

The Study of Intermolecular Inclusion in Cellulose Physical Gels

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In this study, cellulose possessing β -cyclodextrin (β -CD) is employed as a host molecule, and cellulose possessing ferrocene (Fc) is used as a guest polymer. The properties due to the host-guest interactions are presented. The results show that β -CD-cellulose and Fc-cellulose can form inclusion complexes wherein hydrophobic interaction caused by β -CD-cellulose and Fc-cellulose significantly affect the performance of the cellulose gel. A physical gel based on cellulose that can autonomously heal between cut surfaces after 24 h was formed under mild conditions. Moreover, ferrocene redox status affects the hydrophobic interaction, such that the hydrophobic interaction can strengthen the gel strength and affect the self-healing property.

Keywords: Cellulose; Hydrogel; Cyclodextrin; Ferrocene

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INTRODUCTION

Cellulose constitutes the most abundant renewable polymer resource available today. As a biodegradable "green" raw material, it has generally been used in the form of fibers or derivatives for a wide spectrum of products and materials in daily life. Cellulose hydrogels consist of three-dimensional hydrophilic polymer networks, and a wide range of medical, pharmaceutical, and prosthetic applications have been proposed for them.

Supramolecular materials linked by noncovalent bonds have attracted much more attention these days because of their relatively easy modification and their very important and extensive application value, as well as wide applications in catalytic chemistry, materials preparation, life science, information science, nanoscience technology, and many other fields (Aida *et al.* 2012).

Compared with conventional cellulosic materials, cellulose supramolecular materials have many new properties and offer attractive prospects for development. Cellulose supramolecular materials are the most promising materials in this field and have been widely studied, especially the self-assembly characteristics of cellulose graft copolymers (Kang *et al.* 2006; Li *et al.* 2008; Liu *et al.* 2012; Shen *et al.* 2006; Vshivkov and Galyas 2011; Yang *et al.* 2008; Yokota *et al.* 2008; Zhao *et al.* 2010). The responsiveness to the external environment (Ma *et al.* 2010; Wan *et al.* 2007; Yuan *et al.* 2012) such as temperature (Phan *et al.* 2011) and pH (Dou and Jiang 2007; Wang *et al.* 2011), have led to applications across materials science (smart or adaptive materials, information-recording materials) and medicine (drug release carriers) (Bagheri and Shateri 2012; Dou and Jiang 2007; Tan *et al.* 2010; Wang *et al.* 2011). There are few reports on the use of cyclodextrin as a driving force for the environmental response of lignocellulose-based supramolecular assemblies. The formation of supramolecular materials through host-guest interactions is a powerful method to create non-

conventional materials. Supramolecular materials consisting of host and guest polymers have unique features because of their selective complementary interactions. Host–guest interactions are versatile and can be used to prepare supramolecular materials, which have easily tuned switching efficiencies and functions.

Intermolecular hydrogen bonding interactions in cellulose have been reported previously, whereas cellulose physical hydrogels self-assembled with host–guest interactions have rarely been reported. Here, the formation of physical cellulose hydrogels with host-guest interactions is reported employing β -CD-cellulose and Fc-cellulose as a host molecule and guest molecule, respectively. A supramolecular aggregate quickly forms upon mixing cellulose possessing β -CD as a host polymer with cellulose possessing ferrocene as a guest polymer. The redox stimuli properties of the supramolecular aggregate were also studied.

EXPERIMENTAL

Materials

Cellulose, β -cyclodextrin, epichlorohydrin, sodium hydroxide, lithium chloride, N,N-dimethyl acetamide, methylene chloride, ferrocene carboxylic acid, oxalyl chloride, sodium hypochlorite, and glutathione were commercially available and used as received.

Physical Testing

Compressive strength was measured using an Instron 3365 Universal Testing Machine (Norwood, MA) with the following parameters: sampling rate, 10.000 pts/sec; beam speed, 1.0000 mm/min; full scale load range, 0.1000 kN; humidity, 25%; and temperature, 23 °C.

Preparation of Cellulose Gel

Preparation of cellulose -CDs

Cellulose (1 g, 3% wt) was dissolved in sodium hydroxide/urea. To this solution, epichlorohydrin (7 mL) was added. After stirring for 2 h, β -CD (1.1 g) was added and the solution was stirred for another 12 h at room temperature. The polymer product was precipitated with distilled water and washed with distilled water. A cyclodextrin grafting efficiency of 0.32% wt was determined using the phenolphthalein probe method (Wan *et al.* 2004), in which a series of cyclodextrin/phenolphthalein solutions were measured by a spectrophotometer and the cyclodextrin grafting efficiency calculated by means of a standard curve.

In NaOH aqueous solution (0.1 mol/L), cellulose and epichlorohydrin generate epoxy cellulose, which connects the hydroxy of β -cyclodextrin with the epoxy group as a crosslinking bridge.

Synthesis of Fc-COCl

Ferrocenecarboxylic acid (2 g) was suspended in 30 mL of dichloromethane (DCM). Then, oxalyl chloride (2.5 mL) was added dropwise, and the suspension stirred for 3 h at room temperature. The orange suspension turned into a red solution. After evaporating the solvent by a rotary evaporator (RE-5299; Shanghai Yike Instrument), the solid product was collected.

Synthesis of cellulose -Fc

Cellulose (3% w/v) was dissolved in lithium chloride/dimethylacetamide (LiCl/DMAC). The ferrocenecarboxyl chloride solution (10% wt) was added dropwise. After stirring overnight at room temperature, the solution was washed with distilled water (10 times). The orange solid product was collected *via* a centrifuge (5000 rpm, 3 min) and dried for 4 days at 50 °C to obtain cellulose-Fc as a yellow powder. The ferrocene grafting rate was 0.5% wt, as detected by weighing before and after the cellulose reaction.

Synthesis of cellulose gel

The ferrocene-cellulose (0.7% w/v) and cyclodextrin-cellulose (5% w/v) were dissolved in N,N-dimethylformamide (DMF)/lithium chloride solution. The solution was poured into a glass mould in a humid (75% humidity) box at room temperature for 1 to 3 days until the gel was stabilized. For all the samples described in this paper the Fc/CD molar ratio was 1.1.

Oxidation and reduction of Fc groups in the gel

Gels were made into cylindrical samples (diameter 10 mm, height 7 mm). The hydrogel samples were formed using a cylindrical die with a 10-mm diameter. The samples were divided into three groups. One group of samples received no treatment. One group of samples were immersed in a cerium ammonium nitrate (10.59 mM) - DMAC solution at room temperature with shaking for 48 h. One group of samples were immersed in cerium ammonium nitrate (10.59 mM)-DMAC solution at room temperature with shaking for 48 h, then soaked in 1,4-hydroquinone (20.22 mM) /DMAC solution at room temperature with shaking for 48 h.

RESULTS AND DISCUSSION

Characterization

There are different methods that can be used to dissolve cellulose. The three substances cellulose, ferrocene-cellulose, and cyclodextrin-cellulose all can be dissolved well in LiCl/DMF. Therefore, that solvent was selected to carry out the reaction in a homogeneous system.

A detailed assignment of different carbons of cellulose-CDs is shown as Fig. 1a; C1 of glucose units was assigned at 104.6 ppm, C4 of glucose units was assigned at 87.1 ppm, C2, C3, and C5 of glucose units were assigned at 74.2 ppm, and C6 of glucose units was assigned at 62.1 ppm. The carbon atoms connecting cellulose and cyclodextrin were assigned at 84.2, 83.6, 82.9 ppm, which indicates that cyclodextrins successfully grafted onto cellulose.

As can be seen in Fig. 1b, C1 of glucose units was assigned at 104.3 and 103.7 ppm, C4 of glucose units was assigned at 88.2 ppm, C2, C3, and C5 of glucose units were assigned at 74.4 ppm, and C6 of glucose units was assigned at 61.8 ppm. Fc could be found at carbons regions of 124.4-123.0 ppm and 82.8-81.7 ppm, which suggests that ferrocene was successfully grafted to the cellulose under the experimental conditions employed.

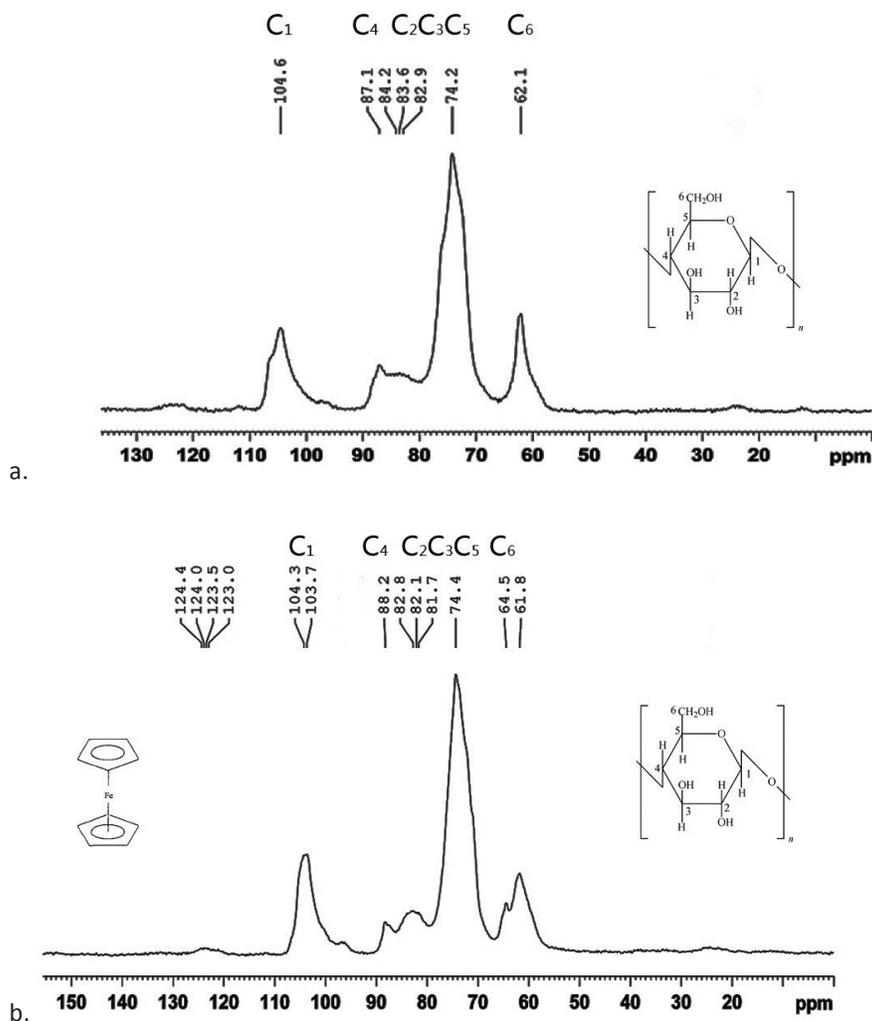


Fig. 1. Characterization of cellulose –CDs and cellulose –Fc. a, ^{13}C -NMR spectrum of cellulose –CDs. b, ^{13}C -NMR spectrum of cellulose –Fc.

Compressive Strength of Fc-Cellulose/ β -CD-Cellulose Hydrogel

To clarify the role of the β -CD and the Fc groups on cellulose, competitive guest or host molecules were added to the β -CD-cellulose /Fc-cellulose gel (Fig. 2).

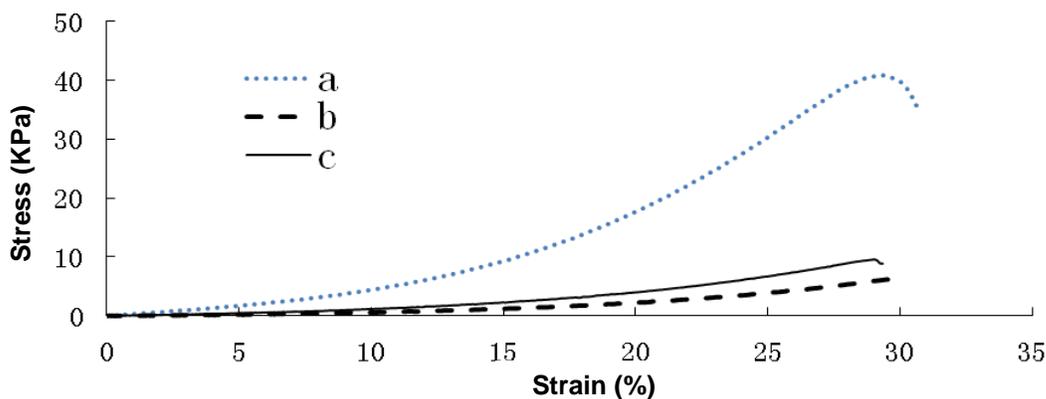


Fig. 2. The compressive strength of competitive agent-treated gels. a. Fc-cellulose/ β -CD-cellulose gel; b. Soaked in adamantane carboxylic acid; c. Soaked in β -CD

Adamantane carboxylic acid (30.35 mM) was used as a competitive guest because the association constant for β -CD is higher than that of Fc. Adding adamantane carboxylic acid to the Fc-cellulose/ β -CD-cellulose gel led to a sharp decrease in the compressive strength, from 41.0 kPa to 6.8 kPa. Similarly, adding β -CD (30.20 mM) as a competitive host into the Fc-cellulose/ β -CD-cellulose gel induced a decrease in compressive strength from 41.0 kPa to 9.8 kPa. The decrease in compressive strength that was caused by competitive guest or host inhibited the formation of an inclusion complex between the β -CD unit of β -CD-cellulose and the Fc unit of Fc-cellulose.

The redox regulation process of supramolecular aggregates containing ferrocene has been studied extensively. The host-guest interaction between the metal ferrocene with β -CD can also be reversibly regulated by oxidation and reduction of the ferrocene. More than 20 years ago, it was reported that the reduced ferrocene effectively forms an inclusion compound with the β -CD, while it is basically impossible for the oxidized ferrocene to form an inclusion compound with the β -CD (Harada and Tkahashi 1984; Matsue *et al.* 1985). The nature of ferrocene in the reduced state is hydrophobic and hydrophilic in the oxidized state. The reversible regulation of the aggregate form of the binary complex can be achieved by changing the redox state of the ferrocene.

Ceric ammonium nitrate was selected as an oxidant and 1,4-hydroquinone as a reductant. The redox behavior of ferrocene was studied by measuring the compressive strength of the gel. The oxidized state (or reduced state) products were prepared by immersing the gel into appropriate amounts of ceric ammonium nitrate (or 1,4-hydroquinone) at room temperature and shaking for 48 h. The compressive strength of the Fc-cellulose- β -CD-cellulose gel was 49.1 kPa (Fig. 3a), and that of the oxidized state gel was 25.3 kPa (Fig. 3b); in contrast, continuous addition of 1,4-hydroquinone to the solution recovered the Fc group, decreasing the compressive strength to 42 kPa (Fig. 3c).

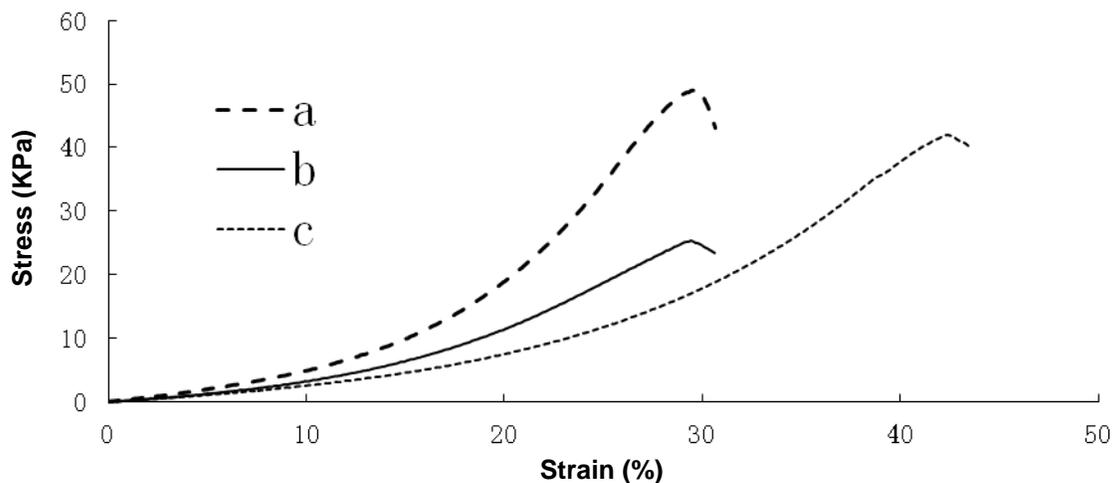


Fig. 3. The compressive strength of different gels. a. Fc-cellulose/ β -CD-cellulose hydrogel; b. Soaked in ceric ammonium nitrate; c. Soaked in 1,4-hydroquinone

The oxidized state of the Fc group (Fc⁺) exhibited a lower compressive strength because of the release of the intermolecular inclusion force, whereas the cellulose hydrogel showed a high compressive strength because of the reduced state of the Fc group when the ferrocene-cellulose and cyclodextrin-cellulose form inclusion complexes. This demonstrates that the intermolecular inclusion force can strengthen the gel. Moreover, the intermolecular inclusion force of cellulose gel exhibits excellent lock and

unlock properties that are controlled by the redox state of the ferrocene. The redox diagram is shown in Fig. 4.

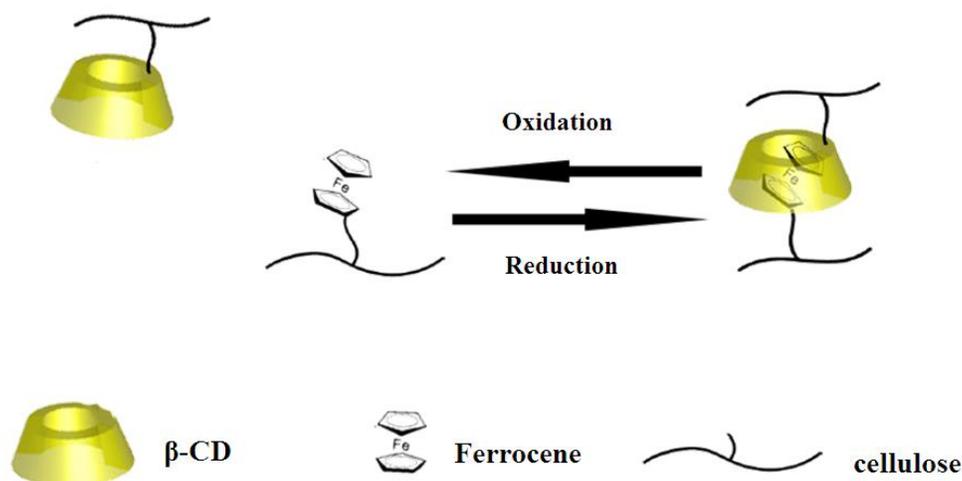


Fig. 4. Redox diagram of cellulose supramolecular aggregates

The Self-healing Property of Cellulose-CDs/Cellulose-Fc Gels

The cellulose-CDs/cellulose-Fc gel was cut in half and then healed to form one gel after 24 h (Fig. 5a).

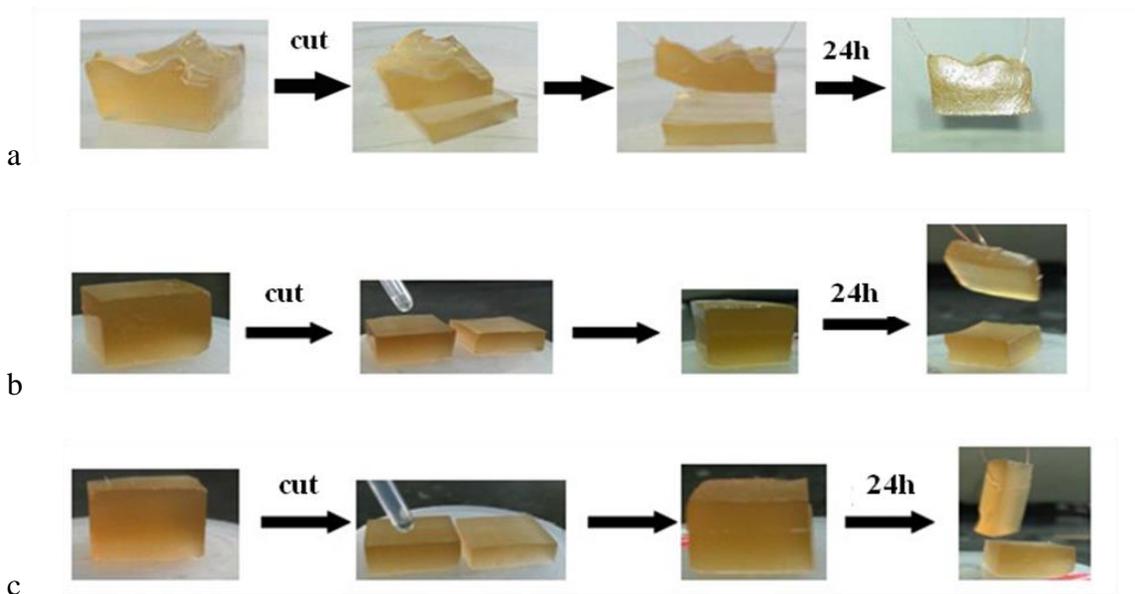


Fig. 5. Self-healing experiments. a. Gel was cut in half and allowed to stand for 24 h before the two pieces were rejoined; b. The cut surfaces were coated with a solution containing a competitive guest (adamantane acid); c. The cut surfaces were coated with a solution containing the host (β -CD)

Competitive guest (adamantane acid) and host (β -CD) molecules were added to the cut plane of the cellulose-CDs/cellulose-Fc gel to investigate the host-guest

interaction between the β -CD and Fc group. The competitive host or guest molecule was placed on the cut surfaces, and the two parts were reattached. After 24 h, the gels with a competitive guest or host did not heal, whereas the sample lacking in competitive compounds healed at room temperature (Fig. 5b, c). These results indicate that the self-healing property is due to the formation of an inclusion complex by β -CD and Fc on the surfaces of the gels.

CONCLUSIONS

1. The host-guest interaction is a powerful method to create supramolecular materials. In this paper, ferrocene and cyclodextrin were grafted onto the cellulose surface to prepare a cellulose physical hydrogel.
2. The intermolecular inclusion force can strengthen the gel.
3. The supramolecular gel has the property of self-healing due to host-guest interactions.
4. The gel product has potential applications in materials that may benefit from autonomous healing upon damage.

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