Biodegradation of Composite Materials

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Fiber-reinforced polymer composites were examined for susceptibility to microbiologically-influenced degradation. Composites, resins, and fibers were exposed to sulfur/iron-oxidizing, calcareous-depositing, ammonium-producing, hydrogen-producing, and sulfate-reducing bacteria (SRB) in batch culture. Surfaces were uniformly colonized by all physiological types of bacteria; however, the microbes preferentially colonized surface anomalies including scratches and fiber disruptions. Epoxy and vinyl ester neat resins, carbon fibers, and epoxy composites were not adversely affected by the microbial species. SRB degraded the organic surfactant on glass fibers. Hydrogen-producing bacteria appeared to disrupt bonding between fibers and vinyl ester resin and to penetrate the resin at the interface. Acoustic emission testing demonstrated reduction of tensile strength in a stressed carbon fiber-reinforced epoxy composite after exposure to SRB.

INTRODUCTION

Fiber-reinforced polymeric composites (FRPC) are commonly used in aquatic environments to replace conventional materials in structural applications. Performance advantages include increased strength-to-weight ratio, hardness, wear and corrosion resistance, stiffness, and improved creep behavior. Modifications during fabrication, such as thermal properties and configurations, can be easily made for specific applications. Although initially more expensive than traditional materials, FRPC remain serviceable for a longer time and provide long-range financial savings. Experimental uses of FRPC in marine heat exchangers, condensers, pumps, shipboard structures, and deep-sea applications are ongoing (Sedriks, 1994).

Unfortunately, little attention has been paid to environmental degradation of FRPC. It was long believed, for example, that fiberglass boat hulls would not suffer the corrosion, biofouling, or deterioration found in conventional materials. However, it is now recognized that all engineering materials become colonized by microorganisms, including bacteria, within hours of exposure in natural waters (Little et al., 1986). Microorganisms grow and produce a viscoelastic layer or biofilm. The environment at the biofilm–material interface is radically different from the bulk medium in terms of pH, dissolved oxygen, and organic and inorganic species (Little et al., 1991). Furthermore, polymeric composites are subject to degradation from moisture intrusion and osmotic blistering (Davis et al., 1983). Although the problems of moisture intrusion and blistering have been studied and can be eliminated by proper manufacturing and maintenance procedures, repair costs and safety risks are high. Polymeric composites are subject to many kinds of environmental degradation. Tucker & Brown (1989a) showed that carbon/polymer composites galvanically coupled to metals are degraded by cathodic reactions in oxygenated seawater. Jones et al. (1991) demonstrated that epoxy and nylon coatings on steel were breached by mixed cultures of marine bacteria.

All phases of FRPC are susceptible to some type of microbial degradation. Phases include fibers, resins, and the fiber–resin interface. Fibers, usually glass or carbon in polymeric composites, provide reinforcement strength with low density. Resin matrices provide load transmission and energy dissipation. Fiber–resin interface bonding is essential for composite integrity. Fibers are not usually degraded by microorganisms, although Pendrys (1989) reported that p-55 graphite fibers were attacked by a mixed culture of Pseudomonas aeruginosa and Acinetobacter calcoaceticus, common soil isolates. Gu et al. (1995) reported fungally-mediated degradation of glass and carbon fibers.
with penetration into the resin matrix. Organic additives to fibers, such as plasticizers and stabilizers, may provide nutrients for microbial growth and ultimate degradation (Upsher, 1976). Polyesters and polyester polyurethane resins are vulnerable to microbial attack, first recognized in vinyl textile industries (Baker, 1978). As a result, fungi and Ps. aeruginosa have been added to quality control testing in that industry. Epoxy resins are considered more resistant to bacterial attack.

Possible mechanisms for microbial degradation of polymeric composites include: direct attack of the resin by acids or enzymes, blistering due to gas evolution, enhanced cracking due to calcareous deposits and gas evolution, and polymer destabilization by concentrated chlorides and sulfides. Any attack may result in loss of strength due to fracture, disbonding, or delamination, and ultimate failure.

This paper reports surface analysis results for an experiment where fiber-reinforced polymeric composites were exposed to bacterial cultures representing physiological types for specific degradation mechanisms. A second experiment attempted to add two important parameters to biodegradation studies: (1) environmental stress applied before and during exposure, and (2) quantification of biodegradation using mechanical testing. A third experiment investigated the effect of biotic exposures on a previously impacted composite.

**EXPERIMENTAL PROCEDURE**

**Experiment I. Microbial exposures for specific degradation mechanisms**

A sulfur/iron-oxidizing bacterium, Thiobacillus ferroxidans, Leathan strain, was maintained in 9K medium (Silverman & Lundgren, 1959). Pseudomonas fluorescens (American Type Culture Collection (ATCC), Rockville, MD, #17571), a calcareous-depositing bacterium originally isolated from polluted seawater, was maintained in a medium containing 0.25 g calcium acetate, 0.4 g yeast extract, 1.0 g glucose, 100 ml distilled water, and adjusted to pH 8.0 using NaOH (Boquet et al., 1973). Lactococcus lactis subsp. lactis, ATCC #19435, an ammonium-producing bacterium, was maintained in brain heart infusion medium (Difco Laboratories, Detroit M1). Clostridium acetobutylicum, ATCC #824, a bacterium previously shown to produce copious amounts of hydrogen from fermentation of sugars, was maintained in a growth medium described by Ford et al. (1990). A mixed facultative/anaerobic marine culture containing SRB was originally isolated from corroded carbon steel in marine service (Jones-Meehan et al., 1994) and maintained in Postgate B (Postgate, 1979) plus 25 gm/l NaCl growth medium. The consortium has been shown to be particularly aggressive in corrosion of copper alloys and degradation of caulks, polymeric coatings, and sealants (Jones-Meehan et al., 1994).

Triplicate coupons of two fiber-reinforced polymer composites—a carbon fiber-reinforced epoxy (T-300) and a glass (S-2) and carbon-reinforced vinyl ester (T-300), were exposed to microbiological cultures for 161 days. The epoxy was cured in a vacuum bag autoclaved at 121°C. Vinyl ester resins were post-cured at 100°C for 8 h. Additionally, carbon fibers, glass fibers, vinyl ester, and epoxy resins were individually exposed for 90 days to SRB and hydrogen-producing bacteria. Glass fibers had been treated with organofunctional silane. All cultures were maintained at room temperature and were periodically refreshed with new media. Triplicate uninoculated controls were maintained under the same exposure conditions. Samples were weighed before and after exposure. Moisture uptake was calculated after the biofilm had been removed with a cotton swab containing acetone and the sample reweighed.

Samples were examined before and after exposure using environmental scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (ESEM/EDS) (Wagner et al., 1992). At exposure conclusion, coupons were fixed in 2% glutaraldehyde, rinsed with distilled water, examined wet for evidence of degradation resulting from microbial activity, and compared to uninoculated controls. Bacterial colonization, distribution, and localized deterioration/disruption were noted.

**Experiment II. Effects of stress applied before and during microbial exposures**

Flat, rectangular lengths of a carbon fiber-reinforced epoxy resin composite (6-ply, unidirectional fiber volume 50%) were prepared
and assembled in 3041 stainless steel loading fixtures at controlled, applied strain levels. Stressed composites were maintained as follows: four sets of two samples each (coupon size 76.2 x 12.7 mm) assembled in 3-point bend fixtures (Fig. 1a) and two sets of two samples each (coupon size 127.0 x 12.7 mm) in 4-point bend fixtures (Fig. 1b). Strain levels were calibrated with a strain-gauged dummy sample and were chosen at levels where mechanical effects would not dominate. In 3-point bend testing (Fig. 1a) the tensile stress is highest under the loading pin on the sample surface opposite the loading pin, while compressive stress is greatest immediately under the loading pin. Strains were applied by turning the loading screw on top of the loading pin. Duplicate sets were maintained at strain levels of 0.4 and 0.6%. In 4-point bend testing (Fig. 1b) samples were maintained at 0.2 and 0.4% strain levels. Tensile stress was approximately uniform along sample length.

Loading fixtures with composite strips were exposed to the previously described mixed, marine facultative culture known to contain SRB. Stressed and nonstressed biotic exposures and sterile controls were maintained anaerobically for 7 months at room temperature and were periodically refreshed with new medium.

One of each of the 3- and 4-point bend assemblies was briefly removed from the culture medium after 1 month exposure for visual inspection for any evidence of galvanic corrosion between the stainless steel loading assemblies and the carbon components of the composite. One area near a stainless steel–composite junction was aseptically swabbed to expose composite surface. Composite samples were examined after exposures using ESEM/EDS as described for Experiment I.

Acoustic emission testing was performed on all samples before and after exposures for mechanical quantification of change in tensile strength. In acoustic emission testing, Piezoelectric transducers are affixed to surfaces and acoustic emissions electronically monitored and recorded. As load is applied to a composite, discrete bursts of acoustic energy characteristic of the physical nature of each composite component and its adhesion to other components are produced (Hamstad, 1986). The goal was to identify and compare loads where a sudden increase (‘knee’) in acoustic hits occurs for each sample. Load was applied in the form of volts (V) where 1 V = 226.8 kg (500 lbs). Acoustic

![Fig. 1. Carbon-reinforced composite coupons as assembled in loading assemblies before microbial exposures (a) 3-point bend and (b) 4-point bend.](image-url)
emission was performed with load levels continued to a final range of 1360–1928 kg (6–8.5 V, 3000–4250 lbs). A 50-dB threshold level was used to lessen interference from the sound of the testing machine.

**Experiment III. Effects of microbial exposures after impact**

Carbon/glass-reinforced composite, assembled in two layers between a rubber layer (prepared according to proprietary specifications) was exposed in a similar manner to the SRB-containing culture previously described and to Key West, FL, natural seawater (35 ppt salinity). The point of impact was visible to the naked eye as a ‘slight dent’ in the composite and was measured for ESEM/EDS relocation after 6 months of biotic and abiotic exposures.

**RESULTS AND DISCUSSION**

**Experiment I**

In all cases, composite, neat resin and fiber surfaces were colonized by all microbial types. Neither the epoxy nor the vinyl ester composites were adversely affected by calcareous-depositing or ammonium-producing bacteria. There was no evidence of attack of resins, and fibers remained embedded within both resins. Composites exposed to sulfur/iron-oxidizing bacteria were covered with crystalline deposits containing iron and sulfur in addition to microbial cells. All surfaces exposed to SRB were black due to the deposition of iron sulfides. No damage to the epoxy composite, epoxy neat resin, carbon fibers, or vinyl ester neat resin could be attributed to the presence and activities of SRB and hydrogen-producing bacteria.

Figure 2a shows unexposed glass fibers, glass fibers exposed to uninoculated medium (Fig. 2b), and glass fibers exposed to SRB in culture medium (Fig. 2c). Glass fibers exposed to SRB lost all rigidity after the 90-day exposure so that the weave pattern was no longer evident. Control glass fibers remained rigid and maintained the original weave pattern. Glass fibers are routinely treated with an organic surfactant used to size the fibers and to facilitate handling. The silane surfactant promotes adhesion between the vinyl ester resin and glass fibers. Microbial degradation of the surfactant by SRB was further demonstrated with ESEM/EDS dot maps of silicon distribution (Fig. 3). Dot maps of control fibers exposed to uninoculated media showed concentrations of silicon within the core of each fiber and small amounts of silicon along the

![Fig. 2. Light microscope micrographs of glass fibers (2x) (a) unexposed, (b) exposed to abiotic culture medium, and (c) exposed to SRB-containing culture.](image-url)
length of each fiber. Similar maps for fibers exposed to SRB showed increased amounts of silicon along the length of the fiber.

Hydrogen-producing bacteria appeared to disrupt bonding between fibers and vinyl ester resin (Fig. 4). The organisms penetrated the resin and disruption of fibers and resin may be due to gas formation within the composite.

Previous work published for moisture uptake for vinyl ester neat resin and the carbon vinyl ester composite indicates that the materials should be saturated after 90 days (Tucker & Brown, 1989b). The neat resin and the carbon vinyl ester composite are typically saturated at 0.78 and 2.25% weight gain, respectively. In the presence of biofilms, moisture uptake was typically 0.1 and
0.9% for the neat resin and composite, respectively. It appears that biofilms may act as a diffusion barrier for water, retarding moisture uptake, a suggestion also observed by researchers exposing composite materials to Galveston Bay, TX, seawater (Stolarski et al., 1993).

**Experiment II**

At the 1-month inspection of composites exposed to the SRB-containing microbial culture, a black, viscous sulfide film was uniformly distributed over composite surfaces (Fig. 5). There were no visible indications of galvanic corrosion, blistering, or bubble formation. Tucker & Brown (1989a) reported blister formation on graphite composites galvanically coupled to mild steel after 3 weeks exposure in aerobic seawater.

After 7 months, ESEM images demonstrated that all composites exposed to the culture had been colonized. Bacteria and/or sulfide crystals were preferentially concentrated along fiber/resin interfaces and in superficial surface scratches (Fig. 6). Figure 7 shows a significant disruption of fibers on one 0.2% strained 4-point bend sample at the point of greatest stress. Bacteria had preferentially colonized the surface anomaly, but the disruption cannot be attributed to their presence.

A number of investigators have shown a correspondence between occurrence of a knee in the hits vs. load plot and the change in acoustic emission behavior (English, 1987). Unstressed/unexposed and unstressed/exposed controls exhibited knees at 1.75 and 1.6 V, respectively (Fig. 8a, b). The 3-point bend/0.4% strain required a higher load to cause a rapidly increased number of hits than for the controls. All other samples (3-point bend/0.6% strain, 4-point bend/0.2% strain, and 4-point bend/0.4% strain) required less load before a rapid change in slope as compared to controls (Fig. 8a, b). Of the 4-point bends, the 0.2% strain sample needed less load than the 0.4% strain sample. Overall, data showed a general trend of knees for stressed biotic samples occurring at lower loads than knees for stressed abiotic samples, suggesting loss in tensile strength as the result of microbial exposures. Plots of initial load levels only (0–2.5 V) are shown in Fig. 8a, b. Fiber fracture was visibly random in all samples at end of loadings.

**Experiment III**

Preferential microbial colonization in areas of fiber fracture and dislocation at points of impact were...
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Fig. 7. Disrupted fibers of exposed, stressed coupon.

observed. No damage resulting from microbial activities can be concluded.

CONCLUSIONS

Epoxy resin and carbon fibers, either individually or in composites, were not degraded by sulfur/iron-oxidizing, hydrogen-producing, calcareous-depositing, or a facultative/anaerobic microbial consortium containing SRB. Bacteria colonized all resins, fibers, and composites. The SRB mixed culture did not degrade neat vinyl ester resin. Microbial degradation of the organic surfactant on glass fibers was documented. Hydrogen-producing bacteria appear to have disrupted fiber-vinyl ester resin bonding with gas production and penetration of the resin. Biofilms may provide a diffusion barrier that retards moisture uptake.

Acoustic emission data indicate that an SRB-containing culture may cause deterioration of stressed carbon-reinforced epoxy composites. These data cannot be considered conclusive because of the small sample size, basic specimen variation, and the lack of an identifiable failure mechanism. Preferential bacterial colonization of surface anomalies was consistently observed.

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Fig. 8. Acoustic emission plots (hits vs. load) for coupons after exposures.
REFERENCES


