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Synthesis and characterization of superabsorbent hydrogels based on hydroxyethylcellulose and acrylic acid

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ABSTRACT

Hydroxyethylcellulose (HEC)/acrylic acid (AAc) copolymer gels with superabsorbent properties were synthesized from aqueous solutions by radiation-initiated crosslinking. The effect of the acrylic acid content on gel properties was determined at different synthesis conditions. The partial replacement of the cellulose derivative with acrylic acid improved the gelation, leading to higher gel fraction and lower water uptake even in very low concentrations (1–5%). In the presence of acrylic acid lower dose and solute concentration was required for the gel synthesis. The molecular properties of the hydroxyethylcellulose also had a major effect on the gelation: higher molecular mass resulted in better gel properties. The acrylic acid also affected the electrolyte sensitivity of the hydrogels: while pure HEC gels were unaffected by the ionic strength of the solvent, the water uptake of HEC/AAc gels decreased with the salt concentration. The sensitivity also depended on the acrylic acid ratio.

1. Introduction

Superabsorbent hydrogels are unique systems with several unique properties, such as very high water absorbing capacity and biocompatibility. There is an increasing demand for them in several fields (Zohuriaan-Mehr, Omidian, Doroudiani, & Kabiri, 2010), especially in various medical applications (Caló and Khutoryanskiy, 2015). While most commercially available products are synthetic polymer-based, the preparation of superabsorbent gels from cheap renewable materials like various polysaccharides (Augst, Kong, & Mooney, 2006; Ismail, Irani, & Ahmad, 2013), amino acids and peptides (Altunbas & Pochan, 2012; Wu, Wu, Mutschler, & Chu, 2012) is also widely studied. The use of such resources is not only more environmentally friendly, but other properties like biodegradability make them preferable in some potential applications, for example in the agriculture. One of the most important renewable resources is cellulose due to its abundance and low cost. While the gel formation of native cellulose is also in-depth investigated, recent studies focus mainly on the potential application of its derivatives due to their water solubility (Chang & Zhang, 2011; Shen, Shamshina, Berton, Gurau, & Rogers, 2016).

Hydroxyethylcellulose (HEC) is one of the most important commercially available cellulose derivatives. It is used as a stabilizer, thickener or coating at several application fields (BeMiller & Whistler, 1993). There is also a large interest towards its potential use for hydrogel synthesis. While the preparation of both physical and chemical gels is widely investigated for the cellulose derivatives, for hydroxyethylcellulose the studies focus on the chemical gelation. A possible method is the free radical crosslinking initiated by irradiation. Gamma-radiation and electron beam (Wach, Mitomo, Nagasawa, & Yoshii, 2003) are frequently used to initiate the reaction as UV irradiation requires the use of photoinitiators (Petrov, Petrova, Tchorbanov, & Tsvetanov, 2007; Velickova, Winkelhausen, Kuzmanova, Cvetovska, & Tsvetanov, 2009). In aqueous solutions the polymer radicals form in the reaction of the reactive intermediates of the water radiolysis (e.g. OH radicals) with the polymer chains (Fei, Wach, Mitomo, Yoshii, & Kume, 2000). The polymer radicals may initiate both crosslink formation and degradation at the same time. It depends mainly on the chemical structure of the polymer which process dominates. The gel formation is influenced by several factors such as the molar properties, atmosphere, irradiation type or absorbed dose (Wach et al., 2003).

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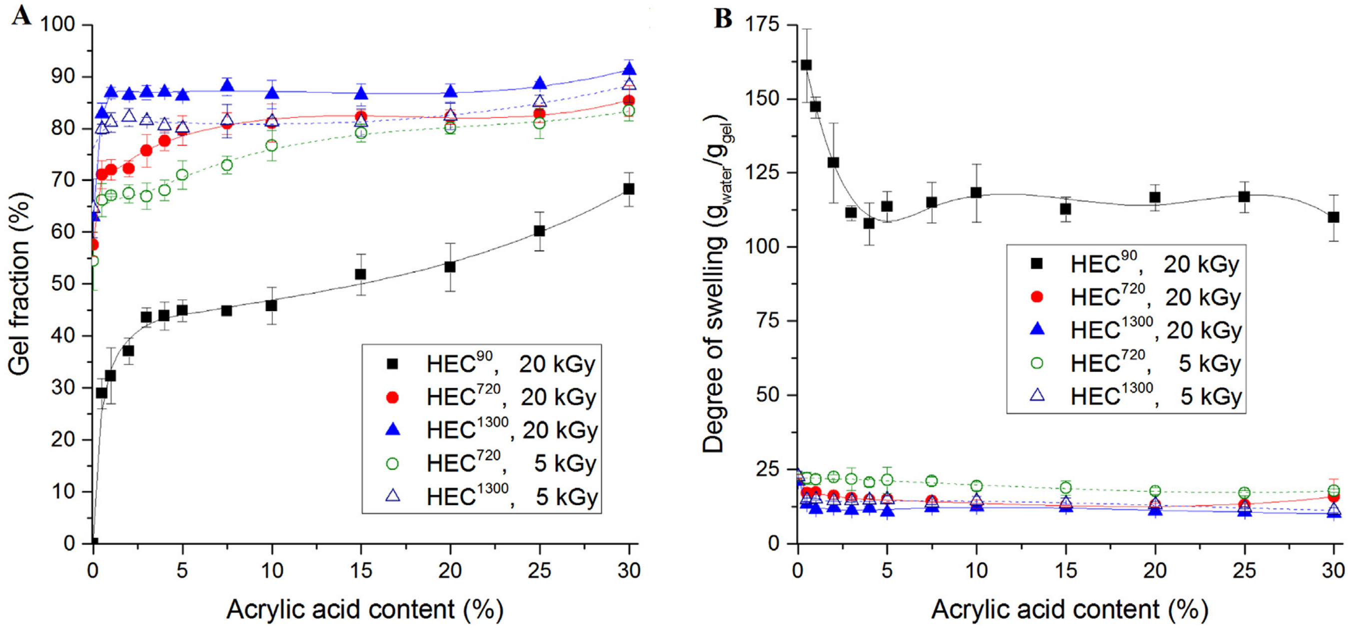

Fig. 1. The effect of the acrylic acid content on the gel fraction (A) and degree of swelling (B) of various HEC/AAc hydrogels (20 w/w% solution).

While such HEC gels showed good swelling properties, they were inferior compared to carboxymethylcellulose gels (Liu, Peng, Li, & Wu, 2005; Wach, Mitomo, Yoshii, & Kume, 2001). However, HEC is a non-polyelectrolyte, thus due to its lower electrolyte sensitivity its application may be advantageous depending on the environment (Fekete, Borsa, Takács, & Wojnárovits, 2014).

A common approach for the modification of gel properties is the introduction of a second polymer into the system: such copolymer gels may have the advantageous properties of both components. Hybrid gels are especially important in the medical field, where more than two polymers are often necessary to fulfill the requirements for their utilization (Jia & Kiick, 2009; Wu, Zhao, Wu, & Chu, 2014). Usually various synthetic polymers or their monomers are used for modification of cellulose derivative gels, for example acrylic acid (AAc) (Bajpai & Mishra, 2004; Fekete, Borsa, Takács, & Wojnárovits, 2016), acrylamide (Al-Kahtani & Sherigara, 2014; El-Mohdy, 2007), polyvinylpyrrolidone (Wang et al., 2007) or polyethylene-glycol (Lee, Nho, Lim, & Son, 2005). Grafting acrylic acid to cellulose or its derivatives is intensively studied due to their large potential in several fields, especially as drug delivery systems (Amin, Ahmad, Halib, & Ahmad, 2012) and wound dressings (Bajpai & Banger, 2014). Acrylic acid has no negative effect on the biocompatibility of the cellulose component, thus such copolymer hydrogels show very low cytotoxicity (Gao et al., 2014; Mohamad, Amin, Pandey, Ahmad, & Rajab, 2014) and good blood compatibility (Boruah et al., 2014). As the compatibility improves with the water content, good swelling properties are also crucial for such systems (Bajpai & Mishra, 2005). The introduction of a polysaccharide component is also beneficial for agricultural applications (Ni, Liu, Lü, Xie, & Wang, 2010) due to pure poly(acrylic acid) superabsorbents degrading very slowly in soil (Wilske et al., 2014). In case of hydroxyethylcellulose/acrylic acid systems, the initiation of the crosslinking is achieved by chemical initiator (Çavuş, Gürdağ, Yaşar, Güüçlü, & Gürkaynak, 2006); solutions generally also contain other additives such as clays (Wang, Wang, & Wang, 2010) or surfactants (Shi, Jietang, & Wang, 2015), as well. While such superabsorbents showed good gel properties, studies were limited to copolymers with very low cellulose derivative content, e.g. a HEC:AAc ratio of 1:6 was generally utilized; the gelling behavior of systems with high HEC content was not studied.

In this work hydroxyethylcellulose gels were modified with the partial replacement of HEC with acrylic acid. Our goal was to improve the gel properties of HEC hydrogels while keeping the hydroxyethylcellulose content as high as possible for a more environmentally friendly, biodegradable superabsorbent. Gamma-irradiation was utilized for the initiation of the gelation; no additives were required for the synthesis, thus avoiding the introduction of toxic components. The effect of the synthesis conditions on the gelation in the presence of the monomer was in depth investigated for three hydroxyethylcellulose samples with different molecular masses. Moreover, the sensitivity of the swelling to the ionic strength of the solvent was also examined for different copolymer gels to gain more information about their potential applications.

2. Experimental

2.1. Materials

Three kinds of HEC powder with identical molar substitution (M_S = 2.5) and differing molar masses (M_v = 90,000 (HEC^{90}), 720,000 (HEC^{720}) and 1,300,000 (HEC^{1300}) Da) were used in combination with acrylic acid monomer (AAc, contains 180–200 ppm MEHQ inhibitor). NaCl was used for swelling studies. All materials were of analytical grade and were purchased from Sigma-Aldrich.

2.2. Synthesis

Aqueous solutions of hydroxyethylcellulose and acrylic acid were prepared. First the acrylic acid was added to deionized water, followed by the HEC powder. Three HEC samples with different molecular masses were used for synthesis. The solute concentration ranged from 1 to 50 w/w%, while the HEC:AAc ratio varied from 100:0 to 70:30. After stirring the highly viscous, paste-like solutions were stored for 24 h at room temperature to improve the homogeneity. Spherical samples of ~1 g were formed and placed in polyethylene bags. The crosslinking step was carried out by gamma-irradiation. ^{60}Co source was used for irradiation, the absorbed dose ranging from 1 to 80 kGy at 9 kGy h^{-1} dose rate.