

Electronic Supplementary Information

Mussel-inspired self-healing of strong and stiff polymer

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1. Chemicals

Acetone, ethanol, methanol, nitric acid (HNO₃, 70%), hydrobromic acid (HBr, 48%), glacial acetic acid (CH₃COOH), hydrochloric acid (HCl, 37%), aluminum chloride anhydrous (AlCl₃), potassium carbonate (K₂CO₃) and Ferric chloride hexahydrate (FeCl₃·6H₂O) were supplied by Tianjin Kermel Chemical Reagent Co., Ltd (China). Chitosan, vanillin, benzyl bromide, sodium borohydride (NaBH₄), ethyl acetate and pyridine were purchased from Sinopharm Chemical Reagent Co., Ltd (China). All chemicals were used as received.

2. Synthesis of nitrocatechol substituted chitosan (CNC)

CNC polymer was synthesized according to the strategy illustrated in Fig. S1.^{1,2,3}

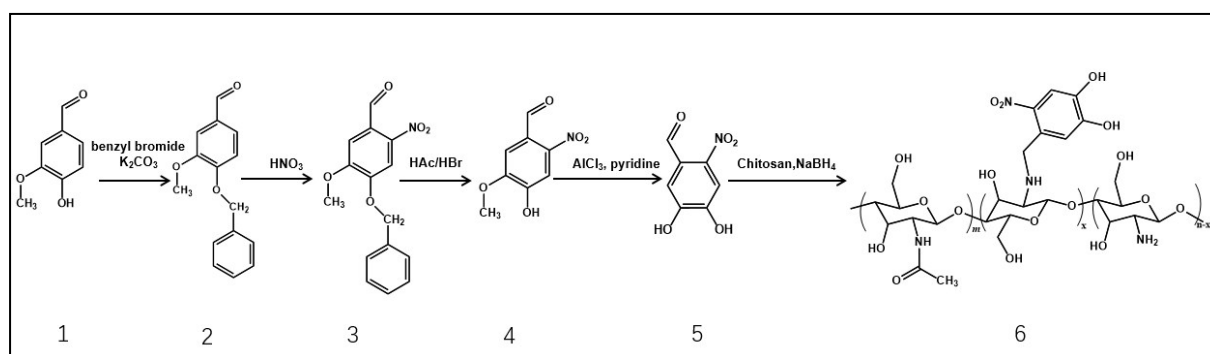


Fig. S1 Synthesis of nitrocatechol substituted chitosan (CNC).

Synthesis of *o*-benzylvanillin (2)

Vanillin **1** (20 g, 0.131 mol), benzyl bromide (22.4 g, 0.131 mol) and K₂CO₃ (8.85 g, 64 mmol) were mixed in 300 mL acetone under stirring. The resulting mixture was refluxed for 12 h and then poured into deionized water to yield white precipitate. The precipitate was recrystallized from ethanol to obtain 30.8 g colorless needles (*o*-benzylvanillin **2**).

Synthesis of *o*-benzyl-6-nitrovanillin (3)

o-Benzylvanillin **2** (30 g, 0.124 mol) was slowly added to concentrated nitric acid at 0 °C. After stirring at 20 °C for 1 h, the mixture was poured into iced water to produce yellow solid. The solid was recrystallized from ethyl acetate to obtain 34.2 g yellowish needles (*o*-benzyl-6-nitrovanillin **3**).

Synthesis of 6-nitrovanillin (4)

o-Benzyl-6-nitrovanillin **3** (34 g, 118 mmol) was added to 240 mL acetic acid under stirring at 85 °C. Later 75 mL hydrobromic acid (48%) was added to the above solution and then heated at 85 °C for 1 h to produce precipitate. The resulting precipitate was filtrated and recrystallized from boiling ethanol to obtain 14 g yellow crystals (6-nitrovanillin **4**).¹

Synthesis of 6-nitroprotocatechualdehyde (5)

6-Nitrovanillin **4** (14 g, 71 mmol), pyridine (21.5 g, 0.259 mol) and AlCl₃ anhydrous (11.5 g, 86 mmol) was mixed in 100 mL ethyl acetate under stirring. The resulting mixture was refluxed for 4 h and then cooled to 50 °C. Later 50 mL iced concentrated HCl was added to the above mixture. The resultant organic layer was washed with water and brine successively, dried with sodium sulfate and then evaporated to yield 8.6 g yellow needles (6-nitroprotocatechualdehyde **5**).²

Synthesis of nitrocatechol substituted chitosan (6)

4 g chitosan was dissolved in 200 mL 3 w/v% acetic acid aqueous solution. 6-nitroprotocatechualdehyde (3.5-14 mmol) was dissolved in 80 mL 50 v/v% methanol aqueous solution. After the above solutions were mixed under stirring for 1~2 h, sodium borohydride was added in small portions until the acidity of the mixture reached pH 9. The resulting precipitate was filtered and dissolved in 150 mL 5 wt% hydrochloric acid. The obtained solution was dropped into 600 mL alcohol to precipitate the polymer. The precipitate was filtered, washed with alcohol and dried in vacuum to produce nitrocatechol substituted chitosan (chitosan-nitrocatechol, CNC).³

Chitosan substituted with catechol (chitosan-catechol, CC) was synthesized by using protocatechualdehyde through the similar reductive amination.

The structure of the CNC was identified by ¹H-NMR spectroscopy (Fig. S2a). The peaks at 7.75 and 6.99 ppm are related to the aromatic protons of the nitrocatechol moiety, while those at 3.10 and 1.97 ppm are assigned to the protons of C2 in the glucose ring and *N*-acetyl groups, respectively.^{3,4} The ¹H-NMR spectrum of CC shows the

aromatic protons of the catecholic moiety at 6.7–7.0 ppm (Fig. S2b).³

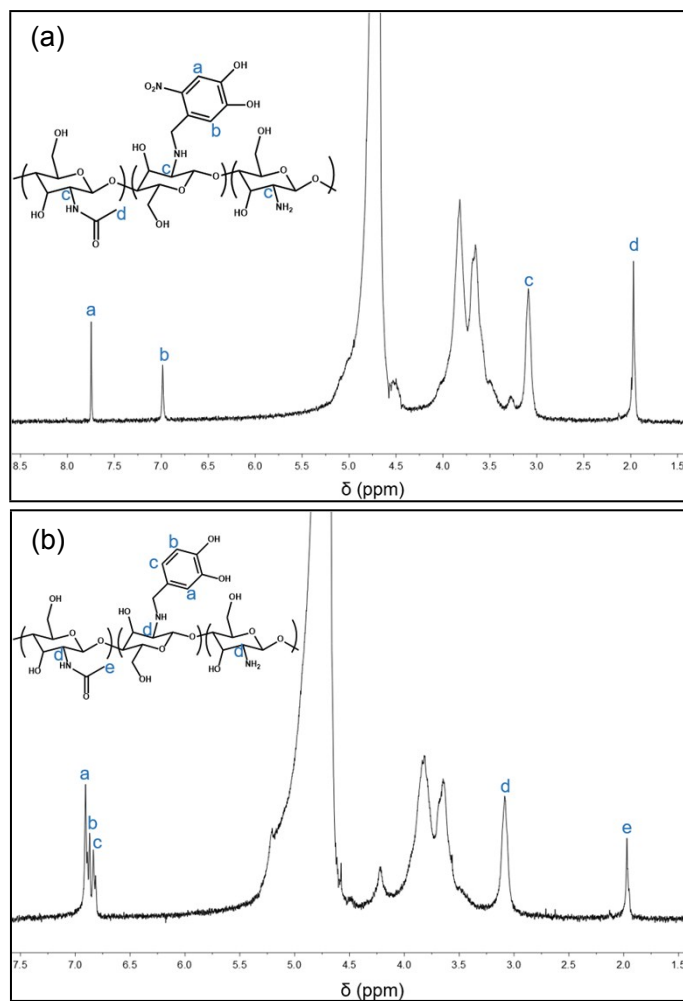


Fig. S2 ¹H-NMR spectra of the (a) CNC and (c) CC polymers.

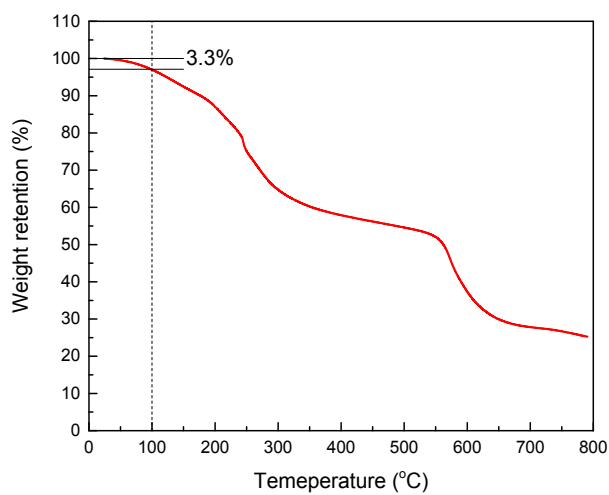


Fig. S3 TGA curve of the CNC filament.

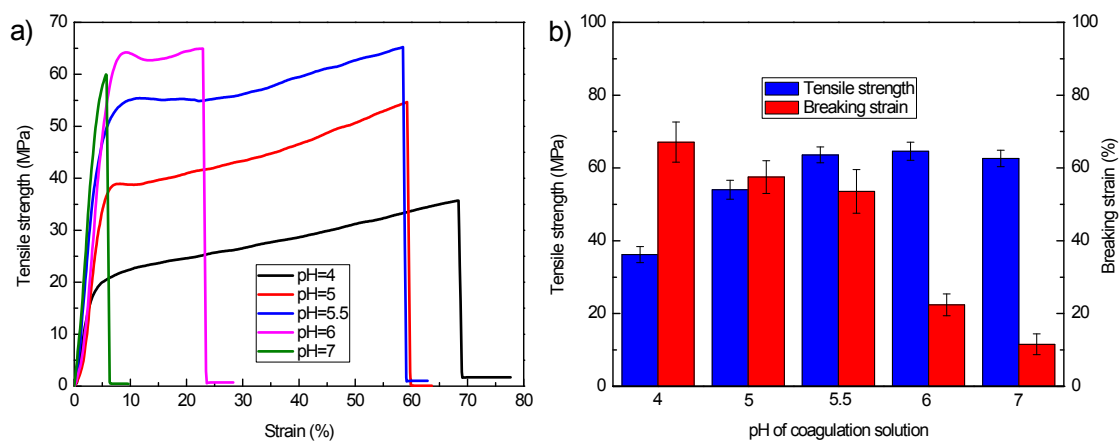


Fig. S4 Effect of the acidity of the coagulation solutions on the mechanical properties of the resulting CNC filaments.

As the pH of the coagulation solution raises, the tensile strength of the CNC filament increases while its breaking elongation decreases. The filament reaches its maximum strength and elongation when the acidity of the solution is pH 5.5 and pH 4, respectively. A balance between the tensile strength and elongation is achieved at pH 5.5. The pH-dependence of the mechanical property is due to the dynamic nature of the Fe-nitrocatechol coordination, as shown by the UV-vis spectra in Fig. S5.

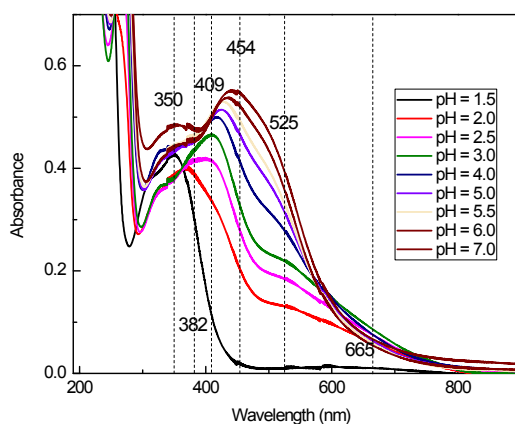


Fig. S5 UV-Vis spectra record the coordination of the CNC polymer with Fe^{3+} at different acidities.

At low pH of 1.5, there is a peak located at 350 nm, which can be ascribed to the protonated nitrocatechol moiety. Two peaks appear at 382 and 665 nm when the acidity of solution is increased to pH 2.0, indicating the formation of mono-Fe-nitrocatechol complex. The peaks shift to 409 and 525 nm as the acidity is increased to pH 2.5-5.0, indicating the formation of bis-Fe-nitrocatechol complexes. As pH is further increased above 5.5, a peak

assigned to tris-Fe-nitrocatechol complex appears at 454 nm.⁵ The UV-vis spectra demonstrate that the stoichiometry of the nitrocatechol-Fe coordination is strongly dependent on pH. Therefore, CNC chains were cross-linked by bis-Fe-catechol coordination when the filament was coagulated in the acidic solution, resulting in relatively low tensile strength but large elongation. In contrast, the filament exhibited high tensile strength and low elongation when it was coagulated in a neutral solution, since its CNC chains were cross-linked by tris-Fe-nitrocatechol complexation.

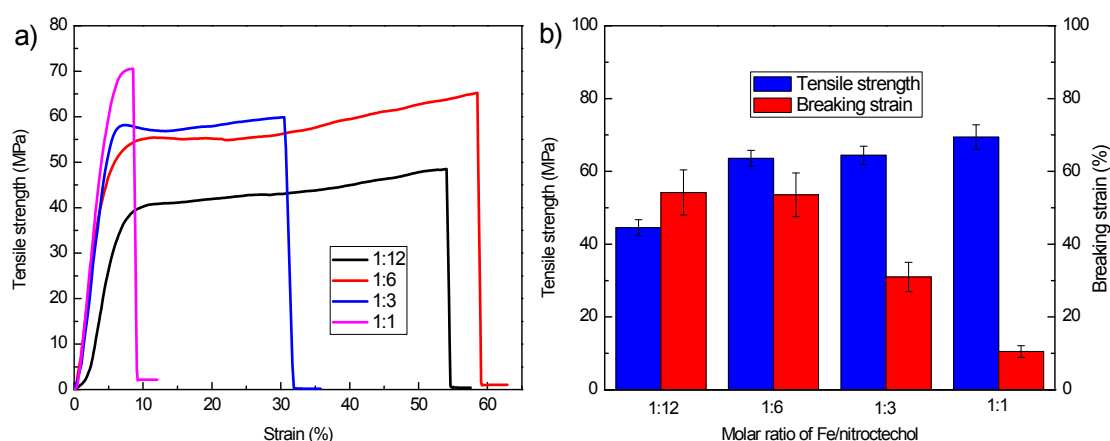


Fig. S6 Effect of the molar ratio of Fe/nitrocatechol on the mechanical properties of the resulting CNC filaments.

The molar ratio of Fe to nitrocatechol also affects the mechanical properties of the CNC filament. Generally, increasing the Fe/nitrocatechol ratio contributes to a higher tensile strength, while lowers the breaking elongation. The variation is attributed to the fact that the molar ratio determines the stoichiometry of the Fe-nitrocatechol coordination. Clearly high Fe/nitrocatechol ratio increases the cross-linking density between CNC polymer chains.

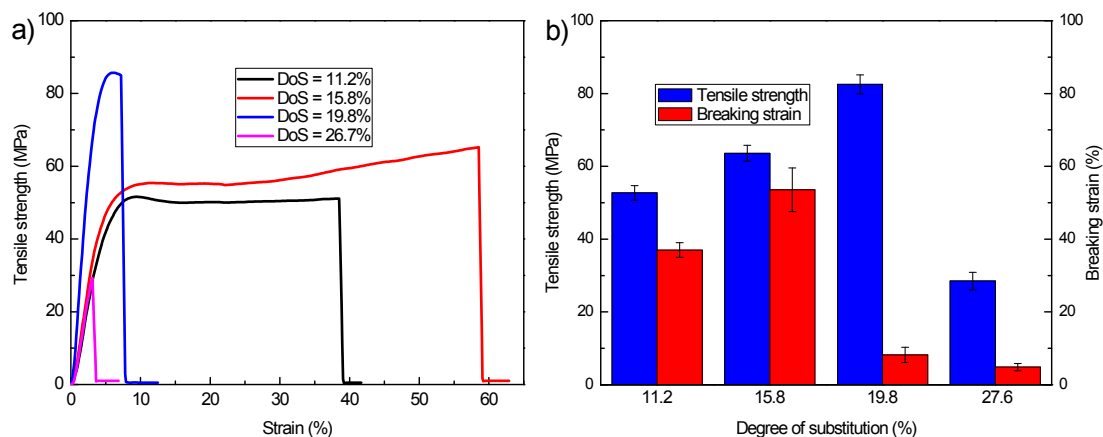


Fig. S7 Effect of the degree of substitution of DA on the mechanical properties of the resulting CNC filaments.

Fig. S7 shows that the CNC filament has the highest tensile strength (82.5 ± 2.6 MPa) when the substitution amount of DA is 19.8%. The largest elongation ($53.6 \pm 6.0\%$) is achieved at the DA substitution degree of 15.8%. However, for the filament has 27.6% DA, it exhibits the lowest tensile strength and elongation. The reason is that the CNC chains are cross-linked by a large amount of nitrocatechol-Fe coordination, and thus greatly increases the rigidity of the resulting polymeric network. In this study, the filament exhibits both high tensile strength (63.6 ± 2.2 MPa) and desirable elongation when the substitution degree is 15.8%.

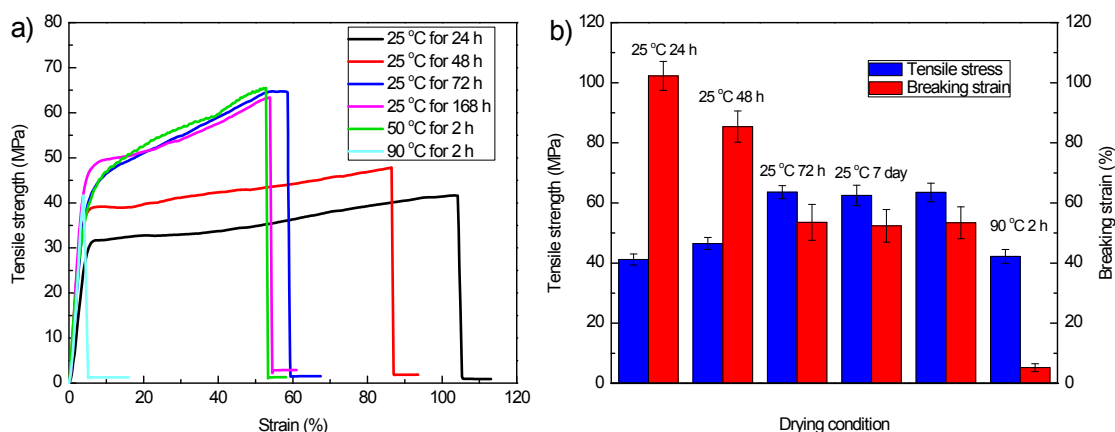


Fig. S8 Effect of drying temperature and time on the mechanical properties of the resulting CNC filaments.

When the filaments are dried at room temperature, prolonging drying time is beneficial for a higher elongation but a lower tensile strength. Both values tend to stable (63.6 ± 2.2 MPa and $53.6 \pm 6\%$, respectively) after drying at 25 °C for 72 h. However, the drying process will be significantly accelerated when the temperature is increased to 50 °C. The filament only takes 2 h to realize the similar mechanical property as that dried at 25 °C for 72 h. Note that the filament dramatically reduced the breaking strain when it was dried at 90 °C for 2 h. The reduction is attributed to the loss of dynamic nature of catechol-Fe coordination in the absence of trace water.⁶ Consequently, energy dissipation becomes difficult when the coordinate bond suffers from external force, leading to the formation and propagation of crack in the filament. The results demonstrate that small amount of water in CNC polymer is crucial for its strength and hardness.

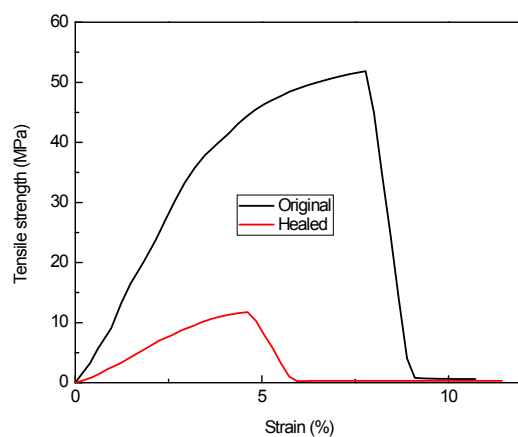


Fig. S9 Tensile stress-strain curves of the CC sample before and after healing. The polymer healed through the same pH variation and heat treatment.



Fig. S10 Flaming behavior of a polypropylene plate.

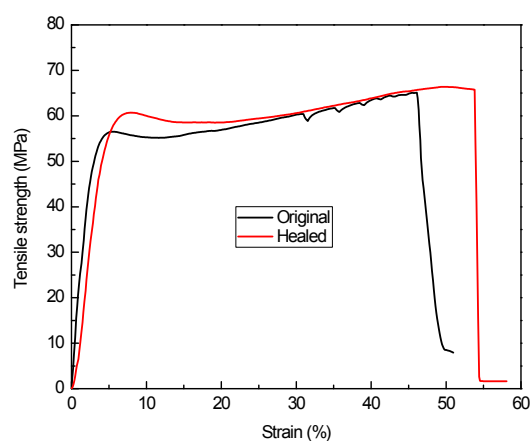


Fig. S11 Stress-strain curves of the toluene-treated CNC filament before and after self-healing.

References

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