

Synthesis and Characterization of Biodegradable Superabsorbent Hydrogels Based on Carboxymethylstarch

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One of the most significant characteristics of today's society in Japan is quite fast aging. Rapid increase of elder population induces many problems in its society. Caring for the elderly people is one of the representatives. Related to this tendency, consumption volume of disposal diapers for the elderly people has been increasing rapidly. One of the key materials in disposal diapers is superabsorbent hydrogels. Superabsorbent hydrogels are polymers with a high capacity of water absorbency because of their lightly cross-linked hydrophilic structure. Since the development of the first superabsorbent hydrogel, starch-*g*-polyacrylonitrile in the 1970's¹⁾, they have been used in various applications such as disposable diapers, sanitary napkins, additives for soil in agriculture and horticulture, water-blocking tapes, controlled drug delivery systems^{2,3)}. The most remarkable success has been in hygiene applications such as disposable diapers and sanitary napkins. Over 80% of superabsorbent hydrogels are currently consumed in these applications.

Nowdays, most of commercially available superabsorbent hydrogels are crosslinked sodium polyacrylates, which are generally produced from petroleum which is one of representative exhaustive resources. Thus, research on superabsorbent hydrogels based on natural resources which is sustainable has been reported. Superabsorbent hydrogels based on natural feedstock include crosslinked poly(amino acids) such as poly(γ -glutamic acid)⁴⁻⁶⁾ and poly(aspartic acid)^{7,8)}, and crosslinked sodium salt of carboxymethylcellulose⁹⁻¹¹⁾. Recently, syntheses of many kinds of superabsorbent hydrogels have been extensively investigated by esterification of polysaccharides with succinic anhydride (SA) by us. Various polysaccharides such as cotton cellulose¹²⁻¹⁴⁾, chitin¹⁵⁾, starch¹⁶⁾, agar¹⁷⁾, extract from sea lettuce¹⁸⁾, chitosan¹⁹⁾, and guar gum²⁰⁾ were employed as feedstock materials of superabsorbent hydrogels. Some of them

exhibited high water absorbency comparable with cross-linked sodium polyacrylates and good biodegradability as well.

Although some superabsorbent hydrogels based on carboxymethylstarch (CMS) are reported so far²¹⁻²³⁾, detailed investigation on relationship between their degree of substitution (DS) and biodegradability are not exhibited yet. So in the present study, we prepared a series of CMS with various DS, crosslinked them with crosslinker, and evaluated water absorbency and biodegradability of crosslinked carboxymethylstarch, to clarify the relationship between DS of CMS and water absorbency and biodegradability.

Experimental

Materials

Starch (Sigma-Aldrich Japan Co. Ltd., Japan), chloroacetic acid (Sigma Aldrich Japan), DVS (Tokyo Chemical Industry Co. Ltd., Japan), and sodium hydroxide (Sigma Aldrich Japan) were commercially available and used without purification. Conventional superabsorbent hydrogel, cross-linked sodium polyacrylate ("Aqua-keep" SA 60) was kindly supplied from Sumitomo Seika Chemicals, Co., Ltd. Cellulose (power, Aldrich Chemical Company, Inc.) for the standard material of biodegradability test was purchased and used as received.

Preparation of hydrogels

Sodium salt of carboxymethylstarch (CMS) was prepared according to Fig. 1. In 500 mL round bottom flask, starch (10 g), isopropyl alcohol (200 g), sodium hydroxide (8.0 g, 3.3 mol for hydroxyl group of starch) dissolved in water (20 g) were charged, and stirred for 30 min at room temperature. Chloroacetic acid (5.83 g, 1.0 mol for repeating unit of starch) dissolved in isopropyl alcohol (20 g) was added

in the flask, and stirred for 30 min at room temperature. Then the flask was warmed for 90 min at 90°C with stirring. After cooling to room temperature, the reaction mixture was poured into 75% methanol (400 mL) with stirring and stored overnight. The precipitate was separated by filtration with nylon fabric, and reprecipitated in methanol (400 mL). The reaction product was dried under reduced pressure to give off-white product.

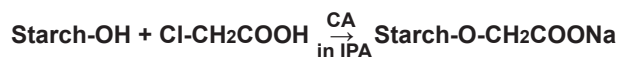


Fig. 1 Preparation scheme of CMS

CMS thus obtained was crosslinked with DVS (Fig. 2). CMS (1 g) was dissolved in pure water (4.0 g). DVS (5, 10, 20, 50 mol% for repeating unit of CMS) was added to the CMS solution. 10% aqueous solution of sodium hydroxide was added to the mixture and vigorously stirred to start the reaction. After 1 h at room temperature, 1 mol/L of hydrochloric acid (5 g) was added to the reaction mixture to terminate the reaction. To the mixture, methanol was added to separate the reaction product. After the filtration, the solid product was dried under reduced pressure, finely cut with mixer, and screened through a 16-mesh sieve to give light brown granule product.

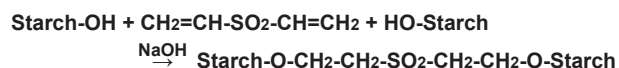


Fig. 2 Crosslinking reaction scheme of CMS with DVS

Measurement

Water absorbency of the product was measured by the so-called “tea-bag method” with the reference to Japanese Industrial Standard, JIS K 7223. Nylon tea-bag whose size is 200mm and 100mm in length and width, was prepared by heat sealing, and the superabsorbent sample (0.2g) was charged in it. The tea-bag was immersed in pure water at 25°C. After 10 min treatment in water, the tea-bag was picked up from the water, and excess water was drained for 5min. 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 sample.

Again, the teabag was dipped for 20 min, and picked up

for 5 min to evaluate absorbency (total treatment time: 30 min). Absorbency after 1 h, 3 h, 24 h, and so on, was estimated in the same way.









Biodegradability of the superabsorbent hydrogels was measured at 25°C for 25 days with reference to JIS K 6950 (ISO 14851) in which the sample was placed in activated sludge. 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.

Results and Discussion

Preparation of CMS

CMS with different DS was prepared by changing feed amount of chloroacetic acid. The results was listed in Table 1. As is obvious from Table 1, weight of reaction products gradually increased with feed amount of chloroacetic acid, which indicates that the DS value of reaction product increased with feed amount of chloroacetic acid. Further, all of the reaction products in the present study was soluble in water, so they were crosslinked with DVS.

Table 1 Appearance and solubility of CMS with different feed amount of chloroacetic acid

CA in feed	0.2mol	0.5mol	0.7mol	1.0mol
Appearance of products (weight)	 9.23g	 10.31g	 11.46g	 14.17g
Solubility of products in water	 soluble	 soluble	 soluble	 soluble

All of the CMS prepared in the present study were crosslinked by changing the feed amount of DVS. Eventually, gelation was observed with all of the CMSs crosslinked with different feed amount of DVS.

Water absorbency of crosslinked CMS

Water absorbency of CMS crosslinked by DVS is shown in Fig. 3. In general, crosslinked CMS prepared with higher feed amount of chloroacetic acid exhibited higher water absorbency. And for each crosslinked CMS, higher water absorbency was observed with lower feed amount of DVS. Consequently, 0.7 mol of chloroacetic acid and 5 mol % of

DVS was optimal among those examined, reaching ca. 130 g/g in pure water.

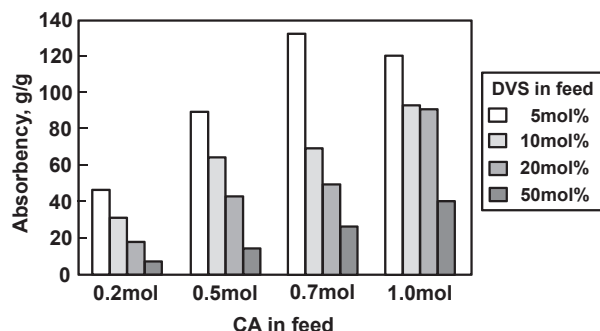


Fig. 3 Water absorbency of crosslinked CMS with different feed amount of chloroacetic acid

Water absorbency of crosslinked CMS was compared with crosslinked sodium polyacrylate which is commercially available and carboxymethylcellulose (CMC) crosslinked with DVS. As shown in Fig. 4, water absorbency of crosslinked CMS was somewhat lower than those of crosslinked sodium polyacrylate and crosslinked CMC.

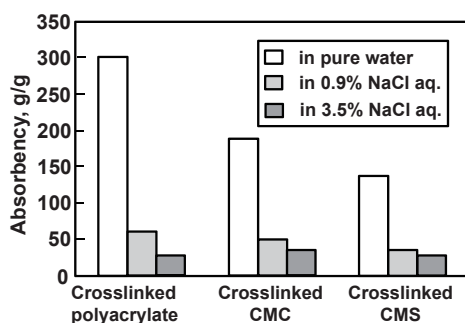


Fig. 4 Comparison of water absorbency of crosslinked CMS with some hydrogels

Biodegradability of crosslinked CMS

Biodegradability of the reaction product crosslinked by DVS is listed in Fig. 5. Uncrosslinked starch exhibited excellent biodegradability. Biodegradation speed of crosslinked CMS was affected by the feed amount of chloroacetic acid, that is, DS of CMS; smaller feed amount of chloroacetic acid resulted in better biodegradability. It is noteworthy that the sample with 0.7 mol of chloroacetic acid and 5 mol % of DVS exhibited some biodegradability, which indicates compatibility of crosslinked CMS for water absorbency and biodegradability is not so bad.

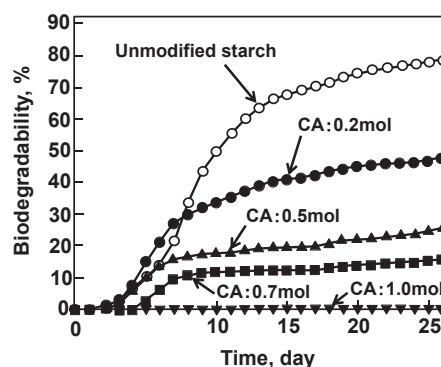


Fig. 5 Biodegradability of crosslinked CMS with different feed amount of chloroacetic acid

Summary

CMS prepared with different feed amount of chloroacetic acid was crosslinked with different feed amount of DVS. Relationship between DS of CMS, feed amount of DVS, and water absorbency and biodegradability was investigated. Among those examined, CMS prepared with 0.7 mol of chloroacetic acid and crosslinked with 5 mol % of DVS exhibited relatively higher water absorbency and some biodegradability

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