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Research Article

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Double-Network Carboxymethyl Chitosan Grafting Polyacrylamide/Alginate Hydrogel Compositions Adapted to Achieve High Stretchable Properties

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Abstract

Double-network hydrogels with high mechanical strength have been synthesized using the carboxymethyl chitosan, alginate, and acrylamide. Separate gel of chitosan, alginate, and acrylamide is brittle and is easily broken into fragments under a modest stretching. The hydrogels were composed of three kinds of polymer, alginate is composed of a combination of ionically first network, and carboxymethyl chitosan grafting alginate is composed of a ductile covalently second network, forming a double-network structure, which, despite containing 86% water, can stretched to 11.5 times their initial length. This ionically and covalently crosslinked structure may expand the scope of hydrogel applications.

Keywords: Carboxymethyl chitosan; Alginate; Acrylamide; Hydrogel introduction

Introduction

Hydrogels are three-dimensional crosslinked polymeric structures which are able to swell up to thousands of time their own weight in the aqueous environment. The absorbed fluids are hardly removable even under some pressure. They have important applications in the field of medicine, pharmacy, biotechnology, foods, cosmetics, and agriculture. In many applications, the use of hydrogels is often severely limited by their mechanical properties. For example, the poor mechanical stability of hydrogels used for cell encapsulation often leads to unintended cell release and death [1], and low toughness limits the durability of contact lenses [2]. Hence, synthesis and investigation of specific and new hydrogels with high absorbency and mechanical strength has been the goal of several research groups in the past decades. Polyacrylamide have been widely studied and applied in different biomedical fields because of their good swelling behaviors and chemical stability [3,4]. Among these, high mechanical property hydrogels have been extensively investigated for potential use in pharmacy and biotechnology [5-12]. On the other hand, chitosan is a potentially useful pharmaceutical material because of its good biocompatibility and low toxicity [13-15]. More recently, many studies have been conducted to fabricate hydrogels about chitosan grafting PAM with superabsorbency, temperature sensitivities, pH-sensitivity and swelling kinetics [16-23]. All of these properties of chitosan grafting PAM hydrogels make them important materials in controlled drug delivery [3,4], wastewater treatment [3,17-19], molecular separation [21], and several technical applications.

However, most chitosan grafting hydrogels suffer from a lack of mechanical toughness, and only a few applications have been realized. Double-network (DN) structure has attracted much interest in this area as they can improve mechanical strength of hydrogels. Herein we describe, on the basis of this principle, the synthesis of chitosan grafting PAM hydrogels with high mechanical strength. DN hydrogels be prepared by carboxymethyl chitosan, alginate, and acrylamide with one step method. This practical one-step method for hydrogel synthesis is relatively simple and easy. Alginate form the ionically first network by crosslinking of calcium sulfate, chitosan and acrylamide form the covalently second network by copolymerization and crosslinking in the presence of N,N-methylene bisacrylamide and potassium persulfate. In this method, hydrogels synthesized through crosslinking copolymerization of carboxymethyl chitosan, alginate, and acrylamide shows special mechanical properties.

Experimental

Materials

Carboxymethyl chitosan, alginate, calcium sulfate and acrylamide, N,N-methylene bisacrylamide and potassium persulfate were of analytical grade and used without further purification.

Preparation of hydrogel

Certain amounts of carboxymethyl chitosan1.75 wt%)alginate1.75 wt%and acrylamide (9.8 wt%) were added to a three-neck reactor and dissolved in 86 wt% distilled water, equipped with a mechanical stirrer. After degassing the solution in a vacuum chamber, we added the potassium persulfate, 0.005 the weight of acrylamide, as a initiator for polyacrylamide, and N,N-methylene bisacrylamide (0.0006 the weight of acrylamide) as the crosslinker for polyacrylamide, and calcium sulphate slurry ($CaSO_4 \cdot 2H_2O$), 0.005 the weight of alginate, as the ionic crosslinker for alginate. The solution was poured into a glass mould measuring 75.0×75.0×3.0 mm^3, covered with a 3-mm-thick glass plate. The gel was cured in one step with heated 50°C in a vacuum oven for 6 hour.

Results and Discussion

Mechanism of hydrogel formation

A general reaction mechanism for the carboxymethyl chitosan, acrylamide and alginate of the hydrogel is shown in Figure 1. We have synthesized extremely stretchable and tough hydrogels by mixing three

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substance: ionically crosslinked alginate, and covalently crosslinked carboxymethyl chitosan-graft-polyacrylamide (the grafting polymer was formed via a simple free radical copolymerization. Alginate form theionically first network by crosslinking of calcium sulfate, each alginate chain contains a large number of G blocks, many of which form ionic crosslinks with G blocks on other chains when enough Ca^{2+} ions are present. In an aqueous solution, the G blocks in different alginate chains form ionic crosslinks through divalent cations, resulting in a network in water and then forming an alginate hydrogel. By contrast, carboxymethyl chitosan and acrylamide form the covalently second network by copolymerization and crosslinking in the presence of N,N-methylene bisacrylamide and potassium persulfate. The latter involves two steps. In the first step, the grafting polymer is synthesized in the absence of a crosslinking agent. And in the second step, the synthesized polymer is crosslinked using N,N-methylene bisacrylamide. Hydrogels was prepared by simultaneous grafting copolymerization and by crosslinking of a crosslinking agent in solution.

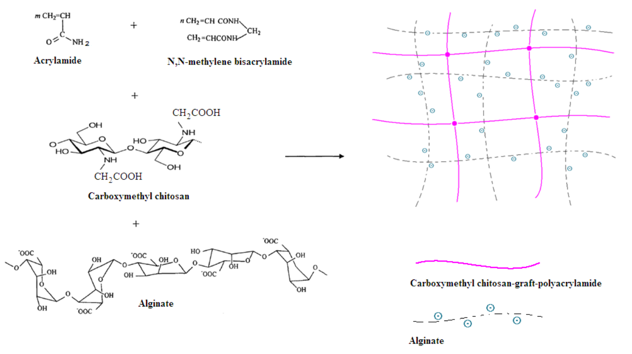

Figure 1: Schematic of carboxymethyl chitosan-graft-polyacrylamide/alginate hydrogel.

Spectral characterization

FTIR spectrum of the hydrogel was shown in Figure 2. Two sharp absorption peaks shown at 2340 and 1670 cm^{-1} are attributed to stretching of -CN and $-CONH_2$ groups, respectively.

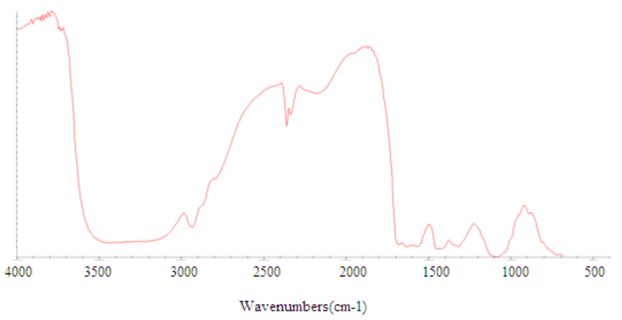

Figure 2: FTIR spectrum of the carboxymethyl chitosan-graft-polyacrylamide/alginate hydrogel.

The absorption modes at 1700, 1550 and 1410 cm^{-1} can be attributed to carbonyl stretching of COOH groups and asymmetric and symmetric stretching modes of carboxylate groups, respectively. The stretching band of -NH overlapped with the -OH stretching band of the carboxylic groups.

Mechanical properties of the hydrogel

Most hydrogels do not exhibit high stretchability. Here we report the synthesis of hydrogels forming ionically and covalently crosslinked networks. Although such gels contain 86% water, they can be stretched beyond 10 times their initial length Figure 3. The extremely stretchable hybrid gels are even more remarkable when compared with the alginate and polyacrylamide. The hydrogel was tested by INSTRON 3365 (Instron series automatic material testing system 8.27.00the stretching rate: 100mm/min). The stress and stretch at rupture were, respectively, 111 kPa and 11.5 for the hybrid gel, 3.7 kPa and 1.2 for the alginate gel, and 11 kPa and 6.6 for the polyacrylamide gel. Thus, the properties at rupture of the hybrid gel far exceeded those of either of its parents. One possible structure reason for the high stretchability may because the ionically and covalently networks are highly crosslinked. The DN-gels have already been shown to be superior to conventional gels in mechanical properties. The load sharing of the two networks may be achieved by entanglements of the polymers, and by possible covalent crosslinks formed between the amine groups on polyacrylamide chains and the carboxyl groups on alginate chains.

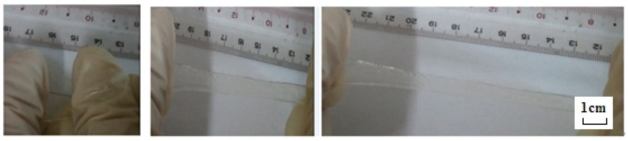

Figure 3: The hybrid gel is highly stretchable.

Conclusions

A novel high stretchable hydrogel composed of carboxymethyl chitosan, polyacrylamide and alginate DN was synthesized by a crosslinking copolymerization route in the presence of N,N-methylene bisacrylamide, potassium persulfate and calcium sulfate. The structure of the hydrogel was characterized by Fourier transform infrared spectroscopy. Although such gels contain 86% water, the stress and stretch at rupture were, respectively, 111 kPa and 11.5 for the hybrid gel. Hydrogels of superior stiffness, toughness and stretchability recoverability will improve the performance in applications of cell encapsulation and contact lenses, and will probably open up new areas of application for this class of materials.

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