Self-Healing, Liquid-Based Coatings for Corrosion Control

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Abstract

Localized corrosion involves the selective attack of a metal at a small, exposed site. This can be particularly devastating for load-bearing structures like bridges, which can fail catastrophically even with very little material loss. Unfortunately, such corrosion is very hard to prevent, predict, and detect.

Corrosion can be prevented by barrier coatings, which isolate metal from reactive environments. However, pinholes and other minor damage to the coating expose small areas of metal and can eventually lead to localized corrosion.

An example can be found with the two-dimensional material graphene, which has been highlighted as a potential anti-corrosion material due to its impermeability to moisture and molecules. Contrary to this expectation, a graphene coating may actually accelerate the degradation of the metal it was intended to protect if it is not free of defects.

One strategy for mitigating such corrosion is to design barrier coatings to be self-healing, so that they spontaneously repair themselves when scratched. Our lab has designed a self-healing coating based on the idea that low-viscosity liquids can readily flow and reconnect. Such liquids, however, typically do not form stable coatings on metal surfaces. To address this problem, we have developed anti-corrosive oil coatings that can be stabilized on metal without sacrificing the liquid’s free-flowing properties.

By mixing low-viscosity silicone oil with graphene-based microcapsule thickeners to make a coating we call “r-GO/oil,” we can create films that flow when scratched but otherwise remain
immobilized on metal surfaces. These coatings can repeatedly self-heal millimeter-scale scratches, be readily painted onto metal underwater, and protect metal from corrosion for extended periods of time.

We also show that these self-healing coatings are not limited to graphene-based microcapsules and silicone oil, but rather is materials agnostic. We demonstrate several coatings that are fabricated using commercially available oils and particles, and discuss further basic science experiments and potential applications.
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1 Introduction

1.1 Corrosion

Defined as “the destructive attack of a metal by its reaction with the environment” by the scientist Edward McCafferty (1), corrosion costs the United States a staggering $276 billion every year in terms of maintenance, repair, and material damage (2). This number does not even consider the indirect costs of corrosion, such as the price of labor associated with managing corrosion or the loss of potential revenue due to disruptions in the supply chain of a product.

Figure 1.1.1. The cost of corrosion in five major industry categories, according to a 1998 study. The total cost of corrosion of the five industry sectors listed, which totaled $137.9 billion, were extrapolated to the entire U.S. economy to estimate the total annual cost of corrosion ($276 billion). Adapted from Reference (2).
Corrosion is expensive because of society’s dependence on metals for their affordability, availability, and performance. Bridges, planes, automobiles, wires, phones, power lines, canned foods, and many more goods and structures rely on metals to operate and function. As can be seen from the range of these examples, corrosion impacts almost every sector of industry, from infrastructure to production and manufacturing (see Figure 1.1).

The study of corrosion, however, is not limited to monetary expenses, and is necessary to maintain the safety and productivity of many sectors in society. Because corrosion causes metals to dissolve (see Figure 1.1.2), it can drastically reduce a metal’s structural integrity. For example, corrosion can reduce the maximum load that a metal can sustain, i.e. its tensile strength, as well as its ductility – the length that the material can be stretched before failure. This decline in structural integrity, or “mechanical property,” is of particular import for “load-bearing structures” such as metal scaffolds and jets, which must tolerate a certain amount of weight in order to remain safe for their users.

Figure 1.1.2. An aluminum wire placed in a solution of hydrochloric acid (HCl) is dissolved away within one hour.
1.2 Localized Corrosion

Localized corrosion is a type of corrosion that occurs at small, unprotected areas of metal such as scratches and pinholes. This contrasts the most well-known type of corrosion, “uniform corrosion,” which occurs uniformly over the entire surface of a metal. An example of uniform corrosion can be found, for instance, in a rusted metal fence that is covered with rust, while localized corrosion would lead to small, rusted-over holes in parts of the fence (see Figure 1.2.1).

Figure 1.2.1. (a) A steel bolt experiences uniform corrosion, as indicated by the rust uniformly covering the surface of the metal. (b) A stainless-steel fixture experiences localized corrosion at an area where a protective coating has been removed. Images adapted from Reference (3).
Localized corrosion can be particularly damaging to a metal for two reasons: (1) because it is difficult to prevent, predict, or detect – unlike uniform corrosion, which can be readily predicted and prevented – and (2) because it can cause a system to catastrophically fail even if a negligible amount of material is lost. One notable example of localized corrosion’s potentially devastating implications is the collapse of the Silver Bridge in Ohio in 1967, which caused about 50 people to die. The bridge’s mechanical failure was attributed to two small holes, roughly 2 to 3 mm in diameter, that were found in the bridge’s supporting structure. (4)

1.3 Localized Corrosion Lowers Effective Area and Induces Stress Concentrators

Localized corrosion can degrade a metal’s mechanical properties through two mechanisms: (1) by decreasing the cross-sectional area of the corroded metal, and (2) by inducing “stress concentrators” – areas that experience a concentration, or amplification of force due to geometrical discontinuities – in the metal.

1.3.1 Reduced Cross-Sectional Area

Both uniform and localized corrosion can lead to a metal with a lower overall cross-sectional area. As shown by Equation 1.3.1, the stress (or pressure) $P$ experienced by a metal will increase with decreased cross-sectional area $A$, which is defined as the area of the material that is perpendicular to an applied uniaxial stress, assuming that the force $F$ is constant.
\[ P = \frac{F}{A} \]

**Equation 1.3.1.** The equation for stress, where \( P \) = pressure (or stress), \( F \) = applied force, and \( A \) = cross-sectional area

However, unless a significant portion of the metal is corroded away at one spot, or the metal structure in question already has a very small area, reduced cross-sectional area by itself is not expected to contribute substantially to a metal’s reduced mechanical properties. As a proof-of-concept experiment, we examine how the cross-sectional area \( A \) of an aluminum wire decreases after being immersed in a solution of HCl. In the experiment, an aluminum wire with a diameter of 0.51 mm was immersed in a solution of 2 M HCl for roughly 20 minutes, resulting in a final diameter of roughly 0.50 mm. Based on **Equation 1.3.1**, and taking into account the equation for a circle, the stress on the metal would only increase by about 4 percent. This result suggests that a decrease in cross-sectional area is unlikely to have significant negative impact on structures found outside of a controlled laboratory environment, especially for structures whose original cross-sectional \( A \) is very large. For example, some types of steel corrode in saltwater at roughly 0.55 mm (0.02 inches) per year (5). Since load-bearing structures often have parts that are much wider than 0.55 mm, a small reduction in cross-sectional area due to uniform corrosion is unlikely to lead a metal structure to fail unless the corrosion was left unaddressed for years.

On the contrary, reduced cross-sectional area *at one spot* can have a drastic impact on a metal’s properties, due to the formation of stress concentrators.
1.3.2 Stress Concentrators

As shown in Figure 1.3.1, reducing cross-sectional area in one location, as is the case in localized corrosion, can lead to “stress concentrators” at the surface of the metal. Stress concentrators experience much greater load than expected from simply an analysis of cross-sectional area, due to the presence of geometrical discontinuities such as cracks and notches. As a result of this increased load, cracks can form and then propagate through the material.

Figure 1.3.1. Crack formation and propagation at a site of localized corrosion. When a small part of a metal is exposed to the surrounding environment, such as if its protective film locally breaks down, corrosion at that site can lead to cracks that can propagate throughout the material, causing the metal to fail earlier than expected. Image obtained from Reference (1).

An introduction to the theory behind stress concentrators is shown in Figure 1.3.2(a), which shows two cracks – an internal crack (with a width of $2a$) in the center of a material being pulled uniaxially with a stress of $\sigma_0$, and a surface crack on the side of the material with a width of $a$. The math describing both types of cracks is equivalent, since the relevant parameter $a$ in the equation (shown below) only corresponds to the width of the surface crack, which in an ideal case is half the size of the internal crack.
As shown in Figure 1.3.2(b), the material experiences a maximum stress $\sigma_m$ at the tip of the crack, which has a radius $\rho_t$ describing the curvature at the tip of the crack.

This maximum stress is given by Equation 1.3.2:

$$\sigma_m = 2\sigma_0 \left( \frac{a}{\rho_t} \right)^{\frac{1}{2}}$$

**Equation 1.3.2.** The maximum stress $\sigma_m$ experienced by a material with a surface crack of width $a$ (or internal crack of width $2a$), which is being pulled uniaxially with a stress of $\sigma_0$. $\rho_t$ is the radius of curvature at the tip of the crack.

Dividing both sides of **Equation 1.3.2** by $\sigma_0$ yields **Equation 1.3.3**, which describes the “stress concentration factor” $K_t$. The factor $K_t$ describes the ratio by which an applied force is amplified at the crack tip. The equation thus shows that deeper and sharper cracks (which correspond to larger $a$ and smaller $\rho$, respectively) yield higher stress concentration factors.

$$K_t = \frac{\sigma_m}{\sigma_0} = 2 \left( \frac{a}{\rho_t} \right)^{\frac{1}{2}}$$

**Equation 1.3.3.** Calculation of the stress concentration factor $Kt$, obtained by dividing each side of Equation 1.3.2 by $\sigma_0$.

At sites of localized corrosion, then, the metal is expected to experience a very large stress concentration. Localized corrosion leads to pits that could indeed have low radius of curvature $\rho_t$ (e.g. on the order of microns or nanometers) and a large $a$ depending on the penetration depth of corrosion and the microstructure of the metal, which may lead to areas that are more susceptible to corrosion. (6) If the applied stress at the tip of the pit is amplified by a large enough factor (i.e., $K_t$ is very large), the metal may exceed a crack initiation threshold and begin to crack. This typically occurs when $a$ is 10 times larger than $\rho_t$. Left unaddressed, the crack may continue to
propagate through the material until the metal experiences failure. Otherwise, if the metal exceeds the yield stress of the metal, the structure may begin to plastically and permanently deform.

Figure 1.3.2. Stress concentrators in a material being pulled uniaxially with a stress of $\sigma_0$. (a) A stress concentrator can occur at an internal crack having a width of $2a$, or at a surface crack with a width of $a$. The radius of curvature of the internal crack is denoted by $\rho_i$. (b) The maximum stress $\sigma_m$ experienced by the material occurs at the tip(s) of the crack. Adapted from Reference (7).

In this thesis, we are interested in designing coatings intended to mitigate such localized corrosion. The materials in these coatings are chosen to reduce localized corrosion’s impact on a metal’s mechanical properties.
1.4 Corrosion Prevention with Barrier Coatings

1.4.1 The Electrochemistry of Corrosion

Corrosion occurs via two half-cell reactions: oxidation, in which a solid piece of metal loses electrons and becomes oxidized (so that the metal acts as the “anode”); and reduction, in which another material such as hydrogen gains electrons and becomes reduced (so that the material acts as the “cathode”) (8). The driving force behind these reactions is the occurrence of a potential difference between the anode and cathode when they are placed in electrical contact, which causes electrons to be transferred from one material to another.

The cathode can vary depending on the pH of the solution. As an example, Equations 1.4.1 and 1.4.2 describe these electrochemical reactions in an acidic solution:

\[ M \rightarrow M^{n+} + ne^- \] (oxidation of metal) \hspace{1cm} 1.4.1

\[ 2H^+ + 2e^- \rightarrow H_2 \] (reduction of hydrogen) \hspace{1cm} 1.4.2

In neutral or basic solutions, the reaction described in Equation 1.4.2 does not proceed at a significant rate due to a much lower concentration of hydrogen ions. In this case, electrons in the metal can still react with oxygen and water to form hydroxyl ions:

\[ O_2 + H_2O + 4e^- \rightarrow 4OH^- \] \hspace{1cm} 1.4.3

These hydroxyl ions can, in turn, react with anodic products such as Fe\(^{2+}\) to form corrosion products. Indeed, Fe\(^{2+}\) is essential for the formation of rust (or Fe(OH)\(_3\)), which is a partially oxidized form of the corrosion product iron (II) hydroxide, Fe(OH)\(_2\).
If the metal remains exposed to a corrosive environment, both oxidation and reduction will continue to occur, resulting in the metal’s sustained dissolution.

1.4.2 Barrier Coatings

Because corrosion occurs via reactions that require the metal to be in both chemical and electrical contact with its environment, “barrier coatings” such as spray-on anti-rust paints – which form a physical barrier to the outside environment to improve its lifetime and durability – can act to prevent corrosion by electrically isolating the metal from a reactive environment.

1.4.2.1 Organic and Inorganic Coatings

Barrier coatings work because they are typically made of polymers or other materials that have low permeability to moisture and corrosive chemicals, preventing electrochemical reactions from occurring between the metal and the corrosive environment. An example of such a coating is shown in Figure 1.4.1, which shows a commercially available anti-rust paint that has been painted onto steel bars to protect the metal from corroding.

Effective corrosion control depends on the design and selection of materials used in the barrier coating. Polymers such as epoxies and alkyds, which can be designed to have good adhesion to the coating to prevent moisture and oxygen from infiltrating to the metal, are typically used in barrier coatings. Inorganic compounds such as oxides and carbides can also be used as they are typically impermeable to moisture, but they are quite brittle and can crack. (9)
Figure 1.4.1. A barrier coating prevents an underlying metal from corrosion, as indicated by the rust formed on the uncoated part of this metal. Adapted from Reference (10).

1.4.2.2 Sacrificial Anodes as Barrier Coatings

Aside from the organic and inorganic compounds used in barrier coatings, another type of barrier coating uses another metal to protect a structure of interest from corroding. In this case, a metal of interest is coated with another metal that exhibits higher reactivity in the corrosive environment. This type of coating – termed a “sacrificial anode” – is preferentially etched away when both metals are placed in a corrosive solution. Sacrificial anodes have been employed to prevent the corrosion of a number of structures, (1) including the hulls of ships and the inner surface of storage tanks – where typically, magnesium, zinc, or aluminum is used to protect steel.

Sacrificial anodes employ galvanic corrosion, which occurs when two metals in electrical contact are immersed in an electrolyte solution. Due to a potential difference occurring between the two metals, the more reactive metal serves as the anode and is corroded away preferentially due to the removal of electrons, while the less reactive serves as the cathode and remains protected.
This behavior can be predicted via an “activity series” like the one shown in Figure 1.4.2, where any element to the right of any one item will act as the anode when galvanic corrosion occurs. Furthermore, the more separated two elements are in the series, the more likely they will experience galvanic corrosion and, typically, the higher the rate of corrosion they will experience.

![Activity Series Diagram](image)

**Figure 1.4.2.** An activity series of metals in seawater. Items to the right of an element in the list will serve as the anode when the two metals are electrically connected and placed in a corrosive environment. Adapted from Reference (11).

### 1.4.2.3 Galvanic Corrosion’s Effect on Localized Corrosion

Though sacrificial anodes and other forms of galvanic corrosion can help mitigate the corrosion of an underlying metal, care should still be taken when selecting the appropriate materials during engineering design.

For example, if a less reactive (i.e. cathodic) metal is mistakenly employed as the sacrificial anode, galvanic corrosion can lead to the accelerated and preferential etching of an underlying metal at sites of localized corrosion. At such spots, a small area of underlying metal and a large area of protective metal are both exposed to a corrosive environment. Since the total anodic and cathodic currents are equal, the difference in exposed surface area causes the two metals to experience different current densities – defined as the amount of electric current (i.e. rate of electron flow) per unit area. In particular, the metal that has a smaller area exposed to the corrosive environment is expected to experience a larger current density (i.e., a faster electron flow) than the coated metal. (12)
If the larger-area material is cathodic to that of the smaller-area material, the smaller, anodic area will experience accelerated corrosion, especially near the interface between the two metals where ionic transport is greatest between the two metals. The surface-area effect is illustrated in Figure 1.4.3, where two same-sized pieces of aluminum foil are coated with different surface areas of graphite and immersed in a solution of 2 M HCl for roughly 15 minutes (Figure 1.4.3a). The aluminum foil with a larger amount of graphite (Figure 1.4.3b) corrodes away more quickly than the other sample, as indicated by the faster evolution of bubbles.

**Figure 1.4.3.** Surface-area effect of galvanic corrosion. (a) Strips of aluminum foil coated with different ratios of graphite are taped to the bottom of a crystallization dish and immersed in 2 M HCl. (b) In 15 minutes, the aluminum foil with a higher surface area of graphite corrodes away more quickly, as shown by the faster evolution of bubbles at the uncoated part of the foil.

The effect of galvanic corrosion on localized corrosion is illustrated in the proof-of-concept experiment described in Figure 1.4.4. As shown in Figure 1.4.4a, an aluminum wire was painted with a barrier coating. The coating was then removed using a swab with a width of 5 mm, and 0.01 mL of 0.1 M HCl was dropped at the point of scratch to simulate localized corrosion. (This technique was chosen over complete immersion within HCl to ensure that corrosion was localized to the point of the scratch. As mentioned in previous sections, pinholes within a coating can be
difficult to detect, which could potentially impact the experiment.) After 30 minutes, the wire was washed with water, dried, and finally tensile-tested to gauge its mechanical property.

4 different types of aluminum wires were examined – 2 coated wires, 1 uncoated wire, and 1 new wire. The two coated wires were covered with a commercially available polymer paint – which is expected to experience localized corrosion but not galvanic corrosion – and graphite – which is expected to experience both galvanic and localized corrosion. In particular, graphite should lead to the accelerated corrosion of aluminum at the point of scratch according to the activity series depicted in Figure 1.4.2, and after taking into consideration the surface-area effects shown in Figure 1.4.3. The graphite coating should have a much larger surface area than aluminum at the point of scratch and thus quicken aluminum’s corrosion. To verify whether graphite would indeed act as the cathode in the experiment, the potential difference between graphite and aluminum in HCl was measured as -0.57 V. The negative voltage value confirms that graphite indeed acts as the cathode in this experiment.

As seen in Figure 1.4.4b, all 4 wires experience negligible mass loss. However, a graphite-coated wire experiences a significant reduction in tensile strength, defined as the maximum load that the metal can sustain. The tensile strength of the graphite-coated wire is about 20 percent lower than all the other wires – showing that material loss, a common standard for gauging corrosion, does not necessarily show the complete picture of corrosion’s impact on mechanical properties. (It should also be noted that the wires shown in Figure 1.4.4b only correspond to single data points. However, these results are representative of the data set, which is tabulated in Table 1.4.1. For each result in the table, 5 wires were measured.)
**Figure 1.4.4.** Examining the effects of galvanic corrosion on localized corrosion. (a) An aluminum wire is coated and then “scratched.” A drop of 0.1 M HCl is then placed on the exposed metal and the wire is tensile-tested. (b) The 4 samples tested in this experiment. Mass retention and tensile-strength retention are compared to those of a “before” state or new wire. The results shown are representative of the data set, which is further described in Table 1.4.1.

To clarify the cause of the graphite-coated wire’s reduced tensile strength, SEM images were taken of each of the 4 wire samples near the point of fracture (**Figure 1.4.5**). As can be seen in the image, the bare and the polymer-coated wire both experience superficial corrosion, whereas the graphite-coated wire sustains many small pinholes near the interface between the wire and the coating, as would be expected from galvanic corrosion. These small pinholes should thus serve as stress concentrators that may lead the wire to fail earlier than expected.
<table>
<thead>
<tr>
<th></th>
<th>Mass retention (%)</th>
<th>Tensile strength retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>New wire</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Etched bare wire</td>
<td>95.8 ± 3.9</td>
<td>105.9 ± 20.5</td>
</tr>
<tr>
<td>Polymer-coated wire</td>
<td>97.1 ± 2.0</td>
<td>106.9 ± 10.6</td>
</tr>
<tr>
<td>Graphite coated wire</td>
<td>97.9 ± 1.4</td>
<td>79.0 ± 11.0</td>
</tr>
</tbody>
</table>

**Table 1.4.1.** Mass and tensile strength retention of the four wires tested in **Figure 1.4.4**. For each data point, 5 wires were measured.

Finally, tensile strength is just one mechanical property that can be affected by corrosion. Other properties that can be impacted include the ductility and toughness – which can, as with the tensile strength, all be derived from a stress-strain test.

**Figure 1.4.5.** SEM images of the wires from **Figure 1.4.4** near the point of fracture. Whereas the polymer-coated wire and bare wires experience superficial corrosion, a graphite-coated wire suffers many small pinholes, especially near the interface between the wire and the coating.
The experiments depicted in Figure 1.4.4 highlight the main idea behind our paper “A cautionary note on graphene anti-corrosion coatings,” (I1) which forms the next chapter of this thesis. The paper focuses on the potential application of graphene, a two-dimensional material made out of carbon atoms connected together in a honeycomb lattice (see Figure 1.4.6), for anti-corrosion.

Graphene’s structure confers several exceptional properties unto the material, such as excellent chemical stability. Indeed, graphene – and graphite, which consists of graphene sheets stacked on one another – are quite difficult to oxidize; the oxidation of graphite, for example, requires strong oxidants such as potassium permanganate. (I3)

Figure 1.4.6. Schematic of the two-dimensional material graphene, which consists of an atom-thick layer of carbons connected in a honeycomb lattice (red circle).

Graphene’s high chemical stability and high surface area at first suggest that the material may be applied as a barrier coating, since these properties imply that graphene could shield metals from corrosive materials such as water and oxygen. And if the graphene layer is made thin enough, the
coating could be deposited with little material, drastically decreasing the weight of the coating. (14) This further increases the potential usefulness of graphene coatings – for example, a lighter coating on a ship could mean less drag and better fuel efficiency.

Contrasting typical polymer coatings, however, graphene also has high electrical conductivity. Though some authors have suggested that this property of graphene improves its anti-corrosion capabilities by providing an alternative pathway for electron conduction (15), this argument also assumes that graphene will remain defect-free throughout its lifetime.

If graphene is not defect-free, galvanic corrosion is expected to occur at the defects on the graphene surface. Since the driving force for galvanic corrosion is the difference in electrical potential between the two metals, galvanic corrosion should take place no matter the size of the defect (e.g. atomic scale, mesoscale, bulk scale), so long as the metals are electrochemically connected. One study (16) showed, for example, that “atomic scale galvanic cells” can occur within Al-Cu-Mg alloys, where the galvanic cell occurred between Cu-rich phases and the surrounding matrix. The authors noted that the effect has been seen in microsized defects as well, although it becomes much more noticeable at larger scales.

In practice, pure graphene coatings are not expected to be completely defect-free. Large-scale, defect-free graphene is very difficult to achieve in practice. This can result from a number of reasons, including the processing method used to fabricate graphene, poor or uneven deposition onto a metal surface, and the mechanical removal of the material from the metal surface, such as by a scratch.
2 A cautionary note on graphene anti-corrosion coatings

Material in this chapter is reproduced in part with permission from Reference (11), “A cautionary note on graphene anti-corrosion coatings” by Chenlong Cui, Alane Tarianna O. Lim, and Jiaxing Huang; Nature Nanotechnology, 12, 834-835. (2017).

Graphene is impermeable to all molecules (17). This excellent barrier property and its chemical stability have motivated recent interest in using graphene as an anti-corrosion coating for metals (15). It is not surprising that a perfect piece of graphene flake can indeed shield the metal underneath it from chemical reactions. But for graphene coatings to protect metals in practical applications, especially for load-bearing functions, a few issues must be addressed first. For example, pinholes, cracks or scratches on the coatings could lead to accelerated local corrosion, owing to galvanic coupling between graphene and metal. Even with very low mass loss, such local corrosion can weaken the material catastrophically.

Galvanic reactions occur at the junction between dissimilar metals, where the more reactive (that is, anodic) metal preferentially corrodes to prevent the degradation of the other (18) (the galvanic sequence, which sorts common metals by their tendency to corrode, is listed in Figure 1.4.7a). This effect is used in many corrosion-inhibition coatings, in which a sacrificial anodic layer is applied to protect a metal. An example is zinc-plated steel, in which the anodic zinc coating acts as a barrier when fully covering the metal. More importantly, on development of pinholes or cracks, the zinc can act as a sacrificial anode to retard the corrosion of any exposed steel (Figure 1.4.7b). In contrast, galvanic coupling of steel with a more noble (that is, cathodic) metal results in the opposite effect, in which steel is preferentially attacked upon exposure to the corrosive
environment. A notable example is the galvanic corrosion of the iron armature in the Statue of Liberty, which came into contact with the statue’s copper skin after its insulating separator failed (19).

Pinhole-free cathodic coatings can be used to protect steel, as with tin-plated cans, because the cathodic metal (tin) is more resistant to corrosion and can act as a barrier. If the coating is not pinhole-free or is damaged (for example, scratched), however, galvanic corrosion of steel will occur in those defect spots (Figure 1.4.7c). Moreover, because the area of the anode (steel) is much smaller than that of the cathode (tin), the corrosion rate of steel will be accelerated in order to balance the electron flow at the anode and cathode. Therefore, minor defects in a cathodic coating can lead to surprisingly severe corrosion in exposed areas (20).

Barrier coatings with minor cracks or scratches can still effectively retard uniform corrosion of the metal. But even without noticeable mass loss or change in the overall appearance, localized corrosion through the exposed areas can greatly reduce properties such as the strength and toughness of a metal (1). This is because localized corrosion tends to propagate through the more reactive sites in the metal, such as along grain boundaries (Figure 1.4.7d), and it does not take much loss of metal to develop fatal cracks. To demonstrate this effect, we coated a brass wire with a plastic coating. When the coating is pinhole-free the wire can resist corrosion in hydrochloric acid for weeks. However, with a scratch in the coating, the wire loses over 20% electrical conductivity, over 50% tensile strength and over 90% toughness, while losing less than 0.2% mass.

Although graphene is an excellent barrier material1, two disadvantages must be borne in mind when using it for anti-corrosion applications. First, graphite (that is, multilayer graphene) is
more noble than most common metals (Figure 1.4.7a), and one would expect metal corrosion to be accelerated at the graphene–metal interface, as has indeed been observed (21, 22). In fact, earlier studies have already noted the problem of galvanic corrosion between carbon and steels when carbon-fibre-reinforced plastics are applied to strengthen steel girders (23). In principle, as a cathodic material, graphene anti-corrosion coatings could work just like tin-plating on steel: a defect-free and continuous graphene coating that completely covered a metal surface would prevent uniform corrosion. However, it is not trivial to create continuous graphene coatings on metal objects with complex geometries, whether single-layered or multilayered. Next, even if such coatings can be made, graphene thin films, once damaged during use, are likely to lead to accelerated local galvanic corrosion. To avoid this, graphene coatings must be made pinhole-free and sufficiently durable to resist scratching.

For applications in which only the mass or properties related to the appearance of metals are important, localized corrosion may not be a concern. In those few cases, graphene can be useful as an ultrathin anti-corrosion coating. For metals used in load-bearing structures, localized corrosion is dangerous but very hard to prevent, predict or detect. Therefore, one should be especially cautious about whether graphene actually promotes localized corrosion.

To make use of graphene’s barrier properties for anti-corrosion applications, the disadvantages of cathodic coatings should be mitigated. For example, an insulating material (such as a polymer) could be inserted to break the galvanic coupling between graphene and metal (24). Graphene–polymer composite coatings would be more durable, easier to apply and more scratch-resistant. Such coatings should have well-dispersed graphene sheets to ensure low overall permeability to gas or liquid. Galvanic corrosion can be alleviated or even reversed if the work
function of the graphene coating can be tuned to become anodic to metal. One possible solution is to add anodic materials, such as zinc, to graphene–polymer coatings, as indicated in recent trials (25). Additionally, localized corrosion could be stifled if graphene-based coatings can self-heal, so that the surface can withstand minor damage (26). Finally, the brass wire example acts as a reminder to researchers pursuing graphene’s anti-corrosion applications: in addition to monitoring mass loss or surface degradation, it is perhaps even more important to monitor those material properties relevant to specific applications.
Figure 1.4.7. (a) The galvanic sequence, listing various metals and graphite in order of their tendency to corrode. (b) An anodic coating such as Zn can protect steel even upon scratching. (c) In contrast, with a cathodic coating, local corrosion at scratches accelerates. (d) Localized corrosion can seriously weaken the metal despite little mass loss, by etching through grain boundaries.
3 Potential Implications for Corrosion Standards

In addition to the materials design problem described in our paper, “A cautionary note on graphene anti-corrosion coatings” (11), care should be taken to ensure that the coating and material of interest have been appropriately evaluated for a given application. This may include tests that fall outside the purview of a well-defined corrosion standard. A brief overview of such considerations is provided in this chapter.

3.1.1 Potential Limitations of Commonly Used Corrosion Tests

3.1.1.1 Mechanical Testing in Common Corrosion Standards

Many standards for corrosion and mechanical testing are designed by ASTM International, an organization that develops and publishes technical standards on a variety of materials and services for the international scientific community.

Some ASTM corrosion standards are described in Table 1.4.2. While this list is by no means exhaustive, it represents standards that are commonly cited in the scientific literature to evaluate the corrosion of metals. In particular, the first two standards in Table 1.4.2 (G46-94 – Standard Guide for Examination and Evaluation of Pitting Corrosion, and G31-12a – Standard Guide for Laboratory Immersion Corrosion Testing of Metals) are often cited by researchers when evaluating the corrosion resistance of metals, including cases where a comparison is provided between uncoated and coated metals.

As discussed in the paper, such data is indeed useful but can be supplemented with mechanical tests to show corrosion’s impact on metals used in e.g. load-bearing structures. Unfortunately,
many standards do not explicitly require mechanical testing, even if the technique is mentioned as an advantage. For example, the standard for evaluating pitting, G46-94 (27), mainly describes how users can visualize characteristics such as the geometry and density of the pits on a metal. Though it includes a section at the end labeled “Loss in Mechanical Properties,” and states that “if pitting is the pre-dominant form of corrosion and the density of pitting is relatively high, the change in a mechanical property may be used advantageously to evaluate the degree of pitting,” such wording does not necessarily indicate that the reader of the standard should use mechanical testing. Because of this, the user may forego mechanical testing even if it may be useful, additional information for a particular study.

Another example can be found in ASTM standard G31-12a (28), which details procedures for laboratory corrosion tests that utilize immersion to test the effects of corrosion on a material. Section 10.5 of this standard states that “it may be desirable to make quantitative mechanical tests, comparing the exposed specimens with uncorroded specimens reserved for the purpose, as described in section 7.2.” 7.2 describes mechanical properties that are commonly used to compare materials that have undergone corrosion such as tensile strength and percent elongation, the latter of which can help evaluate the embrittlement of a material. At the end, this section refers users to ASTM Standard E8 (29), which describes standard test methods for tensile testing.

In summary, ASTM 31-12a does suggest that users could use mechanical properties to gauge the extent of corrosion. However, the choice is left to the discretion of the user. In cases where mechanical property is relevant, therefore, it may be advisable to perform additional tests on mechanical property after other standards have been addressed. For example, what is the tensile strength of a material that has sustained a given pit density and penetration? And is this result
reproducible within a small range of error? This may entail selecting an appropriate corrosive environment and structure geometry such that the tests can be normalized from specimen to specimen.

<table>
<thead>
<tr>
<th>ASTM standard</th>
<th>Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>G46-94</td>
<td>Standard Guide for Examination and Evaluation of Pitting Corrosion</td>
<td>Covers ASTM procedures that can be used in characterizing pitting corrosion, including mass loss, visual inspection, and measuring pit penetration.</td>
</tr>
<tr>
<td>G31-12a</td>
<td>Standard Guide for Laboratory Immersion Corrosion Testing of Metals</td>
<td>Describes procedures for laboratory corrosion tests, in addition to factors that may influence test results.</td>
</tr>
<tr>
<td>G61-86</td>
<td>Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys</td>
<td>Describes a procedure for conducting cyclic potentiodynamic polarization measurements in order to determine the susceptibility of metal alloys to localized corrosion. The potential at which the anodic current increases rapidly is measured, with more noble potentials correlating to increased resistance to corrosion.</td>
</tr>
</tbody>
</table>

Table 1.4.2. Some ASTM standards for evaluating corrosion. The top two standards (ASTM standards G46-94 (27) and ASTM G31-12a (28)) include clauses on mechanical testing, while the last one (G61-86 (30)) does not.

However, it should be noted that not all corrosion standards contain clauses on the potential advantages of mechanical testing. For example, ASTM G61-86 (30), which details procedures for potentiodynamic polarization measurements, states that electrochemical measurements may help elucidate the localized corrosion susceptibility of a metal compared to others, but does not explicitly mention mechanical testing.

3.1.1.2 Note on Accelerated Corrosion Tests

One concern that may arise during corrosion testing may be that the tests are designed to accelerate the corrosion of a specific material. As such, they may not appropriately simulate real-
life conditions, even if they do address “worse” scenarios (in terms of corrosive environments, strain rate, etc.) than a metal would experience in the real world.

Accelerated testing, however, could still be useful for selecting the appropriate material for a given goal. Tests are designed to qualitatively simulate the impact of corrosion on different materials, which should ideally be compared with field tests in order to verify whether they sustain the same corrosion mechanisms and produce similar results (e.g. whether a list of given materials exhibits the same order of corrosion susceptibility out in the field). (31)

Thus, corrosion tests that include mechanical testing could be designed with this issue in mind. Such tests could illustrate the impact of different corrosive environments on different metals. For example, the tensile strength, ductility, and toughness of a coating-metal system for different metals or coatings could be evaluated. A case study using aluminum wires is further illustrated in the next section.

3.1.2 Example Case Studies in Mechanical Testing

As mentioned in the previous section, mechanical tests can highlight aspects of corrosion that may be difficult or even impossible to predict using typical corrosion tests. For example, corrosion standards may not be able to reflect how different mechanical properties are affected by corrosion, or whether a given metal will corrode during galvanic corrosion despite its lower corrosion susceptibility.

An example is highlighted in Table 1.4.3, where three different metal-coating systems – a graphite-coated aluminum wire, a zinc-coated aluminum wire, and an uncoated aluminum wire were tested. (Here, the zinc coating was chosen to serve as a comparison to the graphite coating.
In contrast to the graphite-coated aluminum wire, where the underlying aluminum is anodic to graphite and is thus expected to preferentially corrode, zinc was measured to be anodic to aluminum and is therefore expected to serve as a sacrificial anodic coating. After coating, the wires were scratched to simulate localized corrosion and then placed in a bath of 1 M HCl for 24 hours. Tensile tests were then performed to gauge the impact of localized corrosion on metal wires.

Two significant observations can be extrapolated from Table 1.4.3. First, though our paper on graphene coatings (11) shows a proof-of-concept experiment in which a wire’s tensile strength, toughness, and potentially other properties are reduced after exposure to a corrosive solution, it is not always clear how the mechanical properties of a wire will be impacted by corrosion. As can be seen in the table, the graphite-coated wire experiences a significant reduction in ductility, as indicated by its drastically reduced strain-to-failure when compared to the control wire. This occurs even though the graphite-coated wire has experienced the least mass loss.

Secondly, localized corrosion does indeed have an impact on the mechanical properties of a wire. Although zinc seems to perform the best in retaining the mechanical properties of the wire (and is expected to do so based on the prior observation that it acts as a sacrificial anode), it does not completely retain the mechanical properties of the wire as expected. This seems to indicate that zinc’s ability to protect aluminum may be limited by the distance of the edge of the zinc to the aluminum wire, as well as the concentration and composition of the corrosive environment.

These results serve to highlight the ways mechanical tests can serve to supplement other corrosion tests for different metals and corrosive environments. Importantly, the coated aluminum wire system in the table is quite different from that described in the paper (11), which involved a brass wire that had been coated with a polymer coating, scratched, and then immersed in 5.5 M
HCl for a couple of weeks. As an example of the ways that mechanical properties among different metals can differ, the brass wire in the paper experienced a 50 percent decrease in tensile strength. In contrast, the tensile strength of the graphite-coated aluminum wire did not drastically deviate from that of a new wire even though graphite is expected to accelerate the corrosion of the wire more than that of a polymer coating.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Number of samples</th>
<th>Mass loss (percent)</th>
<th>Tensile strength (MPa)</th>
<th>Strain to failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite-coated</td>
<td>8</td>
<td>3.98 ± 2.91</td>
<td>78.1 ± 12.5</td>
<td>0.11 ± 0.05</td>
</tr>
<tr>
<td>Zinc-coated</td>
<td>8</td>
<td>12.1 ± 2.68</td>
<td>83.0 ± 18.0</td>
<td>0.22 ± 0.02</td>
</tr>
<tr>
<td>Uncoated</td>
<td>10</td>
<td>18.7 ± 5.6</td>
<td>69.6 ± 8.85</td>
<td>0.22 ± 0.03</td>
</tr>
<tr>
<td>Control</td>
<td>4</td>
<td>0</td>
<td>88.2 ± 28.4</td>
<td>0.30 ± 0.03</td>
</tr>
</tbody>
</table>

Table 1.4.3. Results from tensile tests conducted on aluminum wires that had been coated, scratched, and immersed in 1 M HCl for 24 hours to simulate localized corrosion. The graphite-coated wire exhibits the lowest ductility, as indicated by its low strain to failure. Meanwhile, the zinc-coated wire appears to prevent the wire from experiencing significant reductions in tensile strength and ductility, although localized corrosion still appears to have reduced the wire’s ductility.

Finally, these results should extend to mechanical properties that are not necessarily evaluated by the tensile test. Though tensile tests can shed many useful insights on, the ductility of a material and its behavior under tensile load, one may wish to test how the material performs under other conditions such as compression, bending, or fatigue. As an example, the impact of a saltwater environment on the fatigue properties of four metal alloys is shown in Figure 1.4.8 (32).
Figure 1.4.8. Impact of corrosion on the fatigue properties of four metal alloys: stainless steel, 15% chromium steel, an aluminum-copper-magnesium alloy, and 0.5% carbon steel. Immersion in a saltwater environment (dashed line) reduced the fatigue limits of each of the metals evaluated. Adapted from Reference (32).

For Figure 1.4.8, “S-N” fatigue curves, which illustrate the maximum stress that a material can be subject to at a given load cycle before it fails, was measured for each of the four metals.
evaluated. As can be seen in the figure, a corrosive environment may introduce a fatigue limit at lower stresses and significantly reduce the fatigue limits of the metals.

### 3.1.3 Stress-Corrosion Cracking Tests

As discussed in Section 3.1.1.2, though accelerated testing can qualitatively highlight how corrosion can impact the properties of a metal – and provide these insights within a short time span – it may be prudent to combine these results with more “accurate” testing.

To this end, corrosion standards that more accurately simulate “real-life” conditions have also been designed. Additionally, if mechanical properties are of interest, one category of corrosion standards does appear to simulate practical scenarios that can have a profound impact on the properties of a material – stress-corrosion cracking tests.

A brief overview of stress-corrosion cracking (or SCC) tests is given below. SCC is defined as the cracking induced from a combination of stress and a corrosive environment. This phenomenon can embrittle a material and lead to the premature failure of a structure even below its yield stress as a result of localized (i.e. microscopic) plastic flow (33). Many microfeatures and microprocesses may be involved in stress-corrosion cracking, which are described in Figure 1.4.9 (34). As can be seen in the figure, the material can interact with the environment in a number of ways to cause a crack to occur.
Standards for stress-corrosion cracking involve the immersion of a test specimen within a corrosive environment and simulate real-life scenarios in three different ways (35):

- By testing statically loaded, smooth samples, which may simulate how the structural integrity of a material changes as it is constantly exposed to a certain load. This may provide useful information on the time required for crack initiation or the threshold
stress required for a crack to initiate; however, it has been found that this value may differ depending on parameters such as the surface finish.

- By testing statically loaded, precracked samples, which may simulate how the structural integrity of a material changes as it is constantly exposed to a certain load, after the material has sustained a crack of a specific geometry. The stress intensity factor, for example, is assumed to increase as the crack length increases.

Such a test can be used to derive a graph like the one shown in Figure 1.4.10, which describes the typical progression of crack propagation. Two values, $K_{\text{ISCC}}$ and $K_{1c}$, are noted in the x-axis, which are both instances of the stress intensity factor or stress concentration factor $K$ (an example of which can be calculated using Equation 1.3.3 for the case of an elliptical crack within the material). In particular, $K_{\text{ISCC}}$ is the critical stress intensity factor for stress-corrosion cracking, while $K_{1c}$ is the critical stress intensity leading to fracture. Both are experimentally determined for a given metal and environment.

Figure 1.4.10 also shows that crack propagation normally occurs via three stages. In Stage 1, the crack-propagation rate increases with $K$; in stage 2, the crack-propagation rate plateaus at a certain velocity and becomes independent of $K$; and in stage 3, the crack growth increases at a large rate until $K_{1c}$ is reached.
This test may therefore provide useful information on the crack propagation rate of a material after it has been placed under load in a specific corrosive environment.

**Figure 1.4.10.** A typical curve describing crack propagation within a material. Typically, crack propagation can be observed in 3 stages, with the threshold stress intensity for stress-corrosion cracking dictated by the threshold stress intensity $K_{\text{ISCC}}$. In Stage 1, the crack-propagation rate increases with the stress-intensity factor. In Stage 2, the crack-propagation rate becomes independent of the stress-intensity factor. In Stage 3, the crack growth rate increases until the material fractures at the critical fracture stress intensity $K_{\text{IC}}$. Adapted from Reference (35).

- By subjecting the material to a slow strain rate ($10^{-7}$ to $10^{-5}$ s$^{-1}$) within an inert environment, and comparing results to similar tests conducted within a corrosive environment. Such slow strain rate tests can benchmark a number of parameters, including the time to failure, reduction in ductility, tensile strength, susceptibility to...
cracking, and toughness. (36) As with many of the other ASTM corrosion tests and standards, standards on stress-corrosion cracking choose environments which may simulate the ones that could be encountered in applications. Two such standards are listed in Table 1.4.4.

<table>
<thead>
<tr>
<th>ASTM standard</th>
<th>Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>G36-94 (37)</td>
<td>Standard Practice for Evaluating Stress-Corrosion-Cracking Resistance of Metals and Alloys in a Boiling Magnesium Chloride Solution</td>
<td>Describes a procedure for determining the susceptibility of metals to cracking in a hot chloride environment, which may simulate contaminated boiler water.</td>
</tr>
<tr>
<td>G37-98</td>
<td>Standard Practice for Use of Mattson’s Solution of pH 7.2 to Evaluate the Stress-Corrosion Cracking Susceptibility of Copper-Zinc Alloys</td>
<td>Describes a procedure for determining the susceptibility of brass alloys to cracking in Mattson’s solution, which may simulate the performance of the materials in ammonia-containing environments.</td>
</tr>
</tbody>
</table>

Table 1.4.4. Some ASTM standards on stress-corrosion cracking, which simulate different corrosive environments that may be encountered in real-life applications.

Thus, stress-corrosion cracking may be able to provide additional, valuable insights into the impact of corrosion on a material’s mechanical properties. However, as these tests can take months to complete, they may not be ideal for certain situations. These tests could be verified against other, accelerated forms of corrosion tests (such as by immersing a metal in a given solution and then performing a tensile test) in order to determine their effectiveness and accuracy.

3.1.4 Conclusion

Several aspects of corrosion tests and standards, especially ASTM, have been discussed in this chapter:
• While the lack of information on mechanical tests may not be an issue for certain applications, mechanical tests should ideally be used in conjunction with these standards when load-bearing structures are evaluated. Such tests, which include tensile and fatigue testing, can help highlight how material systems differ from one another.

• However, many of the corrosion standards commonly cited in the literature do not require mechanical testing to be performed or do not explicitly mention mechanical testing in their clauses.

• Some corrosion standards, such as those that detail immersion tests commonly used for experiments, include clauses that suggest mechanical tests “may be desirable.” While this allows for the possibility of mechanical tests to be conducted, the choice of whether to conduct e.g. tensile testing is left to the discretion of the user.

• When choosing a test to gauge mechanical properties, users should take into consideration a number of factors, such as whether an “accelerated” test indeed evaluates the phenomenon a user is trying to study.

• Stress-corrosion cracking tests could more realistically simulate the impact of corrosion on load-bearing structures, but they are often take a long time to complete. Thus, these tests could be evaluated against accelerated tests to properly verify whether they qualitatively predict the same results.
4 Self-Healing Oil Barrier Coatings

Material in this chapter is reproduced and adapted in part with permission from Reference (38), “Self-healing Microcapsule Thickened Oil Barrier Coatings” by Alane Tarianna O. Lim, Chenlong Cui, Hee Dong Jang, and Jiaxing Huang; Research, (2019).

4.1 Abstract

Low-viscosity oils could potentially act as self-healing barrier coatings because they can readily flow and reconnect to heal minor damages. For the same reason, however, they typically do not form stable coatings on metal surfaces. Increasing viscosity helps to stabilize the oil coating, but it also slows down the healing process. Here, we report a strategy for creating highly stable oil coatings on metal surfaces without sacrificing their remarkable self-healing properties. Low-viscosity oil films can be immobilized on metal surfaces using lightweight microcapsules as thickeners, which form a dynamic network to prevent the creep of the coating. When the coating is scratched, oil around the opening can rapidly flow to cover the exposed area, reconnecting the particle network. Use of these coatings as anti-corrosion barriers is demonstrated. The coatings can be easily applied on metal surfaces, including those with complex geometries, both in air or underwater, and remain stable even in turbulent water. They can protect metal in corrosive environments for extended periods of time, and can self-heal repeatedly when scratched at the same spot. Such a strategy may offer effective mitigation of the dangerous localized corrosion aggravated by minor imperfections or damages in protective coatings, which are typically hard to prevent or detect, but can drastically degrade metal properties.
4.2 Main Text

4.2.1 Introduction

Barrier coatings can retard corrosion by isolating underlying metal from reactive environments (39). Pinholes and other minor damages (e.g., cracks and scratches) in the coating only expose small areas of metal. However, reactions at these sites can develop into dangerous localized corrosion, which can lead to catastrophic failure of the overall material system even with very little mass loss (40, 41). Since these defects are hard to prevent, predict or detect, responsive coatings that can self-repair would be very useful for mitigating localized corrosion. There have been a number of strategies for making self-healing coatings that can fix damages autonomously (42). At the molecular level, systems with reversible bonding (43) can be triggered to reestablish connections, preventing cracks from propagating. Repairing larger cracks requires the delivery of healing agents to damaged areas. For example, microcapsules (44) and vascules (45) containing monomers and initiators can be embedded in a polymer coating, which, upon rupture, release the liquids to rapidly fill a crack, polymerize and solidify.

Since fluid readily flows and reconnects, materials with such liquid-like properties would be ideal for self-healing purposes. However, for the same reason, low-viscosity fluid does not form stable coatings. On the other hand, high-viscosity liquid (e.g., a grease) can form very stable coatings, but it does not flow easily to heal scratched areas. Continuous layers of low-viscosity oils can be stabilized on a surface with patterned pinning sites, which essentially restructures the liquid films into interconnected small reservoirs. These oil films can then act as protective barriers to isolate the substrate from water (46-50). Here, we report another strategy for fabricating liquid-
based self-healing coatings, in which low-viscosity oil films are immobilized on metal surfaces by a dynamic network of lightweight colloidal capsules. At the macroscopic scale, the oil coating is thickened and becomes creep-resistant on metal surfaces. But at the microscopic scale, the oil trapped within the particle network is still highly fluidic, and can readily flow and reconnect when the network is broken by a scratch, thus retaining the extraordinary self-healing capability of the oil. The coatings can be applied on demand on metal surfaces as anti-corrosion barriers, even from underwater. They are pinhole-free, stable in high turbulence and highly corrosive environments, and can self-heal up to hundreds of times, making them a promising option for underwater anti-corrosion applications.

4.3 Results and Discussion

4.3.1 Microcapsule-thickened oil

Oil can be gelled or thickened by molecule-, polymer- or particle-based additives, which form an extended network in oil to stop its free flow (51). Since barrier coatings are often applied to vertical surfaces, lightweight, low-loading-level particle thickeners would be preferred, as they do not significantly increase the weight of the oil layer. Thus, hollow microcapsules of reduced graphene oxide (r-GO) with an apparent density of around 0.12 g/cm$^3$ (Figure 4.3.1a and Figure 4.3.1b) are chosen as the model particle thickener for all the studies below.

The microcapsules are made by spray-drying a mixture of graphene oxide sheets and polystyrene colloids of around 200 nm in diameter, followed by thermal annealing to reduce graphene oxide and remove the polystyrene beads (see Materials and Methods). The resulting microcapsules are made of interconnected voids of around 200-250 nm in diameter with thin
graphene walls of less than 10 nm. They are sufficiently robust and resilient during handling. As shown in Figure 4.3.1c, r-GO microcapsules can increase the viscosity of silicone oil by 1000 times at just about 5 wt. % loading. Optical microscopy observation confirmed that the r-GO microcapsules indeed form an extended network in the oil (Figure 4.3.1d).

Figure 4.3.1. Low-viscosity oil thickened by r-GO microcapsules. (a) SEM and (b) TEM images of the r-GO capsules. (c) Effect of particle loading on the viscosity of a low-viscosity silicone oil (red, dashed line). (d) An optical microscopy image taken near the edge of a thickened oil film on glass slide, confirming a network structure of r-GO capsules. Thicker parts of the film are hard to image due to overlapping particles.

Heavier hollow microcapsules made of poly(o-methoxyaniline) or silica were also tested, but much higher loading levels (e.g., 15-35 wt. %) are required for the resulting coatings to achieve similar increases in viscosity. The drastic thickening effect of r-GO microcapsules is primarily attributed to their light weight. r-GO microcapsules also have a few other desirable properties. Our earlier work (52) demonstrated that similarly prepared r-GO capsules could absorb oil well,
allowing them to stay wetted by and immersed in the oil rather than floating on the surface. The black color of r-GO also facilitates direct visual inspection and optical microscopy observation of the oil coating.

4.3.2 Stability of r-GO/oil coating on metal surfaces

Figure 4.3.2 shows that coatings made from the r-GO thickened oil are remarkably stable in air and under water. As shown in Figure 4.3.2a and Figure 4.3.2b, a drop of low-molecular-weight silicone oil with viscosity of around 0.02 Pa·s readily flows down a slope of Al foil (Figure 4.3.2), while the same oil loaded with r-GO capsules (around 5 wt. %, hereafter denoted as r-GO/oil) sticks to the foil firmly (Figure 4.3.2b). The thickened oil has a viscosity of around 40 Pa·s. In a control experiment, high-molecular-weight silicone oil with even higher viscosity (around 100 Pa·s) was tested, which can also form a stable coating on Al foil. However, when immersed under water, the high-viscosity oil film gradually dewets (Figure 4.3.2c) due to the added interfacial tension between oil and water. In contrast, the r-GO/oil coating remains stable. The r-GO/oil coating is capable of resisting lateral compressive stresses induced by the surface tension of water and hinders the shrinkage of the oil film, which may be attributed to the jamming of the particles (Figure 4.3.3).

The r-GO/oil coating can withstand highly turbulent water. Figure 4.3.2d shows a coated copper wire immersed in a whirlpool generated by magnetic stirring, from 600 rpm to the maximum stirring speed of 1200 rpm. The coating remains intact after days of vigorous stirring. Under these stirring conditions, the linear velocities of water around the wire are estimated to be in the range of 0.5 to 1 m/s using a dye-tracking method (see Materials and Methods), which are on par with the typical flow rates of rivers (53).
Figure 4.3.2. Stability of r-GO/oil coating on metal. (a) Photos showing a drop of dyed silicone oil (viscosity: around 0.02 Pa·s) flowing down a tilted Al foil in only 10 seconds. (b) In contrast, a drop of r-GO/oil is firmly pinned. (c) Photos showing coatings of r-GO/oil (top) and a high-molecular-weight silicone oil (bottom) of even higher viscosity (around 100 Pa·s), which is dyed red for the convenience of observation. Both coatings are initially stable in air, but when placed under water, the silicone oil film dewets and shrinks within 60 minutes. In contrast, the r-GO/oil coating remains stable. (d) The r-GO/oil coating on a copper wire (1.02 mm diameter) remains stable in a vigorously stirred water bath for days. The inset indicates the position of the wire in the bath.
Figure 4.3.3. Illustration of Figure 4.3.2c. (Left column) When neat silicone oil is placed in water, the interfacial tension between oil and water causes the oil to shrink. (Right column) When particle-thickened silicone oil of similar viscosity is placed in water, the particles prevent the oil droplet from shrinking. This is attributed to the jamming of the particles.

4.3.3 Barrier performance of r-GO/oil coating

The r-GO/oil coating can indeed act as a barrier to protect metal against corrosion over extended periods of time. A 3-electrode electrochemical cell (Figure 4.3.4a) consisting of platinum as the counter electrode, an Al wire as the working electrode, and Ag/AgCl as the reference electrode was used to evaluate the barrier performance of the r-GO/oil film in a solution of 1 M (3%) HCl.

The potentiodynamic polarization curve of a bare Al wire (Figure 4.3.4b, purple line) shows anodic and cathodic branches typically associated with the corrosion of a metal in a solution. In contrast, the same experiment performed on a r-GO/oil coated Al wire (Figure 4.3.4b, red line) results in a nearly flat line around zero current, indicating that the r-GO/oil coating insulates the underlying Al from reacting with the electrolyte solution, and thus prevents metal corrosion.

Figure 4.3.4c and Figure 4.3.4d show the long-term anti-corrosion performance of r-GO/oil coating. An Al wire immediately starts to react upon dipping in 20% HCl solution (Figure 4.3.4c, left), generating H2 bubbles on its surface.
Figure 4.3.4. r-GO/oil barrier coating protects metal against corrosion. (a) Schematic drawing illustrating a 3-electrode electrochemical setup to evaluate the r-GO/oil film's anticorrosion performance in 1 M (3%) HCl. (b) Potentiodynamic polarization curves of uncoated (purple line) and coated (red line) Al wires, showing that the r-GO/oil film indeed acts as a barrier and prevents the underlying Al from reacting with HCl. (c) An Al wire (1.02 mm diameter) is severely etched after just one hour in concentrated HCl 5.5 M or 17% HCl. (d) In contrast, an Al wire coated with r-GO/oil film remains intact after at least 3 months.
After one hour, the immersed part of the wire is almost entirely etched (Figure 4.3.4c, right). However, an r-GO/oil-coated wire (Figure 4.3.4d, left) stays intact after being immersed in this highly corrosive solution for at least 3 months (Figure 4.3.4d, right). Some coated wires were found to be intact after being immersed for over a year.

The r-GO/oil film adheres well to many types of metal surfaces (e.g., Cu, Fe, Al and their alloys), even those with complex geometries or sharp corners, on which oil film tends to dewet. An example is demonstrated in Figure 4.3.5a and Figure 4.3.5b, showing the survival tests of an Al foil boat placed on a sea of 2M HCl. The boats are loaded with a methylene blue dye solution to indicate leakage. Without a barrier coating, the Al boat is rapidly etched by HCl. It starts to leak after a few minutes and completely dissolves in 20 minutes (Figure 4.3.5a). In contrast, the boat coated with an r-GO/oil film is well protected and remains intact after the dye solution (Figure 4.3.5b) or even the entire HCl bath dries out. The r-GO/oil coating can be conveniently applied to metal surfaces on demand, even from underwater, simply with a brush to yield a pinhole-free barrier coating (see photos in Figure 4.3.5c and Movie S1) capable of stopping ongoing corrosion.

4.3.4 Self-healing property of r-GO/oil coating

While the r-GO/oil coating exhibits remarkable stability, it does not lose the self-healing properties of the oil. The coating is capable of healing sub-millimeter to millimeter scale scratches in seconds, as shown in the snapshots in Figure 4.3.6a to Figure 4.3.6d (also see Movie S2).

Optical microscopy observation (Figure 4.3.6e to Figure 4.3.6g, also see Movie S3) reveals that when a scratch breaks part of the particle network, nearby oil immediately starts
flowing to the exposed area and brings new particles to reestablish the network. The flow of particles stops after the coating is healed (Figure 4.3.6h).

Figure 4.3.6i to Figure 4.3.6l show coatings that have been applied to aluminum wires. They demonstrate that the coating can quickly self-heal in both water (Figure 4.3.6i) and in 5% and 10% HCl (Figure 4.3.6j and Figure 4.3.6k, respectively) when scratched. Eventually, when immersed in 20% HCl solution, the evolution of H2 bubbles at the scratched area is too fast to allow the r-GO/oil coating to recover (Figure 4.3.6l). This self-healing behavior can also be seen in open-circuit current measurement (Figure 4.3.6m of an Al wire coated with r-GO/oil immersed in 1 M (3%) HCl. When the coating is scratched, a small area of the metal is exposed, triggering a current spike that gradually decays to near zero within a few seconds, indicating that the coating has self-healed. The coating can self-heal multiple times in succession. The duration of the current spikes matches the time scale of the self-healing behaviors observed in Figure 4.3.6a to Figure 4.3.6d.

Although only 3 consecutive scratching-healing cycles were shown in the electrochemical test shown in Figure 4.3.6m, r-GO/oil coating is actually quite tolerant to scratches and can self-heal up to hundreds of times at the same spot. The drawing in Figure 4.3.7 illustrates an exhaustive scratch test on a r-GO/oil coated wire immersed under water. A soft rod made of polydimethylsiloxane (PDMS) is attached to the minute hand of a clock, so that it can repeatedly scratch the immersed wire at the same location once every minute. As long as there is a sufficient reserve of oil to flow to the scratched area, and extra capsules above the percolation threshold to reconnect the broken network, the r-GO/oil coating sustains scratching and self-heals repeatedly (also see Movie S4).
Figure 4.3.5. r-GO/oil can form stable coating on metal of complex geometry and can be applied from underwater. (a) An Al foil boat placed on 2 M HCl solution is damaged after just 8 minutes, indicated by the leakage of methylene blue solution, and completely dissolves away after 20 minutes. (b) Another Al boat coated with an r-GO/oil film stays intact after a day, when the dye solution has dried out, showing that the coating is stable on metal surface with complex geometry and sharp corners. (c) r-GO/oil film can be brushed onto an already immersed Al wire under water to protect it from reacting with concentrated HCl. As a control, a bare Al wire is also immersed, which immediately starts to bubble (dashed red circle) due to reaction with HCl.
Figure 4.3.6. Self-healing property of r-GO/oil coating. ((a)-(d)) Snapshots showing that a scratch about 0.5 mm wide fully heals in seconds (scale bar = 0.5 mm). ((e)-(h)) The corresponding optical microscopy images reveal that oil can rapidly flow to the scratched area, followed by reorganization of particles to reestablish the network (scale bar = 50 μm). ((i)-(l)) Self-healing of r-GO/oil coating when scratched in (i) water, (j) 5% HCl, (k) 10% HCl, and (l) 20% HCl. The position of the scratch is indicated by the red arrows. The healing time in more concentrated HCl solution increases since the flow of oil to the exposed area is increasingly hindered by H2 evolution at faster etching rate. In 20% HCl, the rate of H2 evolution is too fast to allow self-healing to proceed. (m) Open-circuit current of an Al wire coated with r-GO/oil immersed in 1 M (3%) HCl during a scratch test. When the coating is scratched, a small area of the metal is exposed. The resulting local corrosion triggers a spike in the current that quickly dissipates within a few seconds, indicating that the coating has self-healed to restore its protective barrier property.
Figure 4.3.7. Exhaustive scratching and healing test. As shown in Movie S4, a PDMS rod with a diameter of around 1 mm is attached to a clock hand to repeatedly scratch an r-GO/oil-coated wire, at the same spot, once every minute.

Therefore, although a small piece of the coating is removed during each scratch, the coating shown in Figure 4.3.7 repeatedly heals even after 180 scratches. After 240 scratches, the damage on the coating becomes visible, when the remaining amount of r-GO/oil becomes insufficient to completely cover the wire.

4.3.5 Mitigation of localized corrosion with self-healing coating

The scratch-tolerant, self-healing properties of r-GO/oil coatings make them an effective type of barrier for mitigating localized corrosion. A proof-of-concept experiment is shown in Fig. Figure 4.3.8a, in which brass wires are first protected with a barrier coating, then scratched to expose a small area to simulate localized corrosion, before immersing them in highly corrosive solutions (5.5 M HCl) for 2 weeks. A hard polymer coating is tested as a control to illustrate the importance of the self-healing capability of the barrier coating. Typical corrosion tests often
measure the mass loss of metals. Such measurements do not reflect the drastic degradation of mechanical properties by localized corrosion, which can occur with negligible mass loss \((41, 54)\).

![Diagram of experimental procedure](image)

**Figure 4.3.8.** The r-GO/oil coating is scratch-tolerant and protects metal wires from localized corrosion. (a) Schematic illustration of the experimental procedure testing the effects of localized corrosion on the mechanical properties of brass wires. A wire is first coated with a barrier film and then scratched to expose a small area before being immersed in etching solution \((5.5 \text{ M or } 17\% \text{ HCl})\). After etching, tensile tests are performed to directly evaluate corrosion-induced damage. (b) Representative stress-strain curves of an unetched wire, etched wire, etched wire with an unhealable coating, and etched wire with the r-GO/oil coating. (c) A bar graph summarizing changes in tensile strength and the mass of the wires tested in (b). The unprotected wire loses nearly 40\% of mass and over 90\% of strength after 1 week. The polymer-coated wire has negligible mass loss, even after 2 weeks, but its strength is decreased by about half, due to localized corrosion at the scratch. The wire coated with the self-healing r-GO/oil film retains its original mechanical properties and is not affected by the scratch.

Therefore, tensile tests are performed to directly evaluate the damage in mechanical properties as a result of localized corrosion on the wires. **Figure 4.3.8b** shows representative stress-strain curves of a number of brass wire samples before and after etching. **Figure 4.3.8c** compares the
percentages of tensile strength and mass of these wires after etching, relative to those of the unetched wire.

Without a protective barrier, the wire loses nearly 40% of its mass and over 90% of its strength after just 1 week. The wire coated with a hard polymer barrier experiences negligible mass loss after 2 weeks, but its strength decreases by about 50% due to localized corrosion at the scratched area (see SEM images in Figure 4.3.9).

![SEM images](image)

**Figure 4.3.9. SEM images of etched brass wire samples used in Figure 4.3.8.** (a) The surface of a new wire is relatively smooth before etching. (b) After etching in 5.5 M (17%) HCl for 7 days, the surface is highly corroded and roughened. (c) A wire protected by the r-GO/oil coating shows no signs of corrosion even after 14 days of etching. (d) Significant, localized corrosion occurs at the scratched area of the brass wire protected by the polymer coating.

In fact, even without the intentionally made scratch, the polymer-coated wires still suffer significant property degradation from corrosion due to pinholes, which are hard to prevent and detect (see Figure 4.3.10). In contrast, with the r-GO/oil’s rapid self-healing capability, the wire
coated with r-GO/oil retains its original mechanical properties even after being immersed in the etchant solution for 2 weeks.

Figure 4.3.10. Localized corrosion through pinholes can drastically degrade the properties of metal wires. (a) Stress-strain curve of a brass wire protected with an unscratched polymer coating after being immersed in 5.5 M (17%) HCl for 14 days, compared to that of a pristine wire. The etched wire experiences no detectable mass loss, but obvious reduction in strength and ductility. (b) SEM examination of the etched wire reveals microcracks on the wire, likely due to localized corrosion through some hard-to-detect pinholes on the coating.
4.3.6 Conclusion

In conclusion, by using lightweight microcapsules as thickening agents, even low-viscosity oil can form continuous, highly stable, protective barrier coatings on metal surfaces. Such oil coatings are intrinsically pinhole-free, and they can quickly self-heal many times when they are scratched, making them potentially useful as an on-demand or urgent solution for protective barrier applications. Although most of the work presented here is demonstrated with r-GO microcapsules, the described strategy is largely materials agnostic, and should be applicable to a wide range of lightweight particles. The design and fabrication of other coatings is discussed in a later chapter.

Other variations of the r-GO coatings described in this chapter can also be taken into consideration. For example, the particles can potentially be loaded with other materials to render additional functions to enhance the barrier coatings.

4.4 Materials and Methods

4.4.1 Materials

Graphene oxide (GO) sheets were synthesized through a modified Hummer’s method (55) as reported elsewhere (56). Polystyrene colloids were prepared through emulsion polymerization (57). Reduced graphene oxide (r-GO) capsules are made by an aerosol-assisted synthesis method based on a previous report (52), using a spray dryer (Buchi Nano Spray Dryer B-90). A mixture of 1 L 2 mg/mL GO sheets and 100 mL polystyrene colloids (200 nm diameter) was sprayed at 80 oC, which yielded GO-wrapped polystyrene beads. r-GO capsules were obtained by heating the product under argon at 600 °C for 4 hours, which reduced GO and removed the sacrificial polymer template. The apparent density of the capsules was determined to be 0.12 g/cm³ by measuring the
volume of a known mass of powder within the end of a cylindrical pipette tip. SEM images of the r-GO capsules were taken with an FEI Nova 600 SEM. TEM images were taken with a JEOL ARM300F GrandARM transmission electron microscope. These particles were added to oil at various weight fractions to adjust viscosity. Various types of oils such as household vegetable oils, household sunscreen oils, light mineral oils and silicone oils were tested, all of which worked for self-healing coatings. Silicone oil was chosen as the model system due to its high stability against degradation and low solubility in water. Low-molecular-weight (viscosity 20 cSt, \textit{i.e.}, around 0.02 Pa·s) and high-molecular-weight (viscosity 100,000 cSt, \textit{i.e.}, around 100 Pa·s) silicone oils were purchased from Sigma-Aldrich. A number of metal wires were tested, including brass, copper, steel and aluminum. The wires were briefly polished with sandpaper and washed with ethanol to remove any existing surface coating. Hollow spheres of poly(o-methoxy)aniline (average diameter: 2.27 µm, average wall thickness: 191 nm) and silica (average diameter: 3.94 µm, average wall thickness: 223 nm) were synthesized using methods in the literature (58, 59).

4.4.2 Viscosity measurement (Figure 4.3.1c)

Viscosities of the r-GO/oil coatings were measured on an Anton Paar Physica MCR 300 rheometer with a cone-and-plate (lower loading levels) or parallel plate geometry (higher loading levels). Typically, 0.5 g of particle/oil coating was subjected to shear rates from 0.1 to 100 rad/s to measure the resulting shear stresses. The viscosity at 0.1 rad/s was chosen for comparison.

4.4.3 Stability under shearing water (Figure 4.3.2d)

Copper wires (1.02 mm diameter) coated with r-GO/oil films were immersed in a water bath, which was stirred at a nominal speed of 600 and 1200 rpm for 1-2 weeks. The linear shear
velocity of water is estimated to be 0.5 to 1 m/s using a dye tracking method, in which a droplet of concentrated dye solution is dispensed into the whirlpool and tracked using a camera in slow motion mode (240 fps). The initial linear velocity of this droplet (e.g., within the first 100 ms, before it becomes too diffuse) was calculated to represent the linear flow rate of the whirlpool.

4.4.4 Electrochemical tests (Figure 4.3.3a, Figure 4.3.3b and Figure 4.3.6m)

The anti-corrosion performance of r-GO/oil on aluminum in a 1 M (3%) HCl solution was evaluated using an Autolab electrochemical interface instrument (PGSTAT 302N). The electrochemical cell (illustrated in Figure 4.3.3a) was a three-electrode setup consisting of platinum (counter electrode), a freshly polished aluminum wire that was either bare or coated with r-GO/oil (working electrode) and Ag/AgCl (reference electrode). The polarization curves (Figure 4.3.3b) were measured from -0.3 V OCP to 0.3 V OCP at a scan rate of 0.001 V/s and a step size of 0.01 V. To investigate the electrochemical behavior of self-healed scratches (Figure 4.3.6m), the open-circuit current of an r-GO/oil-coated Al wire immersed in the same electrochemical cell was monitored at a time increment of 0.2 s. The wire was scratched with a plastic pipette tip to induce localized corrosion.

4.4.5 Anti-corrosion tests (Figure 4.3.3c, Figure 4.3.3d, Figure 4.3.4a and Figure 4.3.4b)

An uncoated Al wire (1.02 mm diameter) (Figure 4.3.3c) and another coated with r-GO/oil film (Figure 4.3.3d) were immersed into 5.5 M (17%) HCl. Al boats shown in Figure 4.3.4a and Figure 4.3.4b were made from foil by folding and floated on a solution of 2 M HCl in a 100 mm
diameter petri dish. 0.2 mL of 0.1 wt. % methylene blue solution was loaded in the boats as color indicator of leakage.

4.4.6 Visual and optical microscopy observation of self-healing property (Figure 4.3.6, Movies S2 and S3)

r-GO/oil coating was applied onto a glass slide and swiped with a 200 µL pipette tip to generate scratches that are about 0.5 to 1 mm wide. Optical microscopy images (Nikon Eclipse TE2000-U) were recorded using a monochrome interline CCD camera (Photometrics, CoolSNAP HQ2).

4.4.7 Exhaustive self-healing test (Figure 4.3.7 and Movie S4)

A metal wire coated with r-GO/oil was fastened horizontally under water. A polydimethylsiloxane (PDMS) rod with diameter around 1 mm was used to scratch the coating repeatedly at the same spot. The PDMS rod was attached to the “second” hand of a ticking clock, so that it scratched the coated wire once per minute.

4.4.8 Evaluating corrosion-induced degradation of mechanical properties (Figure 4.3.8, Figure 4.3.9 and Figure 4.3.10)

Brass wires were first coated with r-GO/oil or Rust-Oleum 2X (a polymer-based anti-corrosion paint) and then scratched with a razor blade to generate small slits that are around 0.3 mm wide. Wires with scratched coatings were immersed into 5.5 M (17%) HCl (1 week for uncoated wires, 2 weeks for coated wires). Stress-strain curves were obtained using a Bose ElectroForce 5500 tensile tester. SEM images of the wire surfaces after corrosion were taken with
an FEI Nova 600 SEM. In control experiments, wires coated with the paint, but unscratched, were also immersed in HCl to show the effect of pinholes, which are hard to prevent and detect during the coating process.

4.5 Supplementary Movies

Many of the figures in this paper were extracted from movies taken during the experiments. These movies can be viewed here: https://spj.sciencemag.org/research/2019/3517816/.

**Movie S1.** Brushability of r-GO/oil coating under water. An r-GO/oil film is readily applied to an aluminum wire under water with a paintbrush. After the wire is completely coated, another aluminum wire is fastened next to the coated wire and HCl is added. The uncoated wire reacts with the added HCl, as shown by the formation of bubbles on the wire surface, while the coated wire remains protected.

**Movie S2.** Macroscopic visualization of self-healing r-GO/oil coating. An r-GO/oil film on a glass microscope slide is scratched with a pipette tip and observed to heal within seconds. This healing process can be readily seen by eye.

**Movie S3.** Microscopic visualization of self-healing r-GO/oil coating. A scratch breaks the particle network within the coating. As the freed low-viscosity oil flows into the scratch, it carries lightweight microcapsules towards the scratch, which reorganize to reestablish the network.

**Movie S4.** Repeatability of self-healing. A strip of PDMS attached to the “second” hand on a clock scratches a self-healing coating at one spot. The clock can be left running to test the number of times the coating can be scratched at the same location.
5 Additional Results on r-GO/oil

This text was not included in the original text of the paper presented in the previous section, “Self-healing microcapsule thickened oil barrier coatings” and is intended to supplement the interpretation of various results presented in the article as well as provide further insights into the applications and mechanism of r-GO/oil.

5.1 Electrochemical Corrosion Tests (Figure 4.3.4 and Figure 4.3.6)

The following section details some of the background behind the electrochemical tests performed in the paper and provides additional results.

5.1.1 Examining Electrochemical Behavior with Tafel Plots

The effectiveness of a barrier coating can be gauged by means of a “Tafel plot,” an ideal example of which is shown in Figure 5.1.1. A Tafel plot shows the relationship between current and voltage for an electrochemical system and is obtained by sweeping the voltage between an anode of interest (in this case, the corroding metal) and a cathode (another metal, like platinum, which is more noble than the anode) about the equilibrium potential of the system – also known as the “open-circuit potential.” The absolute value of the plot is then taken to obtain an anodic and cathodic branch, which respectively describe the oxidation and reduction reactions of the corrosive system as they become the dominant reaction.
Figure 5.1.1. Ideal and non-ideal Tafel plots. (a) An example of an ideal Tafel plot. The intersection of the cathodic (“Reduction,” purple line) and anodic (“Oxidation,” yellow line) branches provide the equilibrium potential $E_{\text{rev}}$ and equilibrium current $i_0$ of the system, which correspond respectively to the potential and current at which corrosion is reversible. (b) A non-ideal Tafel plot, which exhibits nonlinear behavior. A linear extrapolation (purple and orange lines) can still be performed to obtain the equilibrium potential and current.

At equilibrium, the reaction described in Equation 1.4.1 – the general reaction for the oxidation of a metal – is reversible. This reversible reaction occurs at the potential $E_{\text{rev}}$ and current $i_0$, which is found at the intersection of the two lines in Figure 5.1.1a. By applying an “overpotential” (which is defined as potential that is different than $E_{\text{rev}}$), the reaction is made to proceed predominantly in one direction:

- At $E > E_{\text{rev}}$, the metal will be oxidized: $M \rightarrow M^{n+} + n\text{e}^-$
- At $E < E_{\text{rev}}$, the metal will be reduced: $M^{n+} + n\text{e}^- \rightarrow M$

An ideal Tafel plot like the one in Figure 5.1.1a shows a linear relationship between
the applied voltage and measured current on the working electrode, which acts as the anode. This ideality assumes that back reactions can be neglected and that there are no other effects that would change the linearity of the measurement.

In reality, Tafel plots exhibit nonlinear behavior at potentials near the corrosion potential and at potentials far beyond the corrosion potential due to back reactions at small potentials and, at larger potentials, effects such as resistance drops and concentration polarization, in which corrosion occurs so rapidly that it is limited by the diffusion of ions to the interface. (1)

A linear Tafel plot can still be extrapolated from a measurement to extract a corrosion potential $E_{rev}$ (Figure 5.1b). This corrosion potential can then be used to qualitatively evaluate the corrosion susceptibility of different materials in a given corrosive environment, with more positive $E_{rev}$ corresponding to lower corrosion susceptibility. Using this information, the relative order of metals ranked on their corrosion susceptibility can be determined. Note that this information does not necessarily correlate to a given corrosion rate. While corrosion rates can be extracted from a Tafel plot, the equations assume that only uniform corrosion takes place and can underestimate the amount of mass loss resulting from localized corrosion. (60)

5.1.2 Extrapolating the Effectiveness of a Barrier Coating from a Tafel Plot

Even with its limitations, the Tafel plot can help characterize the effectiveness of a coating, especially when it is compared to an uncoated system. A coated metal should have a more positive $E_{rev}$ and lower $i_0$ than its uncoated counterpart if the coating is indeed acting against corrosion. (61) This is due to the following reasons: (1) Applying a more positive voltage to the corrosion
potential causes the system to corrode at a faster rate. This suggests that a metal that is associated with a more positive $E_{\text{rev}}$ on the Tafel plot is more resistant to oxidation (i.e. less likely to be corroded), since more potential is needed to drive the metal to oxidize. (2) If a coated metal corrodes at a lower current than an uncoated one, this indicates that the rate of mass transport for the coated system is lower, suggesting that it will take longer to oxidize.

![Tafel plots](image)

**Figure 5.1.2.** Tafel plots obtained of a bare aluminum wire (black) and an aluminum wire coated with an anti-corrosion paint (red) in 1 M HCl solution. The polymer-coated wire exhibits a more positive $E_{\text{rev}}$ and lower $i_0$ than the uncoated system, indicating that the coating reduces the wire’s corrosion susceptibility.
These trends can be seen in Figure 5.1.2, which shows Tafel plots taken of a bare aluminum wire and a similar wire coated with an anti-rust polymer coating in 1 M HCl solution. When the linear Tafel plot is extrapolated from both graphs, the polymer-coated wire exhibits a more positive $E_{rev}$ and a lower $i_0$, indicating that the wire is protected from corrosion.

It should be noted, however, that the graph does not seem to indicate that the aluminum wire completely protects the wire from corrosion. The presence of a well-defined $E_{rev}$ and $i_0$ indicates that some corrosion does take place – possibly due to incomplete coating coverage on the wire, or if the wire is not completely impermeable to the acid in which it was placed. This observation is corroborated by Figure 4.3.10, which shows that wires that have been covered with an anti-rust paint can still experience corrosion, as indicated by cracks seen on an SEM image of the wire after the paint has been removed.

![Figure 5.1.3](image.png)

Figure 5.1.3. Tafel plot obtained of an aluminum wire covered with a plastic pipette and immersed in a 1 M HCl solution. The noisiness of the curve indicates that the wire is insulated from its surrounding environment.
As shown in Figure 5.1.3, a wire that has been completely insulated from corrosion should result in a noisy curve that is centered near zero, indicating that the wire and the solution are not electrically connected. In this experiment, the wire had been placed within a plastic pipette and then immersed within acid. A similar result was indeed observed in our r-GO coating (Figure 4.3.4b) but does not necessarily indicate that the coating yields better anti-corrosion performance than a typical anti-rust coating, as the plastic paint may not have completely covered the wire for the test in Figure 5.1.2. More tests could be conducted to verify whether the anti-rust coating in Figure 5.1.2 indeed insulates the wire from acid.

5.2 Characterizing the Effectiveness of Underwater Coating

The effectiveness of underwater coating can be monitored via a system’s open-circuit current, which is the steady-state current of a system at equilibrium, when no overpotential is applied. An example of an open-circuit current measurement is shown in Figure 4.3.6m, in which the self-healing of a scratch in the r-GO/oil coating can be visualized as a spike in the open-circuit current of the system, with the decay time of the spike corresponding to the visual healing time of the scratch. If the system is protected by the coating (i.e. no defects can be found along the coating) the open-circuit current of the system should be zero. Indeed, experiments not shown here showed an increasing current if the coating even exposed a very small area of metal.

With this in mind, one may still question whether painting over an unhealed scratch – as in the case where the scratch is too large for the coating to heal property – protects the metal from corrosion, or whether the underwater painting experiment performed in Figure 4.3.5c prevents corrosion despite preventing the formation of bubbles in a control (uncoated) aluminum wire.
To test this question, an open-circuit current measurement was performed on a coated aluminum wire that had been immersed into 1 M HCl, scratched, and then repaired via painting. In this case, the scratch was too wide for the coating to self-heal. The results are shown in Figure 5.2.1.

![Graph](image)

**Figure 5.2.1.** Open-circuit current measurement of an aluminum wire that was coated with r-GO/oil and then immersed into 1 M HCl before being scratched at around 213 seconds and then repainted at 240 seconds. Before the scratch is repaired manually, the current increases significantly, indicating that the metal is being corroded. After the scratch is repaired, the current goes back to zero, indicating that the wire is protected again.

As seen in the figure, the coating initially protects the metal from corrosion as indicated by a flat line near zero. Once the coating is scratched, the current increases and continues to increase
until the scratch is repaired – at which point the current again flatlines to zero. This experiment was designed such that the scratch covered an area that could be easily addressed with a paintbrush. For a larger scratched area, we would expect the current to show a decreasing trend with increasing coated surface area as the coating is painted onto the metal, before finally flatlining when the entire wire is coated entirely.

5.3 Aesthetics

While the results in our paper (62) showed that r-GO/oil can indeed protect a metal against corrosion and allow it to retain its mechanical properties, one potential concern of an anti-corrosion coating is how effectively it can maintain the aesthetics of a protected system, as appearance can be used as a qualitative indicator of the performance and state of a material.

Indeed, the visual inspection (i.e. appearance) of a corroded metal is often used as a preliminary means of diagnosing the form of corrosion that a metal has sustained and may influence the perception of and trust in a structure that has been exposed to a corrosive environment. For example, a superficial scratch in a large structure can potentially give the impression of a weak structure even if this is not the case. (63)

To show how the coating can protect a metal’s aesthetic appearance, a penny half-coated with r-GO/oil (Figure 5.3.1a and Figure 5.3.1b) was immersed in a solution of hydrogen peroxide (10 mL) and 10 M HCl (0.5 mL) for 10 minutes. After the coating is removed (Figure 5.3.1c), the right side of the penny retains its pristine appearance. Optical microscopy (Figure 5.3.1d) confirms that the corrosion was limited to the uncoated area.
Figure 5.3.1. r-GO/oil can preserve the appearance of the metals it protects. (a) A pristine penny (b) is half-coated with r-GO/oil and immersed in a solution of hydrogen peroxide and 10 M HCl. (c) After removing the penny from the solution and rinsing it with water, the right side of the penny maintains its pristine appearance. (d) Optical microscopy shows that corrosion was limited to the uncoated area.

5.4 Rheological Measurements

Our coating system can be characterized as a non-Newtonian fluid due to its different flow behaviors at different stresses. Thus, rheology – which is the study of the flow of matter – can help us more rigorously examine the behavior of our coating. In this chapter, various tests were conducted to probe into the self-healing mechanism of r-GO/oil.
5.4.1 Shear-Thinning Behavior and Thixotropy

Shear-thinning is a property of liquids in which a liquid exhibits lower viscosity (i.e. flows more) when it is subject to shear, with lower viscosities occurring with higher shear rates. The material is observed to return to a higher viscosity when the shear stress is lifted, with the time of restoration dependent on factors such as the relaxation of a thickening network. Thixotropy refers to the ability of a material to fully recover its initial viscosity after being subject to a shear force. (64)

![Graph showing shear-thinning behavior of a self-healing r-GO oil at room temperature.](image)

**Figure 5.4.1.** Shear-thinning test of a self-healing r-GO oil at room temperature. The self-healing oil exhibits shear-thinning behavior, as seen by the decrease of viscosity with shear rate.
r-GO/oil should be considered a shear-thinning system since its self-healing involves a drop in, and then subsequent recovery of, an initially higher viscosity. This behavior should contrast that of silicone oil, which is expected to exhibit the same viscosity regardless of the shear force applied due to its Newtonian nature. (65) To verify the shear-thinning nature of the r-GO/oil, the viscosity of a self-healing r-GO/oil at room temperature was measured at different shear rates using an Anton-Paar MCR 302 rheometer. As expected, the viscosity decreases with increasing shear rate, which is characteristic of shear-thinning liquids.

Another question related to the rheological behavior of r-GO/oil may be whether the system fully recovers its initial viscosity after it self-heals (i.e. shear-thins). Such behavior can be probed with the three interval thixotropy test (3iTT), which measures the structural regeneration of a coating using three intervals (66):

1. A very low shear rate is applied to the coating to simulate behavior at rest.
2. After some time, the very low shear rate is removed and a high shear rate is applied to simulate the structural breakdown of a coating as it is applied to a surface. This action significantly reduces the coating viscosity for a set period of time.
3. The high shear rate is removed and a very low shear rate is again applied to the coating to simulate the structural regeneration of the coating at rest, after it has been applied to a surface. A typical coating is expected to fully recover its initial viscosity.

In an ideal coating, the viscosity should exhibit an almost instantaneous recovery of its initial viscosity, as seen in Figure 5.4.2.
Figure 5.4.2. Ideal result of a three internal thixotropy test (3iTT). When a shear force is applied to a coating at rest, the coating viscosity is expected to significantly decrease (left dashed line). The coating is then expected to remain at this lower viscosity until the shear force is removed (right dashed line), at which point the coating returns to its initial viscosity. Adapted from Reference (66).

Since r-GO/oil can be considered a weak and purely colloidal gel, it is not expected to fully recover its viscosity as it may be very difficult to recover the gel’s initial microstructure after it has been sheared. Indeed, some studies have indicated that the reproducibility of thixotropy tests on colloidal gels may be compromised due to this irreversibility. (67)

A 3iTT test (Figure 5.4.3) was performed on a self-healing r-GO/oil system. In this test, which was provided as a preset on the Anton-Paar MCR 302 rheometer, the coating was subject to a shear rate of 1 s\(^{-1}\) for 25 seconds, before being subject to a shear rate of 100 s\(^{-1}\) for 50 seconds. The shear rate was then decreased back to 1 s\(^{-1}\) for the rest of the experiment.

As expected, following the removal of the higher shear stress at 75 seconds, r-GO/oil does not return to its initial viscosity, which is consistent with our expectations that the gel may not
recover its initial viscosity due to the irreversible breakdown of its network structure. Instead, the 
\( r\)-GO/oil exhibits an initial stress overshoot upon the cessation of the shear force, followed by 
gradual progression to a lower but steady final viscosity. This observation implies that only partial 
recovery may also occur when the coating is scratched, since a scratch removes some particles and 
may also cause local imbalances in network density when the coating levels to heal the scratch. 
The self-healing mechanism is explored more on page 98.

\textbf{Figure 5.4.3.} 3iTT test of a self-healing \( r\)-GO/oil system. After about 25 seconds, the coating at 
rest is subject to a much higher shear rate, causing its viscosity to drop significantly. After the high 
shear rate is removed, the coating recovers some of its initial viscosity.
5.4.2 Yield Stress

Yield-stress fluids are characterized by their tendency to flow when they are subject to a stress of some critical value called the yield stress. Otherwise, the fluid does not flow. Researchers have divided these behaviors into a liquid and a solid regime that are both characterized by a sharp deviation in rheological behavior (68).

In the case of r-GO/oil, the yield stress describes the minimum amount of force needed to break the bonds between the individual particles, allowing the liquid to flow. The yield stress is thus crucial to understanding the r-GO/oil’s self-healing behavior, since a minimum stress is required to break the network and initiate flow to self-heal the sample.

The yield stress can be measured a number of different ways, though the veracity of whether these measurements truly measure a well-defined yield stress has been the subject of intense debate. This can be complicated by the thixotropic nature of our sample, which may result in a yield stress that is not well-defined. Nevertheless, measuring the yield stress can provide insights on certain aspects of the r-GO/oil coating – such as its resistance to gravity (Figure 4.3.2b) and turbulence (Figure 4.3.2d).

The technique used to measure the yield stress follows the oscillatory measurements described in Bonn et al. (69). In particular, the yield stress can be characterized as the stress measured at the crossover between the elastic modulus G’ and the loss modulus G”, which is a well-defined point on the graph.

Thus, to measure the yield stress of a self-healing r-GO/oil system, oscillatory measurements were performed on the Anton-Paar MCR 302 rheometer by varying the shear strain
from 0.1 to 100 at a frequency of 1 rad/s. This measurement, shown in Figure 5.4.4, results in a yield stress of about 5 Pa for the self-healing oil.

**Figure 5.4.4.** Determining the yield stress of a self-healing r-GO/oil. The yield stress is taken as the stress $\sigma$ (blue line) measured at the crossover point of the elastic modulus $G'$ (black line) and the loss modulus $G''$ (red line), indicating a transition from solid-like to liquid-like behavior. The yield stress for this particular system is 5 Pa.

The implications of this measurement are summarized in the following sections.
5.4.2.1 Creep Resistance (Figure 4.3.2b)

A fluid that resists slipping down an angled or vertical plane must be able to counteract gravity. Since the yield stress must be exceeded before flow initiates in a sample, a creep-resistant fluid like the r-GO/oil should have a yield stress that counteracts gravity for a given thickness of liquid.

The stress experienced by a fluid on a vertical plane can be described by Equation 5.4.1 (70):

$$\tau_y = \rho gh$$

**Equation 5.4.1.** Relation between the yield stress of a fluid and the gravitational stress acting on a fluid when it is placed on an vertically inclined plane. If $\rho gh > \tau_y$, then the fluid slides down the plane.

In this equation, $\tau_y$ is the yield stress, $\rho$ is the density of the coating, $g$ is the gravitation acceleration, and $h$ is the thickness of the coating on a vertically inclined plane.

Using this relation, the maximum thickness of r-GO/oil that can be placed onto a vertical surface before the coating drips can be predicted by solving for $h$. Plugging in $\tau_y = 5$ Pa (measured in the previous section), $g = 9.81$ m/s$^2$, and $\rho = 0.82$ g/mL, the maximum thickness of the coating is found to be 0.6 mm. This value is consistent with measurements taken of multiple self-healing r-GO/oil coatings, which were found to be in the range of 0.4 – 0.6 mm.

5.4.2.2 Resistance to Water Turbulence (Figure 4.3.2d)

Similarly, the resistance of the oil to water turbulence can also be predicted by the yield stress, as the oil is able to resist being swept away by the turbulent flow. Such behavior can be attributed to the ability of the oil to resist flow.
A quick calculation can provide a first estimate on the resistance of the r-GO/oil to turbulent water. This behavior can be estimated via the drag force equation (Equation 5.4.2) (71):

\[
P_D = \frac{C_D V^2}{2}
\]

**Equation 5.4.2.** The drag force equation, which calculates the pressure \(P_D\) acting on a body of a certain cross-sectional geometry from the drag-coefficient \(C_D\) and the velocity of the fluid \(V\).

In this equation, \(P_D\) is the pressure exerted on a body of a certain cross-sectional geometry by a fluid, \(V\) is the velocity of a fluid, and \(C_D\) is the drag-force coefficient, which changes based on the cross-sectional geometry on which the drag force is acting.

The linear velocity of water estimated in the paper (62) was 0.5 to 1.0 m/s. Assuming a drag coefficient \(C_D = 1.9\) for a rectangular cross-section such as a metal wire, the pressure experienced by the metal wire is calculated to be from 0.24 to 0.95 Pa, which is about 5 to 20 times less than that of the yield stress. Therefore, although the wire appeared to experience a large turbulent force, the coating was not expected to be swept away from the wire. Using the same equation, the maximum velocity at which the water could theoretically flow before removing the coating would be 2.3 m/s, which is found at a \(P_D\) of 5 Pa (chosen to match the yield stress) and a \(C_D\) of 1.9.

Despite these promising results, it should be noted that such equations do not take into account many of the interactions that could be present in the r-GO/oil-and-turbulent-water system. For example, the drag-force equation assumes laminar, not turbulent, flow, and does not take into account the hydrophobicity of the r-GO/oil. Therefore, a more rigorous fluid-dynamics simulation could be performed in order to properly understand the behavior of the r-GO/oil in turbulent water.
5.5 Mechanism of Self-Healing

5.5.1 Self-Healing Versus Stability: Control Experiments with Grease and Oil

r-GO/oil’s ability to self-heal macroscale scratches is attributed to length-scale-dependent viscosity. That is, oil does not flow at the macroscale but does flow at length scales large enough to heal scratches of up to a millimeter in width. The control experiments described in this section are designed to show the behavior of oils that do not act like r-GO/oil for various reasons – including a highly viscous particle-thickened oil (grease), high-viscosity silicone oil, and a low-viscosity oil.

5.5.1.1 Grease

As seen in Figure 5.5.1, a commercially available high vacuum grease from Dow Corning (DC-150) was scratched with a pipette tip to determine its macroscopic self-healing capability. The high-vacuum grease, which was dyed with Oil Red O to improve visualization, is comprised of the particle thickener amorphous silica, silicone-based oils, and other ingredients, making it a particle-thickened oil that has a much higher viscosity (8830 Pa·s) than r-GO/oil (0.02 Pa·s).

Due to the grease’s much higher viscosity, the grease does not heal itself after it is scratched (Figure 5.5.1b) and remains scratched indefinitely on the macroscale (Figure 5.5.1c). However, similar to the r-GO/oil, grease is expected to protect a metal against corrosion due to its hydrophobicity and remain stable underwater due to particle jamming (Figure 4.3.3, right side).
Examining the self-healing capability of grease. (a) A commercially available high-vacuum grease from Dow Corning, which is dyed red for visualization, (b) is scratched with a pipette tip. (c) 15 minutes later, the scratch still remains unhealed, showing that the grease does not self-heal.

To test grease’s stability underwater, grease was spread onto an aluminum wire and immersed into 1 M HCl. The grease’s protection was then characterized with a potentiodynamic polarization curve, shown Figure 5.5.2. The current flatlines at zero, confirming that a thick layer of grease coated onto an aluminum effectively insulates the wire from an acidic environment.

This observation, however, does not necessarily preclude the idea that grease does not self-heal. Based on the same principle of length-scale-dependent viscosity described in the paper (62), the oil could potentially flow at much smaller length scales to heal defects at scales much smaller than a millimeter. However, due to a much higher concentration of particles, which would lead to a drastic increase in the interparticle forces within the grease compared to those in r-GO/oil, the base oil of the grease is not expected to move particles even if oil does flow into the scratch. This prevents the oil from self-healing.
5.5.2 Potentiodynamic polarization curve of an aluminum wire coated with grease, and then placed in 1 M HCl. The current flatlines at 0, indicating that the wire is insulated from the acidic environment.

5.5.1.2 High-Viscosity Oil

Contrasting the low-viscosity oil present in r-GO/oil and other particle-thickened oils, high-viscosity silicone oil contains a significant number of high-molecular-weight polymer chains, which may take a long time to rearrange and move. (72) High-viscosity silicone oil is therefore expected to exhibit similar viscosity at all length scales, and, similar to grease, will not heal when scratched. Furthermore, high-viscosity silicone oil is unstable underwater and will recede into a
droplet due to the compressive stresses induced by the tension present at the oil-water interface (Figure 4.3.2c), significantly hindering its applicability as a protective coating.

Such ramifications are demonstrated by the proof-of-concept experiment shown in Figure 5.5.3, where an aluminum foil boat experiment similar to that depicted in Figure 4.3.5 was conducted. The bottom of an aluminum boat filled with a blue dye leakage indicator was coated on the bottom with a silicone oil of viscosity 100 Pa⋅s and then placed on top of a bath of 1 M HCl (Figure 5.5.3a). While initially the bottom surface of the boat was completely coated with the high-viscosity silicone oil, the droplet receded within a few minutes (Figure 5.5.3b, red arrow) due to the tension present at the oil-water interface.

![Figure 5.5.3](image)

**Figure 5.5.3.** Retraction of high-viscosity silicone oil at the oil-water interface. (a) An aluminum boat is coated on the bottom with 100 Pa⋅s silicone oil and then placed onto a bath of 1 M HCl. (b) Although the boat is temporarily protected, the high-viscosity oil recedes into a droplet (indicated by the red arrow) within a few minutes, causing the acid to contact the metal surface.

### 5.5.1.3 Low-Viscosity Oil

The previous sections show that both grease and high-molecular-weight silicone oil cannot be used as self-healing liquids due to their high viscosity. However, since the mechanism of self-healing is highly dependent on the viscosity of the oil, can low-viscosity liquid be used to protect
oil without particle thickeners in the appropriate situations? One example could be oil that is only spread onto horizontally aligned surfaces so that creep resistance is no longer a factor.

Control experiments were performed by scratching two low-viscosity oils – silicone oil and octylidodecanol, a commercially available oil typically used for cosmetics – with the edge of a wooden stick under the microscope. The substrate is glass. As shown in Figure 5.5.4a and Figure 5.5.4b, low-viscosity liquid can heal scratches on the order of a few seconds or less, with healing times that are dependent on the width and depth of the scratch as well as the thickness of the coating. For example, much faster self-healing times were sometimes observed (Figure 5.5.5). These discrepancies could be attributed to the pipette “cutting through” the liquid to expose the bottom (or near-bottom) surface in the case of Figure 5.5.4.

It is expected that the self-healing behavior of r-GO/oil is more similar to the behavior shown in Figure 5.5.4 rather than Figure 5.5.5. In comparing r-GO/oil to the pictures in Figure 5.5.4, the height difference between the bottom and top edges of the scratch is expected to be more similar, since a particle network causes the liquid to support a larger thickness. The driving force behind self-healing is further discussed in Section 5.5.3.

However, low-viscosity liquids are limited in self-healing applications. Even if the surface is horizontal so that the need for creep resistance is minimized, the low-viscosity liquid must, at equilibrium, be of a height that allows the coating to level or self-heal, since too thin of a coating is not expected to self-heal effectively. Furthermore, as is seen for the case of high-viscosity oil, these low-viscosity liquids can also only be used in environments that do not cause them to retract (Figure 5.5.3) – for example, air – even though they can self-heal.
Figure 5.5.4. Scratching low-viscosity liquids under the microscope. Low-viscosity (a-b) silicone oil (viscosity = 0.02 Pa·s) and (c-d) octyldodecanol (viscosity = 0.04 Pa·s) were scratched with the edge of a wooden stick, which was chosen to cut “through” the liquids to the top of a glass slide. The scratches heal within seconds, which is consistent with the self-healing time of r-GO/oil.

Figure 5.5.5. Fast healing of low-viscosity oil. (a) A low-viscosity silicone oil (0.02 Pa·s) that is scratched (b) heals in less than a second. Contrasting Figure 5.5.4, the scratch does not “cut through” to the glass surface, allowing the scratch to be healed much more quickly. The mechanism of self-healing is further discussed in Section 5.5.3.
5.5.1.4 Summary

The experiments summarized in the previous sections provide comparisons to r-GO/oil, whose length-scale-dependent viscosity enables it to protect metal surfaces at any angle from corrosion, in both air and aqueous environments. Whereas r-GO/oil can resist both corrosion and creep while retaining its self-healing capability, however, low- and high-viscosity oils, including high-viscosity particle-thickened oils such as grease, can only exhibit either stability or self-healing. The results are summarized in Table 5.5.1.

<table>
<thead>
<tr>
<th>Type of liquid</th>
<th>Self-healing?</th>
<th>Stable underwater?</th>
</tr>
</thead>
<tbody>
<tr>
<td>r-GO/oil</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Grease (high-viscosity, particle-thickened oil)</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>High-viscosity silicone oil</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Low-viscosity silicone oil</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>

Table 5.5.1. Summary of Section 5.5.1. r-GO/oil can self-heal macroscopic scratches within seconds and is stable underwater due to particle jamming. In contrast, high-viscosity oils and low-viscosity oil only exhibit either stability or self-healing, even though all types of oils can protect a metal from corrosion due to their hydrophobicity.

5.5.2 Further Experiments on the Stability of r-GO/oil Underwater

As discussed in prior sections, r-GO/oil is stable underwater due to the presence of particles within the oil, which physically resist jamming. If this is the case, then r-GO/oil should be able to resist compression regardless of the concentration of particles within the oil – although lower-weight concentration r-GO/oils, which have a lower-density particle network, should have a lower resistance to compression.
To test this hypothesis, different weight concentrations of r-GO/oil (0.1 wt.%, 1 wt. %, 3 wt. %, and 5 wt. % r-GO capsules in 0.02 Pa·s silicone oil) were painted onto aluminum foil. Water was then added to the bath containing the painted substrate. (Figure 5.5.6). The particles were photographed 3 times: before adding water, just after adding water, and 1 hour after.

![Figure 5.5.6. Stability of r-GO/oil underwater. r-GO/oil of different weight concentrations (0.1 wt. %, 1 wt. %, 3 wt. %, and 5 wt. %) were painted onto an aluminum foil surface (shown in legend at bottom) before water was added to the containing bath. 3 wt. % and 5 wt. % r-GO/oil remain unchanged throughout the process, 0.1 wt. % and 1 wt. % oil are moved due to the introduction of water. The oil droplets remain stable on the surface after displacement.

As can be seen in the figure, the particles indeed prevent the oil droplet from retracting. For the three highest weight concentrations, the introduction of water does not cause the oil to recede, although water can move the oil around depending on the concentration of the particles (Figure 5.5.6, 0.1 wt. % and 1 wt. %). Furthermore, in the 0.1 wt. % suspension, multiple oil-containing droplets form, with the diameter of the droplet dependent on the layout of the particles within. A larger cluster or network, for example, enables a larger droplet to be stabilized.
Taken together, these results indeed confirm that the particles resist the compressive stresses resulting from the oil-water interface, and that a significant network is not required for such resistance to occur.

\[
P = \frac{2\sigma}{R}
\]

**Equation 5.5.1.** The pressure difference between the outside and inside of a spherical drop of liquid. Here, \( P \) is the pressure difference, \( \sigma \) is the surface tension, and \( R \) is the radius of the droplet.

The amount of pressure that the particles must resist can be estimated by calculating the pressure that a drop of liquid experiences across a liquid/gas or liquid/liquid interface (46). **Equation 5.5.1** shows the pressure drop across the interface of a spherical drop of liquid immersed in another gas or liquid. For this equation, \( P \) is the pressure difference, \( \sigma \) is the surface tension of the liquid, and \( R \) is the radius of the droplet. The surface tension of silicone oil increases by about 20 mN/m when it is placed in water (73). Therefore, a spherical drop with a radius of 0.01 m that is immersed in water would experience about 0.4 Pa more than the same drop left within air. This value is expected to change with the diameter of the droplet, with bigger droplets experiencing less of a change in pressure.

### 5.5.3 Driving Force of Self-Healing

#### 5.5.3.1 Role of Viscosity and Surface Tension

The mechanism of self-healing in the paper (62) is attributed to length-scale-dependent viscosity: upon rupturing the particle network comprised of r-GO microcapsules, the released oil can readily flow to heal the scratch, bringing with it capsules that can reform the network. This
phenomenon, as discussed in previous sections, can be rheologically probed by examining the yield stress and shear-thinning, thixotropic behavior of an r-GO/oil sample.

Figure 5.5.7. The different fates of a coating after it is applied to a surface. r-GO/oil will exhibit “good” self-healing if it is able to level onto a surface properly. Adapted from Reference (74).

However, these measurements do not necessarily answer a fundamental question – the driving force that is responsible for the healing of liquids. This question can be answered by looking at what happens to a liquid that contains surface irregularities, such as a film that has just been coated onto a substrate. These films are typically modeled as healing sinusoidal irregularities, as shown by the top picture in Figure 5.5.7.
Furthermore, depending on factors such as the composition and thickness of the coating, the film can undergo different processes after being coated onto a substrate (74), which are further depicted in Figure 5.5.7. In the figure, the branches labeled “leveling” and “dewetting” are relevant to liquid-based self-healing systems, since the coatings’ self-healing property relies on their ability to remain in a liquidlike state. Ideally, a self-healing coating should properly level after it has been scratched.

Leveling – and in fact, all of the pre-drying processes above – is significantly affected by viscosity and surface tension, which must be balanced in order to achieve acceptable leveling. Experimentally, an example of the “balancing act” between surface tension and viscosity is shown in Figure 5.5.8, which shows how the leveling of a powder coating is affected when viscosity or surface tension is changed.

According to Reference (74), viscosity and surface tension can lead to defect growth within the coating in several ways. Low viscosity, for example, enhances capillary-driven flow away from geometrical discontinuities such as corners and edges, and also promotes gravity-driven flow down the surface of the metal. Meanwhile, high surface tension can cause a liquid to form pinholes because of high contact angles, which often are the consequence of high surface tension, or surface
tension gradients, where Marangoni flow effects promote flow from areas of low to high surface tension.

**Figure 5.5.8.** Operability diagram for the leveling of a powder coating. A proper balance between viscosity and surface tension should be achieved for a coating to properly level (i.e. fall within the “region of acceptable flow”). Adapted from Reference (74).

However, surface tension gradients arising from differences in particle concentration do not appear to be responsible for the self-healing capability of r-GO/oil. The surface tensions of
both a bare silicone oil and an r-GO-capsule-thickened oil were compared via the capillary rise method (75), which relies on measuring the height that a liquid climbs in a capillary tube.

The surface tension can be estimated by Equation 5.5.2, which shows that the surface tension $\sigma$ is a function of the density $\rho$, the height of the liquid $h$, the acceleration due to gravity $g$, and $a$, the radius of the capillary tube.

$$\sigma = \frac{1}{2} \rho h g a$$

**Equation 5.5.2.** Estimating the surface tension $\sigma$ of a liquid from the capillary rise method. $\sigma$ is a function of the liquid’s density $\rho$, the height $h$ that the liquid rises within the tube, the acceleration due to gravity $g$, and the radius of the capillary tube $a$.

In this experiment, the edge of a glass pipette tip (diameter = 0.55 mm) was touched to a small bath of silicone oil (0.02 Pa·s, $\rho = 0.971$ g/mL) and the resulting height $a$ was measured to be 5.51 mm, yielding $\sigma = 14.44$ mN/m. The same experiment was then conducted on a 2.3 wt. % r-GO/oil with a density of 0.837 g/mL, which was determined by dividing the total weight of the capsules and oil by the total volume of the capsules and oil, assuming that the density of silicone oil is 0.971 g/mL. The r-GO/oil rose to a height of 7.33 mm, yielding a surface tension value of 16.55 mN/m. Therefore, an r-GO-rich phase of an r-GO/oil suspension is expected to have a surface tension that is greater than that of the r-GO-poor phase.

However, this result is counterintuitive to the self-healing nature of r-GO/oil since Marangoni flow drives liquid flow from lower to higher areas of surface tension, such that the oil should actually travel from regions having a low concentration of particles to those with a high concentration of particles. We suggest that while Marangoni flow could influence the self-healing
capability of r-GO/oil, it is not the dominant mechanism, since the surface tension gradient that would arise in low versus high weight fractions of r-GO/oil would act to oppose self-healing. (76)

5.5.3.2 Role of Capillarity in Self-Healing

The main driving force for self-healing instead appears to be the curvature induced at the surface of the coating when it is scratched (Figure 5.5.9). This curvature leads to a height difference and therefore a pressure difference $\Delta P$ that drives the coating to resolve the height difference, i.e. to heal. Furthermore, since the scratch tends to remove oil from the oil layer, the coating levels into a shorter height $h_2$. This appears to be the case both for neat oil (Figure 5.5.9, top) and self-healing r-GO/oil (Figure 5.5.9, bottom). It should be noted that surface tension, which acts to minimize the surface area of the coating, does play a role in this capillary-driven self-healing, even if the leveling of the coating is not dominated by surface tension gradients.

Indeed, the leveling of the coating is dominated mainly by capillarity rather than gravity. This is confirmed by calculating the capillary length $l$ for neat silicone oil which is given by Equation 5.5.3, where $\sigma$ is the surface tension of the liquid, $\rho$ is the density of the fluid, and $g$ is the gravitational acceleration:

$$l = \sqrt{\frac{\sigma}{\rho g}}$$

Equation 5.5.3. Calculating the capillary length $l$ of a liquid. Here, $\sigma$ is the surface tension of the liquid, $\rho$ is the liquid density, and $g$ is the gravitational acceleration.
The capillary length describes the length below which capillary effects dominate those of gravity. Therefore, capillarity dominates if the thickness of the liquid is less than \( l \). (46)

Plugging in the values for neat silicone oil (\( \sigma = 0.02 \text{ N/m}, \ \rho = 971 \text{ kg/m}^3, \text{ and } g = 9.81 \text{ m/s}^2 \)) yields an \( l \) of 1.44 mm. Although the exact value for the surface tension of r-GO/oil was not rigorously measured, it is expected to have a higher \( \sigma \) based on the qualitative results yielded from the capillary-rise experiment. This, combined with r-GO/oil’s lower \( \rho \), suggests that r-GO/oil should have a larger capillary length \( l \) than silicone oil.

Since the r-GO/oil equilibrates to a height of about 0.6 mm (see Section 5.4.2.1), self-healing does not appear to result from gravity, either. This is further confirmed by the observations that the coating can self-heal when it is flipped upside down and then scratched (not shown), and that the coating self-heals vertically tilted scratches from the sides rather than from top to bottom.

The results of Figure 5.5.9 are also seen in the clock experiment, in which r-GO/oil is cut many times at the same spot (Figure 4.3.7), r-GO/oil returns to a level height after it has healed. The observation that the r-GO/oil can be cut a limited number of times suggests (1) that oil and particles are removed with each swipe, as is indeed observed, and (2) that the number of times that oil can self-heal at the same location is limited by the width of the scratch and the height of the surrounding oil layer.

5.5.3.3 Role of Unjamming in Self-Healing

Another component of self-healing is the ability of the liquid to transport particles back into the point of scratch. Though this is certainly driven by the equilibration of concentration gradients
via diffusion and other processes, the rupture of the particle network plays a key role in the transport of particles during self-healing.

Figure 5.5.9. Leveling mechanism of r-GO/oil self-healing coating. Initially, an oil with a thickness of $h_1$ is scratched. The scratch induces a pressure difference at the highest and lower points of the scratch. This curvature difference causes the coating to level to a lower thickness $h_2$.

A proof-of-concept experiment showing the role of particle-network rupture in the self-healing of r-GO/oil is shown in Figure 5.5.10. In this experiment, two drops of r-GO/oil were pained side-by-side onto a piece of aluminum foil with a small gap separating them. Two oil bridges were then drawn onto the foil to connect the two r-GO/oil dots, though the bridges themselves were not connected to one another. Afterwards, the area near the top oil bridge was cut, causing particles to rush through the top oil bridge – contrasting the bottom oil bridge, where particles did not travel after the cut was made.

The experiment shows that diffusion alone may not be sufficient to induce the particle-thickened oil to self-heal – at least, within the timeframe of a few seconds as has been observed in the paper. If this were the case, simply introducing an oil bridge would introduce a concentration gradient between the two drops of r-GO/oil, causing the oil bridge to “self-heal” and fill with particles and connecting the two drops of r-GO/oil together.
Figure 5.5.10. The role of unjamming in self-healing. (a) Two drops of r-GO/oil were painted next to one another on a piece of aluminum foil, with a small gap separating them. Two oil bridges were then between the r-GO/oil to connect them. (b) The area near the top oil bridge was then cut (top blue arrow), causing particles to rush through the top oil bridge within a few seconds of the cut. In contrast, particles did not travel through the bottom oil bridge, which was left undisturbed or “uncut” (bottom blue arrow).

Rather, the act of scratching causes the particle network to collapse suddenly at a local point, allowing particles near the point of scratch to move into the scratch.

5.5.3.4 Aside on Computational Experiments

A number of groups, including Orchard (77) and Kumar (76), have shown that film irregularities in both Newtonian and non-Newtonian fluids can be modeled as sinusoidal disturbances whose rate of leveling depends on factors such as the height, viscosity, and surface tension of the coating and the width of the scratch. More quantitative experiments or simulations
could be performed to determine the maximum dimensions that can be healed within a time $t_0$, though such simulations are outside the scope of this thesis.

## 5.6 Biofouling

Biofouling is the undesired adhesion and growth of biofilms, such as those comprising of algae, bacteria, plankton, and other marine life, on underwater surfaces (78). Biofouling can negatively impact the properties of a number of marine systems – for example, by significantly increasing the drag acting on a ship and drastically increasing its power consumption requirements (79).

In a study conducted by Aizenberg et al., liquid-infused surfaces based on silicone oils have been shown to improve the biofouling characteristics of camera-guided medical instruments such as endoscopes, whose video quality can be significantly compromised through exposure to biological fluids (80). To show this, the authors infiltrated silicone oil of various viscosities into a glass surface that had been roughened with silica particles and a polymer. The oil acted as a transparent lubricant that prevented blood and mucus from adhering to the surface, improving the camera’s visual feedback.

In a similar manner, r-GO/oil could potentially be used to prevent the biofouling of metal surfaces underwater. In analogy to the liquid-infused surfaces, r-GO microcapsules within the silicone oil would act as the “roughened surface” into which low-viscosity silicone oil infuses. The low-viscosity silicone oil could then act as a lubricant that prevents biofilms from adhering to the surface of the metal.
Figure 5.6.1. Anti-biofouling capabilities of r-GO/oil. (a) (left) A glass microscope slide was wrapped with aluminum foil and then immersed into a water bath in which *C. vulgaris* (green algae) was cultured. (middle, right) After removing the slide from the bath, the algae remained adhered to the foil even after the slide was rinsed with water. (b) (left) Another microscope slide was wrapped with aluminum foil, coated with r-GO/oil, and then immersed into a water bath in which algae was cultured. (middle, right) After removing the slide from the bath, the algae was easily removed from the r-GO/oil-coated surface after rinsing it with water. This shows that algae does not strongly adhere to r-GO/oil.

To demonstrate the anti-biofouling capabilities of r-GO/oil, the following experiment was conducted. As shown in Figure 5.6.1, an aluminum-foil-wrapped glass slide was immersed in a bath of *C. vulgaris* (green algae), which was cultured following a 16 hours/8 hours light/dark cycle in Alga-Gro fresh water, a proprietary algae-growing medium provided by Carolina. The same was done for a glass slide that was wrapped in aluminum foil and then coated with r-GO/oil. After one week, the samples were removed from the bath and then gently rinsed under running water.
As can be seen by comparing the middle and right columns of Figure 5.6.1, the algae is rinsed off easily from the r-GO/oil-coated aluminum foil, whereas the algae remains adhered to the uncoated aluminum foil after rinsing. This observation indeed confirms that the r-GO/oil drastically decreases the adhesion of the algae to the metal surface, suggesting its potential application as an anti-biofouling oil layer.

5.7 r-GO/oil as Water Repellant

Since r-GO/oil is hydrophobic, the material system could potentially be used as a water-repelling layer that can be easily coated onto a metal surface. In this regard, a droplet of water placed onto the r-GO/oil should bead up and easily roll on the surface of r-GO/oil.

The water repellency of r-GO/oil is demonstrated in Figure 5.7.1. For this image, r-GO/oil was painted onto an aluminum-foil-wrapped glass slide. Then, water was dropped onto the r-GO/oil and the slide was tilted (Figure 5.7.1a). The water droplet is seen to roll towards the right edge of the r-GO/oil within a few seconds (Figure 5.7.1b). This droplet, furthermore, can be rolled in any direction that the slide is tilted. In a control experiment (not shown), the water droplet remained adhered to the surface of the aluminum foil even when the foil was tilted vertically, further confirming the water repellency capabilities of r-GO/oil.
Figure 5.7.1. Water repellency of r-GO/oil. (a) Water is dropped onto the r-GO/oil layer of an aluminum-foil-wrapped glass slide, which is then tilted. The water droplet begins rolling towards the direction indicated by the right arrow. (b) Within 1 second, the water has neared the right edge of the r-GO/oil.

This property of r-GO/oil suggests that r-GO/oil could be useful in a number of applications that require water repellency, including those where r-GO/oil protects a metal underwater. Water repellency, for example, may be a significant factor in r-GO/oil’s resistance to turbulent water (Figure 4.3.2d). The result could also indicate r-GO/oil’s potential application in reducing the drag force acting on an underlying metal.

5.8 Aside on the Wettability of r-GO/oil

r-GO/oil’s creep resistance can be attributed to four main properties: (1) the light weight of r-GO microcapsules, which do not significantly increase the weight of the oil layer; (2) the oil-absorption/thickening capabilities of r-GO microcapsules, which prevent r-GO microcapsules from separating from (i.e. sedimenting or floating to the top of) the silicone oil layer; (3) the
wettability of r-GO by silicone oil; and, perhaps most significantly, (4) the observation that silicone oil can spread easily on a number of surfaces, which is attributable to its low surface tension.

Indeed, silicone oil is observed to spread completely or significantly on several metals, including aluminum, copper, and steel. A contact angle experiment using aluminum (not shown) demonstrates that aluminum is completely wet by the silicone oil used to fabricate r-GO/oil. This behavior contrasts mineral oils or alcohols with large R groups, which form an observable contact angle with metals and are thus observed to adhere less well to a tilted metal surface (and e.g. sag) even if they self-heal and exhibit a yield stress.

Thus, the wettability of a metal (or other material) surface by the base oil of a self-healing liquid system should be taken into consideration when optimizing the system’s performance. This could be rectified through a number of ways if the oil in question cannot be substituted. For example, the metal surface could be chemically functionalized. If that is not possible, then a paint primer that adheres well to both the protected surface and the r-GO/oil (without compromising its self-healing capability) could be fabricated.

5.9 Conclusions

In this chapter, various properties and applications of r-GO/oil were further probed to provide a fuller picture of the self-healing oil’s capabilities. These are briefly described in the following bullet points.

- r-GO/oil electrically insulates the underlying metal from a corrosive environment, as demonstrated through potentiodynamic Tafel plots. In particular, r-GO/oil yields a similar plot to that obtained for a wire that has been completely isolated from a surrounding
solution. Regardless of the coating, however, care should be taken during such measurements to ensure that the plots indeed reflect the actual behavior of the coating rather than the presence of pinholes.

- Open-circuit current measurements confirm that painting r-GO/oil onto a metal surface underwater indeed protects it from corrosion.

- One possible consideration for a self-healing coating is whether it maintains the aesthetics of the protected metal. For example, appearance is commonly used to quickly diagnose an issue.

- Rheological measurements provide further insight into the stability of the coating, such as its resistance to creep and turbulence, as well as the mechanism of self-healing as the r-GO/oil recovers to a higher viscosity. Such measurements may also shed insights on the mechanical behavior of the coating at higher temperatures, which could potentially be probed more in the future.

- r-GO/oil was compared to different controls, such as a high-viscosity oil, a commercially available particle-thickened oil (i.e. a grease), and a low-viscosity fluid. Contrary to the other samples, r-GO/oil can both self-heal and remain stable underwater.

- The mechanism of self-healing is attributed to the leveling of the coating. The main contribution to leveling appears to be the curvature of the coating induced by the scratch, which causes capillary-driven flow towards the scratch.

- r-GO/oil could be used as a slippery layer to prevent biofouling. Experiments with green algae indicated that the slipperiness of r-GO/oil prevents algae from adhering well to the
surface of a coated metal layer. The organism can be easily washed off by rinsing gently with water.

- r-GO/oil can also be used to repel water. A droplet of water placed on an r-GO/oil-coated surface will roll easily on top of the oil when tilted. In contrast, a droplet of water placed on a metal surface such as aluminum will tend to stick to the surface of the metal even when it is tilted.

- r-GO/oil’s creep resistance is due in large part to the low surface energy of silicone oil, which enables it to spread completely on many surfaces.
6 Other Self-Healing Systems

Since r-GO/oil involves only two main “ingredients” – a thickener and a compatible (i.e. wettable) liquid – many liquid-based, self-healing systems should be obtainable from other combinations of thickeners and liquids, including those made from r-GO microcapsules and oils other than silicone oil. In particular, the main factors that seemed to enable the self-healing of r-GO/oil were: (1) silicone oil’s ability to wet r-GO microcapsules; (b) the r-GO microcapsules’ light weight, oil absorption, and, potentially, size range; and (c) the formation of a particle network. These criteria and others are discussed in the following sections.

6.1 Colloidal Gels and Network Formation

The dynamic, self-healing, thickened liquid can be characterized as a colloidal gel – which is defined a gel in which the thickeners are colloids (suspensions of nano- to micrometer sized particles) rather than polymers. The formation of this particle network in the case of r-GO/oil can be seen in Figure 6.1.1, in which optical microscopy was used to visualize the network structure of r-GO/oil at four different weight concentrations. Following the progression that characterizes many colloidal gels (81), r-GO microcapsules initially disperse as single particles in solution, which aggregate into flocs through attractive forces (see Figure 6.1.2, which shows that r-GO microcapsules can detach and reattach to other r-GO microcapsules as they are diffusing through a low-viscosity oil, indicating the presence of weak attractive forces between the particles). As weight concentration is increased, a percolating network forms throughout the gel consisting mainly of these aggregates. Finally, as concentration continues to increase, the network densifies into smaller pockets of oil.
Figure 6.1. Network formation of r-GO/oil. Optical microscopy was used to visualize the network structure of r-GO/oil at four different weight concentrations: 0.1 wt. %, 1 wt. %, 3 wt. %, and 5 wt. %. At very low weight concentrations (e.g. 0.1 wt. %), r-GO microcapsules remain as separate particles or aggregate into flocs. As particle concentration increases, however, the network percolates (1 wt. %) and then densifies further (3 and 5 wt. %).

The densification of r-GO/oil’s particle network is verified in Figure 6.1.3, where a 5 wt. % r-GO/oil is visualized at different magnifications under an optical microscope. In contrast to the 1
wt. % image of Figure 6.1.1, which shows much larger oil pockets in the sample, the network in Figure 6.1.3 is comprised of much smaller oil pockets. This appears to indicate that the network formation of r-GO/oil cannot be attributed to purely attractive forces between the particles, which should cause the particles to aggregate over time rather than form a stable, space-spanning network. For example, preliminary tests with carbon black (not shown) suggested that the suspensions do not self-heal nor remain stable when they are mixed with silicone oil at the same carbon volume fraction as that of a self-healing r-GO/oil. After a few days, the carbon black particles are typically observed to aggregate, significantly increasing the volume of oil that flows freely and decreasing the coating’s ability to self-heal effectively.

(a) (b) (c)

Figure 6.1.2. Attractive forces between r-GO microcapsules. (a) While diffusing through the liquid, particles are seen (b) detaching and (c) reattaching to other particles, suggesting the presence of weakly attractive forces between the particles.
Figure 6.1.3. Network densification of r-GO/oil. A 5 wt. % r-GO/oil is visualized under an optical microscope at different magnifications. The network is seen to comprise of oil pockets that are around 10-20 μm in length and width.

6.2 Examples of Self-Healing Particle-Oil Systems

Since particle thickening is a mechanism that is not limited to the r-GO/oil system, a number of other self-healing systems based on liquids and particle thickeners can be fabricated. A wide range of particles and oils were mixed together at different weight fractions and tested. Particle systems included silica in various form factors, carbon particles of various shapes and sizes, and commercially available polymers. Oil systems included sunscreen oils, mineral oil, vegetable oils, alkanes of varying chain lengths, and silicone oils. A selection of these systems is presented in this section, along with additional notes and comments.
6.2.1 Self-Healing Time Lapses for Two Different Systems

Two systems that successfully self-healed are shown below. These systems exhibit similar self-healing behavior to r-GO/oil – for example, healing within the same timescale and qualitatively exhibiting similar behaviors of particle transport.

6.2.1.1 Silica in Sunscreen Oil

The self-healing time lapse for a self-healing system of silica (VM-2270, Dow Corning, 5-15 microns particle size) in 2-ethylhexyl trans-4-methoxycinnamate, an oil commonly found in over-the-counter sunscreen, is shown in Figure 6.2.1. Similar to r-GO/oil, the oil first heals, bringing with it particles that reconnect the network. The flow of particle stops once the network has been reconnected.

![Figure 6.2.1](image)

**Figure 6.2.1.** Self-healing time lapse of silica particles in a sunscreen oil. After a scratch is made in the oil, the oil flows to heal the scratch, bringing with it particles that reconnect the network. The flow of particles continues after the edges of the oil have healed. The self-healing time is approximately 5 seconds.

6.2.1.2 Polymer Microspheres in a Long-Chain Alcohol

The self-healing time lapse for a system consisting of commercially available polymer microspheres and a long-chain alcohol, octyldodecanol. The polymer microspheres are obtainable as Expancel 461 DE 20 d70, a thermoplastic copolymer containing methyl acrylate,
acrylonitrile, and other ingredients. This system also exhibits similar self-healing behavior to r-GO/oil.

Figure 6.2. Self-healing time lapse of commercially available polymer microspheres in a long-chain alcohol, octyldodecanol. After a scratch is made in the oil, the oil flows to heal the scratch, bringing with it particles that reconnect the network. The flow of particles continues after the edges of the oil have healed. The self-healing time is approximately 10 seconds.

6.2.1.3 Potential for Transparent and Colored Coatings

One potential advantage of the silica and polymer self-healing coatings described above is that they either are transparent due to index matching, or white (see Figure 6.2.3 for an example of a white self-healing coating). The latter type of coating could potentially yield colored self-healing coatings when combined with the appropriate oil or polymer dye.

Figure 6.2.3. Snapshots taken of a self-healing coating that is composed of commercially available polymer microspheres and octyldodecanol, whose self-healing time lapse on the microscale is also depicted in Figure 6.2.2. The white color of the coating suggests that either the polymer
microspheres or the oil could be combined with appropriate dyes to yield differently colored coatings, extending the aesthetic range of the coating.

6.2.1.4 Note on Self-Healing Capabilities Versus Other Properties

It should be noted that though the particle-oil systems described in this section can self-heal, further tests should be conducted to see whether they can demonstrate all the other properties exhibited by r-GO/oil in the original paper (62). As mentioned in Section 5.8, r-GO/oil’s creep resistance can be largely attributed to the low surface energy of silicone oil, which enables it to wet many surfaces. In contrast, many other oils exhibit a higher surface tension as well as a noticeable contact oil on metal surfaces, which would hinder the creep resistance capabilities of these self-healing oils.

6.2.2 Viscosity vs. Concentration Curves for Several Self-Healing Systems

The viscosity versus concentration curves for three different self-healing systems containing silicone oil – r-GO/oil, hollow silica microspheres fabricated using the procedures described in (58), and hollow poly(o-methoxylaniline) microspheres fabricated using the procedures describe in (59) – are shown in Figure 6.2.4. The concentrations and viscosities of self-healing systems are indicated by the dashed orange line.
Figure 6.2.4. Concentration versus viscosity for three different particle-silicone oil systems. The dashed orange line, which intersects with the r-GO/oil at 5 wt. % and the other systems at higher weight percent, indicates the compositions at which self-healing coatings were fabricated. This data may suggest that self-healing coatings can be fabricated at a range of concentrations just below the gel point of the coating systems, although more work is needed to properly assess this behavior for a wider range of liquids and particle compositions.

Notably, self-healing systems could potentially be fabricated within a narrow range of particle concentrations, i.e. before the viscosity begins increasing dramatically at the gel point of the system (82). Such behavior was also observed to be the case for the non-silicone-oil system depicted in Figure 6.2.3 (viscosity vs. concentration graph not shown), though more work needs to be done to verify that this observation is indeed the case for a wide range of particle and oil systems.
6.2.3 Effects of Wettability, Density, and Oil Absorption on Particle Thickening

Several patterns were observed while we were attempting to identify self-healing systems. These notes are described in this section.

6.2.3.1 Wettability

Particle thickening cannot occur if the oil cannot wet the particles in question. An example is shown in Figure 6.2.5, which shows hydrophilic perlite spheres on a layer of 2-ethylhexyl trans-4-methoxycinnamate, a type of oil that is commonly used in over-the-counter sunscreen products. Here, the oil is dyed red for visualization. As can be seen in the figure, the oil does not wet the particles and so cannot be thickened by them.

Figure 6.2.5. Perlite microspheres are insoluble in 2-ethylhexyl trans-4-methoxycinnamate, a type of oil used in sunscreen. The oil is dyed red to aid visualization.

6.2.3.2 Density and Oil Absorption

Density plays a large role in the stability of the self-healing coating. If the density of the particle does not match that of the oil, for example, lightweight particles are expected to float to
the top of the oil while heavier particles are expected to sediment. Thus, an initially self-healing coating may separate into particle-rich and particle-poor phases.

Density can also impact the self-healing capability of the coating. For example, silica has a higher density ($\rho = 2.65 \text{ g/cm}^3$) than silicone oil ($\rho = 0.971 \text{ g/cm}^3$). As shown in Figure 6.2.6, a scratch in a coating containing porous silica does not induce the paint to self-heal. This is most likely because the particles was too heavy for the oil to carry back into the scratch, even though the freed oil was able to flow back into the scratch. In this case, the oil may still be able to remain pinned to the surface if the dimensions of the scratch are below the oil’s capillary length. However, the oil at this spot may still be unstable underwater (Figure 4.3.3).

Indeed, though some coatings made from silica do self-heal, such as the one in Figure 6.2.1, many were not as effective at self-healing as, for instance, the polymer-oil system in Figure 6.2.3, and either did not carry particles back into the point of scratch or carried fewer particles back into the point of scratch. The flow of the oil also induced by the scratch may play a role in determining how much of, and whether, the particle network can reconnect. Other silica-based coatings did not self-heal after a certain time had elapsed, possibly due to sedimentation within the coating layer.
Figure 6.2.6. An coating made of porous silica and oil at a self-healing concentration does not self-heal after it sustains a scratch. This may be attributed to the heavier weight of the silica particles compared to that of the oil, which are not carried with the oil when it flows back into the scratch.

Density can typically be offset by the wettability and oil absorption capability of the particle itself, which allows the particle to effectively match the density of the oil. For instance, the r-GO microcapsules in this work were estimated to have a density of about 0.12 g/cm$^3$, which is about 8 times lower than that of silicone oil. However, since the microcapsules have a high oil-absorption capability (about 960 mL silicone oil/100 mL r-GO microcapsules, data from experiment) and are highly wettable by silicone oil, the liquid can enter and surround the particles to stabilize them. Similar strategies of using hollow spheres with a hole for liquid entry (such as is the case for the polymer in Figure 6.2.4 when viewed under SEM) can also be performed.

Wettability also appears to play a major role, as the commercially available polymer used in Figure 6.2.3 has a density of about 0.06 g/cm$^3$ – about 14 times lower than that of octyldodecanol’s (ρ = 0.838 g/cm$^3$) – and does not have nearly as high of an oil absorption capacity as the r-GO
microcapsules (54 mL linseed oil/100 mL Expancel, data provided by company), yet appears to form a relatively stable self-healing coating. One caveat is that a very slight oil layer is observed at the bottom of the bottle, suggesting that the Expancel suspension may still not be as stable as r-GO/oil.

6.3 Summary: Characteristics of Self-Healing Systems

A number of particle systems were tested by dropping dyed particle-oil dispersions on water in two different tests.

For this test, arrays of petri dishes were filled halfway with water. Then, specific amounts (200 μL, 400 μL, 600 μL, 800 μL) of different types of oils dyed with Oil Red O were added to the surface of the water. Afterwards, 9.4 mg of particles were added to the surface and the systems were left overnight.

A second set of tests were conducted in which an array of microwells were filled halfway with water. Then, 200 μL of oil were added to the wells and 9.4 mg sample were added. If the oil is absorbed, then the same test was conducted with 400 μL, etc.

These tests enabled us to quickly characterize the wettability and oil-absorption capabilities of many particle systems, and to identify potential self-healing systems. Particle systems included Expancel polymer microspheres and hollow glass bubbles (diameter: 2-120 μm) and perlite microspheres (10-120 μm) from Cenostar Corporation; a hollow polymer-silica-titanium complex (28 μm), hydrophobic silica shells, cellulose beads, and nylon spheres (TR-1) from Kobo Products; silica silylate and DC 9506, a type of silicone particle, from Dow Corning;
fumed silica (Aerosil R805 and R202); multi-walled carbon nanotubes; activated carbon (large particle size); and talc.

The oils tested included silicone oil, light mineral oil, vegetable oil, 2-ethylhexyl methoxycinnamate, and 1-octanol.

Other systems, including wood chips from American Wood Fibers (Standard Softwood Grade and Hardwood grade, both with a size range of 75 to 125 microns) and expanded graphite sonicated in oil, were also tested but were not included in these high-throughput tests.

Based on the high-throughput tests, the following characteristics were found to be conducive to the formation of self-healing liquid systems.

**Figure 6.3.1.** Examples of (a) good versus (b) bad wettability of particles. (a) Silica shells in 200 μL silicone oil. (b) Perlite microspheres in 400 μL sunscreen oil. It should be noted that good wettability does not necessarily lead to a successful self-healing coating.

- Good wettability of particles by the oil, which can be tuned by the hydrophobicity of the particle surface (e.g. through surface functionalization). An example of good versus bad wettability is seen in **Figure 6.3.1.** Particles that exhibited no or partial wettability (e.g.
hydrophilic hollow glass bubbles in vegetable oil) with an oil were observed to disperse poorly within the oil matrix.

Indeed, particle dispersion appears to be significant to self-healing systems, as particles that exhibited lower oil absorption than our r-GO microcapsules in silicone oil, but which exhibited high dispersive capability in oil (as gauged by the formation of a network rather than aggregated flocs) when they were mixed with the oil later were able to form successful self-healing systems. This was found, for example, in the case of Expancel microspheres in octyldodecanol. It should be noted, however, that Expancel is seen to float within the oil, leaving a thin oil layer on the bottom – most likely due to its low oil-absorption capabilities. Thus, Figure 6.3.2 shows an example of good versus bad dispersibility. (a) consists of a hollow polymer-silica-titanium complex in 800 μL 1-octanol, while (b) consists of silica shells in 200 μL silicone oil. Well dispersed systems are seen to exhibit a more uniform color, as seen in (a).

- Good dispersion of particles within the oil, as seen by the lack of particle aggregation, are conducive to the formation of self-healing systems. An example of good versus bad dispersibility is shown in Figure 6.3.2, which shows that well dispersed systems show a more uniform color. Carbon black particles and carbon nanotubes added to oil were found to have good wettability and good oil absorption (at least 400 μL of oil for 9.4 mg
particles). However, these systems tend to aggregate after a certain period of time, most likely due to van der Waals forces and the high surface contact area between the spheres.

- Particle size exceeding roughly 1 micron in diameter but below roughly 30 microns in diameter, as observed from experiments – though more tests should be conducted to determine whether an exact size threshold exists for creating self-healing systems. As noted by Kapur et al. (83), who developed a model for predicting the yield stress of zirconia suspensions in water, the theoretical maximum yield stress is inversely proportional to the particle size \( d \), suggesting that larger particle sizes would proportionally decrease the yield stress of the system and require either a much thinner liquid or a much higher loading to achieve the same stability.

The Expancel system consists of particles in the size range of roughly 15-25 \( \mu \)m in diameter is able to successfully create self-healing systems. However, wood chips and glass beads, which contained spheres of much higher diameters (about 100 \( \mu \)m) were not able to self-heal even if they were wetted by the oil. On the other hand, much smaller systems like carbon black particles (which are roughly 5 nm in diameter) were found to not self-heal even though they were able to thicken the oil.

Based on rheological tests, the following characteristics were found to be consistent for self-healing systems:

- A finite yield stress of 14 Pa or below for a silicone oil or thickened silicone oil system.

According to Equation 5.4.1, a fluid remains adhered to a vertically inclined surface if its weight, described by \( \rho gh \), is equal to or less than the yield stress \( \tau_y \). Thus, the yield
stress can be predicted by the ratio $\tau_y / \rho h = g = 10 \frac{m}{s^2}$. It can be seen from this expression that $\tau_y = g$ when $\rho h = 1$, and the value of $\tau_y$ should be equal to 9.81 Pa if the liquid is to remain adhered to the surface. The order of magnitude of this prediction agrees with experiments, which mostly fall in the 1-10 Pa range.

For this case ($\rho h = 1$), the following calculation can be done to predict yield stress. Since either oil-absorbing, lightweight particles or density-matched particles are expected to remain suspended in a given oil solution, the maximum density of the system is the density of the fluid itself. In this case, the density of silicone oil is 971 kg/m$^3$. Thus, the thickness of the system is given by $h = 1/(971 \text{ kg/m}^3)$, or about 1 mm.

Further criteria can be extrapolated by calculating the capillary length of silicone oil, which is the maximum thickness of the fluid. This maximum thickness is calculated to be roughly 1.4 mm, meaning that $\rho$ must be equal to or greater than 690 kg/m$^3$ in order for the liquid to remain adhered to the surface. The “greater than” case is compensated for by a lesser thickness. Thus, the range of densities that should work for silicone and thickened silicone oil systems is 690 – 971 kg/m$^3$, and the range of heights from approximately 1 mm to 1.4 mm.

It can also be seen that this expression also allows for lower $\tau_y$ (if $\rho h < 1$) and higher $\tau_y$ (if $\rho h > 1$). However, even if both maximum values for $\rho$ and $h$ are used (in the case that the system is purely liquid and that the liquid is at its capillary height), the maximum
value of \( \rho h \) is 1.4, meaning that the maximum value of \( \tau_y \) is 14 Pa. Thus, the predicted values for yield stress lie below 14 Pa, which is indeed consistent with experiments (which lie in the range of approximately 1 to 10 Pa, with a few results in the \( 10^{-1} \) and \( 10^{-2} \) Pa range). The yield stress cannot be 0, as this corresponds to a freely flowing liquid.

- Viscosity near the gel point of the particle-oil system as seen in a viscosity-concentration curve. This viscosity of self-healing system is typically found near or at the inflection point of a viscosity-concentration curve, with a small range of concentrations able to make self-healing systems.

In order to create a self-healing system for underwater applications or any applications requiring creep resistance, the following characteristic is helpful:

- \( 0^\circ \) contact angle of the particle-thickened liquid on a metal substrate, both in air and underwater. This enables the self-healing oil to remain wetted to the surface despite its orientation in different environments.

In summary, the following characteristics are helpful in fabricating self-healing systems with application in both air and underwater environments.

- Good wettability of particles by the oil
- Good dispersion of particles within the oil, as indicated by a more uniform suspension color
• Particle size exceeding roughly 1 micron in diameter but below roughly 30 microns in diameter (although more work should be done to determine whether there is an exact size threshold)

• A yield stress of below 14 Pa but above 0, which enables the particle-liquid system to resist creep

• Viscosity near the gel point of the particle-oil system as seen in a viscosity-concentration curve

• 0° contact angle of the particle-thickened liquid on a metal substrate, both in air and underwater

6.4 Conclusions

In this chapter, various self-healing coatings were presented and discussed, following an overview of the properties that could allow for the fabrication of self-healing coatings. The main takeaways of this chapter are listed below.

• Self-healing coatings can be characterized as colloidal gels whose particle network densifies (i.e. forms smaller oil pockets) as concentration increases, rather than forming larger aggregates that cause the network to destabilize over time. The formation of the particle network is attributed in part to weakly attractive forces that enable the particles to detach and reattach, though further work is needed to properly understand the forces involved in gel formation.

• Self-healing coatings are not limited to r-GO/oil and can be made from a wide variety of particles and liquids. Two systems – silica in a sunscreen oil and commercially available
polymer microspheres in a long-chain alcohol – are presented as examples of this materials-agnostic aspect of self-healing. These coatings enable other capabilities as well, such as the potential to make transparent coatings or coatings whose color can be tuned with the appropriate dye.

- Self-healing coatings appear to be fabricated at a narrow range of concentrations found just below the gel point in a concentration versus viscosity graph.

- Further considerations are provided for the user who wishes to make a self-healing coating. For example, oil absorption enables particles to effectively match the density of the oil they are in, which helps stabilize them within the liquid medium. Wettability can also play a large role in the stability of the self-healing coating.

- Self-healing coatings share a number of properties, including complete wettability and viscosity characteristics.
7 Future Work

Though much work has been done to identify different self-healing systems and their potential applications, future projects can further diversify the understanding and applications of self-healing, liquid-based coatings.

7.1 Further Probing the Properties of Self-Healing Systems

Previous sections provided an overview of the properties that could enable the successful fabrication of a self-healing system, including wettability and oil absorption. However, more work can be done to provide a full picture of why these particle thickeners work. Doing so would enable potential users to easily identify coatings for their particular situation.

7.1.1 Potential Application of Polymers as Self-Healing Coatings.

A few control studies were conducted to see whether e.g. a low concentration of polymers could lead to the fabrication of self-healing coatings. These experiments, which were performed with gelatin/water and polymethylmethacrylate/water, seemed to indicate that polymers exhibited a high degree of crosslinking and so could not self-heal. Indeed, one of the main arguments that we posit for using particles is that the “oil pockets” within polymers may be of too low of a size-scale to heal millimeter-level damage.

However, this may not be applicable to all polymers. Thus, future studies could test factors that could be relevant to the fabrication of self-healing coatings such as the degree of crosslinking, the molecular weight, and the degree of hydrophobicity of the polymer.
7.1.2 Effect of Wettability for Particle-Oil Systems

Along the same lines as varying the degree of hydrophobicity for polymer systems, selected particle systems could be chemically functionalized to varying degrees and then mixed with an oil to fabricate self-healing coatings. The effectiveness of self-healing, measured qualitatively on the bulk scale by eye and through the microscope to determine whether the particle network reconnects, could be gauged. If a more systematic study is required, perhaps a simple apparatus could be developed to scratch the coating with the same width and force every time.

7.1.3 Effect of Size and Shape of Particles

The effect of size and shape on the formation of self-healing coatings could be further probed. In terms of size, we could vary the size of the particle but retain the same volume fraction as that used for self-healing, as well as the composition. For example, activated carbon from the same batch but of different sizes could be mixed with silicone oil and tested. It is expected that smaller sized particles will prevent self-healing at the same volume fractions, since the particles should experience a significantly larger contact area on their surfaces. This is thus expected to increase the attraction between particles – which, if large enough, can potentially prevent the particle network from being broken and carried over by the oil after the coating is scratched.

Furthermore, the form factors of the particles (e.g. rods, grains, plates, spheres) could be varied as they are expected to influence both the viscosity of the coating at different weight fractions and the self-healing of the coatings. For example, rods may realign with the self-healing cut, which may enable faster self-healing but less effective thickening.
7.1.4 Effect of Oil Absorption

One hypothesis for the effectiveness of r-GO/oil is the microcapsules’ high oil absorption, which enables the oil to effectively match the density of the liquid medium despite having drastically different density (see Section 6.2.3.2). Thus, processing a particle so that it better absorbs oil – such as by improving its wettability and/or introducing pores/pockets into the particle through chemical or physical processes – or comparing the capabilities of different particles having the same oil absorption, could help provide further clues on the role of oil absorption in self-healing.

7.1.5 Fabricating Colored Coatings

Although r-GO/oil is an effective self-healing system, it is limited aesthetically by its black color. As stated in Section 6.2.1.3, the ability to make white and transparent coatings could enable the fabrication of coatings with a color other than black. In this vein, oil-compatible dyes can be selected to fabricate self-healing coatings. Rheological measurements should ensure that the behavior of the dyed oil, and thus that of the dyed coating, should at least qualitatively match the behavior of r-GO/oil.

7.2 Further Applications of r-GO/oil and Other Self-Healing Systems

Much of the work on self-healing systems to date has been their potential application in localized corrosion. However, r-GO/oil and other self-healing systems based on oil could also be applied in a wide range of applications that utilize their water-repelling capabilities (Section 5.7),
their slipperiness (Section 5.6), and their unique deformation capabilities as a microscopically liquid system. Since r-GO/oil has been established, it may be prudent to begin these studies with r-GO/oil before exploring their applicability to other self-healing systems. Thus, this section focuses on applications for r-GO/oil.

### 7.2.1 Probing r-GO/oil at High Temperatures

The capabilities of r-GO/oil and other self-healing systems could be probed at different temperatures, especially those relevant to specific applications. Rheology tests combined with other qualitative measurements could provide a much fuller picture of the mechanisms behind r-GO/oil’s behavior at different temperatures.

For instance, though the r-GO/oil is a promising self-healing system, all previous results were conducted at room temperature. Since underwater applications can span a range of temperatures, the rheological behavior of r-GO/oil was probed at different temperatures ranging from 25 to 100 °C. Some rheological tests are shown below.

The shear-thinning behavior of the oil was measured on the Anton-Paar MCR 302 rheometer (Figure 7.2.1) through oscillatory measurements, where the apparent viscosity $\eta^*$ was measured at shear rates ranging from 0.1 to 100 rad/s.
Figure 7.2.1. Shear-thinning behavior of an r-GO/oil system at different temperatures. Contrary to expectations, the apparent viscosity $\eta^*$ of the oil increases with increasing temperature.

As expected, the oil exhibits shear-thinning behavior at all temperatures, as indicated by the decrease in apparent viscosity with increasing angular frequency. Contrary to our expectations, however, the shear-thinning liquid exhibits *increased* apparent viscosity with increasing temperature for all shear rates measured. Typically, liquids exhibit the opposite effect – decreased viscosity with increasing temperature, which is attributed to the ability of the molecules within the liquid to move more rapidly.
To further probe this behavior, oscillatory measurements of r-GO/oil were taken. Both $G'$ (Figure 7.2.2) and $G''$ (Figure 7.2.3) of r-GO/oil increase with increasing temperature, which at first glance appears contradictory. The increasing loss modulus, which characterizes r-GO/oil’s liquidlike behavior, seems to indicate that r-GO/oil flows more readily at higher temperatures. However, the increasing elastic modulus, which characterizes r-GO/oil’s solidlike behavior, appears to suggest that the r-GO/oil becomes more rigid with increasing temperature as well.

The increased $G'$ may be explained by a network of increasing stiffness, which is possibly related to the increased tendency of colloids to aggregate at higher temperatures. (84, 85). The r-GO/oil’s increased stiffness should thus be verifiable by the yield stress, which measures the difficulty of breaking apart the bonds in the network, with increasing yield stress corresponding to a higher stiffness.

Thus, a series of yield-stress measurements on a self-healing r-GO/oil system was performed. The results are summarized in Table 7.2.1. Please note that the yield-stress value for r-GO/oils occurs within a range depending on, amongst other factors, the concentration of microcapsules within the network, the homogeneity of the mixture, the shear history of the sample, and the ability of the network to recover its microstructure.

Furthermore, as seen in Figure 7.2.3, the loss modulus of the r-GO/oil also increases with increasing temperature, suggesting that the oil within the system flows more readily, as is typical of liquids that are heated. This increased tendency of oil to flow at higher temperatures is further visualized in Figure 7.2.4, which shows an r-GO/oil that has been subject to increasing temperatures. Upon close inspection, the edge of the oil travels farther from the edge of the network.
as temperature is increased, suggesting that the oil indeed flows more readily at higher temperatures. Taken together, these results agree with the trends observed in both $G'$ and $G''$.

**Figure 7.2.2.** The elastic modulus $G'$ of an r-GO/oil taken at different temperatures. The elastic modulus increases with increasing temperature.
Temperature (°C) | Yield stress (Pa)
---|---
25 | 0.027
50 | 0.34
75 | 1.1
100 | 2.3

Table 7.2.1. Yield-stress measurements of an r-GO/oil at different temperatures. The yield stress increases with increasing temperature, implying that the network stiffens as heat is added.

Figure 7.2.3. The loss modulus $G''$ of an r-GO/oil taken at different temperatures. Like the elastic modulus seen in Figure 7.2.2, the loss modulus increases with increasing temperature.
Figure 7.2.4. Optical microscopy of an r-GO/oil taken at (a) 25 °C, (b) 50 °C, and (c) 75 °C. Close examination of the picture reveals that the liquid layer moves outward with increasing temperature. The blue line provides a reference point for showing the movement of the edge.
In addition to the results described below, r-GO/oil could be scratched in heated water and re-evaluated for its stability underwater, its creep resistance, and anti-corrosion properties. At higher temperatures, for example, oil is expected to exhibit less viscosity, which may allow for faster self-healing at the cost of reduced creep resistance. These results could also be compared to a self-healing coating based on lower-viscosity silicone oil at room temperature, with the viscosity of that oil matching the viscosity of the heated, initially higher-viscosity oil at higher temperatures. Such a study would enable us to further see whether temperature indeed plays a role in influencing the microstructure of r-GO microcapsules.

7.2.2 Probing r-GO/oil at Low Temperatures

The effects of lowered temperature (i.e. near or below freezing) could also be interesting to probe for r-GO/oil and other self-healing systems. For example, a thickened oil could provide a means of preventing ice from nucleating and thus growing on the surface of a metal (86). The base oil should furthermore have a freezing temperature lower than that of the minimum temperature needed for the application. Silicone oil, for example, should be applicable for outside winter applications due to its low pour point of about -100 °C.

When this is accomplished, a preliminary experiment can be conducted on an e.g. r-GO/oil-coated surface versus uncoated surface to qualitatively assess the anti-frost capabilities of r-GO/oil. Afterwards, a more systematic study can be conducted in the following manner: An r-GO/oil-coated surface is placed in a chamber with controlled humidity and temperature for a set amount of time. By visualizing the coverage area of the ice for different conditions, we can probe the time and length scales of ice nucleation on r-GO/oil.
7.2.3 Utilizing the Deformation Capabilities of r-GO/oil

Since the r-GO/oil is still largely liquid, it can be used as a deformable but stable layer on a number of surfaces. Experiments showed, for example, that the r-GO/oil can stretch to about 5 times its original length (Figure 7.2.5). This deformation capability of r-GO/oil could find potential application as a protective layer for pieces that are difficult to coat completely, such as those that might be found in electronics.

![Figure 7.2.5.](image)

**Figure 7.2.5.** The deformation capability of r-GO/oil. (Left) r-GO/oil was painted onto a rubber band, (right) and then stretched. r-GO/oil can stretch up to 5 times its original length without breaking due to its largely liquidlike character.

7.3 Conclusions

This chapter describes several future experiments to further probe the basic science and applications of self-healing, liquid-based coatings – namely by conducting systematic studies on various types of particles, probing different temperature conditions, and utilizing the liquid-like layer that r-GO/oil and other self-healing systems provide.
8 References

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