POLYURETHANE-GRAPHENE NANOCOMPOSITES FOR CORROSION-RESISTANT
COATINGS

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ABSTRACT

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Corrosion is a prevalent concern throughout the world, causing significant monetary and safety concerns. Research has been dedicated to developing cost-effective solutions for corrosion that will also meet increasingly stringent environmental regulations. The recently discovered nanomaterial graphene has been proposed as a potential component in anticorrosion technology due to its strong air and water barrier properties. However, graphene is a relatively expensive, difficult to synthesize material. By incorporating it into nanocomposites, its properties can be exploited even at low concentrations. Previous work has been conducted involving the preparation of anticorrosive polystyrene-graphene nanocomposites; these materials were found to be effective long-term barriers for corrosion.

Although the polystyrene-graphene nanocomposites were effective in impeding corrosion on metal substrates, their ease of application left some room to be desired. Painting a substrate is currently the most commonly used method for corrosion prevention, but polystyrene is not typically used in paints due to its incompatible properties with these formulations. If somehow anticorrosive nanocomposites could be incorporated into coatings, the ease of application could be greatly improved. Polyurethanes are commonly used as binders for coatings, so the fabrication and characterization of polyurethane-graphene nanocomposites for use in anticorrosive coatings was chosen as the premise for this project.

A number of different physical and chemical nanocomposites were prepared using lab-synthesized graphene and graphene oxide, as well as commercial graphene. Both two component waterborne and solventborne polyurethanes were employed, and nanocomposites were prepared by both physical and chemical methods. The nanocomposites were coated on cold-rolled steel panels and subjected to salt spray testing in conjunction with control panels in order to analyze their anticorrosive properties. Nanocomposite films were also characterized to determine how their thermal and mechanical performance compared to control coatings.

Despite promising studies that supported the anticorrosive capabilities of graphene, this project found that graphene may not be ready for integration into viable coatings systems. Its complex structure and properties made uniform dispersion throughout polyurethane seemingly unachievable, no matter how many different formulations were attempted. To prepare well-dispersed polyurethane-graphene nanocomposite coatings, new components would definitely be required to prevent aggregation of graphene. These components may already be commercially available, but most likely would have to be developed specifically for these formulations. Without these components, the anticorrosive properties of polyurethane-graphene nanocomposites cannot be accurately studied.

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1. Introduction

1.1. Corrosion Issues

In 2012, annual corrosion costs in the United States exceeded \$1 trillion dollars.¹ Worldwide, these costs are more than double this amount and are continuing to grow year after year. In addition to the monetary burdens of corrosion, other problems can be observed as well. Structures and machinery that corrode are typically more susceptible to failure, which can lead to serious consequences. In 2013, an oil pipeline in eastern China suddenly exploded, killing 62 people and injuring many more.² The monetary cost of this explosion was over \$125 million dollars, and significant parts of the city were destroyed. This incident was determined to be a result of a corroded underground pipe, which was slowly leaking oil into the surrounding area and producing vapors that could easily be ignited by a tiny spark. To prevent incidents like this, a large amount of money and research are being invested to combat the expensive and dangerous problem of corrosion.

1.1.1. The Mechanism of Corrosion

In order to find solutions for corrosion, its mechanism of action must be fully understood. Corrosion refers to the oxidation of a metal, resulting in the formation of metal oxide on the surface.³ This is a destructive process, as the bulk metal material is depleted to create the oxide. Metals can corrode through contact with a number of different oxidizing agents, most commonly oxygen. Specifically, the corrosion of iron will be investigated, as the subject of this study is cold-rolled steel. Steel is an alloy composed of iron, carbon, and other elements that serve to enhance its strength. Cold-rolled steel tends to be more susceptible to corrosion than hot-rolled steel, but it is also stronger, making it a necessary

component of many applications.⁴ When the iron in steel corrodes, this damage can affect the entire substrate.

Corrosion of iron occurs in the presence of water and is composed of simultaneous redox reactions.⁵ Iron atoms dissolve into water at the surface of the substrate, leaving a net negative charge in the metal. Corrosion often occurs at a location where the metal is stressed, allowing the metal ions to more easily break free of the surface. This is an oxidation reaction occurring at the anode, and is shown in Equation 1.

Next, the electrons released upon oxidation of iron react with oxygen gas at the surface of the metal. This is a reduction reaction occurring at the cathode, shown in Equation 2.

The overall reaction for this process is shown in Equation 3.

Rust, or iron oxide, is formed when the Fe^{2+} ions generated in Equation 1 react with oxygen, as shown in Equation 4.

The overall equation for the corrosion of iron can be found in Equation 5.

Corrosion occurs more readily when salts are present, as these increase the conductivity of water, allowing corrosion reactions to occur at a more rapid rate.⁴ Soluble salts can also aid in the formation of insoluble corrosion products such as ferric hydroxide on the substrate, further damaging it. The presence of salts is also believed to impede corrosion by certain mechanisms, for example, available sodium ions in solution can form sodium

hydroxide, which has been observed to break down iron oxide layers on steel. In addition to salt concentration, pH is also an important factor in corrosion. Corrosion occurs most rapidly in acidic conditions; however, between pH values of 4 and 10, the rate of corrosion is independent of pH. Above pH 10, the rate begins to decrease.

1.1.2. Current Corrosion Prevention Methods

There are already a few corrosion prevention options that are implemented today. Material choice can be a big factor for preventing corrosion, as certain metals and alloys are far more prone to corrosion than others. However, using a different material is not always an option, depending on performance requirements and monetary limits. Sacrificial anodes can also be employed; these have more negative electrochemical potential than the material they are protecting, which means that they will corrode preferentially in corrosive conditions. These are often used for applications such as ship hulls, but they have to be inspected and replaced relatively frequently, which can be time consuming. They also alter the surface of the material they are placed on, which can be an issue for certain applications.

The most common method of corrosion prevention is coating or plating the surface of the metals.⁶ Outdoor architectural paints can help prevent corrosion, but under harsh environmental conditions (such as high-salt environments), they become ineffective after a short period of time. The Golden Gate Bridge uses this type of paint as a corrosion barrier, but it must be painted year-round to prevent rust and the corresponding structural damage. Coating surfaces with primers containing high concentrations of zinc can also provide cathodic protection against undesired corrosion.⁴ These primers react to form zinc oxide, which can act as a barrier coating in these areas. Unfortunately, zinc is a fairly expensive material, and these primers require 50-90 weight percent zinc to be effective. Additionally,

since they are formulated above the critical pigment volume concentration (CPVC), the primers typically lack the ductility to be used on many steel substrates, and can crack or flake after application, rendering them ineffective for corrosion inhibition.

Certain passivating pigments can also be added to coatings to help provide anodic protection for metals. Chromate and lead salts are effective passivating agents that have been commonly employed in coatings.⁴ The corrosion inhibition mechanism for these agents is fairly complex and is not completely understood; the pigments are believed to work by forming a protective oxide layer around anodic sites, stopping further corrosion reactions from occurring at the anode. Unfortunately, both chromate and lead salts are toxic, and many have been banned for use in coatings. Other nontoxic alternatives have been developed, but these tend to not be as effective as chromate and lead pigments.⁷

1.1.3. The Call for New Anticorrosion Technology

Although there have been some effective developments in terms of anticorrosion technology, most of these developments do not offer feasible, inexpensive long-term solutions that also meet increasing environmental regulations. In order to save money and prevent equipment failure, researchers are looking into safer, more cost-effective solutions that will fight corrosion over long periods of time. Carbon-based anticorrosive technology is especially prevalent in current studies.

1.2. Graphene and Graphene Oxide

1.2.1. Structure and Properties

Graphene is a promising nanomaterial known for its highly ordered structure and excellent conductive properties. It is currently considered to be the world's strongest and thinnest material, and has potential applications that range from long-lasting car batteries

to superabsorbent aerogels. The unique properties of graphene lie in its structure, which consists of a two-dimensional monolayer of carbon atoms sp^2 -bonded together in a hexagonal matrix, as shown in Figure 1. The pi electrons are delocalized inside the matrix, and can travel freely throughout the structure. This makes graphene a zero-bandgap semiconductor, which means that it does not need electrical potential in order to be conductive.⁸ This property results in extremely high conductivity and has sparked an immense amount of interest in graphene-related research and technology.

Figure 1. The structure of graphene.

The tight-knit, hexagonal structure of graphene creates a matrix that is impermeable to most atoms and molecules, including water and oxygen. This unique barrier property has been proposed for use in a number of different applications, especially for water purification and desalination. Holes of a specific size can be introduced into the matrix, allowing for only molecules of a specific size to travel through and excluding all others. Graphene has also been studied as a corrosion barrier. By blocking the interaction of water and oxygen molecules at the surface of a metal, graphene could potentially inhibit oxidation in that location.

Due to its size and structure, graphene has poor solubility in a number of solvents.⁹ It is very hydrophobic and will rapidly precipitate out of a variety of solutions, forming aggregates. To obtain stable, homogenous dispersions of graphene, surface modification techniques or dispersing additives are usually required. Surface modification of nanomaterials tends to be a tedious and expensive procedure, and dispersing additives introduce extra costs into formulations. For this reason, many experiments are conducted with graphene oxide, a close counterpart to graphene that retains many of its desired properties and is much more dispersible in a wide variety of solvents.

Graphene oxide is composed of graphene sheets containing various oxygen functional groups including alcohols, carboxylic acids, and epoxides. These groups are primarily located on the outer edges of the graphene oxide sheets, but there are also some distributed across the surface of the sheets.¹⁰ The functional groups disrupt the delocalized electron network, which makes the conductivity of graphene oxide much lower than that of pure graphene.¹¹ The conductivity can be restored by reducing it, eliminating a number of these functional groups and forming a more uniform sp^2 hybridized network. The barrier properties of graphene oxide are comparable to those of graphene; although functional groups on graphene oxide produce defects in the structure, the overall structure remains relatively impermeable to oxygen and water molecules. For this reason, graphene oxide could also be explored as a potential anticorrosive additive for coatings.

1.2.2. Current Synthetic Methods

One of the main burdens to graphene-related research is its availability. Most current production methods for graphene are extremely expensive, have low yields, or produce low-quality graphene that would not be useable for most applications. Almost all

commercially available graphene is produced by three main methods: chemical vapor deposition, ultrahigh vacuum annealing of silicon carbide, and reduction of graphene oxide obtained from graphite.

The most commonly used commercial method for graphene synthesis is chemical vapor deposition (CVD). A schematic of this can be found in Figure 2. For this method, a substrate is heated in a reaction chamber in the presence of gaseous hydrocarbons.¹² At high temperatures, the carbon atoms become dissociated and form graphene on the surface of the substrate. When performed correctly, this procedure produces high quality graphene films; however, it is relatively expensive and has a low yield. For this reason, it is not economically feasible for large-scale graphene production. In addition, it is often extremely hard to separate the graphene films from the substrate; most current separation methods cause extensive damage to the graphene structure. For this reason, the films usually must be left on the substrate, preventing them from being incorporated into many different applications.

Figure 2. Synthesis of graphene using chemical vapor deposition.¹³

Ultrahigh vacuum annealing of silicon carbide is another commercial method for graphene synthesis. This method currently produces the highest quality graphene sheets available; however, it is also very expensive. This process involves heating silicon carbide at high temperature and low pressure.¹⁴ Graphene precipitates from the surface of the substrate, retaining the size and shape of the substrate. This is a small-scale production method and is not practical for producing large amounts of graphene for incorporation into most commercial applications.

1.2.3. Modified Hummer's Method

A third graphene production method that has been explored involves the reduction of graphene oxide, which can be synthesized in bulk through a variety of mechanisms. One such mechanism is called the Hummer's Method, and is illustrated in Figure 3. This method exploits the structure of the inexpensive material graphite, which is essentially composed of stacked layers of graphene, held together by Van der Waals interactions. These layers can be broken apart by oxidation with potassium permanganate and sulfuric acid, forming individual graphene oxide sheets decorated with a variety of functional groups. The functional groups include carboxylic acids, hydroxyl groups, and aldehydes. The graphene oxide is highly soluble in water and will gel at high concentrations. Residual ions from the oxidation treatment can be removed through extensive washing steps or by precipitation.

Figure 3. Schematic for preparation of graphene using a modified Hummer's Method.

Graphene oxide can be either thermally or chemically reduced to obtain graphene. One concern of thermal annealing is that the process will introduce additional functional groups onto the sheets rather than fully reducing them. The structures of the sheets can also be damaged at high temperature, impacting the properties. One huge benefit of thermal reduction is that it is typically a much more cost-effective procedure than chemical reduction. A few different conditions can be used to chemically reduce graphene oxide; however, perhaps one of the safest and most inexpensive of these is hydroiodic acid at elevated temperatures. For this method, dried graphene oxide is suspended in concentrated hydroiodic acid and rapidly stirred in an oil bath at 55 °C. As the reaction proceeds, the reduced graphene oxide sheets become more insoluble in solution, eventually precipitating out at the top. The precipitate can then be collected by filtration and washed using deionized water and ethanol to remove residual ions.

1.3. Polyurethanes

Polyurethanes are a class of polymers prepared using step-growth polymerization, typically between alcohol and isocyanate groups. Polymer units are joined together by carbamate (urethane) linkages. Polyurethanes can be made from a huge range of starting materials and tailored to fit many specific applications, from flexible foam cushions to high performance adhesives. Although they are mainly used for construction and transportation, they have a huge role in the coatings industry, functioning as binders as well as additives for paints.

1.3.1. Precursors

To make polyurethanes, isocyanate groups are reacted with other functional groups, forming urethane linkages. Isocyanate groups have the formula “R-N=C=O” and are

extremely electrophilic. They react rapidly with nucleophilic compounds such as amines and alcohols, and will also readily react with water. Different reactions result in the formation of different types of bonds, which lead to different polymer properties.

Polyurethanes can be made from aromatic or aliphatic polyisocyanates.¹⁵ Figure 4 shows examples of both types. Aromatic isocyanates are less expensive than aliphatic isocyanates, but they can also cause yellowing in the final polymer, which can be undesirable for coatings. Aliphatic isocyanates are more expensive but typically produce more durable polyurethane coatings. Aromatic isocyanates react more rapidly than aliphatic isocyanates, which can be considered either a positive or a negative attribute depending on the application.

Figure 4. Hexamethylene diisocyanate (HMDI) and toluene diisocyanate (TDI), two of the most common isocyanates used for polyurethane production. HMDI is an aliphatic isocyanate, while TDI is an aromatic isocyanate.

Polyisocyanates are often classified by their functionalities, or the number of isocyanate groups found on each molecule.¹⁵ Higher functionality polyisocyanates tend to react and form crosslinked networks more rapidly than lower functionality polyisocyanates, resulting in shorter cure times. Shorter cure times produce harder, more brittle films, which can be less than ideal for anticorrosive applications. If a coating cracks and flakes off a substrate,

that region of the substrate will be susceptible to corrosion and subsequent degradation. Even so, longer cure times are also not always ideal for certain applications. If a coating does not cure fast enough, it can undergo sagging, potentially opening up defects in the film where corrosion can occur. For this reason, polyisocyanates must be carefully tailored to achieve the final film properties desired for specific applications.

Isocyanates are also extremely toxic compounds; this is probably one of the largest drawbacks of making and using polyurethanes. These compounds can be inhaled or absorbed through the skin and have high toxicity even at small concentrations. Among other things, they can cause severe respiratory problems and skin irritation to exposed areas.¹⁶ They are also classified as chemical sensitizers, meaning that they can lower a person's sensitivity after exposure, causing adverse reactions (such as asthma attacks) upon future encounters with the compounds. People who work with isocyanates on a fairly regular basis have to be extremely careful to avoid exposure to these compounds, as sensitization could severely limit their careers in addition to the health risks.

Typically, polyisocyanates are reacted with polyols to make polyurethanes. Often, the polyol is supplied in a prepolymer resin, which helps increase the ease of application and facilitates rapid crosslinking. Polyols can be made from polyester, acrylic, or polyether-based components.¹⁵ As with polyisocyanates, polyols come in different functionalities which can affect reactivity and crosslinking. Because of undesirable side reactions that can occur between isocyanate groups and other formulation components, the concentration of isocyanate groups in a polyurethane formulation is often slightly higher than the concentration of hydroxyl groups.

1.3.2. Polymerization Mechanism

Figure 5 outlines the various reactions involved in polyurethane polymerization. When an isocyanate group reacts with an alcohol group, this forms a urethane linkage. This is the primary polymerization mechanism for polyurethanes, but other side reactions can also occur. Isocyanates can react with urethane groups to form allophanates. If there is water present in the reaction mixture, isocyanates will react with it to form urea and carbon dioxide. Carbon dioxide and amides are formed when isocyanates react with carboxylic acid groups. The production of gas can be useful for making polyurethane foams, but bubbles can be extremely detrimental to coatings. Often defoaming agents are utilized when preparing polyurethane coatings to prevent this from occurring.

Figure 5. Reactions involved in polyurethane formation.

1.3.3. Use in Coatings

Polyurethanes are an integral component in many types of commercial coatings.¹⁶ They are commonly used as binders in architectural paints due to their high pigment wetting capabilities, strength, solvent resistance, and mechanical properties. Urethane linkages are resistant to chemicals and hydrolysis, and hydrogen bonding between polyurethane chains forms a stable physical network, enhancing the durability and keeping pigments in place. Polyurethane systems tend to be much more environmentally friendly and safer than other types of binders. Additionally, they can be formulated from many different components, allowing them to be tailored to fit the requirements of almost any desired application.

1.3.4. Solventborne 2K Polyurethanes

Polyurethane polymerization must take place in some form of solvent to ensure that the different reactive groups are able to fully interact with one another. Due to the strong reactivity of isocyanates, finding a proper solvent for polyurethane polymerization can be a challenging task. Alcohols, carboxylic acids, amines, and water can't be used as solvents for traditional polyisocyanates, as this would cause the solvents to be incorporated into the polyurethane. Organic, typically volatile solvents are used to make 2K solventborne polyurethane coatings. Volatility can be tailored to influence the pot life and cure time of the materials.

Solventborne 2K polyurethane film formation is a relatively straightforward mechanism. These systems begin film formation as soon as the two components are mixed together and crosslinking occurs through the reaction of polyols and polyisocyanates. As solvent evaporates, reactive groups are brought closer together, allowing further interactions to occur. The rate of crosslinking is largely controlled by the functionalities of

the reactive groups and their locations on the molecules. Solvent choice also plays a role in the rate of reaction and also the integrity of the final film.

1.3.5. Waterborne 2K Polyurethanes

Although solventborne polyurethane coatings can have excellent properties and be tailored to fit a variety of applications, the solvents used to prepare them can often pose problems. One large issue is cost. Typically, a large amount of solvent is required to dissolve the various components, and it simply evaporates once the coating is applied. Another issue is the environmental impact. Lately, there has been a huge push from consumers to produce green products with as low of an environmental impact as possible, and the government also imposes regulations to enforce this. Many of the solvents used in solventborne coatings are volatile organic compounds (VOCs), meaning that they participate in the creation of ground level ozone.¹⁷ It is difficult to reduce VOC levels in solventborne polyurethane coatings, as many non-VOC solvents also interact with isocyanates. For this reason, new 2K polyurethane technologies has been developed which use water as the dispersion medium.

Because traditional isocyanates react with water, different components are required to prevent this mechanism. 2K waterborne polyurethanes are typically made using hydroxyl-functional prepolymers (polyols) and hydrophilically-modified polyisocyanates. The polyols contain hydrophilic groups to help keep the polyurethane dispersed throughout the aqueous medium during polymerization.¹⁸ Polyisocyanates for 2K waterborne polyurethanes are typically based on either hexamethylene diisocyanate (HMDI) or isophorone diisocyanate (IPDI). Isocyanates with low viscosities are required in order to

initiate effective polymerization with the hydroxyl groups on the polyol component rather than with the solvent.

To prepare 2K waterborne polyurethanes, the polyol and polyisocyanate components are mixed together. Extremely high shear is applied to the mixture, breaking down the hydrophobic isocyanate phase into small droplets.¹⁶ The polyol prepolymer particles surround the isocyanate droplets, forming associations with the hydrophobic regions of the isocyanates. This helps disperse the isocyanates in the aqueous medium and also limits isocyanate reactions with water molecules in the dispersion. Finally, the isocyanate groups react with hydroxyl groups on the polyols to form urethane linkages. Crosslinking occurs inside these droplets, forming a continuous film as water continues to evaporate. 2K waterborne polyurethane film formation is a much more complex mechanism than that of 2K solventborne polyurethanes.¹⁷

Even with modified precursors, waterborne polyurethanes still can have some drawbacks in comparison to their solventborne counterparts. It is impossible to completely eliminate all reactions between isocyanates and water, which means that some carbon dioxide gas will still be generated during polymerization. There are a couple of solutions to this issue. Defoamers can be added to the formulation, the viscosity of the system during drying can be controlled using rheology modifiers, and polyurethane films can be baked after curing to dissipate bubbles. Curing films at higher temperatures can also decrease these side reactions.¹⁷ The increased hydrophilicity of waterborne polyurethanes can cause some additional problems. Waterborne polyurethanes tend to have poorer water resistance than their solventborne counterparts, which can limit their anticorrosive capabilities. To

address this issue, isocyanates with higher NCO functionalities are typically utilized to make waterborne polyurethanes.¹⁷

1.4. Nanocomposites

Nanocomposites are multiphase materials in which at least one phase has at least one dimension less than 100 nanometers.¹⁸ They can be prepared by either physical or chemical methods.²⁰ Nanocomposites are useful materials because they can integrate the physical and chemical properties of nanomaterials into other bulk materials, such as polymers. Since nanomaterials have a huge surface area to volume ratio, they are able to affect the properties of bulk materials even at very low concentrations, which is a positive attribute when considering their relatively high cost.²¹ The surface area to volume ratio can also make nanomaterials extremely hard to disperse in a number of different solvents and substrates. This one of the main problems that arises when making polymer-based nanocomposites. If the nanomaterial is not well dispersed throughout the polymer matrix, desired nanomaterial properties will not be incorporated into the final product.¹⁹ In addition, poor dispersion or precipitation can introduce defects into the composite, degrading its properties so that the composite is actually worse than the pure polymer.

1.4.1. Methods of Preparation

1.4.1.1. Physical Method

The classification of physical or chemical nanocomposites is based on how the nanomaterial is integrated into the matrix of the material. For physical method nanocomposites, the nanomaterial is mixed into the matrix and dispersed through intermolecular forces. Different dispersing aids can be incorporated during preparation to facilitate better interactions between the components during drying; however, selection of

proper surface chemistries for the various components is necessary to ensure even nanomaterial dispersion and integration throughout the matrix. If the nanomaterial is not properly dispersed, its properties will not be retained in the final product.

1.4.1.2. Chemical Method

For chemical method nanocomposites, nanomaterials are integrated into the matrix through chemical bonding. This typically requires modification of the surface of the nanomaterials to give them functional groups that can bond with the matrix material. This modification can often be time-consuming and expensive; however, it can also help facilitate much better interactions between the nanomaterial and the matrix, resulting in better distribution. Some nanocomposites cannot be prepared without using surface-modified nanomaterials; interactions between the nanomaterial and the bulk are too poor to achieve adequate dispersion. Additionally, sometimes nanomaterials are soluble in wet nanocomposites but precipitate out during drying, causing defects in the final material.

1.5. Previous Work Involving Graphene for Corrosion Resistance

1.5.1. Pure Graphene

Many studies have been conducted to investigate the anticorrosive properties of graphene. Some studies found that it impeded corrosion, while others found it enhanced corrosion. Researchers at UC Berkeley used CVD to coat copper foils with a single layer of graphene, then observed the corrosion of the coated substrates in conjunction with pure copper foils.²² They found that the coated substrates resisted corrosion better than the native substrates over short periods of time (a few hours) at both room and elevated temperatures. However, they found that the coated substrates actually corroded more

extensively than the controls after a month at room temperature, showing that the addition of graphene actually facilitated corrosion rather than impeding it.

The researchers hoped to determine how graphene worked as a short term but not a long term corrosion barrier. They found that in short term experiments, the impermeable structure of graphene prevented the diffusion of water and oxygen molecules at the surface of the copper. However, in long term experiments, some oxygen and water molecules were able to get through defects in the graphene, reacting with the surface at those areas. They also found that the conductivity of the graphene maintained charge transfer between the surface of the metal and the bulk, allowing electrochemical corrosion to continue unhindered. Because corrosion began in regions where there were defects in the graphene structure, corrosion occurred unevenly on the substrate, contributing to increased stress on the substrate and oxide. In some regions of stress, cracking occurred, opening up more areas for corrosion to occur.

Based on the results of this study, applying single layers of pure graphene by CVD would not be a viable method to prevent corrosion. Additionally, the costs and size limits involved with the CVD process would never make this a viable option for anticorrosive technology, even if it was an effective method. Materials manufacturers would not be able to use CVD to coat the huge steel beams required for bridges, for example. Ultrahigh vacuum annealing of silicon carbide would produce a higher quality of graphene with far less defects than CVD; however, the finished product could not be effectively adhered to substrates. Graphene produced by Hummer's Method has more defects than CVD, so this would likely cause even more extensive corrosion than was observed for the coated substrates in the UC Berkeley study.

1.5.2. Polystyrene-Graphene Oxide Nanocomposites

Other studies have focused on incorporating graphene and graphene oxide into polymers to make anticorrosive coatings. As previously mentioned, nanomaterials can affect the properties of materials even at very low concentrations, which would be useful for conserving costs and other resources. In addition, a polymer matrix would also provide additional corrosion protection, as it would be even more difficult for oxygen and water molecules to enter through graphene defects with a surrounding polymer phase present. Also, the incorporation of graphene into a polymer typically also improves the thermal and mechanical properties of the polymer, which can play a role in corrosion protection.²³

Researchers were able to successfully prepare nanocomposites made from polystyrene and 2 weight percent modified graphene oxide.²³ They used graphene oxide modified with both *p*-phenylenediamine and *p*-phenylenediamine/4-vinylbenzoic acid; these functional groups formed chemical bonds with polystyrene to help fully incorporate the nanomaterial into the polymer matrix. They studied the anticorrosive properties of the coatings using electrical impedance spectroscopy and found that the nanocomposites were significantly better at preventing corrosion than pure polystyrene. Using TGA and DMA, they also found that the thermal and mechanical properties of the nanocomposites were superior to those of pure polystyrene, due to reinforcement of the polymer matrix by graphene oxide.

1.6. Premise of Research

The current research project, polyurethane/graphene-based nanocomposites for corrosion resistant coatings, was largely motivated by the study conducted by Yu, *et al.*²³ Although this study was successful in producing nanocomposites that significantly impeded corrosion, these materials could not be easily applied to a large range of substrates

requiring corrosion protection. If graphene could somehow be incorporated into coatings that could simply be painted onto a surface using standard painting equipment, the range of substrates that could benefit from this technology would be vastly expanded. For this reason, polyurethane was chosen as the nanocomposite matrix. Binders for high performance coatings are typically made from polyurethane, so an effective nanocomposite binder could be easily incorporated into a number of different coating formulations.

2K solventborne polyurethanes were the first type of polyurethanes that were explored in this study. Solventborne polyurethanes typically resist corrosion better than waterborne polyurethanes because they are less permeable to water.¹⁷ The first batch of nanocomposites prepared were made from graphene oxide dispersed in tetrahydrofuran (THF), hexamethylene diisocyanate (HMDI), and a commercial polyol, Joncryl 910. These components can be seen in Figure 6. These nanocomposites were prepared by a chemical method; the intention was for isocyanate groups to react with both polyol and graphene oxide functional groups in order to fully integrate graphene oxide into the polymer matrix. As the graphene oxide had initially been prepared in water, solvent replacement techniques were used to ensure that no water remained in the dispersion to react with isocyanate groups.

Figure 6. Components of the first batch of nanocomposites.

Hexamethylene diisocyanate (HMDI) is an aliphatic polyisocyanate that is commonly used as a basis for many highly functionalized, commercial polyisocyanate formulations. Due to its small size and the primary carbon location of its isocyanate groups, it reacts very rapidly. Joncryl 910 is a commercial hydroxy ethyl acrylate polyol. It consists of hydroxyl groups attached to a prepolymer matrix, facilitating easy crosslinking and controllable pot life. Both HMDI and Joncryl 910 are soluble in THF, and THF is one of few common organic solvents that doesn't react with isocyanates. Unfortunately, THF is also a volatile organic compound (VOC). These compounds are increasingly being restricted in coatings formulations; for this reason, coatings companies are trying to eliminate them completely from their formulations. Additionally, commercial coatings formulations typically are not made using isocyanate monomers, because these tend to be more volatile and therefore more dangerous than polymeric isocyanates.²⁴

Graphene oxide precipitated out of the first batch of nanocomposites during drying, and THF was found to be a relatively poor solvent for the nanomaterial. The second batch of nanocomposites used a more developed 2K solventborne polyurethane formulation, complete with a variety of solvents and also a commercial dispersing aid to help facilitate better graphene dispersion throughout the polyurethane matrix. The various components of this formulation can be found in Figure 7. The dispersing aid, BYK-9077, contains chemical groups which attach to the surfaces of carbon black pigments to help keep them dispersed in wet polyurethane formulations. This dispersing mechanism is known as steric stabilization.²⁵ The same component was effective in dispersing carbon nanotubes in other experiments, so it seemed to be a reasonable choice for dispersing graphene in this project. Thermally reduced graphene was used in place of graphene oxide in this formulation, and

the isocyanate component was replaced by Desmodur N3300, which is a commercial aliphatic polyisocyanate composed of a HMDI trimer. The number of isocyanate functional groups varies from molecule to molecule; however, the average functionality is 3.5.²⁶

Figure 7. Components of the second batch of nanocomposites.

Although visually the second batch of nanocomposites appeared to be well-dispersed, these coatings also turned out to be ineffective corrosion barriers, which was determined to be due to poor dispersion of graphene on a microscopic level. In addition, there was also some concern regarding whether or not the thermal reduction of graphene oxide was effective. For this reason, the third batch of nanocomposites were prepared using chemically reduced graphene. The same polyisocyanate and polyol as the second batch of nanocomposites were used in this formulation; however, a different solvent was selected. Solvent choice was thought to be the reason for poor graphene dispersion in the previous formulation, so a variety of solvents were tested before dimethylformamide was selected as the most effective for dispersion of graphene. The components of the third batch of nanocomposites can be found in Figure 8.

Figure 8. Components of the third batch of nanocomposites.

Even with extensive testing and analysis to pick a solvent for the third batch of nanocomposite, graphene was observed to precipitate out of the coating during drying, ultimately causing failure of the coating. There are many different solvents that can effectively disperse graphene; however, most of these also react with isocyanate groups, making them unusable for 2K solventborne polyurethane formulations. However, graphene oxide is highly dispersible in water, so the choice was made to prepare the next batch of nanocomposites using a 2K waterborne polyurethane formulation and graphene oxide. If the nanomaterial could remain well dispersed throughout the formulation during curing, its anticorrosive contributions to the coating could be more thoroughly investigated. The components of the Batch 4 formulation can be found in Figure 9.

Figure 9. Components of the fourth batch of nanocomposites.

Bayhydur 302 is a hydrophilically-modified commercial polyisocyanate based on HMDI.²⁴ Its structure (pictured in Figure 10) is composed of a hydrophobic and a hydrophilic component. The hydrophilic component allows the isocyanate to be dispersed in water during polymerization. Bayhydrol A2695 is a commercial hydroxyfunctional polyacrylic dispersion designed for use in waterborne polyurethane formulations. During polymerization, polyol molecules form associations with the hydrophobic portions of polyisocyanate molecules, causing the isocyanate groups to preferentially react with hydroxyl groups rather than water molecules in solution.¹⁸ Despite this mechanism, some isocyanate groups will still react with water and produce CO_2 , which is why defoamers are always required in waterborne polyurethane formulations. The defoamer employed was Surfynol DF-58, an organo-modified siloxane-based defoamer, which worked by lowering the surface tension of the coating to break up bubbles. A hydrophobically-modified ethoxylated urethane (HEUR) thickener, Acrysol RM-825, was used in this formulation to increase the viscosity of the polyol component to that of the isocyanate component before mixing. This was required to ensure that the two components would be fully integrated during mixing so that the full waterborne polymerization mechanism could properly occur.

Figure 10. Structure of Bayhydur 302.²⁴

Unfortunately, although the fourth batch of nanocomposites appeared to be well dispersed before and after curing, more extensive corrosion was observed on the nanocomposite panels than on the control panels. There were a number of potential reasons for why this occurred, leaving several pathways open for further testing. Perhaps the failure of the coatings could be attributed to the quality of the graphene oxide synthesized in the laboratory. For the purpose of comparison, a commercial graphene dispersion was obtained from a supplier, and was used to make nanocomposites using the same formulation guidelines as the batch four nanocomposites.

Figure 11. Components of the fifth batch of nanocomposites.

The commercial graphene sample was obtained from Applied Graphene Materials and was supplied in a 5.0 weight percent dispersion in water. The commercial graphene was not pure graphene but was actually graphene oxide with a small number of functional groups to sufficiently disperse the nanomaterial in water without precipitation. The pH of

the dispersion was 3, equivalent to the pH of the graphene oxide synthesized in lab. However, the number of functional groups on the commercial graphene were far fewer than on the synthesized graphene oxide, producing a relatively low viscosity dispersion rather than a gel.²⁷

After the batch five nanocomposites were prepared, significant defects were observed in the cured films that had been applied to the cold-rolled steel substrates. These defects looked like tiny air bubbles, and were only observed on the cold-rolled steel samples. None of these defects were observed on the nanocomposites applied to polypropylene. To identify these defects and to try to determine their root cause, a final experiment was set up. This involved preparing 4 samples: a 2K waterborne polyurethane control, a 2K waterborne polyurethane-graphene oxide nanocomposite, and two 2K waterborne-commercial graphene nanocomposites prepared with different amounts of HEUR thickener. The samples were applied to four different substrates (cold-rolled steel, aluminum, polypropylene, and glass) and were observed during curing after 5 minutes, 10 minutes, 20 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, and 24 hours. The samples were also inspected using ocular microscopy for the purpose of defect identification.

1.7. Testing and Analysis

Reduced graphene oxide should be characterized after treatment to ensure that the majority of the functional groups have been removed. X-ray photoelectron spectroscopy (XPS) is a characterization method that is commonly used to do this, although equipment for this is not available at Cal Poly. XPS gives the elemental composition of the surface of a sample; when functional groups are removed through reduction, the elemental

composition of the sample should change from a mix of carbon, oxygen, and hydrogen to predominantly carbon.

One method available at Cal Poly to characterize the graphene oxide and graphene is Fourier Transform Infrared Spectroscopy (FTIR). A FTIR spectrometer works by first subjecting a sample to beams of infrared radiation (IR) at certain frequencies, then recording how much IR the sample absorbs.²⁸ The instrument then converts the recorded data into an interpretable spectrum by using the Fourier transform. The generated spectrum plots % transmittance (or % absorbance) versus the wavenumber of the emitted light. Certain bands on the spectrum are characteristic of specific functional groups, so analysis of the spectrum can indicate which functional groups are present in the sample, including those of contaminants. FTIR can be used to distinguish between graphene oxide and graphene; when graphene oxide is reduced, an absence of functional groups will be observed on the corresponding spectrum.

The graphene oxide, graphene, and nanocomposites were all characterized using thermal gravimetric analysis (TGA). TGA measures the change in mass of a sample as a function of temperature or time. This data can be employed to determine various properties, such as the decomposition temperature of a polymer or nanocomposite. This temperature is dependent on a number of different aspects, including degree of crystallinity, structure, and molecular weight.²⁹ During decomposition, a polymer is broken into small gaseous molecules such as carbon dioxide and water vapor. The thermal stability of polymers can change upon addition of nanomaterials; this is reflected in the decomposition temperature.³⁰ TGA was mainly used to assess the influence of graphene and graphene oxide on the thermal properties of polyurethane.

The graphene and graphene oxide were also characterized using X-ray diffractometry (XRD). This structural analysis method works by probing a sample with x-rays and analyzing the diffraction patterns given off by the sample.³¹ Different crystal structures produce characteristic diffraction patterns that can serve as identifiers. A XRD instrument uses the Fourier transform and Bragg's Law to produce a plot of intensity versus diffraction angle. XRD was used in this experiment to determine if graphene oxide had been sufficiently reduced to graphene. Functional groups on graphene oxide make these molecules bulkier than graphene, causing larger interlayer spacing. If graphene oxide was effectively reduced to graphene, a decrease in interlayer spacing would be observed, as shown by an increase in diffraction angle.³¹

There are a number of different methods that can be used to assess the anticorrosive properties of coatings. The coatings must first be applied to a substrate that is prone to corrosion, such as copper or steel. The coated metals can then be subjected to various short-term test methods, designed to mimic extensive corrosion conditions in a short amount of time. Perhaps the simplest of these tests is immersion corrosion testing.³² In this method, samples are immersed in a salt solution in a closed environment and kept at a constant (sometimes elevated) temperature throughout the experiment. Figure 12 Shows a standard apparatus for this procedure. Multiple samples can be tested at once, and this method can be quicker and more reproducible than other techniques such as salt spray testing.³³ However, it also fails to realistically imitate most outdoor corrosion conditions, which often cycle between wet and dry conditions.³³ For example, it would be useful for determining the potential corrosion of a ship in the ocean, but not as useful for modeling the corrosion of the Golden Gate Bridge.

NOTE 1—A = thermometer port, B = flask, C = specimens hung on supporting device, D = air inlet, E = heating mantle, F = liquid interface, G = opening in flask for additional apparatus that may be required, and H = reflux condenser.

Figure 12. Standard laboratory immersion corrosion testing apparatus.³²

Electrical Impedance Spectroscopy (EIS) is another short-term corrosion testing method. In this method, a coated metal substrate is attached to an electric circuit and immersed in an electrolytic solution.³⁴ Voltages are applied to the substrate at different frequencies and the resulting currents are measured. These currents can be used to calculate the electrochemical impedance of the sample. The higher the impedance of a coating, the more corrosion protection it provides.³⁵ A coating with an impedance greater than $10^9 \Omega$ -

cm^2 at 0.1 Hz is considered to be a good corrosion barrier, while a coating with an impedance less than $10^6 \Omega\text{-cm}^2$ at 0.1 Hz is considered to be a poor corrosion barrier.

EIS is a popular method for corrosion testing because it is rapid, straightforward, and does not degrade the sample. It unfortunately has several drawbacks. The instrument is highly sensitive, and sometimes measures changes in impedance that are not associated with corrosion protection.³⁶ Complex models have to be employed to weed out these measurements, and often these models rely on assumptions that may not be applicable to all systems. Additionally, EIS does not provide a realistic model for how corrosion actually occurs in a system in response to environmental conditions. For this reason, EIS is often used in conjunction with other forms of corrosion testing to accurately assess corrosion protection.

Salt Spray testing is an accelerated corrosion testing method designed to mimic coating performance under very harsh corrosive conditions.⁴ Panels are coated and scribed, and placed in a chamber where they are exposed to a continuous fog of salt solution at a controlled temperature. After a set amount of time, the panels are removed and visually assessed. The anticorrosive properties of multiple coatings can be compared using this method. Unfortunately, this method is susceptible to so many variations that its results are often not very reproducible. Additionally, the constant salt spray doesn't mimic realistic corrosion conditions. To improve the correlation between results and environmental conditions, cyclic corrosion testing is often employed.³³ This method transitions between wet and dry phases of testing, giving a more accurate representation of how corrosion actually occurs in real life.

2. Experimental Methods

2.1. Preparation of Graphene

Graphene oxide was prepared using a modified Hummer's Method. Concentrated sulfuric acid (90 mL, 1.7 mol) and a stir bar were added to a 500 mL round bottom flask. The flask was placed in an ice bath and fuming nitric acid (30 mL, 0.72 mol) was added dropwise to the mixture. The mixture was stirred for 15 minutes, then 3 grams of graphite flakes were slowly added to the flask. The mixture was stirred for another 15 minutes and the ice bath was removed. The mixture was stirred at room temperature for 24 hours, poured into deionized water (1000 mL, 55.51 mol) in an ice bath, then stirred for 5 minutes. Then, the precipitate was isolated by vacuum filtration. The precipitate was resuspended in deionized water and filtered five times to ensure that the pH was higher than 5. The solid was transferred to an empty glass petri dish and dried at 60 °C for 24 hours.

The solid was transferred to ceramic boats and heated to 1050 °C for 15 seconds. The solid was allowed to cool back down to room temperature before it was transferred to a 500 mL round bottom flask with a stir bar. Concentrated sulfuric acid (300 mL, 5.67 mol) was added to the flask. The flask was placed in an ice bath. Potassium permanganate (15 g, 95 mmol) was slowly added to the flask with stirring. A color change from black to dark green was observed. The ice bath was removed once the mixture became stabilized. The flask was placed in an oil bath at 45 °C and stirred rapidly. After 4 hours and 30 minutes, a color change from dark green to light green/grey was observed and the viscosity of the mixture increased significantly.

The mixture was resuspended in deionized water (1000 mL, 55.51 mmol) and placed in an ice bath. A solution of 30% hydrogen peroxide (9mL, 9 mmol) was added slowly to the

mixture and stirred. The solution immediately turned a bright orange color. Initially, attempts were made to isolate the precipitate by vacuum filtration. Due to the high viscosity of the dispersion, these attempts were not successful. Fortunately, centrifugation proved to be much more promising. The graphene oxide was washed and isolated using about 20 rounds of centrifugation at 20,000 rpm. Throughout the process, a color change from bright orange to dark brown was observed. The viscosity of the mixture also increased significantly after washing.

A sample of the graphene oxide was chemically reduced to form graphene. The sample was dried in the oven at 60 °C overnight. The dried graphene oxide (1.5 grams) was reacted with concentrated hydroiodic acid (200 mL, 1.46 mol) at 55 °C for 48 hours. The reduced graphene was washed using centrifugation at 20,000 RPM. The sample was washed in water 5 times, then in ethanol for 10 times. The samples were sonicated for 20 minutes between every other wash. The final product was dried first under a heat lamp and then in an oven at 50 °C for 24 hours.

2.2. Chemical Method Nanocomposites

2.2.1. Batch 1

A tube of wet graphene oxide was resuspended in THF and washed 6 times in order to completely eliminate the water in the tube. The concentration of graphene oxide in THF was determined by weighing a drop of the sample before and after drying. The concentration was found to be 29 mg/mL.

Table 1. Components of Batch 1 nanocomposite formulation

Component		Amount
Part 1	Joncryl 910 (71%)	6.09 g
	Graphene in THF (29 mg/mL)	1.92 mL
Part 2	1,6-Diisocyanatohexane	4.87 mL

The Batch 1 nanocomposites were prepared by first mixing the components of Part 1 in a Thinky cup for 30 seconds in a Thinky mixer. The polyol was added using weigh by difference, and the graphene and isocyanate components were added using micropipettes. Next, Part 2 was added to the cup and the mixture was mixed for 60 seconds. 5 mil drawdowns were prepared on cold-rolled steel and polypropylene sheets. The samples were allowed to cure at room temperature for 24 hours.

The steel panels were scribed and placed in the Q-Fog, following the ASTM B117 guidelines.³⁷ The nanocomposites were also analyzed using TGA and DSC.

TGA Procedure:

- a. Equilibrate at 25 °C
- b. Ramp at 20 °C/min to 600 °C
- c. Mark end of cycle

DSC Procedure:

- a. Ramp 20 °C/min to 200 °C
- b. Ramp -10 °C/min to -50 °C
- c. Ramp 10 °C/min to 200 °C
- d. Mark end of cycle.

2.3. Physical Method Nanocomposites

2.3.1. Batch 2

Table 2. Components of Batch 2 nanocomposite formulation

Component		Amount
Part 1	Joncryl 910 (71%)	8.00 g
	Methyl n-amyl ketone	0.3530 g
	Dichlorobenzene	0.1100 g
	n-Pentyl propionate	0.0800 g
	BYK-9077	0.0161 g
	Thermally reduced graphene	0.0459 g
Part 2	Desmodur N3300	1.19 g
	Butyl acetate	0.0980 g

The Batch 2 nanocomposites were prepared by a similar mechanism to the Batch 1 nanocomposites. The components of Part 1 were added to a Thinky cup using weigh by difference and vortexed for 90 seconds. Next, the components of Part 2 were added to the cup and the mixture was vortexed for another 90 seconds. 5 mil drawdowns were prepared on cold-rolled steel and polypropylene sheets. The panels were allowed to cure at room temperature for 24 hours and were then baked in the oven at 60 °C for 24 hours.

The steel panels were scribed and placed in the Q-Fog, following the ASTM B117 guidelines. The nanocomposites were also analyzed using TGA and DSC, according to the procedure in Section 2.2.1.

2.3.2. Batch 3

The solubility of chemically reduced graphene oxide was tested in n-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), tetrahydrofuran (THF), dichlorobenzene (DCB), dimethyl sulfoxide (DMSO), and dimethoxyethane (glyme). These solvents were chosen due to their highly polar nature and their inability to react with isocyanates in

polyurethane formulations. Dispersions containing 1 wt% graphene were prepared in all of the above solvents. A drop of BYK-9077 dispersing aid was added to each in each sample to improve dispersion. The samples were sonicated for 45 minutes and then shaken rapidly for 24 hour. Finally, the samples were visually examined to determine which solvent was most effective.

Table 3. Components of Batch 3A nanocomposite formulation (0% graphene)

Component		Amount
Part 1	Joncryl 910 (71%)	4.00 g
	DMF	4.00 mL
	Chemically reduced graphene	0.00 g
Part 2	Desmodur N3300A	0.59 g

Table 4. Components of Batch 3B nanocomposite formulation (0.5% graphene)

Component		Amount
Part 1	Joncryl 910 (71%)	4.00 g
	DMF	4.00 mL
	Chemically reduced graphene	0.0233 g
Part 2	Desmodur N3300A	0.59 g

Table 5. Components of Batch 3C nanocomposite formulation (1.0% graphene)

Component		Amount
Part 1	Joncryl 910 (71%)	4.00 g
	DMF	4.00 mL
	Chemically reduced graphene	0.0462 g
Part 2	Desmodur N3300A	0.59 g

Table 6. Components of Batch 3D nanocomposite formulation (1.5% graphene)

Component		Amount
Part 1	Joncryl 910 (71%)	4.00 g
	DMF	4.00 mL
	Chemically reduced graphene	0.6960 g
Part 2	Desmodur N3300A	0.59 g

Graphene appeared to be most dispersible in DMF, so this solvent was chosen for the remaining formulations. The specified amounts of graphene for formulations 3B, 3C, and 3D were added to 3 separate 50 mL round bottom flasks. DMF (10 mL, 0.13 mol) was added to each flask. Stir bars were also added to the flasks and rubber septa were attached. The flasks were stirred on high for 3 days using a standard stir plate. The samples were removed from the stir plate. A drop of formulation 3B was removed and examined under the optical microscope. Large black aggregates were observed.

The samples were sonicated for 60 minutes and inspected again under the optical microscope. The aggregates, although much smaller, were still black, indicating that the graphene was poorly dispersed. DMF (90 mL, 1.2 mol) was added to each sample. The samples were stirred at high speed for 3 days. The samples were sonicated again for 60 minutes and then examined under the microscope. The particles appeared much smaller and were transparent for the most part, indicating that the graphene was well-dispersed.

A rotary evaporator was used to remove about 80 mL DMF from each sample. A high vacuum was used to remove solvent until only 4 mL remained in each sample. Formulations 3A-3D were prepared according to the formulation guidelines in Tables 3-6. First, the Joncryl 910 was added to a Thinky cup and vortexed for 30 seconds to ensure that all of the polyol was at the bottom of the cup. Next, the graphene/DMF dispersion was

added to the cup and mixed for 120 seconds in the Thinky mixer. Finally, the Desmodur N3300A was added to the cup and the mixture was vortexed for an additional 90 seconds in the mixer.

6 mil drawdowns were prepared on cold-rolled steel panels and glass slides. The panels were allowed to cure at room temperature for 24 hours and were then baked in the oven at 60 °C for 48 hours. The steel panels were scribed and placed in the Q-Fog, following ASTM B117 guidelines. The nanocomposites were also analyzed by TGA and DSC, following the procedure outlined in Section 2.2.1.

2.3.3. Batch 4

Table 7. Components of Batch 4A nanocomposite formulation (0% graphene oxide, pH adjusted with NaOH)

Component		Amount
Part 1	Bayhydrol A 2695	63.40 g
	Surfonyl DF-58	0.73 g
	Acrysol RM-825	3.00 g
Part 2	Bayhydur 302	34.74 g
Part 3	Deionized water, pH adjusted with NaOH	51.1200 g

Table 8. Components of Batch 4B nanocomposite formulation (0.5% graphene oxide, pH adjusted with NaOH)

Component		Amount
Part 1	Bayhydrol A 2695	63.40 g
	Surfonyl DF-58	0.73 g
	Acrysol RM-825	0.50 g
Part 2	Bayhydur 302	34.74 g
Part 3	Deionized water	14.1975 g
	Graphene oxide (1.329 wt%), pH adjusted with NaOH	36.9225
	BYK 346	1.3378 g

Table 9. Components of Batch 4C nanocomposite formulation (0% graphene oxide, pH adjusted with H₂SO₄)

Component		Amount
Part 1	Bayhydrol A 2695	63.40 g
	Surfonyl DF-58	0.73 g
	Acrysol RM-825	4.00 g
Part 2	Bayhydur 302	34.74 g
Part 3	Deionized water, pH adjusted with H ₂ SO ₄	51.1200 g

Table 10. Components of Batch 4D nanocomposite formulation (0.5% graphene oxide)

Component		Amount
Part 1	Bayhydrol A 2695	63.40 g
	Surfonyl DF-58	0.73 g
	Acrysol RM-825	0.40 g
Part 2	Bayhydur 302	34.74 g
Part 3	Deionized water	14.1975 g
	Graphene oxide (1.329 wt%)	36.9225
	BYK 346	1.3378 g

Table 11. Components of Batch 4E nanocomposite formulation (0% graphene oxide, non-pH adjusted)

Component		Amount
Part 1	Bayhydrol A 2695	63.40 g
	Surfonyl DF-58	0.73 g
	Acrysol RM-825	3.00 g
Part 2	Bayhydur 302	34.74 g
Part 3	Deionized water, pH adjusted with NaOH	51.1200 g

Table 12. Components of Batch 4F nanocomposite formulation (1.0% graphene oxide)

Component		Amount
Part 1	Bayhydrol A 2695	63.40 g
	Surfonyl DF-58	0.73 g
	Acrysol RM-825	0.00 g
Part 2	Bayhydur 302	34.74 g
Part 3	Deionized water	15.0000 g
	Graphene oxide (1.329 wt%)	73.8450 g
	BYK 346	2.6756 g

All of the nanocomposites were prepared separately using a high-speed paint disperser. For Batch 4A, the Bayhydrol A 2695 was first added to a metal paint can and stirred at 205 RPM. Next, the Surfonyl DF-58 was added to the mixture and the speed was increased to 404 RPM. The deionized water from part 3 was adjusted to pH 8 using a few drops of diluted NaOH and added to the mixture. The speed was increased to 700 RPM. The viscosity was examined using a spatula, and Acrysol RM-825 was added until the formulation reached a viscosity similar to that of Bayhydur 302. The sample was stirred for 5 minutes at 1000 RPM. Finally, the Bayhydur 302 was added to the mixture and the stirring speed was increased to 1400 RPM. The mixture was stirred for an additional 5 minutes. 5 mil drawdowns were prepared immediately on cold-rolled steel panels and polypropylene sheets. After 30 and 45 minute increments, additional 5 mil drawdowns were prepared on cold-rolled steel panels to determine pot life.

For Batch 4B, the graphene oxide dispersion was added to the required volume of deionized water and the pH was adjusted to 7.5 using a few drops of 6M NaOH. The specified amount of Bayhdrol A 2695 was added to a metal paint can and stirred at 150 RPM. Then, the Surfonyl DF-58 was added to the can and the speed was adjusted to 355 RPM. The graphene oxide dispersion was added to the paint can and the speed was adjusted

to 700 RPM. The viscosity was examined using a spatula, and Acrysol RM-825 was added until the formulation reached a viscosity comparable to that of Bayhdur 302. The sample was stirred for 5 minutes at 1000 RPM. The Bayhdur 302 was added to the mixture and the stirring speed was increased to 1500 RPM. The mixture was allowed to stir for an additional 5 minutes. 5 mil drawdowns were prepared immediately on cold-rolled steel panels and polypropylene sheets. After 30 and 45- minute increments, additional drawdowns were prepared on cold-rolled steel panels to estimate pot life.

For Batch 4C, the Bayhydrol A 2695 was first added to a metal paint can and stirred at 220 RPM. Next, the Surfonyl DF-58 was added to the mixture and the speed was increased to 422 RPM. The deionized water from part 3 was adjusted to pH 3 using a few drops of diluted H_2SO_4 and added to the mixture. The speed was increased to 675 RPM. The viscosity was examined using a spatula, and Acrysol RM-825 was added until the formulation reached a viscosity similar to that of Bayhydur 302. The sample was stirred for 5 minutes at 1247 RPM. Finally, the Bayhydur 302 was added to the mixture and the stirring speed was increased to 1759 RPM. The mixture was stirred for an additional 5 minutes. 5 mil drawdowns were prepared immediately on cold-rolled steel panels and polypropylene sheets. After 30 and 45-minute increments, additional 5 mil drawdowns were prepared on cold-rolled steel panels to determine pot life.

For Batch 4D, the graphene oxide dispersion was added to the required volume of deionized water. The specified amount of Bayhdrol A 2695 was added to a metal paint can and stirred at 200 RPM. Then, the Surfonyl DF-58 was added to the can and the speed was adjusted to 470 RPM. The graphene oxide dispersion was added to the paint can and the speed was adjusted to 1146 RPM. The viscosity was examined using a spatula, and Acrysol

RM-825 was added until the formulation reached a viscosity comparable to that of Bayhdur 302. The sample was stirred for 5 minutes at 2060 RPM. The Bayhdur 302 was added to the mixture and the stirring speed was increased to 3000 RPM. The mixture was allowed to stir for an additional 5 minutes. 5 mil drawdowns were prepared immediately on cold-rolled steel panels and polypropylene sheets. After 30 and 45-minute increments, additional drawdowns were prepared on cold-rolled steel panels to estimate pot life.

For Batch 4E, the Bayhydrol A 2695 was first added to a metal paint can and stirred at 150 RPM. Next, the Surfonyl DF-58 was added to the mixture and the speed was increased to 355 RPM. The deionized water from part 3 was added to the mixture and the speed was increased to 500 RPM. The viscosity was examined using a spatula, and Acrysol RM-825 was added until the formulation reached a viscosity similar to that of Bayhydrol 302. The sample was stirred for 5 minutes at 1000 RPM. Finally, the Bayhdur 302 was added to the mixture and the stirring speed was increased to 1400 RPM. The mixture was stirred for an additional 5 minutes. 5 mil drawdowns were prepared immediately on cold-rolled steel panels and polypropylene sheets. After 30 and 45-minute increments, additional 5 mil drawdowns were prepared on cold-rolled steel panels to determine pot life.

For Batch 4F, the graphene oxide dispersion was added to the required volume of deionized water. The specified amount of Bayhdrol A 2695 was added to a metal paint can and stirred at 361 RPM. Then, the Surfonyl DF-58 was added to the can and the speed was adjusted to 416 RPM. The graphene oxide dispersion was added to the paint can and the speed was adjusted to 2373 RPM. The viscosity was examined using a spatula, and no Acrysol RM-825 was needed to increase the formulation viscosity to be comparable to that of Bayhdur 302. The sample was stirred for 5 minutes. The Bayhdur 302 was added to the

mixture and the stirring speed was increased to 3048 RPM. The mixture was allowed to stir for an additional 5 minutes. 5 mil drawdowns were prepared immediately on cold-rolled steel panels and polypropylene sheets. After 30 and 45-minute increments, additional drawdowns were prepared on cold-rolled steel panels to estimate pot life.

The nanocomposites were allowed to dry at ambient conditions for 48 hours. The panels were baked at 60 °C for 2 hours to remove residual solvent. The steel panels were scribed and placed in the Q-Fog, following ASTM B117 guidelines. The nanocomposites were also analyzed by TGA, DSC, following the procedure outlined in Section 2.2.1. DMA was used to measure the tensile properties and to determine the glass transition temperature of the coatings.

DMA Procedure:

- a. Isothermal for 5 minutes.
- b. Ramp force 0.100 N/min to 3.000 N.

Dynamic Oscillatory Testing Procedure (Multi Frequency-Strain):

- a. Amplitude: 15 μ m, Force Track: 125%, Frequency: 20 Hz.
- b. Ramp 3 °C/min to 150 °C.

2.3.4. Batch 5

Table 13. Components of Batch 5A nanocomposite formulation (0% commercial graphene)

Component		Amount
Part 1	Bayhydrol A 2695	63.40 g
	Surfynol DF-58	0.73 g
	Acrysol RM-825	3.00 g
Part 2	Bayhydur 302	34.74 g
Part 3	Deionized water	51.1200 g

Table 14. Components of Batch 5B nanocomposite formulation (0.5% commercial graphene)

Component		Amount
Part 1	Bayhydrol A 2695	63.40 g
	Surfynol DF-58	0.73 g
	Acrysol RM-825	4.50 g
Part 2	Bayhydur 302	34.74 g
Part 3	Deionized water	41.3117 g
	Commercial graphene (Supplied 5 wt%)	9.8586 g
	BYK 346	1.3378 g

Table 15. Components of Batch 5C nanocomposite formulation (1.0% commercial graphene)

Component		Amount
Part 1	Bayhydrol A 2695	63.40 g
	Surfynol DF-58	0.73 g
	Acrysol RM-825	8.50 g
Part 2	Bayhydur 302	34.74 g
Part 3	Deionized water	31.4973 g
	Commercial graphene (Supplied 5 wt%)	19.6251 g
	BYK 346	1.3378 g

All of the nanocomposites were prepared separately using a high-speed paint disperser. For Batch 5A, the Bayhydrol A 2695 was first added to a metal paint can and stirred at 205 RPM. Next, the Surfynol DF-58 was added to the mixture and the speed was increased to 446 RPM. The deionized water was added and the speed was increased to 771 RPM. The viscosity was examined using a spatula, and Acrysol RM-825 was added until the formulation reached a viscosity similar to that of Bayhydur 302. The sample was stirred for 5 minutes at 1205 RPM. Finally, the Bayhydur 302 was added to the mixture and the stirring speed was increased to 1428 RPM. The mixture was stirred for an additional 5

minutes. 5 mil drawdowns were prepared immediately on cold-rolled steel panels and polypropylene sheets.

For Batch 5B, the commercial graphene was added to the required volume of deionized water and mixed by pipet. The specified amount of Bayhdrol A 2695 was added to a metal paint can and stirred at 223 RPM. Then, the Surfonyl DF-58 was added to the can and the speed was adjusted to 524 RPM. The graphene dispersion was added to the paint can and the speed was adjusted to 789 RPM. The viscosity was examined using a spatula, and Acrysol RM-825 was added until the formulation reached a viscosity comparable to that of Bayhdur 302. The sample was stirred for 5 minutes at 1271 RPM. The Bayhdur 302 was added to the mixture and the stirring speed was increased to 1572 RPM. The mixture was allowed to stir for an additional 5 minutes. 5 mil drawdowns were prepared immediately on cold-rolled steel panels and polypropylene sheets.

For Batch 5B, the commercial graphene sample was added to the required volume of deionized water and mixed by pipet. The specified amount of Bayhdrol A 2695 was added to a metal paint can and stirred at 235 RPM. Then, the Surfonyl DF-58 was added to the can and the speed was adjusted to 500 RPM. The graphene dispersion was added to the paint can and the speed was adjusted to 711 RPM. The viscosity was examined using a spatula, and a large amount of Acrysol RM-825 was added until the formulation reached a viscosity comparable to that of Bayhdur 302. The sample was stirred for 5 minutes at 1235 RPM. The Bayhdur 302 was added to the mixture and the stirring speed was increased to 1528 RPM. The mixture was allowed to stir for an additional 5 minutes. 5 mil drawdowns were prepared immediately on cold-rolled steel panels and polypropylene sheets.

The nanocomposites were allowed to dry at ambient conditions for 96 hours. Defects were observed after curing, so the cold-rolled steel panels were not tested in the Q-Fog. The nanocomposites were analyzed by TGA, following the guidelines in Section 2.2.1, and by DMA, following the guidelines in Section 2.3.4.

2.3.5. Batch 6

Table 16. Components of Batch 6A nanocomposite formulation (0% graphene)

Component		Amount
Part 1	Bayhydrol A 2695	63.40 g
	Surfynol DF-58	0.73 g
	Acrysol RM-825	3.00 g
Part 2	Bayhydur 302	34.74 g
Part 3	Deionized water	51.1200 g

Table 17. Components of Batch 6B nanocomposite formulation (0.5% graphene oxide)

Component		Amount
Part 1	Bayhydrol A 2695	63.40 g
	Surfynol DF-58	0.73 g
	Acrysol RM-825	0.40 g
Part 2	Bayhydur 302	34.74 g
Part 3	Deionized water	14.1975 g
	Graphene oxide (1.329 wt%)	36.9225
	BYK 346	1.3378 g

Table 18. Components of Batch 6C nanocomposite formulation (0.5% commercial graphene, prepared with sufficient thickener to match viscosity of Bayhydur 302)

Component		Amount
Part 1	Bayhydrol A 2695	63.40 g
	Surfynol DF-58	0.73 g
	Acrysol RM-825	4.50 g
Part 2	Bayhydur 302	34.74 g
Part 3	Deionized water	41.3117 g
	Commercial graphene (Supplied 5 wt%)	9.8586 g
	BYK 346	1.3378 g

Table 19. Components of Batch 6D nanocomposite formulation (0.5% commercial graphene, prepared with the same amount of thickener as 6A)

Component		Amount
Part 1	Bayhydrol A 2695	63.40 g
	Surfynol DF-58	0.73 g
	Acrysol RM-825	3.00 g
Part 2	Bayhydur 302	34.74 g
Part 3	Deionized water	41.3117 g
	Commercial graphene (Supplied 5 wt%)	9.8586 g
	BYK 346	1.3378 g

The Batch 6 formulations were prepared separately using a high-speed paint disperser. Each sample was prepared following the same method. First, the Bayhydrol A 2695 was added to a paint can, and stirring was commenced. Next, Surfynol DF-58 was added to the mixture. Then, part 3 of the formulation was prepared separately, mixed, and slowly added to the paint can. The stirring speed was increased and the mixture was stirred for 5 minutes. A small sample (about 2 mL) of the mixture was saved for later. Next, the specified amount of Acrysol RM-825 was added, and the stirring speed was increased. The mixture was stirred for 5 minutes and a small sample (about 2 mL) was saved for later. The stirring speed was increased to a rapid rate and Bayhydur 302 was added to the formulation. The mixture was stirred for 5 minutes at this speed. Four substrates (cold-rolled steel, polypropylene, glass, and aluminum) were wiped down with ethanol to prepare them for drawdowns. 5 mil drawdowns of each batch were prepared on these substrates, and the drawdowns were photographed after 5 minutes, 10 minutes, 20 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, and 24 hours. After curing, all drawdowns were observed using ocular microscopy. The saved samples from the formulations were also analyzed using rheology.

Rheology procedure:

- a. Flow Peak Hold 25°C, 60 s, 100 1/s
- b. Flow Sweep 25°C, 0.001 to 1000 1/s

3. Results and Discussion

3.1. Graphene and Graphene Oxide Characterization

Figure 13. XRD plot for graphene oxide.

Figure 14. XRD plot for chemically reduced graphene oxide.

Figures 13 and 14 show the XRD plots (intensity versus 2θ) for the graphene oxide and chemically reduced graphene oxide. A clear change is observed from Figure 13 to Figure 14: in Figure 13 there is a representative peak for graphene oxide at a 2θ value of 10. This peak represents the interlayer spacing between graphene oxide sheets due to functional groups introduced by oxidation.³¹ This peak is absent in Figure 14, due to the removal of these groups during reduction.³⁰ Instead, Figure 14 has a broad graphene peak at a 2θ value ranging from about 22-24, which shows a decrease in interlayer spacing. Both plots are comparable to published XRD results for graphene oxide and graphene, indicating that graphene oxide was successfully reduced by hydroiodic acid treatment.^{30,31}

Figure 15. FTIR spectrum for graphene oxide.

Figure 16. FTIR spectrum for chemically reduced graphene oxide.

Figures 15 and 16 contain FTIR spectra for graphene oxide and chemically reduced graphene oxide. As in the XRD results, a clear change is seen from one figure to the other. The graphene oxide spectrum contains many characteristic peaks for OH groups (~3200-

3600 cm^{-1}), carboxylic acids ($\sim 1700 \text{ cm}^{-1}$), and other functional groups found in graphene oxide.³⁸ These characteristic peaks are absent in the spectrum for chemically reduced graphene oxide, indicating that the functional groups had been removed from the graphene oxide during hydroiodic acid treatment. Figure 17 shows TGA data for graphene oxide and chemically reduced graphene oxide. At around 150 °C, a significant decrease in weight percent can be observed for the graphene oxide, showing the removal of functional groups during heating. This decrease cannot be seen in the profile for chemically reduced graphene oxide. Based on these results, it was determined that graphene oxide had been successfully reduced to graphene.

Figure 17. TGA profiles of graphene oxide (GrO) and chemically reduced graphene oxide (ChemRed GrO).

3.2. Chemical Method Nanocomposites

3.2.1. Batch 1

Figure 18. Cold rolled steel panels coated with Batch 1 nanocomposites containing 0 and 0.5% graphene oxide, before and after 250 hours of corrosion testing.

Figure 18 shows the corrosion test results for the Batch 1 nanocomposites. As demonstrated by the figure, the addition of graphene oxide actually led to more substrate corrosion than was observed for the control polyurethane panels. THF was found to be a poor long term solvent for the graphene oxide, causing it to precipitate out of the coating after only a short period of time. This led to the formation of craters in the films, disrupting the structure and producing inadequate substrate coverage in certain areas.

Both the control and the nanocomposite were also analyzed with a 4-point probe. Neither coating was conductive, supporting that the graphene oxide was not uniformly dispersed throughout the polyurethane matrix and likely did not react with the isocyanate functional groups as intended.

Table 20. Thermal properties for Batch 1 coatings

	0% Graphene Oxide	0.5% Graphene Oxide
T_g (°C)	70	67
T_d (°C)	200	200

Table 20 contains the TGA and DSC results for the Batch 1 coatings. It appeared that the addition of the graphene oxide slightly raise the glass transition temperature of the coatings; however, it did not have an effect on the decomposition temperature. Although the control panel did have less substrate corrosion than the nanocomposite panel, neither would be considered good anticorrosive coatings. Significant corrosion was visible on both after only 150 hours of corrosion testing, which is much lower than would be accepted for a commercial anticorrosive product. This formulation clearly was not the best for this product and needed to be changed before the next batch.

3.3. Physical Method Nanocomposites

3.3.1. Batch 2

Figure 19. Cold rolled steel panels coated with Batch 2 nanocomposites containing 0 and 0.5% graphene, before and after 1500 hours of corrosion testing.

Figure 19 shows the corrosion test results for the Batch 2 nanocomposites. Although these required a longer corrosion test period than the Batch 1 nanocomposites to distinguish a difference, the substrate coated with the nanocomposite did display more extensive corrosion than the substrate coated with the control polyurethane.

In this batch, no visible precipitation was observed in the dry coatings; however, 4-point probe measurements indicated that the nanocomposite was no more conductive than the control, demonstrating that graphene was not well dispersed throughout the polymer matrix.

Table 21. Thermal properties for Batch 2 coatings

	0% Graphene	0.5% Graphene
T_g (°C)	32	39
T_d (°C)	250	250

Table 21 contains the DSC and TGA results for the Batch 2 coatings. As with the Batch 1 coatings, the addition of graphene increased the glass transition temperature but did not impact the decomposition temperature. The formulation used for this batch was more carefully planned out and could be considered more commercially sound than the Batch 1 coatings; unfortunately the solvents and the dispersing aid were ineffective in adequately dispersing graphene throughout the coating.

The dispersing aid used in the Batch 2 nanocomposites employed steric effects to stabilize graphene in the polyurethane matrix. Other studies have reported successful dispersion of graphene in polymers using specifically designed compatibilizers. Some of these compatibilizers work through pi-stacking rather than steric stabilization. The structure of graphene makes pi-pi stabilization conducive to its dispersion in various mediums in which it would otherwise be insoluble. If such a compatibilizer could be synthesized and implemented in this system, the dispersibility of graphene would likely improve significantly, which could have an effect on the corrosion resistant properties of the nanocomposites.

3.3.2. Batch 3

Figure 20. Cold rolled steel panels coated with Batch 3 nanocomposites 3A and 3B containing 0 and 0.5% graphene, before and after 400 hours of corrosion testing..

Figure 21. Cold rolled panels coated with Batch 3 nanocomposites 3A and 3C containing 0 and 1.0% graphene, before and after 400 hours of corrosion testing.

Figure 22. Cold rolled steel panels coated with Batch 3 nanocomposites 3A and 3D containing 0 and 1.5% graphene, before and after 400 hours of corrosion testing.

In this batch of nanocomposites, extensive efforts were put forth to ensure that the graphene remained well dispersed in DMF. Optical microscopy confirmed that the graphene did not form aggregates in the dispersion, even at high concentrations of graphene. Unfortunately, once the DMF/graphene dispersion was mixed with the other components and the coating began to dry, the graphene precipitated out. Before corrosion testing even began, the failure of the nanocomposites at preventing corrosion was predictable.

Figures 20-22 Show that the predictions were indeed correct. At all concentrations of graphene, corrosion was more extensive in the nanocomposites than in the polyurethane control. The 3C nanocomposite containing 1.0% graphene demonstrated the worst corrosion; almost the entire panel was covered with rust. Corrosion was also relatively bad on the control panel, especially after only 400 hours in the corrosion chamber. This simple formulation, similar to the Batch 1 coatings, was not an effective coating with or without the incorporation of graphene.

Table 22. Thermal properties for Batch 3 coatings

	0% Graphene	0.5% Graphene	1.0% Graphene	1.5% Graphene
T_g (°C)	1.6	8.0	6.6	9.1
T_d (°C)	275	250	260	256

Table 22 contains the DSC and TGA results for the batch 3 coatings. Graphene was found to increase the glass transition temperature and decrease the decomposition temperature of the coatings. This batch of nanocomposites once again reinforced the importance of developing a good control coating, which should be done before the graphene is incorporated. This ensures that both time and materials are conserved and gives more valuable results.

3.3.3. Batch 4

Figure 23. Unstripped cold rolled steel panels coated with Batch 4 coatings 4A and 4B containing 0 and 0.5 % graphene oxide, both adjusted with NaOH, before and after 500 hours of corrosion testing.

Figure 23 shows the coated panels 4A and 4B before and after 500 hours of corrosion testing. Before the coatings were peeled from the panels, the extent of corrosion between the control and nanocomposite-coated panels appeared similar. In fact, the control-coated panel appeared to have several regions of pitting corrosion which could not be observed

in the nanocomposite-coated panel. Extensive blistering was observed throughout the entire surface of the nanocomposite, while blistering was not observed on the control panel.

Figure 24. Stripped cold rolled steel panels originally coated with Batch 4 coatings 4A and 4B containing 0 and 0.5% graphene oxide, both adjusted with NaOH, after corrosion testing.

Figure 24 shows the 4A and 4B panels after the coatings were removed. The corrosion profile of the control panel remained very similar after the panel was stripped while the corrosion profile of the nanocomposite panel changed significantly. Extensive corrosion was observed over the entire surface of the nanocomposite panel, covering the surface of the panel evenly rather than emanating from the original scribe as was observed for the control panel. Air and water molecules were able to freely penetrate through the nanocomposite coating and react with the surface of the cold rolled steel. This may have

occurred through defects introduced by blistering. The nanocomposite was clearly a very poor corrosion barrier, perhaps the worst of all the prepared nanocomposites.

Figure 25. Unstripped cold rolled steel panels coated with Batch 4 coatings 4C and 4D containing 0 and 0.5 % graphene oxide, before and after 500 hours of corrosion testing. The pH of the graphene oxide was not adjusted in the 0.5% coating, but the pH of the 0% coating was modified with H_2SO_4 .

Figure 25 shows the coated panels 4C and 4D before and after 500 hours of corrosion testing. As in Figure 23, both coated panels appeared to have a similar degree of corrosion between the two. 4C and 4D seemed to be less corroded than their respective 4A and 4D counterparts, however. Some pitting corrosion could be seen through the clear control coating. Extensive blistering was observed throughout the nanocomposite but not the control coating.

Figure 26. Stripped cold rolled steel panels originally coated with Batch 4 coatings 4C and 4D containing 0 and 0.5% graphene oxide after corrosion testing. The pH of the graphene oxide was not adjusted in the 0.5% coating, but the pH of the 0% coating was modified with H_2SO_4 .

Figure 26 shows the 4C and 4D panels after the coatings were stripped away. As in Figure 24, the corrosion profile of the control panel remained the same, while the nanocomposite panel showed much more extensive corrosion after the coating was removed. The 4D panel corroded significantly less than the 4B panel, and corrosion seemed to be most concentrated near the site of the original scribe. Patches of corrosion that seemed to be consistent with blisters on the film were also observed on the 4D panel. The slightly better anticorrosive performance of these coatings compared to the 4A and 4B coatings could potentially be attributed to the difference in pH. The water components of the 4A and 4B coatings were adjusted with a few drops of NaOH to bring the pH to 8 (matching

the pH of the polyol component). The pH of the 4C water component was brought down to 3 using H_2SO_4 to match the pH of the graphene oxide/water component for 4D.

Figure 27. Batch 4 control panels, before and after 500 hours of corrosion testing. The first panel shows the non-pH adjusted formulation (4E), the second shows the increased pH formulation (4A), and the third shows the decreased pH formulation (4C).

Figure 27 compares the three Batch 4 control panels to further investigate the effects of pH and ion content on corrosion. The panel coated with the non-pH adjusted control shows the smallest creep from the scribe, while the panel coated with the NaOH-adjusted control shows the largest creep from the scribe in addition to extensive pitting corrosion. The pH of all of the final coatings (both the nanocomposites and controls) remained around 8-9, despite the pH adjustments to the water components. At pH values ranging from 4 to 10, corrosion is independent of pH.⁴ Therefore, it would have been expected for all of the controls to have consistent levels of corrosion. The changes in corrosion patterns throughout the control panels could be attributed to ions introduced by the addition of

strong acids and bases. Ions increase the conductivity of water, allowing corrosion to occur at a more rapid rate.

Figure 28. Cold rolled steel panels coated with Batch 4 coatings 4C and 4F containing 0 and 1.0% graphene oxide, before and after 500 hours of corrosion testing. The pH of the graphene oxide was not adjusted in the 1.0% coating, but the pH of the 0% coating was modified with H_2SO_4 .

Figure 28 shows the corrosion test results for the coated panels 4C and 4F before and after 500 hours of corrosion testing. As with the 0.5% graphene nanocomposite, much more extensive corrosion was observed for the nanocomposite than for the control. Corrosion did not simply extend outward from the scribe; it covered the entire surface of the panel. Clearly the nanocomposite was unable to protect the steel surface from interaction with air and water molecules, allowing corrosion to freely occur on areas covered by the coating.

The reason for failure of all of the Batch 4 nanocomposites is not entirely known, but there are some potential explanations. Even though graphene oxide is highly dispersible in water, its dispersibility in the final polyurethane was not fully investigated. No visible graphene oxide precipitation was observed in the final films (as was observed for the Batch 3 nanocomposites); however, precipitation still could have occurred on a microscopic level.

Upon further analysis, the final nanocomposite films appeared to have some tiny air bubbles trapped under the surface. These defects may have allowed air to penetrate the films and interact with the surface. These bubbles were likely caused by isocyanate reactions with functional groups on the graphene oxide. When isocyanate groups react with water and carboxylic acids, carbon dioxide is produced as a by-product. In waterborne polyurethane formulations, some reactions with water are inevitable. However, these bubbles were not observed in the control coatings, indicating that they probably resulted from isocyanate reactions with carboxylic acids on the graphene oxide. This issue could potentially be fixed in future formulations by adjusting the NCO:OH ratio to account for the additional reactive groups introduced by the graphene oxide.

Table 23. Thermal properties for Batch 4 coatings

	4A 0% Graphene Oxide, pH adjusted with NaOH	4B 0.5% Graphene Oxide, pH adjusted with NaOH	4C 0% Graphene Oxide, pH adjusted with H₂SO₄	4D 0.5% Graphene Oxide, pH not adjusted	4E 0% Graphene Oxide, pH not adjusted	4F 1.0% Graphene Oxide, pH not adjusted
T_g (°C)	63	53	63	60	63	60
T_d (°C)	260	234	270	257	251	269

The TGA data shown in Table 23 showed some potential correlations between decomposition temperature and the incorporation of graphene. For the 4A and 4B formulations and the 4C and 4D formulations, the decomposition temperatures of the nanocomposites were lower than those of the controls. However, the decomposition temperature of 4D nanocomposite was very similar to the decomposition temperature of the 4A control, and the decomposition temperature of the 4F nanocomposite was higher

than most of the controls. Perhaps some of the temperature differences could be attributed to the pH of the formulations and the effect on their general stabilities.

Because of the complexity of these waterborne coatings, it was impossible to accurately pinpoint their glass transition temperatures using DSC, even at a wide range of scan rates. Instead, dynamic oscillatory testing was used to assess the glass transition temperatures of these coatings. For the most part, the glass transition temperatures seemed to be relatively unaffected by both incorporation of graphene and pH. For some reason, the 4B formulation had a much lower glass transition temperature than the other coatings. This thermal behavior was similar to the decomposition trend, where the same formulation had the lowest decomposition temperature of all of the coatings. Somehow, incorporating both sodium hydroxide and graphene oxide disrupted the structural integrity of the nanocomposite, making it more receptive to thermal energy and subsequent breakdown.

Figure 29. Stress versus strain plot showing the Young's moduli of the Batch 4 coatings 4A and 4B containing 0 and 0.5% graphene oxide, pH of both adjusted with NaOH.

Figure 29 Shows the DMA data for the NaOH-adjusted Batch 4 coatings 4A and 4B. The Young's was shown to decrease significantly from 1154 MPa to 232 MPa upon addition of graphene oxide. These results are opposite of what would be expected for an ideal nanocomposite; typically the addition of nanomaterials increases the Young's modulus of a polymer, as long as these nanomaterials are well dispersed throughout.³⁹ The fact that the Young's modulus decreased upon the addition of graphene oxide indicates that this addition may have disrupted the structure of the polyurethane matrix, potentially due to inadequate dispersibility of graphene throughout the matrix.

Figure 30. Stress versus strain plot showing the Young's moduli of the Batch 4 coatings 4C and 4D containing 0 and 0.5% graphene oxide, pH of both adjusted with H_2SO_4 .

Figure 30 Shows the DMA data for the H_2SO_4 -adjusted Batch 4 coatings 4C and 4D. As in Figure 29, the Young's modulus significantly decreases from 897 to 220 MPa upon the addition of graphene oxide. The change in Young's modulus is not as large as observed between 4A and 4B, but it is still significant. Again, it can be assumed that the addition of graphene disrupted the polyurethane matrix through aggregation.

Figure 31. Stress versus strain plot showing the Young's moduli of the Batch 4 control coatings (non-pH adjusted [4E], pH-adjusted with NaOH [4A], and pH-adjusted with H₂SO₄ [4C]).

Figure 31 compares the Young's moduli of the three different Batch 4 control coatings. The control which was not pH modified had the highest Young's modulus of 2724 MPa. Control 4A, which was adjusted with NaOH to raise its pH had the second highest Young's modulus of 1154 MPa. Control 4C, which was adjusted with H₂SO₄ to lower its pH had the lowest Young's modulus of 897 MPa. Modifying the pH of the formulation (even by a small degree) had a very significant impact on the structure of the coating, contributing to the dramatic decrease in Young's modulus.

Figure 32. Stress versus strain plot showing the Young's moduli of the Batch 4 nanocomposite coatings 4B and 4D, adjusted with NaOH and H₂SO₄, respectively.

Figure 32 compares the Young's moduli of the two Batch 4 nanocomposite coatings. The coating that was adjusted with NaOH to achieve a higher pH had a Young's modulus of 232 MPa, while the coating that used non-pH adjusted graphene oxide had a slightly lower Young's Modulus of 220 MPa. This was consistent with the control coatings where the lower pH formulation had a lower Young's modulus, although the change was not very significant.

Figure 33. Stress versus strain plot showing the Young's moduli of the Batch 4 nanocomposite coatings 4C (0% graphene oxide, pH adjusted with H_2SO_4) and 4E (1.0% graphene oxide, not pH adjusted).

Figure 33 compares the Young's moduli of the 1.0% graphene oxide nanocomposite and the control coating adjusted with H_2SO_4 . The Young's modulus of the nanocomposite (404 MPa) was about half of that of the control coating (899 MPa). This behavior was consistent with the previous nanocomposites, indicating that the presence of graphene oxide may have disrupted the integrity of the polyurethane matrix, potentially due to its poor dispersion throughout the matrix.

Figure 34. Stress versus strain plot showing the Young's moduli of the Batch 4 non-pH adjusted 0.5% and 1.0% graphene oxide nanocomposite coatings 4D and 4E, respectively.

Figure 34 Compares the Young's moduli of the non-adjusted 0.5% and 1.0% graphene oxide nanocomposites. The 1.0% nanocomposite had a Young's modulus of 404 MPa, while the 0.5% nanocomposite had a modulus of 222 MPa. It appeared that although the graphene oxide was not fully dispersed in the 1.0% nanocomposite, it was not as detrimental to the integrity of the matrix as the graphene oxide at the 0.5% loading. The reason behind this was not fully known. Perhaps the higher concentrations of graphene oxide served to reinforce certain regions of the nanocomposite, contributing to a slightly higher Young's modulus for the coating.

3.3.4. Batch 5

After the Batch 5 nanocomposites were prepared and allowed to cure, a significant number of defects were observed in the coatings that had been applied to cold-rolled steel substrates. These defects were not observed in the films applied to polypropylene sheets. They consisted of small bubble-like features distributed across the entire surface of the films. The formation of bubbles is not uncommon in waterborne polyurethane formulations; when isocyanate groups react with water, carbon dioxide is produced. If carbon dioxide becomes trapped in the coating and is unable to escape before curing, it will be retained in the final film. Bubbles and other defects weaken coatings and make them more permeable to air, water, and other solvents. Bubbles would not be desirable in a film designed for effective corrosion protection. For this reason, the decision was made to not subject the cold-rolled steel panels to corrosion testing; rapid failure was almost guaranteed due to the defects.

Table 24. Thermal properties for Batch 5 coatings

	5A 0% Commercial Graphene, pH adjusted with H₂SO₄	5B 0.5% Commercial Graphene, pH not adjusted	5C 1.0% Commercial Graphene, pH not adjusted
T_g (°C)	61.98	57.98	57.50
T_d (°C)	270	286	271

Although the films on the steel panels had visible defects, the films on the polypropylene sheets did not, and were therefore able to be analyzed using TGA, DMA, and dynamic oscillatory testing. The thermal data for these films can be found in Table 24. Although a

slight decrease in glass transition temperature was observed upon addition of graphene, the decomposition temperatures of the nanocomposites were higher than that of the control. It appeared that the addition of graphene at 0.5 weight percent served to reinforce the structural integrity of the coating, causing it to require more thermal energy to decompose.

Figure 35. Plot showing the Young's moduli of the Batch 5 coatings containing 0, 0.5%, and 1.0% commercial graphene.

Figure 35 Compares the Young's moduli for the three batch 5 coatings. The control film had the highest Young's modulus of 896 MPa. The nanocomposite containing 1.0% graphene had the lowest Young's modulus of 155 MPa. The 0.5% graphene nanocomposite had an intermediate Young's modulus of 322 MPa. The 0.5% Batch 5 nanocomposite had a higher Young's modulus than the corresponding 0.5% Batch 4 nanocomposite, but the

1.0% Batch 5 nanocomposite had a much lower Young's modulus than its Batch 4 counterpart. The decrease in mechanical properties in the nanocomposites in comparison to the control could be associated with poor dispersion of graphene throughout the polymer matrix. Graphene aggregation can disrupt the hydrogen bonding network between polyurethane chains, leading to microphase separation.³⁹

Rather than performing corrosion testing, time was dedicated to determining the cause and identity of these defects. If the defects really were bubbles caused by isocyanate reaction with water, why were bubbles observed only on the cold-rolled steel panels and not on the polypropylene sheets? The exact same coating had been applied to both substrates. Defects that were this pronounced were not observed for the Batch 4 nanocomposites coated on cold-rolled steel; however, extensive bubble-like defects were found on the Batch 4 nanocomposites that had been applied to polypropylene. The Batch 4 nanocomposites were prepared using graphene oxide with a large number of functional groups, while the Batch 5 nanocomposites were prepared using graphene with only a few functional groups. The presence of functional groups likely had an effect on the polarity and interfacial interactions of these nanomaterials, which could be a factor in the defects observed on the different substrates.

During the preparation of the Batch 5 nanocomposites, a large amount of HEUR thickener was required to raise the viscosity of the polyol component to match the viscosity of the isocyanate component. The amount of thickener required was much higher than was required for both the control and the Batch 4 nanocomposites. Using a larger amount of thickener significantly shortened the pot life of the nanocomposites, which could have prevented generated carbon dioxide bubbles from escaping the coatings during curing. This

was proposed as a mechanism for the defects on the Batch 5 nanocomposites; however, this mechanism would not explain why defects were only observed on the cold-rolled steel panels and not on the polypropylene sheets.

Because the defects were only present on certain substrates, surface energy effects seemed to be a contributing factor in defect formation. An experiment was designed to better investigate these effects. Four different coatings were prepared: a 2K waterborne polyurethane control, the Batch 4 0.5% graphene oxide nanocomposite (4B), and two Batch 5 0.5% graphene nanocomposites, one made with the same amount of thickener as the control and one made with the required amount of thickener to match the viscosity of the isocyanate component. The coatings were applied to four different substrates with a wide range of surface chemistries: cold-rolled steel, aluminum, glass, and polypropylene. After application, the coatings were photographed at set time increments in order to observe their behavior during curing. The coatings were also examined using microscopy to gain more information about the structure of the defects.

3.3.5. Batch 6

Figure 36. Curing of the 2K waterborne polyurethane control on an aluminum panel after 5 minutes, 10 minutes, 20 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, and 24 hours.

Figure 36 shows the curing behavior of the 2K waterborne polyurethane control on aluminum. As seen in the images, air bubbles were formed after application. These disappeared after 30 minutes, however, and could not be observed in the final film. The absence of bubbles was confirmed using optical microscopy, pictured in Figure 37. In this image, all that is visible is the texture of the aluminum panel.

Figure 37. Optical microscopy image for sample 6A on aluminum, 100X magnification.

Figure 38. Curing of the 2K waterborne polyurethane control on a glass panel after 5 minutes, 10 minutes, 20 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, and 24 hours.

Figure 38 Shows the curing behavior of the 2K waterborne polyurethane control on the glass substrate. The final film had an orange peel texture. No air bubbles could be detected in the final film through visible observation; however, upon inspection with the optical microscope, a few small bubbles were observed, randomly distributed throughout the film. An image of this can be found in Figure 39.

Figure 39. Optical microscopy image for sample 6A on glass, 100X magnification.

Figure 40. Curing of the 2K waterborne polyurethane control on a polypropylene sheet after 5 minutes, 10 minutes, 20 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, and 24 hours.

The curing behavior of the 2K waterborne polyurethane control can be observed in Figure 40. As on the glass substrate, an orange peel texture was observed in the final film. No bubbles were observed during visible inspection of the final film. The absence of bubbles was confirmed through ocular microscopy, as pictured in Figure 41.

Figure 41. Optical microscopy image for sample 6A on polypropylene, 100X magnification.

Figure 42. Curing of the 2K waterborne polyurethane control on a cold-rolled steel panel after 5 minutes, 10 minutes, 20 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, and 24 hours.

The curing behavior of the 2K waterborne polyurethane control on cold rolled steel can be observed in Figure 42. Some bubbles were initially formed after application; however, these disappeared from the film after 20 minutes. None were observed in the final film, as confirmed by ocular microscopy, which is shown in Figure 43. For the 2K waterborne polyurethane control, bubbles were only observed in the coating on the aluminum panel but were absent in the coatings on the other three substrates.

Figure 43. Optical microscopy image for sample 6A on cold-rolled steel, 100X magnification.

Figure 44. Curing of the polyurethane-graphene oxide nanocomposite on an aluminum panel after 5 minutes, 10 minutes, 20 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, and 24 hours.

Figure 44 shows the curing behavior of the 2K waterborne polyurethane-graphene oxide nanocomposite on aluminum. The appearance of the film remained relatively the same throughout curing, and no bubbles were observed through visible inspection. However, when the samples were inspected using an optical microscope, a large number of small bubbles were observed. An image of this can be found in Figure 45.

Figure 45. Optical microscopy image for sample 6B on aluminum, 100X magnification.

Figure 46. Curing of the polyurethane-graphene oxide nanocomposite on a glass panel after 5 minutes, 10 minutes, 20 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, and 24 hours.

Figure 46 shows the curing behavior of the 2K waterborne polyurethane-graphene oxide nanocomposite on glass. Bubbles could be visually observed on the edges of film during drying after only 20 minutes. After 24 hours, a myriad of bubbles could be observed across the entire surface of the film. The texture created by these bubbles could be physically felt through contact with the surface. Upon inspection with the optical microscope, more bubbles of a much larger size than were found in any of the previous films were observed, as shown in Figure 47.

Figure 47. Optical microscopy image for sample 6B on glass, 100X magnification.

Figure 48. Curing of the polyurethane-graphene oxide nanocomposite on a polypropylene sheet after 5 minutes, 10 minutes, 20 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, and 24 hours.

Figure 48 shows the curing behavior of the 2K waterborne graphene oxide-polyurethane nanocomposite on polypropylene. Bubbles were observable on the dry edges of the film after 30 minutes. Once the film was completely cured, large bubbles could be observed across the entire surface of the film. The texture created by the bubbles could be easily felt by simply running a finger over the surface. When the films were inspected under the optical microscope (as shown in Figure 49) they appeared identical to the corresponding films on the glass panels.

Figure 49. Optical microscopy image for sample 6B on polypropylene, 100X magnification.

Figure 50. Curing of the polyurethane-graphene oxide nanocomposite on a cold-rolled steel panel after 5 minutes, 10 minutes, 20 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, and 24 hours.

Figure 50 Shows the curing behavior of the 2K waterborne graphene oxide-polyurethane nanocomposites on cold rolled steel. After about an hour of curing, tiny bubbles were observed in the film. These were retained in the final film after curing was complete. The bubbles were inspected using an ocular microscope (Figure 51) and were found to have similar appearance to those observed in the film on the aluminum panel. They were smaller than those observed on the glass and polypropylene sheets. Bubble formation is especially common in 2K waterborne polyurethane formulations because carbon dioxide is produced when isocyanate groups react with water. However, these defects were not observed in the control coatings, indicating that they must have resulted from the incorporation of graphene oxide. Graphene oxide contains carboxylic acid functional groups which produce carbon dioxide as a by-product when reacted with isocyanates. By adjusting the amount of excess isocyanate in the formulations, the amount of bubbles could likely be reduced.

Figure 51. Optical microscopy image for sample 6B on cold-rolled steel, 100X magnification.

The type of surface also appeared to have an impact on the appearance of the defects observed in the films. Steel and aluminum form oxides in the presence of air, which makes

their surfaces more polar than those of glass or polypropylene. Variances in polarity and surface energy can influence the wettability of a substrate, which can, in turn, influence the size of bubbles that are retained in the coatings.⁴⁰

Figure 52. Curing of the polyurethane-commercial graphene nanocomposite (6C) on an aluminum panel after 5 minutes, 10 minutes, 20 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, and 24 hours.

Figure 52 shows the curing behavior of the 2K waterborne polyurethane-commercial graphene nanocomposite (prepared using excess thickener) on aluminum. There appeared to be some issues with wettability, as small regions of dewetting could be seen during curing and in the final film. Besides this, other defects such as air bubbles were not observed in the final film. This was confirmed using optical microscopy, as shown in Figure 53.

Figure 53. Optical microscopy image for sample 6C on aluminum, 100X magnification.

Figure 54. Curing of the polyurethane-commercial graphene nanocomposite (6C) on a glass panel after 5 minutes, 10 minutes, 20 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, and 24 hours.

Figure 54 Shows the curing behavior of the 2K waterborne polyurethane-commercial graphene nanocomposite (prepared using excess thickener) on glass. No bubble formation was observed during curing or in the final film. The sample appeared to have good wettability on the glass substrate. The films were inspected using microscopy (shown in Figure 55) and no bubbles or other defects were observed.

Figure 55. Optical microscopy image for sample 6C on glass, 100X magnification.

Figure 56. Curing of the polyurethane-commercial graphene nanocomposite (6C) on a polypropylene sheet after 5 minutes, 10 minutes, 20 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, and 24 hours.

Figure 56 Shows the curing behavior of the 2K waterborne polyurethane-commercial graphene nanocomposite (prepared using excess thickener) on polypropylene. As with the sample on the glass substrate, no bubble formation was observed during curing or in the final film. The sample appeared to have good wettability on the substrate. The films were inspected using ocular microscopy (shown in Figure 57) and no bubbles or other defects were observed.

Figure 57. Optical microscopy image for sample 6C on polypropylene, 100X magnification.

Figure 58. Curing of the polyurethane-commercial graphene nanocomposite (6C) on a cold-rolled steel panel after 5 minutes, 10 minutes, 20 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, and 24 hours.

Figure 58 Shows the curing behavior of the 2K waterborne polyurethane-commercial graphene nanocomposite (prepared using excess thickener) on cold-rolled steel. The formation of bubble-like defects was observed after 20 minutes, and these defects were retained in the final film. Through simple visual inspection, the defects appeared to indeed be air bubbles trapped inside the film. However, upon inspection under the ocular microscope, no air bubbles could be observed, as evidenced by Figure 59. The microscopy image appeared very similar to that for the control coating on steel; even if the sample was moved around on the stage, no defects could be found.

Figure 59. Optical microscopy image for sample 6C on cold-rolled steel, 100X magnification.

Figure 60. Curing of the polyurethane-commercial graphene nanocomposite (6D) on an aluminum panel after 5 minutes, 10 minutes, 20 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, and 24 hours.

Figure 61. Optical microscopy image for sample 6D on aluminum, 100X magnification.

Figure 62. Curing of the polyurethane-commercial graphene nanocomposite (6D) on a glass panel after 5 minutes, 10 minutes, 20 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, and 24 hours.

Figure 63. Optical microscopy image for sample 6D on glass, 100X magnification.

Figure 64. Curing of the polyurethane-commercial graphene nanocomposite (6D) on a polypropylene sheet after 5 minutes, 10 minutes, 20 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, and 24 hours.

Figure 65. Optical microscopy image for sample 6D on polypropylene, 100X magnification.

Figure 66. Curing of the polyurethane-commercial graphene nanocomposite (6D) on a cold-rolled steel panel after 5 minutes, 10 minutes, 20 minutes, 30 minutes, 1 hour, 3 hours, 6 hours, and 24 hours.

Figure 67. Optical microscopy image for sample 6D on cold-rolled steel, 100X magnification.

Figures 60, 62, 64, and 66 show the curing behavior of the 2K waterborne polyurethane-commercial graphene nanocomposite (prepared using the same amount of thickener as sample 6A) on the various substrates. Figures 61, 63, 65, and 67 show the corresponding ocular microscopy images for these samples. This formulation had identical behavior to the polyurethane-commercial graphene nanocomposite (6C) prepared using excess thickener. Because the behavior of the two samples was the same, this ruled out the possibility that the defects observed could be attributed to thickener concentration. Additionally, the optical microscopy images of these samples confirmed that the defects observed were not actually air bubbles, and were therefore not caused by isocyanate reaction with water and carboxylic acids. Because defects could only be observed on the samples coated on cold-rolled steel, surface energy differences were determined to be the most probable cause of defect formation. The defects were believed to be microphase separation, which is a common issue encountered when preparing nanocomposites.

Graphene as a material is highly nonpolar and, like other nanomaterials, often has issues with aggregation when incorporated into other materials.³⁹ Polyurethane coatings with

good barrier properties require a uniform polymer matrix composed of a complex hydrogen-bonding network between polymer chains. If graphene is added to polyurethane and aggregates before the polymer crosslinks, this can interfere with the hydrogen bonding network and cause microphase separation between the graphene and the polyurethane matrix. Nanophase separation is linked to a decrease in mechanical properties, which was observed in this experiment. The nanocomposites containing graphene had significantly lower Young's moduli than the control coatings, indicating that aggregation did occur.

Nanophase separation probably led to defects on all of the substrates; however, the reason that significant defects were only visibly observed on the steel panels was most likely attributable to the surface energy and polarity of the substrate. Of all the four substrates, steel is the most polar due to its rapid formation of an iron oxide layer in the presence of air. When the nanocomposites were applied to the substrate, poor interactions between highly nonpolar graphene and the polar substrate likely drove the graphene particles away from the substrate, causing aggregation and subsequent microphase separation to occur at a faster rate. To confirm this explanation, additional tests and better characterization techniques (such as scanning electron microscopy) would be required.

4. Future Work

Although none of the attempts to produce anticorrosive polyurethane-graphene nanocomposites were successful, there is still potential for this technology to be developed and implemented. If this project were to be continued, the dispersibility of graphene in polyurethane would have to be significantly improved. There are a number of different dispersing additives that may be more effective for graphene-polyurethane systems, and compatibilizers could be designed and synthesized specifically for this project. Graphene itself can also be modified with specific functional groups that can greatly improve its dispersibility in polyurethane. In order to weed out potential sources of error and contamination, it would be advisable to begin with commercial graphene in future formulations. Additionally, nanocomposites can be synthesized in a number of different ways, perhaps the method that was employed in this work was not the most effective way to ensure even graphene dispersion in polyurethane.

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