Supporting Information

Algae-Mussel-Inspired Hydrogel Composite Glue for Underwater Bonding

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Iron Crosslinking and Surface Adhesion

Since dopamine that is complexed with Fe^{3+} would not be able to interact with surfaces through catechol groups, we sought to understand how the addition of Fe^{3+} may affect the adhesive portion of the composite glue. To investigate this, contact adhesion tests were performed using a microindentation system. 0.1 mL of aqueous dopamine solution (D-DI); aqueous dopamine, Fe^{3+}, and tris(hydroxymethylaminomethane) solution (D-Fe-Tris); or a commercial cyanoacrylate-based aquarium glue, CorAffix Gel (CAG, Two Fishes) were injected and sandwiched between a hemispherical polydimethylsiloxane (PDMS) probe and a microscope glass slide. The probe was held at a known position (where a force of 20 mN was detected without the presence of the mixtures) for 12 hours, then retracted from the glass slide at a rate of 0.1 μm/s.

CAG showed low adhesive strength, which is most likely due to its difficulty in chemically bonding to the glass. Interestingly, the D-Fe-Tris system showed extremely similar adhesive strength to the D-DI system. This may suggest that interactions with Fe^{3+} do not appear to significantly weaken the adhesion of the dopamine. One possible explanation for this is that oxidized dopamine at the surface may prefer to interact with the surface rather than the Fe^{3+} ions. While this test does not fully remove the cohesive contributions of Fe^{3+} to the system, it does suggest that for the standard composition of algae-mussel glue, Fe^{3+} is not weakening the final adhesion.

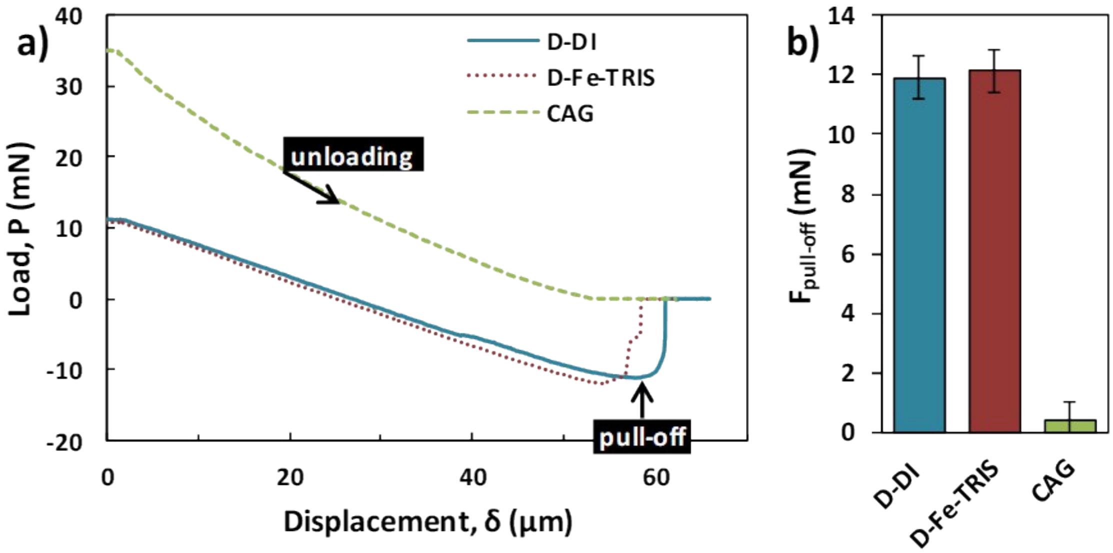

Figure S1: (a) Unloading curve for a hemispherical polydimethylsiloxane (PDMS) probe in contact with a glass slide. The two substrates were joined together using aqueous dopamine solution (D-DI); aqueous dopamine, Fe^{3+}, and tris(hydroxymethylaminomethane) solution (D-Fe-Tris); or commercial aquarium glue (CAG). (b) Resulting adhesive pull-off forces measured for the D-DI, D-Fe-Tris, and CAG systems.

Sequential and Pre-mixed Application Methods

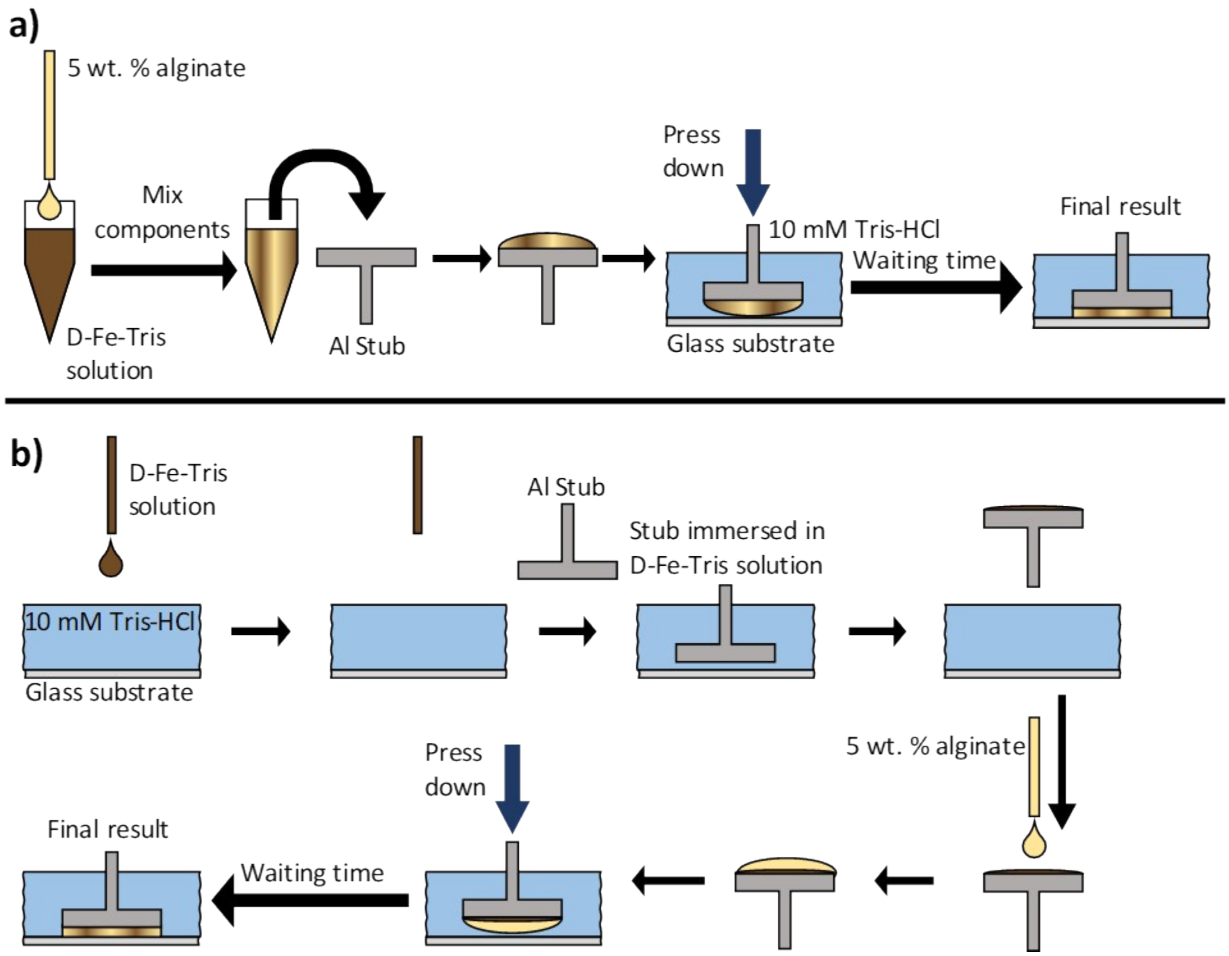

Figure S2: Schematic detailing the procedure for (a) pre-mixed application; and (b) sequential application of algae-mussel glue. The two solutions used are a dopamine-iron-Tris solution (D-Fe-Tris) and a 5 wt. % alginate solution in deionized water.

Equilibrium Water Content

To investigate the water content of the gel at equilibrium, samples of aluminum stubs glued to glass slides were made using the sequential method. The stubs and slides were weighed before forming the gel; after gel formation, the outside surfaces of the samples were gently dried with Kimwipes, with a second weighing to determine the mass of the swollen gel. Finally, the samples were dried in an oven at 90 °C overnight and weighed to determine the mass of the dried gel (with the difference between swollen and dried gels providing the mass of water). This was used to acquire a weight percentage of water, which was 64.0 ± 29.4 %.

Viscoelastic Behavior

In order to investigate the viscoelastic behavior of the algae-mussel glue, tensile holding tests were carried out, where aluminum stubs were glued to glass slides using the same technique as for general adhesion testing in this work. The method used was similar to that of stress relaxation tests, and the inclusion of the time domain was intended to give insight into viscoelastic properties. Instead of pulling on the stub until failure, the stub was pulled until a force of 50 g was felt, and then held at constant strain. At this fixed displacement, the change in force over time was measured and recorded, with Figure S2 showing a typical force-time plot. One interesting behavior that is immediately apparent from Figure S2 is that while the force initially decreases over time, it then begins to increase again, reaching a value close to the initial force at the fixed strain. At first, the force appears to drop to 25% of its initial value, before rising back up to 95% of the initial force. To make sure this surprising result is valid, we repeated the experiment multiple times, and performed additional tensile holding tests with cyanoacrylate-based glue in both dry and submerged conditions (to confirm this result was not due to external factors).

The lowering of the tensile force is likely due to the ionic crosslinks breaking to release the stress; however, the cause for the following increase in force is unclear. One possible explanation is that the alginate chains and dopamine complexes could tighten and pull on the gel when they reform in new positions. While this is not direct evidence of self-healing capability, it does suggest the composite glue has some ability to reform bonds that are broken – at least those that are broken as part of releasing stress.

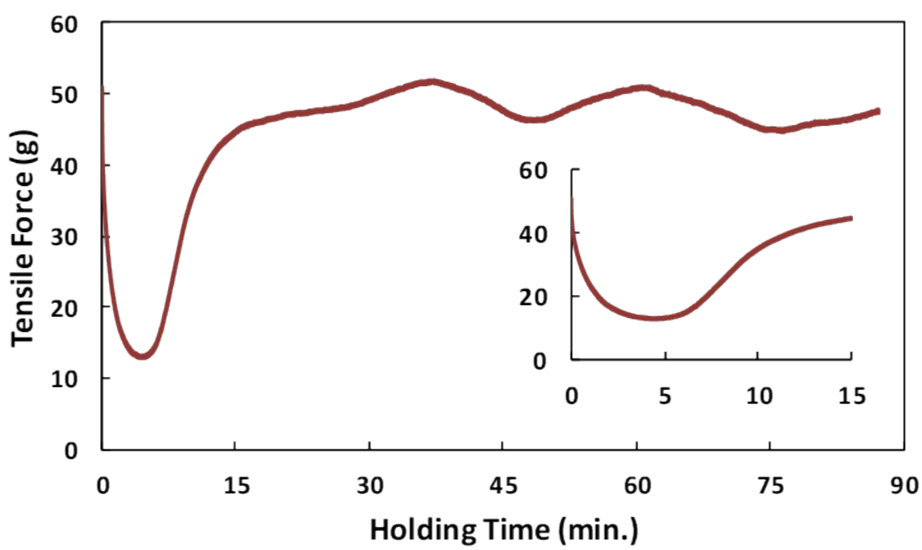

Figure S3: A plot of force vs. holding time for a constant strain applied to an aluminum stub bonded to a glass slide with algae-mussel glue. The insert shows a closer view of the first 15 minutes of holding time.

Curing Time Dependence

Differing curing times can result in strikingly different behaviour, so the effects of this were examined for the algae-mussel composite glue, along with a version without dopamine, and CAG (Figure S3). CAG showed high adhesive strength initially, but weakened over time, likely once again due to its lack of chemical bonding with glass. The composite glue and pure alginate-Fe^{3+} showed similar strengths with 30 min cure times, but the composite glue became stronger at longer cures, plateauing after 2 hours of curing time. This bond appeared to be permanent;

samples after two hours of joining were placed in deionized water, and the joints were still intact over two weeks later. In contrast, the alginate-Fe^{3+} system became weaker at longer curing times; this behaviour of the two systems suggests that part of alginate's role in adhesion may be holding the system in place until the polydopamine can form and adhere more strongly to the surfaces over time.

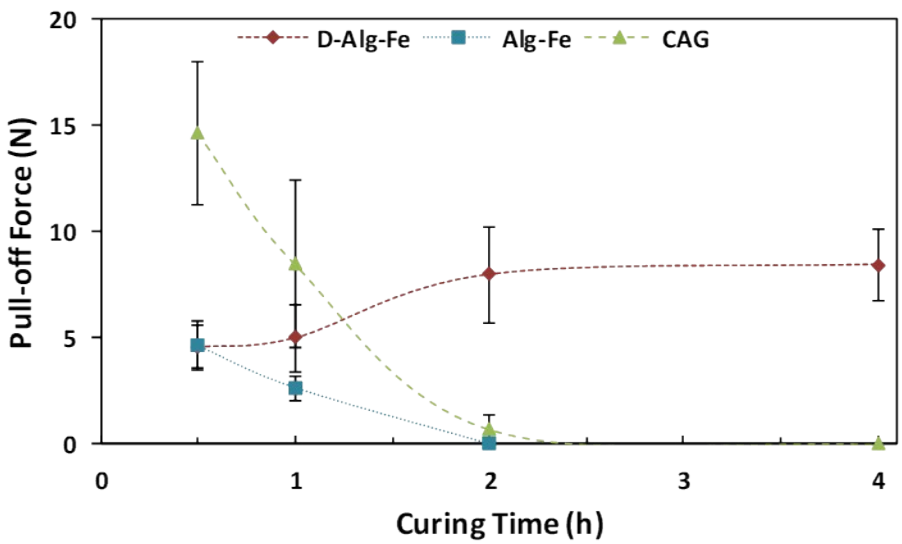

Figure S4: Tensile pull-off force for aluminum stubs bonded to glass slides for varying curing times using dopamine, alginate, and Fe^{3+} in Tris (D-Alg-Fe), alginate and Fe^{3+} in deionized water (Alg-Fe), and CorAffix Gel commercial aquarium glue (CAG). Lines are provided as a visual guide.