Research Article

Binding Cellulose and Chitosan via Intermolecular Inclusion Interaction: Synthesis and Characterisation of Gel

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A novel cellulose-chitosan gel was successfully prepared in three steps: (1) ferrocene- (Fc-) cellulose with degrees of substitution (DS) of 0.5 wt% was synthesised by ferrocenecarboxylic acid and cellulose within dimethylacetamide/lithium chloride (DMAc/LiCl); (2) the β -cyclodextrin (β -CD) groups were introduced onto the chitosan chains by reacting chitosan with epichlorohydrin in dimethyl sulphoxide and a DS of 0.35 wt%; (3) thus, the cellulose-chitosan gel was obtained via an intermolecular inclusion interaction of Fc-cellulose and β -CD-chitosan in DMA/LiCl, that is, by an intermolecular inclusion interaction, between the Fc groups of cellulose and the β -CD groups on the chitosan backbone at room temperature. The successful synthesis of Fc-cellulose and β -CD-chitosan was characterised by ¹³C-NMR spectroscopy. The gel based on β -CD-chitosan and Fc-cellulose was formed under mild conditions which can engender autonomous healing between cut surfaces after 24 hours: the gel cannot self-heal while the cut surfaces were coated with a solution of a competitive guest (adamantane acid). The cellulose-chitosan complex made by this method underwent self-healing. Therefore, this study provided a novel method of expanding the application of chitosan by binding it with another polymer.

1. Introduction

Chitosan is a partially deacetylated polymer of N-acetyl glucosamine. It is essentially a natural, water-soluble derivative of cellulose with unique properties [1]. Chitosan is usually prepared from chitin and chitin has been found in a wide range of natural sources [2] (crustaceans, fungi, insects, annelids, molluscs, coelenterate, etc.) [1, 2]. Chitosan is used in many applications (flocculant [3, 4], clarifier [5–7], fibre [8, 9], film [10–12], and wound healing promoting agent [13, 14]). Cellulose and chitosan have similar molecular structures, with the same β -glycoside linkages. The main difference is the presence of primary amino groups at the C-2 positions in chitosan, where cellulose has hydroxyl groups. The presence of active groups in chitosan's molecular structure allows for easy chemical modification. Cellulose and chitosan are both biocompatible, nontoxic, and naturally occurring biopolymers that have been used extensively for biomedical applications.

In recent years, many studies of the different applications of chitosan and especially of chitosan blends with cellulose have been undertaken [3–24]. The complex based on cellulose and chitosan is to be studied as a fibre [8, 9], a film [3, 8, 10–12], hydrogen [7, 15], and microspheres [5, 16, 17] and be used as a drug carrier [17, 18], wound healing promoting agent [14, 15], a medical material [17], a food packaging material [11], an adsorbent [3–7], and as a range of other functional materials [15, 20–23]. The preparation of cellulose-chitosan composite materials has involved two main strategies: physical mixing [6, 8, 13] and covalent bonding [24, 25], whereas cellulose-chitosan hydrogel binding with host-guest interactions has never been reported before. This method differed with physical mixing in that it incorporated a “lock” formed by the Fc and β -CD groups between cellulose and chitosan molecules: the gel prepared by this method with Fc-cellulose and β -CD-chitosan by self-assembled Fc and β -CD groups in the absence of chemical cross-links was also novel. The incorporation of “locks” ensured a uniform mixing system and the

FIGURE 1: Infrared spectra of cellulose-Fc (a), chitosan-CDs (b), and the inclusion compound (c).

“locks” in this Fc- β -CD system made the materials smart in such a manner as to allow them to respond by their “locking” and “unlocking” behaviour [26–29]. The potential responsive properties present this kind of gel with a wider range of applications. The aim of this research was to modify the cellulose and chitosan and to prepare an Fc-cellulose/ β -CD-chitosan gel.

2. Experimental

2.1. Materials. Cellulose (DP380), chitosan (DP465), 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. IR spectra were recorded by FTIR (Nicolet iN10 Thermo Fisher Scientific, China) in the region of 400 to 4000 cm^{-1} . Compressive strengths were measured using an Instron 3365 Universal Testing Machine (Norwood, MA, USA) with the following parameters: sampling rate, 10.000 points/s; beam speed, 1.0000 mm/min; full-scale load range, 0.1000 kN; humidity, 25%; and temperature, 23°C. The gel samples were formed using a 10 mm diameter cylindrical die.

2.2. Preparation of Cellulose-Chitosan Gel

2.2.1. Preparation of Chitosan-CDs. β -CD and isopropanol were dissolved in dimethyl sulphoxide (DMSO). To this solution, epichlorohydrin and solution (1 mol/L) were added. After stirring for 5 h, chitosan was added and the solution was stirred for another 12 h at room temperature. The polymer product was reprecipitated from distilled water and washed with distilled water. The cyclodextrin grafting efficiency was 0.35% wt, which was detected by the phenolphthalein probe method [30].

2.2.2. Synthesis of Fc-COCl. Ferrocenecarboxylic acid was suspended in dichloromethane (DCM). Then oxalyl chloride

was added dropwise, and the suspension was stirred for 3 h at room temperature. The orange suspension turned into a red solution. After evaporating the solvent, the solid product was collected.

2.2.3. Synthesis of Cellulose-Fc. Cellulose was dissolved in lithium chloride/dimethylacetamide (LiCl/DMAc). The chlorocarbonyl ferrocene solution was added dropwise. After stirring overnight at room temperature, the solution was washed with distilled water. The orange solid was washed with lithium chloride; the solid product was collected by centrifugation and dried for 4 days at 50°C to obtain the cellulose-Fc as a yellow powder. The ferrocene grafting rate was 0.5% wt, which was detected by weighing before and after the cellulose reaction.

2.2.4. Synthesis of Cellulose-Chitosan Gel. The ferrocene-cellulose (0.017 mM) and cyclodextrin-chitosan (0.017 mM) were dissolved in N,N-dimethylformamide (DMF)/lithium chloride solution. The solution was poured into a glass mould in a humid box until the gel had stabilised.

3. Results and Discussion

Figure 1 shows the infrared spectra of the cellulose-Fc (a) and chitosan-CDs (b). According to the curves in (a), absorption was observed at 3380 cm^{-1} (hydroxyl stretch influenced by hydrogen bonding), 1646 cm^{-1} and 1354 cm^{-1} (carbonyl stretch), 1043 cm^{-1} (carboxyl in ethers), and 2920 cm^{-1} (methylene). The characteristic peaks of ferrocene could be found at 1402 cm^{-1} , 1100 cm^{-1} VC-C (cyclopentadienyl ring), and 856 cm^{-1} DC-H (cyclopentadienyl ring). As seen from the curves in (b), the characteristic absorption peaks of chitosan-CDs structures were observed at 1656 cm^{-1} (the stretching vibration of C=O) and at 1591 cm^{-1} (the bending vibration of N-H). The characteristic peaks of ferrocene disappeared from the infrared spectra of the envelope of the

FIGURE 2: ^{13}C -NMR of cellulose-Fc. FIGURE 3: ^{13}C -NMR of chitosan-CDs.

FIGURE 4: Intermolecular inclusion interaction of cellulose-chitosan hydrogel.

(a) (b) (c)

FIGURE 5: Self-healing experiments.

inclusion compound (curves in (c)). This indicated that the cellulose-Fc and chitosan-CDs have been formed in the inclusion complex. Similar findings were reported in the literature [26–28].

Figures 2 and 3 show the solid-state ^{13}C -NMR spectra of the chitin-CDs and cellulose-Fc. As can be seen in Figure 2, the C1 of the glucose units was assigned to 104.3 and 103.7 ppm, their C4 was assigned to 88.2 ppm, C2, C3, and C5 were assigned to 74.4 ppm, and C6 was assigned to 61.8 ppm. Fc could be found at carbon sites in regions between 124.4 and 123.0 ppm and 82.8 and 81.7 ppm; this suggested that ferrocene was successfully grafted to the cellulose by the proposed experimental method. A detailed assignment of different carbons of chitin-CDs was shown in Figure 3: the C1 site of the glucose units was assigned to 104.6 ppm, C4 to 85.4 ppm, C2, C3, and C5 to 74.9 ppm, C6 to 60.5 ppm and 57.0 ppm, carbonyl carbon C7 (connected acetyl group) to 173.0 ppm, and C8 to 23.5 ppm. The carbon atoms connecting cellulose and cyclodextrin were assigned to 80.9 ppm; this indicated that cyclodextrins had been successfully grafted onto chitosan.

Cellulose-chitosan gel was prepared from the solution of ferrocene-cellulose and cyclodextrin-chitosan at room temperature. The schematic diagram of the binding of cellulose and chitosan by an intermolecular inclusion interaction was shown in Figure 4. The gel based on β -CD-chitosan and Fc-cellulose was formed under mild conditions which can engender autonomous healing between cut surfaces after 24 hours (Figure 5). To clarify the intermolecular inclusion interaction between the β -CD and Fc groups on cellulose and chitosan, a competitive guest molecule was coated onto the cut surfaces. Adamantine acid was used as a competitive guest, because the association constant for β -CD ($K_a = 35 \times 10^3 \text{ M}^{-1}$) is higher than that of Fc. A β -CD-chitosan/Fc-cellulose gel was cut in half, and the cut surfaces were coated with a solution of adamantane acid (3 Mm). After 24 h, healing was not observed. These results indicated the formation of an inclusion complex between the β -CD unit of β -CD-chitosan and the Fc unit of Fc-cellulose. The compressive strength (Instron 3365 Universal Testing Machine (Norwood, MA, USA)) of Fc-cellulose/ β -CD-chitosan hydrogel (3 wt%) without cracking was 4.70 kPa, and the compressive strength

of the sample healed after standing for 24 h was 3.42 kPa. Thereafter, the compressive strength of the healed gel can recover 72.77% of its original compressive strength.

4. Conclusion

β -CD-chitosan/Fc-cellulose gel was prepared at room temperature, the β -CD unit of the β -CD-chitosan and the Fc unit of the Fc-cellulose can form inclusion complexes. The cellulose and chitosan can bind by intermolecular inclusion interaction. This research reports the resulting self-healing properties arising from host-guest interactions. The healed gel can recover 72.77% of its original compressive strength. The β -CD-chitosan/Fc-cellulose gel hydrogels have a wide potential for industrial applications including medicine, textiles, sports, cosmetics, and hygiene product manufacture.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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