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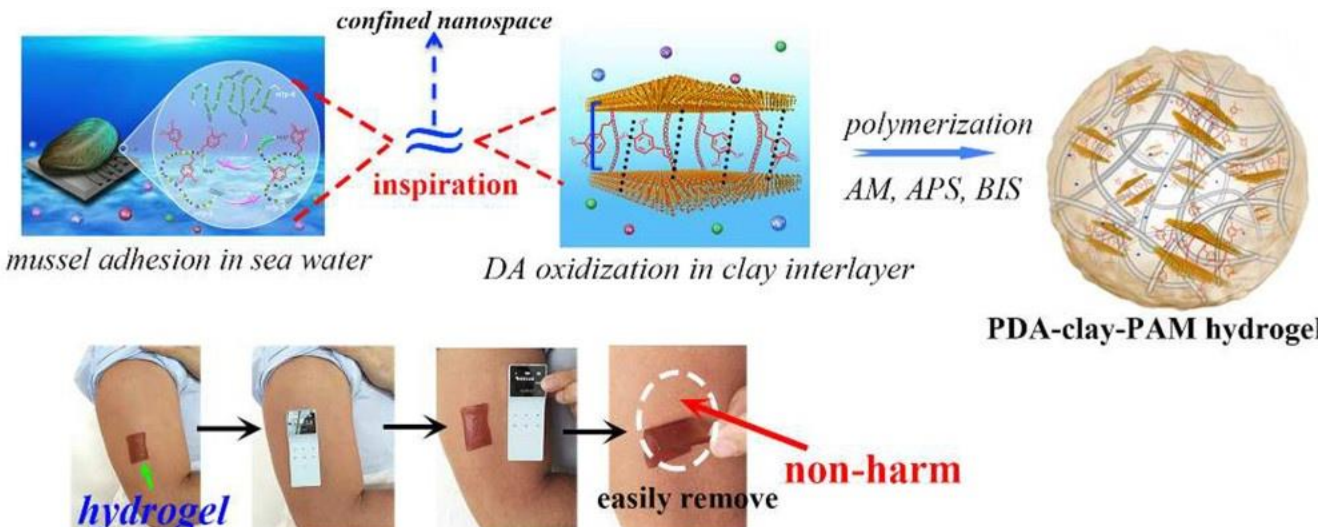
Mussel-Inspired Adhesive and Tough Hydrogel Based on Nanoclay Confined Dopamine Polymerization

Lu Han,[†] Xiong Lu,[*,†,‡] Kezhi Liu,[†] Kefeng Wang,[‡] Liming Fang,[§] Lu-Tao Weng,[∥] Hongping Zhang,[⊥] Youhong Tang,[#] Fuzeng Ren,[∇] Cancan Zhao,[∇] Guoxing Sun,[∥] Rui Liang,[∥] and Zongjin Li[∥]



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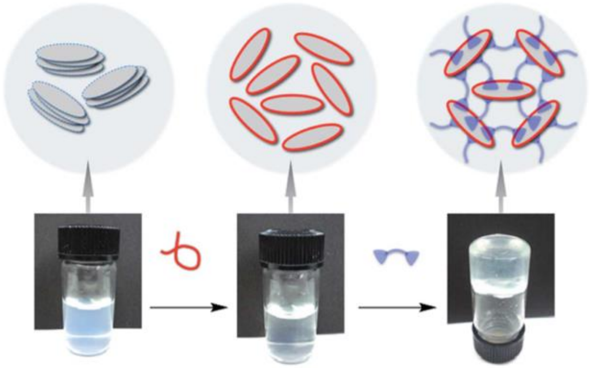
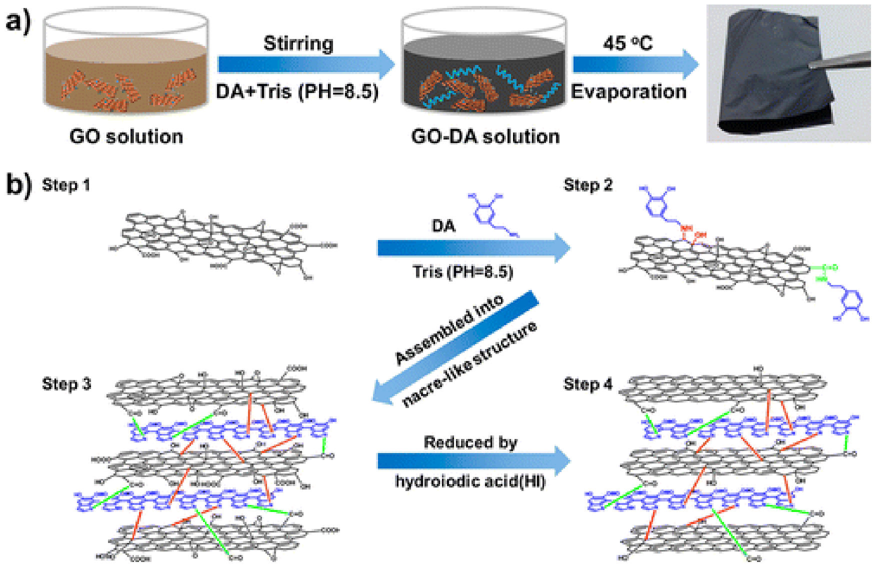
Background work

High-water-content mouldable hydrogels by mixing clay and a dendritic molecular binder



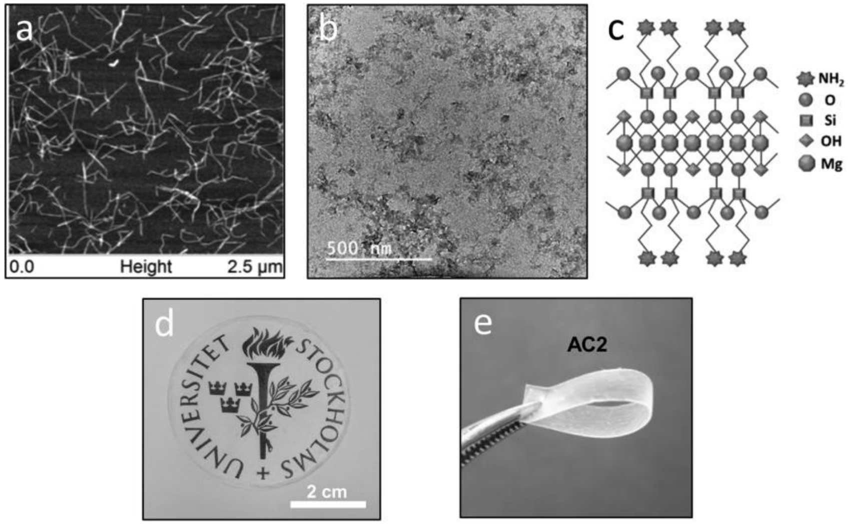
Nat. **2010,** *463*, 339–343

A Strong Integrated Strength and Toughness Artificial Nacre Based on Dopamine Cross-Linked Graphene Oxide



ACS Nano, **2014**, *8* (9), pp 9511–9517

Transparent and Flexible Nacre-Like Hybrid Films of Aminoclays and Carboxylated Cellulose Nanofibrils



*Adv. Funct. Mater.*2017, 28, 1703277

Why this paper?

1. Bioinspired
2. Use of nanoclay and various hydrogel initiators to form biocompatible, adhesive and mechanically strong hydrogel.
3. Detailed understanding of the hydrogel formation.
4. Combination of repeatable adhesive properties and superior mechanical properties to form biocompatible product.

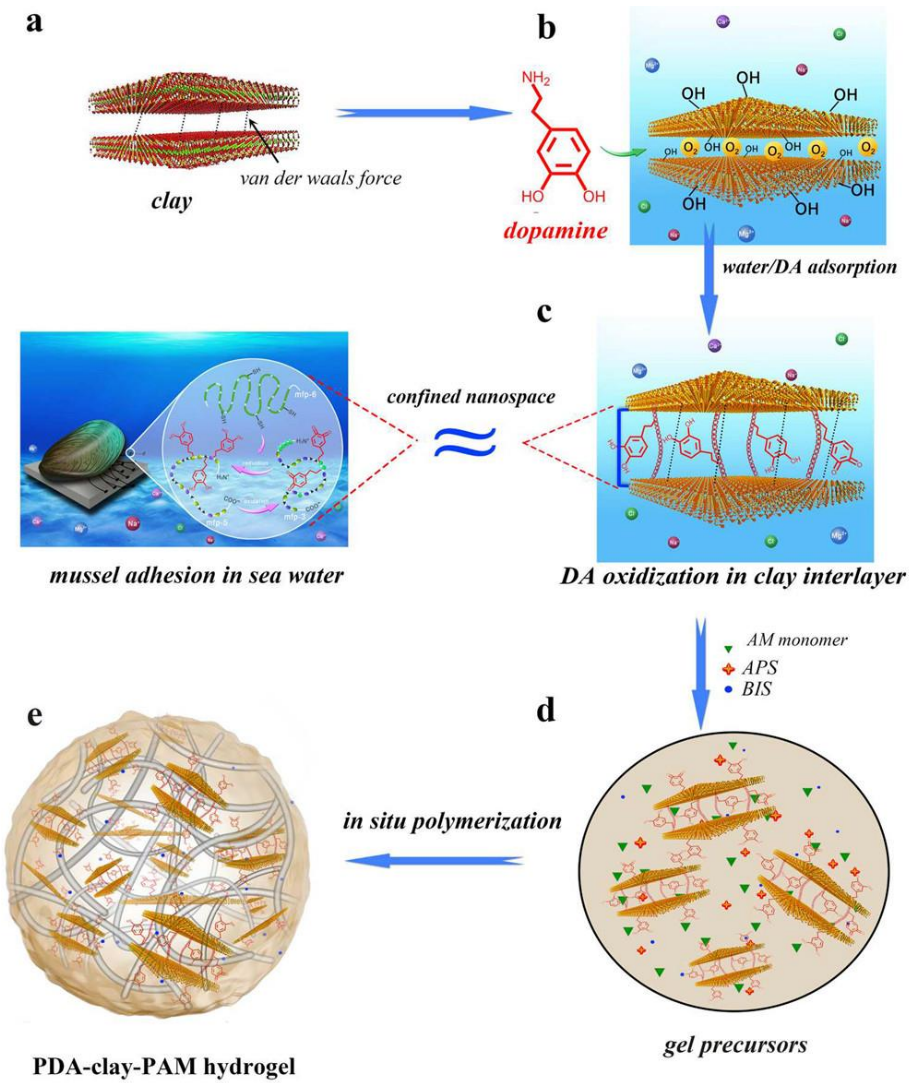
Introduction

1. Adhesive hydrogels are attractive biomaterials for various applications, such as electronic skin, wound dressing, and wearable devices..
2. Adhesive materials should be biocompatible, nontoxic, and nonirritating to human skin.
3. Mussel-inspired adhesive hydrogels with many outstanding properties have shed a light on the design and synthesis of other types of adhesive hydrogels.
4. Most of the mussel inspired hydrogels are having short-term adhesiveness, single usage, and limited reusability.
5. Fabricating a hydrogel with both adequate adhesiveness and excellent mechanical properties remains a challenge.

In this paper

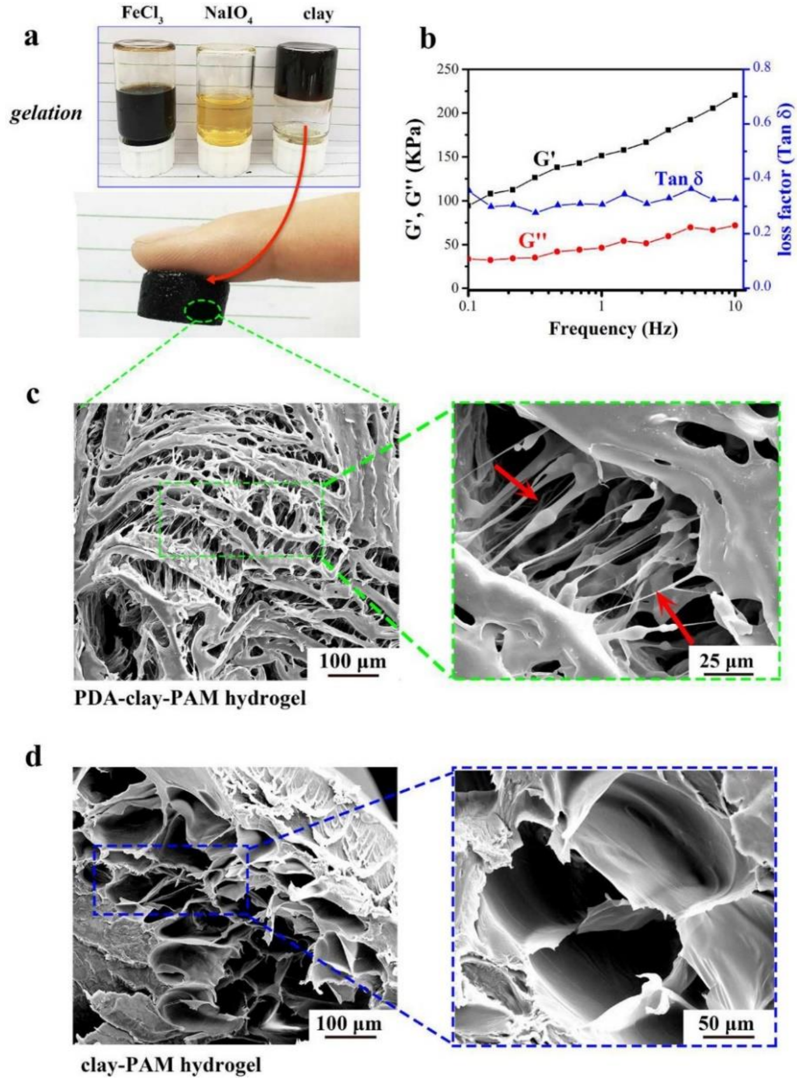
1. In this study, an adhesive and tough polydopamine-clay-polyacrylamide (PDA-clay-PAM) hydrogel based on the mussel-inspired adhesion mechanism and the NC concept has been desgined and synthesised.
2. Unlike previous single-use adhesive hydrogels, our hydrogel showed repeatable and durable adhesiveness.

Design Strategy for the Synthesis of the Polydopamine-Clay-Polyacrylamide Hydrogel.



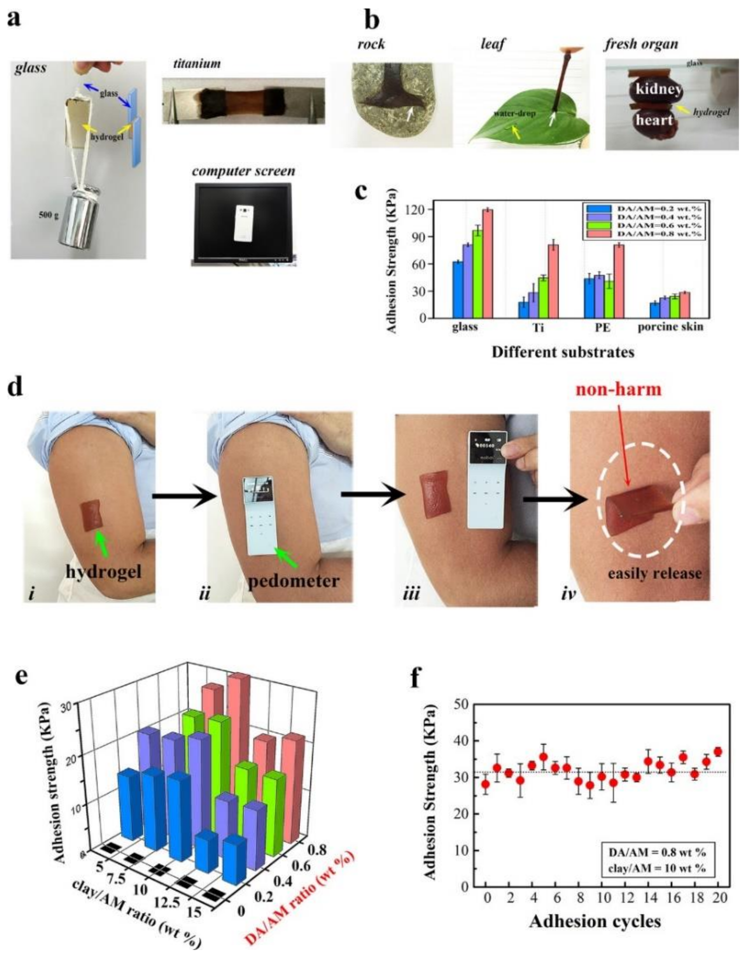
Design strategy for the preparation of PDA-clay-PAM hydrogel. (a) The layered structure of clay nanosheets. (b) DA molecule intercalated into the nanospace between the nanoclay layers. (c) Clay-induced DA oxidization to PDA in its nanospace, and the interlayer of clay nanosheets mimicked the confined nanospace of mussel's plaque. (d) AM monomers, cross-linkers (BIS), and initiator (APS) were added into the PDA-intercalated clay suspensions to form gel precursors. (e) The PDA-clay-PAM hydrogel was formed by in situ polymerization.

Cont…



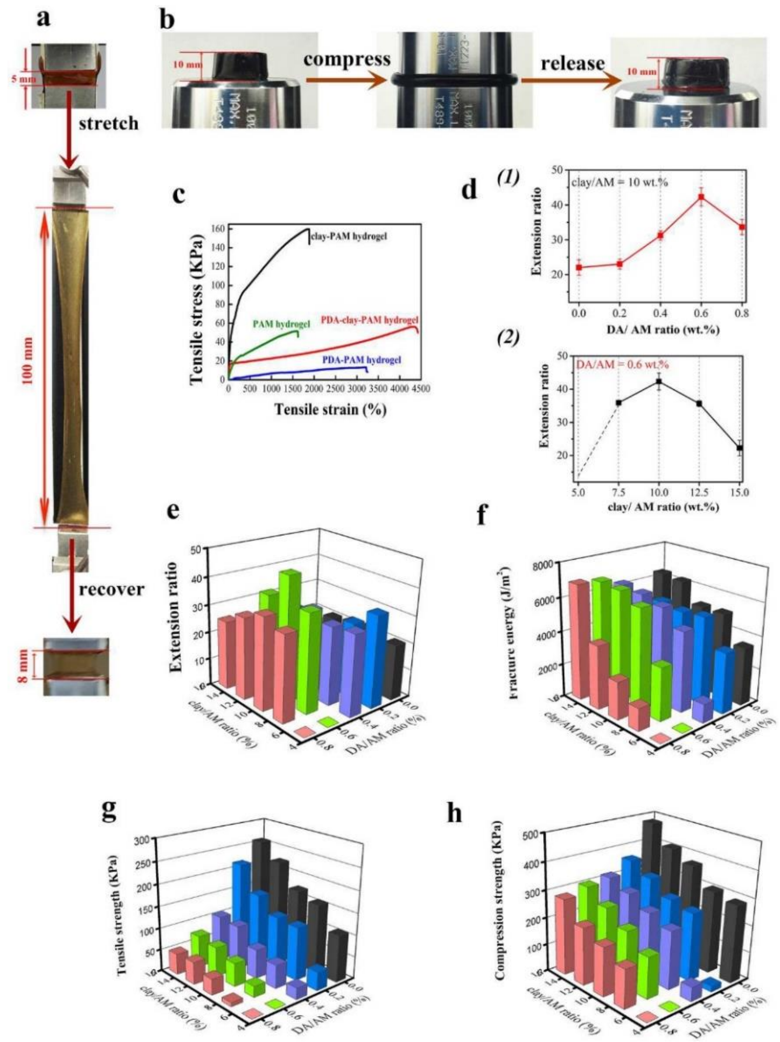
(a) A free-standing PDA-clay-PAM hydrogel (DA/AM = 0.6 wt %, clay/AM = 10 wt %) was obtained when clay was used to oxidize DA, and the PDA-clay-PAM hydrogel tightly adhered on the author's finger. The insert picture shows that a solid hydrogel could not form when clay was replaced by an equal amount of FeCl3 or NaIO4. (b) G′, G″, and loss tangent (tan δ) of a PDA-clay-PAM hydrogel (DA/AM = 0.6 wt %, clay/AM = 10 wt %, water content =80 wt %) as a function of frequency. (c) The structure of PDA-clay-PAM hydrogel (DA/AM = 0.6 wt %, clay/AM = 10 wt %), showing a layered architecture and interconnected networks; the magnified area shows the microfibril structures as indicated by red arrows. (d) The structure of the clay-PAM hydrogel (clay/AM = 10 wt %), showing porous structure; the magnified area shows that no microfibril structures were observed in the pores.

Adhesion Ability



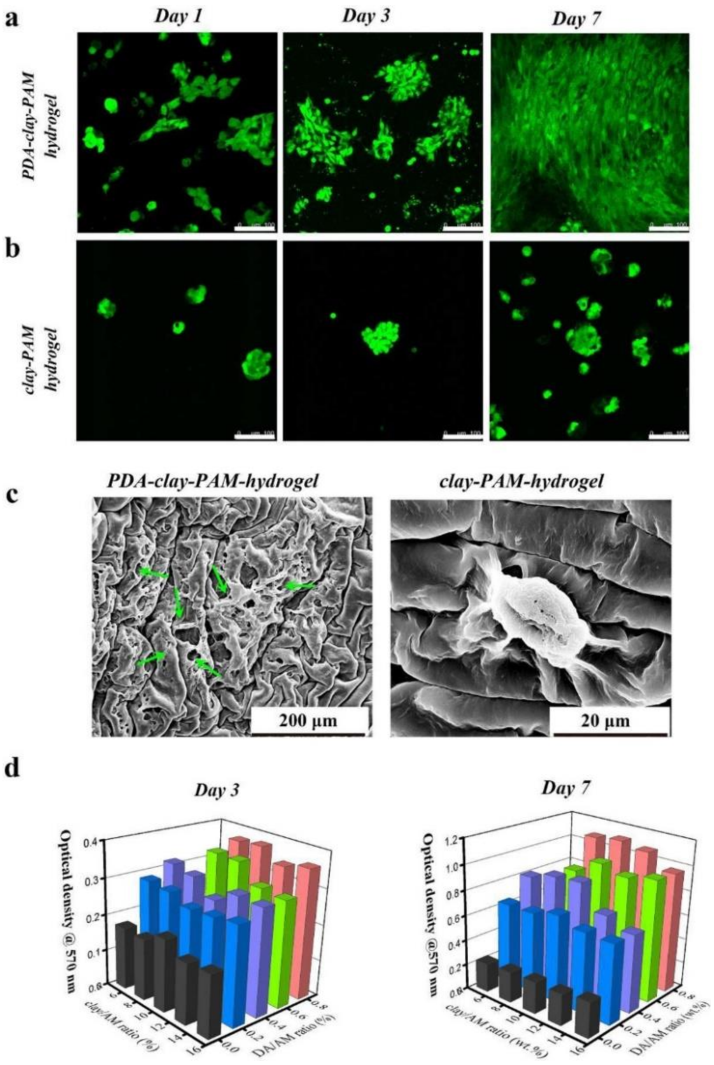
Adhesive property of the PDA-clay-PAM hydrogel. (a) The PDA-clay-PAM hydrogel (DA/AM = 0.6 wt %, clay/AM = 10 wt %) showed excellent adhesion to various surfaces: glass, a piece of hydrogel adhered between two smooth glasses and supported a load of 500 g; Ti, a hydrogel adhered on the Ti surfaces acting as a bridge and sustained a stretch; polymer, a hydrogel adhered on a computer screen and holding a mobile phone on the screen. (b) The hydrogel also exhibited strong adhesion to natural surfaces: hydrophilic rocks, hydrophobic leaves (yellow arrow shows a water droplet), and two fresh organs (liver and kidney of rats). (c) The adhesive strength of the hydrogels (clay/AM = 10 wt %, with DA/AM = 0.2, 0.4, 0.6, and 0.8 wt %) to porcine skin tested by tensile adhesion tests. (d) (i) A piece of hydrogel directly adhered on a human arm, as indicated by green arrow; (ii) a pedometer was attached to the arm through the hydrogel to count steps during arm movement; (iii) the pedometer was detached from the arm after movement had stopped; (iv) the hydrogel was easily peeled off from the arm skin without causing any harm or allergy and no residue remained. (e) The combinatorial study of the effect of DA and clay content on the adhesive strength of the PDA-clay-PAM hydrogels. (f) Repeatable adhesion behavior of the adhesive hydrogel (DA/AM = 0.6 wt %, clay/AM = 10 wt %) using porcine skin as the testing surface.

Mechanical Properties of the Adhesive Hydrogels



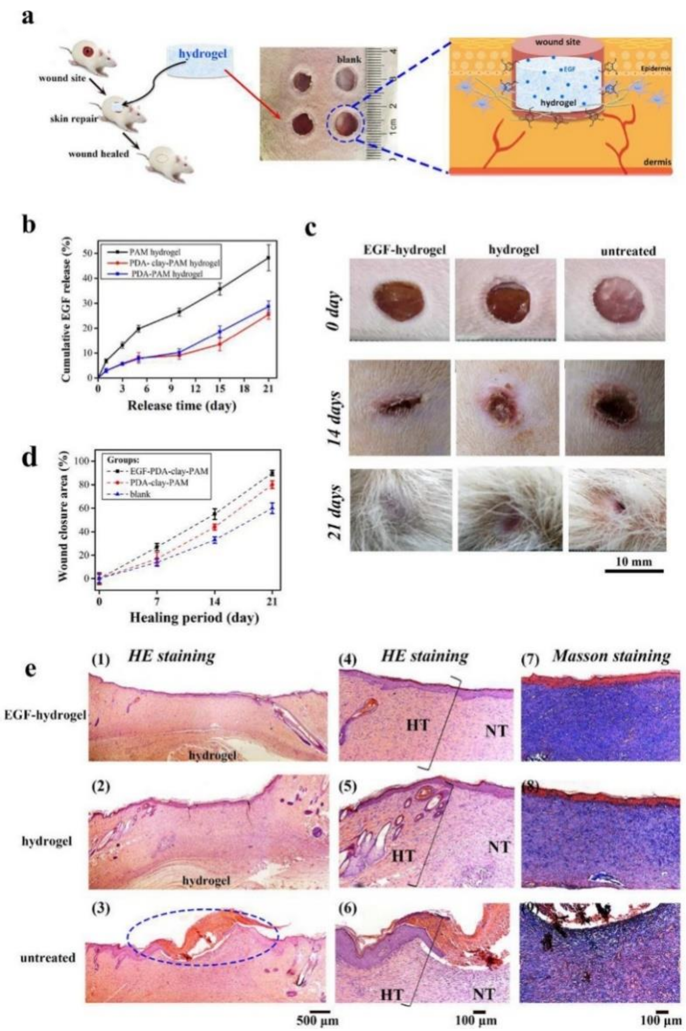
Mechanical properties of the PDA-clay-PAM hydrogel. (a) Digital photo showing the PDA-clay-PAM hydrogel (DA/AM = 0.6 wt %, clay/AM = 10 wt %) was stretched to 20 times of its initial length and the recovery of its initial length after removing the load. (b) The PDA-clay-PAM hydrogel recovered to its original shape after it was compressed up to the strain of 80%. (c) Typical tensile stress–strain curves of PDA-clay-PAM (DA/AM = 0.6 wt %, clay/AM = 10 wt %), PDA-PAM (DA/AM = 0.6 wt %), clay-PAM (clay/AM = 10 wt %), and PAM hydrogels. (d-1) The effect of DA contents on the extension ratio when the clay/AM ratio was 10 wt %. (d-2) The effect of clay contents on the extension ratio when the DA/AM ratio was 0.6 wt %. (e–h) The combinatorial study of the effect of DA and clay contents on the extension ratio (e), fracture energy (f), tensile strength (g), and compression strength (h) of the PDA-clay-PAM hydrogels.

Cell adhesion



Cell behaviors on PDA-clay-PAM hydrogel. (a) CLSM images of fibroblasts adhered on PDA-clay-PAM hydrogels (DA/AM = 0.6 wt %, clay/AM = 10 wt %) and (b) clay-PAM hydrogels (clay/AM = 10 wt %) after 1, 3, and 7 days of culture. The scale bars represent 100 μm. (c) SEM micrographs of fibroblasts cultured on PDA-clay-PAM hydrogel after 3-day culture, indicating numerous cells were well spreading on the PDA-clay-PAM hydrogels; the green arrows indicate filopodia. (2) One typical fibroblast on clay-PAM hydrogel, exhibiting a globular shape without extending filopodia. (d) Cell growth on PDA-clay-PAM hydrogels with various clay and DA content after 3 and 7 days of culture.

Hydrogel as a Wound Dressing



PDA-clay-PAM hydrogel as a wound dressing in a full-thickness skin defect. (a) Schematics of the PDA-clay-PAM hydrogel serving as a wound dressing on the wound sites of rat skin. (b) Cumulative EGF released from PDA-clay-PAM (DA/AM = 0.6 wt %, clay/AM = 10 wt %), PDA-PAM (DA/AM = 0.6 wt %), and clay-PAM hydrogels (clay/AM = 10 wt %) in PBS. (c) Digital photos of the wound after 0, 14, and 21 days of healing. (d) Wound closure of untreated defects and defects treated with EGF-loaded PDA-clay-PAM (DA/AM = 0.6 wt %, clay/AM = 10 wt %), EGF-free PDA-clay-PAM (DA/AM = 0.6 wt %, clay/AM = 10 wt %), PDA-PAM (DA/AM = 0.6 wt %). (e) Photomicrographs showing histological staining of wound sites on day 21. (1–3) Overview of the defects treated by EGF-loaded PDA-clay-PAM hydrogel and PDA-clay-PAM hydrogel and untreated defect. (4–6) The interface between the newly regenerated tissue (NT) and host skin tissue (HT). (7–9) Masson staining of the collagen deposited in the defects.

Conclusions

1. Demonstration of a tough and adhesive PDA-clay- PAM hydrogel inspired by the adhesion mechanism of mussels.
2. By borrowing the concepts from mussel adhesion chemistry and using clay-induced NC, the PDA-clay-PAM hydrogel realizes the optimal integration of high adhesive strength and
3. high toughness.
4. The adhesiveness of the hydrogel is attributed to the presence of a sufficient number of free-catechol groups in the hydrogel.
5. Although the hydrogel exhibits strong adhesion, it can be easily released without hurting skin, which is very meaningful for meeting practical clinical needs.
6. The superior mechanical properties are ascribed to the presence of covalent and noncovalent cross-linked polymer networks and clay nanoreinforcements.
7. Inclusion of PDA is a feasible method for developing a tough cell- and tissue-adhesive hydrogel