Tough and anti-swelling naturally derived adhesives by long-chain toughening and electrostatic attraction

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EXTENDED ABSTRACT

Simultaneous achievement of anti-swelling properties and strong tissue adhesion in hydrogel adhesives is crucial for their medical applications. In this paper, an effective strategy combining long-chain toughening and electrostatic attraction induced anti-swelling is proposed. Natural macromolecular hydrogel adhesives composed by loosely crosslinked macromolecular network and polyelectrolyte microspheres is designed. The hydrogel can achieve intrinsic toughening by increasing the chain length of the polymer network. And by introducing polyelectrolyte microspheres, excellent anti-swelling property is achieved through the electrostatic attraction between polyelectrolyte microspheres and the polymer network. The prepared hydrogel adhesive was able to achieve up to 100 J/m^2 adhesion energy with a variety of porcine tissues, and the hydrogel showed excellent anti-swelling properties with swelling ratio of 1.13 at 37°C for 24 h in wet environment. By changing the influencing factors, the anti-swelling mechanism of the hydrogel was investigated, and the design basis for the anti-swelling hydrogel was provided.

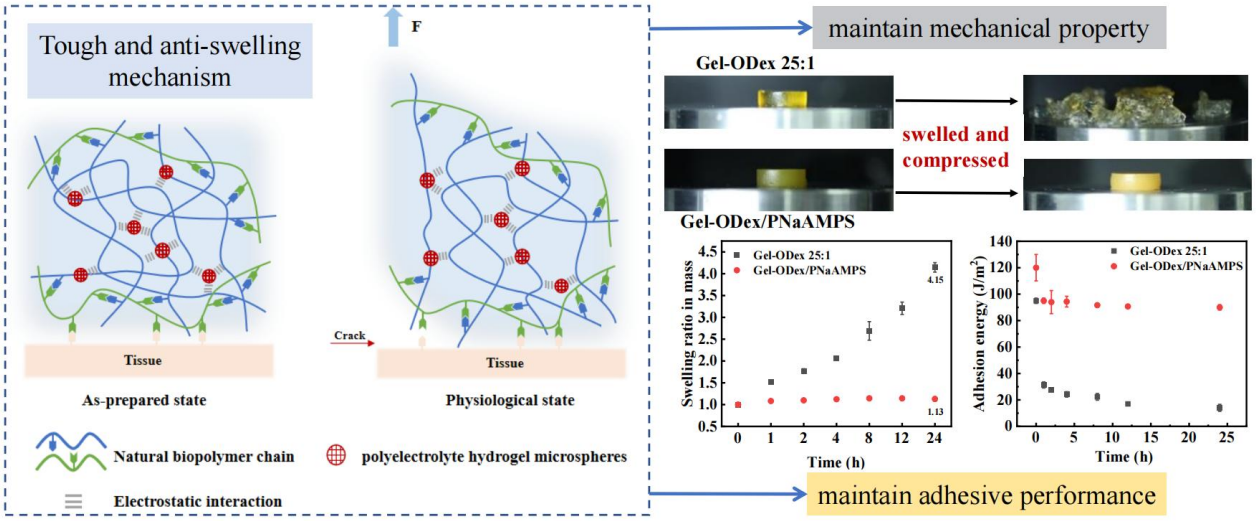

Figure 1. Schematic of the tough and anti-swelling mechanism induced by long-chain and polyelectrolyte microspheres.

SECTIONS

Introduction

Using tissue adhesives to replace sutures and staples in surgery for minimally invasive wound sealing and repairing is of great importance in medical science. Natural macromolecular hydrogel adhesives (NMHA) have attracted much attention due to their biocompatibility, biodegradability, injectability and mechanical compliance with tissues. However, the naturally derived adhesives still need to overcome two key challenges to achieve clinical applications: First, it needs to form tough adhering interface with tissues so as to withstand high mechanical loads in living organs. Second, it needs to avoid massive swelling which may weaken the adhesion and compress the adjacent organs .

Herein, we realize tough and anti-swelling NMHA by applying the long chain mechanism to the hydrogel synthesis and resolving the performance conflicts through a strategy combining long-chain toughening and electrostatic attraction. Most natural macromolecules, such as proteins and polysaccharides, are usually characterized by having a long polymer chain with an isoelectric point. In physiological environment, natural macromolecules usually carry a net charge. Based on this feature, we design the natural macromolecular hydrogel adhesives with two parts: the loosely crosslinked macromolecular network and polyelectrolyte hydrogel microspheres (Figure 1). The macromolecular network has pendant functional groups to form bonds with tissue. And it also has long polymer chains between two crosslinking points to work as elastic dissipater for energy dissipation, which ensures high interfacial toughness of the hydrogel adhesive. The polyelectrolyte hydrogel microspheres carry opposite charges toward the macromolecules, which are distributed in the macromolecular network and physically entangle with the macromolecular chains, attracting surrounding macromolecular chains through electrostatic interaction to suppress the swelling of macromolecular network. As a result, tough and anti-swelling natural macromolecular hydrogel adhesives can be achieved.

Results and discussions

In this work, we used oxidized dextran (ODex) and A-type gelatin (Gel), which were widely used in NMHA, to form the long-chain macromolecular network. And we also introduced poly(2-acrylamido-2-methylpropane sulfonic acid sodium) (PNaAMPS) microgel as the oppositely charged polyelectrolyte microspheres.

We changed the mass ratio between gelatin and oxidized dextran to adjust the chain length. The hydrogel with Gel/OD=25:1 was more stretchable with improved mechanical performances and the fracture toughness increased nearly tenfold, which demonstrated the long-chain toughening mechanism. By applying the long-chain Gel-ODex/PNaAMPS hydrogel adhesive to various porcine tissues, we proved its efficient adhesion to different types of tissues with all adhesion energies over ~100 J/m^2.

To demonstrated the anti-swelling capacity induced by polyelectrolyte microspheres, we immersed the hydrogel samples in deionized water for 24 h and evaluated the dynamic swelling behaviors. The swelling ratio of Gel-ODex/PNaAMPS hydrogel rarely changed with immersing time, and the volume changes of the hydrogel was at the low level of 10% compared with Gel-Odex hydrogel. To demonstrate the influence of swelling on the mechanical properties of hydrogel adhesives, we compared the compression properties of hydrogel samples before and after swelling. When after swelling, the Gel-ODex hydrogel without polyelectrolyte microspheres became noticeably brittle as the swollen gel was broken into pieces under compression, while the Gel-ODex/PNaAMPS could still maintain itself. While for the Gel-ODex/PNaAMPS hydrogel, the compressive strengths and modulus decreased no more than 5%, and its adhering interface with porcine skin could also remain over 70% of the maximum adhesion energy after submerging in water over 24 h.