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MICROBIAL DEGRADATION OF STRESSED FIBER REINFORCED POLYMERIC COMPOSITES

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ABSTRACT

Reduction of tensile strength was demonstrated for carbon fiber reinforced epoxy resin composite strips after exposure to sulfate-reducing bacteria (SRB) in batch culture. Composite strips were maintained in a stressed condition in 3- and 4-point bend fixtures before and during exposure. Exposed surfaces were examined microscopically for bacterial colonization, fiber disruption and disbonding. Mechanical testing and acoustic emission (AE) examinations were used to evaluate degradation of tensile strength.

Keywords: polymeric composites, microbial degradation, mechanical testing, acoustic emission

INTRODUCTION

Fiber reinforced polymeric composite materials are used in many aquatic environments. With high strength-to-weight ratios and improved stiffness for high performance, these materials surpass conventional metals and alloys for many structural applications. Unfortunately, little attention has been paid to environmental degradation. 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 after exposure in natural waters.[1] 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.[2] Furthermore, polymeric composites are subject to degradation from moisture intrusion and osmotic blistering.[3] Although the problems of moisture intrusion and blistering have been studied[4] and can be eliminated by proper manufacturing and maintenance procedures,[5] repair costs and safety risks are high.

Polymeric composites are subject to many kinds of environmental degradation. Tucker and Brown[6] showed that carbon/polymer composites galvanically coupled to metals are degraded by cathodic reactions in seawater. Jones et al.[7] demonstrated that epoxy and nylon coatings on steel were breached by mixed cultures of marine bacteria. Pendrys[8] reported that p-55 graphite fibers were attacked by a mixed culture of *Pseudomonas aeruginosa* and *Acinetobacter calcoaceticus,* common soil isolates. 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.

Wagner et al.[9] reported results of polymeric composite exposures to bacterial cultures representing physiological types for specific degradation mechanisms. They showed that the carbon fiber reinforced epoxy and a glass and carbon reinforced vinyl ester were preferentially colonized by bacteria at fiber/resin interfaces. Degradation of an organic surfactant on glass fibers by sulfide-producing SRB and disruption of fiber-vinyl ester resin bonding by hydrogen-producing bacteria were observed. This paper is an extension of those experiments and represents an attempt to add two important parameters to biodegradation studies: (1) an environmental stress was applied to samples before exposure and (2) mechanical impact of microbiological colonization and sulfide production was quantified.

EXPERIMENTAL PROCEDURE

Samples

Flat rectangular lengths of a carbon fiber[(1)] reinforced epoxy resin[(2)] composite ((fiber volume (V_f 50%)) were prepared and assembled in 304L stainless steel loading fixtures at Texas A&M University, Department of Mechanical Engineering, for controlled applied strain levels. Two groups of stressed composites were used as follows: 4 sets of 2 samples each (each coupon 76.2 mm × 12.7 mm) assembled in 3-point bend fixtures (Figure 1) and 2 sets of 2 samples each (each coupon 127.0 × 12.7 mm) in 4-point bend fixtures (Figure 2). 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 (Figure 1) 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. Duplicate sets were maintained at strain levels of 0.4% and 0.6%. Strains were applied by turning the loading screw on top of the loading pin. In 4-point bend testing (Figure 2) samples were maintained at 0.2% and 0.4% strain levels. Tensile stress was approximately uniform along sample length.

Exposure Conditions

Loading fixtures with composite strips were exposed to a facultative, mixed culture known to contain SRB. The culture was originally isolated from a corrosion failure of a carbon steel waster piece on a surface ship,[10,11] and maintained in Postgate B plus 25 gm/L NaCl growth medium.[12] The consortium has been shown to be particularly aggressive in the corrosion of copper alloys and degradation of caulks, polymeric coatings, and sealants. Biotic exposures and abiotic controls were maintained anaerobically for 7 months at room temperature and were periodically refreshed with one-third volume new medium.

Surface Analysis

Samples were examined before and after exposure using environmental scanning electron microscopy coupled with energy-dispersive x-ray analysis (ESEM/EDS).[13] Bacterial colonization, distribution, and localized deterioration/disruption were noted.

One each of the 3- and 4-point assemblies was briefly removed from the culture medium after 1 month exposure for visual inspection of any evidence of galvanic corrosion between the stainless steel loading assemblies and the graphite components of the composite. One area near a stainless steel/composite junction was aseptically swabbed to expose composite surface.

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(1)Type IM7, Hercules Advanced Materials and Systems Co., Magna, UT 84044
(2)Tactix 556, Dow Chemical Co., Midland, MI 48674

Mechanical Testing

Tensile testing was performed according to ASTM D3039-76[(3)] and compared to nonstressed, nonexposed and nonstressed, exposed controls. Tests were performed using a hydraulic testing system with 5 kips load cell under displacement control mode. Displacement rate was 1.27 mm/min, giving a strain rate of 0.05 in/in/min. Coupons were prepared for testing by bonding one inch fiberglass/epoxy tabs with bevels to each sample. Longer 4-point coupons were first trimmed to 76.2 mm. Test gauge length was about 25.4 mm. Tensile strength of the fibers is rated by the manufacturer as 400 ksi for V_f=62%. Calculated strength expected for identical fibers at V_f=50% is 322.5 ksi with an applied load of 2560.6 kg (5645 lb) required for failure. One coupon of each set was used for tensile testing.

Acoustic emission (AE) is a nondestructive technique that offers many advantages in monitoring of damage in materials: high sensitivity to any process or mechanism that generates stress waves, real-time capability, and ability to locate damage regions.[14] 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. Piezoelectric transducers are affixed to surfaces and acoustic emissions electronically monitored and recorded. A 50-decibel threshold level was used to lessen interference from the sound of the testing machine. AE testing was performed on one coupon of each set with load levels continued to final range of 1360–1928 kg (6–8.5 V, 3000–4250 lb).

RESULTS AND DISCUSSION

Surface Analysis

At the 1-month inspection a black, viscous sulfide film was uniformly distributed over composite surfaces (Figure 3). There were no visible indications of galvanic corrosion, blistering, or bubble formation. Tucker and Brown reported blister formation on graphite composites galvanically coupled to mild steel after 3 weeks exposure in aerobic seawater.[15]

After 7 months, macroscopic colonies of SRB appeared as wrinkles in the otherwise smooth sulfide layer surface (Figure 4). ESEM images demonstrated that all composites had been colonized by SRB. SRB and sulfide crystals were preferentially concentrated along fiber/resin interfaces and in superficial surface scratches (Figure 5 a,b,c). A significant disruption of fibers was observed on one 0.2% stressed 4-point bend sample at the point of greatest strain (Figure 6). Bacteria had preferentially colonized the surface anomaly (Figure 6 a,b), but the disruption cannot be attributed to their presence.

Mechanical Testing

Tensile tests were stopped without failure at 2,154 kg (4,750 lb) due to system load limitations.

Acoustic emission plots represent acoustic emission events as a function of load level (one volt=226.8 kg (500 lb)). A number of investigators have shown a correspondence between a knee in the curve and the change in AE behavior.[16] A rapid change in slope is related to an increased number of acoustic hits. Unstressed/unexposed and unstressed/exposed controls exhibited knees at 1.75 and 1.6 V, respectively (Figure 7 a,b). The 3-point bend (0.4% strain) required a higher load to cause a rapidly increased number of hits than for controls (Figure 7c). 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 (Figure 7 d,e,f). Of the 4-point bends, the 0.2% sample needed less load than the 0.4% sample. Plots of initial load levels only are shown in the figures. Fiber fracture was visibly random in all samples at conclusion of loadings.

[(3)]ASTM, Philadelphia, PA 19103

CONCLUSIONS

Seven of eight stressed composite strips showed apparent reduction of mechanical strength as a function of load after exposure to SRB. These data are indicative that SRB may cause deterioration of stressed graphite reinforced epoxy composites, but cannot be considered conclusive because of the small sample size, basic specimen variation, and the lack of identifiable failure mechanism.

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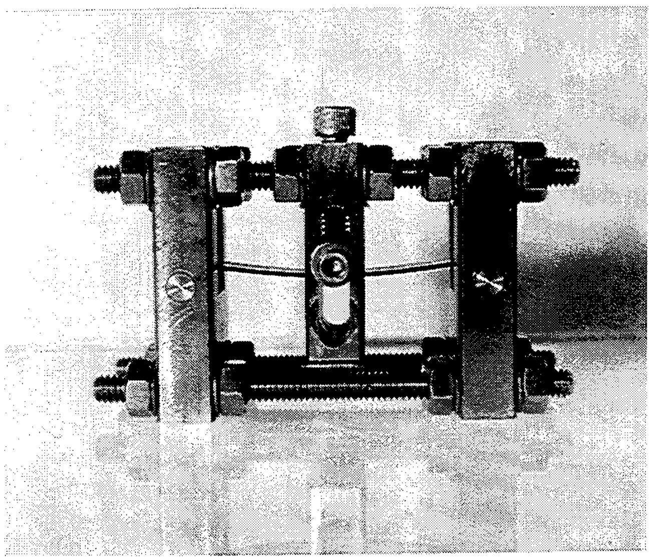

FIGURE 1 — Composite coupon as assembled in 3-point bend loading assembly before exposure

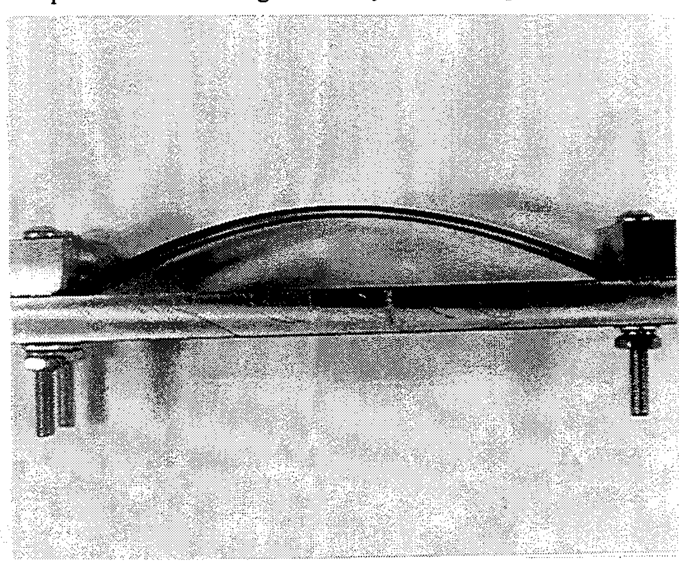

FIGURE 2 — Composite coupon as assembled in 4-point bend loading assembly before exposure

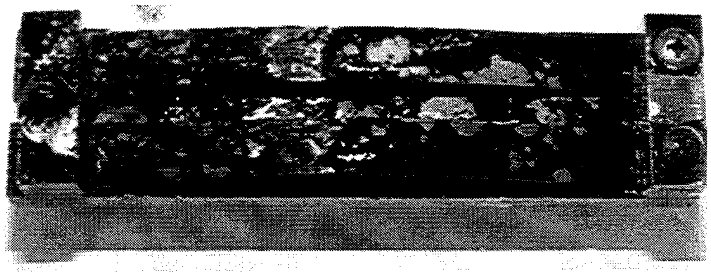

FIGURE 3 — Sulfide film on coupon surface at 1 month examination

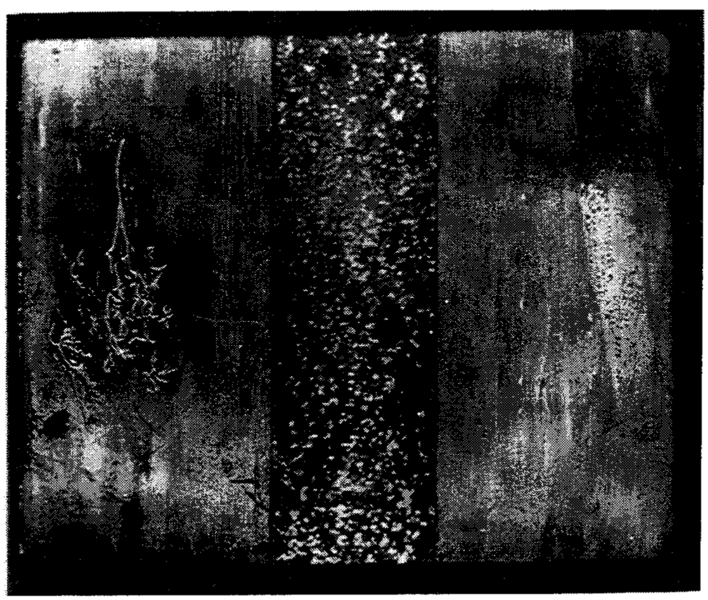

FIGURE 4 — Coupon surface after 7 months exposure (3×)

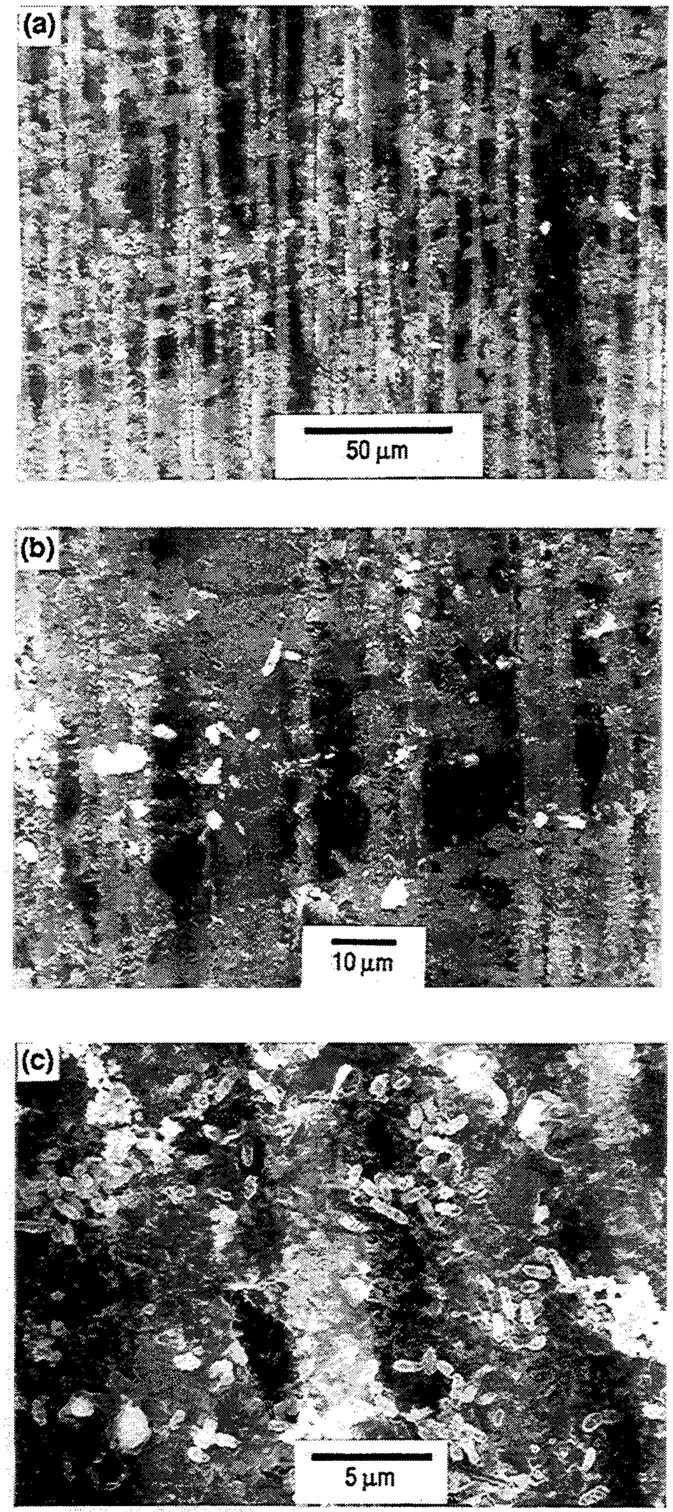

FIGURE 5 — (a,b,c) Bacteria and crystals preferentially distributed along fiber/resin interface

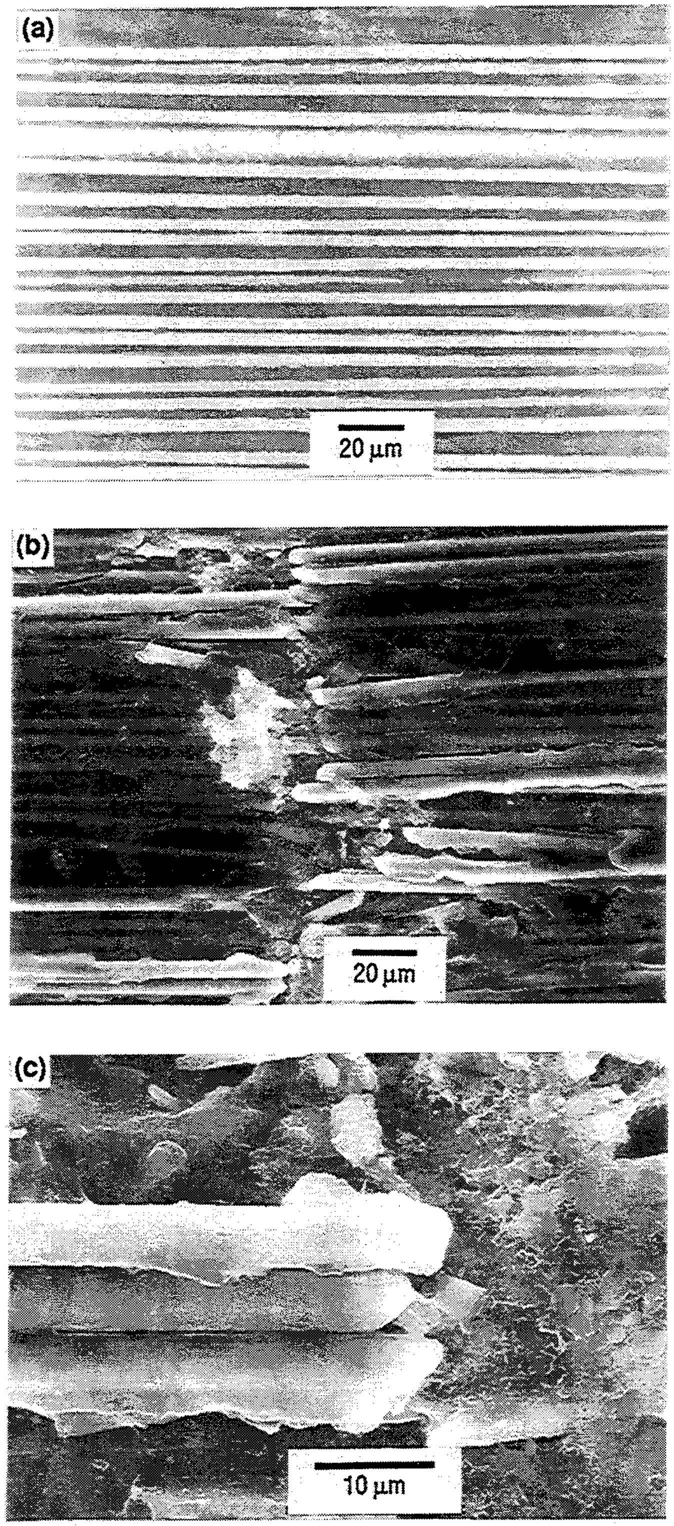

FIGURE 6 — (a) Fibers of unexposed, unstressed coupon and (b, c) disrupted fibers of exposed, stressed coupons at point of greatest applied strain

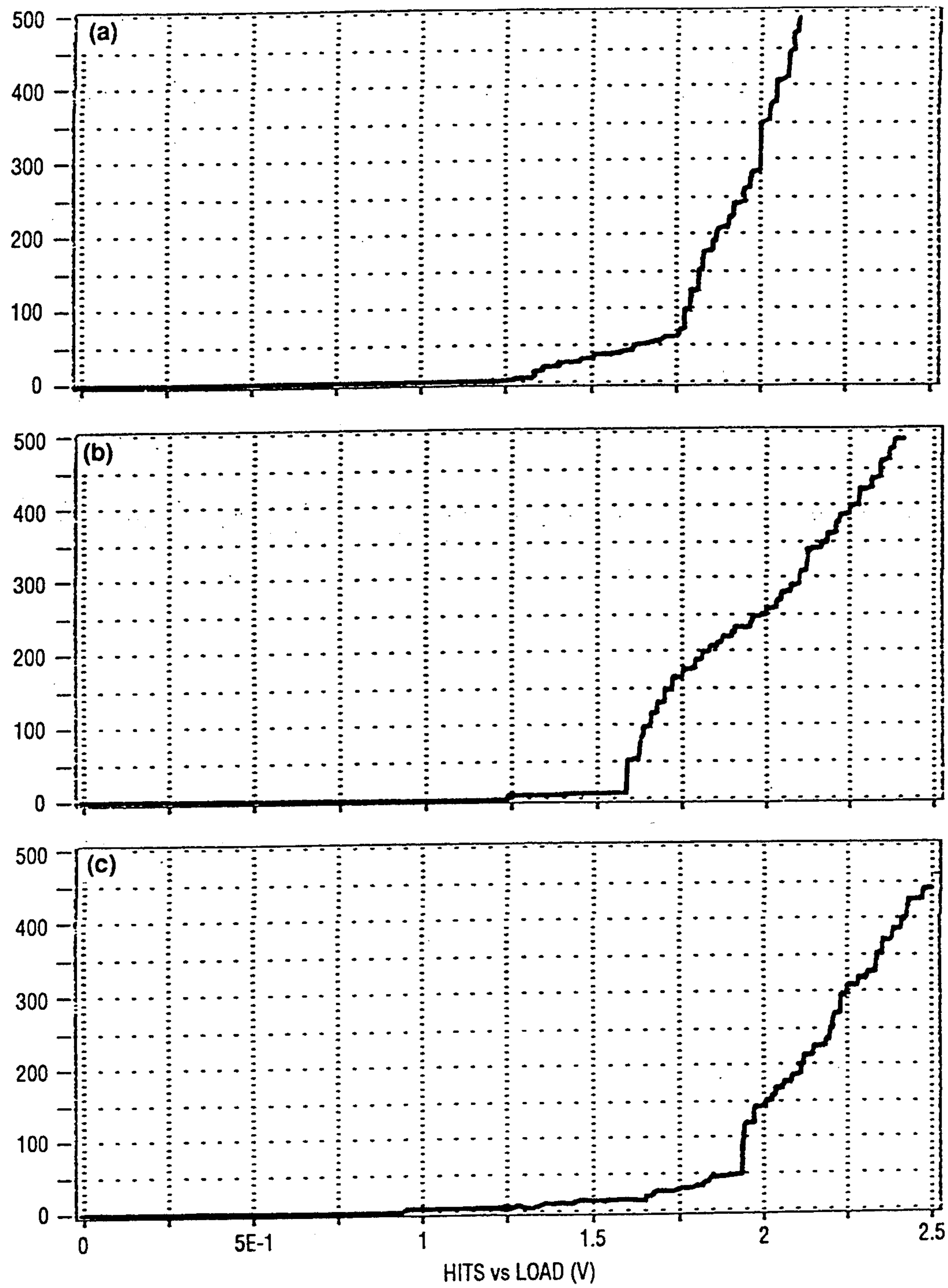

FIGURE 7 — AE plots of hits vs. V (load): (a) control—unstressed, unexposed, (b) control —unstressed, exposed, and (c) 3-point bend, 0.4% strain

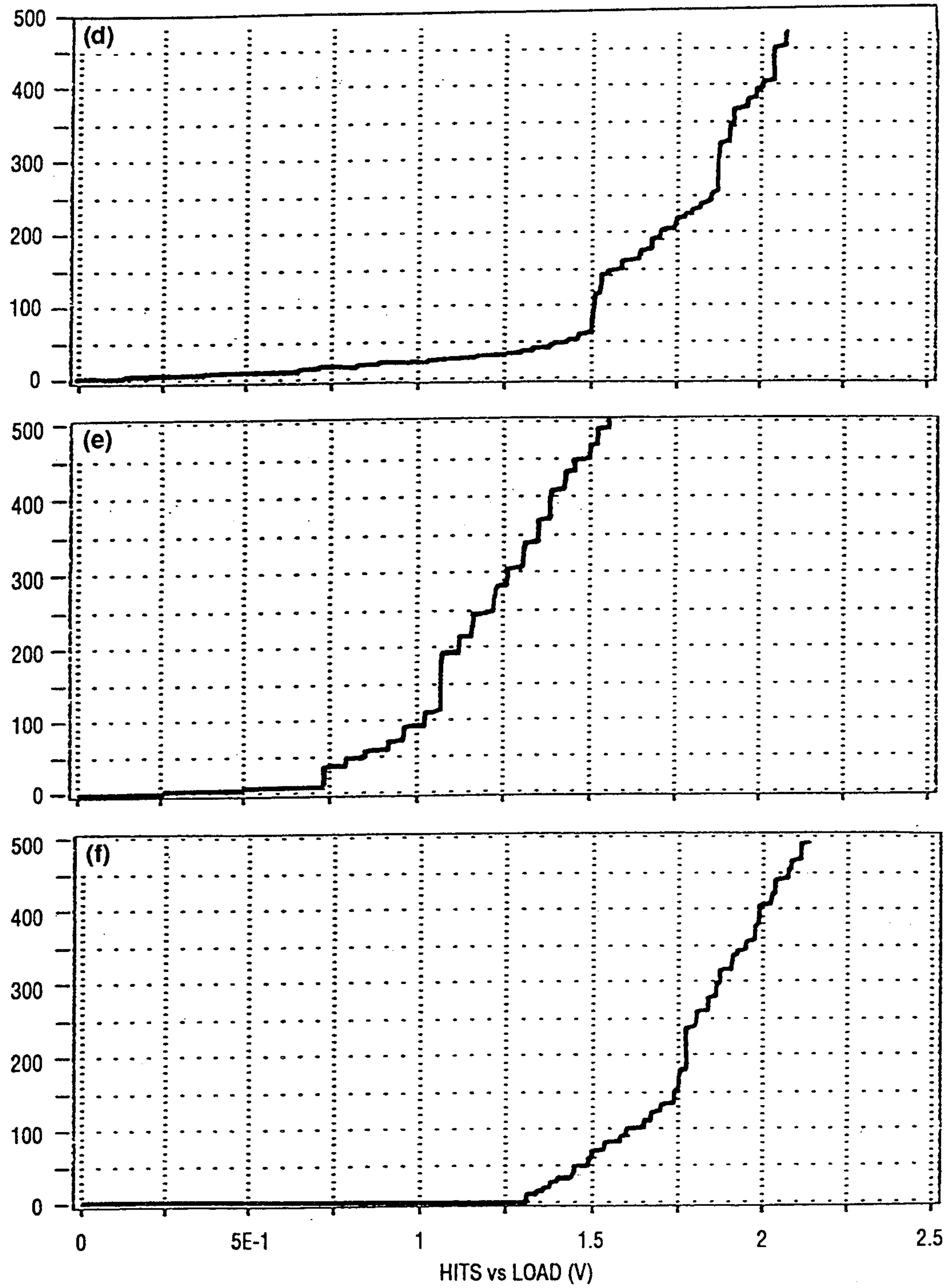

FIGURE 7 — (cont.) (d) 3-point bend, 0.6% strain, (e) 4-point bend, 0.2% strain, and (f) 4-point bend, 0.4% strain.

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