Advances in Polymer-to-Metal Bonding for Underwater Environments

Two Years of R&D Yield Better Materials for Polymer-to-Metal Adhesion, Promising Longer Service Life of Electrical Connectors

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Bonding of organic polymers to inorganic surfaces is hardly new technology. Ancient Sumerians and Babylonians used asphalt and pitch for floor covering and paving. Naturally occurring polymers were used by the ancient Egyptians to varnish their sarcophagi. After thousands of years, these organic coatings are still at least partially intact.

That may be true for the dry desert, but when it comes to polymer to mineral coatings submerged in water, survivability may be measured in hours. Few agents are as destructive to organic bonds as bionic water. (Water naturally has two ionic forms —HO^-, H_3O^+—as well as being a polar molecule.)

The 1940 evolution of composite plastics filled with glass fiber for structural material replacement of aluminum and steel brought on the discovery of this troubling phenomenon. Prolonged exposure to moisture severely degraded the composite's strength-to-weight ratio. The loss of strength demonstrated the power of the intruding water to debond resin from hydrophilic glass.

The same phenomenon has been confronted in many other circumstances, particularly in undersea applications where organic polymer moldings and coatings debond from metals. Paint coatings have received considerable study for underwater applications due to the hydrolyzation problem. The past 15 years of naval experience reveal susceptibility of rubber-to-metal bonded materials outboard ship where electrical connectors fail because of overmold polymers debonding. Connector/cable assemblies rated for 15 years of continuous ocean submersion may fail in as little as a few months before a new ship has even left the dock.

Studies attributed cathodic action between the connector shell in the electrolytic ocean water and ship hull sacrificial zinc plates as a major contributor to the failure. Credit for recent significant contributions goes to Naval Sea Systems Command, Naval Weapons Systems Center, TRI, General Dynamics/Electric Boat Division, Naval Research Laboratory, and BIW Connector Systems. Researchers are in agreement that water with high alkalinity, resulting from the cathodic action, attacks the polymer/metal bond interface.

Beginning at the Edge

The cathodic action begins at the exposed edge of the polymer-to-metal interface. The delamination appears to creep along the interface until the overmolded boot of the connector (or any other polymer-to-metal bond) completely delaminates. However, the rate of delamination is dependent on a number of variables with the nature of the polymer being very significant; polyurethane delaminates many times faster than neoprene. On the other hand, polyethylene has not yet revealed a failure mode although inadequate test data are available.

Cathodic action occurs naturally in the marine environment in the presence of dissimilar metal structures. Since typical connectors of underwater assemblies are made of relatively noble metals, such as Monel, stainless steel, and titanium compared to the sacrificial zinc plates on ship hulls, a battery current results with the ocean water acting as an electrolyte. The connector and the zinc form the electrodes of a battery.

Electrons flow from the zinc (anode) through the steel ship hull to the connector shell (cathode). The electrons leaving the zinc produce a positive zinc ion that dissolves in the seawater. Positive and negative ions diffuse through the seawater between

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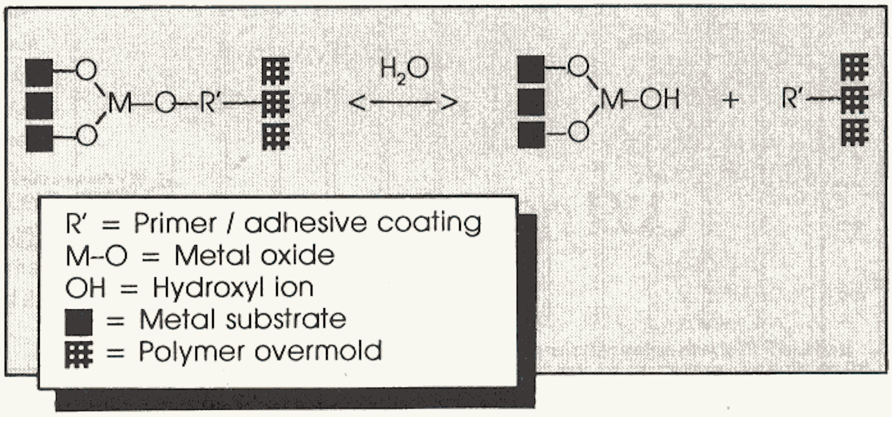


Chemical equation is for equilibrium state polymer-to-metal adhesion in moisture.

the electrical connector shell and the zinc plate to complete the electrical circuit. This is more precisely defined as *electrolytic conductance* by anions and cations.

The electrolytic reactors produce a problem; the caustic OH^- ion is released at the connector shell. Under conditions that allow buildup of the OH^-, pH level can rise from the normal sea level of 8.2 to perhaps 11 to 12 pH. Organic polymers typically used in manufacture of underwater connectors begin to break down at that high pH level—especially the adhesive bond between the overmolded sealing boot and the connector shell.

Once the seal fails, the connector is flooded and electrical failure is probable.

Because the connector shell is the cathode in this reaction that seems to lead to delamination of the connector boot, the term *cathodic delamination* seems appropriate.

Further research indicates cathodic action is an incomplete description of the noted debonding process and, after 50 years of intensive study, debate continues on the mechanism of bonding and debonding between polymers and metals. Recent studies not only confirm that polymer/metal bonds *will hydrolyze* in the presence of moisture but lead to the understanding that *consequential debonding cannot be stopped.* High pH environments, a consequence of cathodic action in the environs of ship hulls, especially aggravate the condition. In addition, thermal shock is found to be a major factor in debonding.

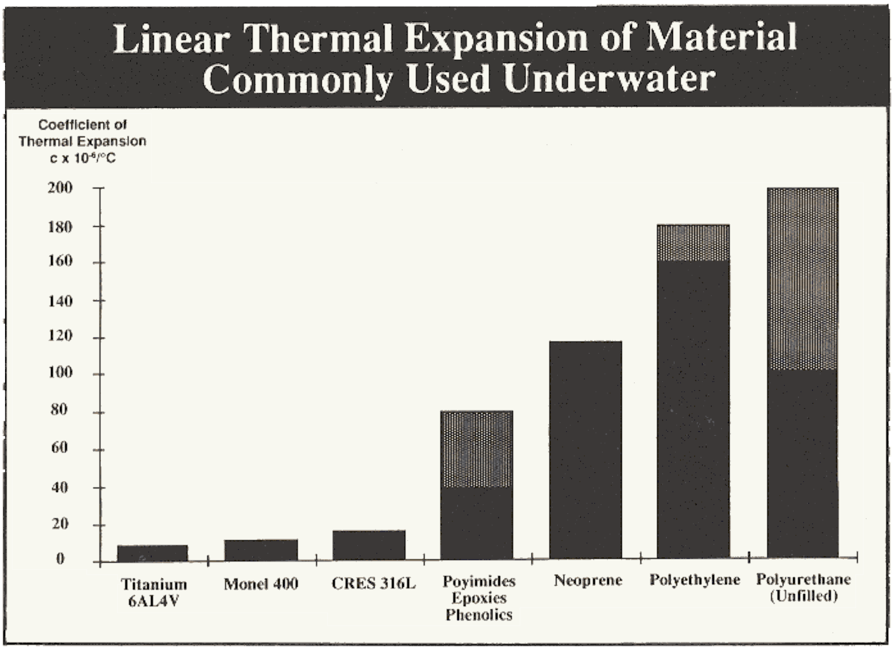
The debonding mechanism, particularly cathodic debonding, recently received significant attention. Naval Sea Systems Command, through NWSC at Crane, Indiana, and the Naval Research Laboratory (Florida) funded studies at Texas Research Institute. Various connector configurations were tested. The focus of the effort was to stimulate industry suppliers to develop solutions to the problem and produce a reliable long term polymer-to-metal bond—with a 15-year service life as the target. The test report is available from NWSC.

The principle product derived from that research, BONDiT®, is a reliable metal-to-polymer bonding system able to withstand long service in continuously submerged ocean environments, subjected to caustic chemical attack by cathodic action and thermal shocks, and compatible with existing field service practices.

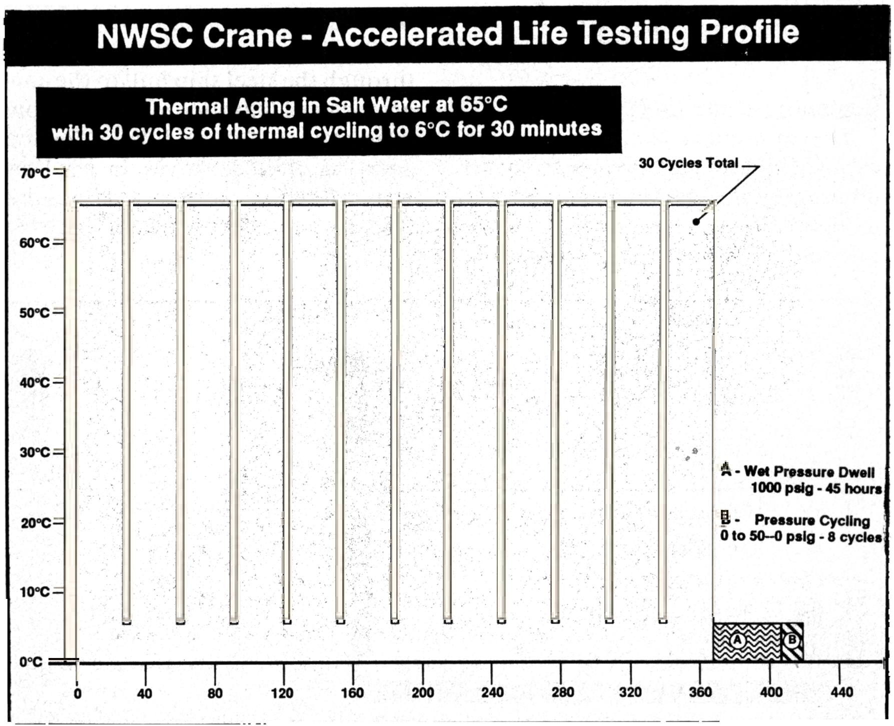
Understanding Adhesion Failure

Additional research at BIW has lead to a better understanding of the debonding mechanism. Assuming a good bond initially, there are two primary contributors to adhesion failure: Polymer/substrate interface stresses and water desorption. In practice these work together to reduce a good cohesive bond to a failure.

It is well established that moisture will travel through a polymer to reach the interface and proceed by diffusion along the interface beginning at any exposed polymer-to-metal interface. The diffusion along the interface is as much as 450 times faster than through the polymer. However, depending on geometry and material, moisture may saturate the polymer and fill the interfacial region faster than the moisture flow along the interface. Typical polymer satu-



Comparison above shows thermal expansion coefficients for materials commonly used underwater. Below is NWSC accelerated life testing profile.



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ration ranges widely from 0.015 to 24 percent of mass, while the interfacial region saturation remains relatively constant at 3.0 to 3.5 percent of surface area regardless of the polymer, the hydrophilic nature of the mineral surface being the biggest determinant.

There is little doubt a saturated interface *hydrolyzes* the polymer/metal bonds. However, the reaction is reversible and, hence, if the interface is dried, the bonds will return to their former state.

When in equilibrium in the moisture environment, a percentage of each side of the equation exists with individual metal/polymer bonds having some probability of being in either state. Equilibrium constants determine the probability and correspondingly which side of the equation is favored. In any case, some percentage of debonding will exist—it's unavoidable.

Variables such as activation energies, bond temperature, bond chemical structure, and pH of the water have significant effects on the probability.

In and of itself, the equilibrium bond conditions may be satisfactory for the application. Bond failure occurs only when the interfacial region separates beyond the range that dispersion forces can act to induce chemisorption. Thermal stress constitutes the most significant of the mechanical stresses in a typical application, causing separation. Polymer coefficients of thermal expansion range from two times to 20 times that of common metals.

For polymers having adequate bond density, this does not pose a problem barring actual fracture of the bulk material. However, with a lowered bond density resulting from hydrolysis of the interfacial region, the thermal expansion of the polymer causes the polymer to physically break away from the metal interface thereby permanently breaking the bond.

Another Stress Factor

Another factor causing stress is swelling due to moisture absorption by the polymer. The degree of swelling is dependent on the pH level of the bond interface and nature of the polymer—polyurethane having very hydrophilic qualities and polyethylene very low; that is, hydrophobic. Since the metallic substrate will not swell, the adhesive-substrate interface

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is the plane of discontinuity and resulting stress buildup. When this accompanies desorption by water (hydrolyzation of the adhesive bond) and thermal shock in the desorbed adhesive, then *failure in adhesion inevitably results.*

A fourth factor is also clearly evident. The cathodic environment increases the available OH- ions at the exposed edges of the interface. That moves the equilibrium point of the reaction in favor of debonding. Further increase in the pH moves the equilibrium constants so far in favor of debonding that virtually no organic / mineral interface can withstand the chemical attack. Any mechanical stress at that "loose" edge initiates complete debonding of the polymer from the mineral substrate.

Blistering illustrates the same phenomenon, commonly seen in paint on metal substrate. As the moisture penetrates through the polymer to the hydrophilic metal surface, microscopic irregularities and contaminants offer sites on the metal surface to form oxidation-reduction reactions.

Multicomponent BONDiT

BONDiT is a multicomponent system to provide high moisture resistant metal-to-polymer bonds. It provides a moisture- and thermal-shock-resistant substrate for a wide range of polymers as a tie coating to metal substrate. It is designed with constants that greatly favor the bonding side of the chemical equation.

The constants of the individual polymer/metal bond give it a probability 10^4 greater than those commonly in use today. Designed to also reduce the moisture concentration significantly at the interface, it moves the equilibrium constants in favor of bonding.

The BONDiT system is designed to "manage" thermal stresses and provide a balanced transition from rigid metal to high expansion polymers, such as polyurethanes.

Accelerated life tests (ALT) conducted at BIW demonstrate bond survival rate improvements of 3,000 percent over common systems in use today. In all cases, the bulk adherent failed under adhesion pull tests, before and after accelerated aging, with such overmold materials as polyurethane, neoprene, and LDPE. ALTs run at Texas Research Institute under the direction of NWSC show no degradation of the BONDiT system.

The entire system works together to provide a reliable bond between the metal substrate and the overmolded polymer. The BONDiT system is proven to withstand environment of moisture, cathodically active conditions, and thermal and mechanical stress.

Specifications and Applications

Normal operating temperatures for BONDiT are -40° to 150°F. The material will maintain adhesion to metal substrate up to temperatures of 400°F in superheated water or steam and certain oils, albeit with decreasing bond strength proportional to increasing temperature above 200°F. Peel strength exceeds 180 pounds per inch width at 75°F and impact of 52 inch-pounds. Thermal shock tests employed include -40° to 150°F water of 180 cycles, 60° to 200°F water of 30 cycles, and 75° to 400°F water and oil of 14 cycles. Accelerated moisture soak tests run at 150° and 195° in excess of 400 hours continuous submersion produced no bond failures. BONDiT sustained soak tests in 11.5 pH, 195°F salt water in excess of 250 hours before evidencing bond weakening.

ALTs conducted by NWSC and NRL at Texas Research on a submarine mission profile, including elevated temperatures of 66°C and thermal shocks to 6°C in cathodically active sea water, demonstrated no failure modes in excess of ten equivalent year cycles.

Applications include virtually any configuration of metal. Tested metals range from 316 stainless steel and 4130 steel to Monel 400, titanium, and aluminum. Commercial and military marine applications include sonar cable assemblies and towed arrays and coating of ROV masts requiring overmolding of acoustical rubber. /st/

Robert E. Lindberg is a consultant to BIW Connector Systems and developer of the BONDiT system. Another of his recently developed underwater products is the polyethylene cable splice kit that allows cable repair without the use of a thermoplastic press. It permits field repairs with the use of a standard heat gun. Lindberg holds a B.S.E.E. and B.S. in physics from California Polytechnic University and a masters in business marketing and finance.