

Synthesis and Properties of Superabsorbent Hydrogels Based on Guar Gum and Succinic Anhydride

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ABSTRACT: Synthesis of novel superabsorbent hydrogels has been investigated with the reaction of guar gum and succinic anhydride (SA), using of 4-dimethylaminopyridine as esterification promoter and water or dimethylsulfoxide (DMSO) as reaction solvent, followed by NaOH neutralization. Hydrogels prepared in water exhibited somewhat higher water absorbency than those prepared in DMSO; its maximum water absorbency in pure water and aqueous 0.9% NaCl solution was ca. 200

g/g and 80 g/g, respectively. These values were considerably higher than those of hydrogels obtained from starch in a similar way. The products in this study biologically degraded up to 70–80% after 10 days in activated sludge, which shows their excellent biodegradability. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 612–616, 2009

Key words: guar gum; hydrogel; swelling; biodegradation

INTRODUCTION

Superabsorbent hydrogels are loosely crosslinked hydrophilic polymers, which can absorb large amount of water or saline solution. For these unique characteristics, they have been used in various applications such as disposal diapers, additives for soil in agriculture, and medicine for drug delivery systems.¹ Most of commercially available superabsorbent hydrogels are crosslinked sodium polyacrylates with extremely high molecular weight, and they have no biodegradability. So, 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.¹

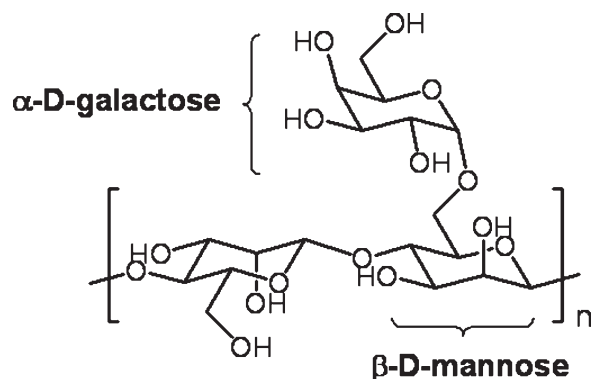
Guar gum is a polysaccharide obtained from the endosperm in guar that is a leguminous plant. It has interesting characteristics such as high water-thickening potency. Thus, it can be used in various multi-phase formulations; as an emulsifier because it helps to prevent oil droplets from coalescing, and/or as a stabilizer because it helps to prevent solid particles from settling.² Guar gum is one of representative galactomannans which consist of (1-4)-linked β -D-mannopyranose backbone with branchpoints from their 6-positions linked to α -D-galactose. Since molar ratio of mannopyranose to galactose of guar gum is

ca. 2, the idealized chemical structure of guar gum can be depicted as shown in Scheme 1. Guar gum possesses high molecular weight (50,000–8,000,000), which is suitable for raw material of superabsorbent hydrogels, because high molecular weight of the polymer is one of the indispensable factors to attain high water absorbency. Several kinds of hydrogels based on guar gum are reported so far; interpenetrating polymer network of guar gum and poly(acrylic acid),³ poly(methacrylic acid),⁴ poly(*N*-isopropylacrylamide)⁵; graft polymer based on guar gum such as guar gum-*g*-poly(acrylic acid),⁶ guar gum-*g*-poly(acrylonitrile),⁷ guar gum-*g*-poly(*N*-isopropylacrylamide)⁸; guar gum crosslinked with glutaraldehyde.⁹

Recently, we have investigated biodegradable superabsorbent hydrogels by esterification of cotton cellulose,¹⁰ chitin,¹¹ and starch¹² with succinic anhydride (SA). It was found that hydrogels were obtained without any crosslinking procedure, when 4-dimethylaminopyridine (DMAP) was employed as esterification promoter, which indicates the formation of crosslinking structure between hydroxyl group of polysaccharides and SA. Thus, it is an interesting subject to investigate the synthesis of superabsorbent hydrogels from guar gum and SA in a similar procedure, because chemical properties of guar gum are different from those of starch in spite of their structural analogy.

This article describes a study on the synthesis of superabsorbent hydrogels from guar gum and SA in various reaction conditions. Novel biodegradable superabsorbent hydrogels have been successfully

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Scheme 1 Idealized chemical structure of guar gum.

obtained, and their properties have been clarified. These results were compared with those obtained from starch.

EXPERIMENTAL

Materials

Guar gum (Sigma Aldrich, Japan) as a starting material was commercially available and used without purification. Intrinsic viscosity ($[\eta]$) of guar gum measured in water at 30°C by using Ubbelode-type viscometer was 10.0 dL/g, which indicates its high molecular weight. DMAP was purchased from Tokyo Chemical Industry. Dimethylsulfoxide (DMSO) and other chemicals were employed as received. Starch (from potato, Aldrich), raw material of hydrogel for comparison, was purchased and used as received.

Preparation of superabsorbent hydrogels

Hydrogels in this study were prepared according to Scheme 2. As an example, the procedure for synthesizing superabsorbent hydrogel in water at room temperature is described in detail. In 200 mL Erlenmeyer flask, guar gum (1.0 g, 2.1 mmol for repeating unit) was dissolved in water (99 g) under stirring at room temperature for 24 h. DMAP (2.38 g, 19.4 mmol, molar ratio for hydroxyl group of guar gum: 1.05) was added under stirring. After dissolution of DMAP, SA (1.86 g, 18.5 mmol, molar ratio for hydroxyl group of guar gum: 1) 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 poured into methanol (500 mL) under stirring, and then neutralized with aqueous NaOH solution (conc. 10%, 7.42 g, 18.5 mmol). The solid was dried under reduced pressure, finely cut with mixer, and screened through a 16-mesh sieve to give off-white granule product.

Structural analysis

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

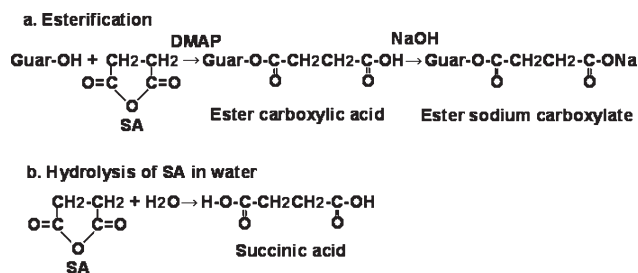
The degree of substitution (DS) of the reaction product was determined by titration method. All of ester linkage was saponified by NaOH, and the amount of remained excess NaOH was determined by titration with HCl. The procedure in detail is as follows. A total of 0.2 g of the sample was weighed accurately and placed in 200 mL plastic flask. Fifty milliliters of distilled water was added to the flask, and stirred overnight at room temperature. Thirty milliliters of 0.1N NaOH was added and heated at 50°C for 3 h. After cooled to room temperature, titration was conducted with 0.1N hydrochloric acid using phenolphthalein as indicator. Molar quantity of ester linkage was determined and ester linkage per repeating unit shown in Scheme 1 was thus calculated as DS.

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 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 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 2 h, and picked up for 5 min to evaluate absorbency (total treatment time: 3 h). Absorbency after 24 h and so on was evaluated in the same way.



Scheme 2 Synthetic route from guar gum and SA.

Further, absorbency in 0.9% NaCl aqueous solution was investigated similarly, which is corresponding to that of physiological saline.

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

RESULTS AND DISCUSSION

Preparation and structure of hydrogels

Hydrogels were successfully obtained from guar gum and SA in DMSO and water. In water, hydrolysis of SA is competitive to esterification. The latter seems predominant to the former according to the experimental results shown below.

Figures 1 and 2 are the IR spectra of guar gum and the reaction products prepared in DMSO and water, respectively (feed molar ratio of SA: 1, 5 and 20). Absorption bands due to C=O stretching of ester are observed at 1735 cm⁻¹ in both samples prepared in DMSO and water. Absorption intensity at 1735 cm⁻¹ of samples prepared in water (Fig. 2) seems stronger than those prepared in DMSO (Fig. 1), which indicates DS value of the former is larger than those of the latter (see below). Furthermore, absorption bands due to unsymmetrical stretching of

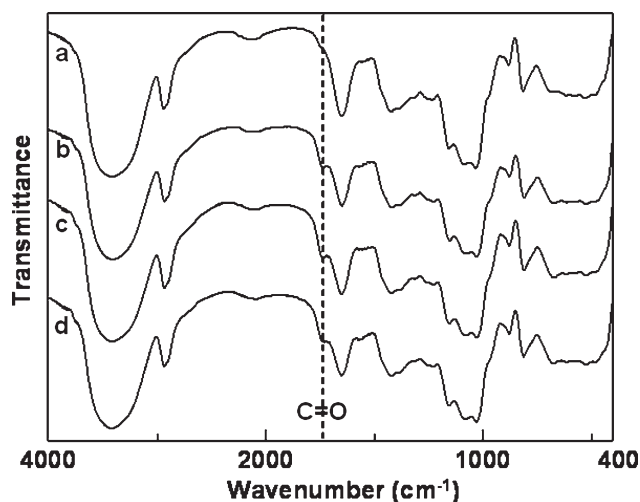


Figure 1 IR spectra of guar gum and the reaction products prepared in DMSO. (a) Guar gum, (b) SA feed ratio of 1, (c) SA feed ratio of 5, (d) SA feed ratio of 20.

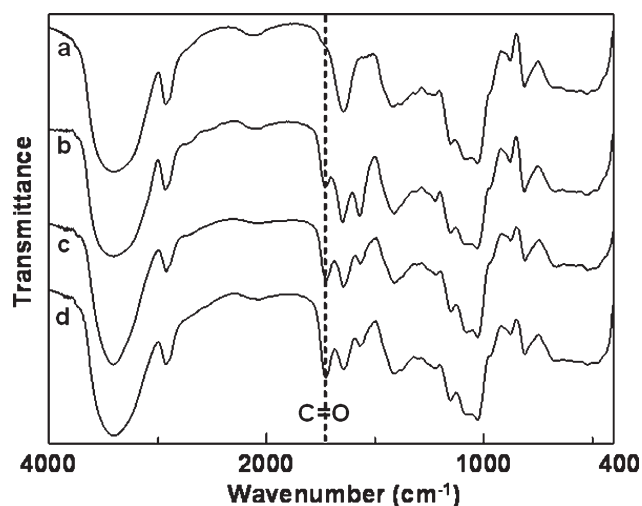


Figure 2 IR spectra of guar gum and the reaction products prepared in water. (a) Guar gum, (b) SA feed ratio of 1, (c) SA feed ratio of 5, (d) SA feed ratio of 20.

carboxylic anion are observed at 1550 cm⁻¹ in the reaction products obtained in water. Absorptions at 1735 cm⁻¹ and 1550 cm⁻¹ are absent in original guar gum. These results indicate the formation of ester by the reaction between guar gum and SA.

To determine DS of the reaction products, titration with hydrochloric acid after alkali saponification of the reaction products was carried out. As shown in Table I, DS value of the sample prepared in DMSO was almost constant, irrespective of SA feed amount. On the other hand, DS value of those prepared in water gradually increased with the feed amount of SA. DS value of the samples prepared in water was totally higher than those prepared in DMSO; this tendency is coincident with IR analysis data shown above, but different from those prepared from starch; DS value of the sample based on starch prepared in DMSO was totally higher than those in water.¹² As shown in Scheme 1, guar gum has nine hydroxyl groups per repeating unit, which means that the maximum DS value of the reaction product could be 9. Therefore, DS values in this study (0.5–1.9) are considerably smaller than the corresponding hydrogels made from starch (0.2–1.4), which has only three hydroxyl groups per repeating unit.

TABLE I
DS of Products Determined by Titration

Solvent	SA feed ratio	DS
DMSO	1	0.5
	5	0.6
	20	0.6
Water	1	0.7
	5	1.4
	20	0.9

Water absorbency and biodegradability

All the esterification products in this study were insoluble in water, and turned out to be hydrogel without any crosslinking process, just like the case of cotton cellulose, chitin, and starch. So, evaluation of water absorbency was carried out with aforementioned esterification products. Figure 3 shows time dependence of absorbency of products prepared in DMSO by changing the feed amount of SA. Products prepared in DMSO swelled gradually, but exhibited low absorbency, regardless of the SA feed amount; ca. 60–80 g/g after 96 h treatment.

On the other hand, as shown in Figure 4, products prepared in water exhibited higher water absorbency than those obtained in DMSO. As the SA feed amount increased, the absorbency inversely decreased, and the absorbency of the sample with SA feed amount of 1 was the highest among those examined, reaching ca. 200 g/g after 96 h treatment. These results suggest that higher DS value does not always induce high water absorbency. Therefore, the relationship between polymer structure and water absorbency is not clear at present and still under investigation.

In Figure 5, maximum absorbency in pure water and aqueous 0.9% NaCl solution of some hydrogels are compared. Hydrogel based on guar gum prepared in water absorbed more pure water and NaCl solution than those based on starch. In the case of starch-based hydrogel, products obtained in DMSO showed higher water absorbency than those obtained in water.¹² In contrast, in the case of guar gum, products obtained in water showed higher absorbency than those in obtained in DMSO. As a whole, water absorbency of hydrogels seems to correspond to their DS value; in general the higher DS is, the higher water absorbency is. For absorbency in aqueous NaCl solution, hydrogels prepared from guar gum absorbed higher than those prepared

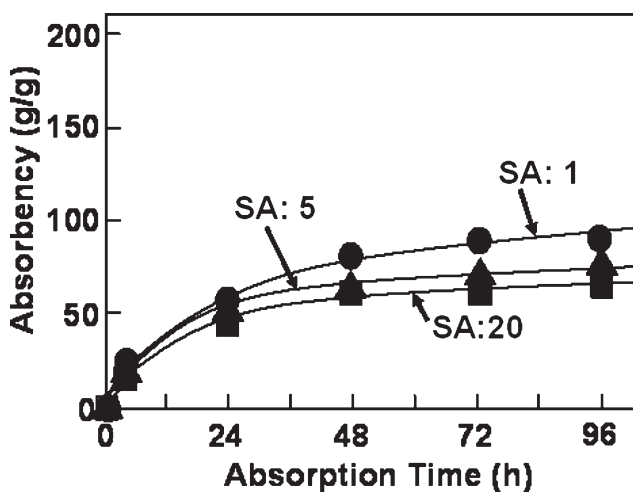


Figure 3 Absorbency of products prepared in DMSO.

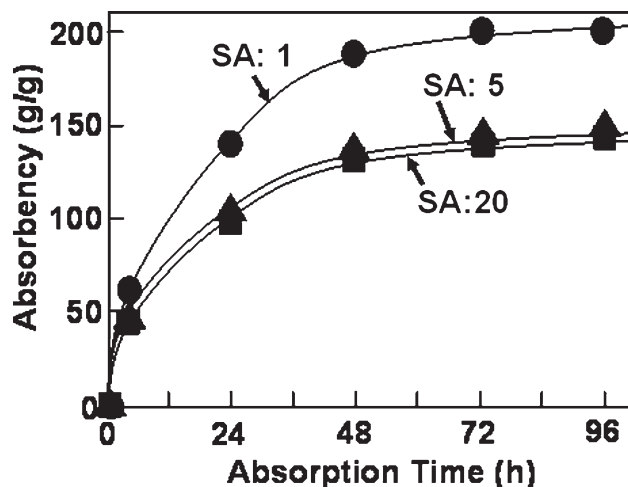


Figure 4 Absorbency of products prepared in water.

from starch. Thus, guar gum has turned out to be a more suitable starting material to attain high water absorbency than starch when the preparation method in this study is employed. The reason why absorbency behavior of the hydrogels based on guar gum is different from that of the hydrogels based on starch is not clear at present. One possible reason is that starch is more susceptible to hydrolysis during preparation than guar gum.

Figure 6 shows biodegradability of various materials based on guar gum by continuous BOD method. The appearance of samples was granule before evaluation, but it turned to be in swollen state immediately, and gradually dissolved into activated sludge during evaluation. As shown in Figure 6, the activated sludge degraded ca. 80% of unmodified guar gum for 10 days. Similarly, products prepared in water exhibited excellent biodegradability, irrespective of feed amount of SA. The hydrogels made in DMSO exhibited similar biodegradability to that of the hydrogels made in water. Further, as shown in Figure 6, their biodegradation speed was higher than that of cellulose, a standard material for

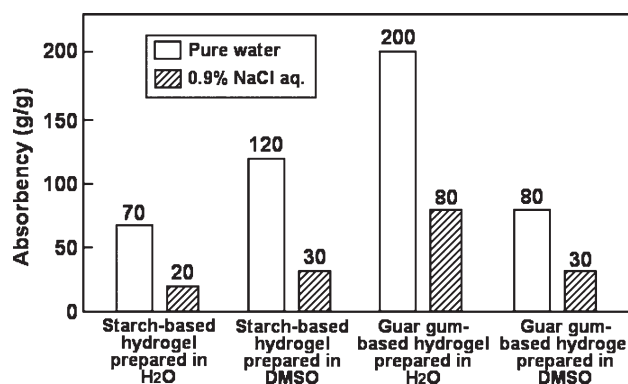


Figure 5 Comparison of absorbency with various super-absorbent hydrogels.

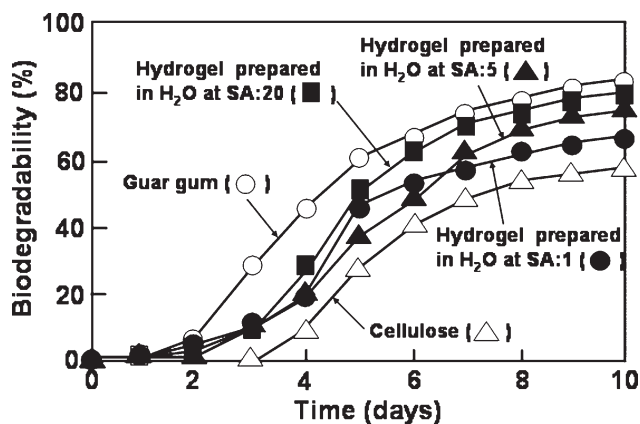


Figure 6 Biodegradability of various materials evaluated at 25°C.

biodegradability. On the other hand, reaction products from starch showed lower biodegradability than cellulose.¹² Thus, biodegradability of the hydrogels based on guar is higher than that of hydrogels based on starch. As a consequence, hydrogels in this study have proved to have excellent biodegradability together with high water absorbency.

CONCLUSIONS

Novel biodegradable hydrogels were successfully prepared by simple procedure, i.e., esterification of

guar gum with SA in water, followed by NaOH neutralization. Hydrogels were obtained without any specific crosslinking agent. The maximum absorbency in pure water was ca. 200 g-water/g-dry gel. Hydrogels prepared in this study exhibited excellent biodegradability in activated sludge. Thus, the present hydrogels are expected to be useful for biomedical and agricultural applications.

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