

POLYFIBROBLAST: A SELF-HEALING AND GALVANIC PROTECTION ADDITIVE

Progress Report #6

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14. ABSTRACT The goal of this project is to develop a primer additive that mimics the self-healing ability of skin by forming a polymer scar across scratches. Designed to work with existing military grade primers, Polyfibroblast consists of microscopic, hollow zinc tubes filled with a moisture-cured polyurethane-urea (MCPU). When scratched, the foaming action of a propellant ejects the resin from the broken tubes and completely fills the crack. No catalysts or curing agents are needed since the polymerization is driven by ambient humidity.					
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1 Summary

Silane adhesion promoters have been more widely evaluated for their ability to improve the spreading of the healing resin across the surface of the exposed scratch. We find that the surface activity of these surfactant-like molecules impairs the formation of the polymer skin layer; however, octadecyl trimethoxy silane in particular appears to improve healing across all scratch widths *even in the absence of significant polyurethane resin*. PPG continues to improve the quality control of their larger batch synthesis, and are investigating alternative drying methods.

2 Project Goals and Objectives

The project has completed its experimental microcapsule processing stage and has begun its experimental paint testing phase. For the next three months, we will synthesize Polyfibroblast with different types and concentrations of silane adhesion promoters to determine which formulation best prevents corrosion according to ASTM measurements. The final milestones are that (1) shelf life will be sufficient to survive one week at 100°F and 100% relative humidity without loss of liquid volume fraction by mid August, and (2) PPG will demonstrate the capability to synthesize enough Polyfibroblast filler to make 1-gallon batches of primer by early September.

3 Key Accomplishments

3.1 Silane Adhesion Promoters

The silane adhesion promoters being evaluated for the Polyfibroblast formulation are as follows:

- Octadecyltrimethoxy silane (OTS): Hydrophobic silane best known as a mold release, OTS forms a self-assembled monolayer and makes the surface very hydrophobic and nearly impenetrable to water.
- Isocyanatopropyltrimethoxy silane (ITS): This silane forms a covalent bond with both the oxide layer of the underlying steel and the polyurea resin released from the microcapsules. It is nearly ideal for promoting adhesion in this system.
- Glycidoxypyltrimethoxy silane (GPS): This silane presents an epoxy group that can react with amines in the polyurea to form a covalent bond. The fact that it reacts more slowly than ITS makes it easier to process, but it may take longer to develop stronger adhesion with the polyurea scar.
- Methacryloxypropyltrimethoxy silane (MPTMS): With an exposed vinyl group, this silane does not form a covalent bond with the polyurea scar, but it will have better contact adhesion with the polymer scar than OTS.
- Aminopropyltrimethoxy silane (APS): This silane reacts with the polyurea resin before the microcapsules even form. Unfortunately, this reaction immediately gels the resin.

Contrary to expectations, OTS delivered the greatest improvement to scratch healing. OTS normally functions as a mold release. It forms a self-assembled monolayer whereby each molecule stands perpendicular on the surface and packs closely so that no gaps exist between

adjacent molecules. It presents a surface of CH₃ groups that repel water, but also prevent strong interactions with any adjacent polymer.

Per MIL-P-26915 specification and with guidance from ASTM D870 and D1308, scratches were individually immersed in separate 1000 mL beakers filled with ~850 mL of deionized (DI) water at 38°C for 24 hours. Upon removal, the panels were rinsed with water, blotted dry, and inspected for changes in appearance (blistering, cracking, etc.). The level of corrosion in each scratch was graded on a 0-4 scale, where 0 represents 100% rust and 4 represents no rust. Table I and Figure 1 below show that OTS improves the corrosion resistance across wide, narrow, and intermediate scratch widths. Perhaps most notably, even the 80% OTS sample—which essentially consists of pure OTS with a polyurea shell—exhibits excellent healing ability. This finding supports the hypothesis from last month's report that claims that self-assembled monolayers may provide corrosion protection apart from any polymer scar that may form over them.

Table I: Rust scores for Polyfibroblast primer samples with varying types and concentrations of silane adhesion promoters. Each sample is immersed in water for 24 hours in deionized water at a temperature of 100°F. A rust score of 0 corresponds to 0% rust, and a score of 4 corresponds to no rust along the length of the particular scratch.

Sample Name	Rust Score 0.125 in. 0-4	Rust Score 0.032 in. 0-4	Rust Score 0.016 in. 0-4	Rust Score 0.014 in. 0-4	Rust Score 0.003 in. 0-4
Silicone oil 1	3	4	4	4	4
Silicone oil 2	2	3	4	3	3
5% OTS 1	0	0	0	0	4
5% OTS 2	3	3	3	2	4
10% OTS	4	4	4	4	1
5% ITS	0	0	1	4	3
10% ITS	1	0	0	0	4
10% MPTMS	3	2	0	0	2
20% MPTMS	1	2	0	0	4
80% OTS	3	4	2	4	4

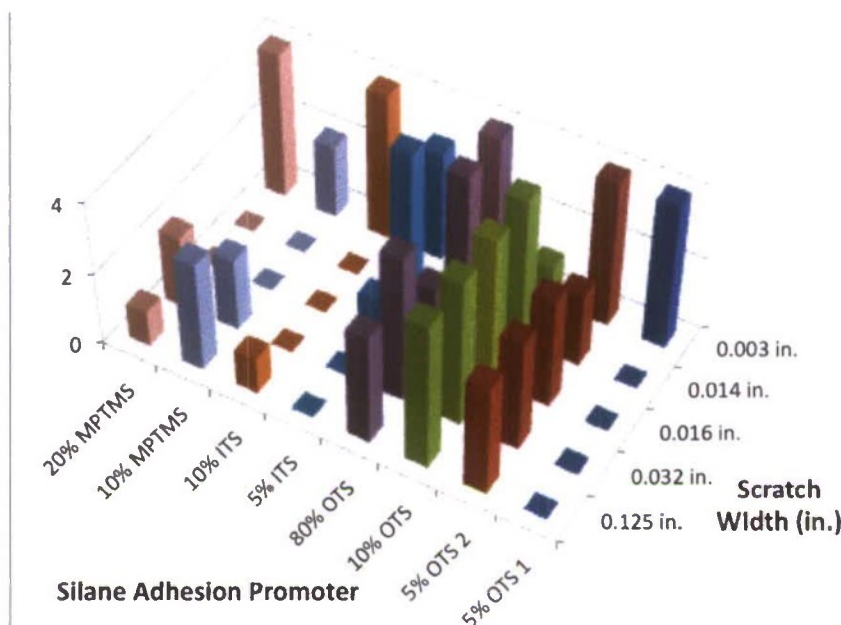


Figure 1: Graphical representation of Figure 1. Note how OTS-infused samples displayed the greatest resistance to corrosion.

3.2 Reaction Kinetics

The extent of polymerization was tracked using thermogravimetric analysis (TGA). For this method, small samples are weighed to a high degree of accuracy and then the resulting mass loss is recorded as a function of temperature. In the present system, the liquid outgases around 240°C and the solid polymer outgases around 350°C. The relative mass loss at each temperature corresponds to the solid fraction of liquid and solid, respectively. The solid fraction is shown below in Figure 2.

After repeating these experiments a third time, we were able to determine that the early time measurements cannot be obtained with greater accuracy due to the fragility of the thin polymer skin layer. Figure 2 therefore represents the finalized data.

Additional dynamic scanning calorimetry (DSC) measurements have shown that the glass transition temperature of the cured polymer is approximately 58°C. Interestingly, this temperature lies between room temperature and 70°C. Previously we showed that microcapsules synthesized at 70°C suffered from unacceptable levels of internal polymerization. We hypothesized that glassy polymer skin layers prevented internal polymerization at room temperature and rubbery polymer skin layers allowed internal polymerization at high temperatures. This new DSC measurement strongly supports this hypothesis.

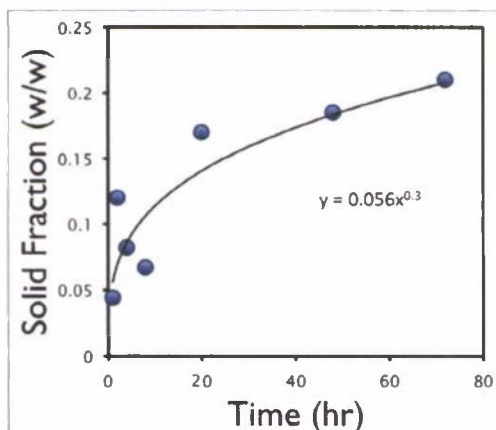


Figure 5: Thermogravimetric analysis of microcapsules showing the weight fraction of polymer as a function of time. The solid fraction reaches 17% after 24 hours and then only slowly increases to about 20% by day 3.

3.3 Scale Up

Scale up efforts at PPG continue, and they now focus increasingly on quality control. Early batches suffered from thinner than usual metal shells, resulting in decreased shelf life. One 200 g batch did not survive more than one week in water, unlike samples made in 20 g batches. After repeating the protocol with greater attention to purification, microcapsules with thick metal shells were again successfully synthesized.

3.4 Drying

Since freeze-drying is not a viable option for industrial synthesis of the microcapsules, PPG continues to investigate alternatives such as solvent displacement, spray drying, and using a fluidized bed. To date, solvent drying has not yet been successful in displacing water without damaging the integrity of the microcapsules. For example, water may be displaced by a polar solvent, such as isopropanol, followed by a second solvent, such as toluene, which has an even lower water content. Although the final product dries without clumping, the resulting microcapsules have shorter shelf life than freeze-dried samples.

Spray drying and the fluidized bed have not been tested yet, but PPG has recently completed extensive installation work and safety preparation in advance of these experiments. Both techniques will be rolled out in upcoming weeks.

3.5 Presentations and Publications

Lance Baird presented recent results at the Polymers Gordon Research Conference held at Mount Holyoke College, in South Hadley, MA on June 12-17.

4 Next Steps

4.1 PPG: Drying, Painting, and Characterization

PPG's primary focus in the upcoming month will be (i) investigate solvent drying, spray drying, and fluidized beds as alternatives to freeze drying, (ii) spray test panels with Polyfibroblast in several primer resins, (iii) compare the performance of the different Polyfibroblast-modified primers with respect to ASTM hardness, adhesion, QUV, and salt spray measurements.

4.2 APL: Silane Optimizations

Formulation improvements will be investigated along two tracks: (i) incorporate silane adhesion promoters into the original Polyfibroblast formulation to determine which type and concentration most effectively prevent corrosion, (ii) test the original Polyfibroblast formulation with different ratios of zinc powder to determine which level achieves the best balance between self-healing and galvanic protection.