



Soft, tough, and flexible curdlan hydrogels and organogels fabricated by covalent cross-linking



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ABSTRACT

Soft, tough and flexible curdlan (CD) hydrogels were fabricated by covalent cross-linking of CD using ethylene glycol diglycidyl ether (EGDGE) as a cross-linker. The mechanical properties of the gels were investigated by uniaxial compression test. CD hydrogels showed non-linear elastic behavior. The elastic modulus of CD hydrogels was 0.004–0.011 kPa. CD hydrogels were highly tough and did not fracture under compression to 90% strain at the maximum. The gels could retain water during compression, and no water was squeezed out from the gel. In addition, CD hydrogel could recover the original shape and elastic modulus after 90% compression, indicating its high flexibility. Subsequently, hydroxyl groups of CD hydrogels were acetylated in acetic anhydride and pyridine system to give hydrophobic property, and novel CD organogels were obtained. CD organogel were swollen in chloroform and resistant to repeated drying and swelling treatment in chloroform.

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1. Introduction

Polysaccharides are attractive material for soft material science due to their biocompatibility, biodegradability, or bio-activities [1]. Many kinds of polysaccharides, such as cellulose [2], agarose [3], gellan gum [4], alginate [5], curdlan [6], are known to form hydrogels. Hydrogels are self-standing soft material that is highly swollen in a liquid water and have been extensively studied for many application areas such as medical, food, or bio-engineering sciences [7–9]. Curdlan (CD) is a polysaccharide composed of β -(1 → 3)-D-glucose units which is produced by *Alcaligenes faecalis* [10–12]. CD has high molecular weight more than a couple tens kDa, and attractive bio-based material that can be obtained from nature [1]. CD forms a gel by heating and are used in cosmetics or food industry [13–16]. However, most of hydrogels of polysaccharide are normally very brittle and have low mechanical strength, which has been restricting an application of polysaccharide-based hydrogels as industrial material. Improvement and designing of mechanical properties of hydrogels, such as toughness or elasticity is crucial issue to utilize polysaccharide

hydrogels for biomedical or engineering application.

There have been some reports on polysaccharide-based hydrogels with high mechanical properties. Double network gels consisting of gelatin and cellulose are known to have high toughness and high elasticity, and they are expected to be suitable for artificial tendon or cartilage which are categorized as hard tissue [17]. Interpenetrating hydrogels consisting of alginate and polyacrylamide have also been reported as a soft hydrogels with high mechanical properties [18,19]. Polyacrylamide are widely used as a contact lenses and its further application for biomedical field is expected, but toxicity of acrylamide monomer has been concerned. Regarding the mechanical property of hydrogels, polysaccharide-based gel that has softness, toughness and flexibility at the same time, has not been reported to our knowledge. Such kind of hydrogels would be novel class of bio-based hydrogels and could be applicable for artificial soft tissue in tissue-engineering or regeneration studies.

Chemical crosslinking is a one of the effective way to improve mechanical strength and water retention ability of the gels [19–23]. Ethylene glycol diglycidyl ether (EGDGE) is available as a cross-linking reagent for polysaccharides, and is suitable reagent for biomedical application because it is amphiphilic and can be removed from the human body [22,24]. Herein, we describe

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preparation of covalently cross-linked CD hydrogels with soft, tough and flexible properties, and demonstrated their excellent elastic behavior to repeated compressing. Furthermore, CD organogels are obtained by acetylation of CD hydrogels and their unique swelling behavior for repeated drying and swelling treatments are also described.

2. Experimental

2.1. Materials

CD was purchased from Wako Pure Chemical Industries, Ltd (Japan). Ethylene glycol diglycidyl ether (EGDGE) and sodium hydroxide (NaOH) were purchased from Tokyo Chemical Industry Co., Ltd. (Japan), and Kanto Chemical Co., Inc. (Japan), respectively. All reagents were used without further purification.

2.2. Fabrication of CD hydrogels

The representative procedure for fabrication of CD hydrogel (CDg-1) is as follows; To a 4% NaOH aqueous solution (25 ml) of CD (1.0 g), EGDGE (1.0 ml, 1.1 molar equivalent to anhydroglucose unit (AGU)) was added dropwise. A solution was stirred for 1 min and poured into a glass mold with 10 mm diameter and 10 mm height, and set at room temperature to allow gel formation for 1 day. The obtained cross-linked gels were removed from the mold in distilled water (1 L), and then, acetic acid was added to neutralize NaOH. The gels were further washed for 2 days with distilled water to remove residual reagents. The CDg-2 and -3 were prepared by varying concentration of CD and EGDGE as listed in Table 1. The molar ratio of NaOH to EGDGE was set to 4 molar equivalent.

2.3. Fabrication of agar hydrogel

Agar gels were fabricated as follows: Agar (2 g) was dissolved hot distilled water (98 ml) and poured into a mold with 10 mm diameter and 10 mm height, and set at room temperature for 3 h to allow gel formation.

2.4. Fabrication of organogels

The hydrogels were immersed in ethanol and the media was subsequently exchanged by acetic anhydride/pyridine. The gels in acetic anhydride/pyridine mixed media were heated at 70 °C for 3 days. The obtained organogels were washed by chloroform to remove acetic anhydride and pyridine.

2.5. Media composition of the gels

The media composition of the gels was calculated from the weights of the swollen gel and the dried gel; The media composition (wt %) = $(1 - [\text{dried gel}]/[\text{swollen gel}]) \times 100$. Dried hydrogels and organogels were obtained by freeze-drying or vacuuming.

2.6. Compression test

Compressive test was carried using EZ-test (Shimadzu, Japan) to measure mechanical properties of the hydrogels. The hydrogels were compressed perpendicular to the height direction by parallel metal plates connected to a load cell at 1 mm/min at room temperature. The elastic modulus (E) was determined by the average slope over the strain ratio range of 10–20% in the stress-strain curve which was considered as a linear region. To determine elastic modulus, five specimens were used and the data were averaged for each gel. Strain rates (%) were referenced to the initial height of the gel. For the repeated compressing test, the one specimen was used for five times to obtain strain-stress curves, and the recovery rates (%) were calculated as the relative height of the CD gel after compressing to its original height.

3. Results and discussion

3.1. Fabrication of CD hydrogels

The CD was cross-linked using EGDGE in NaOH aq. solution as described in Fig. 1. EGDGE is considered to form ether bond between epoxy group and hydroxyl groups of CD in alkaline solution. Three different CD hydrogels, namely, CDg-1, -2, and -3 were obtained by varying the amount of EGDGE as listed in Table 1. As can be seen in the images in Fig. 2, the self-standing hydrogels were successfully obtained and the gels prepared with higher EGDGE concentration formed more swollen gel in the order of CDg-1 > -2 > -3. Water composition of CDg-1, -2, and -3 was 97.2, 95.4, and 94.8% respectively, and decreased in the order of CDg-1 > -2 > -3 with decrease in EGDGE (Table 1). This result is opposite to the common tendency that media composition of a gel decreases with increase in cross-linker [25,26]. We attribute this result to poor cross-linking efficiency caused by steric hindrance that occurs when more cross-linker was added. The relative molar amount of EGDGE to AGU of CD for CDg-1, -2, and -3 is 1.1, 0.4 and 0.2, respectively. In the case of CDg-1, all AGU is theoretically substituted by at least one epoxy group. There might be steric hindrance for next cross-linking reaction between another epoxy group and hydroxyl group of different CD chain, and as a result, free hydroxyl group was formed by cleavage of epoxy group. This might be one reason for the result that media composition became higher when more cross-linker was loaded.

3.2. Compressive mechanical properties of CD hydrogels

Compressive mechanical property of CD hydrogels was investigated by uniaxial compression test. Fig. 3 shows stress-strain curves of CD hydrogels under uniaxial compression to 50% and 90% strain. CD hydrogels showed non-linear elastic behavior. The gels were quite tough and fracture stress could not be determined. The elastic modulus of CD hydrogels is listed in Table 2 with a comparison with other polysaccharide-based gels or gelatin gels. The elastic modulus of CD-1, -2, and -3 hydrogels were 0.004, 0.006, and 0.011 MPa, respectively. Elastic modulus tended to increase in the order of CDg-1 < -2 < -3 with a decrease in EGDGE. This

Table 1
Characteristics of cross-linked CD gels.

| Gels | CD (g) | H ₂ O (mL) | EGDGE (mL) | [EGDGE]/[AGU] (mol/mol) | NaOH (g) | Water composition of hydrogels (wt %) | CHCl ₃ composition of organogels (wt %) | CHCl ₃ composition of re-swollen organogels (wt %) |
|-------|--------|-----------------------|------------|-------------------------|----------|---------------------------------------|--|---|
| CDg-1 | 1.0 | 25 | 1.0 | 1.1 | 1.0 | 97.2 | 99.5 | 99.2 |
| CDg-2 | 1.0 | 25 | 0.4 | 0.4 | 0.4 | 95.4 | 99.0 | 99.2 |
| CDg-3 | 1.0 | 25 | 0.2 | 0.2 | 0.2 | 94.8 | 98.1 | 98.2 |

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