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Synthesis of carboxymethylcellulose/acrylic acid hydrogels with superabsorbent properties by radiation-initiated crosslinking

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HIGHLIGHTS

- CMC/AAc hydrogels were prepared by radiation-induced crosslinking.
- Gelation required lower dose and solute concentration in CMC/AAc solutions.
- Increased AAc concentration improved the gel fraction at the expense of water uptake.
- In mild synthesis conditions CMC/AAc gels had better properties than pure CMC gels.
- Substitution of CMC with AAc up to 10% proved to be the most effective.

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ABSTRACT

Superabsorbent hydrogels were prepared by gamma irradiation from aqueous solutions of carboxymethylcellulose (CMC) and acrylic acid (AAc) with varying CMC:AAc ratio. By partially replacing the CMC with AAc the gelation increased and led to a higher gel fraction and lower water uptake. Moreover, the gelation required significantly milder synthesis conditions. Decreasing both the dose and the solute concentration in the presence of AAc led to gels with higher gel fraction and higher degree of swelling compared to pure CMC gels. Increasing the AAc content up to 10% proved to be very effective, while very high AAc content (over 50%) hindered the gelation process.

1. Introduction

Carboxymethylcellulose (CMC) is one of the major low-cost, commercially available derivatives of cellulose with a wide array of industrial applications (Heinze and Koschella, 2005). An interesting potential application is the preparation of hydrogels with superabsorbent properties (Chang and Zhang, 2011). CMC has several advantageous properties for gel synthesis, such as good water solubility and the presence of reactive hydroxyl and carboxymethyl groups. The non-toxic nature and biocompatibility of such gels is advantageous for biomedical applications (Caló and Khutoryanskiy, 2015). Moreover, its good biodegradability in soil is advantageous for its use in agriculture and forestry (Nie et al., 2004). Cellulose derivative gels are prepared from aqueous solutions with several crosslinking methods. While common crosslinking agents such as divinylsulfone (Sannino et al., 2004) and epichlorohydrin (Chang et al., 2010) are effective for the chemical crosslinking of CMC, they are mostly used for the synthesis of various CMC copolymer gels. However, pure CMC gels were also prepared with several non-toxic crosslinkers like citric acid (Demitri et al., 2008) and fumaric acid (Akar et al., 2012). The gelation can also be achieved without crosslinkers by free-radical crosslinking. Moreover, with high-energy irradiation no initiator is required for the synthesis (Fei et al., 2000; Liu et al., 2002).

Besides pure CMC gels copolymers with other monomers such as acrylamide (Ibrahim et al., 2007; Heimvichian et al., 2014) or acrylic acid (AAc) were also prepared. Carboxymethylcellulose/

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acrylic acid hydrogels were previously synthesized by using crosslinking agent/initiator system (Bajpai and Mishra, 2004) and electron beam irradiation (Said et al., 2004; El-Naggar et al., 2006). In the latter method gels with high gel fraction and moderate swelling properties were prepared successfully. However, it should be noted that relatively low carboxymethylcellulose concentration was used (4.2 w/v% as opposed to the acrylic acid concentration of 10–50 w/v%) and high absorbed doses (50–80 kGy) were required. As pure concentrated solutions of CMC can also form gels by high-energy irradiation, the gelation of CMC/AAc solutions with low AAc content should be also examined.

In the present work we prepared gels using high concentration aqueous solutions of carboxymethylcellulose and acrylic acid with different blend ratios. The aim of this work is to form gels at milder synthesis conditions and to achieve better gel properties compared to the pure CMC gels reported in our previous study (Fekete et al., 2014) by substituting a part of the cellulose derivative content with acrylic acid while keeping the AAc concentration relatively low.

2. Experimental

2.1. Materials

Carboxymethylcellulose Na-salt (M_w=700,000 g mol^{-1}, D_S=0.9, properties provided by the manufacturer) and acrylic acid (anhydrous, contains 180–200 ppm monomethyl ether of hydroquinone (MEHQ) as inhibitor) of analytical grade were purchased from Sigma-Aldrich. No purification was used.

2.2. Synthesis

Aqueous solutions of CMC and AAc were prepared from 5 to 40 w/w% solute concentrations. The CMC:AAc ratio varied from 100:0 to 20:80. First, the acrylic acid was mixed with the water, and then the CMC powder was added to the solution. After stirring the solutions were stored at room temperature for 24 h to improve homogeneity. Spherical samples formed from the paste-like solution were put into polyethylene bags. The solutions were irradiated with ^{60}Co γ-source at a dose rate of 9 kGy h^{-1} with an absorbed dose from 1 to 80 kGy. Three samples were used during the measurements to determine the standard deviation.

2.3. Gel fraction

The sol fraction was removed by immersing the samples in deionized water for 48 h (1000:1 liquid ratio). Swollen gels were removed by a metal sieve and dried to constant weight at 60 °C. The gel fraction (GF) was calculated from the dry gel weight before (w_0; calculated from the solution concentration) and after (w_1) the process

$$GF\ (\%) = \frac{w_1}{w_0} \times 100 \tag{1}$$

2.4. Degree of swelling

Dried, washed (see Section 2.3) samples were immersed in deionized water. After 24 h, gels were removed from the water and weighted. The degree of swelling (Q) was calculated from the weight of the swollen (w_s) and the dry gel (w_d)

$$Q\left(\frac{g_{water}}{g_{gel}}\right) = \frac{w_s - w_d}{w_d} \tag{2}$$

2.5. Composition of the hydrogel

ATR–FTIR spectra were recorded using ATI Mattson Research Series FTIR spectrometer. The accessory contained a ZnSe flat plate with a nominal incident angle of 45°. Gel samples were prepared by freeze-drying after immersion in water for 48 h. The spectra were recorded from 4000 to 500 cm^{-1} at a resolution of 8 cm^{-1}, averaged from 128 scans.

3. Results and discussion

Three synthesis parameters (absorbed dose, solute concentration and CMC:AAc blend ratio) were varied to determine their effect on the gel properties. ATR–FTIR spectroscopy was used to characterize the composition of the crosslinked samples.

3.1. Absorbed dose

The effect of the dose on gel properties was determined at three different CMC:AAc ratios (Fig. 1). Gel formation occurred only over a critical absorbed dose. Acrylic acid-free solutions

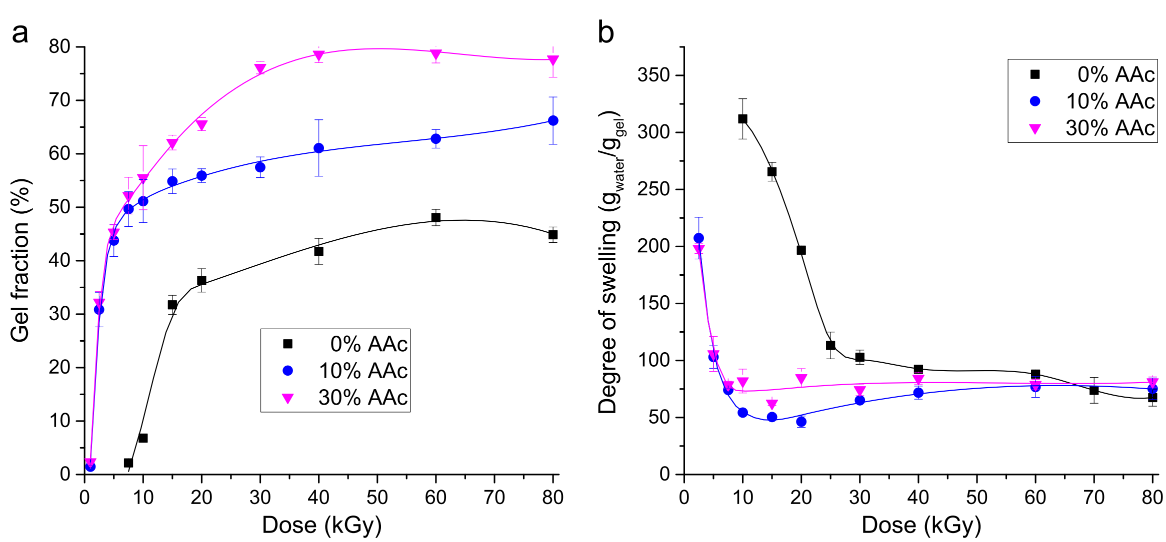

Fig. 1. Effect of the absorbed dose on gel fraction (a) and degree of swelling (b) for CMC/AAc gels with different AAc content (20 w/w% solution).