Carboxymethyl Starch Cross-Linked by Electron Beam Radiation in the Presence of Acrylic Acid Sensitizer: Postprint

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Abstract

Carboxymethyl starch (CMS) can be cross-linked by electron beam radiation to form a biocompatible and environment-friendly hydrogel at a high absorbed dose and a condensed CMS concentration. Acrylic acid (AAc) can be used as a sensitizer in order to reduce the absorbed doses to an acceptable certain level. At an absorbed dose of 3 4 kGy, the gel content of crosslinked CMS can be obtained about 50% with 5% (w/w) AAc concentration used. The compressive strength of CMS samples increased with increasing their cross-linked densities due to raising absorbed doses. The swelling ratio of cross-linked CMS was also attainable at a maximum of 50 times in the distilled water. The enzymatic degradation of cross-linked CMS was carried out in acetate buffer pH 4.6 with 0.1% α-amylase enzymatic solution incubated at 40^{o}C for 6 h. The crosslinked CMS samples were degraded slower than uncrosslinked CMS ones. The results indicated that the highly cross-linked CMS was almost fully degradable when the enzymatic hydrolysis was performed during 6 h. The FT IR spectra of cross-linked CMS in the presence of AAc were examined to observe the carboxyl group of AAc in the structure of cross-linked CMS. The hydrophilic of cross-linked CMS surface was determined by a contact-angle analysis.

Full Text

Preamble

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Abstract

Carboxymethyl starch (CMS) can be cross-linked by electron beam radiation to form a biocompatible and environment-friendly hydrogel at high absorbed doses and condensed CMS concentrations. Acrylic acid (AAc) can be used as a sensitizer to reduce the absorbed doses to an acceptable level. At an absorbed dose of 3–4 kGy, a gel content of about 50% can be obtained for crosslinked CMS when using 5% (w/w) AAc concentration. The compressive strength of CMS samples increased with increasing cross-linked densities due to higher absorbed doses. The swelling ratio of cross-linked CMS was also attainable at a maximum of 50 times in distilled water. The enzymatic degradation of cross-linked CMS was carried out in acetate buffer pH 4.6 with 0.1% α-amylase enzymatic solution incubated at 40°C for 6 h. The crosslinked CMS samples degraded slower than uncrosslinked CMS ones.

The results indicated that the highly cross-linked CMS was almost fully degradable when enzymatic hydrolysis was performed for 6 h. The FTIR spectra of cross-linked CMS in the presence of AAc were examined to observe the carboxyl group of AAc in the structure of cross-linked CMS. The hydrophilicity of the cross-linked CMS surface was determined by contact-angle analysis.

Keywords: Sensitizer, Carboxymethyl starch, Crosslinking, Biodegradation, Electron beams, Radiation, Hydrophilic

Introduction

Crosslinked HEMA hydrogel was investigated in 1960 for its hydrophilic character and biocompatible potential [**?**]. Later, hydrogels combining natural and synthetic polymers have attracted interest in fields such as controlled drug release, wound dressing, cell encapsulation, tissue engineering, and as matrices for repairing and regenerating a wide variety of tissues and organs [**?**, **?**]. Hydrogels are called chemical gels when they form covalently crosslinked networks. A hydrogel can absorb from dozens to thousands of times its dry weight in water [**?**]. Polysaccharide derivative hydrogels may be crosslinked by irradiation under paste-like conditions. Hydrogels can form from radiation crosslinking of carboxymethyl cellulose (CMC), carboxymethyl starch, carboxymethyl chitin, and condensed carboxymethyl chitosan concentrations (higher than 10%). These hydrogels swelled well in water and were biodegradable [**?**].

Radiation crosslinking of carboxymethyl starch (CMS) was carried out at paste-like concentrations (20–50%). It was proved that the amylopectin region in CMS was predominantly responsible for crosslinking of CMS [**?**]. The gel strength of

CMC treated with irradiation combination (5–10 kGy) with acid immersion was 100 times higher than that of CMC untreated with acid [**?**]. The relationship between structure and drug release of CMS has mutual influence of drying procedures and its degree of substitution [**?**]. Biodegradability of blend hydrogels based on CMC and CMS was evaluated. The ratio of CMC part to CMS one in the blend influenced radiation crosslinking characterizations such as gel fraction, swelling degree, gel strength, and biodegradability [**?**]. Electron beam crosslinking of CMS at high absorbed dose of 50 kGy, at 50% (v/v) concentration has been investigated with gel content obtained max. 87.1%. Radiation crosslinked CMS was used to remove iron in aqueous solution [**?**].

2.1 Materials

Sodium carboxymethyl starch EMSIZE CMS-150 (Mw=600 kDa, DS=0.85, Emsland Stärke, Germany); α-amylase enzyme (Himedia, India); acrylic acid (BASF, Germany); acetic acid, sodium acetate, calcium chloride ($CaCl_2$) (China); distilled water were used during the experiment.

2.2 Preparation of CMS Hydrogel

The formulation of 35% CMS and 1% AAc was prepared as follows: 350 g of CMS powder was weighed and placed into a 2 L beaker with 650 mL of distilled water available. The mixture was stirred at room temperature for 2 h to obtain a homogeneous state, and then 9.5 mL of AAc was added while the system continued stirring for an additional 1 h. The paste-like CMS mixture was packed in polyethylene bags and stood overnight before irradiation on an electron beam accelerator with 10 MeV and 15 kW power (UERL-10-15S2, Russia) at absorbed doses of 3.5, 7.0, 10.5, and 14 kGy. Drying of the sample was performed at 70°C for 15 h. The dried CMS was then ground into 300 mesh particles. Similarly, samples of 35% CMS with additions of 3% and 5% AAc were also formulated. A blank sample of 35% CMS without AAc was prepared following the above-mentioned steps.

2.3 Determination of Characteristic Properties of Crosslinked CMS

2.3.1 Gel Content

0.15 g of sample covered by stainless steel net was extracted in a Soxhlet instrument with distilled water as solvent for 24 h. The sample was dried in an oven at 70°C overnight, kept in desiccators for 4 h before weighing. The gel content was expressed as follows:

$$\text{Gel content } (\%) = (W_g/W_i) \times 100$$

where W_i and W_g are the weights of initial dry CMS and extracted dry CMS with hot water, respectively.

2.3.2 Swelling Ratio

0.5 g of sample was weighed and immersed in 100 mL of distilled water for 48 h. The swollen CMS gel was taken out, excessive water on the surface of the sample absorbed with tissue paper, and then weighed. The swelling ratio (the amount of water absorbed by the CMS gel) was defined as follows:

$$\text{Swelling ratio (g/g)} = (W_s - W_g)/W_g$$

where W_s is the weight of the swollen CMS gel.

2.3.3 Compressive Strength

The strength of the gel immersed in water was tested on a Strograph V 10-C tester (Toyoseiki, Japan). Maximum stresses at 50% compression were measured for cylindrical formed gel.

2.3.4 Enzymatic Degradation

25 mg of sample was weighed and placed in tubes with screwed caps containing 4 mL of acetate buffer solution at pH 4.6, 1 mL of 0.1% $CaCl_2$ solution, and 1 mL of 0.1% α-amylase solution (10^6 cfu/mL). The tubes were incubated at 40°C in a thermostat bath. The experimental cycle was carried out for 6 h; every hour, one sample was taken out, filtered by filter paper, washed with distilled water several times, dried at 70°C overnight, stored in desiccators for 4 h, and then weighed until its weight was constant. Loss of CMS gel weight was determined as follows:

$$M(\%) = [(m_0 - m_1)/m_0] \times 100$$

where M, m_0, and m_1 are the weight percentage of lost dry CMS gel, weight of initial dry CMS gel, and of residual dry CMS gel, respectively.

2.3.5 FT IR Spectra

FTIR spectra of the gel with 3% AAc and without AAc that were irradiated at 10.5 kGy were measured by FTIR 8400S spectrophotometer (Shimadzu, Japan).

2.3.6 Hydrophilic (Wetting Property) Analysis

Contact angle measurement of swollen CMS gel membranes with AAc at various concentrations and without AAc was performed on the Contact Angle Instruments, GmbH, System OCA (Dataphysics Germany) at 25°C.

3.1 Gel Content

Figure 1 [Figure 1: see original paper] shows the change of EB absorbed doses in gel content of CMS in the presence of acrylic acid sensitizer at concentrations of 0, 1, 3, and 5% (w/w). Gel content of CMS increases with increasing absorbed doses and AAc concentration. At the optimal dose of around 3–4 kGy, a gel content of 60% can be obtained, except at lower AAc concentrations where gel contents are attainable at a low value of 20%–30% at 7 kGy. Without AAc, the gel content in crosslinked CMS is the lowest.

3.3 Compressive Strength at 50% Compression

Figure 3 [Figure 3: see original paper] shows the relationship between EB absorbed doses and maximum stress at 50% compression of CMS gel (sometimes called gel strength) with different AAc concentrations. The gel strength of CMS gel increases with increasing doses. The increase of AAc concentration also leads to increased strength. This means that the gel strength increases with higher durability of the gel due to increased crosslinking as seen in Fig. 3.

3.2 Swelling Ratio

Figure 2 [Figure 2: see original paper] shows the effect of absorbed doses on swelling ratio of CMS in the presence of acrylic acid sensitizer at concentrations of 0%, 1%, 3%, and 5%. The water absorbed reduces with increase of absorbed doses and AAc concentration, which is consistent with crosslinking theory of a predominantly crosslinked polymer. The swelling ratio of CMS gel decreases to a minimum at 3–4 kGy. At doses higher than 5 kGy, the water absorbed in CMS gel almost remains unchanged. This can be explained that crosslinked CMS gel makes network space in the structure smaller. When doses increase higher than 10 kGy, there is an increase of water uptake of CMS without AAc due to partial degradation of CMS gel.

3.4 Enzymatic Degradation of CMS Gel

Figure 4 [Figure 4: see original paper] shows hydrolyzed time of CMS gel at various EB absorbed doses versus weight loss of CMS gel. The slow hydrolyzation of CMS gel with α-amylase enzyme at 3.5 kGy absorbed dose and 5% AAc concentration reveals that the crosslinking of CMS gel was optimal compared to other CMS gels at higher absorbed doses (7, 10.5, 14 kGy) and lower AAc concentrations (1 and 3%), which were anticipated to be a certain region of CMS gel radiation-degraded at high doses. Crosslinked CMS gels with added AAc sensitizer probably degraded in enzymatic media at a significant level.

3.5 FT IR Spectra

Figure 5 [Figure 5: see original paper] shows the FTIR spectra of CMS with or without AAc sensitizer. A peak at 1728 cm^{-1} is assigned to the carboxyl group (-COOH) of acrylic acid in the CMS chain. Another peak appearing at 1161 cm^{-1} is referred to as the -C-O group in CMS.

3.6 Wetting Property of CMS Gel Membrane

Figure 6 [Figure 6: see original paper] shows the effect of absorbed doses on wettability of CMS gel membrane at 5% AAc concentration measured indirectly by contact angle technique. Contact angle measured for CMS gel increases with increasing absorbed doses. This means that hydrophilicity of CMS gel membrane reduces with increased crosslinking ability at 5% AAc concentration. It suggests that the selection of a suitable EB absorbed dose for practical application of CMS gel such as cosmetics and personal care (face mask) should have a highly relative wettability.

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4 Conclusion

AAc plays an essential role as a sensitizer for reduction of absorbed doses in EB radiation crosslinking of CMS. The results indicated that AAc accelerates CMS crosslinking through increasing gel content and gel strength of CMS gel. The CMS gel with physical characteristics comprising 60%–70% gel content and 70–80 (g/g) swelling ratio can be formed by EB radiation crosslinking at 35% CMS, 3%–5% AAc concentration at 3–4 kGy absorbed dose.

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Note: Figure translations are in progress. See original paper for figures.