissolve cellulose without any pretreatment. Thus, we examined the preparation of cotton-based superabsorbent hydrogels in LiCl/NMP and in TBAF/DMSO and compared the properties of the products.

In both LiCl/NMP and TBAF/DMSO, cotton cellulose gradually dissolved at room temperature, and this indicated its high molecular weight and high crystallinity. DMAP was employed as an esterification catalyst because it is effective especially for the esterification of secondary or tertiary hydroxyl groups.<sup>16</sup> During esterification, gelation was observed, and this indicated the formation of a crosslinking structure. In this case, physical crosslinking due to coulombic interactions between carboxylic acid formed during esterification and DMAP is supposed to form because DMAP is a divalent tertiary amine compound [Scheme 2(a)]. This physical crosslinking structure should disappear after neutralization by NaOH, and the linear polymer should be regenerated [Scheme 2(b)], but a hydrogel was obtained as the final reaction product. This probably occurred because another crosslinking structure formed; that is, the partial formation of a diester between ester carboxylic acid and



**Figure 1** IR spectra of cotton cellulose and the reaction products: (a) cotton cellulose, (b) a hydrogel prepared in LiCl/NMP at room temperature, (c) a hydrogel prepared in LiCl/NMP at 60°C, (d) a hydrogel prepared in TBAF/DMSO at room temperature, and (e) a hydrogel prepared in TBAF/DMSO at 60°C. The SA feed ratio to cellulosic hydroxyl groups was 20.

cellulosic hydroxyl groups was presumed to occur, as shown in Scheme 2(d). Excess SA in the reaction system might behave as a dehydrating agent under non-aqueous conditions.

Figure 1 presents the IR spectra of cotton cellulose and the reaction products (feed molar ratio of SA = 20, reaction temperature = room temperature). Absorption bands due to the C=O stretching of ester and antisymmetrical stretching and symmetrical stretching of carboxylic anions can be observed at 1760, 1550, and 1400  $\text{cm}^{-1}$ , respectively, for the reaction products. These absorptions were absent for cotton cellulose. This indicates the formation of an ester and salt of carboxylic acid by the reaction between hydroxyl groups in cotton cellulose and carboxylic anhydride groups of SA, followed by NaOH neutralization.

To determine the DS of the reaction product, titration by hydrochloric acid after alkali saponification of the reaction product was carried out. The results are shown in Table I. As the feed amount of SA increased, the DS value increased. When the SA feed ratio was 20, DS was around 3, indicating that almost all hydroxyl groups had been replaced with ester carboxylic acid groups. This value was much higher than that of commercially available CMCs (0.5–1.6). When the reaction temperature was 60°C, DS considerably increased also when the SA feed ratio was less than 20. In general, products prepared in LiCl/NMP possessed slightly higher DS values than those prepared in TBAF/DMSO.

### Water absorbency and biodegradability

Figure 2 shows the time dependence of the absorbency in water of superabsorbent hydrogels prepared in

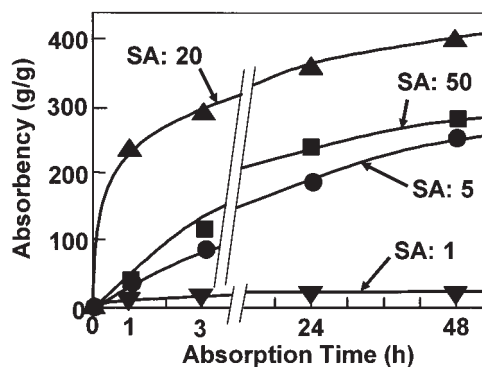
**TABLE I**  
DS Values of Products as Determined by Titration

Solvent	Reaction temperature	SA feed ratio	DS
LiCl/NMP	Room temperature	1	<0.1
		5	0.75
		20	2.6
	60°C	1	0.74
		5	2.4
		20	3.0
TBAF/DMSO	Room temperature	1	<0.1
		5	0.3
		20	2.5
	60°C	1	0.45
		5	1.4
		20	2.4

LiCl/NMP at room temperature through changes in the SA feed amount. When the feed ratio of SA was 1, the product hardly absorbed water. As the SA feed ratio increased, the absorbency became higher, except for an SA feed ratio of 50, and when the SA feed ratio was 20, the absorbency was the highest among those examined, reaching about 250 g/g after 1 h of treatment and about 400 g/g after 48 h of treatment. These values are comparable to those of the conventional sodium polyacrylate superabsorbent hydrogel (ca. 300 g/g; shown later in Fig. 6).

As shown in Figure 3, superabsorbent hydrogels prepared in LiCl/NMP at 60°C absorbed a considerable amount of water, regardless of the SA feed amount. This result corresponds to the fact that the DS value was much higher when the esterification reaction was performed at 60°C. However, the maximum absorbency was about 350 g/g and was somewhat lower than the maximum absorbency of that prepared at room temperature with an SA feed ratio of 20.

Superabsorbent hydrogels prepared in TBAF/DMSO at room temperature showed absorption behavior similar to that of hydrogels prepared in LiCl/NMP at room temperature; that is, the absorbency



**Figure 2** Absorbency of superabsorbent hydrogels prepared in LiCl/NMP at room temperature.

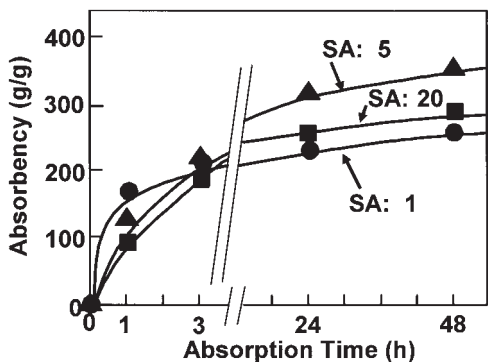


Figure 3 Absorbency of superabsorbent hydrogels prepared in LiCl/NMP at 60°C.

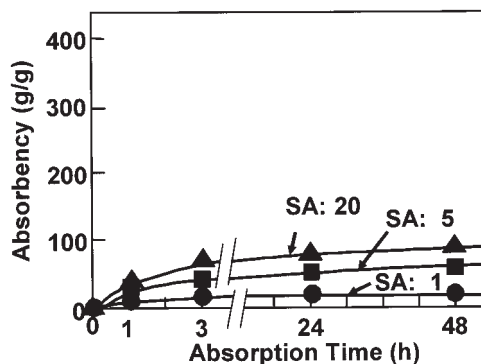


Figure 5 Absorbency of superabsorbent hydrogels prepared in TBAF/DMSO at 60°C.

increased as the SA feed amount increased (Fig. 4). Slightly lower absorbency than that of hydrogels prepared in LiCl/NMP seemed to correspond to a lower DS value.

As is well known, the degree of crosslinking is one of the important factors for determining the absorbency of superabsorbent hydrogels.<sup>1,2</sup> Unfortunately, in this study, it was difficult to estimate the degree of crosslinking because the ester linkage of the diester was indistinguishable from that of ester sodium carboxylate. The degree of crosslinking of hydrogels shown in Figures 2–4 is, however, not supposed to have a big difference mutually because the DS value directly affected water absorbency.

As shown in Figure 5, superabsorbent hydrogels obtained in TBAF/DMSO at 60°C showed very low absorbency, regardless of the SA feed amount. The reason for this low absorbency despite the high DS value is not clear at present. One possible interpretation is that at a high reaction temperature, the formation of diester crosslinking proceeded predominantly, and it restricted chain expansion in water and also restricted water absorbency. The crosslinking point is still under investigation. Consequently, LiCl/NMP

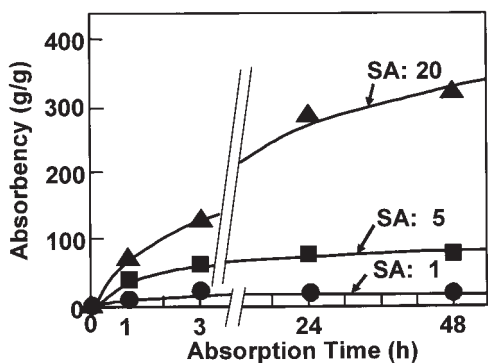


Figure 4 Absorbency of superabsorbent hydrogels prepared in TBAF/DMSO at room temperature.

has proved to be a more suitable solvent system than TBAF/DMSO for attaining high water absorbency.

The absorbency of superabsorbent hydrogels prepared in LiCl/NMP remained relatively high even in aqueous NaCl solutions, compared with that of the sodium polyacrylate superabsorbent hydrogel (Fig. 6). The absorbency of the former was about 100 g/g in a 0.9% aqueous NaCl solution and about 80 g/g in a 3.5% aqueous NaCl solution, and that of the latter was 60 and 30 g/g, respectively. These results should be emphasized because superabsorbent hydrogels should absorb salt solutions in many applications.

For comparison, we also tried to prepare superabsorbent hydrogels from cellulose powder instead of cotton cellulose. The reaction conditions were as follows: in LiCl/NMP, at room temperature, and with an SA feed ratio of 20. The absorbency of the hydrogel prepared from cellulose powder was far lower than the absorbency of that prepared from cotton cellulose, as shown in Figure 6. The intrinsic viscosity of the cellulose powder measured in LiCl/NMP at 30°C with an Ubbelohde-type viscometer was 0.56 dL/g, whereas that of cotton cellulose was as high as 15.6

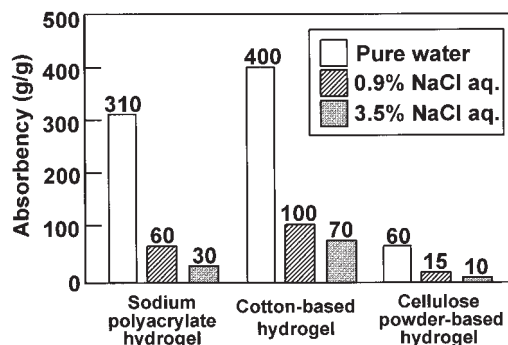
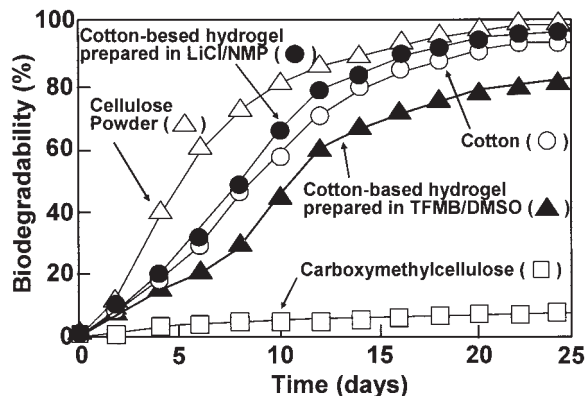


Figure 6 Comparison of the absorbency with various superabsorbent hydrogels prepared in LiCl/NMP. The SA feed ratio to cellulosic hydroxyl groups was 20, the reaction temperature was room temperature, and the absorption time was 48 h.



**Figure 7** Biodegradability of various materials evaluated at 25°C. The SA feed ratio to cellulosic hydroxyl groups was 20, and the reaction temperature was room temperature.

dL/g. Thus, the difference in the absorbencies of that prepared from cotton and that prepared from cellulose powder was due to the difference in their molecular weights. As a result, it was confirmed that an extremely high molecular weight of the polymer is indispensable for attaining high water absorbency for the procedure of this study.

The biodegradability of various materials measured by continuous BOD testing is shown in Figure 7. Superabsorbent hydrogels derived from cotton cellulose biodegraded almost completely after 25 days. This biodegradation speed was comparable to that of cotton. On the contrary, CMC degraded only about 10% after 25 days. A possible reason is that CMC contains a sodium carboxylate group via an ether linkage that is stable and hard to degrade, and this superabsorbent hydrogel contains it via an ester linkage that is susceptible to hydrolysis. This structural difference may affect the biodegradability. As a result, the superabsorbent hydrogels prepared in this study proved to have excellent biodegradability together with high water absorbency.

## CONCLUSIONS

Novel biodegradable superabsorbent hydrogels were successfully prepared by a simple procedure, that is, the esterification of cotton cellulose with SA, followed by NaOH neutralization. Hydrogels were obtained

without any specific crosslinking agent when DMAP was employed as an esterification catalyst, and this indicated that the introduction of hydrophilic side groups and crosslinking proceeded simultaneously. The absorbency of the products strongly depended on the reaction conditions, that is, the kind of solvent, the SA feed amount, and the reaction temperature. The maximum absorbency in pure water was about 400 g of water/g of dry gel. Furthermore, they exhibited higher absorbency in aqueous NaCl solutions than the conventional sodium polyacrylate superabsorbent hydrogel, and this should be emphasized from a practical point of view. The hydrogels prepared in this study degraded almost completely after 25 days in activated sludge, and this showed that they retained excellent biodegradability although they underwent chemical modification. This is worthy of special mention because in many cases, the derivatization of cellulose decreases biodegradability.

The synthesis of biodegradable superabsorbent hydrogels from other polysaccharides (chitin, chitosan, starch, etc.) with a similar procedure is under investigation.

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