

Synthesis and Characterization of Superabsorbent Hydrogels Based on Carboxymethylcellulose

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(Received January 5, 2021)

One of the most serious characteristics of today's society in Japan is quite fast aging. Rapid increase of elder population induces many problems in its society. Caring for these elderly people is one of the representatives. Related to this tendency, consumption volume of disposal diapers for the elderly people has been increasing recently. As is well known, 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 crosslinked 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.

Nowadays, 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 carboxymethylcellulose (CMC)⁹⁻¹¹⁾. 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 crosslinked sodium polyacrylates and good biodegradability as well.

Although some superabsorbent hydrogels based on CMC are reported as shown above, 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 CMC with various DS, crosslinked them with crosslinker, and evaluated water absorbency and biodegradability of crosslinked CMC, to clarify the relationship between DS of CMC and water absorbency and biodegradability.

Experimental

Materials

Cotton cellulose (Daisan Co. Ltd., Japan), chloroacetic acid (Sigma Aldrich Japan), divinylsulfone (DVS, Tokyo Chemical Industry Co. Ltd., Japan), and sodium hydroxide (Sigma Aldrich Japan) were commercially available and used without purification. Conventional superabsorbent hydrogel, crosslinked 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 CMC was prepared according to Fig. 1. In 500 mL round bottom flask, cotton cellulose (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 cotton cellulose) 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.

CMC thus obtained was crosslinked with DVS (Fig. 2).

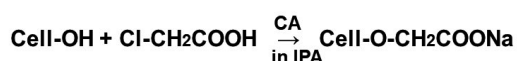


Fig. 1 Preparation scheme of CMC

CMC (1 g) was dissolved in pure water (4.0 g). DVS (10, 20, 40, 60, 100 mol% for repeating unit of CMC) was added to the CMC 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.

Measurement

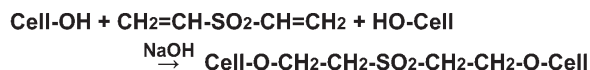


Fig. 2 Crosslinking reaction scheme of CMC with DVS

IR spectra of reaction products were recorded on a HORIBA FT-710 spectrophotometer (KBr disk).

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 20 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 CMC and crosslinked CMC

CMC 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, DS of reaction products gradually increased with feed amount of chloroacetic acid. Further, almost all of the reaction products in the present study was soluble in water, except for the case of CA feed amount of 0.5 mol, probably due to its low DS value.

Table 1 Appearance and solubility of CMC with different feed amount of CA









CA in feed	0.2mol	0.5mol	0.7mol	1.0mol
Appearance of products (DS)	 0.44	 0.72	 0.90	 1.36
Solubility of products in water	 insoluble	 soluble	 soluble	 soluble

Fig. 3 shows the IR spectra of the reaction products by changing feed amount of CA. Absorption band due to C=O stretching of carboxylic group is observed at ca. 1700 cm⁻¹ in the reaction products. And this absorption increased as feed amount of CA. This indicates the introduction of carboxylic acid by the reaction between hydroxyl group in cotton cellulose and CA.

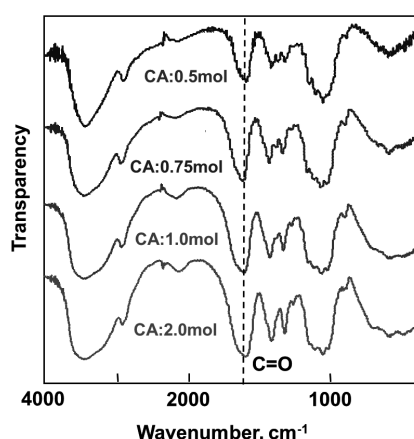


Fig. 3 IR spectra of CMC prepared with different feed amount of CA

As a next step, all of the water-soluble CMC prepared in the present study were crosslinked by changing the feed amount of DVS. Eventually, gelation was observed with all of the CMCs crosslinked with different feed amount of DVS.

Water absorbency of crosslinked CMC

Water absorbency of CMC crosslinked by DVS is shown in Fig. 4. In general, crosslinked CMC prepared with higher feed amount of chloroacetic acid exhibited higher water absorbency. And for each crosslinked CMC, higher water absorbency was observed with 40 mol % of the DVS feed amount. Consequently, 2.0 mol of CA and 40 mol % of DVS was optimal among those examined, reaching ca. 400 g/g in pure water.

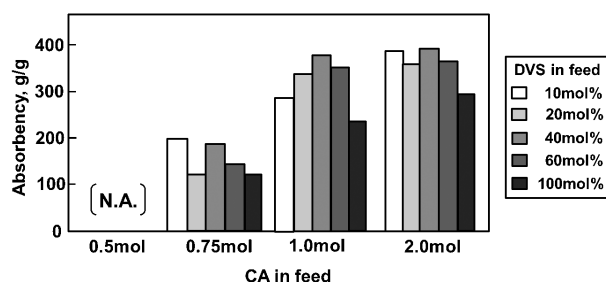


Fig. 4 Water absorbency of CMC crosslinked with DVS in pure water

Water absorbency of crosslinked CMC with different feed amount of CA in pure water and salt water was exhibited in Fig. 5. As shown in Fig. 5, water absorbency of crosslinked CMC increased with feed amount of CA.

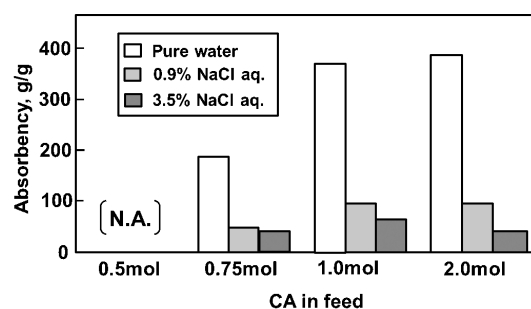


Fig. 5 Comparison of water absorbency of crosslinked CMC

Biodegradability

Biodegradability of the reaction product crosslinked by DVS is listed in Fig. 6. Unmodified cellulose exhibited excellent biodegradability. Biodegradation speed of crosslinked CMC was affected by the feed amount of CA, that is, DS of CMC; smaller feed amount of CA resulted in better biodegradability. It is noteworthy that the sample with 0.75 mol of CA exhibited only low biodegradability, which indicates compatibility of crosslinked CMC for water absorbency and biodegradability is not so good. This result has shown that compatibility of crosslinked CMC is worse than that of crosslinked carboxymethylstarch (CMS) prepared similarly²¹⁾.

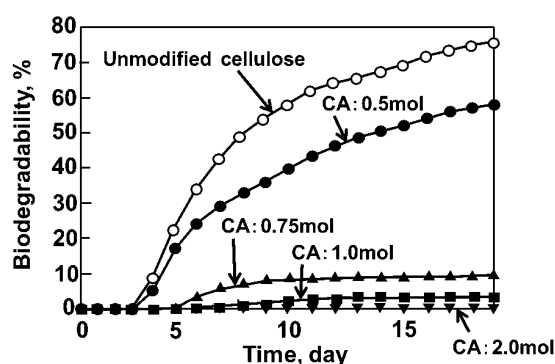


Fig. 6 Biodegradability of crosslinked CMC with different feed amount of CA

Summary

CMC prepared with different feed amount of CA was crosslinked with different feed amount of DVS. Relationship between DS of CMC, feed amount of DVS, and water absorbency and biodegradability was investigated. Among those examined, CMC prepared with 1.0 mol and 2.0 mol of CA crosslinked with 40 mol % of DVS exhibited high water absorbency but low biodegradability. On the other hand,

CMC prepared with 0.5 mol of CA crosslinked with 40 mol % of DVS good biodegradability but low water absorbency. From these experimental results, compatibility of water absorbency and biodegradability of crosslinked CMC is not worse than those of crosslinked CMS.

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