Carbohydrate Polymers 137 (2016) 59–64

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Biocompatible cellulose-based superabsorbent hydrogels with antimicrobial activity

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ARTICLE INFO

Article history:
Received 15 September 2015
Received in revised form 6 October 2015
Accepted 15 October 2015
Available online 19 October 2015

Keywords:
Cellulose hydrogel
Superabsorbent property
Biocompatible
Antimicrobial activity

ABSTRACT

Current superabsorbent hydrogels commercially applied in the disposable diapers have disadvantages such as weak mechanical strength, poor biocompatibility, and lack of antimicrobial activity, which may induce skin allergy of body. To overcome these hassles, we have developed novel cellulose based hydrogels via simple chemical cross-linking of quaternized cellulose (QC) and native cellulose in NaOH/urea aqueous solution. The prepared hydrogel showed superabsorbent property, high mechanical strength, good biocompatibility, and excellent antimicrobial efficacy against *Saccharomyces cerevisiae*. The presence of QC in the hydrogel networks not only improved their swelling ratio via electrostatic repulsion of quaternary ammonium groups, but also endowed their antimicrobial activity by attraction of sections of anionic microbial membrane into internal pores of poly cationic hydrogel leading to the disruption of microbial membrane. Moreover, the swelling properties, mechanical strength, and antibacterial activity of hydrogels strongly depended on the contents of quaternary ammonium groups in hydrogel networks. The obtained data encouraged the use of these hydrogels for hygienic application such as disposable diapers.

1. Introduction

Superabsorbent hydrogels are lightly crosslinked polyelectrolyte polymer networks with unique absorption capacity of up to several hundred times of their dried weight (Chang, Duan, Cai, & Zhang, 2010). They have been widely used in many fields such as drug delivery systems, tissue engineering, immobilization of protein and cells, agriculture and horticulture, and sanitary products (Sharma, Dua, & Malik, 2014; Zhang, Wang, & Wang, 2007; Zohuriaan-Mehr, Omidian, Doroudiani, & Kabiri, 2010; Chang & Zhang, 2011; Gawande & Mungray, 2015). Superabsorbent hydrogels were industrially developed in Japan and USA as early as 1980s for hygienic application, such as baby diapers and feminine napkins, which originated from the product of hydrolysis of starch-*g*-polyacrylonitrile in 1970 (Kabiri, Omidian, Zohuriaan-Mehr, & Doroudiani, 2011). The global demand for superabsorbent hydrogels is increasing and reaches 1.9 million metric tons in 2015 (Zhang et al., 2014). However, lack of biocompatibility and biodegradability is the major hassle for the present superabsorbent materials used worldwide as they are made from petroleum based monomers like acrylic acid and acrylamide. The remedy for this problem is to design the hydrogels by using natural polymers which usually would be biocompatible and biodegradable, but they have inferior mechanical properties compared to petroleum based polymers (Spagnol et al., 2012).

The techniques to improve the mechanical properties of hydrogels include increasing the cross-linking density and incorporation of inorganic materials or suitable polymers (Huang et al., 2007; Gong, Katsuyama, Kurokawa, & Osada, 2003; Haraguchi & Li, 2005). However, the former resulted in the decrease of swelling ratio of hydrogels while the latter need add new components to hydrogel networks. So these approaches were inapplicable to develop superabsorbent hydrogels with good mechanical strength. In our previous works, we found that cellulose with stiff molecular chains could act as support ingredient in the hydrogel networks and superabsorbent hydrogels can be obtained by introducing other hydrophilic polymers into the networks (Chang, He, Zhou, & Zhang, 2011; Chang, Duan, & Zhang, 2009). Therefore, it may be a

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http://dx.doi.org/10.1016/j.carbpol.2015.10.057
0144-8617/

Table 1
Conditions for the preparation of QC/cellulose hydrogels.

Code	QC		Cellulose	Weight ratio	Swelling ratio
	M_w ($\times 10^{-4}$)	DS	M_w ($\times 10^{-4}$)	QC/cellulose	g/g
Gel9-2	9.4	0.23	9.4	9:1	206.6
Gel9-4	9.4	0.42	9.4	9:1	337.3
Gel9-6	9.4	0.61	9.4	9:1	433.9
Gel25-2	25.6	0.28	9.4	9:1	247.1
Gel25-4	25.6	0.44	9.4	9:1	607.5
Gel25-6	25.6	0.69	9.4	9:1	983.9

relatively simple, cost-effective, and green approach way to fabricate cellulose based superabsorbent hydrogels.

Traditional diapers are breeding grounds for harmful bacteria after absorbing urine, which seriously threaten human health. To avoid the growth of bacteria and provide a healthy environment for baby skin during usage of a diaper, the antimicrobial activity of products is essential and new technique must be developed to suit the needs. Among the various antimicrobial agents, metallic nanoparticles have shown broad spectrum antibacterial activity (Cui et al., 2012; Loo et al., 2015), but both metallic nanoparticle and their syntheses may cause environmental toxicity or biological hazards (Kittler, Greulich, Diendorf, Koller, & Epple, 2010; Cheng, Betts, Kelly, Schaller, & Heinze, 2013; Sharma, Yngard, & Lin, 2009). Fortunately, modification of cellulose fibers with bactericidal species, such as quaternary ammonium, β-cyclodextrin with ciprofloxacin, siloxane sulfopropylbetaine, and *N*-halamine siloxanes, has become a facile way to endow them with antibacterial performance (Roy, Knapp, Guthrie, & Perrier, 2008; Dong et al., 2014; Ren et al., 2008; Chen et al., 2011). These results demonstrated that the effective modification of cellulose fiber can enhance the antibacterial performance of cellulose materials. Almost all studies confined only to modify the surface of cellulose fibers, but the technique to covalently incorporate bactericidal species into cellulose hydrogel networks have not been reported. Therefore, we attempt to introduce quaternary ammonium groups into hydrogel networks by solution blending of cellulose solution and quaternized cellulose solution, aiming to develop novel hydrogel materials with good mechanical strength, superabsorbent property, biocompatibility and antimicrobial activity. This paper reports the preparation of cellulose based hydrogels through chemical cross-linking cellulose and quaternized cellulose in NaOH/urea aqueous solution, besides the evaluation of superabsorbent properties, mechanical properties, biocompatibility, and antimicrobial activities of hydrogels, as well as the influence of chemical structure of quaternized cellulose on the properties of hydrogels.

2. Experimental

2.1. Materials

Two kinds of cellulose samples (cotton linter pulps) were supplied by Hubei Chemical Fiber Co. Ltd. Their weight-average molecular weights (M_w) were determined by static laser light scattering (DAWN DSP, Wyatt Technology Co.) to be 9.4×10^4 and 2.56×10^4. 3-Chloro-2-hydroxypropyltrimethylammonium chloride was purchased from Guofeng Fine Chemical Co. Ltd. (Shandong, China). Epichlorohydrin (ECH), sodium hydroxide (NaOH), and urea were from Chemical Agents, Ltd. Co. (Shanghai, China) without further purification. The *Saccharomyces cerevisiae* was obtained from European *S. cerevisiae* Archive for Functional Analysis (Frankfurt, Germany). And other biochemical reagents were purchased from Thermo Fisher Oxoid (Shanghai, China).

2.2. Fabrication of cellulose based hydrogels

Quaternized celluloses (QC) were synthesized by quaternization of cellulose with 3-chloro-2-hydroxypropyltrimethylammonium chloride in NaOH/urea aqueous solutions according to our previous method (Chang et al., 2011). Their degree of substitutions (DS) were determined by an elemental analyzer (CHN-O-Rapid, Hanau, Germany) (see Table 1). For the preparation of hydrogels, cellulose was dissolved in 7 wt% NaOH/12 wt% urea aqueous solutions at low temperature, while QC was also dissolved in 7 wt% NaOH/12 wt% urea aqueous solutions at room temperature. Then, QC and cellulose solution were mixed with a weight ratio of 9:1 to obtain a 3 wt% polymer concentration. 1 mL ECH as crosslinker was added to 10 g QC/cellulose mixed solution under stirring, and reacted at 60 °C for 2 h. Finally, the hydrogels were taken out and immersed in ultrapure water to remove the residual NaOH, urea and un-reacted ECH to get pure samples. Hydrogels were coded as Gel9-2, Gel9-4, Gel9-6, Gel25-2, Gel25-4, and Gel25-6, according to the molecular weight and DS of QC (Table 1).

2.3. Characterization

The dried samples were analyzed in KBr discs by FTIR (Perkin Elmer Spectrum One, Wellesley, MA, USA) in the region of 400–4000 cm^{-1}. The mechanical properties of the hydrogels were measured on a universal testing machine (CMT6503, Shenzhen SANS Test Machine Co. Ltd., Shenzhen, China). Swelling ratios of the hydrogels in the ultrapure water at 37 °C were measured by the gravimetric method (Chang et al., 2011). The swelling ratio was calculated as

$$\text{Swelling ratio} = \frac{W_s}{W_d} \quad (1)$$

where W_s is the weight of the swollen gel after equilibrium at 37 °C, and W_d is the weight of the gel in the dry state.

2.4. Cell viability assay

Hydrogels samples were sterilized in an autoclave at 150 °C for 15 min before the cells were cultured. L02 cells (5×10^4 cells per well) were seeded on the surface of the sterilized hydrogel matrices in Dulbecco's modified Eagle's medium (DMEM, Sigma) with 10% FBS, and incubated at 37 °C. After incubation at 37 °C for 48 h, the medium was removed. Fresh medium (1 mL) and MTT (60 μL, 5 mg/mL) were added to each well, followed by 4 h of incubation at 37 °C. Subsequently, the supernatant was carefully removed, and 1 mL DMSO was added to each well. The absorbance of the solution was measured with microplate reader (Bio-Rad 550) at 570 nm to determine the Optical Density (OD) value. The cell viability was evaluated by MTT assay using the cells cultured on the cell culture plate as control and calculated as follows:

$$\text{Cell viability} = \left(\frac{\text{OD}_{\text{gel}}}{\text{OD}_{\text{control}}}\right) \times 100\% \quad (2)$$