DoD Corrosion Prevention and Control Program

Self-Repairing Polymer Networks for High-Performance Coatings

Final Report on Project F12-AR12

Brooke A. Divan, Richard G. Lampo, and Lawrence Clark

September 2018

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Self-Repairing Polymer Networks for High-Performance Coatings

Final Report on Project F12-AR12

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Final report

Approved for public release; distribution is unlimited.

Prepared for Office of the Secretary of Defense (OUSD(AT&L))
Washington, DC 20301-3090

Under Project F12-AR12, “Self-Repairing Polymer Networks for High-Performance Coatings”
Abstract

This project demonstrated the capabilities of a self-repairing additive in a polyurethane topcoat (MIL-PRF-85285 Type II, Class H) applied to the exterior hangar doors in the severely corrosive environment at Corpus Christi Army Depot, Texas. Many conventional coatings when scratched or abraded, may develop corrosion that can lead to rapid deterioration of the substrate steel. The demonstrated self-repairing coating system was also applied to test panels exposed to atmospheric weathering and salt fog testing for 2,000 hours. While the self-repairing coating showed promise on the test panel exposure tests, the system was not able to protect the steel hangar doors due to the excessive mechanical impacts and stresses they are subjected to during daily operations. Department of Defense implementation of the demonstrated self-repairing coating is not currently recommended for use on infrastructure. Further evaluation would be needed to match the self-healing capabilities of the demonstrated coating with lighter-duty steel infrastructure components not subjected to the degree of impact and abrasion as the subject hangar doors. Because the self-repairing coating system did not perform any better than the conventional control coating in this project, the return on investment was zero.
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Preface

This demonstration was performed for the Office of the Secretary of Defense (OSD) under Department of Defense (DoD) Corrosion Prevention and Control (CPC) Program Project F12-AR12, “Self-Repairing Polymer Networks for High-Performance Coatings.” The proponent was the U.S. Army Office of the Assistant Chief of Staff for Installation Management (ACSIM), and the stakeholder was the U.S. Army Installation Management Command (IMCOM). The technical monitors were Daniel J. Dunmire (OUSD (AT&L) Corrosion), Ismael Melendez (IMPW-E), and Valerie D. Hines (DAIM-ODF).

The work was performed by the Materials Branch of the Facilities Division (CEERD-CFM), U.S. Army Engineer Research and Development Center, Construction Engineering Research Laboratory (ERDC-CERL). A portion of the work was performed under contract with Mandaree Enterprise Corporation (MEC), Warner Robins, GA. At the time of publication, Vicki L. Van Blaricum was Chief, CEERD-CFM; Donald K. Hicks was Chief, CEERD-CF, and Michael K. McInerney, CEERD-CFM, was the ERDC CPC Program Coordinator. The Deputy Director of ERDC-CERL was Dr. Kiran-kumar Topudurti, and the Director was Dr. Lance D. Hansen.

The following personnel are gratefully acknowledged for their support and assistance in this project:

- Harry Falcon, Jr., Maintenance and Construction Branch Chief, Facilities Engineering Management Division, Corpus Christi Army Depot, TX.
- Dr. Marek Urban, KMA Maxis, Inc., Hattiesburg, MS, for contributions developing and formulating a self-repairing network additive for polyurethane coatings.
- Susan A. Drozdz (retired), Chemist, ERDC-CERL
- Alfred D. Beitelman, Chemist, ERDC-CERL, for onsite inspection during surface preparation and painting of the hangar doors.

The Commander of ERDC was COL Ivan P. Beckman, and the Director was Dr. David W. Pittman.
## Unit Conversion Factors

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1 Introduction

1.1 Problem statement

The Department of Defense (DoD) spends billions of dollars annually to prevent and control the effects of corrosion on metal infrastructure (Herzberg et al. 2014). Coatings are generally recognized as the “first line of defense” for protecting steel structures (Shaw and Kelly 2006). The need for better-performing and more cost-effective coatings is of ongoing interest within the Army and the DoD.

Coatings applied to steel structures for corrosion protection are routinely subjected to cuts and scratches during normal operations or maintenance. If deep enough, these cuts and scratches expose the steel substrate to moisture and other elements that then cause corrosion. This impact creates significant continual maintenance from the effects of corrosion and paint failure on steel structures (e.g., fuel/water storage tanks, utility piping, metal buildings, and bridges).

Regular maintenance and repair of coatings is routinely deferred because of the expense and time constraints imposed by mission-required facility operations. The lack of routine coating maintenance results in the development of rust, pitting, and under-film corrosion. Such coating failures, if not repaired for an extended period, will cause significant damage and ultimately increase the cost and time requirements for facility maintenance or rehabilitation.

Epoxy primers, overcoated with a polyurethane topcoat, have a proven track record of being a very effective corrosion protection coating system for steel in harsh environments. However, these systems become compromised when damaged by frequent mechanical impact and abrasion, thus reducing the coating’s protective performance. Development of self-repairing coatings that heal themselves when damaged (maintaining protection from the effects of corrosion) could increase the service life of coatings, reduce the cost of maintenance, and mitigate corrosion damage to critical infrastructure. Effective self-repairing coating systems could reduce facility life-cycle costs of Army assets around the world.
1.2 Objective

The objectives of this project were to demonstrate and validate the benefits of an innovative, self-repairing polyurethane coating for infrastructure application and to assess the self-healing and corrosion-protection abilities of the coating in such applications.

1.3 Approach

Hangar doors at Corpus Christi Army Depot (CCAD; Corpus Christi, TX) were selected to provide a rigorous performance test in a highly corrosive environment. CCAD has 100 sliding, heavy-duty, steel hangar door leaves (Figure 1) that were scheduled for repainting at an estimated cost exceeding $1,000,000. These doors, due to the purpose for which they are designed, are subjected to frequent, heavy impacts and abrasion during normal operations. These operational factors amount to a challenging test environment for performance testing of a self-repairing coating.

Figure 1. Hangar door leaves at the CCAD before coating application.

The demonstrated coating consisted of MIL-DTL-24441/20, Formula 150 Type III epoxy primer and an intermediate coating of MIL-DTL-24441/31, Formula 152 Type IV. The self-healing topcoat was based on MIL-PRF-85285 Type II, Class H polyurethane topcoat. An innovative additive P/N ADT-100 supplied by KMA Maxis, Inc., of Hattiesburg, Mississippi, was
incorporated into this topcoat for the purpose of initiating self-healing activity at damaged portions of the topcoat. This coating system was applied to selected hangar door leaves and test panels as described below:

- One hangar door leaf, which was abrasive-blasted to near-white condition (SSPC-SP 10).
- Steel atmospheric exposure test panels that were abrasive-blasted to near-white condition (SSPC-SP 10).
- Steel test panels for accelerated laboratory testing, which were abrasive-blasted to near-white condition (SSPC-SP 10).
- A control door leaf and control steel test panels, blasted to near-white condition (SSPC-SP 10), to which the coating system was applied without the self-repairing additive in the topcoat.

1.4 Metrics

The four metrics used to assess the performance of the demonstrated self-repairing coating system to generate a self-healing action and improve the useful service life of the coating system were as follows:

1. Using bare metal coupons exposed to the atmosphere, assess the corrosivity level of the site at CCAD per ASTM G1.
2. As compared to the control coating system, assess the ease of use and effectiveness of the self-repairing coating system to control corrosion on the hangar door leaves per ASTM D1654.
3. As compared to the control coating system, assess the effectiveness of the self-repairing coating system to control corrosion on the outdoor exposure test panels per ASTM D1654.
4. As compared to the control coating system, assess the effectiveness of the self-repairing coating system to control corrosion on test panels after they were subjected to 2,000 hours of salt fog per ASTM B117.

The above-referenced standards and additional standards described below were used to execute this demonstration:

- ASTM D4417, “Standard Test Methods for Field Measurement of Surface Profile of Blast Cleaned Steel,” and SSPC-VIS 1, “Guide and Reference Photographs for Steel Surfaces by Dry Abrasive Blast Cleaning,” were used in the surface preparation of the steel test panels and hangar door panels.
• The Society for Protective Coatings (SSPC) standard, SSPC-SP 10/NACE 2, “Near-White Blast Cleaning,” was used as a standard for surface preparation on the hangar doors and steel test panels.

• SSPC-PA 2, “Measurement of Dry Coating Thickness with Magnetic Gages,” was used in measuring the coating thickness on the steel test panels and hangar doors.

• ASTM D1014, “Standard Practice for Exterior Exposure Tests of Paints and Coatings on Metal Substrates,” was used in the preparation and coating of all test panels.

• ASTM B117, “Standard Practice for Operating Salt Spray (Fog) Apparatus,” was used for salt spray testing of coated and scribed steel test panels.

• ASTM D1654, “Standard Test Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments” (Procedure A–Method 2 and Procedure B), was used in the evaluation of the scribed coated test panels.

• ASTM D610, “Standard Practice for Evaluating Degree of Rusting on Painted Steel Surfaces,” was used in the evaluation of the coated test panels in the unscribed area.

• ASTM G1, “Standard Practice for Preparing, Cleaning, and Evaluation of Corrosion Test Specimens,” was used to evaluate mass loss experienced by bare metal coupons fabricated from copper, 1010 steel, and three aluminum alloys (2024-T3, 6061-T6, and 7075-T6) that were installed on an atmospheric corrosion test rack erected near the hangar doors and exposed to the environment for 6–12 months.

• ASTM B825, “Standard Test Method for Coulometric Reduction of Surface Films on Metallic Test Specimens,” was used to determine the amount of silver chloride (AgCl) deposited on the surface of a silver coupon installed on an atmospheric corrosion test rack.
2 Technical Investigation

2.1 Technology overview

An additive has been developed for urethane coatings that provides self-repairing capability. Urethane resins can be synthesized with functional groups that are activated upon mechanical damage to the coating film (Urban 2009; Ghosh and Urban 2009). Those activated sites will bond together to repair or heal the polymer network. Figure 2 illustrates the basic concept that relies on orchestrated chemical modifications of polymeric networks with specific pending groups (squares) that become reactive upon network rupture. These groups, upon exposure to UV solar radiation, will react with other reactive ends and result in self-repair.

This concept has been incorporated into an innovative, self-repairing urethane coating system for maximum protection of the structure, even after mechanical damage to the coating. This concept is very different from previous self-healing coatings that incorporate microcapsules containing reactive healing agents. With the self-repairing network concept, there is no issue with shelf life or with loss of function as the applied coating ages.

![Figure 2. Schematic of self-repairing polymer networks.](image_url)

Figure 2 illustrates polyurethane (PUR) networks that were allowed to crosslink under ambient conditions to form solid films mechanically damaged by creating a visual scratch of about 10–50 μm. Figure 3, A1 illustrates a mechanical damage of self-repairing oxetane-substituted chitosan polyurethane (OXE-CHI-PUR) films. When the damaged area is exposed to ultraviolet (UV) light for 15 min (Figure 3, A-2) and 30 min (Figure 3,
A-3), the damaged area vanishes. Also, the upper part of Figure 3 illustrates infrared (IR) images during the self-repair process, which provide essential molecular-level information from the repaired area. This information reveals that the crosslinking reactions resulting from the covalent bonding of cleaved ends of ether linkages of OXE are most likely responsible for self-repair.

**Figure 3. Example of self-repairing process upon exposure to UV light over 0–30 min.** (courtesy of Dr. Marek Urban).

In this demonstration, the polyurethane topcoat had to be modified with an additive to create the self-repairing properties because the polyurethane paint system was not available with the additive as an off-the-shelf commodity. Initial work was conducted by KMA Maxis, Inc. to determine a solvent vehicle for the self-repairing additive that was compatible with the MIL-PRF-85285 Type II, Class H coating for mixing at the time of field application of the coating. This work tested various solvent vehicles with polysaccharides for compatibility with the polyurethane topcoat. The testing resulted in polysaccharides being placed in dimethylformamide as a
vehicle with the best compatibility and performance results. This dimethylformamide and polysaccharide solution was then produced as ADT-100 and provided by KMA Maxis, Inc., along with mixing instructions for addition to the polyurethane topcoat prior to application to the hangar doors. The top coat was then applied over an epoxy primer coating system of MIL-DTL-24441/20, Formula 150 and MIL-DTL-24441/31, Formula 152, Type IV. (See Appendix A for more information about the self-repairing coating concepts.)

2.2 Field work and installation of the technology

The aircraft hangars at CCAD are located in a very corrosive environment, being located directly next to Corpus Christi Bay. This corrosive environment made CCAD an ideal site selection for the evaluation of the self-repairing coating evaluation. Hangar 47 was chosen for the test and is the last one in the row. The door leaves (Figure 4) painted in this demonstration are facing east. The overall condition of all hangar doors is very poor as a result of severe corrosion and age (built circa 1948). CCAD is planning to fully restore the doors in the future. However for this evaluation, the outside of the lower portion of the door leaves on the east side of Hangar 47 were prepared and painted with an epoxy polyamide primer, epoxy polyamide intermediate coat, and the MIL-PRF-85285 Type II, Class H polyurethane topcoat. This work included the evaluation of another coating system as part of CPC Project F12-AR14 (Divan, Lampo, and Clark 2018). The polyurethane topcoat with self-repairing additive was applied only to door leaves 6, 7, and 8 (Figure 4). The coating system on door leaf 1 was the control for the assessment, so it did not receive the self-healing additive.
2.2.1 Surface preparation

The hangar doors were pressure washed to remove all soil and loose contaminants from the surface prior to the start of the abrasive blasting operation. The hangar doors were found to contain lead-based paint. In order for the doors to be prepared by abrasive blasting to the requirement of SSPC SP 10 (NACE No. 2), “Near White Blast Cleaning,” a full containment system was erected for lead abatement and surface preparation (Figure 5).

Figure 5. Containment system in place for abrasive blasting operation needed to remove lead-based paint.
An aggressive, angular profile was achieved to 2–3 mils for improved coating adhesion. The surface profile was measured using ASTM D4417, Method C. In addition, testing of the surface to determine the roughness profile was done using a Testex micrometer. This system uses replica tape (Figure 6), which is rubbed onto the substrate and then measured with the Testex micrometer (Figure 7) to determine the average height of the profile. Additionally, the door surfaces were visually inspected for SSPC-VIS 1 comparison for compliance. Figure 8 shows the doors after abrasive blasting and lead paint removal.

Figure 6. Press-on replica tape.

Figure 7. Testex micrometer.
2.2.2 Coating application

The coating process consisted of priming with epoxy polyamide primer MIL-DTL-24441/20 (Formula 150, Type III) green, once all surface preparation had been completed. This primer application was followed by applying the intermediate epoxy primer coat MIL-DTL-24441/22 (Formula 152, Type III) white, and it was finished with a polyurethane topcoat MIL-PRF-85285, Type II, Class H (Red FED-STD-595, color number 20062) to comply with United Facility Guide Specification (UFGS) for paint, UFGS 09 97 13.27, “Exterior Coating of Steel Structures.” All coatings were applied per the manufacturer’s specifications and instructions for mixing the ADT-100 (Appendix B).

The following photographs show the application of

- Epoxy polyamide primer, MIL-DTL-24441/20 (Formula 150, Type III) green (Figure 9);
- Epoxy intermediate coat MIL-DTL-24441/22 (Formula 152, Type IV) white (Figure 10); and
- Polyurethane Topcoat MIL-PRF-85285, Type II, Red FED-STD-595 color number 20062 (Figure 11).
Figure 9. Applying MIL-DTL-24441/20 (Formula 150, Type III).

Figure 10. Applying MIL-DTL-24441/31 (Formula 152, Type IV).
At the time the coating system was applied, surface preparation was monitored to determine compliance with minimum requirements (Section 2.2.1). Paint thicknesses were also measured at the time of application and again after 12 months. The total coating thickness at many locations exceeded the contract requirement of a recommended 7-9 mils. Figure 12 shows the approximate location where coating thickness was measured on each door panel.1 Table 1 lists the coating thicknesses taken at each of four locations on each of the six panels per each door. The average coating thickness was within the required minimum parameters.

Figure 12. Indication (with white markings) of thickness measurement locations on each panel of a hangar door.

---

1 The bottom part of each door leaf is made up of six panels welded together to form the door (readily discernible in Figure 11).
Table 1. Coating thicknesses.

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<tr>
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<td>2</td>
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<tr>
<td></td>
<td>3</td>
<td>13.5</td>
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2.3 Technology monitoring

In order to evaluate the performance of this coating system and its effectiveness, the following assessments were accomplished:

- A weather station was placed behind the exposure test rack (Figure 13), and it was used (along with an atmospheric corrosion test rack) to assess corrosion potential.
- Test panels of 1010 steel that measured 3 in. x 6 in. were prepared at the test site. These panels received the same preparation process and coating on site as the hangar doors.

2.3.1 Test panel legend

As stated previously, a set of 12 steel test panels were prepared for each coating and surface preparation. The explanation of the panel labeling legend is as follows:
First number = surface prep (1=SSPC SP-10)
Second number = paint system (see section 2.3.2 below)
The number after the dash is the individual test panel in the set of 12.

Example: S11 is Surface Prep 1 (SSPC SP-10), Paint System 1 (Control).

### 2.3.2 Paint systems

The project used two coating systems, as listed below – one being a control system and the other being the demonstrated system with the self-repairing additive. (Note that this project was completed in conjunction with another CPC demonstration project [F12-AR14] regarding a different concept for a coating system for corrosion prevention and control. Coating system #2 below was used in that other project)

1. Control coating system – MIL-DTL-24441 Formula 150, MIL-DTL-24441 Formula 152, MIL-PRF-85285 Type II, Class H.
2. System #2 does not apply to the self-repairing coating demonstration.

### 2.3.3 Surface preparation

The surface was prepared by abrasive blast per SSPC-SP10/NACE 2 for near-white metal. Surface preparation and coating application was monitored and documented.

A test rack was installed at the site, and panels were scribed and placed on the rack for atmospheric exposure (Figure 13). Panels were also submitted for accelerated weathering laboratory testing per ASTM B117.
Figure 13. Test panel atmospheric exposure rack with weather station visible behind it.
3 Discussion

3.1 Results

3.1.1 Measurement of corrosivity at site

An assessment to establish the corrosivity of the environment at the CCAD site was completed by measuring the weight loss on five bare-metallic coupons mounted on an atmospheric corrosion test rack after 6 months and 12 months of exposure at the test site. Weight loss data and calculations are presented in Appendix C. It was determined that the corrosivity at this location is, as expected, very high.

3.1.2 Evaluation of coatings on hangar doors

The 12-month visual inspection of the hangar doors found significant scrapes and coating damage to the doors that resulted from manual operation of the doors (Figure 14). The majority of areas where coating damage has occurred were significant and not just minor nicks from tools, bumping equipment, etc. The demonstrated coating system is weathering well after 12 months and shows no sign of oxidation. In areas where paint damage resulted in exposure of the steel substrate, however, rust is evident. The self-repairing material was not overcoming the mechanical impacts the coating was subjected to (Figure 15). The self-repairing capability of the additive to the MIL-PRF-85285 Type II, Class H is apparently not capable of healing the coating for this level of damage, as no evidence of any healing was detected in the damaged areas.
3.1.3 Accelerated laboratory tests

Test panels were subjected to salt spray/fog testing in the laboratory for 2,000 hours per ASTM B117, and they were then evaluated per ASTM D1654. The complete laboratory report is provided in Appendix D.
In Table 2, the sample numbers are those listed in the laboratory report (Appendix D). Samples 3 and 9 are the self-repairing paint system, and samples 4 and 6 are the control paint system. When assessed per ASTM 1654, Procedure A, the panels with the self-repairing additive are rated a 7 and 6 for rust swell at 1,000 hours, and a 6 and 10 for corrosion creep at 2,000 hours. These ratings are in comparison to the control panels without the self-repairing additive, which were rated at 6 and 5 at 1,000 hours and 4 and 5 at 2,000 hours).

Rust swell is defined as the distance from the center of the scribe to the edge of the rust prior to the area being scratched clean (ASTM D1654, Procedure A, modified). The rust swell analysis was done at 1,000 hours in order to not damage the 2,000 hour data. Per ASTM D1654, a numerical rating of 10 is the highest rating with rust creepage (i.e., the distance the rust penetrates outward from the scribe) at 0 mm. At the other end, a numerical rating of 0 means that the measured rust creepage was greater than 16 mm. The unscribed area on the test panel was also rated using ASTM D610 where a rating of 10 means no visible corrosion.

The results of the ASTM B117 testing indicate that the MIL-PRF-85285 Type II, Class H paint system with the self-repairing additive outperformed the control MIL-PRF-85285 Type II without the self-repairing additive (Table 2).

### Table 2. Test panel ratings for self-repairing coating system after salt fog exposure per ASTM B117.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Sample No.</th>
<th>Rust Swell Rating at 1,000 hr (mm)*</th>
<th>Creep from Scribe Rating at 2,000 hr (mm)+</th>
<th>Rating for Unscribed Areas#</th>
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<td>S13-1</td>
<td>3</td>
<td>7 (193)</td>
<td>6 (2.50)</td>
<td>10</td>
</tr>
<tr>
<td>S13-8</td>
<td>9</td>
<td>6 (251)</td>
<td>10 (0)</td>
<td>10</td>
</tr>
<tr>
<td>S11-5</td>
<td>4 (control)</td>
<td>6 (2.24)</td>
<td>4 (5.13)</td>
<td>10</td>
</tr>
<tr>
<td>S11-7</td>
<td>6 (control)</td>
<td>5 (4.18)</td>
<td>5 (4.27)</td>
<td>10</td>
</tr>
</tbody>
</table>

*Per ASTM D1654, Procedure A, modified.
+Per ASTM D1654, Procedure A.
# Per ASTM D1654, Procedure B (which refers to ASTM D610 for the rating).
3.1.4 Outdoor exposure testing

Some examples of panels placed on the outdoor exposure rack after 12 months exposure are shown in Figure 16–Figure 17.

Figure 16. Test panel S13-2: self-repairing additive in MIL-PRF-85285 Type II, Class H. (Note that visible “spots” are not corrosion but result from application technique.)

Figure 17. Test Panel S11-2: control MIL-PRF-85285 Type II, Class H.
Final evaluation of the test panels indicated that only minor corrosion (a tight oxide film) formed in the scribed areas. No topcoat lifting, blistering, or undercutting at the scribed edge, or corrosion product residue on the back side of the test panels was detected on any of the fully coated test panels. No corrosion was noted in the unscribed areas.

When assessed per ASTM 1654, Procedure A, these outdoor exposure panels are rated 10 for corrosion creep from the scribe. Even though the test site has a very corrosive environment, 12 months of exposure was not long enough to reliably project long-term coating system service life. Continued observation of the atmospheric exposure panels would be needed to reliably assess life-cycle coating system performance.

### 3.2 Lessons learned

There were no significant issues or problems involved with incorporating the self-repairing additive when mixing the components for the polyurethane topcoat or the application of the self-repairing coating on the hangar doors. All work was conducted without incident.

However, there were two lessons learned from this project, as explained below.

One important lessons learned was the overestimation of a self-repairing coating’s capability to take the normal impacts that these hangar door leaves are subjected to in everyday use. The demonstrated results make it obvious that the polyurethane coating system, with or without the added self-repairing material, is not sufficiently tough for the demonstrated application’s level of impact.

The second lesson learned it that although the mechanisms for the self-repairing coating is a proven concept (Urban 2009; Appendix A), some experimental testing at increasing degrees of mechanical impact and cutting (i.e., through the coating) should have been conducted to simulate various infrastructure applications before applying the system to the hangar doors. This type of testing could have led to a more realistic and successful demonstration of the self-repairing technology.
4 Economic Summary

4.1 Costs

Total project costs for this project were $703,900, as shown in Table 3. An estimated breakdown of costs for the field demonstration are shown in Table 4.

<table>
<thead>
<tr>
<th>Description</th>
<th>Amount, $K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Labor (including $25K from CCAD DPW)</td>
<td>160.1</td>
</tr>
<tr>
<td>Contract for development of self-repairing additive *</td>
<td>246.8</td>
</tr>
<tr>
<td>Contracts for field demonstration **</td>
<td>257.0</td>
</tr>
<tr>
<td>Travel</td>
<td>20.0</td>
</tr>
<tr>
<td>Reporting</td>
<td>15.0</td>
</tr>
<tr>
<td>Air Force and Navy participation</td>
<td>5.0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>703.9</strong></td>
</tr>
</tbody>
</table>

* With Dr. Marek Urban at the University of Southern Mississippi
** Includes $56.5k provided by CCAD for coating application contract.

<table>
<thead>
<tr>
<th>Item</th>
<th>Description</th>
<th>Amount, $K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Labor for project management and execution (including $20K from CCAD)</td>
<td>78.9</td>
</tr>
<tr>
<td>2</td>
<td>Travel for project management</td>
<td>15.0</td>
</tr>
<tr>
<td>3</td>
<td>Cost for coatings and preparation materials</td>
<td>12.5</td>
</tr>
<tr>
<td>4</td>
<td>Subcontract for coating formulation</td>
<td>89.1</td>
</tr>
<tr>
<td>5</td>
<td>Contract for coating application (from CCAD)</td>
<td>56.5</td>
</tr>
<tr>
<td>6</td>
<td>Paint waste removal (CCAD DPW)</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td><strong>Total</strong></td>
<td><strong>257.0</strong></td>
</tr>
</tbody>
</table>

4.2 Return on investment (ROI) computation

While the self-repairing coating technology showed some promise at the test panel level, the self-repairing coating system, as demonstrated on the hangar door leaves for this project, is not recommended for use on any infrastructure components that would be subject to a similar degree of abrasion and mechanical damage.
The estimated return on investment (ROI) in the original project management plan (PMP) assumed the following:

- Painting 100 hangar doors at an estimated total cost of $1.15M.
- The hangar doors coated with a “standard” coating would need to be repainted every 5 years.
- The hangar doors coated with the self-repairing coating system would not need to be repainted for 19 years.

Given a total planned project execution cost of $1M, the originally calculated ROI was 6.1. However, since the demonstrated self-repairing coating system did not perform any better than the “standard” coating system in this project, the assumed benefits of extending the repainting cycle would not be realized, and the final ROI for the overall Project would, therefore, be zero.
5 Conclusions and Recommendations

5.1 Conclusions

This demonstration of a self-repairing additive used in a MIL-PRF-85285 Type II, Class H coating system has shown that its performance was improved over the control coating system by the evaluation criteria used (ASTM D1654, Procedure A) over a limited exposure period of 12 months. However, it could not be determined that improvement in performance was a direct result of the self-repairing additive healing of the damaged sites in the demonstrated coating system. The small benefit shown does not warrant inclusion of this self-healing topcoat into DoD criteria or specifications. In addition, the poor results of the coating system on the hangar door leaves implies that the self-repairing capability of the coating is not effective for substrates subjected to frequent or intensive levels of mechanical impact and abrasion.

5.2 Recommendations

5.2.1 Applicability

Currently, the research team does not recommend use of the self-repairing additive until further evaluation and testing show conclusive evidence of advantages for applications that will produce a positive ROI.

5.2.2 Implementation

Based on the results of this project that showed the self-repairing property was not robust enough to repair coating damage caused by the normal operations in the subject hangar, the self-repairing polyurethane coating system cannot be recommended for implementation on DoD infrastructure. Additional assessments, as suggested below, are required before such a recommendation might be obtainable.

5.2.3 Future work

Recommended follow-on work includes a detailed laboratory study to determine the level of mechanical damage in real-world situations that the demonstrated coating is capable of repairing and producing a positive ROI. It would also be beneficial to determine the types and amounts of impact and abrasion damage that the coating can self-repair over a sustained time. Follow-on assessment of this self-repairing coating technology
should attempt to identify applications for military aircraft, vehicles, and equipment that receive significant amounts of minor, everyday coating damage that promotes corrosion but that might be small enough for a self-repairing coating to be able to self-“heal.”
References


Appendix A: Research and Development of a Self-Repairing Additive

Progress Report
Correlating Early Protective Coatings Material Characterization and Properties with Corrosion Related Failures via Real and Accelerated Corrosion Testing in Model and Commercial Systems

Submitted to: Richard Lampo
U.S. Army Engineer Research & Development Center
Construction Engineering Research Laboratory
Champaign, IL 61826-9006

Submitted by: Merek Urban
Clemson University
Department of Materials Science and Engineering
Clemson, SC 29631

Objectives:
- Development of a new generation of self-healing two-component polyurethanes
- Understand processes governing the formation of self-healing two-component polyurethanes

Mission-Oriented Accomplishments:
- Significant advances in modification of polyurethane chemistry and the use of non-toxic polysaccharides and glucose-based materials for use in diversified military and civilian applications have been made. Although more testing and studies are required for these systems to be commercialized, this project allowed us to identify and formulate future strategies for the development of potentially commercial products that exhibit self-healing attributes.
- Other potential avenues of these technologies have been identified and ultimately will be pursued if funding becomes available.

Scientific Accomplishments:
- The presence of specific crosslinkers that exhibit stable and self-repairing capabilities allowed us to achieve diffusion and reactivity controlled polymeric coatings.
- Understanding and modifications of polyurethane chemistries resulted in new discoveries that offer self-repairing attributes.
- During the course of this work novel molecular level non-destructive evaluation methods were identified and enhanced. Specifically, significant advances were made in imaging and corrosion detection using internal reflection IR imaging (IRIR) and Raman imaging.
- Three manuscripts (one published, two in preparation) and one patent resulted from this research. Appendix 1 provides a copy of the manuscript and the patent.

November 13, 2014
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5. Self-Repairing Mechanisms ....................................... 16
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   Manuscript entitled "Self-Repairing Polyurethane Networks by
   Atmospheric Carbon Dioxide and Water."
   Patent PCT/US14/49661; Ref. 9662-60-WO was filed.
1. Objectives

The objective of this study was to develop self-healing polyurethanes (PUR) by chemical modifications of PUR networks. In general, for polymers, several self-healing approaches have been proposed which utilize temperature, electromagnetic radiation, and/or chemical surroundings (pH, ionic strength, concentrations, and redox reagents).[1] However, these approaches still require human intervention to provide the energy source. Our natural surroundings offer natural energy, such as sunlight, water, air, and wind. Can synthetic materials repair damages utilizing these sources with minimal human intervention? These studies were undertaken to utilize natural resources and develop polyurethane networks capable of self-repair.

2. Approaches

- **Synthesis and formulation of polyurethane (PUR) networks**

  PUR films were prepared by reacting hexamethylene diisocyanate trimer (HDI) with polyethylene glycol (PEG) in DMF using overhead agitation at 500 rpm with a small four-blade polycarbonate impeller in a 50 ml three-neck reaction flask at 25°C for 10 min. The molar ratio of HDI/PEG = 2/3 were utilized while maintaining 38% (v/v) solids in DMF. Dibutyltin dilaurate (DBTDL) is utilized as a catalyst at a concentration of 2.5×10⁻³ mol/L. Such mixtures were applied to obtain an approximate film thickness of 1 mm on a PTFE substrate at 75°C and dried for 4 days. Reactions between hydroxyl (OH), isocyanate (NCO), and H₂O resulting in PUR and PUA segments as well as gaseous CO₂. The PUR networks are shown in Figure 1, A.

![Figure 1](image)

**Figure 1.** Reactions of isocyanate (NCO) groups of HDI and hydroxyl (OH) of PEG in the presence of H₂O generate CO₂ during PUR formation.

- **Development of self-repairing polyurethane networks**

  To develop self-repairing polyurethane networks, we incorporated methyl o-D-glucopyranoside (MGP), which is a monosaccharide, into crosslinking
reactions of HDI and PEG following the same procedure. These reactions were also catalyzed by 2.5×10⁻⁶ mol/L DBTDL to form MGP modified polyurethane (MGP-PUR) networks. The ratio of HDI/PEG/MGP = 1:0.68:0.02 was used, so that two out of four OH groups are reacted, forming urethane linkages. Chemical structure of the crosslinked network is shown in Figure 2A.

![Diagram of MGP-PUR network](image)

**Figure 2A.** Reactions of NCO groups of HDI and OH of PEG and MGP in the presence of H₂O result in MGP-PUR network formation. Each network linkage and/or component is identified as follows: PUA- polyurea, HDI- hexamethylene diisocyanate trimmer, PUR- polyurethane, PEG- polyethylene glycol, MGP- methyl-D-β-glucopyranoside.

The MGP-PUR networks are composed of complex chemical makeup. To examine how each component affect the self-healing property, various saccharides, catalysts and chain extenders were also utilized. Figure 4A listed the saccharides that have been utilized for this purpose, including mono saccharides- glucose (GLC), fructose (FRU), rhamnose - ribose (RBI), and polysaccharides - cellulose (CLB), and pullulan (PLL). There are many other types of mono/poly saccharides, but are not utilized in this study due to stability and solubility obstacles. Glycerol with three OH groups is also reacted into PUR network as a control. As known, urthane formation reaction requires the presence of a catalyst. Selectivity toward formation of urthane or urea varies using different catalysts. They may also participate in self-healing. For such reasons, different catalysts are utilized including dibutyltin dilaurate (DBTDL), zinc acetate (Zn(OAc)₂), cerium(III) acetylacetonate hydrate (Ce(C₅H₇O₂)₃· xH₂O), and copper(II) chloride (CuCl₂). Three concentrations 0.5×10⁻⁶, 1×10⁻⁶, and 10×10⁻⁶ mol/g are utilized. Another main component in the modified PUR networks is the chain extender. Flexibility, hydrophobicity, H-bonding ability can be adjusted choosing different chain extenders. Besides PEG (Mₘ ~300 g/mol), Polyester-block-polyether α, ω-diol of similar molecular weight (Mₘ ~468 g/mol),

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acrylic polyol, alkyd diol including 1,4-butanediol, 1, 6-hexanediol and 1, 12-dodecanediol are also utilized. The ratio of HDI-NCO/polyol-OH/saccharide unit-OH = 1: 0.45:0.55. For each saccharide unit, only 2 OH groups are reacted with NCO, and only these 2 OH are accounted as saccharide unit-OH.

![Saccharide structures](image)

Figure 3. Various saccharides that are incorporated into PnR networks.

3. Characterization

- Optical analysis of self-repairing properties

Controlable mechanical damage was achieved by creating scratches with precisely controlled dimensions using custom built computerized Micro-Cut instrument that facilitates control of the depth, speed and load during damage. In a typical experiment, a speed of 5 mm/s and a depth of 100 µm were utilized to obtain a 20 µm width and 100 µm deep scratches. Self-healing events were recorded using Leica DM2500 M microscope at 20× magnifications along with time. 3D optical images were generated by analyzing the shades of optical images using ENVI software (The Environment for Visualizing Images, Research Systems, Inc.) version 3.5.

Self-healing of such damaged samples were first examined in the air at room temperature. Relative humidity in the lab at a temperature of 25°C was 28%. In order to identify which gaseous in the air contributes to self-repairing, the damaged samples were then exposed to various gaseous environments, including N₂, O₂, CO₂, H₂O (relative humidity (RH) 28% in N₂), and combinations of components. RH 28% was achieved in a closed chamber using saturated magnesium chloride (MgCl₂) aqueous solution.

- Dynamic mechanical analysis (DMA) and recovery of mechanical properties after self-repairing

Mechanical properties were measured using dynamic mechanical analysis (DMA) on a TA instrument Q800 DMA. Rectangular specimens having a size of 15.73 mm×8.09 mm×1.07 mm were tested at a frequency of 10 Hz. Dynamic mechanical properties were measured from -100°C up to 80°C while heating at 2°C/min. Dynamic moduli and mechanical damping (tan δ) were analyzed using...
TA Universal Analysis 2000. The measured glass transition temperature \(T_g\) for MGP-PUR at maximum tan \(\delta\) is 54 ± 1°C.

Nano-indentation measurements were performed on a Ti 950 Tribolndenter equipped with a diamond Berkovich probe. Storage modulus was measured at 220 Hz frequency, 4 μN dynamic load, and a peak force of 1000 μN. Tensile stretch test was carried out on Instron 4502 at room temperature (25°C) at a rate of 2 mm/min. Repaired MGP-PUR for tensile stretch test was prepared by cutting and physically separating the film, followed by attaching the separated parts together. After self-repair under ambient conditions for 30 min, the film was subject to tensile test.

- Spectroscopic analysis

Internal reflection infrared images (IRIRI) were obtained using a Cary 600 series Stingray system equipped with internal reflection IR imaging providing 1 micron spatial resolution. This system consists of a Cary 680 spectrometer, a Cary 620 FTIR Microscope, an Image IR focal plane array (FPA) image detector, and germanium (Ge) imaging crystal. The IR images were collected using the following spectral acquisition parameters: under sampling ratio 2, rapid-scan speed 5Hz, number of images per step 64, and spectral resolution 4 cm\(^{-1}\). Image processing was performed using ENVI software (The Environment for Visualizing Images, Research Systems, Inc.) version 3.5. Traces showing IR spectra inside and outside damage were averaged over 20 spectra.

Microscopic attenuated total reflectance Fourier transform infrared spectra (μATR FT-IR) were obtained using an Agilent Cary 680 FT-IR single-beam spectrometer setting at 4 cm\(^{-1}\) resolution. A 2 mm diamond crystal, and maintain constant contact pressure between crystal and the film specimens was used. All spectra were corrected for spectral distortions and optical effects using Urban-Huang algorithm. Raman spectra were recorded using a Renishaw inVia Raman microscope equipped with a computer controlled three-axis encoded (X, Y, Z) motorized stage, a RenCam CCD detector, and a Leica microscope (DM2500 M). The 760 nm diode laser at 100mW power provided an excitation source. The films were placed on the gold surface and an acquisition time of 60 sec was used.

Energy-dispersive X-ray (EDX) spectroscopy was collected on Hitachi Variable Pressure Scanning Electron Microscope (SEM) SU6600 equipped with EDX system at a working distance of 10mm, an accelerating voltage of 20 kV, and variable pressure mode (30 Pa). Weight % atoms of carbon (C), oxygen (O), nitrogen (N), and tin (Sn) inside and outside the scar were measured using points collection mode, and each averaged over 5 points. Molecular structure of equilibrated center of chelation complexes was obtained using Avogadro software. The geometry optimization was produced under UFF force field.
4. Analysis of the Results

- Self-repair properties of modified PUR networks

Results shown in Figure 4, A illustrate that MGP-PUR networks are able to self-repair under such conditions within 30 mins after damage, while PUR networks without crosslinked MGP do not exhibit these unique attributes (Figure 2, C). Self-repair cannot be observed when the damaged samples were exposed to various gaseous environments, including \( \text{N}_2 \), \( \text{O}_2 \), \( \text{CO}_2 \), \( \text{H}_2\text{O} \) (RH 28% in \( \text{N}_2 \)). The results are shown in Figure 5, A-D. However, exposure to pure \( \text{CO}_2 \) at 28% RH facilitates MGP-PUR network repair (Figure 5, E). When network components, including the saccharide, chain extender, and the catalysts, are varied, as detailed in Approaches section, self-repair properties of each polymer network are summarized in Table 1.
Figure 5. Optical images of damaged MGP-PUR networks exposed to: A – N₂, B – O₂, C – CO₂; D – H₂O vapor (23% RH in N₂), E – CO₂–H₂O mixture (RH 23%).

Table 1. Self-healing ability of modified PUR networks when saccharides, chain extender, and catalysts are varied.

<table>
<thead>
<tr>
<th>Varying saccharides</th>
<th>MGP</th>
<th>GLC</th>
<th>FRU</th>
<th>CLB</th>
<th>PLL</th>
<th>GLY</th>
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<tbody>
<tr>
<td>Self-healing</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
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<tr>
<td>Varying chain extender</td>
<td>PEG</td>
<td>Polyester-urea-polyether polyol</td>
<td>Acrylic Polyol</td>
<td>Allyl Diol</td>
<td></td>
<td></td>
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<tr>
<td>Network components</td>
<td>HDI inimer, PUR, and DBTDL</td>
<td>HDI inimer, MGP, and DBTDL</td>
<td>HDI inimer, PEG, and MGP</td>
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<td></td>
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<tr>
<td>Self-healing</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Varying Catalyst</td>
<td>DBTDL</td>
<td>Zn(OAc)₂</td>
<td>CuCO₂–H₂O₂</td>
<td>CuCO₂</td>
<td></td>
<td></td>
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<tr>
<td>Network Components</td>
<td>HDI inimer, PEG, and MGP</td>
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<tr>
<td>Self-healing</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td></td>
<td></td>
</tr>
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</table>

- Analysis of mechanical properties and self-repairing efficiency of MGP-PUR

MGP-PUR network catalyzed by DBTDL was chosen as the model system for further studies because of MGP’s stability compared with GLC and FRU, and its low cost compared to CLB. Storage (E), loss (E’) moduli, and tan δ were measured using dynamic mechanical analysis (DMA). Figure 6 shows DMA results for PUR (A) and MGP-PUR (B). The glass transition temperature (T_g) of PUR increases from 2°C to 54°C by covalent incorporation (crosslinking) of MGP into PUR networks. MGP-PUR has strong mechanical property, and can self-heal at room temperature.
Mechanical properties of undamaged and repaired MGP-PUR specimens were also analyzed. MGP-PUR films were cut into two pieces. Self-repair was conducted by re-attaching two separated pieces under ambient conditions, followed by stress-strain measurements. Figure 7 summarizes the results which show that incorporation of MGP to form MGP-PUR networks results in the
Increase of the Young's modulus (E) from 3.58 for PUR to 77.7 MPa in MGP-PUR. The maximum stress of undamaged MGP-PUR is 12.97 MPa at the maximum elongation of 227%. Upon self-repair, the maximum stress diminishes to 3.38 MPa at 48% elongation.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Young's modulus (MPa)</th>
<th>Elongation at break (%)</th>
<th>Stress at maximum load (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MGP-PUR</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>undamaged</td>
<td>77.7</td>
<td>227</td>
<td>12.97</td>
</tr>
<tr>
<td>repaired</td>
<td>50.3</td>
<td>48.1</td>
<td>3.38</td>
</tr>
<tr>
<td>PUR</td>
<td>9.58</td>
<td>42.2</td>
<td>0.75</td>
</tr>
</tbody>
</table>

**Figure 7** A - Stress-strain curves of a - undamaged MGP-PUR, b - repaired MGP-PUR, and c - neat PUR. Young's moduli, elongation at break, and stress at maximum load are summarized in part B. Optical images C illustrate: C-1 - undamaged MGP-PUR film; C-2 - put and physically separated MGP-PUR film; C-3 - physically attached previously separated parts; and C-4 - self-repair film after 30 mins.

We created a scratch on a MGP-PUR film and measured storage modulus $E'$ inside the scratch using nano-indentation at the oscillation depth of 200 nm. During ~30 min of self-repair, the $E'$ values inside the scratch increase from ~1.9 to ~4.5 GPa. Table 2 summarizes these results. Notably, there is an initial drop of the $E'$ values from ~1.9 to ~1.1 GPa, followed by expected increase to reach ~4.5 GPa. For the undamaged MGP-PUR, the $E'$ values are ~2.8 GPa. The initial drop of the $E'$ values (during the first 10 min) is likely attributed to the adsorption of CO$_2$ and H$_2$O capable of plasticizing damaged network, thus enhancing segmental mobility of cleaved segments. Comparison of the stress-strain and storage moduli measurements shows different rates of the recovery. The storage moduli were measured inside scratch, whereas the stress-strain curves were...
obtained from bulk measurements. Under stress-strain experimental conditions, CO₂ and H₂O diffusion to the inside part of damage is limited, thus not all bonds can be re-formed during the timeframe of these experiments. This is reflected in lower maximum stress/elongation at break after repair. In contrast, when scratch is created and nano-indentation experiments are performed, CO₂ and H₂O may easily diffuse into damaged areas, thus reaching full recovery of the E' values.

Table 2. Storage modulus (E') of MGP-PUR inside newly created scratch and outside of the scratch measured as a function of time at the oscillation depth of ~200 nm.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Storage modulus (E') inside scratch (GPa)</td>
<td>1.9±0.1</td>
<td>1.1±0.05</td>
<td>2.9±0.3</td>
<td>4.5±0.5</td>
</tr>
<tr>
<td>Storage modulus (E') outside scratch (GPa)</td>
<td>2.3±0.1</td>
<td>2.7±0.1</td>
<td>2.8±0.2</td>
<td>2.6±0.3</td>
</tr>
</tbody>
</table>

- Analysis of chemical events during damage-repair cycle

Results from optical and mechanical analysis clearly demonstrate that the covalent incorporation of MGP into PUR networks catalyzed by DBTDL facilitates self-repair under CO₂ and H₂O atmosphere. The question is what molecular processes may govern this unique behavior, and what molecular entities are formed as a result of autonomous repair? To identify molecular events responsible for self-repair of MGP-PUR we followed chemical changes during damage-repair cycle using internal reflection IR imaging (IRIRI). This analytical tool, complimented by Raman spectroscopy, allows us to determine chemical changes inside scratch during damage-repair cycle with a spatial resolution of ~1 μm. Figure 6, A and B illustrate optical images recorded 1 (A) and 30 mins (B) after damage. Figure 8, A-1 - A-5 and B-1 - B-5 show the corresponding IRIRI images collected from 30×30 μm² area of the 1680 (A-1 and B-1), 1556 (A-2 and B-2), 1427 (A-3 and B-3), 1376 (A-4 and B-4), and 1045 (A-5 and B-5) cm⁻¹ bands that are most sensitive to damage-repair cycle. While χ-y directions identify spatial distribution of these bands, their intensity changes (z-direction) are also reflected in color variations (red-high; blue-low). The corresponding spectra recorded inside scratch (a/a') and outside (b/b') damaged area are shown in Figure 8, A-1 - A-5 and B-1 - B-5.

As manifested by the band intensity and color changes of IRIRI images collected 1 min after damage (Figure 8, A-1 - A-5), and the corresponding IR spectra in Traces A'-1 - A'-5 in Figure 2, multiple bond cleavage occur upon mechanical damage.
1) The 1680 cm\(^{-1}\) band due to H-bonded urethane C=O stretching vibrations decreases, while the 1715 cm\(^{-1}\) band due to the non-H-bonded urethanes increases (Figure 8, A-1 and A'-1), indicating cleavage of PUR bond and dissociation of H-bonding.

2) Increase of the 1620 cm\(^{-1}\) band due to N-H deformation of primary amines (NH\(_2\)) (Figure 8, A'-1) resulting from breakage of urethane C-N and C-O bonds and subsequent hydrogen abstraction is observed.

3) The C-O bond dissociation in PEG segments is manifested by the decrease of the 1350 cm\(^{-1}\) band (C-H deformation of ether linkages) (Figure 8, A'-4). H-bonding dissociation is further substantiated by the decrease of the N-H and O-H stretching vibrations at 3346 cm\(^{-1}\) (Figure 9), which overshadows spectroscopic changes due to hydrolysis of ether segments.

Also, the bands at 1558 (Figure 8, A-2 and A'-2), 1427 (Figure 8, A-3 and A'-3), and 1376 (Figure 6, A-4 and A'-4) cm\(^{-1}\) exhibit slight intensity increase 1 min after damage, which significantly increase during self-repair process. The increases of the 1142, 1100, and 1045 cm\(^{-1}\) bands (Figure 8, A-5 and A'-5) attributed to C-O stretching vibrations result primarily from conformational changes of HCO groups of MGP, C-O-C groups of PEG, and/or PEG/PUR C-O-C linkages. In summary, C-N and C-O covalent bond cleavage as well as urethane H-bonding dissociation are the main observed molecular events dominating mechanical damage.
Figure 8. A - Optical image of MGP-PUR film 1 min after damage. B - optical image of MGP-PUR film self-repaired 30 min after damage. Analyzing the traces on the original 2-D optical images using Envi program generated the 3-D depth profiles of the optical images. Images A1 through A5 represent 3D intensity distributions of vibrational bands at 1680 cm⁻¹, 1558 cm⁻¹, 1427 cm⁻¹, 1376 cm⁻¹, and 1045 cm⁻¹ (A-5) recorded from a square marked on Figure 2. Traces A-1 through A-5 represent IR spectra collected from areas a and b of images A-1 through A-5 respectively (a - spectra collected inside scratch 1 min after damage; b - spectra collected from undamaged area). Images B1 through B5 represent 3D intensity changes of vibrational bands at 1680 cm⁻¹, 1558 cm⁻¹, 1427 cm⁻¹, 1376 cm⁻¹, and 1045 cm⁻¹ (B-5) recorded from a square marked on Figure 2. Traces B-1 through B-5 represent IR spectra collected from areas a and b' of images B-1 through B-5 (a' - spectra collected from damaged area after repair; b' - spectra collected from undamaged area).
Figure 9. ATR-FTIR spectra of damaged and repaired MGP-PUR networks obtained from RIRI images (Figure 2 of the Main Document). The spectra were collected from marked square areas in Figure 2: A-1 through A-5 and B-1 through B-5. a – inside a scratch 1 min after damage; b – undamaged area 1 min after damage; c – damaged area after repair; d – undamaged area after repair.

Figure 8. B illustrates the results of spectroscopic analysis after repair under atmospheric CO₂ and H₂O (28% RH and 25°C). The intensity decreases of the urethane C=O stretching bands at 1715 and 1680 cm⁻¹ (Figure 8, B-1 and B-2) are detected, whereas the band at 1558 cm⁻¹ (Figure 8, B-2 and B-2) increases. This is attributed to Sn-chelation with C=O entities of MGP during repair of MGP-PUR networks. Even though only 10⁻¹⁷ mol/g concentration levels of DBTDL were used to catalyze MGP-PUR network formation, significant increases of the bands due to DBTDL vibrations at 1558 cm⁻¹ (Sn·······O=C), 1376 cm⁻¹ (C-H bending) (Figure 8, B-4 and B-4), 2856 and 2923 cm⁻¹ (C-H stretching) (Figure 9) are detected in repaired areas. These observations are attributed to chelation and conformational changes of DBTDL during repair. We utilized energy-dispersive X-ray spectroscopy (EDX) to measure Sn concentrations inside and outside scratch. Figure 10 shows that indeed Sn content remains unchanged. However, the concentration levels of carbon increase in the repaired area. The above data show that, in addition to CO₂ and H₂O atmosphere, MGP and DBTDL play a significant role during self-repair process. When copper(II) chloride (CuCl₂) was utilized as a catalyst in the same MGP-PUR networks, no self-repair was observed. Thus, only specific reactions catalyzed by DBTDL will facilitate PUR self-repair.
To verify spectroscopic changes under atmospheric CO₂ and H₂O, we conducted a series of controlled experiments in which concentrations of MGP, HDI monomer and DBTDL were varied, and interactions of individual components in the context of self-repair of MGP-PUR were examined. Specifically, MGP and HDI monomers were reacted following the same procedure as for MGP-PUR networks by varying MGP-HDI monomer ratios: MGP-HDI = 1.0:5 (a), 1:1(b), 1:1.5 (c) and 1:2 (d). These ratios correspond to 1, 2, 3, and 4 OH groups of M3P reacted with NCO groups. For each ratio, three concentrations of DBTDL, 0.2×10⁻³, 1×10⁻³, 2×10⁻³ mol/g, were used. All specimens were analyzed using ATR FT-IR. Figure 11 shows the results of ATR FT-IR analysis, and indicates that the degree of Sn–O–C chelation is the strongest when, on average, two OH groups of MGP are reacted with NCO. If MGP is not utilized at all, instead of Sn–O–C chelation manifested by significant increase of the 1588 cm⁻¹ band due to CCH deformations of the MGP ring resulting from conformational changes of the ring substituents upon chelation,[5] this is shown in Figure 8, B-4 and B-4 as well as in Figure 11. Considering that OH groups in C2 and C6 positions of MGP exhibit highest reactivity compared to C3 and C4 (Figure 2) whereby C6 is greater than C2,[6] when only C6 OH react with NCO, no chelation is observed. However, when OH in C2 position is reacted, chelation with DBTDL is the strongest. As identified in Figure 8, A, dissociation of covalent bonds occurs during mechanical damage. The question is whether these bonds reform, and what structural entities result from repair. IR/RI analysis collected on a repaired scar revealed the following changes:

1) Increase of the urethane C-N stretching band intensities at 1247 cm⁻¹ along with the decrease of N-H stretching at 3346 cm⁻¹ (Figure 8). These changes are caused by reformation of urethane linkages.
2) In the C-O region, the 1142 cm\(^{-1}\) band due to OCH\(^{+}\) bending of MGP decreases, and the 1045 cm\(^{-1}\) band due to C-O stretching vibrations continues to increase (Figure 8, B-S and B-S).\(^{[5]}\) These changes result from reactions of MGP-OH with NCO groups. The same changes are detected for 1142 and 1045 cm\(^{-1}\) bands in the control experiments in which hydroxyl on MGP was reacted with NCO (Figure 11).

3) The increase of the C-H bending vibrations at 1427 cm\(^{-1}\) (Figure 7, B-3 and B-3) due to asymmetric C-H deformation next to tertiary amides further substantiates these network rearrangements. Thus, reformation of C-O and C-N bonds occur as a result of substitution of the C3 and C4 OH groups of MGP.

4) Two new bands at 1750 (Figure 7, B-1) and 1127 cm\(^{-1}\) (Figure 7, B-5) due C=O and C-O-C stretching, which were not observed before, are detected (Figure 7, B-1 and B-5). Their presence is attributed to carbonate linkage formations.\(^{[7]}\)

IRIR images collected from MGP-PUR specimens in damaged and undamaged areas after 30 min exposure to N\(_2\), H\(_2\)O, and CO\(_2\) did not exhibit such intensity changes due to bond reformation. When damaged MGP-PUR network is exposed to CO\(_2\), the band at 1565 cm\(^{-1}\) due to C=O stretching of DBTDL increases. The formation of Sn and MGP-urethane complex or substitution of MGP-OH is not observed under these conditions. These data indicate that CO\(_2\) gas molecules interact with DBTDL in damaged areas, but in order to reform covalent linkages, the presence of both H\(_2\)O and CO\(_2\) is required.
Figure 11  A - ATR FT-IR spectra of MGP-HDI specimens prepared with the following MGP-HDI monomer ratios: 1:0.5 (Traces a (--)), 1:1 (Trace b (--)), 1:1.5 (Trace c (--)), and 1:2 (Trace d (--)). B - ATR FT-IR spectra of MGP-HDI specimens prepared using the same MGP-HDI monomer ratios as in Figure 5A, A with varied DBTDL concentration levels. Spectra a'-a'', b'-b'', c'-c'', and d'-d'' correspond to 1:0.5 (Traces a), 1:1 (Trace b), 1:1.5 (Trace c), and 1:2 (Trace d) ratios of Figure 4A. For each ratio, three concentrations of DBTDL, 0.2×10⁻⁶ (--), 1×10⁻⁶ (--), and 20×10⁻⁶ (-- mol/g, were used.

It should be noted that during a single internal reflection experiment using Ge crystal such as in IRIRI experiments, when bonds are ruptured by mechanical forces, the Ge probe is in contact with the surface. At 45° angle of incidence, the signal carrying chemical information comes from approximately ~650 nm depth.[8] Assuming that the top 10 nm of surface contain 100% of cleaved bonds, the overall detected signal will consist of roughly 98.5% of unreacted (~650 nm depth) and 1.5% of cleaved bonds (~10 nm). Therefore, anticipated intensity changes are in the range of 1.5% of the overall band intensities. In an effort to confirm that relatively small changes are attributed to damage-repair cycle, control experiments utilize larger quantities of reactants. Thus, they
provide confirmation and evidence that even small intensity changes in multiple IRIRI experiments are due to damage-repair cycle.

Further spectroscopic evidence for chelation and covalent C-O and C-N bond reformation is provided by Raman analysis (Figure 12). The most sensitive bands at 1412, 888, and 861 cm\(^{-1}\) are due to urethane and carbonate vibrations. These bands increase as a result of bond reformation and repair. Thus, the primary event is the Sn chelation with MGP-urethane, and covalent substitution of MGP-OH moieties leading to the formation of urethane and carbonate linkages.

![Figure 12](image)

Figure 12: Raman spectra of MGP-PUR collected from. Trace a - damaged areas after 30mins. Trace b - undamaged areas.

5. Self-Repairing Mechanism

Supported by spectroscopic evidence discussed in Figure 8, the mechanism of MGP-PUR self-repair under atmospheric conditions is proposed as depicted in Figure 13. A depicts free radical generation and \(H\) abstraction leading to the formation of free OH and NH\(_2\) groups as a result of mechanical damage. The proposed mechanism for self-repair is shown in Figure 13, B. Facilitated by initial coordination with \(H\_2O\), Sn complexes with MGP through chelation with the neighboring MGP-OH and urethane C=O groups to form a ring structure (a). This intermediate was spectroscopically identified as Sn---O=C chelated ring and molecular modeling shown in Figure 13, C identified that this complex curing self-repair is energetically most favorable conformation. The next step involves \(CO\_2\) insertion into Sn-O bonds to form carbonate moieties.
(Figure 13, B(b)). It should be noted that the majority of CO$_2$ insertion reactions to Sn-O bonds are conducted under 1 atm of CO$_2$.[9-11] Reactions shown in Figure 13 occur upon MGP-urethane and Sn complexation facilitates CO$_2$ insertion (b) and subsequent carbonate (c) and urethane (d and e) formation. During this step, metal carbonate moieties shown in Figure 13, B(b) are subject to nucleophilic attack. As shown spectroscopically, three main nucleophilic sites are present after damage: PEG-DH after cleavage of PEG C-O-C bonds, NH moieties of urethanes, and NH$_2$ resulting from cleavage of urethane linkages. Reactions with PEG-DH nucleophiles result in formation of carbonate linkages (Figure 13, B(c)), and N-H and NH$_2$ groups result in the reformation of urethane linkages (Figure 13, B(d) and (e) respectively). Although kinetics of each of these reactions remains to be determined, these reactions facilitated self-repair of MGP-PUR networks. Table 1 indicates that self-healing also occurs when Zn(OAc)$_2$ and Ce(C$_2$H$_5$O$_2$)$_3$ • xH$_2$O are utilized as catalysts instead of DBTDL, but no self-heal occurs when CuCl$_2$ is used. While the self-healing mechanism involving Zn(OAc)$_2$ and Ce(C$_2$H$_5$O$_2$)$_3$ • xH$_2$O will be further studied, it should be noted that, similar to DBTDL, Zn(OAc)$_2$ also has been reported as an effective catalyst for CO$_2$ reactions.[12] but CuCl$_2$ is not.

In summary, sugar moieties were incorporated into crosslinked polyurethane (PUR) networks in an effort to achieve self-repairing in the presence of atmospheric carbon dioxide (CO$_2$) and water (H$_2$O). When methyl-$\alpha$-D-glucopyranoside (MGP) molecules are reacted with hexamethylene diisocyanate trimer (HDI) and polyethylene glycol (PEG) to form crosslinked MGP-polyurethane (PUR) networks, these materials are capable of self-repairing in air. This process requires atmospheric amounts of CO$_2$ and H$_2$O thus resembling plant's behavior of carbon fixation during photosynthesis cycle. Molecular processes responsible for this unique self-repair process involve physical diffusion of cleaved network segments as well as the formation of carbonate and urethane linkages. Unlike plants, MGP-PUR networks require no photo-initiated reactions, thus are capable of repairs in darkness under atmospheric conditions.
Figure 13. A - Covalent bond cleavage of MGP-PUR networks due to mechanical damage; B - Proposed repair mechanism leading to carbonate and urethane formation; C - Optimized molecular structure of MGP-urethane during Sn complexation that leads self-repair.

References


Self-Repairable Polyurethane Networks by Atmospheric Carbon Dioxide and Water

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Abstract: Sugar monomers were incorporated into cross-linked polyurethane (PUK) networks in an effort to achieve self-repairing in the presence of atmospheric carbon dioxide (CO₂) and water (H₂O). When methyl-1,4-glycolurilopropionate (MGP) monomers are reacted with hexamethylene diisocyanate triurate (HDI) and polyethylene glycol (PEG) to form cross-linked MGP-polyurethane (PUR) networks, these materials are capable of self-repairing in air. This process requires atmospheric amounts of CO₂ and H₂O, thus resembling plant behavior of carbon fixation during the photosynthesis cycle.

Molecular properties responsible for this unique self-repair process involve physical diffusion of uncrosslinked segments as well as the formation of carbonate and urethane linkages. Unlike plants, MGP-PUR networks require no photo-initiated reactions, and they are thus capable of repair in darkness under atmospheric conditions.

Materials properties that extend their lifetimes, thus reducing the environmental footprint, play a crucial role in today's developments of new technologies. Among particularly impressive properties of materials is their ability to self-repair. Recent studies have shown that reversible breaking and reforming of dynamic covalent[11][12] or non-covalent bond[13] induced by temperature, electromagnetic radiation, and/or chemical surroundings (pH, ionic strength, concentrations, and roles reactions) can be beneficial in numerous applications. However, the use of environmental gases in the self-repair of materials has never been explored. It is, however, well-established that plants assimilate carbon dioxide (CO₂) and water (H₂O) to produce organic compounds, thereby releasing oxygen (O₂).[15] As a result, carbohydrates are produced, and the carbon fixation cycle is one of the essential steps in this process. Can man-made materials utilize atmospheric gases to recover themselves? Notably, the use of CO₂ as a raw material to produce organic compounds has been explored, and many successful reactions of CO₂ with methanol, diol, and cyclic ethers to produce dimethyl carbonates, cyclic carbonates, and polycarbonates have been reported.[16][17] Furthermore, under certain catalytic conditions, CO₂ also reacts with primary or secondary amines to form amides and ureas.[18] Interestingly enough, when polyurethanes (PUR) are synthesized in the presence of H₂O vapor, CO₂ as well as polyurethane (PUA) can be generated. The PUR networks shown in Figure 1.A are produced by reacting polyoxyethylene glycol (PEG) and hexamethylene diisocyanate triurate (HDI), resulting in PUR and PUA segments as well as gaseous CO₂. If such a PUR network is mechanically damaged, during which C-C, N-H, and other linkages are cleaved, CO₂ and H₂O will not facilitate self-repair. However, if carbohydrates with multiple OH groups are incorporated into PURs, will CO₂ and H₂O be able to regenerate mechanically damaged network bonds? To test this hypothesis, we incorporated monomeric additives, such as methyl-1,4-glycolurilopropionate (MGP) containing four reactive OH groups, into cross-linking reactions of HDI and PEG. These reactions were catalyzed by dibutyltin dilaurate (DBTDL) to form MGP containing polyurethane (MGP-PUR) networks. Figure 1.B illustrates the reactions leading to MGP-PUR formation. Such networks were subjected to controllable mechanical damage.

Figure 1.C illustrates that indeed, the MGP-PUR networks are capable of self-repair in air under ambient conditions (see the Supporting Information for details regarding MGP-PUR network preparation and damage-repair cycles).

In contrast, when the same damaged MGP-PUR network is exposed to pure N₂, O₂, CO₂, or H₂O (28% RH in N₂), no self-repair occurs. The results of these experiments are illustrated in the Supporting Information, Figure S1A-D. However, exposure to pure CO₂ at 28% RH facilitates MGP-PUR network repair (Figure 1.D). For comparison, PUR networks without cross-linked MGP (Figure 1.E) do not exhibit these unique attributes. These results clearly demonstrate that the covalent incorporation of MGP into PUR networks catalyzed by DBTDL, such as shown in Figure 1.B, facilitates self-repair under CO₂ and H₂O atmosphere. The question is then what molecular processes may govern this unique behavior, and what molecular entropies are favored as a result of repair.

To identify molecular events responsible for self-repair of MGP-PUR, we followed chemical changes during the damage-repair cycle using internal reflection IR imaging (IRR). This analytical method, complemented by Raman spectroscopy, allows us to determine chemical changes localized within the damage-repair cycle with a spatial resolution of about 1 μm. Figure 2A and B illustrate optical images recorded 1 min (A) and 30 min (B) after damage. Figures 2A-A-1 and Figure 2B-1-1 show the corresponding IRR images collected from 30 x 30 μm² areas of the 1080 (A-1) and
As manifested by the band intensity and color changes of IR/UV images collected 1 min after damage (Figure 2. A-1: A-5) and the corresponding IR spectra in traces A-1-A-5 in Figure 2, multiple bond cleavages occur upon mechanical damage. The 1660 cm⁻¹ band due to H-bonded urethane C=O stretching vibrations decreases, while the 1700 cm⁻¹ band due to the non-H-bonded urethane increases (Figure 2.A-1 and A-5), indicating the cleavage of PUR bond and dissociation of H-bonding. Furthermore, the increase of the 1660 cm⁻¹ band owing to N-H deformation of primary amines (NH) (Figure 2A-A) resulting from breaking of amine C-N and C=O bonds and subsequent hydrogen abstraction is observed. The C=O bond dissociation in PUR segments is manifested by the decrease of the 1350 cm⁻¹ band (C–H deformation of aliphatic chains; Figure 2A-A) H-bonding dissociation is further substantiated by the decrease of the N-H and O-H stretching vibrations at 3346 cm⁻¹ (Supporting Information, Figure S2), which overshadow spectroscopic changes that are due to hydrolysis of other segments. Also, the bands at 1586 (Figure 2A-2 and A-3) and 1427 (Figure 2A-3 and A-5) and 1350 cm⁻¹ (Figure 2A-A and A-5) exhibit a slight intensity decrease 1 min after damage, which significantly increases during self-repair process. The increases of the 1142, 1000, and 1045 cm⁻¹ bands (Figure 2A-3 and A-5) attributed to C–O stretching vibrations result primarily from conformational changes of HCO groups of MGP, C=O groups of EPG, and/or EPG-PUR-C=O linkages. In summary, C=N and C=O covalent bond cleavage as well as amine H-bonding dissociation are the most observed molecular events dominating mechanical damage.

Figure 2. Illustrates the results of x-ray spectroscopic analysis after repair under atmospheric CO₂ and H₂O (20% RH and 25°C). The intensity decreases of the amine C–O stretching bands at 1713 and 1680 cm⁻¹ (Figure 2B-1 and B-3) are detected, whereas the band at 1586 cm⁻¹ (Figure 2B-2 and B-2) increases. This is attributed to Sn chelation with C–O entities of MGP during repair of MGP-PUR networks. A significant increase of the bands due to DIHTDL vibrations at 1588 cm⁻¹ (Sn–O–X), 1376 cm⁻¹ (C=H bending) (Figure 2B-4 and B-4, and 2686 and 2923 cm⁻¹ (C–H stretching; Supporting Information, Figure S2) are detected in repaired areas. These observations are attributed to chelation and conformational changes of DIHTDL during repair. We utilized energy-dispersive X-ray spectroscopy (EDX) to measure Sn content inside and outside the Sn-exposed area. The Sn content inside remains unchanged (Supporting Information, Figure S2). However, the concentrations of carbon increase in the repaired area. In summary, the above data show that CO₂ and H₂O atmosphere along with MGP and DIHTDL play a significant role during self-repair process. When copper(II) chloride (CuCl₂) was utilized as a catalyst in the same MGP-PUR networks, no self-repair was observed (Supporting Information, Figure S1). It should be noted that CuCl₂ is capable of catalyzing and
facilitating repairs of poly(dimethylsiloxane)-poly(urethane) (PDMS-PUR) cross-linked networks. Thus, only specific reactions catalyzed by DBTDL will facilitate PUR self-repair.

To verify spectroscopic changes under atmospheric CO₂ and H₂O, we conducted a series of controlled experiments in which concentrations of MGP, HDI monomer and DBTDL were varied, and interactions of individual components in the content of self-repair of MGP-PUR were assessed. We reacted MGP with HDI monomer at various stoichiometric ratios, and for each MGP:HDI monomer ratio, we varied DBTDL concentration levels. ATR FTIR analysis (Supporting Information, Figure S4) showed that the degree of Si–O–C chelation is the strongest when, on average, two OH groups of MGP are reacted with NOC. If MGP is not utilized at all, instead of Si–C–O–C chelation manifested by significant increase of the 1558 cm⁻¹ band shifts to 1565 cm⁻¹ (Supporting Information, Figure S5). These results are further substantiated by the decrease of the 1355 cm⁻¹ band owing to C–O–C deformations of the MGP ring resulting from conformational changes of the ring substituents upon chelation (Figure 2 B–4 and B–4; Supporting Information, Figure S4). Considering that OH groups in C2 and C6 positions of MGP exhibit highest reactivity compared to C3 and C4 (Figure 1B), whereby C6 is greater than C2 while only C6 OH react with NOC, no chelation is observed. However, when OH in C2 position is reacted, chelation with DBTDL is the strongest.

As identified in Figure 2A, dissociation of covalent bonds occurs during mechanical damage. The question is whether these bonds scavenge, and what structural entities result from...
repair. IR/ATR analysis collected on a repaired area revealed the increase of the subsequence C–N stretching band intensity at 2347 cm⁻¹ along with the decrease of N–H stretching at 3346 cm⁻¹ (Supporting Information, Figure S2). These changes are caused by modification of urethane linkages. In the C–O region, the 1712 cm⁻¹ band owing to C=O stretching vibration continues to increase (Figure 2B–5 and B–5'–5). These changes result from reactions of MPEG-OH with NCO groups. The same changes are detected for 1142 and 1045 cm⁻¹ bands in the control experiments in which OH-enriched MPEG was reacted with NCO (Supporting Information, Figure S4). The increase of the 1372 cm⁻¹ band at 1472 cm⁻¹ (Figure 2B–5 and B–5') is that due to asymmetric C–H deformation to tertiary amide. Further substantiate these network reorganizations. Thus, reactions of C–O and C–N bonds occur at a result of substitution of the C5 and C4 OH groups of MPEG. Furthermore, two new bands at 1750 cm⁻¹ (Figure 2B–1) and 1273 cm⁻¹ (Figure 2E–5) that are due to C–O and C–O–C stretching, which are not observed before, are detected (Figure 2B–2 and B–5'). Their presence is attributed to carbonate linkage formation. It should be noted that these spectroscopic changes are only detected in the presence of CO₂ and N₂ (Supporting Information, Figure S6). In summary, formations of urethane and carbonate functional linkages are primarily responsible for self-repair of MPEG–PUR network. Further spectroscopic evidence for cleavage and resultant C–O and C–N bond reformation is provided by Raman analysis (Supporting Information, Figure 2F). Thus, the primary event is the 2n cleavage with MPEG-urethane, and subsequent substitution of MPEG-OH moieties leading to the formation of urethane and carbonate linkages.

Mechanical properties of unrepaired and repaired MPEG–PUR specimens were also analyzed. MPEG–PUR film films were cut into two pieces. Self–repair was conducted by reattaching two separated pieces under ambient conditions, followed by strain–strain measurements (for video footage of the process, see the Supporting Information). The results are summarized in the Supporting Information, Figure S8, which show that incorporation of MPEG–PUR network can improve the strength of the Young's modulus (η) from 3.5 MPa to 77.7 MPa in MPEG–PUR. The maximum stress of unrepaired MPEG–PUR is 12.0 MPa at the maximum elongation of 227%. Upon self–repair, the maximum stress diminishes to 3.3 MPa at 48% elongation. In another experiment, we created a scratch on a MPEG–PUR film and measured storage modulus η inside the scratch (nanoindentation) at the elongation depth of 200 μm. During about 60 s of self-repair, the η values inside the scratch increase from about 1.9 to about 4.5 GPa (Supporting Information, Table S1). Notably, there is a significant drop of the η values from 1.9 to 1.5 GPa followed by expected increase to reach about 4.5 GPa. For the unrepaired MPEG–PUR, the η values are about 2.5 GPa. The initial drop of the η values (within the first 10 s) is likely attributed to the adsorption of CO₂ and H₂O capable of participating damaged network, thus enhancing segmental mobility of cleaved segments. Comparison of the stress–strain and storage modulus measurements show different rates of the recovery. The storage modulus were measured inside the scratch, whereas the stress–strain curves were measured from bulk measurements. Under such–strain experimental conditions, CO₂ and H₂O diffusion to the inside part of damage is limited, thus all bands can be recovered during the healing phase of these experiments. This is reflected in a lower maximum stress/elongation at breaking after repair. In contrast, when the scratch created and nano–indentation experiments are performed, CO₂ and H₂O may easily diffuse into damaged area, thus reaching full recovery of the η values.

Stopped by spectroscopic evidence discussed in Figure 2, the reactions of MPEG–PUR self–repair under atmospheric conditions is depicted in Figure 3. Figure 3A depicts that two main molecular events that are due to mechanical damage are free radical generation and H abstraction. The proposed mechanism for self–repair is shown in Figure 3B. Facilitated by initial oxidation with H₂O, an encounter with MPEG through cleavage with the neighboring MPEG–OH and aromatic C–O groups to form a ring structure (a). This intermediate was spectrally identified as Sn–O–C–Cl cleavage ring and molecular modeling shown in Figure 3C identified that this complex during self–repair is energetically more favorable configuration. The next step involves CO₂ insertion into Sn–O bonds to form carbonate moieties (Figure 3B). It should be noted that the majority of CO₂ insertion reaction is Sn–O bonds are conducted under 1 atm of CO₂. Reactions shown in Figure 3 occur upon MPEG–anthracene and Sn complexation facilitate CO₂ ionization (b) and subsequent carbonate (c) and anthracene (d) formation. During this process, the secondary moieties shown in Figure 3B are subject to inductive attack. As shown spectroscopically, three main meso–aromatic sites are present: ether damage, MPEG–OH after cleavage of FEG–C–O–C–Bonds (N–H) moieties of anthracene, and N–H resulting from cleavage of urethane linkages. Reaction with MPEG–OH moiety results in formation of carbonate linkages (Figure 3Bc), and N–H and N–H groups result in the formation of urethane linkages (Figure 3Bd) and (e) respectively. Although cleavage of each of these reactions tension to be determined, these reactions facilitated self–repair of MPEG–PUR networks.

In summary, we developed thermosetting polyurethane network containing cross-linked sugar moieties capable of self–repair under atmospheric conditions at ambient temperatures without intervention. By incorporating sugar moieties into polyurethanes, these materials are able to react with atmospheric CO₂ and H₂O and regenerate covalent linkages capable of bridging cleaved network segments. Mechanical properties are recovered during self–repair process. These materials resemble behavior of plants during photomorphogenesis, but unlike plants, MPEG–PUR networks require no photo–initiated reactions and are capable of repairing in the dark or in air.

Experimental Section
Methyl 3-(4-hydroxy-3,5-dimethyl-4-isoazolyl)propanoate (MDG), polyethylene glycol (PEG), hexamethylene diisocyanate (HDI monomer), N,N-dimethyl-formamide (DMF), chloroform, and dichloromethane (DCM) were used as received.
amide (DMF), ethylendiaminotetraacetic acid (EDTA, or edetate), hydrochloric acid (HCl), and magnesium chloride (MgCl2) hydrate were purchased from Sigma-Aldrich Co., triethanolamine, and hexamethyldisilazane (HMDS) from MERCK. N,N,N-Tris(hydroxymethyl)propyl trimethoxysilane (KH550) was purchased from Momentive Performance Materials Inc.

MGP-PUR films were prepared by reacting HDI trimer with MGP and PEG in DMP using overnight agitation at 50°C with a small amount of diethyl ether. The reaction mixture was filtered and the solvent was removed. The resulting solid was dried under vacuum at 100°C for 24 h. MGP-PUR networks were formed by reacting MGP trimer, PEG, and MGP using stoichiometric amounts of NCO and OH groups.

The molar ratio of HDI trimer/PEG/MG-P = 10:40:0.81 were utilized while maintaining 38% (w/w) solids. This ratio was utilized to react two out of four OH groups of MGP with NCO. The surfaces were applied to obtain an approximate film thickness of 250 nm (2.4 μm) on a PTFE substrate at 75°C and cured for 48 h.

Specimen damage was achieved by creating scratches with a guided diamond cutter using a custom-built computerized micro-cut instrument that facilitated control of the depth, speed, and load during damage. In a typical experiment, a speed of 5 mm/s and a depth of 100 μm were utilized to obtain a 20 μm width and 100 μm deep scratches. Optical images were collected using Leica DMR200D microscope. SD optical images were generated by analyzing the shades of optical images using ENVIS software (The Environment for Visualizing Images, Research Systems, Inc.) version 3.2. Relative humidity (RH) was controlled by utilizing enclosures containing saturated magnesium chloride solutions (RH = 25 ± 2%) and mon-

Figure 3. A) Contact hardness testing of MGP-PUR networks due to mechanical damage. B) proposed repair mechanism leading to carbosilane formation; C) optimized molecular structure of MGP-polyester during in compression that seed self-repair.
Appendix B: Instructions for Self-Repairing Additive and MSDS

Mixing Instructions: ADT 100

ADT - 100 is an additive designed and formulated solely for the use with SIMCO Coatings Inc. 2-component MIL-PRF-85285 polyurethane coating consisting of Components A and B.

SURFACE PREPARATION

The same cleaning and surface procedures should apply as for all MIL-PRF-85285 topcoats.

MIXING INSTRUCTIONS

Shake SIMCO Coatings Inc. MIL-PRF-85285 polyurethane color Component A (MIL-PRF-85285) for 10 minutes before admixing. Shake component ADT-100 (in one quart container) for 10 minutes. If transparent tiny crystals are present, additional shaking time should be allowed.

Admix Component A (MIL-PRF-85285) and Component ADT 100 (KMA Maxis, Inc.) by volume:

1. Remove 0.4 quart of Component A (MIL-PRF-85285) from 1-gallon container and store it in separate container.
2. Admix the entire content of Component ADT 100 can (each can contains 0.3 quarts of ADT 100) with the remaining Component A in 1-gallon container.

After complete mixing, add Component B (MIL-PRF-85285) by volume:

1 quart of Component B (MIL-PRF-85285)

Pot life is 4 hr minimum, but immediate spraying is recommended after admixing.

Note: Since 20 gallons of paint are supplied by Simco, Inc., after removal of 0.4 quarts of Component A from each 1-gallon container, there will be 2 gallons of Component A left over. In order to fully utilize Component A, two additional ADT 100 component cans were prepared, making a total of 22 cans of ADT 100. Please, note that in order to use the remaining two gallons of Component A/ADT 100, the same protocol should be followed. Two additional quarts of Component B from Simco, Inc. will be needed.

APPLICATION

This product can be applied using the same application equipment as Simco Coatings, Inc. MIL-PRF-85285 topcoats.
MATERIALS SAFETY DATA SHEET

MANUFACTURER'S NAME: KMA Maxis, Inc.
72 St. Anne's Drive
Hattiesburg, MS 39401
Date of preparation: 10/07/13

FOR 24 HOURS EMERGENCY ASSISTANCE
CALL - CHEMTREC
CHEMTREC®, Inside the USA: 800-424-9300
CHEMTREC®, Outside the USA: 001-703-527-3887

SECTION I - PRODUCT IDENTIFICATION

PRODUCT NUMBER: ADJ-100
PRODUCT NAME: ADDITIVE FOR SELF-HEALING
PRODUCT CLASS:
IMIS RATING:
HEALTH: 2
FLAMMABILITY: 2
REACTIVITY: 0

SECTION II - HAZARDOUS INGREDIENTS

<table>
<thead>
<tr>
<th>INGREDIENT</th>
<th>CAS #</th>
<th>WEIGHT PERCENT</th>
<th>OCCUPATIONAL EXPOSURE LIMITS</th>
<th>VAPOR mbar @ 20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>N, N-Dimethylformamide</td>
<td>68-12-2</td>
<td>&gt;60</td>
<td>10 TEL (PPM) 10 PEL (PPM)</td>
<td>4.9</td>
</tr>
<tr>
<td>Skin</td>
<td></td>
<td>5 (Vacated)</td>
<td>10 TWA: 10 (Vacated) TWA: 30 mg/m³</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TWA: 10 ppm</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TWA: 30 mg/m³</td>
<td></td>
</tr>
<tr>
<td>Polysaccharide derivative</td>
<td>not available</td>
<td>&lt;40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

SECTION III - PHYSICAL DATA

BOILING RANGE: 153°C / 307.4°F  VAPOR DENSITY: (AIR = 1.0)  EVAPORATION RATE: (BUTYL ACETATE = 1.0)  %VOLATILE VOLUME: WT/GAL: VOLATILE ORGANIC COMPOUND (VOC)

SECTION IV - FIRE AND EXPLOSION DATA

FLAMMABILITY CLASSIFICATION: FLAMMABLE
FLASH POINT: 58°C / 136.4°F
AUTOIGNITION TEMPERATURE: 445°C / 833°F
EXPLOSION LIMITS
  UPPER: 15.2 VOL %
  LOWER: 2.2 VOL %

EXTINGUISHING MEDIA: Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide. Cool closed containers exposed to fire with water spray.

SPECIFIC HAZARDS ARISING FROM THE CHEMICAL: Flammable. Risk of ignition. Containers may explode when heated. Vapors may form explosive mixtures with air. Vapors may travel to source of ignition and flash back.

SECTION V - HEALTH HAZARD DATA

ACUTE TOXICITY
Oral LD50: LD50 Oral - rat - 2,800 mg/kg
Inhalation LC50: LC50 Inhalation - rat - 4 h - 9 - 15 mg/l
Dermal LD50: LD50 Dermal - rabbit - 1,500 mg/kg
Skin corrosion/irritation
Serious eye damage/eye irritation
MUTAGENIC EFFECTS
CARCINOGENICITY
REPRODUCTIVE TOXICITY
Teratogenicity
POTENTIAL HEALTH EFFECTS
Inhalation
Ingestion
Skin
Eyes

Skin - Human - Mild skin irritation - 24 h
Eyes - rabbit - Moderate eye irritation
Mutagenic effects have occurred in humans
There are no known carcinogenic chemicals in this product
May cause congenital malformation in the fetus.
May be harmful if inhaled. Causes respiratory tract irritation.
May be harmful if swallowed.
Causes skin irritation.
Causes eye irritation.

SIGNs AND SYMPTOMS OF EXPOSURE
Warning: intolerance for alcohol can occur up to 4 days after dimethylformamide exposure. N,N-dimethylformamide is considered to be a potent liver toxin, Vomiting, Diarrhoea, Abdominal pain. To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

Additional Information
RTECS: LQ2100000

SECTION VI– REACTIVITY DATA
CHEMICAL STABILITY:
HAZARDOUS REACTION:
CONDITIONS TO AVOID:
MATERIALS TO AVOID:
HAZARDOUS DECOMPOSITION PRODUCTS:
Stable under recommended storage conditions.
No data available
Heat, flames and sparks.
Strong oxidizing agents
Hazardous decomposition products formed under fire conditions. - Carbon oxides, nitrogen oxides (NOx)

SECTION VII– TRANSPORTATION INFORMATION
U.S. DEPARTMENT OF TRANSPORTATION
PROPER SHIPPING NAME: PAINT
HAZARD CLASS: 3
PACKING GROUP: III
UN-No: Not available
REPORTABLE QUANTITY (RQ): 100 lbs
MARINE POLLUTANT: No
POISON INHALATION HAZARD: No

SECTION VIII– SPILL OR LEAK PROCEDURES
PERSONAL PRECAUTIONS:
Use personal protective equipment. Avoid breathing vapours, mist or gas. Ensure adequate ventilation. Remove all sources of ignition. Evacuate personnel to safe areas. Beware of vapours accumulating to form explosive concentrations. Vapours can accumulate in low areas.

ENVIRONMENTAL PRECAUTIONS:
Prevent further leakage or spillage if safe to do so. Do not let product enter drains.

METHODS FOR CONTAINMENT AND CLEAN UP:
Soak up with inert absorbent material. Keep in suitable, closed containers for disposal. Remove all sources of ignition. Use spark-proof tools and explosion-proof equipment.

WASTE DISPOSAL METHOD:
Burn in a chemical incinerator equipped with an afterburner and scrubber but exert extra care in igniting as this material is highly flammable. Offer surplus and non-recyclable solutions to a licensed disposal company. Contact a licensed professional waste disposal service to dispose of this material.

SECTION IX– SAFE HANDLING AND USE INFORMATION
HANDLING:
Use only under a chemical fume hood. Wear personal protective equipment. Do not get in eyes, on skin, or on clothing. Do not breathe vapors or spray mist. Keep away from open flames, hot surfaces and sources of ignition. Use
only non-sparking tools. Use explosion-proof equipment. Take precautionary measures against static discharges.

STORAGE:
Keep containers tightly closed in a dry, cool and well-ventilated place. Keep away from heat and sources of ignition.

PERSONAL PROTECTION:
Engineering measures:
Use only under a chemical fume hood. Ensure that eyewash stations and safety showers are close to the workstation location. Ensure adequate ventilation, especially in confined areas. Use explosion-proof electrical/ventilating/lighting/equipment.

Eye/face Protection:
Wear appropriate protective eyeglasses or chemical safety goggles as described by OSHA’s eye and face protection regulations in 29 CFR 1910.133 or European Standard EN166.

Skin and body protection:
Wear appropriate protective gloves and clothing to prevent skin exposure.

Respiratory Protection:
Follow the OSHA respirator regulations found in 29 CFR 1910.134 or European Standard EN 149. Use a NIOSH/MSHA or European Standard EN 149 approved respirator if exposure limits are exceeded or if irritation or other symptoms are experienced.

SECTION X– FIRST AID MEASURES

EYE CONTACT:
Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes. Immediate medical attention is required.

SKIN CONTACT:
Wash off immediately with plenty of water for at least 15 minutes. Immediate medical attention is required.

INHALATION:
Move to fresh air. If breathing is difficult, give oxygen. Do not use mouth-to-mouth resuscitation if victim ingested or inhaled the substance; induce artificial respiration with a respiratory medical device. Immediate medical attention is required.

INGESTION:
Do not induce vomiting. Call a physician or Poison Control Center immediately.

NOTES TO PHYSICIAN:
Treat symptomatically.

SECTION XI– SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING:
Keep away from heat, sparks, open flames.

OTHER PRECAUTIONS:
Drums stored in direct sunlight may build pressure.
Appendix C: Corrosion Potential Assessment for CCAD

Classification method

A corrosion severity classification for this site at Corpus Christi Army Depot (CCAD) was developed to evaluate coatings used in this project. This was accomplished through placing a portable weather station at the site and collecting weather data for one year, placing an atmospheric corrosion test rack at the site, and conducting visual inspections during semi-annual site visits.

Monitoring

Weather station

A weather station (similar to Figure C1) was installed to measure and record environmental characteristics throughout the 12-month exposure period. The station measured temperature, relative humidity, wind speed and direction, solar radiation, dew point, and rainfall. The weather station was powered by a solar panel and a rechargeable battery. A data logger was used to store the measurements which were recorded every 12 hours by the rain gauge and every 30 minutes by all other sensors. Data were downloaded manually to a laptop coming during on-site inspections. The data logger and each sensor were powered by a rechargeable battery connected to a solar panel. The data logger has a storage capacity to continue storing data at 30-minute intervals for approximately 2.5 years. Upon reaching full capacity, the data logger will truncate the oldest data point to create room for new incoming data.

Atmospheric coupon rack

An atmospheric coupon rack to determine the relative corrosivity of the site was attached to an exposure rack at the site. The coupon rack was similar to the one in Figure C2, except there were only two stacks of coupons used. The corrosion coupons in each stack included silver, copper, 1010 steel, and three aluminum alloys: 2024 T3, 6061 T6 and 7075 T6 and measured 1 inch wide by 4 in. long by 1/16 in. thick. Theses coupon were collected after 6 and 12 months of exposure. The mass of each coupon was
recorded before being exposed to the test environment. The silver coupon was tested for chloride deposition in accordance with ASTM B825. The remaining coupons were analyzed for mass loss in accordance with ASTM G1.

**Figure C1.** Weather station similar to one used at CCAD.

**Figure C2.** Atmospheric corrosion test rack.
Assessments, weather, corrosion coupon rack

Weather data was analyzed using response functions from the ISO 9223:2012 *Corrosion of Metal and Alloys – Corrosivity of Atmospheres – Classification, Determination and Estimation* (see Figure C3). Sulfur dioxide (SO₂) measurements were not collected; however due to the location of CCAD, it was assumed that the deposition of SO₂ would be equal to zero milligrams per square meter per day. The amount of chloride (Cl) deposition was calculated using ASTM B825 *Coulometric Reduction of Surface Films on Metallic Test* of the silver coupon. The equations used are reproduced as Figure C3. Corrosion classifications per ISO 9223:2012 are listed in Table C1. A further description of typical atmospheric environments related to the estimation of corrosivity categories is given in Table C2.
Figure C3. ISO 9223:2012 response equations for four standard metals.

\[
\text{Equation (1) for carbon steel:}
\]
\[
r_{\text{corr}} = 1.77 \cdot P_d^{0.52} \exp(0.020 \cdot \text{RH} + f_{\text{St}}) + 0.102 \cdot S_d^{0.52} \exp(0.033 \cdot \text{RH} + 0.040 \cdot T)
\]
\[
N = 128, R^2 = 0.85
\]

\[
\text{Equation (2) for zinc:}
\]
\[
r_{\text{corr}} = 0.0129 \cdot P_d^{0.44} \exp(0.046 \cdot \text{RH} + f_{\text{Zn}}) + 0.0175 \cdot S_d^{0.57} \exp(0.008 \cdot \text{RH} + 0.085 \cdot T)
\]
\[
f_{\text{Zn}} = 0.038 \cdot (T - 10) \text{ when } T \leq 10 \text{ °C; otherwise } -0.071 \cdot (T - 10)
\]
\[
N = 114, R^2 = 0.78
\]

\[
\text{Equation (3) for copper:}
\]
\[
r_{\text{corr}} = 0.0053 \cdot P_d^{0.26} \exp(0.059 \cdot \text{RH} + f_{\text{Cu}}) + 0.0102 \cdot S_d^{0.27} \exp(0.036 \cdot \text{RH} + 0.049 \cdot T)
\]
\[
f_{\text{Cu}} = 0.126 \cdot (T - 10) \text{ when } T \leq 10 \text{ °C; otherwise } -0.080 \cdot (T - 10)
\]
\[
N = 121, R^2 = 0.88
\]

\[
\text{Equation (4) for aluminium:}
\]
\[
r_{\text{corr}} = 0.0042 \cdot P_d^{0.73} \exp(0.025 \cdot \text{RH} + f_{\text{Al}}) + 0.0018 \cdot S_d^{0.62} \exp(0.020 \cdot \text{RH} + 0.094 \cdot T)
\]
\[
f_{\text{Al}} = 0.009 \cdot (T - 10) \text{ when } T \leq 10 \text{ °C; otherwise } -0.043 \cdot (T - 10)
\]
\[
N = 113, R^2 = 0.85
\]

\[
\text{where}
\]
\[
r_{\text{corr}} \text{ is first-year corrosion rate of metal, expressed in micrometres per year (\(\mu\text{m}/\text{a}\));}
\]
\[
T \text{ is the annual average temperature, expressed in degrees Celsius (°C);}\]
\[
\text{RH} \text{ is the annual average relative humidity, expressed as a percentage (%);}\]
\[
P_d \text{ is the annual average } \text{SO}_2 \text{ deposition, expressed in milligrams per square metre per day [mg/(m}^2\text{-d)}];\]
\[
S_d \text{ is the annual average } \text{Cl}^- \text{ deposition, expressed in milligrams per square metre per day [mg/(m}^2\text{-d)}].\]
Table C1. Corrosion rate, $r_{\text{corr}}$, for the first year of exposure for the different corrosivity categories (ISO 9223:2012).

<table>
<thead>
<tr>
<th>Corrosivity category</th>
<th>Corrosion rates of metals</th>
<th>$r_{\text{corr}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unit</td>
<td>Carbon steel</td>
</tr>
<tr>
<td>C1</td>
<td>g/(m²·a)</td>
<td>$r_{\text{corr}} \leq 10$</td>
</tr>
<tr>
<td></td>
<td>µm/a</td>
<td>$r_{\text{corr}} \leq 1.3$</td>
</tr>
<tr>
<td>C2</td>
<td>g/(m²·a)</td>
<td>$10 &lt; r_{\text{corr}} \leq 200$</td>
</tr>
<tr>
<td></td>
<td>µm/a</td>
<td>$1.3 &lt; r_{\text{corr}} \leq 25$</td>
</tr>
<tr>
<td>C3</td>
<td>g/(m²·a)</td>
<td>$200 &lt; r_{\text{corr}} \leq 400$</td>
</tr>
<tr>
<td></td>
<td>µm/a</td>
<td>$25 &lt; r_{\text{corr}} \leq 50$</td>
</tr>
<tr>
<td>C4</td>
<td>g/(m²·a)</td>
<td>$400 &lt; r_{\text{corr}} \leq 650$</td>
</tr>
<tr>
<td></td>
<td>µm/a</td>
<td>$50 &lt; r_{\text{corr}} \leq 80$</td>
</tr>
<tr>
<td>C5</td>
<td>g/(m²·a)</td>
<td>$650 &lt; r_{\text{corr}} \leq 1500$</td>
</tr>
<tr>
<td></td>
<td>µm/a</td>
<td>$80 &lt; r_{\text{corr}} \leq 200$</td>
</tr>
<tr>
<td>CX</td>
<td>g/(m²·a)</td>
<td>$1500 &lt; r_{\text{corr}} \leq 5500$</td>
</tr>
<tr>
<td></td>
<td>µm/a</td>
<td>$200 &lt; r_{\text{corr}} \leq 700$</td>
</tr>
</tbody>
</table>

NOTE 1 The classification criterion is based on the methods of determination of corrosion rates of standard specimens for the evaluation of corrosivity (see ISO 9226).

NOTE 2 The corrosion rates, expressed in grams per square metre per year [g/(m²·a)], are recalculated in micrometres per year (µm/a) and rounded.

NOTE 3 The standard metallic materials are characterized in ISO 9226.

NOTE 4 Aluminium experiences uniform and localized corrosion. The corrosion rates shown in this table are calculated as uniform corrosion. Maximum pit depth or number of pits can be a better indicator of potential damage. It depends on the final application. Uniform corrosion and localized corrosion cannot be evaluated after the first year of exposure due to passivation effects and decreasing corrosion rates.

NOTE 5 Corrosion rates exceeding the upper limits in category C5 are considered extreme. Corrosivity category CX refers to specific marine and marine/industrial environments (see Annex C).
Table C2. Description of typical atmospheric environments related to the estimation of corrosivity categories (ISO 9223:2012).

<table>
<thead>
<tr>
<th>Corrosivity category</th>
<th>Corrosivity</th>
<th>Indoor</th>
<th>Outdoor</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>Very low</td>
<td>Heated spaces with low relative humidity and insignificant pollution, e.g. offices, schools, museums</td>
<td>Dry or cold zone, atmospheric environment with very low pollution and time of wetness, e.g. certain deserts, Central Arctic/Antarctica</td>
</tr>
<tr>
<td>C2</td>
<td>Low</td>
<td>Unheated spaces with varying temperature and relative humidity, Low frequency of condensation and low pollution, e.g. storage, sport halls</td>
<td>Temperate zone, atmospheric environment with low pollution (SO$_2$ &lt; 5 µg/m$^3$), e.g. rural areas, small towns</td>
</tr>
<tr>
<td>C3</td>
<td>Medium</td>
<td>Spaces with moderate frequency of condensation and moderate pollution from production process, e.g. food-processing plants, laundries, breweries, dairies</td>
<td>Temperate zone, atmospheric environment with medium pollution (SO$_2$: 5 µg/m$^3$ to 30 µg/m$^3$) or some effect of chlorides, e.g. urban areas, coastal areas with low deposition of chlorides</td>
</tr>
<tr>
<td>C4</td>
<td>High</td>
<td>Spaces with high frequency of condensation and high pollution from production process, e.g. industrial processing plants, swimming pools</td>
<td>Temperate zone, atmospheric environment with high pollution (SO$_2$: 30 µg/m$^3$ to 90 µg/m$^3$) or substantial effect of chlorides, e.g. polluted urban areas, industrial areas, coastal areas without spray of salt water or Exposure to strong effect of de-icing salts</td>
</tr>
<tr>
<td>C5</td>
<td>Very high</td>
<td>Spaces with very high frequency of condensation and/or with high pollution from production process, e.g. mines, caverns for industrial purposes, unventilated sheds in subtropical and tropical zones</td>
<td>Temperate and subtropical zone, atmospheric environment with very high pollution (SO$_2$: 90 µg/m$^3$ to 250 µg/m$^3$) and/or significant effect of chlorides, e.g. industrial areas, coastal areas, sheltered positions on coastline</td>
</tr>
</tbody>
</table>

A summary of the weather data collected from October 2015-October 2016 is listed in Table C3. The results from the response equation calculations in Figure C3 are listed in Table C4. This equation also uses the chloride deposition rate determined in the assessment of the atmospheric corrosion coupons.


<table>
<thead>
<tr>
<th>Wind Direction, $\phi$</th>
<th>Wind Speed, mph</th>
<th>Gust Speed, mph</th>
<th>Temp, °F</th>
<th>RH, %</th>
<th>Solar Radiation, W/m²</th>
<th>DewPt, °F</th>
<th>Rain, in</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>244.5691213</td>
<td>9.079089179</td>
<td>14.07402085</td>
<td>74.70637995</td>
<td>62.86330293</td>
<td>341.3688628</td>
<td>48.6881417</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>102.5062393</td>
<td>4.666945834</td>
<td>6.370966329</td>
<td>10.81356208</td>
<td>33.85614551</td>
<td>432.8678342</td>
<td>33.6742968</td>
</tr>
<tr>
<td>Maximum</td>
<td>355.2</td>
<td>40</td>
<td>61.96</td>
<td>94.964</td>
<td>100</td>
<td>1276.9</td>
<td>87.4</td>
</tr>
<tr>
<td>Minimum</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>39.078</td>
<td>1</td>
<td>0.6</td>
<td>-33.2</td>
</tr>
<tr>
<td>Mode</td>
<td>355.2</td>
<td>9.57</td>
<td>12.95</td>
<td>83.467</td>
<td>1</td>
<td>0.6</td>
<td>72.5</td>
</tr>
</tbody>
</table>
Table C4. Atmospheric corrosion severity classification from weather data and ISO 9223:2012 response equation calculations.

<table>
<thead>
<tr>
<th></th>
<th>Steel</th>
<th>Copper</th>
<th>Aluminum</th>
<th>Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rcorr [µm/a]</td>
<td>167.0856</td>
<td>2.1204</td>
<td>4.0829</td>
<td>11.8198</td>
</tr>
<tr>
<td>Classification</td>
<td>C5 (Very High)</td>
<td>C4 (High)</td>
<td>-</td>
<td>CX (Extreme)</td>
</tr>
</tbody>
</table>

The atmospheric corrosion coupon rack placed at the site had coupons removed at 6 and 12 months. These coupons were sent to a certified lab (Applied Technical Services, Inc. [ATS]), and mass loss was measured per ASTM G1-03 on the AL 6061 T6, AL 2024 T3, AL 7075 T6, C 1010, and CDA 101. The silver test coupon had Coulometric Reduction of Surface Films done per ASTM B 825-13. A summary of the test results and classification according to the categories listed in ISO 9223:2012 (Table 1) is listed in Tables C5 and C6. The annual chloride deposition is listed in Table C7. This deposition value is used in the ISO 9223:2012 calculations.

The results from the ISO 9223:2012 analysis of weather data and mass loss testing (Table C5 and C6) suggest the CCAD site is a category 5 (C5) classification of atmospheric corrosion severity. Thus the potential for corrosion at the site is considered very high.

**Corrosion severity site classification**

The results from the ISO 9223:2012 analysis of weather data and mass loss testing (Table C5 and C6) suggest the CCAD site is a category 5 (C5) classification of atmospheric corrosion severity. Thus the potential for corrosion at the site is considered very high.
Laboratory results for six-month coupon exposure

MATERIALS TEST REPORT

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Date</th>
<th>Page</th>
<th>of</th>
</tr>
</thead>
<tbody>
<tr>
<td>D246720-2</td>
<td>September 2, 2016</td>
<td>1</td>
<td>4</td>
</tr>
</tbody>
</table>

Larry Clark  
Mandaree Enterprise Corporation  
812 Park Drive  
Warner Robins, Georgia 31088

Purchase Order #: W9132T-ATS-002-01

Procedure

Test Performed  
Mass Loss Evaluation

Method  
ASTM G1-03 (2011)

Test Material  
Mass Loss Coupons

Results

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Part #</th>
<th>Initial Weight [g]</th>
<th>Final Weight [g]</th>
<th>Δ Weight [g]</th>
<th>Mass Loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDA101</td>
<td>COR124170304100</td>
<td>33.6182</td>
<td>33.5265</td>
<td>.0917</td>
<td>.2727</td>
</tr>
<tr>
<td>C1010</td>
<td>COR123750304100</td>
<td>29.8844</td>
<td>28.0942</td>
<td>1.7898</td>
<td>5.9904</td>
</tr>
<tr>
<td>AL6061T6</td>
<td>COR123400304100</td>
<td>10.1357</td>
<td>10.1243</td>
<td>.0114</td>
<td>.1124</td>
</tr>
<tr>
<td>AL7075T6</td>
<td>COR123470304100</td>
<td>11.0208</td>
<td>10.9644</td>
<td>.0564</td>
<td>.5117</td>
</tr>
<tr>
<td>AL2024T3</td>
<td>COR122990304100</td>
<td>10.6545</td>
<td>10.5994</td>
<td>.0551</td>
<td>.5171</td>
</tr>
</tbody>
</table>

Prepared by: C. Elsberry  
Materials Testing

Approved by: C. Tippens  
Materials Testing

This report may not be reproduced except in full without the written approval of ATS. This report represents interpretation of the results obtained from the test specimen and is not to be construed as a guarantee or warranty of the condition of the entire material lot. If the method used is a customer provided, non-standard test method, ATS does not assume responsibility for validation of the method.
Figure 1: CDA101 after Corrosion Removal

Figure 2: C1010 after Corrosion Removal

Figure 3: AL6061T6 after Corrosion Removal
# MATERIALS TEST REPORT

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Date</th>
<th>Page</th>
<th>of</th>
</tr>
</thead>
<tbody>
<tr>
<td>D246720-2</td>
<td>September 1, 2016</td>
<td>3</td>
<td>4</td>
</tr>
</tbody>
</table>

**Figure 4:** AL7075T6 after Corrosion Removal

**Figure 5:** AL2024T3 after Corrosion Removal
# ACCELERATED ENVIRONMENTAL TEST REPORT

**Ref.** D246720-2  
**Date** September 2, 2016  
**Page** 4 of 4

**Larry Clark**  
Mandaree Enterprise Corporation  
812 Park Drive  
Warner Robins, Georgia 31088  

**Purchase Order #: W9132T-ATS-002-01**

## Procedure

<table>
<thead>
<tr>
<th>Test Performed</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coulometric Reduction of Surface Films on Metallic Surfaces</td>
<td>ASTM B 825-13</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test Material</th>
<th>Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver Test Coupon</td>
<td>None Specified</td>
</tr>
</tbody>
</table>

## Results

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Sample #</th>
<th>Observations</th>
</tr>
</thead>
</table>
| Ag          | COR117520304100 | Reduction Time = 1,670 Seconds  
Total Reduction Charge = 3.053 Coulombs |

---

**ISO 9001**

Prepared by:  
Lloyd Thomas  
Electrical Testing

Approved by:  
Shawn Murray  
Group Manager

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Laboratory results for twelve-month coupon exposure results

### Applied Technical Services, Incorporated

**Materials Test Report**

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Date</th>
<th>Page</th>
<th>of</th>
</tr>
</thead>
<tbody>
<tr>
<td>D246720-6</td>
<td>December 16, 2016</td>
<td>1</td>
<td>4</td>
</tr>
</tbody>
</table>

**Larry Clark**  
Mandarce Enterprise Corporation  
812 Park Drive  
Warner Robins, Georgia 31088

**Purchase Order #: W9132T-ATS-002-01**

#### Procedure

**Test Performed**  
Mass Loss Evaluation

**Method**  
ASTM G1-03 (2011)

**Test Material**  
Mass Loss Coupons

**Requirements**  
None Specified

#### Results

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Part #</th>
<th>Initial Weight [g]</th>
<th>Final Weight [g]</th>
<th>Δ Weight [g]</th>
<th>Mass Loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDA101</td>
<td>COR124170304100</td>
<td>34.5033</td>
<td>34.3808</td>
<td>.1225</td>
<td>.3550</td>
</tr>
<tr>
<td>C1010</td>
<td>COR123750304100</td>
<td>29.0703</td>
<td>25.2272</td>
<td>3.843</td>
<td>13.22</td>
</tr>
<tr>
<td>AL2024T3</td>
<td>COR123400304100</td>
<td>10.1790</td>
<td>10.0676</td>
<td>.1114</td>
<td>1.094</td>
</tr>
<tr>
<td>AL6061T6</td>
<td>COR123470304100</td>
<td>10.0990</td>
<td>9.9926</td>
<td>.0164</td>
<td>.1638</td>
</tr>
<tr>
<td>AL7075T6</td>
<td>COR122990304100</td>
<td>10.8952</td>
<td>10.8246</td>
<td>.0706</td>
<td>.6479</td>
</tr>
</tbody>
</table>

**ISO 9001**

Prepared by: C. Elsberry  
Materials Testing

Approved by: C. Tippens  
Materials Testing

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Figure 1: CDA101 after Corrosion Removal

Figure 2: C1010 after Corrosion Removal

Figure 3: AL2024T3 after Corrosion Removal
Figure 4: AL6061T6 after Corrosion Removal

Figure 5: AL7075T6 after Corrosion Removal
# Accelerated Environmental Test Report

**Ref.** D246720-6  
**Date** December 8, 2016  
**Page** 4 of 4

**Purchase Order #:** W9132T-ATS-002-01

**Larry Clark**  
Mandaree Enterprise Corporation  
812 Park Drive  
Warner Robins, Georgia 31088

## Procedure

**Test Performed**  
Coulometric Reduction of Surface Films on Metallic Surfaces

**Method**  
ASTM B 825-13

**Test Material**  
Silver Test Coupon

**Requirements**  
None Specified

## Results

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Sample #</th>
<th>Observations</th>
</tr>
</thead>
</table>
| Ag 2        | COR17520304100 | Reduction Time = 1,630 Seconds  
Total Reduction Charge = 3.185 Coulombs |

**Prepared by:** Licyaal Thomas  
Electrical Testing

**Approved by:** Mark Elrod  
Manager

---

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Appendix D: Salt Spray Exposure Test Results

Note that the words “painted coupons” used in these results are referred to as “test panels” within the body of this report.

SALT SPRAY EXPOSURE OF PAINTED COUPONS

ATS JOB # D246720-1
PURCHASE ORDER #W9132T-ATS-002-01

Prepared for
LARRY CLARK
MANDAREE ENTERPRISE CORPORATION
812 PARK DRIVE
WARNER ROBINS, GEORGIA 31088

Prepared by ___________ Chris Elshberry, Materials Testing

Approved by ___________ Clinton Tippens, Materials Testing

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Subject
Salt Spray Exposure of Painted Coupons

Material
Painted Coupons

Background and Objective
Mandaree Enterprise Corp. submitted ten (10) scribed painted coupons for salt spray exposure to observe the corrosion resistance.

Test Procedure
The exposure was performed per ASTM B117-16, Standard Practice for Operating Salt Spray (Fog) Apparatus, for 2000 hours. The samples were removed after 1000 hours and evaluated for rust swell per ASTM D1654-08, Standard Test Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments, and photographed. After 2000 hours of exposure, the samples were removed and evaluated per ASTM D1654, Procedure A, Method 1 (Scraping), and photographed.

Requirements
None Specified

Results

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Sample #</th>
<th>Rust Swell 1000 hrs. ASTM D1654-08 (mm)</th>
<th>Creep From Scribe 2000 hrs. ASTM D1654-08 (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S22-7</td>
<td>1</td>
<td>5 (3.45)</td>
<td>10 (0)</td>
</tr>
<tr>
<td>S2-9</td>
<td>2</td>
<td>5 (3.47)</td>
<td>10 (0)</td>
</tr>
<tr>
<td>S13-1</td>
<td>3</td>
<td>7 (1.93)</td>
<td>6 (2.50)</td>
</tr>
<tr>
<td>S11-5</td>
<td>4</td>
<td>6 (2.24)</td>
<td>4 (5.13)</td>
</tr>
<tr>
<td>S21-5</td>
<td>5</td>
<td>6 (2.56)</td>
<td>5 (3.14)</td>
</tr>
<tr>
<td>S11-7</td>
<td>6</td>
<td>5 (4.18)</td>
<td>5 (4.27)</td>
</tr>
<tr>
<td>S12-1</td>
<td>7</td>
<td>5 (3.07)</td>
<td>5 (4.88)</td>
</tr>
<tr>
<td>S12-10</td>
<td>8</td>
<td>5 (4.34)</td>
<td>5 (4.56)</td>
</tr>
<tr>
<td>S13-8</td>
<td>9</td>
<td>6 (2.51)</td>
<td>10 (0)</td>
</tr>
<tr>
<td>S21-12</td>
<td>10</td>
<td>6 (2.32)</td>
<td>10 (0)</td>
</tr>
</tbody>
</table>

See Photographs on Pages 3-8
<table>
<thead>
<tr>
<th>Millimetres</th>
<th>Inches (Approximate)</th>
<th>Rating Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>Over 0 to 0.5</td>
<td>0 to $\frac{1}{64}$</td>
<td>9</td>
</tr>
<tr>
<td>Over 0.5 to 1.0</td>
<td>$\frac{1}{64}$ to $\frac{1}{32}$</td>
<td>8</td>
</tr>
<tr>
<td>Over 1.0 to 2.0</td>
<td>$\frac{1}{32}$ to $\frac{1}{16}$</td>
<td>7</td>
</tr>
<tr>
<td>Over 2.0 to 3.0</td>
<td>$\frac{1}{16}$ to $\frac{1}{8}$</td>
<td>6</td>
</tr>
<tr>
<td>Over 3.0 to 5.0</td>
<td>$\frac{1}{8}$ to $\frac{3}{16}$</td>
<td>5</td>
</tr>
<tr>
<td>Over 5.0 to 7.0</td>
<td>$\frac{3}{16}$ to $\frac{1}{4}$</td>
<td>4</td>
</tr>
<tr>
<td>Over 7.0 to 10.0</td>
<td>$\frac{1}{4}$ to $\frac{3}{8}$</td>
<td>3</td>
</tr>
<tr>
<td>Over 10.0 to 13.0</td>
<td>$\frac{3}{8}$ to $\frac{1}{2}$</td>
<td>2</td>
</tr>
<tr>
<td>Over 13.0 to 16.0</td>
<td>$\frac{1}{2}$ to $\frac{5}{8}$</td>
<td>1</td>
</tr>
<tr>
<td>Over 16.0 to more</td>
<td>$\frac{5}{8}$ to more</td>
<td>0</td>
</tr>
</tbody>
</table>

**Figure 1:** Creep from Scribe Rating Chart
Figure 2: Painted Coupons 1000 Hour Photographs
Figure 3: Painted Coupons 1000 Hour Photographs
Figure 4: Painted Coupons 2000 Hour Photographs (prior to scrape)
Figure 5: Painted Coupons 2000 Hour Photographs (prior to scrape)
Figure 6: Painted Coupons 2000 Hour Photographs (after scrape method)
Figure 7: Painted Coupons 2000 Hour Photographs (after scrape method)
This project demonstrated the capabilities of a self-repairing additive in a polyurethane topcoat (MIL-PRF-85285 Type II, Class H) applied to the exterior hangar doors in the severely corrosive environment at Corpus Christi Army Depot, Texas. Many conventional coatings, when scratched or abraded, may develop corrosion that can lead to rapid deterioration of the substrate steel. The demonstrated self-repairing coating system was also applied to test panels exposed to atmospheric weathering and salt fog testing for 2,000 hours. While the self-repairing coating showed promise on the test panel exposure tests, the system was not able to protect the steel hangar doors due to the excessive mechanical impacts and stresses they are subjected to during daily operations. Department of Defense implementation of the demonstrated self-repairing coating is not currently recommended for use on infrastructure. Further evaluation would be needed to match the self-healing capabilities of the demonstrated coating with lighter-duty steel infrastructure components not subjected to the degree of impact and abrasion as the subject hangar doors. Because the self-repairing coating system did not perform any better than the conventional control coating in this project, the return on investment was zero.