Sustainable Composite Super Absorbents Made from Polysaccharides

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Abstract

Compared to traditional super absorbent polymers using raw materials from petrochemical industry, natural polymer absorbents are more favorable because they are sustainable and biodegradable. In this study, composite absorbents were developed by crosslinking carrageenan with sodium alginate using calcium chloride. Effect of composition on absorption was tested. Absorption was improved by increasing carrageenan content. The super absorbent exhibited the maximal swelling ratio of 13.1 g/g in 0.9% saline water in just 5 minutes. The maximal tensile strength was reached with a value of 12.8 MPa. Water contact angle revealed that carrageenan is more hydrophobic than sodium alginate. Presence of sulfate groups might be a key factor promoting absorption. The scanning electron microscopic images showed that the composite material had a structure with alginate arranged at the outside surface. These results demonstrate that a sustainable and biodegradable absorbent was successfully developed with a matrix of properties for potential application in diapers.

Keywords

Biomaterials; Sustainable super absorbent; Composite materials; Swelling; Mechanical strength

1. Introduction

Super absorbent polymers (SAPs) are capable to absorb a large amount of liquid compared to their own mass. They are widely used in personal care such as baby diapers. However, traditional SAPs are not sustainable because they are made of raw materials derived from petrochemical industry. Moreover, the adverse environmental impact associated with their non-degradability has raised increasing concerns [1]. Though the polymer products are safe to human including babies, monomers may be toxic to workers manufacturing SAPs in a plant. Therefore, demand is growing for super absorbents made from sustainable, biodegradable and natural materials.

It has been well known that natural polymers including carrageenan, konjac glucomannan and agar can absorb a large amount of liquid compared to their own mass. Due to the presence of sulfate group, carrageenan is salt resistant [2], showing potential application in diaper. However, carrageenan is a linear polymer that can finally dissolve in water. Therefore, it should be modified to be applied as SAP. Addition of cross-linking agents can improve material strength and stability. To develop sustainable and biodegradable SAP, a natural cross-linking agent is more favorable than chemicals from petrochemical industry [3]. Alginate sodium is a natural polysaccharide and can be easily cross-linked by 2+ ions [4, 5].

In this study, a composite SAP material was developed using carrageenan as the component to absorb liquid, and calcium alginate as the cross-linking agent. Absorption of saline water was tested. Surface morphology, mechanical strength, water contact angle, IR spectra, scanning electron microscopy (SEM) images and X-ray diffraction (XRD) were examined to understand the structure-property relationships.

2. Material and methods

2.1 Material

Calcium chloride, sodium alginate and sodium chloride were purchased from Sinopharm Chemical Reagent Co., Ltd. Kappa-carrageenan was obtained from Shishi Xieli Ocean Biochemistry Co., Ltd.

2.2 Preparation of the absorbents

Sodium alginate and carrageenan in four mass ratios (0.1 g : 0.4 g, 0.2 g : 0.3 g, 0.3 g : 0.2 g, 0.4 g : 0.1 g) were dissolved in 25 mL distilled water by fast stirring. The total concentrations of the two polysaccharides were kept 20 g/L. The series A1C4, A2C3, A3C2 and A4C1 represent the samples prepared using alginate and carrageenan in the four mass ratios of 1 : 4, 2 : 3, 3 : 2 and 4 : 1, respectively. The prepared solution was subsequently dropped into 0.5% calcium chloride solution using a syringe injector to cross-link for about 2-5 min. The resulting absorbent beads were then dried [6].

2.3 Material characterization

The swelling ratio (SR) was determined in 0.9% NaCl solution at room temperature. The samples were immersed in the saline water for five minutes. After removal of surface water, the wet samples were immediately weighted on an electronic balance. The SR was determined as reported [7]. Samples were prepared using 0.5% calcium chloride solution for cross-linking [7] and then air dried. The tensile strength at break was tested by extension measurements using a tensile tester (UTM 4503) with a crosshead speed of 10 mm/min. Surface morphology was examined using a zoom stereo optical microscope (ZSA302, Chongqing Optical & Electrical Instrument Co., Ltd.). Alginate and carrageenan were mixed in the four mass ratios and then casted on glass slide to make films. Hydrophilicity was estimated using water contact angle measurement as reported after three seconds [8]. IR spectra were obtained with a Nicolet iS50 Attenuated Total Reflection (ATR) infrared spectrometer (Fisher Scientific, USA), in the range from 400 to 4000 cm^{-1}. The morphology of the absorbent on both the inside and outside surfaces was examined by a scanning electron microscope (Nova NanaoSEM 230, FEI, USA). XRD spectra were recorded on a Ultima-IV X-ray diffractometer (Rigaku, Japan).

3. Results and discussion

Fig. 1 shows the capability of the composite materials to absorb 0.9% NaCl saline solution in five minutes. The absorption was related to the ratios of calcium alginate to carrageenan. Increase in carrageenan content improved the absorption. The highest SR was reached with a value of 13.1 for the sample A1C4. Fast absorption makes A1C4 useful for potential application in diapers. The SR of our sample reached 50% of a super absorbent prepared for use in diapers [9]. Alginate can be degraded by microorganisms such as *Pseudoalteromonas elyakovii*, *Sphingomonas sp.* strain A1, etc. [10], while carrageenan can be degraded by *Cellulophaga lytica*, *Pseudoalteromonas atlantica*, etc [11]. Therefore, our sample is totally biodegradable and sustainable, showing advantages over traditional SAPs.

On the other hand, A4C1 had the lowest SR of only 2.9. This implied that carrageenan played an important role in absorption. Carrageenan is composed of repeating units of α-(1-3)-d-galactose-4-sulfate and β-(1-4)-3,6-anhydro-d-galactose. The abundant hydrophilic and sulfate groups promote absorption.

Fig. 1 Effect of composition on swelling

The samples were prepared in a dumbbell shape (Fig. 2A) by a tablet machine with 4 mm width cutting knife for tensile strength measurement. Fig. 2B shows the tensile strength and Fig. 2C shows surface morphology of the samples examined by a zoom stereo optical microscope. Films made of alginate was easy to shrink, resulting in rough surface and a structure with less mechanical strength [7]. In our study, the surface of A4C1 was the most rough, with a tensile strength of only 0.24 MPa. The tensile strength and surface smoothness were improved when the ratio of carrageenan to calcium was increased from 1:4 (A4C1) to 3:2 (A2C3). The most smooth sample A2C3 exhibited a tensile strength as high as 12.8 MPa. It has been proposed that the fast cross-linking process led to polymer folding lumps, causing non-uniformity of alginate films [7, 12]. By blending a proper amount of carrageenan to alginate here, slower cross-linking occurred, enhancing material uniformity and strength. There is an optimum ratio of carrageenan to alginate, above which further increase in carrageenan content reduced the mechanical strength. The tensile strength of A1C4 dropped to10.4 MPa due to insufficient cross-linking. High strength hydrogels had tensile strengths between 10^5-10^7 Pa [13, 14]. Our samples had strengths in the high end compared to those from previous studies. The composite absorbent developed here showed high mechanical strength and fast swelling, two most desirable properties for application in diapers.

Fig. 2 (A) The visual appearance of the specimen; (B) Tensile strength; (C) Surface morphology Absorption can be affected by hydrophilicity or presence of group with high ionization tendency.

It is important to find out the dominating factor in order to further improve absorption. Water contact angles were measured for the composite materials. Contrasting with absorption, samples with higher contents of kappa-carrageenan were more hydrophobic (Fig. 3A). It has been reported that pure kappa-carrageenan had a water contact angle of 68.8^{o} [15] and pure sodium alginate had an initial water contact angle of ~47^{o} [8]. Kappa-carrageenan is more hydrophobic because of the anhydro-D-glactose. As a result, hydrophilicity of the material should not be the dominating factor for absorption. It has been reported that for polyelectrolyte hydrogel, ionic concentration differences between the interior of the hydrogel and the external solution is the dominating swelling force [16]. It is likely here that presence of the sulfate groups on the polymer network is the key factor controlling fast absorption. Therefore, It is possible to further improve absorption rate by introducing more sulfate groups to the carrageenan.

SEM, IR spectroscopy and XRD were performed to further understand the organization of the composite materials. SEM images show that on the inside surface of the absorbent (Fig. 3B), the carrageenan alone had a linear structure, while cross-linked calcium alginate formed a compact network. The two polymers formed a semi-Interpenetrated Polymer Network, enhancing the strength of the absorbent. On the outside surface (Fig. 3C), a more homogenous structure was formed by almost only calcium alginate. Alginate is more hydrophilic, therefore it was rearranged to the outside surface during the cross-linking process. In the IR spectra (Fig. 3D), characteristic bands at 1420 $cm^{-1}$and 1597 cm^{-1} are attributed to asymmetric and symmetric stretching vibrations of COO^{-} groups on the polymeric backbone of calcium alginate [17]. Carrageenan shows a characteristic band at 1258 cm^{-1} due to the sulphate stretch of S=O [17]. The appearance of these bands confirms composite formation. The diffraction patterns (Fig. 3E) indicate the amorphous structure of all samples [17]. The broad peaks at 2θ of ~8.3^{o} and ~20.6^{o} were associated with the carrageenan [17], and gradually disappeared with decreasing carrageenan contents.

Fig. 3 (A) Water contact angles; (B) The inside surface of A1C4; (C) The outside surface of A1C4; (D) IR spectra; (E) XRD

4. Conclusions

A composite absorbent was successfully developed using carrageenan and calcium alginate. The absorbent exhibited fast swelling in saline water and high mechanical strength, a matrix of properties suitable for application in diapers. Kappa-carrageenan is more hydrophobic than alginate, showing a contrasting role in absorption. The novel absorbent is sustainable and biodegradable, providing an alternative to traditional super absorbent polymers.

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Highlights:

- Composite absorbents were prepared using sustainable polysaccharides carrageenan and sodium alginate
- The effect of composition on swelling was studied
- The maximal tensile strength was reached with a value of 12.8 MPa
- The effect of hydrophilicity on swelling was studied
- SEM was performed to reveal structural organization of the composite materials