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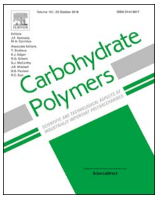

Synthesis of high-strength microcrystalline cellulose hydrogel by viscosity adjustment

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ABSTRACT

Developing hydrogels with enhanced mechanical strength is desirable for bio-related applications. For such applications, cellulose is a notable biopolymer for hydrogel synthesis due to its inherent strength and stiffness. Here, we report the viscosity-adjusted synthesis of a high-strength hydrogel through the physical entanglement of microcrystalline cellulose (MCC) in a solvent mixture of tetrabutylammonium fluoride/dimethyl sulfoxide (TBAF/DMSO). MCC was strategically dissolved with TBAF in DMSO at a controlled ratio to induce the formation of a liquid crystalline phase (LCP), which was closely related to the viscosity of the cellulose solution. The highest viscosity was obtained at 2.5% MCC and 3.5% TBAF, leading to the strongest high-strength MCC hydrogel (strongest HS-MCC hydrogel). The resulting hydrogel exhibited a high compressive strength of 0.38 MPa and a densely packed structure. Consequently, a positive linear correlation was determined between the viscosity of the cellulose solution and the mechanical strength of the HS-MCC hydrogel.

1. Introduction

Hydrogels are attractive biomaterials due to their biocompatible and biomimetic properties (Peppas, Hilt, Khademhosseini, & Langer, 2006). These properties facilitate their usage in bio-related applications including drug delivery systems, tissue-engineering scaffolds, wound dressing, and biomedical devices (Lee & Mooney, 2001; Seliktar, 2012; Sun et al., 2012; Zhao, 2014). However, hydrogels are often limited in practical applications by their typically poor mechanical properties (Huang et al., 2007; Kamata, Akagi, Kayasuga-Kariya, Chung, & Sakai, 2014). For instance, applications of hydrogels such as contact lenses, drug delivery systems, and artificial tissues require high strength (Calvert, 2009; Hernandez, Orive, Murua, & Pedraz, 2010; Maldonado-Codina & Efron, 2004).

Cellulose is a suitable biopolymer for synthesizing a hydrogel with good mechanical properties. Cellulose exhibits high strength, high stiffness, and low density because of its inherent crystalline structure (Zhang, Wu, Gao, & Xia, 2012). Furthermore, its biodegradability, biocompatibility, and renewability are beneficial for bio-related applications (Zhang et al., 2007). In spite of the excellent advantages, native cellulose is often limited for hydrogel synthesis due to its insolubility in water and commonly used organic solvents because its solid crystalline structure interferes with proper dissolution for hydrogel preparation (Choe & Shin, 2015). To overcome the insolubility, soluble derivatives of cellulose including methyl cellulose, hydroxypropylmethyl cellulose, sodium carboxymethyl cellulose, hydroxypropyl cellulose, and hydroxyethyl cellulose have commonly been used in studies of cellulose hydrogel synthesis (Chang & Zhang, 2011; Shen, Shamshina, Berton, Gurau, & Rogers, 2016). However, the strength of cellulose derivative hydrogels is compromised because the derivation prevents the formation of strong hydrogen bonds. Instead of using cellulose derivatives, the synthesis of hydrogels with native cellulose using distinctive cellulose-dissolving solvent systems has been recently reported. Cellulose-dissolving solvent systems belong to four categories: polar solvents, ionic liquids, deep eutectic solvents, and alkali aqueous systems (Shen et al., 2016). Specifically, lithium chloride/dimethylacetamide (McCormick, Callais, & Hutchinson, 1985), *N*-methylmorpholine-*N*-oxide (Biganska & Navard, 2005), sodium hydroxide/urea (Chang, Zhang, Zhou, Zhang, & Kennedy, 2010), choline acetate (Zhang, Benoit, De Oliveira Vigier, Barrault, & Jerome, 2012), ionic liquids (Liu, Sale, Holmes, Simmons, & Singh, 2010) and tetrabutylammonium/dimethyl sulfoxide (TBAF/DMSO) (Kohler & Heinze, 2007) are representative

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Abbreviations: MCC, microcrystalline cellulose; HS-MCC, high-strength microcrystalline cellulose; TBAF, tetrabutylammonium fluoride; DMSO, dimethyl sulfoxide; DP, degree of polymerization; LCP, liquid crystalline phase; DLS, dynamic light scattering; XRD, X-ray diffraction; CI, crystallinity index; FT-IR, Fourier transform infrared; LOI, lateral order index; TGA, thermal gravimetric analysis; IFRP, insoluble fiber reducing power; FE-SEM, field emission scanning electron microscope

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solvent systems utilized to dissolve native cellulose for hydrogel synthesis. Among these solvent systems, TBAF/DMSO has remarkable advantages as a polar solvent because it can rapidly dissolve cellulose at room temperature without changing the mean degree of polymerization (DP) (Heinze et al., 2000). Moreover, TBAF/DMSO is suitable for practical bio-related applications because it is relatively non-toxic and inexpensive (Joshi, Mandhane, Dabhade, & Gill, 2010; Zhang et al., 2015).

The mechanical strength of a physically crosslinked hydrogel is generally enhanced when the physical interactions between polymer chains and chain entanglement are promoted by increasing the polymer concentration and/or DP (Kimura et al., 2015). Alternatively, these hydrogels can be strengthened by forming a liquid crystalline phase (LCP) in the polymer solution, even with a low concentration and/or DP of the polymers. The formation of an LCP enhances the mechanical strength of hydrogels through strong intermolecular interactions and the highly oriented, rigid intrinsic backbones of the liquid-crystalline structure (Song, Zhang, Niu, & Wang, 2010). Interestingly, it has been reported that LCPs are present in solutions of cellulose (Ahn, Kwak, Song, & Kim, 2016; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011).

In this study, we report the synthesis of a high-strength native cellulose hydrogel by controlling the viscosity of solutions of microcrystalline cellulose (MCC) and TBAF/DMSO. A three-step process consisting of dissolution, curing, and exchange was used for synthesizing cellulose hydrogels. During the dissolution step, we dissolved MCC in TBAF/DMSO and adjusted the viscosity of the solution by tuning the ratio of MCC and TBAF concentrations in DMSO. Especially, the highest viscosity was obtained at a specific concentration ratio through the strongest intermolecular interactions among the cellulose chains due to a formation of nanoparticles, the size of which is the smallest at this point. Next, gelation processes in the curing and exchange steps. During the curing step, the cellulose solution thickened due to physical entanglement and slow aggregation of the cellulose molecules. Finally, a high-strength cellulose hydrogel was achieved by exchanging TBAF/DMSO with water and rearranging cellulose molecules during the exchange step. The mechanical strength of hydrogels synthesized using various compositions of MCC and TBAF was examined, and a correlation between the cellulose solution viscosity and the strength of the resulting high-strength MCC hydrogel (HS-MCC) was revealed. As a result, we identified the cellulose hydrogel with the highest strength and analyzed its physicochemical properties, such as its crystallinity, thermal stability, DP, and morphology.

2. Materials and methods

2.1. Materials

MCC (Avicel PH-101) with a mean DP of 170 was purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). TBAF, DMSO, and sodium sulfate were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). Sodium potassium tartrate (Rochelle salt), copper (II) sulfate, sulfuric acid, sodium carbonate, and sodium bicarbonate were obtained from Duksan Co. (Seoul, Korea). Ammonium molybdate tetrahydrate was provided by Daejung Co. (Seoul, Korea), and disodium hydrogen arsenate (hepta-hydrated) was obtained from Wako Ltd. (Osaka, Japan). All reagents and solvents were commercially available and used without purification.

2.2. Measurement of viscosity and molecular size of cellulose solutions

Cellulose solutions containing different ratios of MCC (0–5.0%, w/v) and TBAF (0–31.6%, w/v) dissolved in DMSO were prepared in 50-mL tubes and incubated at room temperature for 5 min. The viscosity of each solution was measured at 25 °C using a rheometer (MCR 102, Anton Paar, Ostfildern, Germany) using a 25-mm parallel plate (PP25, Anton Paar, Ostfildern, Germany) at a shear rate of 10 s^{-1}. The molecular size of cellulose was measured by dynamic light scattering (DLS) using a particle analyzer (ELSZ-1000, Otsuka Electronics Co. Ltd., Osaka, Japan) after the solutions were 10-times diluted with DMSO.

2.3. Preparation of high-strength microcrystalline cellulose hydrogels

To prepare HS-MCC hydrogels, cellulose solutions were prepared composed of varying MCC (2.5%, w/v) and TBAF (1.3–31.6%, w/v) ratios in DMSO. To ensure the solutions were well dispersed, the appropriate amount of TBAF was first added into a 50-mL conical tube containing DMSO, and then MCC was added to each solution. MCC was dispersed in each TBAF/DMSO solution and stirred at room temperature for 1 h. As a result, a transparent solution was obtained, indicating that MCC was well dissolved. In the next step, the resulting cellulose solution was poured into a silicone mold and left overnight at room temperature until it aggregated into a thickened gel. The aggregate was removed from the mold and soaked in water for 10 h to transform the aggregate into a hydrogel through a solvent exchange. To completely remove the TBAF and DMSO from the HS-MCC hydrogel, it was soaked in water for an additional 5 h, during which the water was exchanged every 1 h. After rinsing five more times with running water, the HS-MCC hydrogel was finally obtained.

2.4. Characterization of high-strength microcrystalline cellulose hydrogels

2.4.1. Composition analysis

MCC and the strongest HS-MCC hydrogel were freeze-dried, and their nitrogen and sulfur contents were measured using an elemental analyzer (2400 Series II, PerkinElmer, Waltham, MA, USA). The fluoride content was measured by combustion ion chromatography using an 881 Compact IC Pro (Metrohm AG, Herisau, Switzerland) connected to an automatic quick furnace (AQF-100, Mitsubishi Chemical Analytech, Tokyo, Japan).

2.4.2. Determination of water content

The water content of the strongest HS-MCC hydrogel was calculated using the following equation:

$$\text{Water content (\%)} = [(W - D)/W] \times 100$$

where W (g) is the weight of the strongest HS-MCC hydrogel, and D (g) is the weight of the freeze-dried strongest HS-MCC hydrogel.

2.4.3. Mechanical properties

HS-MCC hydrogels, cylindrically shaped with a diameter of 10 mm and a height of 8 mm, were stored in distilled water for 24 h at 25 °C in prior to measurement. The mechanical properties of the HS-MCC hydrogels were measured using a TA-XT Plus Texture Analyzer (Texture Technologies, Hamilton, MA, USA) equipped with a 50-kg load cell and a 10-mm diameter cylinder probe (*P*/10, 10 mm Delrin). The compressive strength and modulus were determined from stress–strain curves that were recorded at a rate of 2 mm/s while pressing the sample to 90% strain. Each HS-MCC hydrogel was tested in triplicates.

2.4.4. Determination of crystallinity

HS-MCC hydrogels were freeze-dried to conserve the initial swollen state without any structural collapse. X-ray diffraction (XRD) patterns of MCC and the freeze-dried HS-MCC hydrogels were obtained using an X-ray diffractometer (Smartlab, Rigaku Co., Tokyo, Japan). Scans were collected at 2°/min in the 2θ range of 10°–40°. The crystallinity index (CI, %) was calculated using the following equation:

$$\text{CI} = [(I_{002} - I_{am})/I_{002}] \times 100$$

where I_{002} is the maximum intensity of the lattice diffraction of the (002) planes, and I_{am} is the amorphous intensity corresponding to the