REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	23-03-2012
2. REPORT TYPE	Performance/Technical Report (Monthly)
3. DATES COVERED (From - To)	3/23/12 - 4/23/12
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	
5d. PROJECT NUMBER	
5e. TASK NUMBER	FGY25
5f. WORK UNIT NUMBER	
6. AUTHOR(S)	Benkoski, Jason J.
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	

20120504061

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

16a. REPORT	16b. ABSTRACT	16c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON	19b. TELEPHONE NUMBER (Include area code)
U	U	U	UU	7	Jason J Benkoski	240-228-5140

REDD-2012-152

POLYMER CLAW: INSTANT UNDERWATER ADHESIVE

Progress Report #2

Prepared for:

David K. Han
Office of Naval Research
Code 322
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: March 23, 2012 through April 24, 2012
Date of Report: April 24, 2012

TABLE OF CONTENTS

1 Summary

The yield of amine-loaded microcapsules has been improved by modifying vortex speed, formulation, and glassware. The microcapsules have been purified and added to an isocyanate resin to successfully form a pressure-activated adhesive. A number of new caustic materials are being evaluated for their ability to degrade bacterial cellulose. So far NaOH/urea mixtures have caused the most rapid degradation of cellulose. Lastly, modified grill brushes have been fabricated and tested under a compressive load. With 50% of the bristles angled at 30° from the normal, they collapse under a critical load of 40-50 pounds.

2 Project Goals and Objectives

The amine-loaded microcapsules and adhesive putty have been successfully synthesized in the first two months according to schedule. For the next three months, the project plan calls for parallel development of the pressure-activated adhesive, water-activated caustic cleaning agent, and mechanically activated abrasive brush.

3 Key Accomplishments

3.1 Amine Microencapsulation

As described in last month's report, we have developed a method for synthesizing amine-loaded microcapsules using a reverse-phase emulsification. Initially, yields were estimated to be below 75% due to uncontrolled polymerization and droplet coalescence. We tried to address these issues by changing the stirring rate, changing the type of stirring blade, changing the glassware, and adjusting the chemistry. The reaction conditions are given in Table 1 below:

Total Solution Mass (g)	PIB Concentration (g/g)	Nanoclay Concentration (g/g)	Isocyanate 1	Isocyanate 1 Concentration (g/g)	Isocyanate 2	Isocyanate 2 Concentration (g/g)	Amine 1	Amine 1 Concentration (g/g)	Amine 2	Amine 2 Concentration (g/g)	Amine 3	Amine 3 Concentration (g/g)	Spin Speed (RPM)
75	3%	0.3%	TDI	5%		0%	DETA	4%	Low PEI	9%		0%	1500
75	3%	0.3%	IPDI	5%		0%	DETA	7%	Low PEI	7%		0%	
75	3%	0.3%	IPDI	5%	PHMDI	1%	DETA	7%	Low PEI*	7%		0%	8000
75	3%	0.3%	IPDI	5%	PHMDI	1%	DETA	7%	Low PEI	7%		0%	8000
75	3%	0.3%	IPDI	3%	TDI	3%	DETA	7%	Low PEI	7%		0%	1700
75	3%	0.3%	IPDI	3%	TDI	3%	DETA	6%	Low PEI	6%	High PEI	25%	1700
75	3%	0.3%	IPDI	3%	TDI	3%	DETA	12%	High PEI	1%		0%	1700

Table 1: *List of experimental parameters for amine-loaded microcapsule synthesis. The bottom sample on the list produced the highest yield of microcapsules.*

The best results were obtained using a mechanical stirrer in a round bottom flask. A combination of IPDI and TDI were found to produce tougher polymer shells than either by itself, and high molecular weight PEI was crucial for stabilizing microcapsule droplets during the initial addition of isocyanates. An example of microcapsules from this batch are shown in Figure

1, along with a micrograph showing a large amount of liquid released when the microcapsules are broken beneath a glass cover slip. The microcapsules are sufficiently robust to form stable mixtures with IPDI. This crude pressure-activated adhesive has the consistency of toothpaste, and rapidly forms a hard polymer when pressed between a pair of glass slides. The resulting adhesive bond is shown in Figure 2.

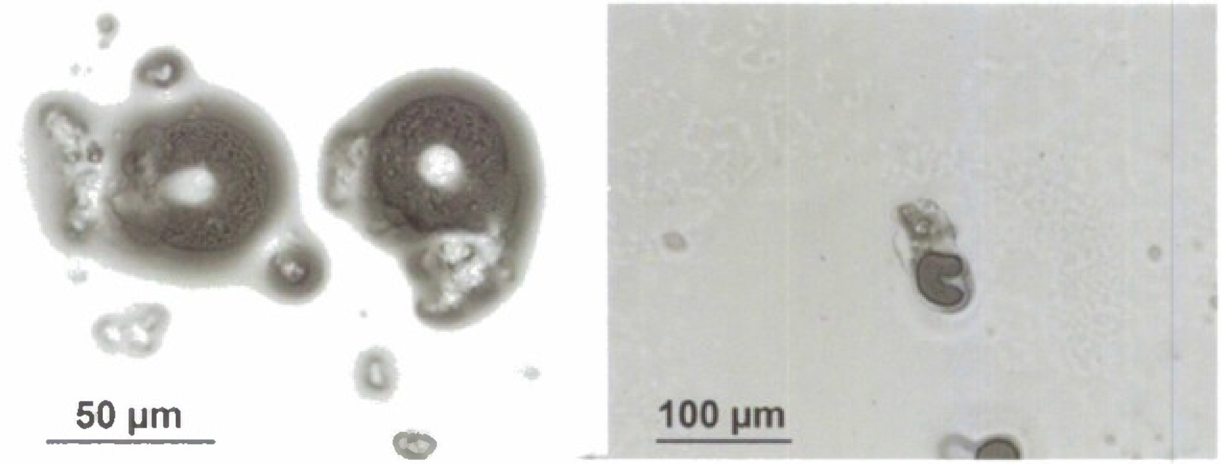


Figure 1: *(left) Optical micrograph of a pair of amine-loaded microcapsules. (right) A microcapsule is crushed between a glass slide and cover slip, revealing its liquid contents.*

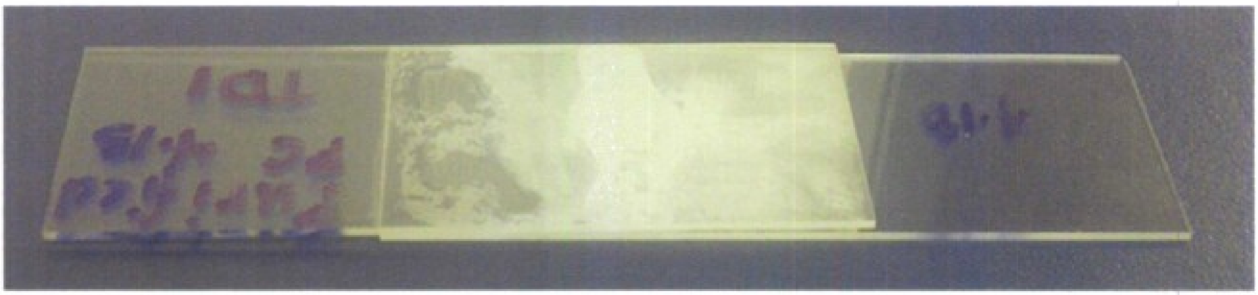


Figure 2: *Two glass slides glued together using a mixture of amine-loaded microcapsules and IPDI.*

3.2 Alternative Caustic Ingredients

In addition to oxalic acid and sodium percarbonate, we have also begun to explore alternative caustics to rapidly break down cellulose. Toluenesulfonic acid is an organic form of sulfuric acid that is more acidic than oxalic acid. Much like oxalic acid, it comes as a dry powder and forms stable mixtures with sodium percarbonate that foam when added to water.

We have also begun to investigate using bases rather than acids to catalyze hydrolysis. NaOH and KOH are currently under evaluation. Unlike the two acids described above, they do not cause the sodium percarbonate to outgas, but they do form stable dry mixtures.

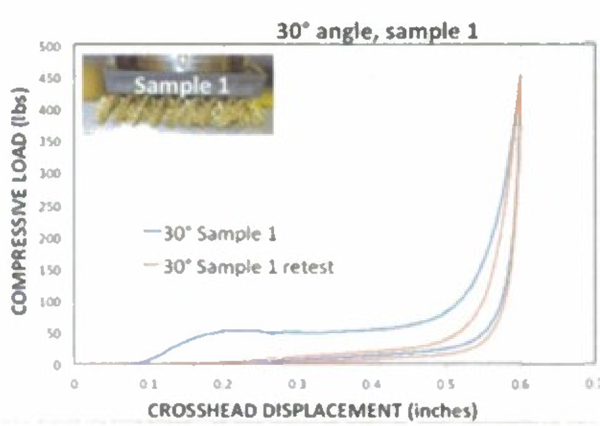
Literature searches have also revealed that urea can be helpful in breaking up the hydrogen bonds in cellulose crystals. This reduces crystallinity and thereby improves the penetration of acids, bases, or radicals. Lastly, we have also begun to evaluate powdered soaps to help loosen and break up debris.

To date, we have not observed dramatic cellulosic breakdown in any of our mixtures. The best performance was from a mixture of sodium hydroxide and urea that caused a bacterial cellulose pellet to decrease in volume by about one half over the course of an hour. Interestingly, this combination worked best at temperatures close to freezing.

3.3 Load-Displacement Testing of Metal Brush

Three grill brushes were modified by pruning and bending the bristles to fixed angles with respect to the normal (Fig. 3). It immediately became clear that the bristle angle would have a large spread about the average. We also observed that the accuracy was limited to about ± 15°. Nevertheless, we prepared three samples by first pruning 50% of the bristles and then bending the remaining bristles with needle-nose pliers.

Figure 3: *(left) Grill brush with 50% of the bristles pruned and bent 60° with respect to the normal. (right) The same but with bristles bent only 30° with respect to the normal.*



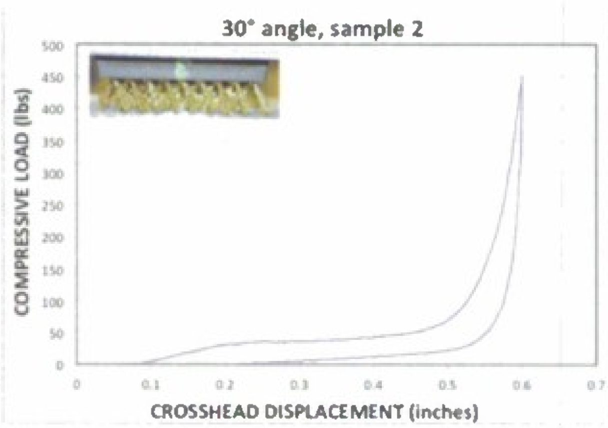


Figure 4: *Load-displacement curves for grill brushes with 50% of the bristles pruned and bent 30° with respect to the normal. All samples were tested in compression. Sample 1 was tested a second time to show that no critical load was observed during the retest.*

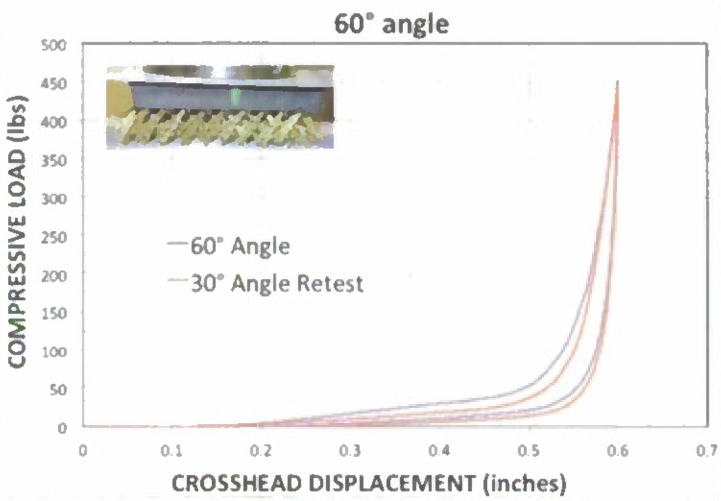


Figure 5: *Load-displacement curve for a grill brush with 50% of the bristles pruned and bent with a 60° angle with the normal. Note the similarity with a 30° sample that was retested. The compressive load gradually rises to about 50 pounds before taking off, and all 0.5 inches of displacement are stored elastically.*

The load-displacement curves in Figure 4 give a critical load of 50 pounds for the first 30° sample and 40 pounds for the second. Observe how the load rises more dramatically at the end of the test after the bristles lie completely flat. About 10 pounds of that load is stored elastically in the bristles when they bounce back after the load is removed. About 0.2 inches of displacement are also recovered. Upon retest, the critical load is no longer observed.

When the bristle angle is increased to 60°, a well-defined critical load is no longer observed (Fig. 5). Bending these bristles to such a large angle has apparently consumed the majority of the available plastic strain. The similarities between the loading and unloading curve indicate that bending the bristles from 60° to 90° is largely elastic. A comparison with the retest of the 30° sample gives further credence to the idea that the bristles naturally bounce back to approximately 60° after they have been bent completely flat.

A critical load is desirable for this application because it would help protect the pressure-activated adhesive prior to use. The overall adhesive system will be designed so that the critical load to collapse the bristles will be greater than the critical load for activating the adhesive.

4 Next Steps

4.1 Pressure-Activated Adhesive

For the time being, the seventh recipe in Table 1 will be used to synthesize microcapsules for the adhesive putty. The adhesive strength will be optimized by varying: (1) the type of commercial isocyanate resin, (2) the ratio of resin to microcapsules, (3) the ratio of DETA and PEI inside the microcapsules, and (4) the microcapsule diameter.

4.2 Water-Activated Caustic

Next month we will employ design of experiments (DOE) to rapidly screen our caustic formulations to identify the combination of ingredients that most rapidly hydrolyzes cellulose. We also plan to identify a method for measuring the hydrolysis kinetics that can also withstand extreme pH values.

4.3 Abrasive Brush

Next month we will perform a more systematic investigation of the effects of bristle angle and bristle density on the critical load for collapse. We will first measure 30°, 45°, and 60° samples with a 50% bristle density. Then we will repeat the study using a 10% bristle density. Our goal is to achieve a critical load of about 10 pounds with a minimal level of residual stress when completely flattened (90° angle).