Mechanism of Degradation of Bismaleimide (BMI) Composites due to Galvanic Reactions Between Metals and Carbon Fiber

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Background

Aerospace structures have hybrid construction with a combination of organic matrix composite and metallic materials. In addition to stiffness improvements, composites have benefits of **corrosion** and **fatigue resistance** enabling effective performance under severe operating conditions. Epoxy resin composites have been used in the vast majority of legacy applications, but **the use of bismaleimide (BMI) resins** in programs (e.g. F-22, F-35) are increasing, **due to their superior strength, toughness, and elevated temperature performance.**

In the early 1990's, **laboratory tests** showed BMI and other imide-based carbon composites were **chemically attacked and severely degraded when coupled with a corroding metal** (e.g. aluminum, steel). While galvanic corrosion of aluminum by carbon epoxy composites is well known and addressed by extensive protection measures, the attack and dissolution of the BMI resin raised additional concern. This issue caused both the Air Force and Navy to place restrictions on the use of carbon reinforced BMI (C/BMI) composites in uninspectable and unreplaceable areas. This is consistent with good design practice that disallows dependency on protective coatings to prevent catastrophic failure.

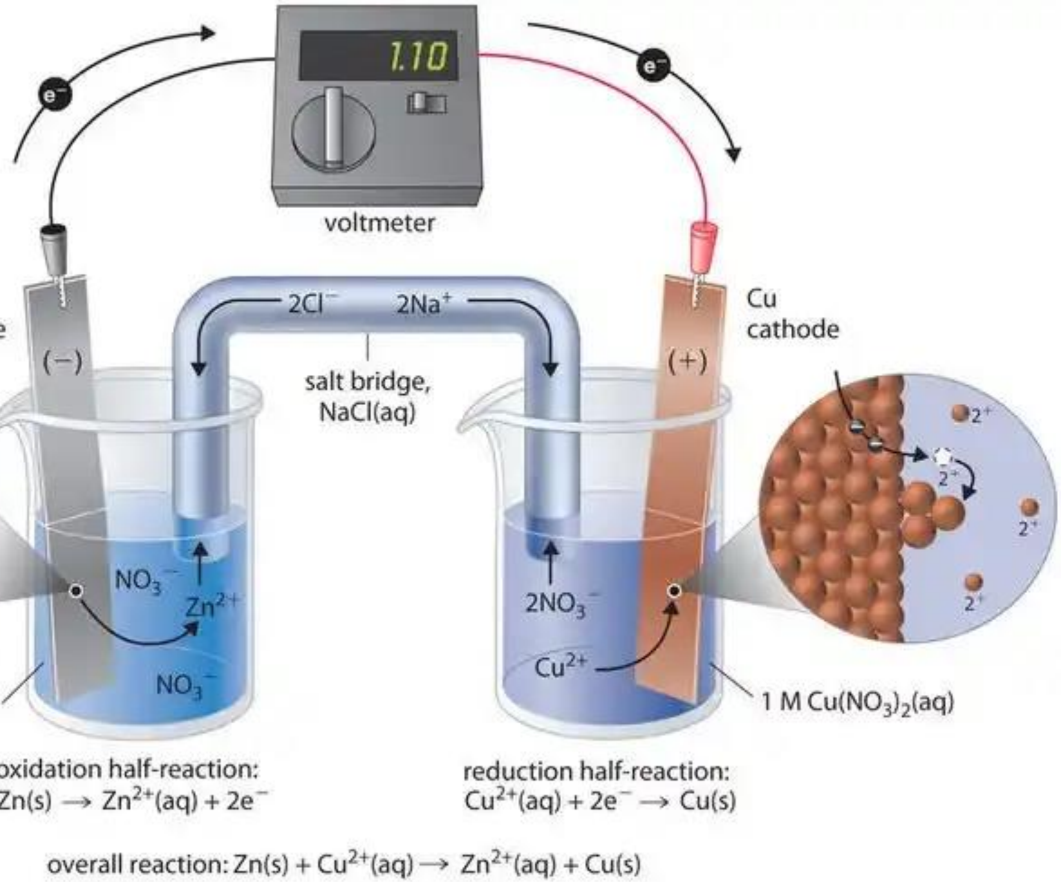
Galvanic Cell

Galvanic Cell

What is Galvanic Cell? An electrochemical cell that converts the chemical energy of **spontaneous** redox reactions into electrical energy

$\Delta G = -nFE$ (Gibbs free energy equation)

ΔG > 0 no spontaneous
ΔG < 0 spontaneous
n = number of electrons
F = Faradays constant
E = Cell's potential

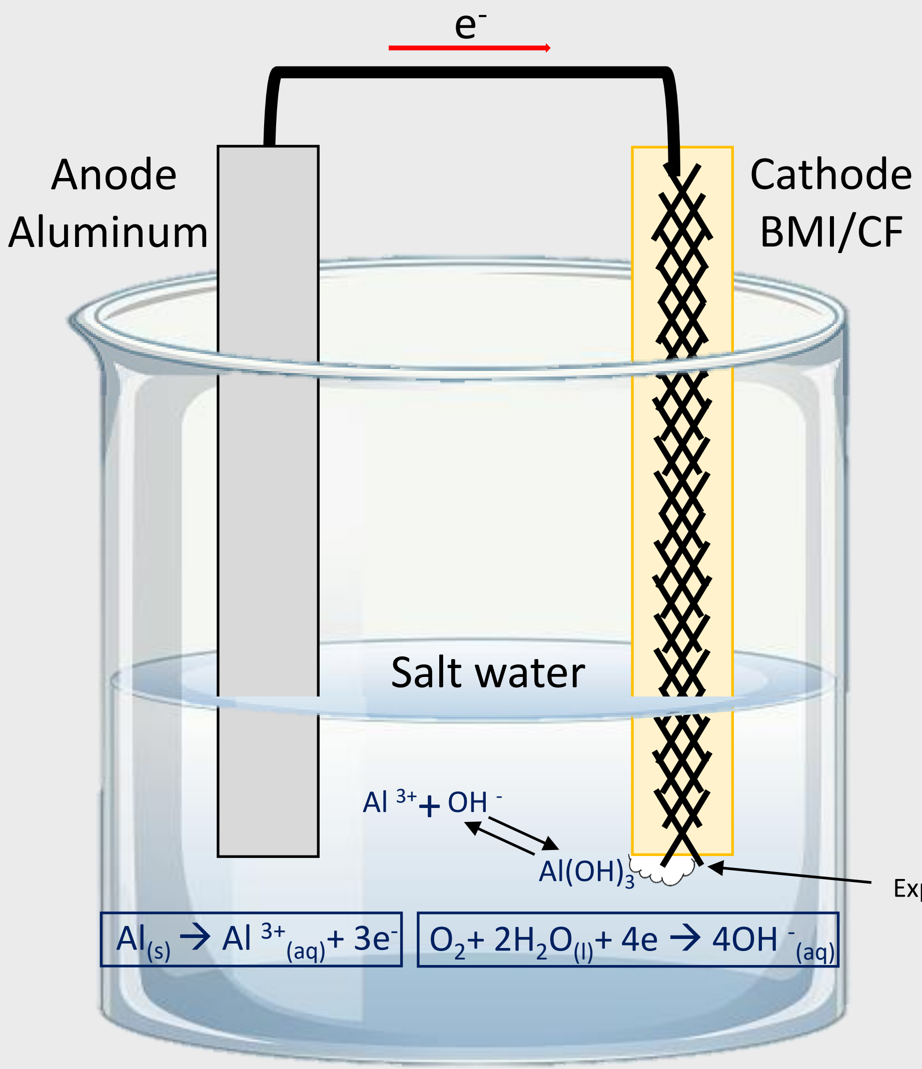


Half Reaction					potential
F_2	+	$2e^-$	⇌	$2F^-$	+2.87 V
Pb^{4+}	+	$2e^-$	⇌	Pb^{2+}	+1.67 V
Cl_2	+	$2e^-$	⇌	$2Cl^-$	+1.36 V
Ag^+	+	$1e^-$	⇌	Ag	+0.80 V
Fe^{3+}	+	$1e^-$	⇌	Fe^{2+}	+0.77 V
Cu^{2+}	+	$2e^-$	⇌	Cu	+0.34 V
$2H^+$	+	$2e^-$	⇌	H_2	0.00 V
Fe^{3+}	+	$3e^-$	⇌	Fe	−0.04 V
Pb^{2+}	+	$2e^-$	⇌	Pb	−0.13 V
Fe^{2+}	+	$2e^-$	⇌	Fe	−0.44 V
Zn^{2+}	+	$2e^-$	⇌	Zn	−0.76 V
Al^{3+}	+	$3e^-$	⇌	Al	−1.66 V
Mg^{2+}	+	$2e^-$	⇌	Mg	−2.36 V
Li^+	+	$1e^-$	⇌	Li	−3.05 V

increasing strength as an oxidizing agent
increasing strength as an reducing agent

Galvanic Reactions Between Metals and Carbon Fiber

Galvanic Reaction between Aluminum and BMI/CF



Net reaction

$$Al^{3+}_{(aq)} + 3OH^-_{(aq)} \rightleftharpoons Al(OH)_{3\,(S)}$$

$$Kps = 1.9 \times 10^{-33}$$

Aluminum/carbon composite systems can have outstanding mechanical properties. Aluminum and carbon fiber reinforced polymer matrix composites (CFRP) are typically considered corrosion resistant when used alone, but can develop severe galvanic corrosion when in physical contact in the same component or structure.

Galvanic Reaction between Aluminum and BMI/CF

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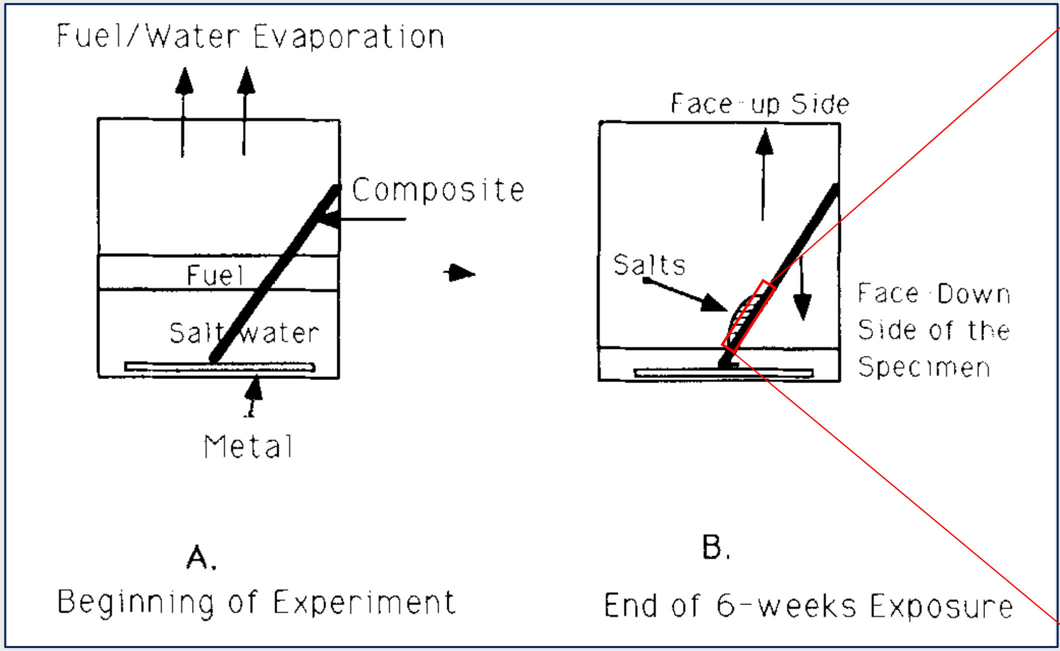

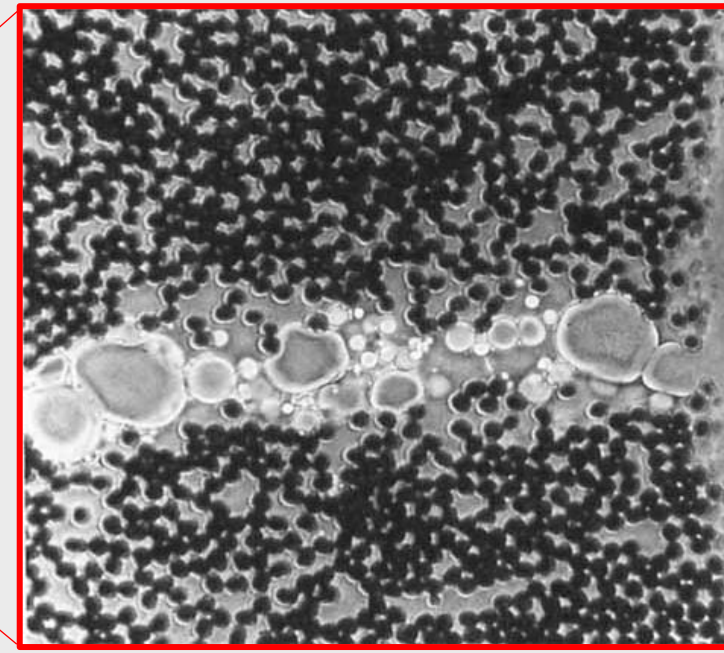

BMI surface

Conclusion

- The aggregation of salts favor the OH^- buildup, which then initiates attacks on **cyclic imide structure.** The presence of moisture and salts and conductive contacts between unprotected metals and imide-type (BMI) carbon fiber composites have been known to constitute the prerequisite conditions for imide-type composite degradation.
- Degradation was found to invariably progress more heavily on the face-up side of the BMI specimens where the white sludges (in the aluminum-composite setup) were deposited.

Characterization of BMI-Graphite/Aluminum Galvanic Couple Using Electrochemical Impedance Spectroscopy (EIS)

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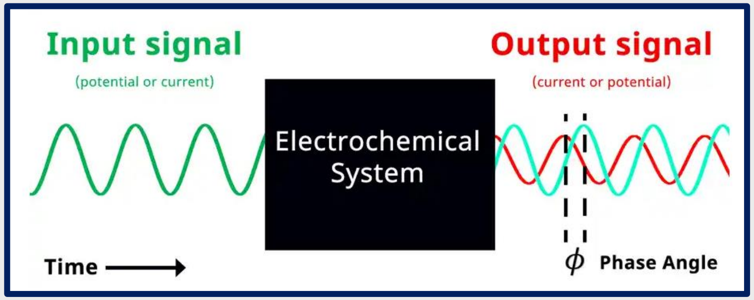
Electrochemical Impedance Spectroscopy (EIS)

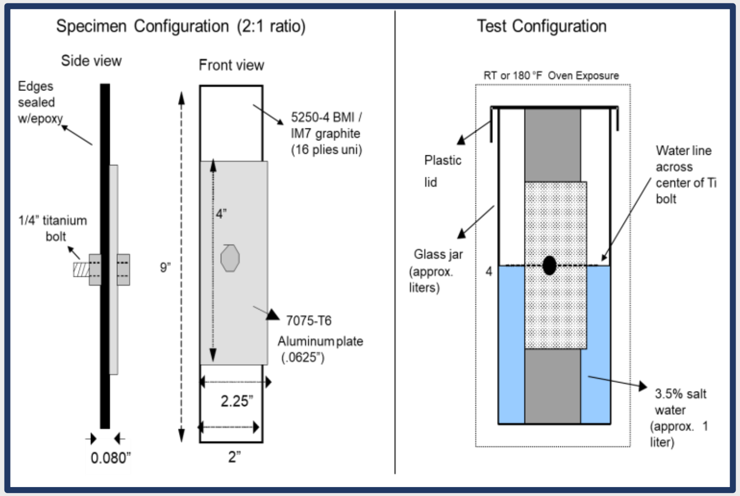
Analytical method used to establish the electrochemical response of a corrosion cell over a wide range of frequencies. This response includes properties such as impedance, capacitance and phase angle.

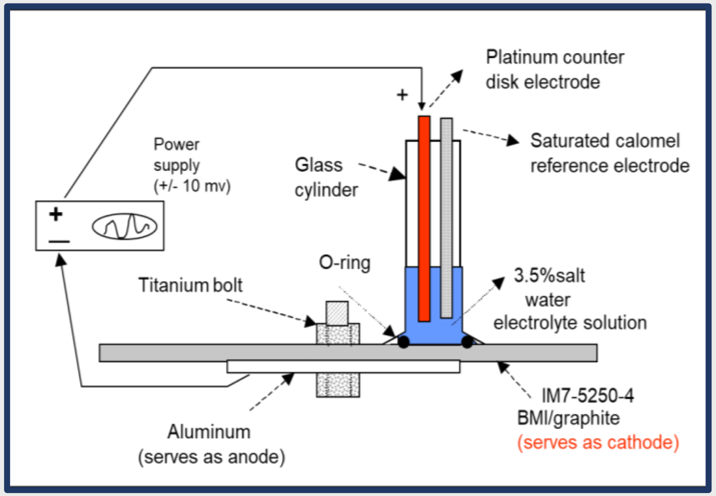
- Used extensively by the coatings industry to measure the efficiency of corrosion-prevention coatings applied to metal substrates.
- Changes in current flow are strongly associated with changes in reaction rate (i.e., corrosion rate) when chemical reactions are taking place in both anode and cathode regions of the electrochemical system.
- Phase angle results are very descriptive of polymer degradation within the galvanic couple.

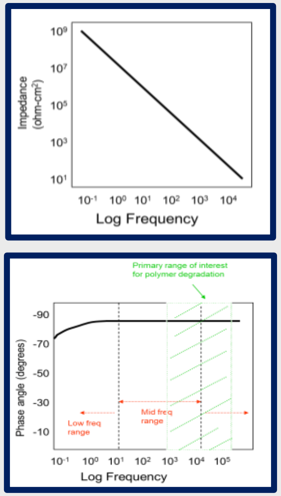


Characterization of BMI-Graphite/Aluminum Galvanic Couple Using Electrochemical Impedance Spectroscopy (EIS)

Objective: Assess Electrochemical Impedance Spectroscopy (EIS) as a viable method to characterize the galvanic cell characteristics of BMI-graphite/aluminum system after exposure to typical Navy aircraft operating environments.







Typical impedance characteristics for undamaged composite material

Conclusion

- The data has demonstrated that the non-destructive EIS technique may help in characterizing and evaluating the degradation of organic resin in resin-graphite composite/metal systems exposed to aggressive elevated temperature salt-water environment.
- Epoxy-resin in epoxy-graphite composite is highly resistive to the development of galvanic couple resulting in diminishing the probable attack by hydroxyl ions/radicals to degrade the polymer-backbone in the epoxy-resin; epoxy resin in the composite provides superior degradation protection in an aggressive environment as compared to BMI resin in the composite.

Degradation Mechanism

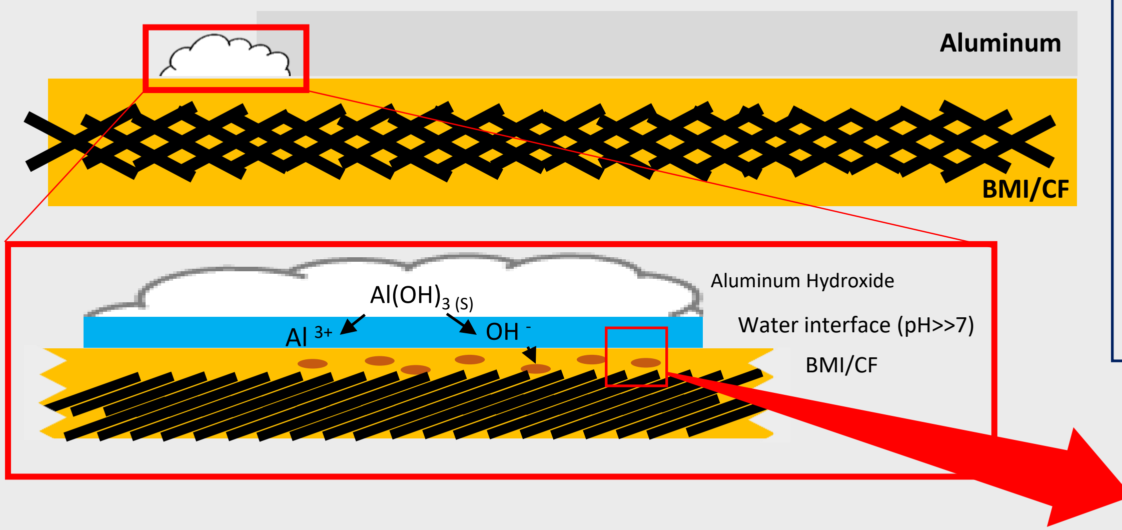
BMI Degradation Mechanism

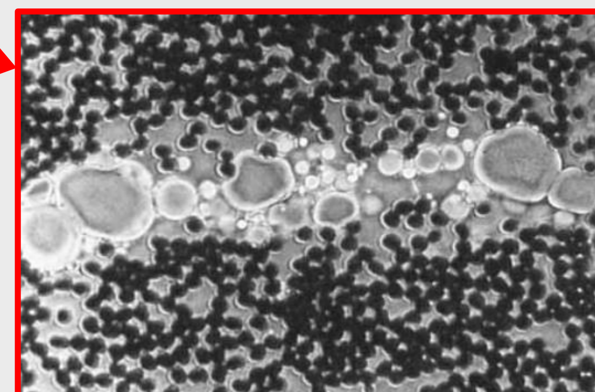
Aluminum crevice corrosion

Crevice corrosion refers to corrosive attack that occur when an aluminum surface is in close proximity to another 'apposing' surface, for example, an oxide or polymer film, a metal bolt in an engineered structure, etc.

Le Châtelier's principle states that if a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium shifts to counteract the change to reestablish an equilibrium.

$$Al(OH)_{3\,(S)} \rightleftharpoons Al^{3+}_{(aq)} + 3OH^{-}_{(aq)}$$



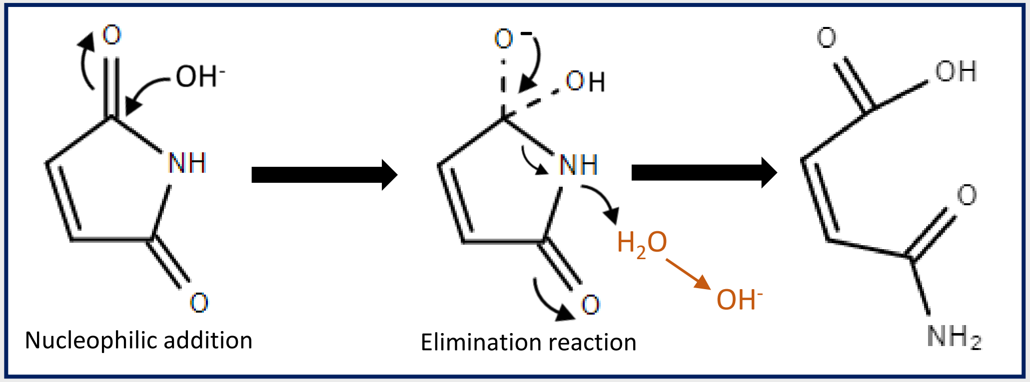


Degraded BMI surface

- A high alkaline environment can be found at the interface between Al(OH)3 and BMI
- It has been known that BMI's or polyimides and other ring forming thermosetting polymers are quite unstable in a basic aqueous solution.

BMI Degradation Mechanism

The Hydrolysis of Maleimide



The hydrolysis of maleimide in alkaline solution

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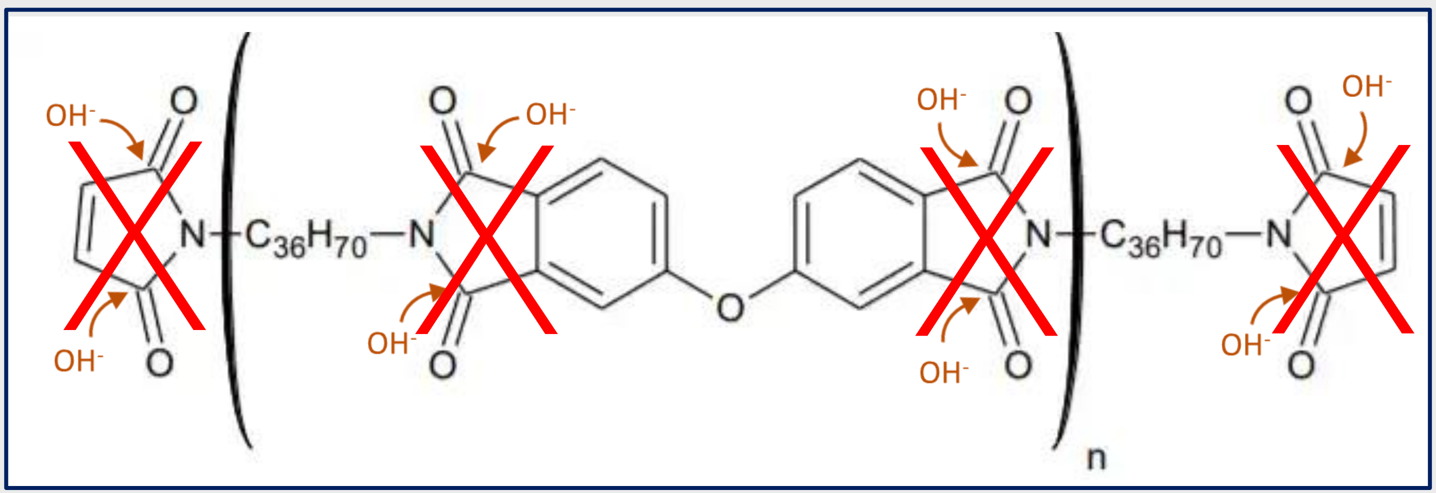
Proposed mechanism for Maleimide hydrolysis

A similar hydrolysis mechanism can be applied to explain the degradation of BMI resin.



Correcting Action

Corrosion of Imide Containing Composites

- In 1998 the team proposed that a layer of fiber glass (cloth or unidirectional) may prevent the degradation of BMI resin material. This layer would be considered non-structural and would act solely as a galvanic isolation medium. Through penetrations are considered risky since the fastener will be in contact with the metal and graphite materials. Wet installation procedures may not alleviate this concern since small cracks in the sealant may be present and no effective NDE technique exists to detect these cracks.

- Imides should be avoided in sump applications or other locations wherein salt water can collect.

- Imides should be avoided in applications where the parts are difficult to inspect and particularly when the components cannot be easily removed for detailed inspection and/or replacement.

- Other uses of these materials have no general prohibitions; rather, they will be reviewed on a case-by-case basis.

- **In a report published in 2001** it was demonstrated that two-sided glass plied films on composite matrix slows down the development of galvanic couple, and thus may extend the useful life of composite structures exposed to salt water environments.

Field Service Report

Field Service Results

Various aircraft vehicles have been examined for the presence of graphite/polyimide corrosion and, to date, non has been found. In May 1990,the General Dynamics prototype **F16-XL** wing skins were examined with video borescopes and ultrasonic hand scanners. The wing skins were fabricated out of USPs (now BP) graphite/V378A,which was bolted to anodized/coated aluminum spars. No polyimide corrosion was observed. Glass scrim covered the entire wing skin and protected it from corrosion. The graphite/polyimide lower strakes of the **AV8B (Harrier)** were investigated and BMI corrosion was not detect

Conclusions:

- Graphite/polyimide degradation occurs when all of the following conditions exist:
  - Pooled electrolyte comes in contact with active metal and graphite of composite.
  - Active metal and graphite are also in physical contact Bare graphite of composite are exposed at aqueous interface.
  - Polyimide degradation occurs as a result of hydroxyl ion accumulation in the thin film of water just above the salt water/fuel interface This accumulation is a result of the galvanic process.
- Degradation as described in this work applies to graphite composites containing an imide linked resin, the phenomena was found to occur in BMI, in condensation polyimides, and in triazines.
- For graphite epoxies, degradation of the type described in this work isn't expected to be risk.
- When the composite is properly treated, standard galvanic protection schemes have been shown to be efficient in preventing polyimide degradation.

RELATIONSHIP OF GRAPHITE/POLYIMIDE COMPOSITES TO GALVANIC PROCESSES

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Questions