N92-22463

CORROSION-PROTECTIVE COATINGS FROM ELECTRICALLY CONDUCTING POLYMERS

Karen Gebert Thompson & Coleman J. Bryan
National Aeronautics and Space Administration
Materials Science Laboratory (DM-MSL-22)
Kennedy Space Center, Florida 32899

Brian C. Benicewicz & Debra A. Wrobleski
Materials Science and Technology Division
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

ABSTRACT

In a joint research effort involving the Kennedy Space Center and the Los Alamos National Laboratory, electrically conductive polymer coatings have been developed as corrosion- protective coatings for metal surfaces. At the Kennedy Space Center, the launch environment consists of marine, severe solar, and intermittent high acid/elevated temperature conditions. Electrically conductive polymer coatings have been developed which impart corrosion resistance to mild steel when exposed to saline and acidic environments. Such coatings also seem to promote corrosion resistance in areas of mild steel where scratches exist in the protective coating. Such coatings appear promising for many commercial applications.

INTRODUCTION

Research in the last decade has brought to light a new class of polymeric materials known as electrically conductive polymers. Many experts have touted this new class of materials as having the potential to combine the conductivity of a metal with the lightweight convenience and chemical resistance of a plastic. The physical and chemical properties of polymers such as high strength-to-weight ratios, toughness, low cost, molecular tailoring of desired properties, and ease of processing into films, filaments, and complex shapes make polymeric materials extremely attractive for many applications. Over the last several years, efforts to develop a new generation of stable and processable conducting polymers appear to be on the brink of success. One such research effort involving the Kennedy Space Center (KSC) and the Los Alamos National Laboratory (LANL) entails the development of corrosion-protective coatings from electrically conductive polymers. This paper discusses the development and testing of these conductive polymer coatings.

BACKGROUND

Until recently, the field of electrically conductive polymers comprised materials with virtually no processability. In the last few years, however, it was discovered that monomers based upon aniline, thiophenes, and pyrroles can be synthesized and polymerized to high molecular weight materials. Through proper control of substituents, polymers have been made that are both soluble in common organic solvents and melt processable below decomposition temperatures. Such breakthroughs demonstrate the potential of producing processable electrically conductive polymers.

The concept of using electrically active coatings for corrosion protection of metal surfaces has recently been addressed by F.C. Jain et. al. [1]. Metallic surfaces can host positive dipole layers when such surfaces adjoin appropriately doped semiconductors to form metal/semiconductor structures. These interfacial space charge layers result in an inherent electric field which opposes the flow of electrons from the metal surface to oxidizing species in the environment, thus lowering the rate of oxidation (i.e., corrosion). It is important to note that the current reduction is due to the existence of an active electronic barrier at the interface, and not to the electrical resistance of the semiconductor film. The electronic barrier may also inhibit corrosion in regions where pinholes exist in the semiconductor layer, since a finite electric field is expected to retard transfer of electrons. This same theory may apply to electrically conductive polymers used as corrosion-control coatings.

A coating with resistance to hydrochloric acid and to corrosion is needed for ground support equipment and structures at KSC. The launch environment consists of a marine, severe solar, and intermittent high acid/elevated temperature environment. The current zinc-rich coatings used on launch structures have the drawback of attack of the zinc moiety by the high concentrations of hydrochloric acid released during a Space Shuttle launch. The KSC and LANL research effort involves the synthesis of electrically conductive polymers, formulation of such polymers into coatings, and subsequent environmental and physical testing of steel specimens coated with these materials. The objective of the study is to formulate these organic coatings to provide easy application, repair, and long term resistance to the KSC launch environment.

COATING PREPARATION AND TESTING

Polymer selection

The research team has synthesized several conducting polymers and prepared solutions of suitable viscosity for casting films. Solvents, casting techniques, and drying conditions have been developed for coating steel coupons with pinhole-free films. For a material to qualify as a candidate for a corrosion-protective coating, selection criteria include ease of preparation and processing, dopability (i.e. increasing conductivity by additives serving as electron donors or acceptors), electrical conductivity, environmental stability, mechanical integrity of film, adhesion to steel, and low cost.

Several conducting polymers were synthesized during the course of the research effort. In some cases specialized monomers were synthesized before subsequent polymerization; in other cases monomers were obtained commercially. Many of the polymers considered were eliminated from the study based upon the qualification criteria listed above. For example, some of the polymers requiring specialized monomer synthesis were eliminated due to high cost to produce such materials. Recent work has encompassed development of methods for coating steel coupons with pinhole-free films of the following pi-conjugated polymers: polyaniline, poly(3-hexyl thiophene), poly(3-octyl thiophene), poly(3-thienylmethylacetate), and poly(3-thienylethylacetate). Figure 1 gives the chemical structures for these polymers.

Adhesion to steel was the main obstacle in the study. Adhesion problems were solved for many of the polymers through efforts such as investigating an appropriate blend of conductive polymer and epoxy and by applying undoped, chemically prepared polymer to the surface of the steel and subsequently doping the coated surface to the conducting state. Once steel samples were coated with candidate materials, the samples were exposed to salt water and to 0.1 M HCl. Results of such adhesion studies concentrated the work effort on polyaniline coatings, which were clearly superior to others tested.

Polyaniline

The oxidative polymerization of aniline to polyaniline was reported in the literature as early as 1862 [2]. Polyaniline was known as "aniline black" and was used as a textile dye. In fact, electrically conductive polymers are intensely colored. Researchers in France in 1967 first reported the electrical conductivity of certain members of the polyaniline family [3]. The electrical conductivity of polyaniline is a function of its oxidation and protonation states. In the polyaniline structure depicted in Figure 2, y represents reduced or benzenoid units, and 1-y represents oxidized or quinoid units. When polyaniline is composed solely of reduced units, the material is colorless and an insulator. When polyaniline is made up solely of oxidized units, the material is black in color and is a readily hydrolyzed insulator. The emeraldine form is the most conductive form and has roughly equal numbers of reduced and oxidized units.

Polyaniline was synthesized chemically according to the method reported in the literature [4]. Ammonium persulfate was the oxidizing agent used. The polyaniline powder was converted to the nonconducting emeraldine base by stirring in an ammonium hydroxide solution. The product was filtered, washed, partially dried, pulverized, and dried to a constant weight.

The emeraldine base of polyaniline can be easily dissolved in organic solvents for application to steel substrates. Once polyaniline is doped to the conducting state, however, the material has limited solubility in organic solvents. Consequently, the surface of the mild steel samples were initially coated with the undoped, chemically prepared polyaniline. This coating of the mild steel coupons was accomplished using solutions of polyaniline in 1-methyl-2-pyrrolidinone (NMP). Dip-coating methods were first used for applying the polyaniline/NMP solutions to the steel, followed by development of a spray method. Both methods provided good coverage and good adhesion of the polyaniline to the steel. Upon drying, the coatings were 1-2 mils (0.001-0.002 in.; 0.03-0.05 mm.) thick.

Once dry, the undoped polyaniline coating was doped to the conducting state. By increasing the electrical conductivity of the polymer, dopants provide the proper electronic environment to impart corrosion resistance and acid resistance to the film. Over twenty-five different dopants were evaluated during the study. The dopants which gave the best results were tetracyanoethylene (TCNE), zinc nitrate, and p-toluenesulfonic acid.

After the coating was doped to a conducting state, a topcoat of cross-linked epoxy was applied to the samples in order to impart improved abrasion resistance to the coating. The epoxy topcoat used on the samples discussed in this paper was Ciba-Geigy Bisphenol A GY 2600 resin cured with a cycloaliphatic/aliphatic amine hardener XU265. The resultant coating was designed to provide the proper electronic environment as well as coating toughness and resistance to harsh environmental conditions.

Corrosion Testing

Polymer-coated steel coupons were tested for corrosion resistance in two different environments via gas/liquid cells. One environment consisted of placing each coupon in an individual vial containing enough 3.5% NaCl solution to cover the coated portion of the coupon. All vials were capped with a rubber septum into which air was bubbled to ensure oxygenation of the solution. In the second environment, a 0.1 M hydrochloric acid (HCl) solution was used in place of a saline solution. Photographs were taken of the samples before exposure to the above environments as well as throughout the testing. In some cases, the tests were carried out for 12 weeks.

To establish a baseline of the corrosion resistance of the conductive polymer-coated samples, control samples of mild steel coated solely with the epoxy coating were tested. The Ciba Geigy epoxy material was chosen because of its use in power plants for coating interior surfaces of stacks emitting sulfur dioxide. The material is reported to exhibit acid resistance [5]. The control samples were tested with the conductive polymer samples in the corrosion tests.

Figure 3 shows photographs of samples before and after twelve weeks of exposure to aerated 3.5% NaCl solution. The photograph on the top left shows mild steel coated only with epoxy before exposure. The sample shown on the top right was sprayed with undoped polyaniline in NMP, then doped with p- toluenesulfonic acid, followed by application of an epoxy topcoat. The sample shown on the bottom left is an epoxy control sample after twelve weeks exposure to the saline solution. Corrosion was evident with the control sample, with pitting throughout the sample and mass loss from the edges of the steel sample observed. The sample on the bottom right is a polyaniline/epoxy sample. No evidence of corrosion was seen, with the edges of the sample still intact and showing no mass loss. Since the polyaniline is dark in color, the coating was scraped off to verify that no corrosion was present. In fact, the polyaniline coating adhered to the substrate so tenaciously that it was difficult to scrape the coating from the steel.

Figure 4 shows photographs of samples before and after twelve weeks of exposure to aerated 0.1 M HCl solution. The photograph on the top left shows mild steel coated only with epoxy before exposure. The photograph on the top right shows mild steel which was sprayed with undoped polyaniline in NMP, then doped with tetracyanoethylene (TCNE), followed by application of an epoxy topcoat. Both samples were scribed before exposure to acid. The photograph on the bottom left shows extensive corrosion on the epoxy control sample after eight weeks in acid. The photograph on the bottom right shows the polyaniline/epoxy sample. No evidence of corrosion was seen, with the scratched surface still shiny.

Many environmental tests have been carried out in saline and acidic oxidizing environments. A marked improvement in the corrosion resistance of mild steel has been observed when using the electrically conductive polymer coatings developed in this research program as compared to mild steel coated solely with epoxy.

Additional Environmental and Physical Testing

Candidate coatings were initially screened by the corrosion tests described above using aerated saline and hydrochloric acid solutions. The best candidate materials are undergoing further testing for determining effective corrosion resistance for mild steel. Testing methods include ultraviolet (UV) radiation testing, electrochemical corrosion testing, accelerated corrosion testing in a salt fog chamber, long term exposure at the KSC beach corrosion testing site, pitting corrosion tests in ferric chloride solution, and electrochemical impedance spectroscopy.

Samples are subjected to high intensity UV radiation in an Atlas Electric Devices Weatherometer. Such UV exposure is used to determine outdoor weathering properties of a material in regard to sunlight and rain. Specimens are exposed to 0.35 Watt/m^2 of 340 nanometer wavelength UV radiation.

The electrochemical corrosion testing utilizes a Model 351-2 Corrosion Measurement System, manufactured by EG&G Princeton Applied Research. The electrochemical cell includes a saturated calomel reference electrode, two graphite rod counter electrodes, a metal specimen working electrode, and a bubbler/vent tube. The electrolyte consists of varied concentrations of HCl solution plus 3.55% NaCl. Electrochemical tests performed include determination of corrosion potential, polarization resistance (per test procedure in ASTM G59 [6],) and cyclic polarization (per test procedure in ASTM G61 [7]).

Accelerated corrosion testing is carried out in an Atlas Corrosive Fog Exposure System Model SF-2000, manufactured by Atlas Electric Devices Company. The solution used for salt fog exposure is a standard 5% NaCl mixture. After each week of exposure to salt fog, the specimens are immersed for one minute in a 1.0 M HCl/alumina mixture to simulate the solid rocket booster effluent created during launch of the Space Shuttle. Following immersion in HCl/alumina, the specimens are allowed to drain and dry overnight and then are returned to the salt fog chamber for the next one week cycle. The inspection procedure includes cleaning, weighing, and visual characterization of the corrosion occurring.

All beach exposure testing is carried out at the KSC Beach Corrosion Test Site, which is located on the Atlantic Ocean approximately one mile south of Launch Complex 39A at KSC. The test site is approximately 100 feet from the mean high tide line, with the orientation of the samples facing east toward the ocean at a 45 degree angle, to receive the full extent of sun, rain, and sea spray. The beach exposure test procedure is based on the test method described by ASTM G50 [8], with the addition of an acid spray. Every two weeks the specimens are sprayed with a 1.0 M HCl/alumina powder slurry, which thoroughly wets the surface of the specimen and which is allowed to remain on the surface of the specimen until dry or rinsed off by rain. The inspection procedure includes cleaning, weighing, and visual characterization of the corrosion.

The pitting corrosion testing in ferric chloride solution is based on ASTM G48, Method A [9]. Specimens are immersed in an aqueous solution of ferric chloride for 72 hours. Following a water rinse and removal of corrosion products, the specimens are dipped in acetone or alcohol and allowed to air dry. Each specimen is weighed and examined visually and at low magnification for signs of pitting.

Electrochemical evaluation of the conductive polymer/steel interface is performed, using alternating current (ac) and direct current (dc) methods. Such methods are used as accelerated test methods. AC impedance measurements made over a range of frequencies utilizes a Model 378 electrochemical measurement system manufactured by EG&G Princeton Applied Research. The dc work utilizes a Model 1000 system manufactured by EG&G. Samples are immersed in aerated, natural seawater collected from the Atlantic Ocean at Cape Canveral, Florida. Electrochemical ac impedance measurements are made at approximately one week intervals for six weeks. Direct current linear polarization resistance measurements are also made periodically, and the corrosion potential is measured as well. Values for polarization resistance are obtained from Nyquist diagrams and from the dc linear polarization data. Values are also calculated for the coating capacitance.

FUTURE STUDIES

Current work is producing improved coatings with greater environmental stability. This work will continue, and corrosion resistance and physical properties of the coatings will be evaluated. Efforts are also underway to establish a working agreement to aid in the commercialization of these coatings. The aim of this agreement would be to develop the capability of manufacturing large batches of these coatings and to subsequently develop methods for coating large structures.

COMMERCIAL APPLICATIONS

Corrosion-protective coatings from electrically-conducting polymers have many commercial applications. Most applications considered thus far regard corrosion protection to equipment exposed to heat, sunlight, saline environments, and other outdoor exposure concerns. There is a great need for such coatings for bridges, for example. Another use is for coating rebar used in concrete. Improved coatings for underground storage tanks are greatly needed. The automotive industry also needs improved coatings--especially for customers living in sea coast environments. The authors of this paper were recently contacted by industry regarding the need for a protective coating on oceanic drilling platform equipment. A need which deviates from outdoor environmental concerns involves an application in a new electrically erodable printing process which requires conductive paths in specific locations on the printing plate. Electrically conductive polymer coatings afford advantages over existing materials in properties including bonding ability, processability, durability, and greater strength-to-mass ratio. In addition to the suggested applications listed herein, there are many commercial applications for an easily processable, electrically-conductive polymer coating with good adhesion and good environmental resistance properties.

REFERENCES

1. Jain, F.C.; Rosato, J.J.; Kalonia, K.S.; Agarwala, V.S.; Corrosion 1986, 42, 700.

2. Letheby, H.; J. Chem. Soc. 15, 161 (1862).

3. Jozefowicz, M.; Yu, L.T.; Belorgey, G.; Buvet, R.; J. of Polymer Science. Part C 16, 2943 (1967).

4. Cao, Y.; Andreatta, A.; Heeger, A.; Smith, P.; Polymer, 30 (12) 2305-11 (1989).

5. "Organic Coatings in Simulated Flue Gas Desulfurization Environments", Electric Power Research Institute Report #CS-5449, Research Project 1871-5, October 1987, H. Leidheiser, Fr., M.L. White, D.J. Mills.

6. ASTM G59-78, Standard Practice for Conducting Potentiodynamic Polarization Resistance Measurements, 1986 Annual Book of ASTM Standards, Volume 03.02, ASTM, Philadelphia, PA, 1986.

7. ASTM G61-78, Standard Practice For Conducting Cyclic Potentiodynamic Polarization Measurements For Localized Corrosion, 1986 Annual Book of ASTM Standards, Volume 03.02, ASTM, Philadelphia, PA, 1986.

8. ASTM G50-76, Standard Practice for Conducting Atmospheric Corrosion Tests on Metals, 1986 Annual Book of ASTM Standards, Volume 03.02, ASTM, Philadelphia, PA, 1986.

9. ASTM G48-76, Standard Test Methods For Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys By The Use Of Ferric Chloride Solution, 1986 Annual Book of ASTM Standards, Volume 03.02, ASTM, Philadelphia, PA, 1986.

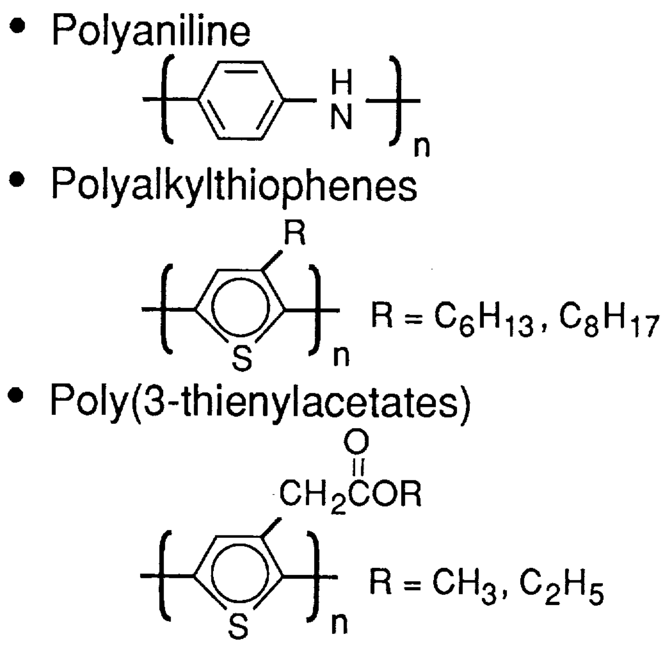


FIGURE 1. ELECTRICALLY CONDUCTING POLYMERS STUDIED

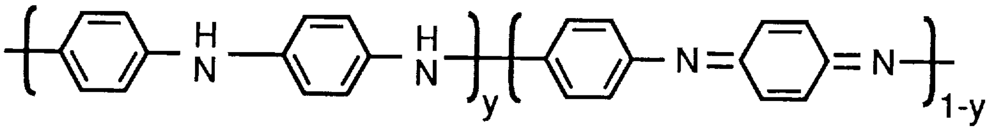
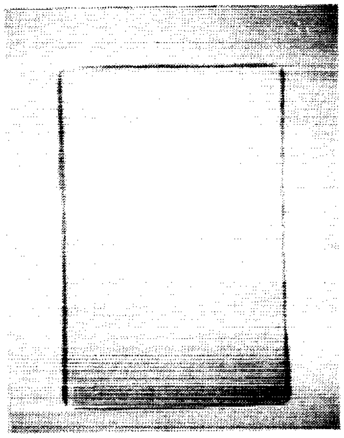
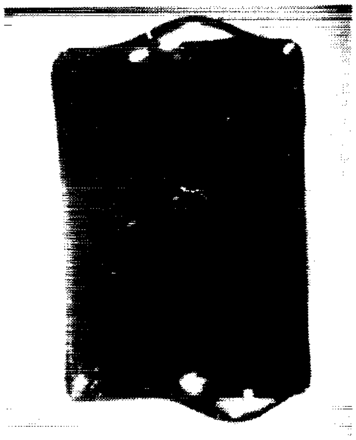
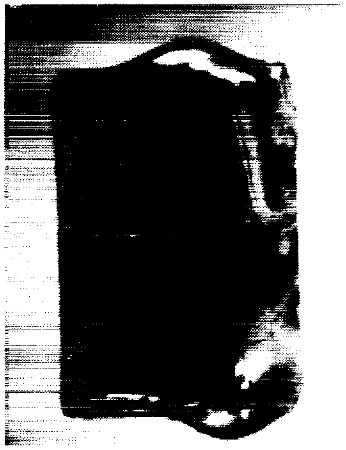
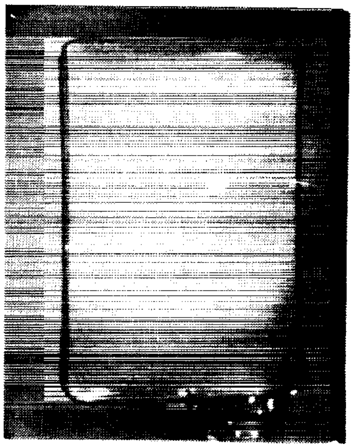
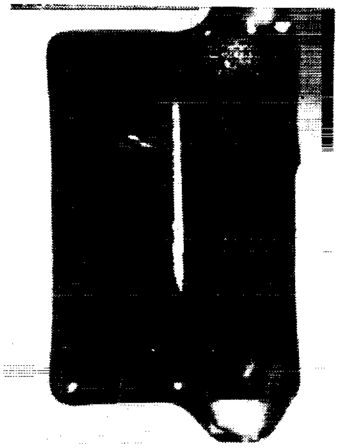
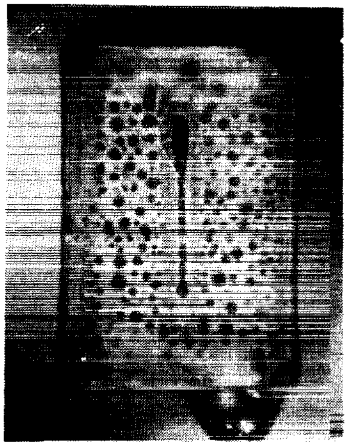


FIGURE 2. POLYANILINE STRUCTURE IN UNDOPED FORM, SHOWING REDUCED AND OXIDIZED UNITS

	Mild Steel Coated Solely With Epoxy	Mild Steel With Polyaniline, p-TolSO$_3$H* Dopant, & Epoxy Topcoat
Photographs of Specimens Before Corrosion Testing		
Photographs of Specimens After 12 Weeks Corrosion Testing		

* p-TolSO$_3$H = p-Toluenesulfonic acid

FIGURE 3. CORROSION TESTING OF COATED STEEL SPECIMENS IN AERATED 3.5 % NaCl. (Magnification: 3X)

	Mild Steel Coated Solely With Epoxy	Mild Steel With Polyaniline, TCNE* Dopant, & Epoxy Topcoat
Photographs of Specimens Before Corrosion Testing		
Photographs of Specimens After 8 Weeks Corrosion Testing		

* TCNE = Tetracyanoethylene

FIGURE 4. CORROSION TESTING OF SCRIBED SPECIMENS IN AERATED 0.1 M HCl. (Magnification: 3X)

ORIGINAL PAGE
BLACK AND WHITE PHOTOGRAPH

MEDICAL ADVANCES: COMPUTERS IN MEDICINE

(Session B5/Room C4)

Wednesday December 4, 1991

- Computation of Incompressible Viscous Flows Through Artificial Heart Devices
- Computer Interfaces for the Visually Impaired
- Extended Attention Span Training System
- Man/Machine Interaction Dynamics and Performance Analysis Capability