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Carbohydrate Polymers 58 (2004) 109–113
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

Radiation crosslinking of carboxymethyl starch

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Received 28 April 2003; revised 19 April 2004; accepted 19 April 2004

Available online 8 September 2004

Abstract

A new biodegradable starch derivative hydrogel, carboxymethyl starch (CMS) hydrogel, was synthesized by irradiation in high concentrated solution (in the so-called paste-like condition). The effect of the solution concentration on the crosslinking of CMS, the properties of formed hydrogel and the biodegradability were investigated. The crosslinking of CMS was induced by irradiation at concentration range from 20 to 50%. One gram of the dry gel formed from the solution at concentration of 40% crosslinked at dose of 2 kGy was able to absorb about 500 and 26 g of distilled water and 0.9% NaCl, respectively. Biodegradation of crosslinked CMS (irradiated in 50% solution at a dose of 5 kGy) by controlled composting was about 40% after 2 weeks which was faster than standard cellulose powder. The contribution of crosslinking in CMS was elucidated from crosslinking behaviors of carboxymethyl amylopectin (CMAP) and carboxymethyl amylose (CMA). The crosslinked CMAP (irradiated at a concentration range from 10 to 50%) reveal higher gel fraction and water-uptake than that of CMA. The amylopectin region in CMS is predominantly responsible for crosslinking of CMS.

Keywords: Radiation; Crosslinking; Carboxymethyl starch; Hydrogel; Carboxymethyl amylopectin; Carboxymethyl amylose; Biodegradation

1. Introduction

Starch is a potentially useful material for biodegradable plastics because it is a natural abundant polysaccharide produced as a storage polymer from many plants (Aggarwal, 1999; Iman, Gordon, Mao, & Chen, 2001; Lörcks, 1998; van Soest & Vliegenthart, 1997) Usually, it has two major components and appears as a mixture of two glycosidic macromolecules which are very different in structure and properties: linear amylose consisting of α-(1 → 4)-linked D-glucose, and amylopectin, having the same backbone as amylose but with myriads of α-(1 → 6)-linked branch points. Starch and its derivatives such as carboxymethyl starch (CMS), hydroxyethyl starch, and hydroxypropyl starch that are soluble in water have been widely used in many industrial applications such as food, medicine and cosmetic fields (Choi & Kerr, 2003; Husband, 1998; Lévy & Andry, 1990; Thevis, Opfermann, & Schänzer, 2000).

Ionizing radiation has been well known as a very convenient tool for modification of polymer materials through crosslinking, grafting and degradation techniques. Such modified materials are used in many products, e.g. foams and automobile tyres which are produced by the radiation crosslinking. Recently, we found that the hydrogels of carboxymethyl cellulose, carboxymethyl chitin and carboxymethyl chitosan in paste-like condition can be prepared by radiation-induced crosslinking (Fei, Wach, Mitomo, Yoshii, & Kume, 2000; Zhao, Mitomo, Nagasawa, Yoshii, & Kume, 2003). However, these original polysaccharides are more expensive than starch. So from that reason usage of the starch derivatives for utilization in the agricultural field seems to be more appropriate. In this article, the crosslinking of carboxymethyl starch (CMS) is reported. Carboxymethyl amylopectin (CMAP) and carboxymethyl amylose (CMA) were irradiated in paste-like condition to elucidate their contribution to the crosslinking of CMS.

2. Experimental

2.1. Materials

All starch derivatives modified from maize starch were received from Gun Ei Chemical Industry Co. Ltd, Japan.

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doi:10.1016/j.carbpol.2004.04.021

The degrees of substitution (DS) were 0.15 for CMS, 0.25 for CMAP and 0.24 for CMA, respectively. All chemicals used were analytical grade.

2.2. Sample preparation and irradiation

CMS powder was added to deionized water, which was then mixed until homogeneous in dilute solution, viscous solution, and highly concentrated solution (paste-like condition) using a hybrid mixer HM-500 (Keyence Co., Ltd, Japan). After that samples were irradiated at dose range of 1–50 kGy. CMAP and CMA were also irradiated at the same dose range in highly concentrated solution.

The irradiation was carried out in polyethylene/nylon blend bag sealed after removal air by a vacuum pump. A dynamitron electron beam accelerator (3 MeV, 25 mA) was used with the following irradiation parameters: acceleration energy 2 MeV, beam current 1 mA, and the dose per pass 1 kGy.

2.3. Gel content and swelling of hydrogel

After irradiation, the CMS, CMAP and CMA dispersions were freeze-dried (freeze dryer FD-550 purchased from Tokyo Rikakikai Co., Ltd, Japan). Then the gel content in the dried samples was estimated by measuring its insoluble part in dried sample after immersion in deionized water for 48 h at room temperature. The gel fraction was calculated as follows

$$\text{Gel fraction } (\%) = \left(\frac{W_d}{W_i}\right) \times 100 \quad (1)$$

where W_i is the initial weight of dried sample after irradiation and W_d is the weight of the dried insoluble part of sample after extraction with water.

The swelling of the crosslinked sample was estimated by Japan Industrial Standard K8150. The dry gel was immersed in deionized water for 48 h at room temperature. After swelling, the hydrogel was filtered by a stainless steel net of 30 meshes. The swelling was calculated as follows

$$\text{Swelling} = \frac{(W_s - W_d)}{W_d} \quad (2)$$

where W_s is the weight of hydrogel in the swollen state.

2.4. Biodegradation method

The microbial biodegradability of the polymer in soil was evaluated by measuring released carbon dioxide (CO_2). Especially designed apparatus—MODA: Microbial Oxidative Degradation Analyzer (Saida Ironworks Co., Ltd), comprised of four independent lines of columns in parallel, was used. Ten grams of the sample along with rinsed sea sand—450 g, and compost—130 g, was placed in the heated reaction column after mixing (Uematsu et al., 2002). Monitored temperature inside the column was 35 °C and the flow of CO_2-free but moisturized air was 30 ml min^{-1}. After flowing through the sample inside the reactor, the air, and CO_2 formed due to polymer decay were passed through a series of columns filled in turn with silica gel, calcium chloride, soda lime and calcium chloride. Ammonia, which was formed from the compost, was trapped in sulphuric acid solution, and water vapor was absorbed into the first two columns (silica gel and calcium chloride). The CO_2 was collected quantitatively by soda lime while water produced during the reaction was caught in the last calcium chloride column. Thus, the mass of produced CO_2 was calculated as a difference in the weight of two last columns (containing soda lime and calcium chloride) at the beginning and during the test. Pure compost mixed sea sand was used as a blank sample and cellulose powder as a reference sample.

3. Results and discussion

3.1. Crosslinking of CMS

CMS with DS 0.15, at a high concentration range of 10–50% solution was strongly kneaded with water in a plastic vessel by using hybrid mixer to obtain a homogeneous mixture and then degassed to remove air prior to irradiation. This is called the paste-like condition. The irradiation of CMS in this state resulted in crosslinking while irradiation of CMS in dilute aqueous solutions below 10% and in the solid state led to a degradation. It was reported that water enhances the mobility of rigid polymer molecule allowing the diffusion of macroradicals and induces in the increasing of radical concentration by the products of water radiolysis (Peppas & Merrill, 1977). The most reactive species were reported to be hydrogen atoms and hydroxyl radicals. Fig. 1 shows the gel fraction of

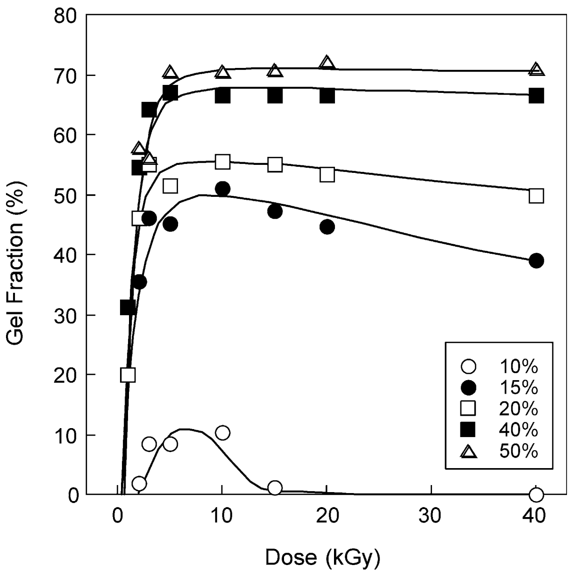

Fig. 1. Effect of concentration on crosslinking of CMS irradiated in vacuum.

CMS crosslinked in paste-like condition at different degree of irradiation. At 10% solution, a small gel fraction is lean at 10 kGy, but the gel disintegrate at 20–40 kGy due to degradation. Even for concentration of 15 and 20%, a decrease in gel fraction was observed at higher dose such as 40 kGy. At higher concentration solution (40, 50%), gel fraction reached 50% at a low dose of 3 kGy and started to saturate at 5 kGy. The dose required for crosslinking of CMS is relatively smaller than that of CMC (Fei et al., 2000). Maximum gel fraction is particularly dependant on the concentration of CMS.

The main chemical effects on polymers subjected to ionizing radiation are crosslinking and degradation by chain scission. Both processes occur simultaneously and their yields determine the final results of irradiation (Chapiro, 1962). If crosslinking predominates over scission, an insoluble macroscopic gel is formed. In this case, the sol–gel analysis allows to estimate parameters of the radiation processing (Chapiro). Gel contents of polymers irradiated in highly concentrated solution was presented. The amount of insoluble fraction (gel) was used to determine soluble part (sol). The ratio of degradation to crosslinking density (p_0/q_0) was estimated by sol–gel analysis and calculated using the Charlesby–Rosiak equation (Olejniczak, Rosiak, & Charlesby, 1991). The p_0/q_0 corresponds directly to obtained gel fraction and it is equal to the half of the scission yield and crosslinking yield ratio; $0.5 \times G_{(s)}/G_{(x)}$ (detailed explanation in Olejniczak et al.). If this p_0/q_0 parameter decreases, the crosslinking occurs more effectively than the scission. Fig. 2 gives p_0/q_0 parameter with corresponding concentration of CMS. The p_0/q_0 parameter decreases with increasing concentration of polymer. At a concentration of 40% solution, the p_0/q_0 parameter is lowest among various concentrations, 40% is the most effective for crosslinking. Thus, irradiation in paste-like condition is effective for crosslinking of CMS. As described in our previous paper, irradiation of carboxymethyl cellulose (CMC), carboxymethyl chitin (CM-chitin), and carboxymethyl chitosan (CM-chitosan) at paste-like condition led to efficient crosslinking (Fei et al., 2000; Zhao et al., 2003). Chemical crosslinkers such as formaldehyde and epichlorohydrin are frequently used for introducing intermolecular bonding of CMS but it is expected that some unreacted chemicals remained in the crosslinked CMS (Iman et al., 2001; Shukla, Rajagopalan, Bhaskar, & Sivaram, 1991; Trimnell, Shasha, & Otey, 1985). On the other hand, crosslinking of paste-like samples was induced only by irradiation and obtained product is of a high purity. This advantage makes radiation crosslinking of CMS superior to the methods mentioned above.

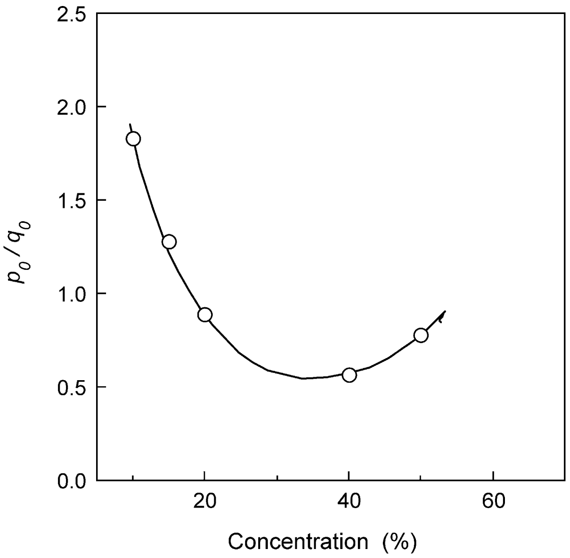

Fig. 2. The p_0/q_0 ratio of crosslinked CMS at high-concentrated solution.

3.2. Swelling and biodegradability of crosslinked CMS

The basic feature of hydrogel is that it can absorb and hold huge amount of solvent in its network structure. This swelling property is a very important factor for its future application of hydrogels. Fig. 3(a) and (b) show the swelling of crosslinked CMS in deionized water and 0.9% NaCl. The swelling in deionized water and 0.9% NaCl decreases with increasing dose as well as with increasing concentration of polymer. This is probably due to dependence on increasing crosslinking density for the CMS gel. The gel crosslinked at concentration 10 and 15% reveals different swelling behavior at higher dose. It is apparent from Fig. 2 that CMS at 10 and 15% degraded with continuous irradiation. Thus, breaking of chain in the gel may be responsible for the increase in swelling above 20 kGy. Gel crosslinked at a concentration of 40% and a dose of 2 kGy absorbs 500 g of distilled water. Swelling of the gel in 0.9% NaCl is 20 times lower than in water. We reported in our previous paper that biodegradable hydrogel of polysaccharide derivative such as CMC has swelling of 360 in water and 60 in 0.9% NaCl (Fei et al., 2000). Swelling in water of the CMS is higher than that of CMC. It is known that starch can dissolve in hot water whereas cellulose does not, due to the strong hydrogen bonds between its molecular chains. According to Larsson (1998), it was reported that branched-type polymer amylopectin aggregated with increasing salt content, the aggregation may have also occurred between amylopectin molecules of CMS.

Biodegradable polymer after use is transformed to carbon dioxide and water by digestion and by bacterial degradation in the soil. This property is an advantageous characteristic of hydrogels developed in agricultural, medical and other fields. Biodegradability of crosslinked CMS as a function of incubation time in the controlled compost is shown in Fig. 4. The biodegradation of unirradiated and crosslinked CMS (irradiated in 50% solution at a dose of 5 kGy) by controlled compost after 2 weeks was about 43.3 and 39.5%, respectively. The biodegradation of unirradiated and crosslinked CMS were

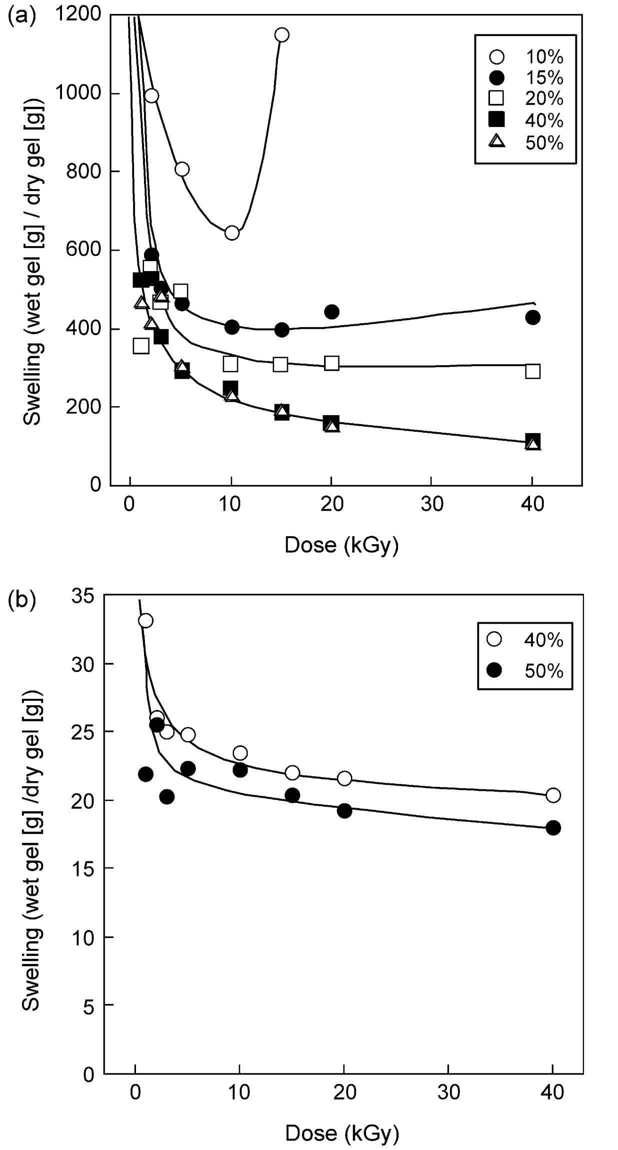

Fig. 3. Swelling of hydrogels of CMS: (a) in distilled water; (b) in 0.9% NaCl.

faster than that of cellulose powder standard. Furthermore, compared to CMC gel (irradiated in 20% solution at a dose of 20 kGy) the value of gel content of CMS is equal, but the degradation of CMS gel is 10 times faster than that of CMC gel after 2 weeks in compost. It is an environmentally acceptable material even after crosslinking. As a result, crosslinked CMS after use undergoes biodegradation by naturally existing microorganisms in the soil.

3.3. Contribution of crosslinking region in CMS

CMAP with DS 0.25 and CMA with DS 0.24 were also irradiated in paste-like condition in order to elucidate their contribution to the crosslinking of CMS. The gel fractions and swelling ratios of crosslinked CMAP and CMA are shown in Figs. 5 and 6, respectively. The crosslinked CMAP had higher gel fraction and water-uptake at high

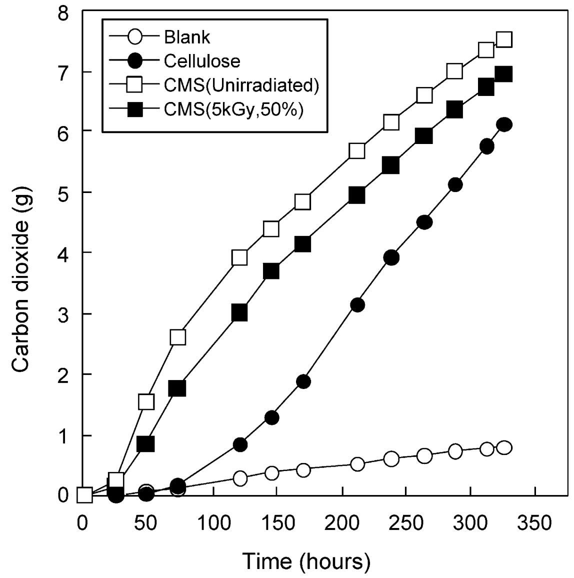

Fig. 4. Biodegradation of hydrogels of CMS using microbial oxidative degradation analysis.

concentration (10–50%) than that of CMA at 50% solution. From the Fig. 5, one can see that gelation behavior of CMAP is similar to CMS (compare to Fig. 1). However, the gel fraction of CMAP at lower doses is higher than that of CMS. CMAP consist of amylopectin has branch-type structure, so that this polymer might form physical gel in high concentrated solution (in paste-like condition) due to entanglements between molecules. CMA did not lead to crosslinking in a concentration range of 10–20% solutions. Only CMAP at a concentration of 50% reveal increase of gel fraction with increasing dose. It is similar to CMC gelation behavior because of their liner structure (Wach, 2002). On the other hand, according to Fig. 6, swelling

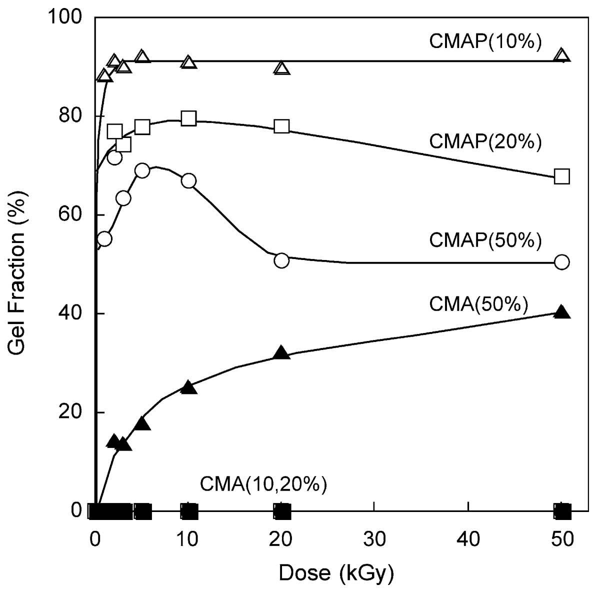

Fig. 5. Influence of irradiation dose on the resulted gel fraction of hydrogels, respectively. Hydrogels of CMAP (open points) and CMA (solid points) formed at high-concentrated solution by irradiation in vacuum.

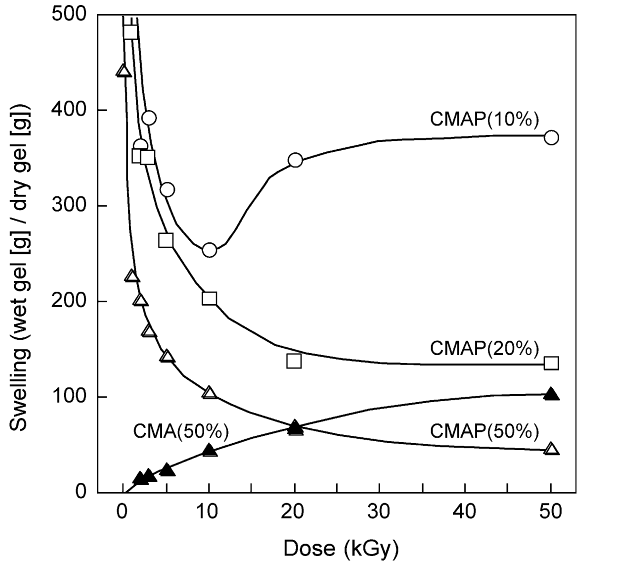

Fig. 6. Swelling of hydrogels of CMAP and CMA in distilled water, respectively.

behavior of CMAP is also comparable to CMS. With increasing dose, CMAP could form a covalently bonded chemical gel. These observations suggest that amylopectin region is predominantly responsible for the crosslinking of CMS. This assumption was further confirmed by the p_0/q_0 ratio. The comparison of p_0/q_0 for CMS, CMAP and CMA irradiated in a concentration of 50% solution are 0.78, 0.36, and 1.28, respectively, estimated by sol–gel analysis on the basis of the Charlesby–Rosiak equation as mentioned above. The factor of CMAP is smaller among that of these polymers. From these results, it is also suggested that amylopectin region is predominantly responsible for the crosslinking of CMS.

4. Conclusion

Hydrogel from starch derivatives were synthesized by ionizing radiation without any additives. It was found that high concentration in aqueous solution, so-called paste-like condition of polymer was favorable for crosslinking. The obtained hydrogel was able to swell significantly by water absorption. The swelling is influenced by the concentration in which the polymer was irradiated and by an applied dose. The hydrogels were biodegradable materials due to keep degrading in controlled compost. The amylopectin region in the starch appears to be predominant in the crosslinking of CMS.

Acknowledgements

We thank Mr Hiroaki Saito (Gun Ei Chemical Industry Co., Ltd, Japan) for providing us with various samples and specifications. One of the authors (Naotsugu Nagasawa) would like to express his gratitude to Dr Radoslaw A. Wach (The University of Tokyo), Ms Lorna S. Relleve (Philippine Nuclear Research Institute), Mr Jaroslaw Wasikiewicz (Gunma University) and Prof. Janusz M. Rosiak (Technical University of Lodz, Poland) for the comments and discussion and Mr Hiroaki Hanaya and Mr Shigeyuki Maniwa (Irradiation Service Division, Japan Atomic Energy Research Institute) for help with the irradiation experiment.

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