

POLYMER CLAW: INSTANT UNDERWATER ADHESIVE

Progress Report #7

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1 Summary

A new adhesive formulation demonstrated a major improvement in cure rate. By replacing the amine crosslinker with glycerine and a catalyst, the fracture energy of the adhesive was too strong to measure by ADCB after only 10 minutes. **When tested underwater, the lap shear adhesion was ~200x stronger than commercial underwater adhesives after 1 hour.** This month also marked the successful construction of the first full prototype of Polymer Claw, which included the adhesive, abrasive, and caustic components.

2 Project Goals and Objectives

For the next 3 months, we will continue the system-level development of Polymer Claw Prototypes. By the end of December, our final milestone is to adhere to a biofouled surface with an adhesive strength of 5 MPa under wet conditions.

3 Key Accomplishments

3.1 Faster Curing Adhesive Formulation

The pressure-activated adhesive already boasted much faster curing times compared to commercial underwater adhesives. Even after 5 minutes, the Polymer Claw adhesive partially solidified, while commercial adhesives were completely liquid after one hour. However, the curing rate was still not fast enough to fully satisfy the CONOPS for this program. The adhesion does not have to reach its final strength at the first instant of contact, but it should be strong enough to remain attached for those first few moments after it is released.

We hypothesized that mixing was our biggest problem. Visual inspection of the adhesive during compression revealed that the amine crosslinker rapidly formed a new polymer membrane with the isocyanate matrix when the microcapsules ruptured. This membrane was good in the sense it was a hard polymer, but it arrested further mixing between the amines and isocyanates. We tried two approaches to solve this problem: reduce the microcapsule size, and decrease the reaction rate. The first approach is straightforward. Smaller microcapsules are more finely dispersed to begin with, so less mixing is required during the rupture process. This approach was tested with modest improvement. The second approach is counterintuitive. Why would reducing the reaction rate accelerate the cure? The thought is that a slower reaction between the isocyanate and crosslinker would improve mixing. We hypothesized that the polymerization rate was mass transport limited rather than reaction rate limited. Ultimately, mixing has to occur prior to polymerization in order to achieve a full cure. The polymerization rate therefore had to be reduced in order to allow more time for the slower mixing process.

The new formulation replaces the polyethylenimine crosslinker with a combination of glycerol and dibutyltin diacetate. Glycerol has three alcohol groups that react with isocyanates to form urethane bonds. Dibutyltin diacetate is a catalyst that is specific for the isocyanate/alcohol reaction. The nice feature of this reaction is that the rate can be tuned by

adjusting the concentration of catalyst. Alcohols normally react 1/200x as fast as amines do with isocyanates, but additional dibutyltin diacetate can close this gap completely. Currently, microcapsules with 1% dibutyltin diacetate and 99% glycerol have shown the best performance. Microcapsules with 10% dibutyltin diacetate did not form properly, so work is underway to determine whether it is possible to increase the cure rates even further by incorporating higher concentrations of catalyst.

3.2 Clamping Force Selection

The primary CONOPS for guiding the development of Polymer Claw is one in which a diver must rapidly attach the adhesive system to the immersed hull of a boat and swim away. It is imperative to ensure that the critical pressure for activating the adhesive is comparable to what a diver can exert under these conditions. In the absence of a field test with trained scuba divers, coming up with an estimate of this force is difficult.

To approximate such loads, we pushed against a load cell that was mounted on a wall. In one scenario, we stood on the floor and pushed as hard as we could without moving backwards. In the second scenario, we pushed while being seated on a chair with rollers. The average force was 41 ± 8 lbs. when standing, and 28 ± 5 lbs. when seated. This corresponds to 6.6 psi and 4.5 psi, respectively, for the area of the grill brush.

Since smaller clamping stresses were hard to apply reproducibly, we chose 6.6 psi as the standard pressure applied to each lap shear sample during curing. These were applied by spring loaded plastic clamps that were calibrated to apply a force in the 3.4-3.7 lb. range over a 0.5 sq. in. area.

3.3 Underwater Lap-Shear Adhesion

The most important test of the improved adhesive is the underwater lap-shear experiment. This measurement is performed by applying the adhesive to one aluminum test strip in air. Next, the adhesive coated strip is immersed in salt water, and it is pressed against a wet aluminum strip that is also immersed in water. A plastic clamp applies a consistent pressure of 6.6 psi, and the whole sample is held underwater until tested on an Instron tensile tester.

Although not a biofouled surface, this test is actually a better indicator of the underwater adhesive performance because it isolates the adhesion performance from the cleaning ability of the caustic paste and abrasive brush. It is a pure indicator of underwater adhesion under controlled conditions. After 24 hours, the Polymer Claw adhesive performed very well (Figure 1). It displayed no decrease in adhesion due to water immersion. It outperformed all but one of the commercial underwater adhesives at long times. The one adhesive that did perform better than Polymer Claw, Loctite, did so at a much reduced strength compared to its own dry adhesive performance.

We note here that Gorilla Glue performed much worse underwater. This finding is interesting because the Polymer Claw adhesive is identical to Gorilla Glue except for the addition of the glycerol-filled microcapsules. Something about the glycerol or 1% dibutyltin diacetate prevented water-assisted crack growth. One would not expect such an adhesion improvement due to these additives because glycerol is a well-known hygroscopic liquid and lubricant. In the

absence of direct measurements, we can hypothesize that the glycerol may improve the surface wetting of the adhesive under these conditions. Perhaps by forming hydrogen bonds with the aluminum oxide it can outcompete water to prevent water-assisted crack growth. Another possibility is that the more rapid cure rate does not allow enough time for water to cause crack growth in the first place. Either way, the wet performance of the Polymer Claw adhesive is a major accomplishment.

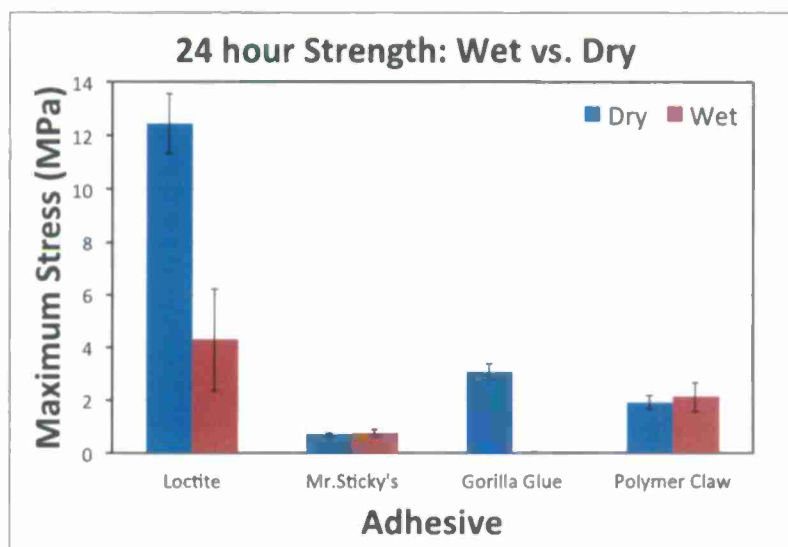


Figure 1: ASTM D 1002 lap shear adhesion stress after 24 hours plotted versus adhesive. Dry samples were prepared and cured in air, whereas wet samples were prepared and cured in salt water. Although Loctite performed the best, Polymer Claw showed no decrease in adhesion due to water immersion.

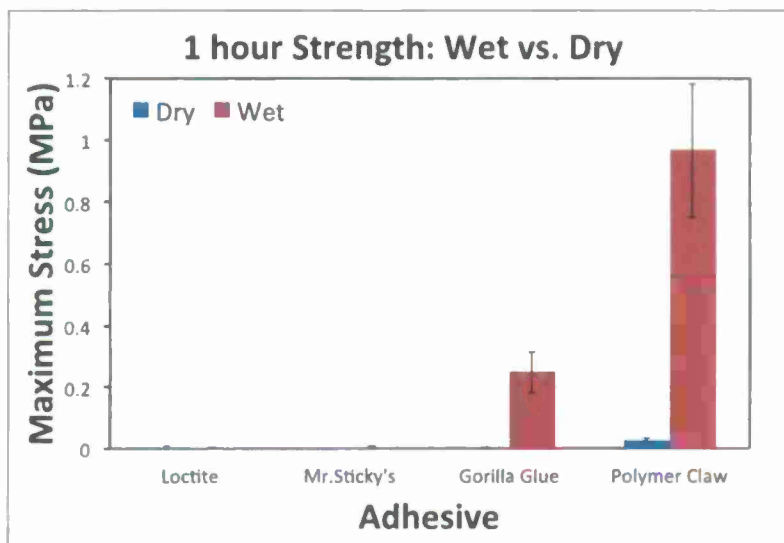


Figure 2: ASTM D 1002 lap shear adhesion stress after 1 hour plotted versus adhesive. Dry samples were prepared and cured in air, whereas wet samples were prepared and cured in salt water. Polymer Claw was nearly 5x stronger than the next best adhesive, but Gorilla Glue can be ruled out, because its adhesion was almost zero at 24 hours. Polymer Claw was 260x stronger than Loctite after 1 hour.

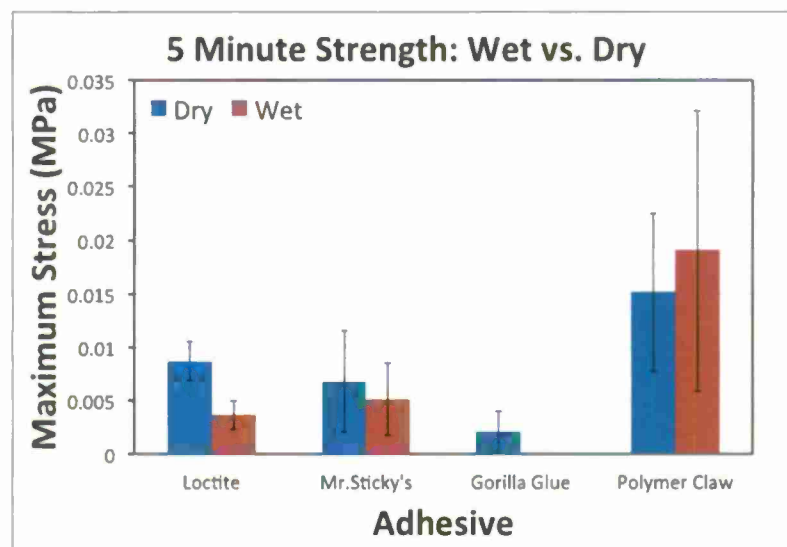


Figure 3: ASTM D 1002 lap shear adhesion stress after 5 minutes plotted versus adhesive. Dry samples were prepared and cured in air, whereas wet samples were prepared and cured in salt water. Polymer Claw was nearly 4x stronger than the next best adhesive.

The 1 hour measurements are where the Polymer Claw adhesive really shined (Figure 2). It achieved a 1 MPa lap-shear strength, which was already half of its strength at long times. The next best adhesive was Gorilla Glue, but we already saw that its adhesion fell to almost zero at long times. **Polymer Claw was 180x stronger than Mr. Sticky's Underwater Glue and 260x stronger than Loctite Underwater Glue** at this point. Part of this increase is due to the fact that water also causes the isocyanate resin to polymerize. The Polymer Claw adhesive should therefore cure faster than water than in air. This trend is also seen for Gorilla Glue, which is also based on isocyanate chemistry.

Finally, Figure 3 shows the performance after 5 minutes. Much like with the dry samples, Polymer Claw was the best adhesive, but the difference is not as dramatic as at 1 hour. Here it was nearly **4x stronger than the next best commercial adhesive**.

3.4 Full Polymer Claw Prototype

The first full Polymer Claw prototype was fabricated by first applying the sulfuric acid paste to the brass bristles of the grill brush and then pipetting the pressure-activated adhesive between the bristles. The whole process only took 15 minutes. When placed in water, neither the adhesive nor the sulfuric acid paste dissolved away. Both were also stable on the benchtop. Their viscosity was therefore sufficiently high to pass basic usability criteria.

When pressed against a glass plate underwater, the bristles collapsed in a controlled manner, and the sulfuric paste spread evenly across the glass. Unfortunately, this prototype did not have an adequate supply of adhesive to bond with the glass. This shortcoming will be easily addressed in future prototypes.

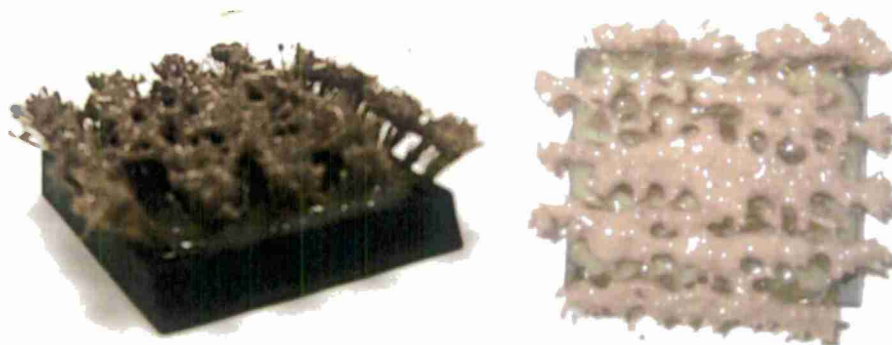


Figure 4: Picture of full Polymer Claw prototype viewed from different angles. The sulfuric acid paste is tan, the adhesive is light yellow, and the plastic backing is dark gray.

4 Next Steps

4.1 Biofouled Surfaces

With the ability to construct full prototypes, the technology is ready for testing on biofouled surfaces. A set of aluminum panels has been suspended in the Chesapeake Bay for several months collecting biofouling. First, they will be used to evaluate the effectiveness of the abrasive brush and caustic paste independently. Next, the paste and brush will be used together on the fouled panels. Finally, the biofouled panels will be used for lap shear measurements with full Polymer Claw prototypes, and the results will be compared with several control adhesives.

4.2 Rheological Measurements

Rheological samples are being shipped out for characterization by a 3rd party measurement services company. Results should be back within two months.

4.3 ADCB Fracture Energy Measurements

The ADCB measurements will continue to be used for further optimization of the pressure-activated adhesive. Since the measurement is not valid for partial liquid adhesives, we will only test at later times, noting the minimum time for which the glass slides break. The time to cohesive failure will then serve as the main metric for comparison, with shorter times corresponding to better adhesives.

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14. ABSTRACT JHU/APL's Polymer Claw is a pressure-activated underwater adhesive that bonds instantly to biofouled surfaces in a single step. The key to this technology is the use of pressure sensitive microcapsules, which release reactive amine crosslinkers into an adhesive putty when pressed against the surface. The amine reacts with the sticky, isocyanate putty to form a tough polyurea. The catalyzed isocyanates likewise bond with alcohols, amines, acids, or oxides on the surface. This technology addresses the issue of biofouling through an abrasive metal brush coated with a caustic gel. Activated by water, the caustic removes plant and animal matter before the adhesive even makes contact with the surface. Pressure from the adhesive putty flattens the metal bristles and displaces the gel to make way for the adhesive. The entire system will be sealed in disposable packaging for safe storage and transport. This aggressive approach meets the Navy's requirements for speed, robust performance in all conditions, and no special training.					
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