

POLYFIBROBLAST: A SELF-HEALING AND GALVANIC PROTECTION ADDITIVE

Progress Report #5

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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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TABLE OF CONTENTS

1	SUMMARY	3
2	PROJECT GOALS AND OBJECTIVES	3
3	KEY ACCOMPLISHMENTS	3
3.1	ELECTROCHEMICAL CHARACTERIZATION	3
3.2	IMPROVED SCRATCH HEALING	5
3.3	ADVANCED FORMULATION	8
3.4	SCALE UP	8
3.5	AGING EXPERIMENTS	8
4	NEXT STEPS	9
4.1	PPG: DRYING, PAINTING, AND CHARACTERIZATION	9
4.2	APL: FULL PRIMER EVALUATION	9

1 Summary

The addition of wetting agents has greatly improved the wetting of the released resin into fresh scratches. Ten percent octadecyltrimethoxy silane (OTS) was particularly good at wetting all scratches from 0.003 to 0.125 in. Since OTS forms a hydrophobic self-assembled monolayer on the surface, this result might mean that acceptable levels of self-repair can be achieved with vanishingly small amounts of resin. In other words, the amount of Polyfibroblast filler could potentially be reduced from, say, 50%, down to 5%, while still achieving our self-healing performance goals.

Electrochemical analysis suggests that the mole fraction of Zn in the alloy is not critical for galvanic protection; however, the long-term performance of the electroless Ni strongly suggests that this system would benefit from the addition of Zn powder. The scale up of the synthesis has reached 200 g batches, approximately 1/5th the final goal. Aging studies show that the microcapsules display better shelf life in hydrophobic solvents compared to polar organic solvents.

2 Project Goals and Objectives

This month marks the milestone for healing 1/32 in. scratches, which were the most difficult to address using last year's formulation. The addition of wetting and adhesion promoting agents to the formulation has successfully solved this problem. Combined with the downselect of the alloy composition and the ability to spray paint, the only two remaining goals for the end of the year are to demonstrate shelf life and scale up to one-gallon batches.

3 Key Accomplishments

3.1 Electrochemical Characterization

Polyfibroblast containing different amounts of zinc (Zn) were tested for their ability to: (i) Generate cathodic protection current on A1008 steel in an aqueous aerated solution of 0.1 M NaCl; and (ii) Polarize the electrode potential of the steel. The Polyfibroblast test specimen consisted of the following mole % zinc: 0%, 2%, 4% and 8%. The Polyfibroblast were coated (on both sides) of a steel or glass surface.

Experimental Setup: Typical electrochemical test consisted of measuring: (i) Current flow between the Polyfibroblast coating and A1008 steel; and (ii) The electrochemical potential between the A1008 steel and a calomel electrode (Hg/HgCl/0.1M NaCl), while connecting and disconnecting (the un-immersed parts of) the steel and the Polyfibroblast using a copper wire. All measurements were made by employing the E-I Noise technique found in the Solartron Electrochemical Analyzer Model SI Model SI 1287.

Results and Discussions: Generally speaking, when steel is subject to cathodic polarization (CP), its electrochemical potential should shift to more negative values relative to its open circuit voltage (OCV) found in the absence of polarization. A negative shift of 100 to 150 mV from the OCV is considered adequate for proper protection against corrosion. However, measuring the shift accurately requires the establishment of a stable OCV prior to the application of the CP. Establishing a stable OCV is feasible for steel immersed in a relatively benign, non-corrosive

solution such as 0.1 M Na_2SO_4 . On the other hand, in 0.1 M NaCl , a stable OCV rarely becomes established due to the non-uniform, specific adsorption of chloride ions on steel that causes localized corrosion, localized variation in pH, etc. Therefore a measure of the potential alone may not provide conclusive evidence about cathodic protection of steel in aqueous sodium chloride solution. An accompanying complimentary measurement of the current is also necessary to ensure that cathodic polarization is effected by the Polyfibroblast.

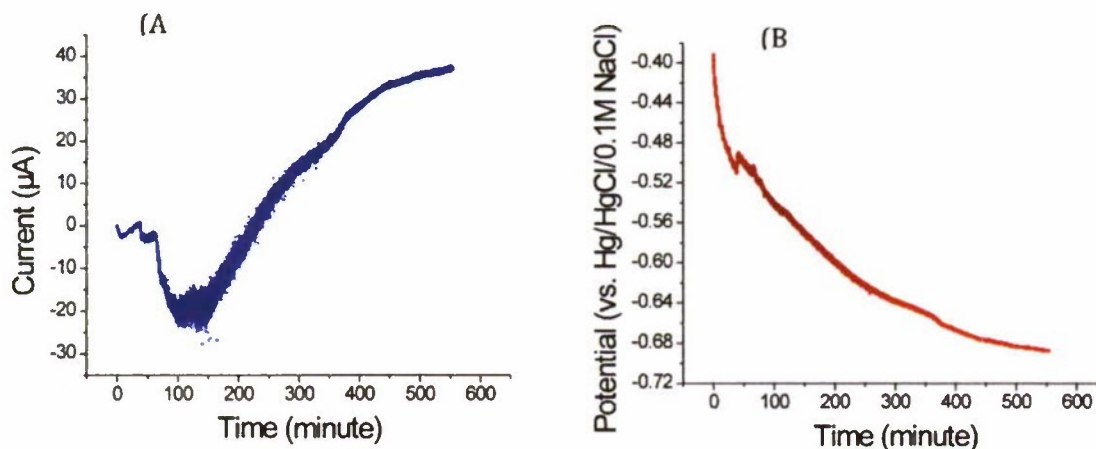


Figure 1: Effect of short circuiting A1008 steel to Polyfibroblast containing 2% Zn, both immersed in aerated aqueous solution of 0.1 M NaCl : (A) Short circuit current (left); and (B) Electrochemical potential of the steel versus a calomel reference electrode (right).

Figure 1A shows the short-circuit current flowing through the steel/electrolyte interface, when the A1008 steel immersed in 0.1 M NaCl was shorted to Polyfibroblast containing 2% Zn. The electrochemical potential between A1008 measured against a calomel reference electrode is shown in Figure 1B. Note that during the current and potential measurements, the electrolyte was under constant aeration to prevent starvation of the solution of dissolved oxygen.

In Figure 1A the direction of the current is negative over the first 250 minutes; the negative sign is indicative of cathodic current through the steel/electrolyte interface. After 250 minutes, the direction current turned positive, indicating cessation of cathodic polarization and the beginning of anodic dissolution of steel; anodic oxidation is analogous to the corrosion of steel. The reversal of current was caused, apparently, not by the depletion of dissolved oxygen (the electrolyte was under aeration during the entire 600 minutes of the test); it was likely caused by the consumption of the elements in the Polyfibroblast that provided CP. The elements that caused CP could have been either Zn or P or both, and the element causing anodic polarization could have been Ni.

It is also interesting and informative to note that the potential data (Figure 1b) indicated a continuous drifting toward negative values relative to the initial (Time = 0 minute) OCV value. Had we not recorded the current simultaneously (Figure 1a), the potential data alone could have been (mistakenly) assumed to be indicative of effective CP. In the light of the current data, it is obvious that the A1003 steel received CP from the Polyfibroblast only for a short period of time; over longer duration, the Polyfibroblast anodically oxidized (corroded) the steel.

The 4% and 8% Zn samples exhibited similar behavior, albeit for a shorter time period. The 4% Zn sample provided CP for 150 minutes, while the 8% Zn sample provided CP for only 40. Interestingly, even the 0% Zn sample provided CP for 30 minutes before the current switched sign. The data are summarized in Figure 2.

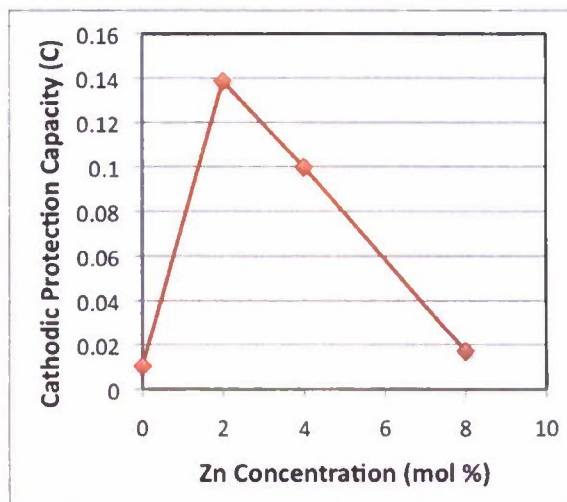


Figure 2: Total integrated cathodic protection capacity (current integrated over time) plotted as a function of Zn concentration in the electroless alloy. The current does not correlate in a simple fashion with zinc concentration due to uncontrolled variables such as exposed surface area, internal resistance, and total amount of material.

Preliminary conclusions: Cathodic protection obtained by A1008 steel from Polyfibroblast containing Ni-P-Zn-plated polyurethane capsules does not depend on the Zn concentration in the plating. The fluctuations in cathodic protection capacity plotted in Figure 2 may result from variations in the thickness of the films, which varied due to the fact that the plating rate decreases with increasing zinc concentration in the plating bath. The short circuit current between A1008 steel and Polyfibroblast remains cathodic for tens to hundreds of minutes, after which it turns anodic. When the current is cathodic, the steel receives some amount of protection against corrosion: larger the current, better the protection; however, the extent of protection appears to be limited. When the current turns anodic, Polyfibroblast could potentially begin to accelerate the rate of corrosion. The take home message from these results, then, is that the addition of zinc powder may be necessary to achieve acceptable levels of galvanic protection.

3.2 Improved Scratch Healing

The resin released by the microcapsules during scratching often absorbs into the surrounding paint rather than wetting the exposed steel. Experiments suggest that self-wetting hinders the ability of Polyfibroblast to consistently repair deep scratches with intermediate widths (0.003 – 0.125 in.). To improve scratch healing, we have added wetting agents to the polyurethane precursor. Unfortunately, amphiphilic substances such as surfactants do not readily emulsify in water. As expected, the surface-active molecules interfere with the interfacial polymerization process. Their presence at the interface either inhibits growth of the polymer shell, or leads to weak films that swell with water (Figure 3). The surfactants could be included neither as an additive to the polyurethane precursor nor as separate microcapsules.

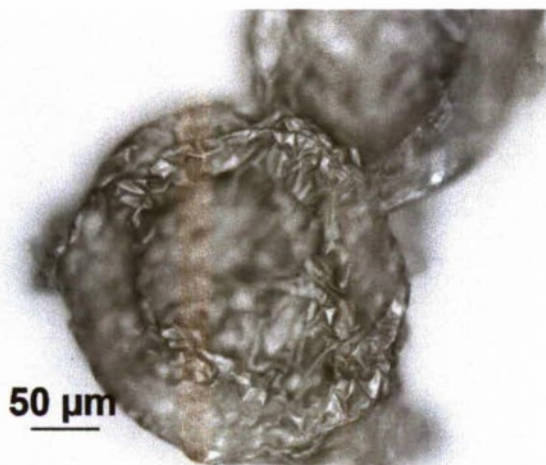


Figure 3: Attempt to encapsulate DABCO 197 surfactant within a polyurea shell. Note the highly wrinkled appearance. The wrinkles appear after the microcapsules soak for an extended time in water.

The next strategy was to incorporate an oily liquid that spontaneously spreads upon a steel surface. Silicone oil was therefore mixed with the resin and microencapsulated. The resulting panels were nearly rust free (Figure 3A). One potential drawback to the use of silicone oil is that it is prone to phase separate from the resin and remain in the liquid phase. While the silicone oil may still provide some protection against water attack as a liquid, the effect is likely short-lived.

The success of silicone oil led to the exploration of silane adhesion promoters. Also possessing the Si-O bond, silanes not only spread spontaneously on steel, but they also couple polymers to the metal surface through the formation of covalent bonds. With many chemistries to choose from, we narrowed down to glycidoxypyriltrimethoxy silane (GPS), aminopropyltrimethoxy silane (APS), isocyanatopropyltrimethoxy silane (ITS), and octadecyltrimethoxy silane (OTS). GPS was eliminated since it is water-soluble. APS could not be used because it reacted too violently with the polyurethane precursor. ITS complicates the microencapsulation procedure, but it is still under investigation due to its ability to form urea or urethane bonds. OTS, on the other hand, incorporated readily into the microcapsules without requiring any adjustments to the synthetic procedure. As seen below in Figure 3B, 10 wt% of the additive nearly arrested corrosion entirely. Except for a small speck of rust in the razor blade scratch, the OTS-modified Polyfibroblast healed all scratches.

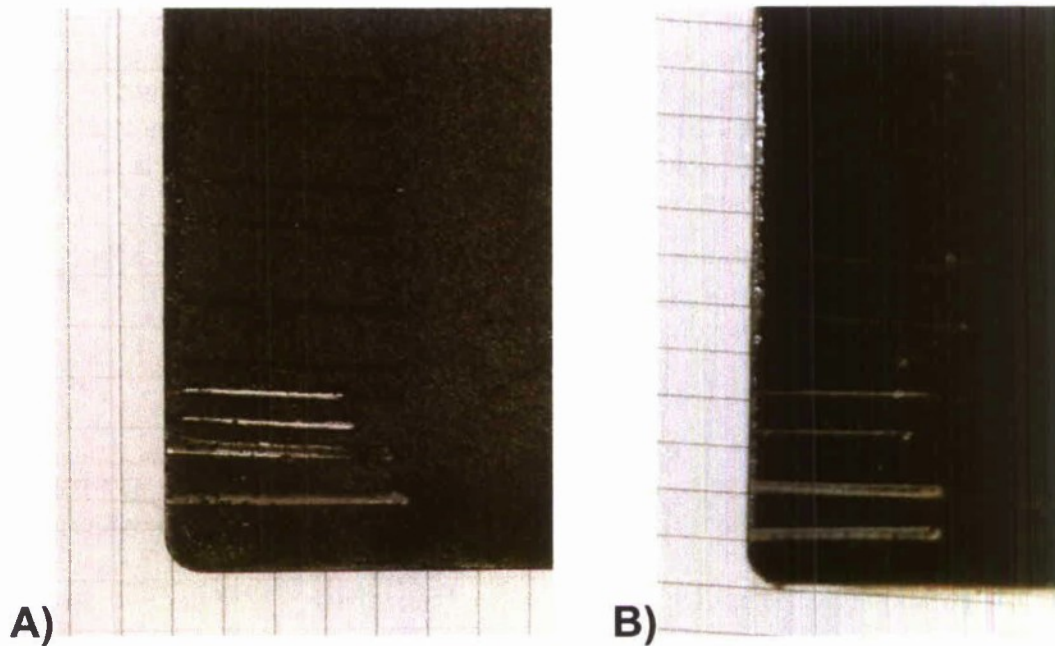


Figure 4: A) Silicone oil-modified Polyfibroblast panel, and B) OTS-modified Polyfibroblast panel after 24 hours of immersion in deionized water at 100°F. Little to no rusting occurred in either panel.

Figure 5 shows fluorescence microscopy of the two samples in Figure 4. Note the presence of fluorescence within both 1/32 in. scratches. What becomes clear is that the resin does not form a thick wetting layer, except in the 0.003 in. (razor blade scratch). Despite its small thickness, the polymer scar efficiently prevents corrosion. The success of OTS in particular suggests that potentially even a self-assembled monolayer (SAM) could be used to heal scratches rather than forming a polymer scar. While a SAM is less robust than a polymer film, one can coat a much greater area with a vanishingly small amount of material. The success of OTS could therefore pave the way to make self-healing coatings with a vastly decreased loading of Polyfibroblast.

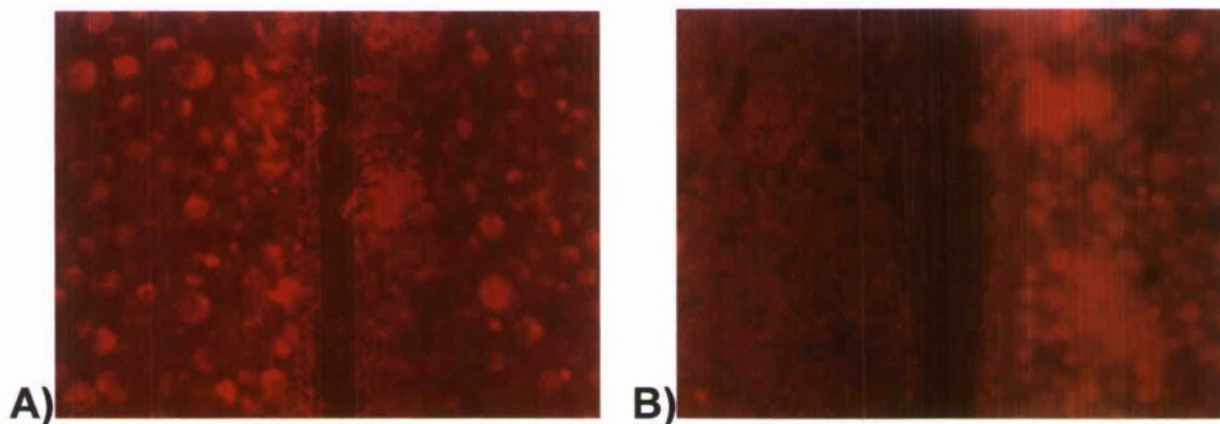


Figure 5: A) Silicone oil-modified Polyfibroblast panel, and B) OTS-modified Polyfibroblast panel after showing the 1/32 in. scratch under fluorescence microscopy. Fluorescence occurs deep within the scratch for both samples, showing that the silicone oil and OTS help the released resin to spread within the scratch and form a moisture barrier.

3.3 Advanced Formulation

Preliminary evidence that hexamethylene diisocyanate (HMDI) forms a more wear resistant polymer than isophorone diisocyanate (IPDI) have spurred interest in using it as a potential replacement. Also driving this change is the lower viscosity of HMDI, which may lead to more thorough scratch healing. Experiments to evaluate wear resistance are underway.

The advanced formulation also addresses deficiencies in the current processing method. It greatly reduces the amount of time required, and eliminates the costly drying step. The advanced protocol cuts the total processing time from about one week to a single day.

3.4 Scale Up

PPG has successfully scaled up to 200 g batches. They have found that the amount of stirring time using the rotor-stator mixer can be reduced to as little as 30 minutes without impacting the particle size. In this manner, multiple batches can be combined in succession to achieve the desired batch size. Observe that the particle size of the combined batch is essentially the average of the two smaller batches.

	Batch 1	Batch 2	Combined Batch	Combined Batch after 18 hours
Surface Weighted Mean (μm)	16.6	19.2	17.9	18.0
Vol. Weighted Mean (μm)	25.1	30.5	27.9	28.0

Table I: Particle size data for microcapsules showing that multiple batches can be combined without adversely affecting the size or size distribution.

3.5 Aging Experiments

To assess the shelf-life of the Polyfibroblast filler, PPG has performed aging experiments where the metal-coated microcapsules are allowed to soak in various solvents for different amounts of time. The weight fraction of liquid is then measured by TGA. As shown in Figure 6, acetone rapidly removes liquid from the microcapsules. Both xylene and Aromatic 100 have little effect, showing only modest decreases in the amount of liquid after 1 week. Tests are currently underway to measure the amount of liquid after 1 month of storage.

The destruction of the microcapsules by acetone had been observed previously when it was tried as a drying method, and has not been observed yet with other solvents. While poor solvent resistance is obviously a concern, these measurements are being performed on the bare microcapsules and not a primer. The more important measurement involves the solvent resistance of a Polyfibroblast-modified primer. Preliminary results suggest that the primers hold up well to most common solvents, but these experiments clearly suggest the need to investigate the solvent resistance of the self-healing primers in greater detail.

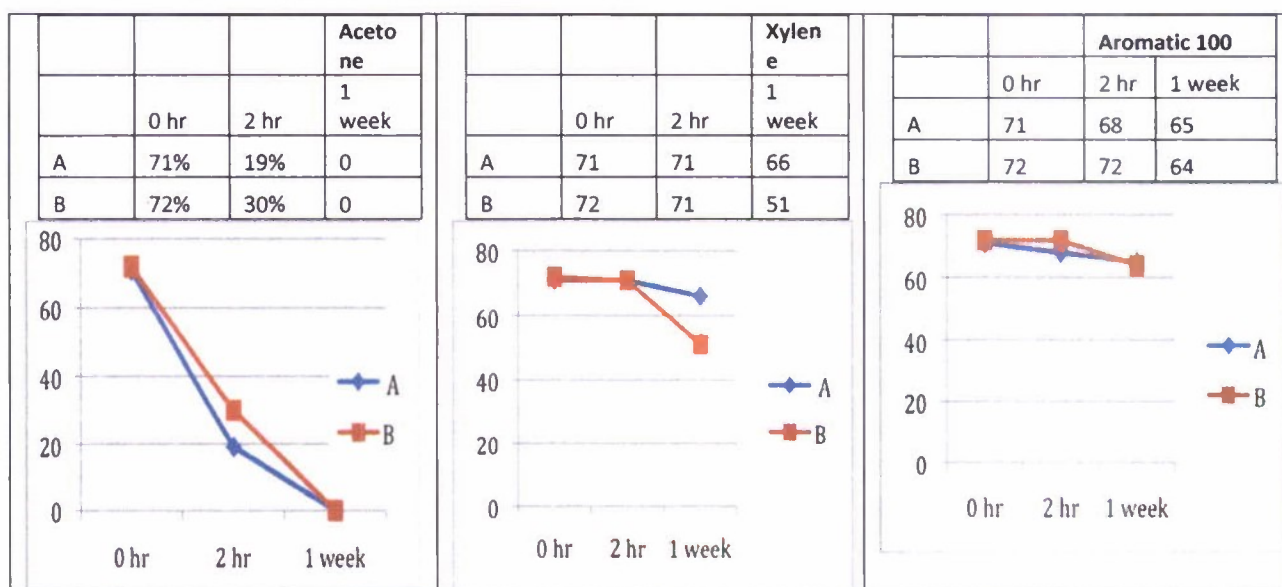


Figure 6: Thermogravimetric Analysis (TGA) of microcapsules aged in acetone, xylene and aromatic 100. The liquid weight % is provided for the virgin sample (0 hr), 2 hours of soaking, and 1 week of soaking. A and B refer to two different samples. Acetone rapidly removed liquid from the samples, but the shelf life was much better in hydrophobic solvents.

4 Next Steps

4.1 PPG: Drying, Painting, and Characterization

PPG's primary focus in the upcoming month will be (i) to continue scale up, (ii) investigate alternatives to freeze drying, (iii) 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: Full Primer Evaluation

With a better understanding of the electrochemistry and the discovery of the effectiveness of silane adhesion promoters, APL will begin to evaluate test panels in larger numbers with respect to moisture resistance. On the galvanic protection side, zinc powder will be incorporated into the primer to assist in galvanic protection, and on the self-healing side, the silane adhesion promoters will be used in different concentrations to obtain the best performance. Special attention will be given to the durability of the OTS/polyurea films, whereas the ITS-modified resin will be studied mostly in terms of processability.