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Synthesis and characterization of novel biodegradable superabsorbent hydrogels based on chitin and succinic anhydride

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Abstract

Synthesis of novel superabsorbent hydrogels has been investigated with the reaction of chitin and succinic anhydride (SA) in the presence of 4-dimethylaminopyridine as esterification catalyst in mixture of tetrabutylammnium fluoride and dimethylsulfoxide (TBAF/DMSO) or in mixture of lithium chloride and *N*-methyl-2-pyrrolidinone (LiCl/NMP), followed by NaOH neutralization. Interestingly, hydrogel was obtained in TBAF/DMSO without any crosslinking agent, which indicated the partial formation of diester between hydroxyl group of chitin and SA. On the contrary, products obtained in LiCl/NMP dissolved out during the absorbency test, which indicates that they consist mainly of linear polymer. The former absorbed water about 300 times of its dry weight, which is comparable with the conventional sodium polyacrylate superabsorbent hydrogel. Further, in aqueous NaCl solution, absorbency of the product hydrogels was higher than the sodium polyacrylate superabsorbent hydrogel. The products biologically degraded up to 70% after 20 days, which shows their good biodegradability.

Keywords: Chitin; Biodegradable; Crosslinking; Hydrogels; Swelling

1. Introduction

Chitin is the second most abundant polysaccharide on the earth next to cellulose, and at least 10 gigatons of chitin are estimated to be synthesized and degraded every year in the biosphere. Chitin is a linear polymer mainly consisting of β-1,4-linked *N*-acetyl-D-glucosamine; its chemical structure is quite similar to that of cellulose, a linear polymer consisting of β-1,4-linked D-glucose. Because of its availability, biodegradability as well as biocompatibility, chitin and its derivatives have been used for a variety of applications such as water treatment, textile and paper, cosmetic, food and health supplements, agriculture and biotechnology (Dumitriu, 1998; Majeti & Kumar, 2000).

Superabsorbent hydrogels are highly swollen, hydrophilic polymer networks, capable of absorbing large amounts of water, or saline solution. For 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 (Buchholz & Graham, 1998; Masuda, 1987). So far, several kinds of chitin-based hydogels mainly for biomedical application are reported; carboxymethylchitin crosslined by electron beam irradiation (Zhao, Mitomo, Nagasawa, Yoshii & Kume, 2003), chitin grafted with poly(acrylic acid) (Tanodekaew et al., 2004), semi-interpenetrating polymer networks of chitin and poly (ethylene glycol) macromer (Kim, Lee, & Cho, 1995), and a mixture of carboxymethylchitin and deacetylated chitin crosslinked by glutaraldehyde (Zhao, Kato, Fukumoto, & Nakamae, 2001).

In the previous study on the synthesis of superabsorbent hydrogels from cotton cellulose and succinic anhydride, we found that hydrogel can be obtained without any crosslinker when 4-dimethylaminopyridine (DMAP) was used as esterification catalyst (Yoshimura, Matsuo, & Fujioka, 2005). Thus, it is an interesting subject to examine whether the hydrogel can be obtained also from chitin and succinic anhydride in the same procedure, because the chemical properties of chitin are markedly different from those of cellulose in spite of their structural similarities. The present paper describes a detailed study on the synthesis

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of superabsorbent hydrogels in various conditions. New biodegradable superabsorbent hydrogels have been successfully obtained from chitin and succinic anhydride, and their properties have been clarified. These results have been compared with those obtained from cotton cellulose.

2. Experimental

2.1. Materials

Chitin (powder, Tokyo Kasei Kogyo, Japan) as a starting material was commercially available and used without purification. Tetrabutylammonium fluoride (TBAF, 70–75% in water, Tokyo Kasei Kogyo, Japan) was heated at 80 °C for 3 h under reduced pressure by use of evaporator to remove water just prior to use. Dimethyl sulfoxide (DMSO) and other chemicals were employed as received. Cellulose powder (20 μm, Aldrich) for the standard material of biodegradability test was purchased and used as received.

2.2. Preparation of superabsorbent hydogels

Superabsorbent hydrogels were prepared according to the Scheme 1. As an example, the procedure for synthesizing superabsorbent hydrogel in mixture of TBAF and DMSO at room temperature is described in detail. Citin (1.0 g, 4.9 mmol for anhydrous *N*-acetylglucosamine unit) was dissolved in 300 ml Erlenmeyer flask in TBAF/DMSO solvent (TBAF 15 g, DMSO 85 g) under stirring at room temperature for 3 days. DMAP (1.26 g, 10.3 mmol, molar ratio for hydroxyl group of chitin: 1.05) was added under stirring. After dissolution of DMAP, succinic anhydride (SA, 4.93 g, 49 mmol, molar ratio for hydroxyl group of chitin: 5) was added to the solution, and the reaction was carried out under stirring at room temperature for 24 h to obtain ester carboxylic acid. The reaction mixture was neutralized with aqueous NaOH solution (conc. 10%, 19.7 g, 49 mmol) and then poured into mixture of methanol (850 g) and water (150 g) under stirring. The isolated reaction product was reprecipitated in methanol (500 g), and filtered. The solid was dried under reduced pressure, finely cut with mixer, and screened through a 16-mesh sieve to give off-white granule product.

Preparation in mixture of lithium chloride (LiCl, 8 g) and *N*-methyl-2-pyrrolidinone (NMP, 92 g) was carried out in a similar way.

2.3. Structural analysis

IR spectra of chitin and the reaction products were recorded on a Jasco FT/IR-410 spectrophotometer (KBr disk).

The degree of substitution (DS) of the reaction product was determined by titration method. All of ester linkage was saponified by NaOH, and the amount of remained excess NaOH was determined by titration with HCl. The procedure in detail is as follows. 0.2 g of the sample was weighed accurately and placed in 500 ml plastic flask. 50 ml of distilled water was added to the flask, and stirred overnight at room temperature. 30 ml of 0.1 N NaOH was added and heated at 50 °C for 3 h. After cooled to room temperature, titration was conducted with 0.1 N hydrochloric acid using phenolphthalein as indicator. Molar quantity of ester linkage was determined and ester linkage per repeated anhydrous N-acetylglucosamine unit was thus calculated as DS.

2.4. Water absorbency

Water absorbency of the product was measured by the tea-bag method (Japanese Industrial Standard, JIS K 7223). Nylon tea-bag whose size is 200 and 100 mm in length and width, were prepared by heat sealing, and the superabsorbent hydrogel sample (0.2 g) was charged in it. The tea-bag was immersed in water at 25 °C. After 2 h treatment in water, the tea-bag was picked up from the water, and excess water was drained for 5 min. The weight of tea-bag and hydrogel was then measured (W_t), and absorbency was calculated according to the following scheme;

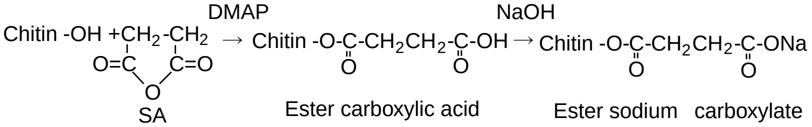
$$\text{Absorbency} = (W_t - W_b - W_p)/W_p$$

where W_b is the weight of blank tea-bag after water treatment, and W_p is the weight of dry superabsorbent hydrogel sample. Again, the tea-bag was dipped for 4 h, and picked up for 5 min to evaluate absorbency (total treatment time: 6 h). Absorbency after 24, 48, and 96 h was evaluated in the same way.

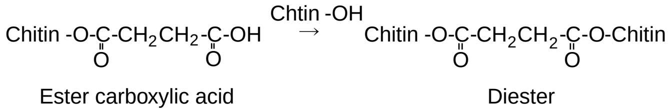
Further, absorbency in aqueous NaCl solution (concentration: 0.9 and 3.5%) was investigated similarly. These concentrations are corresponding to those of physiological saline and seawater, respectively.

2.5. Biodegradability

Biodegradability of the superabsorbent hydrogel was measured at 25 °C for 20 days with reference to JIS K 6950 in which the sample was placed in activated sludge.



Scheme 1. Synthetic route from chitin and SA.



$$\text{Chitin -O-}\underset{\overset{\|}{O}}{C}\text{-CH}_2\text{CH}_2\text{-}\underset{\overset{\|}{O}}{C}\text{-OH} \xrightarrow{\text{Chtin -OH}} \text{Chitin -O-}\underset{\overset{\|}{O}}{C}\text{-CH}_2\text{CH}_2\text{-}\underset{\overset{\|}{O}}{C}\text{-O-Chitin}$$

Scheme 2. Presumed reaction scheme of crosslinking.

The activated sludge was kindly supplied from Tataragawa sewage-treatment plant (Fukuoka, Japan) and used as received. The biodegradability was evaluated by monitoring the biological oxygen demand (BOD) using an OM3001 coulometer of Ohkura Electric Co. Ltd, Japan, which detected the consumption of the oxygen during the evaluation.

3. Results and discussion

3.1. Preparation and structure of superabsorbent hydrogels

In the previous study, we employed a mixture of LiCl and NMP, and a mixture of TBAF and DMSO as a solvent for the synthesis of hydrogels from cotton cellulose and succinic anhydride, because these are different types of aprotic solvent for cellulose (Yoshimura et al., 2005). Among these solvents, LiCl/NMP is also known as the solvent for chitin (Uragami, Ohsumi, & Sugihara, 1981). And in our preliminary experiment, it was found that TBAF/DMSO dissolved chitin as well. Thus we examined preparation of chitin-based superabsorbent hyrogels, both in LiCl/NMP and in TBAF/DMSO, and compared the structures and properties of the products.

In both of LiCl/NMP and TBAF/DMSO, chtin gradually dissolved at room temperature, which indicates its high molecular weight and high crystallinity. When TBAF/DMSO was used as solvent, gelation was observed during esterification, which was also observed in the esterification of cotton cellulose both in LiCl/NMP and in TBAF/DMSO. Gelation seems due to the physical crosslinking between ester carboxylic acid formed during esterification and DMAP, because DMAP is divalent tertially amine compound. This physical crosslinking structure should disappear after neutralization by NaOH and linear polymer should be regenerated, but hydrogel was obtained as final reaction product when TBAF/DMSO was employed as solvent, as shown below. It is probably because other crosslinking structure has formed, i.e. the partial formation of diester between ester carboxylic acid and hydroxyl group of chitin are presumed to occur, as shown in Scheme 2. Excess SA in the reaction system might behave as dehydrating agent under nonaqueous condition. On the contrary, apparent gelation was not observed during esterification when LiCl/NMP was used as solvent. The reason for this is not clear at present, but solvation of LiCl/NMP to chitin might inhibit the formation of crosslinking. To investigate characteristics of each solution, we measured the solution viscosity of chitin and cotton cellulose in LiCl/NMP and TBAF/DMSO, by use of Ubbelode-type viscometer at 30 °C (Fig. 1). Among them, inclination of η_{sp}/c of chitin in LiCl/NMP was different from others, indicating the peculiar interaction between chitin and LiCl/NMP.

Fig. 2 is the IR spectra of chitin and the reaction products (feed molar ratio of SA: 5, reaction temperature: room temperature). An absorption bands due to C=O stretching of ester are observed at 1760 cm^{-1} in the reaction products. This absorption is absent in original chitin. This indicates the formation of ester by the reaction between hydroxyl group in chitin and carboxylic anhydride group of SA. No apparent difference was observed between the products obtained in TBAF/DMSO and LiCl/NMP, except the absorption intensity at 1760 cm^{-1}, which corresponds to the difference of DS value (see below).

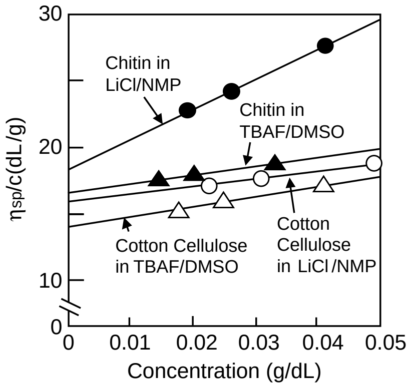


Fig. 1. Solution viscosity of chitin and cotton cellulose measured in TBAF/DMSO and LiCl/NMP at 30 °C.

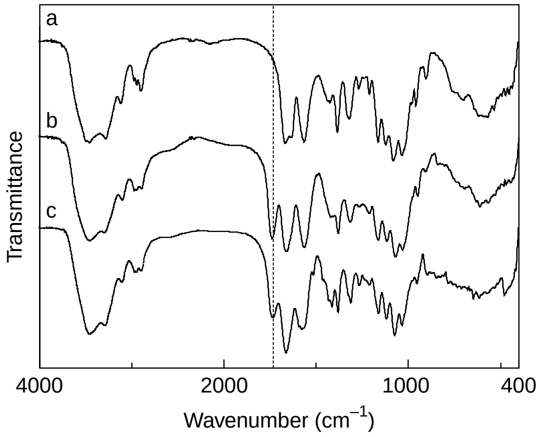


Fig. 2. IR spectra of chitin and the reaction products. (a) Chitin, (b) product prepared in TBAF/DMSO at room temperature, (c) product prepared in LiCl/NMP at room temperature. SA feed ratio to hydroxyl group of chitin: 5.

Table 1
DS of products determined by titration

Solvent	Reaction temp.	SA feed ratio	DS
TBAF/DMSO	r.t.	1	<0.1
		5	0.8
		20	1.2
	60 °C	1	0.2
		5	0.9
		20	1.3
LiCl/NMP	r.t.	1	<0.1
		5	0.3
		20	0.9
	60 °C	1	0.1
		5	0.3
		20	0.9

To determine DS of the reaction product, titration by hydrochloric acid after alkali saponification of the reaction product was carried out. Results are shown in Table 1. As the feed amount of SA increased, DS value gradually increased in each case. And when the SA feed ratio was 20, DS was around 1, indicating almost one hydroxyl group per repeating unit are replaced to ester carboxylic acid group. When the reaction temperature was raised up to 60 °C, DS values were hardly changed. As a whole, products prepared in TBAF/DMSO possessed somewhat higher DS value than those prepared in LiCl/NMP. The difference was the most remarkable when the SA feed ratio was 5 (DS obtained in TBAF/DMSO: 0.8–0.9, that in LiCl/NMP: 0.3).

3.2. Water absorbency and biodegradability

Fig. 3 shows time dependence of absorbency of products obtained in TBAF/DMSO at room temperature by changing the SA feed amount. When the feed ratio of SA was 1, the product hardly absorbed water. As the SA feed ratio increased, the product absorbed water, and absorbency increased slowly but steadily with passage of absorption time. No decrease of absorbency was observed during the test. When SA feed ratio was 5, the absorbency was the highest among those examined, reaching ca. 330 g/g after 96 h treatment. This value is comparable to that of the conventional sodium polyacrylate superabsorbent hydrogel, ca. 300 g/g (see Fig. 7).

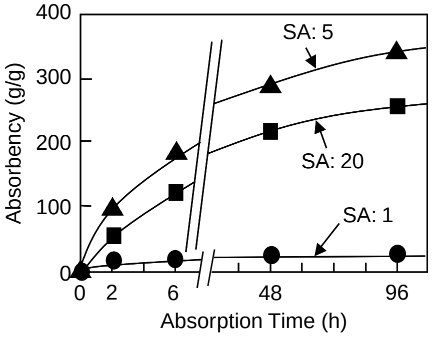


Fig. 3. Absorbency of products prepared in TBAF/DMSO at room temperature.

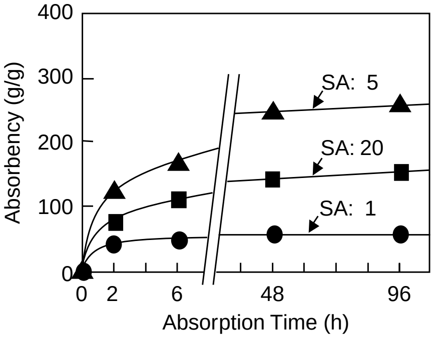


Fig. 4. Absorbency of products prepared in TBAF/DMSO at 60 °C.

As shown in Fig. 4, hydrogels obtained in TBAF/DMSO at 60 °C exhibited similar absorbency to those obtained at room temperature. The product obtained at SA feed ratio of 5 showed the highest water absorbency. However, maximum absorbency was ca. 250 g/g and was somewhat lower than that prepared at room temperature. The reason of lower absorbency of the hydrogels obtained at 60 °C in spite of high DS value is not clear at present. One possible interpretation is that at high reaction temperature, formation of crosslinking proceeded predominantly and it restricted chain-expansion in water, which also restricted water absorbency.

In the case of the products obtained in LiCl/NMP at room temperature, absorbency increased as the SA feed ratio increased, but it gradually decreased after 48 h treatment (Fig. 5). As shown in Fig. 6, products obtained at 60 °C showed similar absorbency behavior to those obtained at room temperature. That is to say, the products obtained at the SA feed ratio of 5 and 20 showed absorbency at early stage, but absorbency decreased after prolonged treatment. It was confirmed that samples obtained in LiCl/NMP hardly remained in the tea-bag after the absorption test, indicating the product had dissolved out of the tea-bag during the test.

Consequently, TBAF/DMSO has proved to be a more suitable solvent than LiCl/NMP to attain high water absorbency, which is in contrast to the results obtained

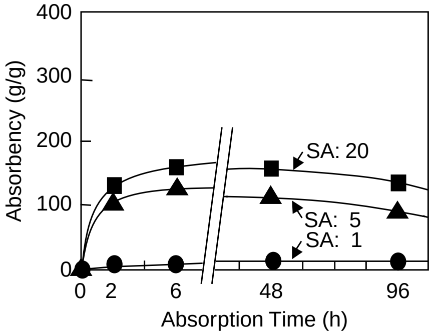


Fig. 5. Absorbency of products prepared in LiCl/NMP at room temperature.

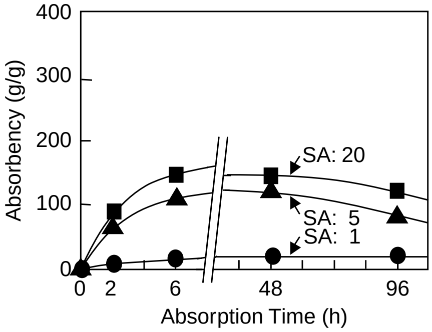


Fig. 6. Absorbency of products prepared in LiCl/NMP at 60 °C.

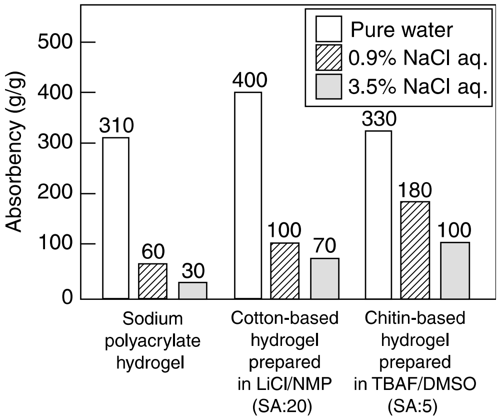


Fig. 7. Comparison of absorbency with various superabsorbent hydrogels.

from cotton cellulose, in which LiCl/NMP afforded better absorbency than TBAF/DMSO (Yoshimura et al., 2005).

Absorbency of superabsorbent hydrogels prepared in TBAF/DMSO remained relatively high even in aqueous NaCl solution, compared with those of crosslinked sodium polyacrylate and hydrogel obtained from cotton cellulose (Fig. 7). This result should be emphasized because superabsorbent hydrogels should absorb aqueous NaCl solution in many applications.

Biodegradability of various materials measured by continuous BOD test is shown in Fig. 8. Biodegradation speed of unmodified chitin was quite fast; it degraded almost completely in 20 days. The products derived from chitin showed good biodegradability; their biodegradation speed was comparable with that of cellulose. Slightly slower biodegradability of the product prepared in TBAF/DMSO than that prepared in LiCl/NMP might be due to higher DS and/or crosslinking structure. As a consequence, superabsorbent hydrogels prepared in the present study has proved to have good biodegradability together with high water absorbency.

4. Conclusion

Novel biodegradable superabsorbent hydrogels were successfully prepared by simple procedure, i.e. esterification of chitin with SA, followed by NaOH neutralization. Hydrogels were obtained without any specific crosslinking agent when TBAF/DMSO was employed as esterification solvent, indicating that the introduction of hydrophilic side group and crosslinking proceeded simultaneously. The maximum absorbency in pure water was ca. 330 g-water/g-dry gel. Further, they exhibited higher absorbency in aqueous NaCl solution than the conventional sodium polyacrylate superabsorbent hydrogel, which should be emphasized from practical point of view. Hydrogels prepared in the present study exhibited good biodegradability in activated sludge. Thus the present hydrogels are expected to be useful for biomedical and agricultural application.

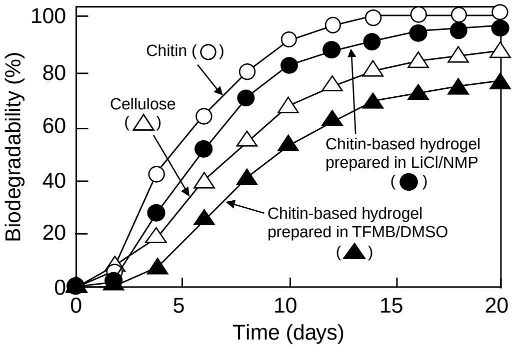


Fig. 8. Biodegradability of various materials evaluated at 25 °C. SA feed ratio to hydroxyl group of chitin: 5, reaction temperature: room temperature.

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