Versatile hydrogel based on polyvinyl alcohol/chitosan/regenerated silk fibroin

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Abstract. Versatile sensors have broad application prospects in human motion detection, health monitoring, wearable electronic devices and flexible electronic skin and other emerging fields. In this work, the enhanced hydrogel was prepared by freezing and thawing process with calcium ion crosslinking. This composite material shows excellent flexibility and elasticity, and after being cut in half, it can automatically heal well in a short time without external force. It shows great potential in flexible and wearable devices.

1. Introduction
With the rapid development of mobile Internet and intelligent terminals, wearable electronic devices have presented a huge market prospect. As one of the core components of wearable electronic devices, flexible wearable sensors have become the focus of attention due to their wide sensitivity range, short response time, portability and comfort [1-3]. Biological hydrogels are three-dimensional network materials formed by cross-linking hydrophilic polymer chains in an aqueous microenvironment [4, 5]. They are chemically or physically crosslinked and have unique structure and mechanical properties, which can be customized according to specific requirements [5]. Compared with other materials, polyvinyl alcohol (PVA) hydrogels have the advantages of good security, high flexibility, good transparency, mild preparation process and extensibility, making them ideal materials for the manufacture of portable wearable sensors [6].

The combination of gelatin, chitosan (CS), cellulose and PVA is a common method to improve the mechanical strength of hydrogels [7-10]. For example, the tensile strength of bacterial cellulose/PVA composite hydrogel prepared by Liu [8] and other gelatin/PVA and Zhao [9] is close to 1 MPa, Wang et al. [10] combined CS and PVA to prepare the hydrogel with sensitivity to the precursor. However,
the materials with high tensile strength, self-healing properties, good water retention and biocompatibility are still needed in practical applications [11].

In existing studies, PVA has been combined with silk fibroin (SF) (a fibroin from silk fiber) to achieve biocompatibility and biodegradability [12]. The addition of SF in PVA hydrogel improved the stability of the hydrogel and significantly increased the water absorption of the gel [13]. In addition, because of its unique microstructure (including beta folding), SF can contribute to the water retention of PVA hydrogels [11].

Herein, a self-healing hydrogel was made by polyvinyl alcohol/chitosan/regenerated silk fibroin (PVA/CS/RSF). It was prepared by calcium ion crosslinking freeze-thaw method and exhibits excellent flexibility and elasticity, and it can automatically heal well in a short time without external force after being cut in half.

2. Experimental
PVA/CS/RSF enhanced hydrogel was prepared by calcium ion crosslinking and freeze-thaw method. The specific preparation process of hydrogel is shown in figure 1. First, the modified PVA solution needs to be prepared. 5 g PVA and 2 g CS were put into a beaker, and heated in a water bath at 90 ℃ for 2.5 h, then cooled to room temperature, and stirred at 1000 rpm to obtain the modified PVA solution.

After that, boiled a small amount of cocoons in 0.2 M NaCO₃ solution for 30 minutes, washed them with deionized water for several times, and then dried them at 60 ℃ for 3 days to obtain degummed fibers. Then, the degummed fibers were stirred and dissolved in the mixed solution of CaCl₂/H₂O/C₂H₅OH (1:8:2) at 85 ℃, and dialyzed it in deionized water for 3 days. The dialysate was then centrifuged at 6000 rpm for 30 minutes to remove suspended particles. Then, RSF solution was obtained from the supernatant. Finally, 10 ml modified PVA solution and 0.2 ml RSF solution were mixed and placed in a glass container and stirred for 2 hours at 2000 rpm at room temperature. Then put the stirred solution in the refrigerator, froze and thawed at minus 20 ℃ for 5 times (2 hours each time). After 10 hours, removed it from the refrigerator, cooled at room temperature, and get PVA/CS/RSF hydrogel from the container.

The morphology was analyzed by scanning electron microscopy (SEM, S-4800).

3. Results and Discussion
The macroscopic properties of functional materials are usually closely related to their microstructures [14 – 16]. The structure of PVA/CS/RSF hydrogel was studied by scanning electron microscope (SEM) as shown in figure 2. The surface of PVA/CS/RSF hydrogel is irregular and there are many holes in the internal structure of the hydrogel, as shown in figure 2 (a-b). The optical image of hydrogels is shown in figure 2 (c), they are pure PVA, PVA/CS, RSF and PVA/CS/RSF from left to right,
respectively. The original pure PVA showed a white appearance, which turned yellow and thicker after introducing CS, RSF. The loading capacity of hydrogel was investigated by hanging a weight on the hydrogel. It is found that the hydrogel can bear a maximum weight of 500 g, as shown in figure 2 (d). The hydrogel can be highly compressed and then returned to its original shape, showing excellent flexibility, as shown in figure 2 (e). Similarly, as shown in figure 2 (f), the original gel is about 4.5 cm in length, and is about 9.3 cm after stretching. It can be stretched to twice its length and then restored to its original state, as shown in figure 1, the physical crosslinking of the hydrogel was not destroyed after stretching, showing excellent elasticity. Therefore, PVA/CA/RSF hydrogel is an ideal material for flexible devices.

Figure 2. (a), (b) Surface and internal images of PVA/CS/RSF hydrogel. (c) Optical image of hydrogels. (d) Bearing capacity test of PVA/CS/RSF hydrogel. (e) The optical images of cylindrical PVA/CS/RSF hydrogel in its initial state, compressed and restored with fingers. (f) Optical images of PVA/CS/RSF hydrogel before, during and after stretching.

Autonomous self-healing is defined as the property that enables a material to repair damage internally and automatically. It usually occurs in prepared materials without the intervention of external stimulation to promote the occurrence or degree of self-healing [17, 18]. As shown in figure 3 (a), there are two original hydrogels. The transparent one is hydrogel without adding RSF, and the yellow one is hydrogel added with RSF. In order to study the self-healing ability of hydrogels after adding RSF, the PVA/CS/RSF hydrogel was cut into two halves on the table, as shown in figure 3 (b). Without any external interference, two hydrogels can heal autonomously in a short time, as shown in figure 3 (c). In order to detect good self-healing, the self-healing hydrogel was picked up vertically for a period of time and swayed around. PVA/CS/RSF hydrogel can support its weight and shake without breaking, as shown in figure 3 (d).
Figure 3. (a) Two original hydrogels with RSF (yellow) and no RSF (transparent). (b) Two cut raw hydrogels. (c) The self-healing condition of the hydrogel after cutting without any external stimulation at room temperature (20 °C). (d) Test whether the PVA/CS/RSF hydrogel can support its own weight without breaking after healing.

4. Conclusions
A self-healing hydrogel was made by polyvinyl alcohol/chitosan/regenerated silk fibroin (PVA/CS/RSF). It has the advantages of simple preparation technology, low material cost, practicability and environmental protection. The composite material shows excellent flexibility and elasticity, and after being cut in half, it can automatically heal in a short time. It shows great potential in wearable devices, human-computer interaction, remote personalized medical data collection and other aspects.

Acknowledgements
This work was supported by the Anhui Collaborative Innovation Project (GXXT-2019-036), Open Research Fund of National Engineering Research Center for Agro-Ecological Big Data Analysis & Application, Anhui University (No. AE201910, AE202001), Open Research Fund of Key Laboratory of Textile Fiber and Products (Wuhan Textile University), Ministry of Education (No. Fzxw2021026).

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