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5.4 Country Report: Japan

Radiation Processing of Polysaccharide Derivatives

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Summary

Carboxymethylcellulose (CMC), carboxymethylstarch (CMS), carboxymethylchitin (CM-chitin) and carboxymethylchitosan (CM-chitosan) form gels when irradiated at paste-like condition. Bedsore prevention mat filled up CMC hydrogel crosslinked by irradiation at paste-like condition was practical applied as a health care products. It was found that CM-chitosan hydrogels have anti-microbial activity and effective as absorbents to remove metal ions. When crosslinked gel sheets of CM-chitin and CM-chitosan were immersed in copper (II) aqueous solution, absorption of Cu (II) were 161 mg/g and 172 mg/g, respectively.

Radiation crosslinking of cellulose derivative such as hydroxypropyl methylcellulose phthalate, (HPMCP) kneaded with aqueous alkali solution and methanol was achieved with EB-irradiation at paste-like condition. The HPMCP gel absorbed organic solvents such as chloroform and pyridine

1. Introduction

Polysaccharides such as cellulose, starch, chitin/chitosan and their derivatives have a variety of application in many fields owning to their unique structure, distinctive properties, safety and biodegradability [1]. In their utilization, many shapes and material properties are required such as hydrogels, which have been widely used in the field of biomedicine and pharmacy. The hydrogels based on polysaccharides and their derivatives have been studied widespread but no radiation crosslinking of polysaccharides and their derivatives have been reported so far. Polysaccharides and their derivatives are typical degradation polymers in radiation processing. But in several studies conducted, it is found that polysaccharide derivatives such as carboxymethylcellulose (CMC), methylcellulose (MC), carboxymethylstarch (CMS) and carboxymethylchitosan (CM-chitosan) undergo crosslinking when irradiated at paste-like condition [2-5]. Polysaccharide derivative powder is kneaded homogeneously with water and then pressed to obtain sheets of suitable thickness for EB irradiation. Irradiated sheets have high gel strength. By this simple technology, biodegradable

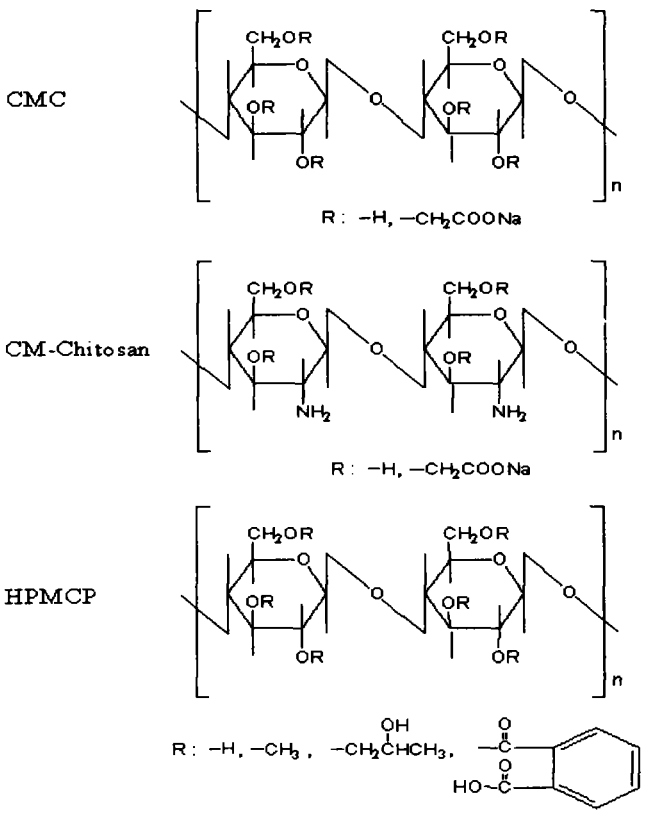
hydrogels are formed.

Radiation crosslinking without any additive in the fabrication process results in a high-purity product. Therefore, the activity of the functional groups of the gel sample for their special adsorption is the same of that of the original material, even after irradiation. Cellulose ethers with hydrophobic substituents and a high degree of substitution have solubility in organic solvent. Hydroxypropyl methylcellulose phthalate (HPMCP), insoluble in water but have good organosolubility due to its high degree of substitution, can be used as oil recovery material. Chitin/chitosan and their derivatives have been used as suitable natural polymers for the collection of metals ions because the amine groups and hydroxyl groups present on the main chain can act as chelation sites for metal ions. To obtain highly efficient adsorbents with high chemical stability for metal ions and organic solvents, we synthesized new types of crosslinked chitin derivatives (CM-chitin/chitosan) and crosslinked cellulose ethers (HPMCP) at paste-like condition with EB irradiation.

In this report, radiation crosslinking behavior of polysaccharide derivatives at paste-like condition and their applications, especially their special adsorptive ability were reported.

2. Materials and Irradiation

Commercial products of CMC, CM-chitin, CM-chitosan, and HPMCP were used in our research work. Scheme 1 showed their structure.



Scheme 1. Structure of samples

All samples were kneaded well with solvent (water or the other) well by a glass bar. The irradiation was carried out in polyethylene / nylon blend bag heat-sealed after removal air by a vacuum pump. Dynamitron electron beam accelerator (3 MeV, 25 mA) was used at the following irradiation parameters: acceleration energy 2 MeV, beam current 1 mA, and the dose per pass 1 kGy.

3. Radiation Crosslinking of Polysaccharides

3.1.1. Effect of degree of substitution and concentration on crosslinking of CMC

CMC aqueous solution was irradiated at a high concentration (10-50%) to produce crosslinkings [2]. The gel fractions of CMC with two different degree of substitution (DS) of 1.36 and 2.2 against delivered dose are presented in Figure 1. Gel fraction rises sharply just after exceeding the gelation point and levels off later. A high concentration in aqueous is favorable for crosslinking. The presence of water enhances the yields of macroradicals. So from the practical point of view, the polymers should be mixed with water well to prepare homogeneous samples. A high DS also was found favorable crosslinking. The CMC with a DS of 2.2 gives the highest gel fraction in high concentration among these samples. It can be explained that intermolecular linkages are a result of ether function.

3.1.2. Application of crosslinked CMC on bedsore prevention

Carboxymethylcellulose (CMC) soft hydrogel is applied as a healthcare product in hospitals and is used as bed mats for operation procedures (Fig. 2). Before operation is conducted, the mat is pre-heated to body temperature (37 °C) using an oven heater. Temperature could be maintained for a long time during operation. The hydrogel mat is shown to disperse body pressure and improve circulation of blood during operation, thus, it could prevent bedsores in patients. This hydrogel converts into fertilizer by degradation of microorganism in soil. In addition, biodegradability is a big advantage of this hydrogel.

3.2. Crosslinking of CM-chitin/CM-chitosan and their application for metal ion adsorption

Crosslinking of CM-chitin and CM-chitosan was also observed at paste-like state (above 10 %) of high concentration (Fig. 3). The crosslinking behavior is similar like CMC. High concentrated paste-like condition was favorable for crosslinking [4, 5]. In the case of CM-chitosan, high degree of deacetylation was found to negatively correlate to crosslinking even if it has a high DS. The hydrogels created from carboxymethylated chitin derivatives, exhibited excellent mechanical properties and good swelling in water. Irradiation of 30% CM-chitin and CM-chitosan sheets gave maximum gel strength of 0.45MPa at 70kGy and 0.75MPa at 50kGy, respectively. Swelling of these gels showed dependence on concentration with irradiation and swelling range is from 20 to 150 g water / 1 g dry gel. These values are less than that of CMC gel. It was found that CM-chitosan hydrogels have anti-microbial activity and effective as absorbents to remove metal ions. In our research, a new type adsorbent based on chitin derivatives (CM-chitin, CM-chitosan) was prepared by irradiation [6]. The adsorption of Cu (II) ions onto these crosslinked chitin derivatives was investigated. Adsorption kinetic studies indicated a rapid removal of Cu (II) ions from aqueous solutions (Fig.4). Also, isothermal adsorption data revealed that Cu (II) could be removed by these cross-linked carboxymethylated chitin derivatives with high efficiency. Adsorption isothermal data could be well interpreted by the Langmuir equation. The uptakes of Cu (II) ions on cross-linked CM-chitin were 161 mg/g, and on cross-linked CM-chitosan was 172 mg/g at pH 5.5. Low pH is favorable for Cu (II) desorption. The Cu (II) ions can be desorbed from the crosslinked matrix rapidly and completely by treatment in diluted HCl solution and at the same time the adsorbents can be regenerated for the use again to adsorb heavy metal ions (Fig.5).

3.3. Crosslinking of HPMCP for organic solvent adsorption

Hydroxypropyl methylcellulose phthalate (HPMCP), a cellulose-ether with a phthalate functional group, is widely used in the pharmaceutical industry because it is less susceptible to hydrolysis than cellulose acetate phthalate. Radiation crosslinking of cellulose derivative having phthalate function (Hydroxypropyl methylcellulose phthalate, HPMCP) kneaded with alkali aqueous solution, was achieved with EB-irradiation at paste-like condition (Fig. 6). Low alkyl chain alcohol, ethers and ketone can be used as the media for radiation crosslinking of HPMCP [7]. The gels have good swelling ability in chloroform and acetone. The HPMCP gel absorbed organic solvents such as chloroform and pyridine. Accordingly, applications for absorbent to adsorption of organic solvent are expected.

References

1. S. Dumitriu et al., *Polysaccharides in Medical Applications.*, Marcel Dekker Inc, New York, 1996.
2. B. Fei, R. A. Wach, H. Mitomo, F. Yoshii, & T. Kume, Hydrogel of biodegradable cellulose derivatives. I. Radiation-induced crosslinking of CMC., *Journal of Applied Polymer Science.*, 78, 278, 2001.
3. N. Nagasawa, T. Kume, & F. Yoshii, Radiation crosslinking of starch derivatives at high concentrated solution., *Carbohydrate Polymers.*, submitted
4. F. Yoshii, R. A. Wach, L. Zhao, N. Nagasawa, H. Mitomo, & T. Kume, Hydrogels of polysaccharide derivatives crosslinked with irradiation at paste-like condition. *Nuclear Instruments and Methods in Physics Research B.* 208, 320, 2003.
5. L. Zhao, H. Mitomo, N. Nagasawa, F. Yoshii, & T. Kume, Radiation synthesis and characteristic of the hydrogels based on carboxymethylated chitin derivatives. *Carbohydrate Polymers.* 51, 169, 2003.
6. L. Zhao, H. Mitomo, N. Nagasawa, F. Yoshii, & T. Kume, Preparation of crosslinked carboxymethylated chitn derivatives by irradiation and their sorption behavior for copper (II) ions. *Journal of Applied Polymer Science*, in press.
7. L. Xu, N. Nagasawa, F. Yoshii, & T. Kume,. Radiation crosslinking of hydroxypropyl methylcellulose phthalate gels in organic solvents. *Journal of Applied Polymer Science.* submitted.

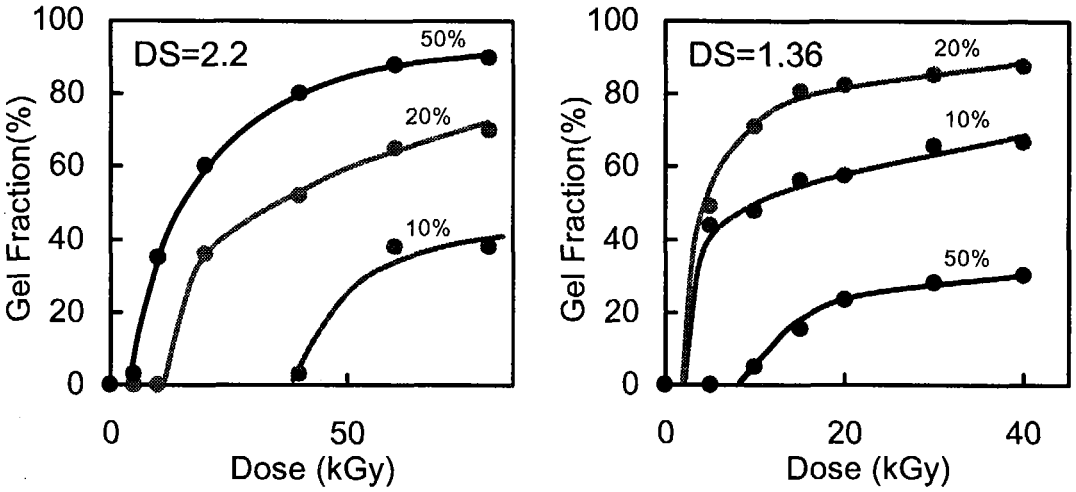


Fig. 1. Crosslinking of CMC by radiation

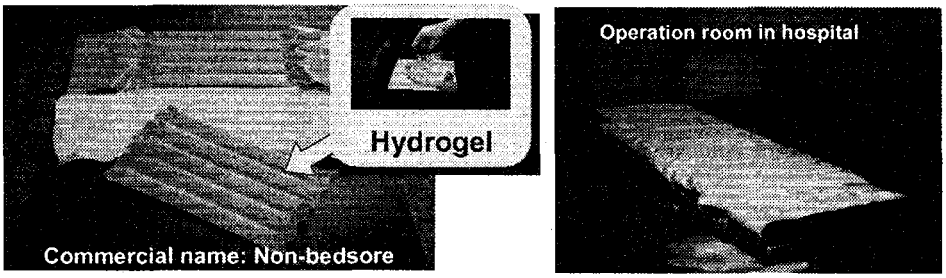


Fig. 2. Healthcare product in hospitals and bed mats for operation procedures

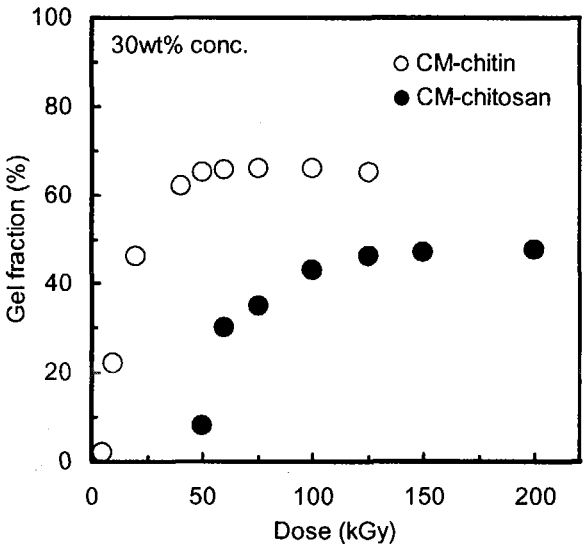


Fig. 3. Effect of irradiation dose on crosslinking of CM-chitin and CM-chitosan.

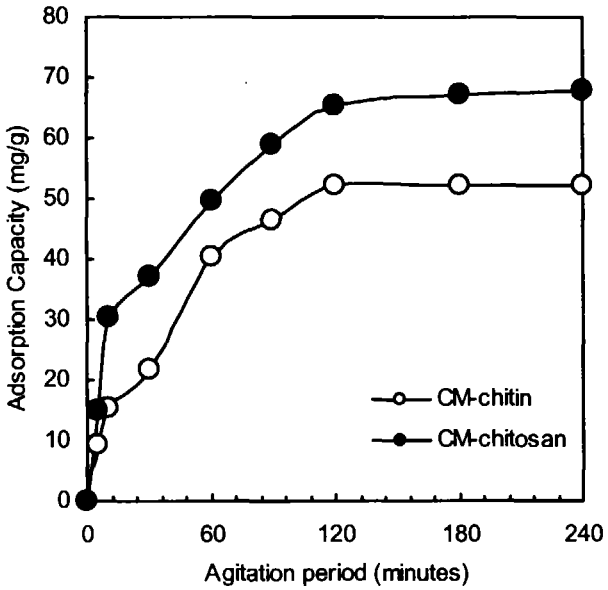


Fig. 4. Absorption kinetics of Cu^{2+} on crosslinked CM-chitin and CM-chitosan.

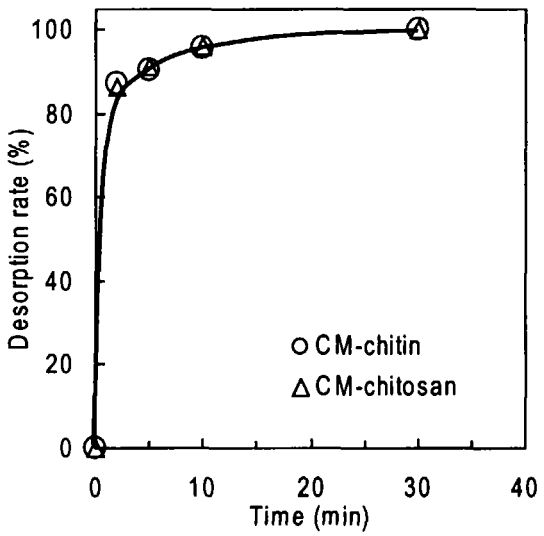


Fig. 5. Desorption kinetics of Cu^{2+} on crosslinked CM-chitin and CM-chitosan.

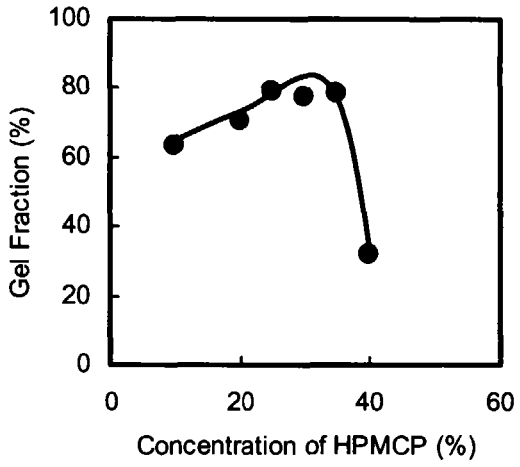


Fig. 6. Radiation crosslinking of HPMCP in 5% Na_2CO_3 solution.