REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
26-08-2013	Performance/Technical Report (Monthly)	7/25/13 - 8/26/13

4. TITLE AND SUBTITLE

Polyfibroblast: A Self-Healing and Galvanic Protection Additive

5a. CONTRACT NUMBER

5b. GRANT NUMBER
N00014-09-1-0383

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Benkoski, Jason J.

5d. PROJECT NUMBER

5e. TASK NUMBER
FGY25

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
The Johns Hopkins University Applied Physics Laboratory
11100 Johns Hopkins Rd
Laurel, MD 20723

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
875 North Randolph Street
Arlington, VA 22203-1995

10. SPONSOR/MONITOR'S ACRONYM(S)
ONR

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for Public Release: Distribution is Unlimited.

13. SUPPLEMENTARY NOTES

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.

15. SUBJECT TERMS
corrosion protection, self-healing, coatings, polymers

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Jason J Benkoski
U	U	U	UU	6	19b. TELEPHONE NUMBER *(Include area code)* 240-228-5140

REDD-2013-323

POLYFIBROBLAST: A SELF-HEALING AND GALVANIC PROTECTION ADDITIVE

Progress Report #3

Prepared for:

Frank Furman
Logistics S&T Thrust Manager
Office of Naval Research
Code 30, Room 1149
875 North Randolph Street
Arlington, VA 22203-1995

Prepared by:

Jason J. Benkoski, Ph.D., Senior Research Scientist
The Johns Hopkins University Applied Physics Laboratory
The Milton S. Eisenhower Research Center
11100 Johns Hopkins Rd, MS 21-N109
Laurel, MD 20723
Tel. (240) 228-5140

Reporting Period: July 25 through August 26, 2013
Date of Report: August 26, 2013

TABLE OF CONTENTS

1 Summary

The investigation of microcapsule shear strength has been completed. Microcapsules with shell thickness greater than 1.1 μm survive normal spray painting conditions. An applied compressive stress on the order of 1 MPa was required to rupture the microcapsules. Dielectric spectroscopy has shown early promise as a nondestructive method for monitoring microcapsule hydrolysis.

2 Project Goals and Objectives

The four milestones for phase IV are given below. For the purposes of tracking our progress, we are currently at the end of month 3 in our revised research plan.

1. Develop on site inspection method for monitoring self-healing and coating health by month 3. (**Completed**)
2. Develop a method for continuous monitoring of OTS degradation by month 5.
3. Demonstrate a method for measuring the fraction of broken microcapsules as a function of shear stress by month 6. (**Completed**)
4. Establish baseline metrics for qualifying batches of microcapsules from the manufacturing process by month 12.

3 Key Accomplishments

3.1 Thin-Shelled Microcapsules

Preliminary measurements of microcapsule shear strength have been completed. In general, the microcapsules easily withstand the shear stress of mixing and spray painting. Our tests have confirmed that, generally, the microcapsules are exceedingly difficult to rupture via fluid stresses. But for the purposes of method development, we intentionally synthesized weaker microcapsules with thinner shells that would yield a measurable result (ie., broken microcapsules).

As noted previously, we synthesized microcapsules with different shell thicknesses by adjusting the reaction time at 90°C. Figure 1 shows the average diameter, liquid fraction, and average shell thickness for this set of microcapsules.

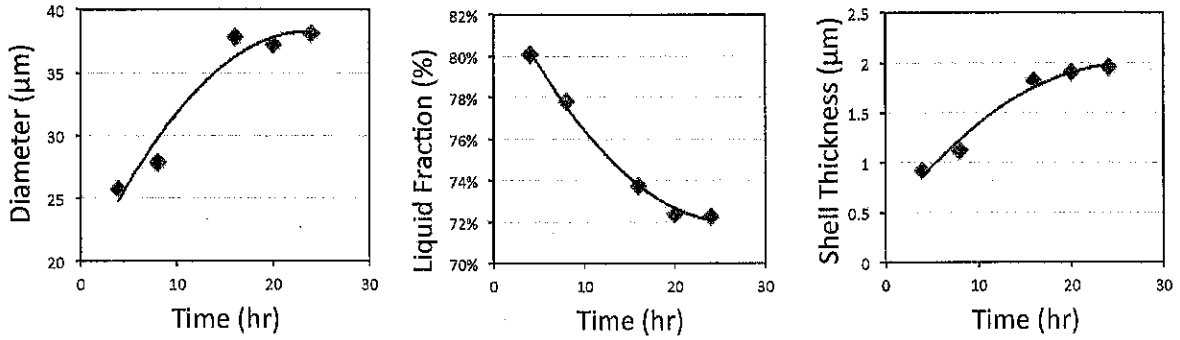

Figure 1: (left) Average microcapsule diameter versus reaction time, (center) mass fraction of liquid versus time, and (right) polymer shell thickness versus time.

3.2 Spray Paint Stress Measurement

Due to the difficulty of breaking the fully cured microcapsules that have been reacted for 24 hours, most of the fluid shear experiments were performed on the microcapsules cured for 4 hours. As seen in Figure 1, these had a polymer shell thickness of approximately 0.9 μm. The first measurement was performed by spraying the microcapsules through a spray gun using a pressure of 206 kPa and a viscosity of 500 cSt. Only the microcapsules with a 0.9 μm shell broke during this test, with approximately 14% broken according to microscopic inspection.

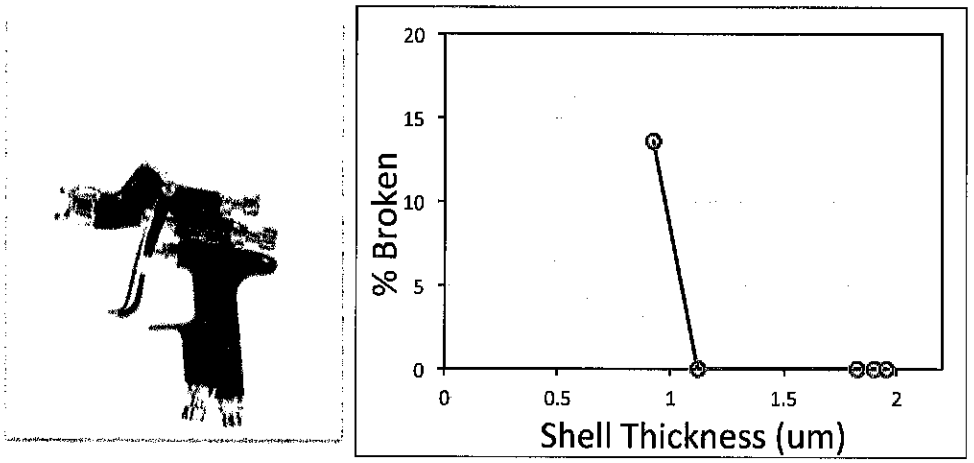

Figure 2: (left) HVLP spray gun used for shear experiments. (right) Fraction of broken microcapsules as a function of shell thickness.

3.3 Couette Viscometer Stress Measurement

Next, microcapsules were tested on a Couette viscometer. The Couette viscometer is shown in Figure 3. It has a maximum speed of 24000 RPM, the fluid has a 35 cSt viscosity, the cup diameter is 51 mm, and the bob diameter is 44 mm, giving a 7 mm gap. Only a small fraction of the 0.9 μm microcapsules broke, even at 24,000 RPM. Only about 7% of the microcapsules broke at that speed according to microscopic inspection.

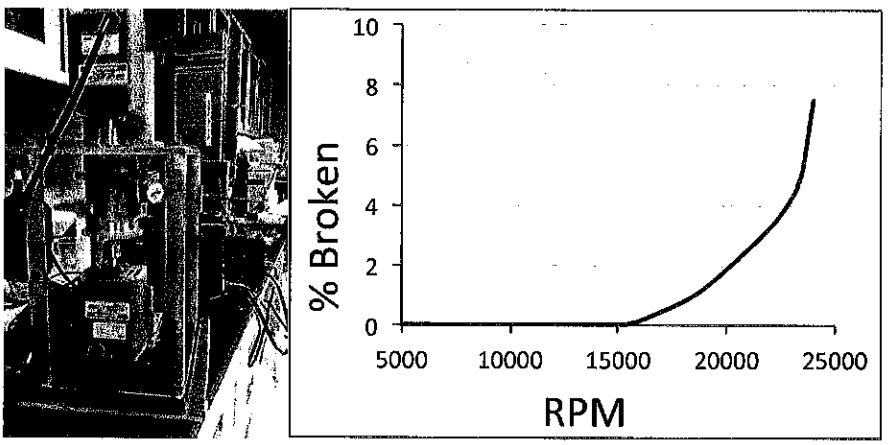

Figure 3: (left) Picture of the Couette viscometer with nested cylinders. (right) Plot of percentage of broken microcapsules with a 0.9 μm shell thickness as a function of rotation speed.

3.4 Compressive Strength

Since shear stresses applied through fluid flow has proven insufficient to rupture the microcapsules using our test equipment, we supplemented the above measurements with a rupture test performed under uniaxial compression. This simple experiment consisted of placing a fixed number of microcapsules between a pair of glass slides. Weights were placed upon the upper slide to measure the percentage of broken microcapsules as a function of applied stress.

Here we calculate a first approximation of the compressive stress by dividing the total force equally among the microcapsules and then dividing by the cross-sectional area.

As seen in Figure 4, the microcapsules do not begin to break until the stress is on the order of 1 MPa. As expected, the thicker microcapsules ruptured at higher stresses than the thinner microcapsules. Further analysis of this measurement technique is necessary, but the initial data suggests greater differentiation among the stronger microcapsules than for the weaker microcapsules. In other words, the critical stress to reach 10% broken microcapsules is not a strong function of shell thickness. The critical stress to reach 70% broken microcapsules is a much stronger function of shell thickness according to this data.

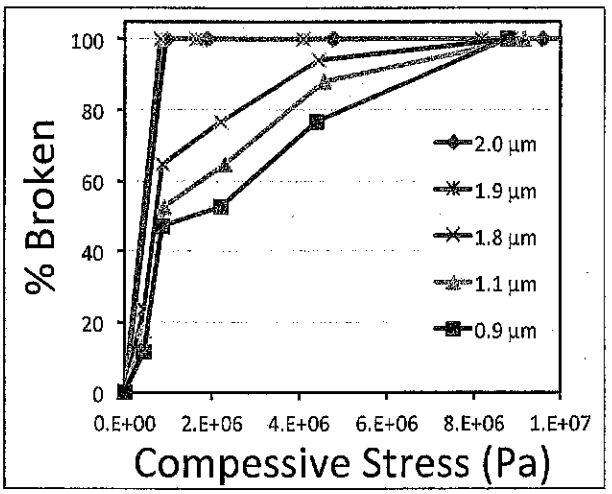

Figure 4: The percentage of broken microcapsules versus compressive stress.

3.5 *In Situ* Hydrolysis Measurements

We are currently developing a method for monitoring microcapsule health using dielectric spectroscopy. By measuring the complex dielectric constant as a function of frequency, we are hoping to probe the quantity of liquid within a self-healing paint. As the liquid hydrolyses, the decreasing quantity of liquid or increasing viscosity should be reflected in the complex dielectric constant. These measurements are performed by patterning electrodes upon a printed circuit board and then applying a self-healing paint over the top. We then apply an alternating electric field across the electrodes and record the complex dielectric constant. At this stage, we are looking for correlations between the known volume fraction of liquid and the real and complex dielectric constant. We are also looking for differences in the frequency dependence of the dielectric constant that might arise from the presence of entrained liquid.

Although currently there appears to be an increase in the real part of the dielectric constant with increasing microcapsule concentration, we are performing additional control experiments to verify it.

3.6 Next Steps

Having completed milestones for both the on site visual inspection and microcapsule strength measurements, our focus will turn towards continuous monitoring of microcapsule hydrolysis

and electrochemical impedance spectroscopy. Currently, dielectric spectroscopy appears to be a promising method. In contrast to infrared spectroscopy, thermogravimetric analysis, and gas chromatography, this method works for microcapsules embedded within a paint better than virgin microcapsules. Not only might it measure the percentage of liquid as a function of time in a nondestructive fashion, but it might also make it possible to monitor microcapsule health under conditions that more closely approximate those while a paint is in service.