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A novel highly stretchable, adhesive and self-healing silk fibroin powder-based hydrogel containing dual-network structure

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ABSTRACT

We have demonstrated a novel strategy to enhance mechanical strength by designing dual-network (DN) structures. The novel self-healing hydrogel system composed of silk fibroin powder (SFP) and polyacrylamide (PAM) combines hydrogen bond supramolecular action. In addition, this system was prepared via a simple one-pot method of copolymerization. The SFP-PAM hydrogels could achieve high mechanical properties. The stress and strain at break were 0.65 MPa and 2250%, respectively. The hydrogels exhibited adhesive and self-healing properties. The fabricated multifunctional SFP-PAM hydrogel shows promise in potential applications in wound dressing and transparent artificial skins for body-adhered signal detection.

1. Introduction

As there are widespread applications of hydrogels, only improving the mechanical properties of hydrogels is insufficient to meet the practical requirements. Hence, preparation of intelligent, strong, and ductile hydrogels is of great significance. The hydrogels have been widely investigated because of their versatile properties ranging from high mechanical strength to multiple properties for extensive applications such as tissue engineering [1], soft robotics [2], stretchable electronics [3,4], and soft devices [5]. However, it has always been a challenge to fabricate an adhesive and self-healing hydrogel that can exhibit robust bonding to the surface or fractured surface of materials while simultaneously maintaining excellent mechanical properties [6].

To overcome the above issues and extend the practical applications of hydrogels, significant efforts have been made to prepare mechanically strong hydrogels with a suitable material system. Silk fibroin powder is a biocompatible component and contains one or more long chains of amino acid residues which can dissolve in water. Silk fibroin hydrogels have shown significant potential in the biomedical engineering field due to their biocompatibility, tunable biodegradability, and non-immunogenicity [7,8].

Herein, a novel silk fibroin powder material system is proposed to obtain a highly stretchable and self-healing hydrogel. The hydrogel composed of silk fibroin powder and polyacrylamide was prepared via physical and chemical crosslinking of copolymerization. The resultant SFP-PAM hydrogel exhibited mechanically robust, adhesive, and self-healing behavior. The SFP-PAM hydrogels would have potential applications in wound dressing, transparent artificial skins, and bioelectrodes for body-adhered signal detection.

2. Experimental section

2.1. Preparation

The aqueous silk fibroin solution was obtained by fibroin powders directly which different from traditional silk-worm cocoons according to the procedures reported previously [9]. The typical procedure for the same is as follows. Firstly, the silk fibroin solution (35 wt%) and acrylamide solution (15 wt%) were mixed in the weight ratio of 3:2 and a homogeneous and transparent mixture solution was formed. Subsequently, a crosslinker (N,N′-methylene diacrylamide, BIS) and initiator (ammonium persulfate, APS) were added into the mixed solution. The resultant solution was injected into a glass mold and the samples were kept at 60 °C for 6 h to complete the free radical polymerization reaction to form the SFP-PAM hydrogel. The hydrogel before sectioning is labelled as original SFP-PAM. When the fracture part hydrogels after self-healing, it is named by self-healing SFP-PAM hydrogel. The original and self healing SFP-PAM hydrogels are of same material.

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2.2. Characterization

The chemical structure and micro-network structure of SFP, PAM, and SFP-PAM hydrogel were analysed via Fourier transform infrared spectrometer (FTIR) (Nicolet-6700, USA) and thermal field emission Scanning electron microscopy (SEM) (SU-70, Japan). Then, the mechanical properties of the original and self-healing SFP-PAM hydrogels were measured by using universal testing machine (Hounsefield H25K, UK). The cross-head speed was 50 mm/min. Three identical dumbbell-shaped specimens were tested for each sample and their average mechanical properties were reported.

3. Results and discussion

The FTIR spectroscopy results for SFP, PAM, and SFP-PAM hydrogels are exhibited in Fig. 1A. The main characteristic peaks of SFP were present at 3297 cm^{-1} (amino groups), 1652 cm^{-1} (carbonyl groups), 1528 cm^{-1}, and 1251 cm^{-1} (N—H bending and C—N stretching vibration). For PAM, 3345 cm^{-1} and 3191 cm^{-1} were the absorption peaks attributed to free and associated amino groups, respectively, and 2930 cm^{-1} and 1456 cm^{-1} were the vibration peaks of methylene. The absorption band at 1120 cm^{-1} is attributed to —C=O stretching vibration [10]. Different from SFP and PAM, the two broad absorption peaks for the SFP-PAM samples at 1626 and 1082 cm^{-1} were due to the new stretching vibrations of the C=O and C—N groups of the PAM or SF in the copolymer system. The position of these peaks is offset by hydrogen bonding [11]. A diagram in Fig. 1B elaborates the mechanism of hydrogen bond formation. Hydrogen bonding is extremely easy between the polypeptide and amide bond molecular chains, which has already been observed in the case of other polymers [12]. To observe the dual network micro-structure of the SFP-PAM hydrogel, the fractured surface of a freeze-dried sample was observed under SEM (see Fig. 1C). Compared to the SFP and PAM hydrogels, the SFP-PAM hydrogel exhibited clear uniform porous network structures. The micrographs reflected that silk fibroin and polyacrylamide formed a continuous phase in all the polymer blends. The pore wall was changed from rough to a filiform surface indicating the adhesive performance.

The self-healing behavior of the hydrogels was also investigated. As shown in Fig. 2A, the original SFP-PAM hydrogel was cut into three sections and one part was stained with Rhodamine B while another one was stained with Brilliant blue. Then, the three pieces of the hydrogels were recombined at room temperature without healing agents or stimulus. After the desired healing time (within 6 h), the cutting interface disappeared. The recombined pieces could also withstand an external force. The diffusion of rhodamine B from one-third to another could be observed directly as the cutting interface disappeared. As shown in Fig. 2B, the original SFP-PAM hydrogels demonstrated a high tensile strength (the stress and strain at break were 0.65 MPa and 2250%). The tensile stress and tensile strain of self-healing SFP-PAM hydrogels were 0.56 MPa and 1800%, which are slightly lower than those of the original hydrogels. It has been reported that pure SF and PAM hydrogels fracture in a brittle manner [13,14]. The self-healing mechanism of the hydrogels was also investigated. Previous studies have shown that the weaker interactions such as hydrogen bonding may provide a promising chance for self-healing materials as long as the spatial density of the bonds is sufficiently high [15]. As shown in Fig. 2C, a network structure built with the addition of SFP can contribute to a high spatial density of the hydrogen bonds

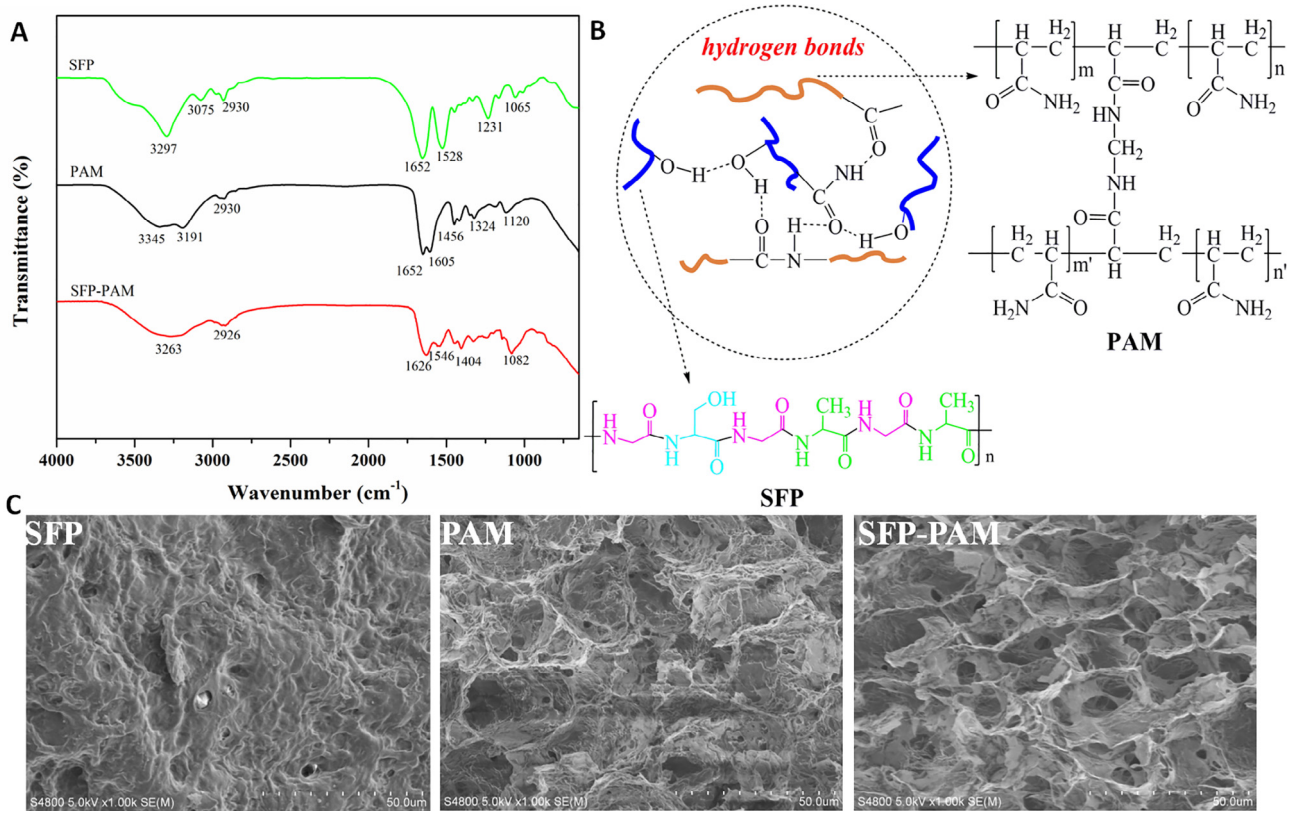

Fig. 1. . (A) FTIR analyses of the hydrogels; (B) the diagram mechanism of hydrogen bond formation; (C) SEM photographs showing cross-sectional morphology of the hydrogels.

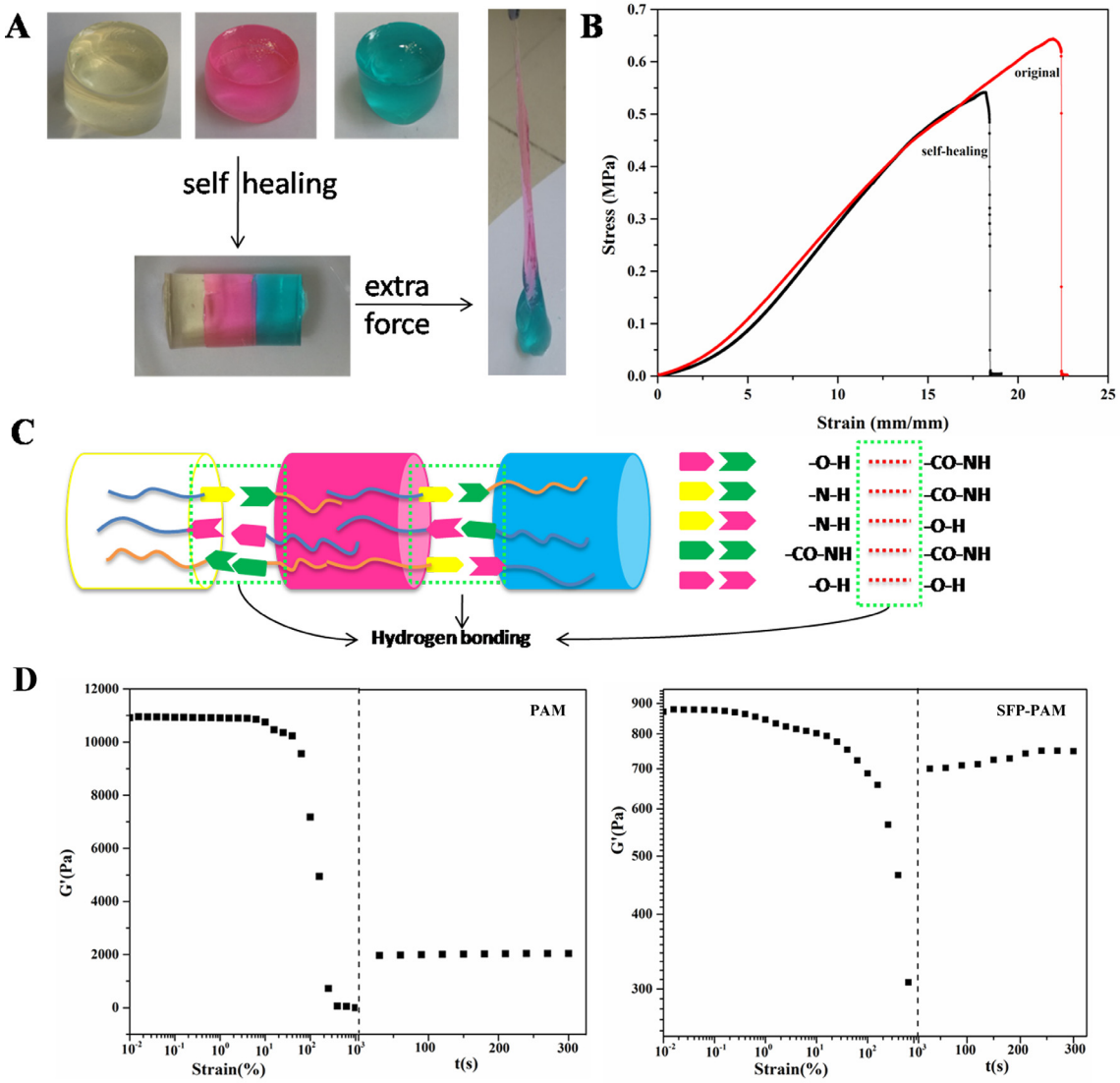

Fig. 2. (A) Photographs showing the self-healing behavior; (B) stress-strain curves of the hydrogels; (C) schematic illustration of the self-healing mechanism of the hydrogel after a cut; (D) rheological test of PAM and SFP-PAM hydrogel.

and more adherent points on the cut surface. This is because silk fibroin contains one or more long chains of amino acid and hydroxyl (see Fig. 1B). When the network of the hydrogel was damaged, the SFP and the PAM chains at the two outermost layers tended to rearrange at the interface via hydrogen bond interactions to allow their groups to reconstruct fresh hydrogen bonds. Hence, the incorporation of hydrogen bonding may effectively provide the hydrogel with a self-healing ability. In order to further investigate the self-healing behavior of PAM and SFP-PAM hydrogels, rheological recovery tests were also performed on the hydrogels. Rheological tests (Fig. 2D) show that the energy storage modulus of self-healing SFP-PAM hydrogels can be nearly restored to the initial value after the damage of large deformation, while the energy storage modulus of PAM hydrogels without self-healing property can only be slightly restored after the damage of large deformation.

As shown in Fig. 3A and Video S1, the silk fibroin powder based hydrogel was highly stretchable and sufficiently tough to be used for complex deformations. The hydrogel could easily stretch repeatedly. The hydrogel film stretched 20 cm, which is four times the original length. Fig. 3B shows that the hydrogel could easily stick on stainless steel ingot and latex gloves. Furthermore, SFP-PAM hydrogels elongated to more than 15 times their original length (1 cm) while not separating from the stainless steel ingot. As shown in Fig. 3C and Video S2, the hydrogel was still firmly attached to the simulative skin when it was stretched and followed the movement of the joint as the finger was bent. The adhesiveness of the hydrogel on the author's fist shows that the formulated hydrogels exhibit an excellent adhesive property. It could be stretched or twisted and could be easily peeled off. In conclusion, the SFP-PAM hydrogels are suitable for complex deformations in real applications.

4. Conclusion

We prepared a novel dual-network structure material system hydrogel. The prepared DN hydrogels exhibited superb mechanical properties as the stress and the elongation at break were 0.65 MPa and 2250%. Moreover, the hydrogels demonstrated adhesive and self-healing properties under ambient conditions owing to hydrogen bonding. The research can broaden the scope of current

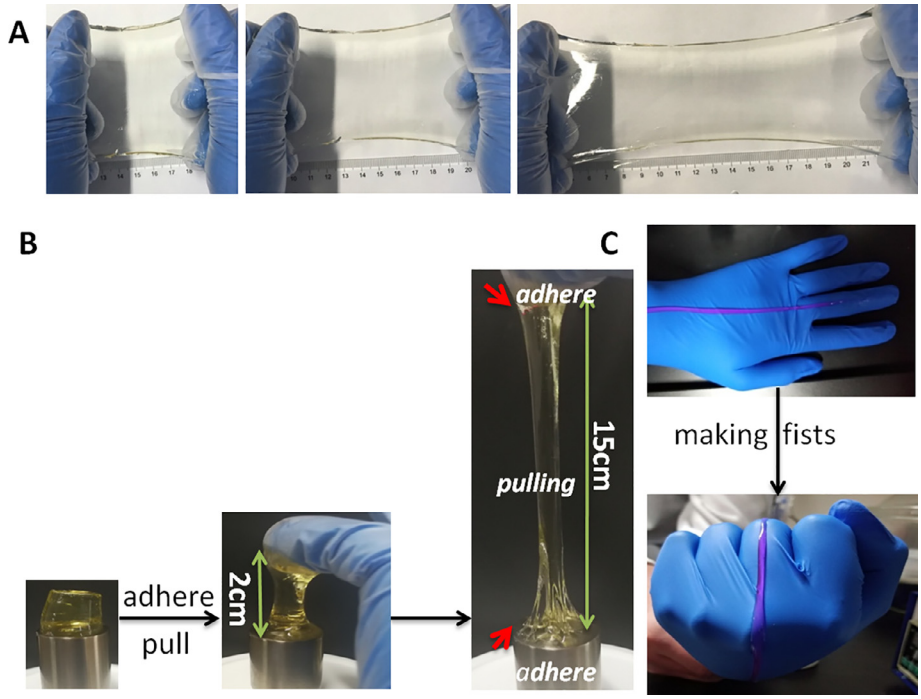

Fig. 3. (A) Photographs of SFP-PAM hydrogel exhibit highly stretchable; (B) adhesive exhibition of SFP-PAM hydrogel; (C) SFP-PAM hydrogel adhering and moving with the finger.

highly stretchable and self-healing hydrogel studies and applications.

Declaration of Competing Interest

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2019.05.129.

References

[1] S. Hong, D. Sycks, H.F. Chan, S. Lin, G.P. Lopez, F. Guilak, K.W. Leong, X. Zhao, Adv. Mater. 27 (2015), 4034-4034.
[2] F. Luo, T.L. Sun, T. Nakajima, T. Kurokawa, Y. Zhao, K. Sato, A.B. Ihsan, X. Li, H. Guo, J.P. Gong, Adv. Mater. 27 (2015) 2722–2727.
[3] C. Larson, B. Peele, S. Li, S. Robinson, M. Totaro, L. Beccai, B. Mazzolai, R. Shepherd, Science 351 (2016) 1071–1074.
[4] L. Han, X. Lu, M. Wang, D. Gan, W. Deng, K. Wang, L. Fang, K. Liu, C.W. Chan, Y. Tang, Small (2017) 13.
[5] M. Liao, P. Wan, J. Wen, M. Gong, X. Wu, Y. Wang, R. Shi, L. Zhang, Adv. Funct. Mater. 27 (2017) 1703852.
[6] J. Xu, Z. Fan, L. Duan, G. Gao, Polymer Chem. 9 (2018) 2617–2624.
[7] L. Shi, F. Wang, W. Zhu, Z. Xu, S. Fuchs, J. Hilborn, L. Zhu, Q. Ma, Y. Wang, X. Weng, D.A. Ossipov, Adv. Funct. Mater. 27 (2017) 1700591.
[8] J. Ming, M. Li, Y. Han, Y. Chen, H. Li, B. Zuo, F. Pan, Mater. Sci. Eng. C Mater. Biol. Appl. 59 (2016) 185–192.
[9] L. Zhao, J. Luo, H. Wang, G. Song, G. Tang, Appl. Thermal Eng. 99 (2016) 495–501.
[10] X. Wang, W. Deng, Y. Xie, C. Wang, Chem. Eng. J. 228 (2013) 232–242.
[11] M.M. Coleman, D.J. Skrovanek, J. Hu, P.C. Painter, Macromolecules 21 (1988) 59–65.
[12] Z.H. Ayub, M. Arai, K. Hirabayashi, Biosci. Biotechnol. Biochem. 57 (2014) 1910–1912.
[13] J. Ma, J. Lee, S.S. Han, K.H. Oh, K.T. Nam, J.Y. Sun, ACS Appl. Mater. Interfaces 8 (2016) 29220–29226.
[14] K. Luo, Y. Yang, Z. Shao, Adv. Funct. Mater. 26 (2016) 872–880.
[15] X. Tong, L. Du, Q. Xu, J. Mater. Chem. A 6 (2018) 3091–3099.