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Fiber-reinforced polymeric composites are susceptible to microbial degradation

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A mixed culture of fungi, enriched from degraded polymeric materials, formed biofilms on coupons of fiber-reinforced polymeric composites (FRPCs). They grew actively in aqueous extracts of the composites under ambient conditions. The data indicate that the fungi utilized the resins or fiber chemical sizing as carbon and energy sources. A progressive decline in impedance from above 10^7 Ohms to below 10^6 Ohms was detected in the inoculated FRPC panels by electrochemical impedance spectroscopy (EIS) after 179 days of incubation, but not on the sterile controls. The degradation proceeds through an initial ingress of water into the resins, followed by degradation of bonding between fiber surfaces and resins and finally separation of fibers from the resins. At the end of EIS study, the extent of disbonding in the inoculated composite was greater than the control observed by scanning electron microscopy. These results suggest that the composite materials are susceptible to microbial attack by providing nutrients for growth.

Keywords: biodeterioration; degradation; disbonding; electrochemical impedance spectroscopy; fungi; polymeric composites

Introduction

Fiber-reinforced polymeric composites (FRPCs) are structural materials widely used in transportation, aviation, and aerospace [2,12,14]. The increasing usage of these materials is primarily due to their high strength, molding flexibility and lower weight compared to metal alloys. It is expected that this class of materials will find more diversified applications in the future. These materials are frequently in contact with moisture and microbial contaminants, resulting in biofilm formation [7,11,14,16].

Fungi can penetrate into the interior of composites composed of fluorinated polyimide resins reinforced with glass fibers [7,11,14]. Both glass and carbon fibers are also susceptible to the growth of microorganisms and formation of microbial biofilms [11]. Since there are several chemically and physically distinguishable constituents in a composite, localized chemical changes resulting from growth and metabolism of microorganisms may accelerate damage to individual constituents and weakening of bonding between resins and reinforcing fibers [11]. Degradation of a composite material may significantly affect its physical integrity and fatigue performance. Data were recently obtained showing growth of microorganisms on composite reinforcing fibers, suggesting the utilization of sizing chemicals from surfaces of graphite carbon fibers by microorganisms as carbon and energy sources [11]. We have also demonstrated that fungi colonize graphite sheets, and electronic packaging polyimides [10]. Information about the effect of microorganisms on the integrity of composite materials is essential for a comprehensive assessment of the potential for microbial damage and for the development of resistant materials.

The objectives of this study were to investigate the nutritional relationship between constituents of composites which are attacked by microorganisms and the growth of microorganisms, and to monitor composite degradation processes by electrochemical techniques in order to elucidate the mechanisms of degradation.

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Materials and methods

Colonization of composite coupons

The FRPC materials were Magnamite IM-6G/3501-6 unidirectional layup with F161/120 style glass prepreg on both sides (Hercules Inc, Magna, UT, USA). They consisted of Hercules 3501-6 epoxy resins with unidirectional reinforced graphite fibers with a layer of crowfoot satin weave epoxy impregnated glass on both sides. The thickness of the composite was approximately 2 mm. Fiber volume was 62% in the composite. The graphite fibers and epoxy resins were cured into flat plates for use as assembly racks. Large pieces were cut into small coupons with dimensions of $10 \times 20 \times 2$ mm. The coupons were sterilized and inoculated with a previously isolated fungal consortium in flasks containing a malt broth medium (Difco Lab, Detroit, MI, USA). The consortium was previously enriched on degraded polymeric materials [10,11]. After 30 days of incubation, samples were prepared for scanning electron microscopic observation.

Growth on composite extracts

Two coupons of the composite were autoclaved in each flask containing 80 ml of a minimum salt medium for 20 min. The salt medium consisted of (g L^{-1}): K_2HPO_4 0.8, KH_2PO_4 0.2, $CaSO_4 \cdot 2H_2O$ 0.05, $MgSO_4 \cdot 7H_2O$ 0.5, $FeSO_4 \cdot 7H_2O$ 0.01, and $(NH_4)_2SO_4$ 1.0. The coupons were

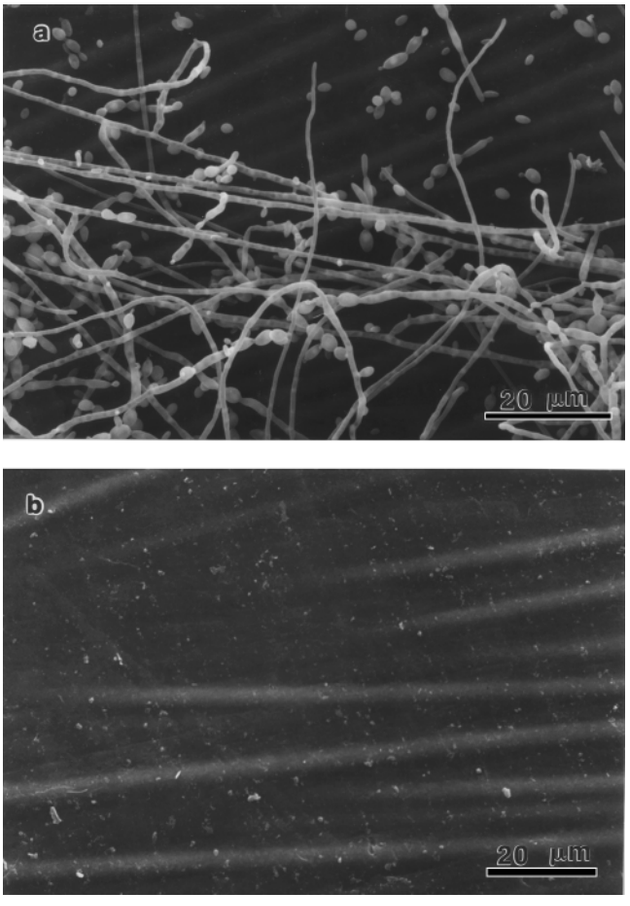

Figure 1 (a) Scanning electron micrograph showing fungal colonization of the surface of an epoxy/graphite fiber composite after 30 days of incubation; (b) SEM of the composite coupons maintained under aseptic conditions for 30 days.

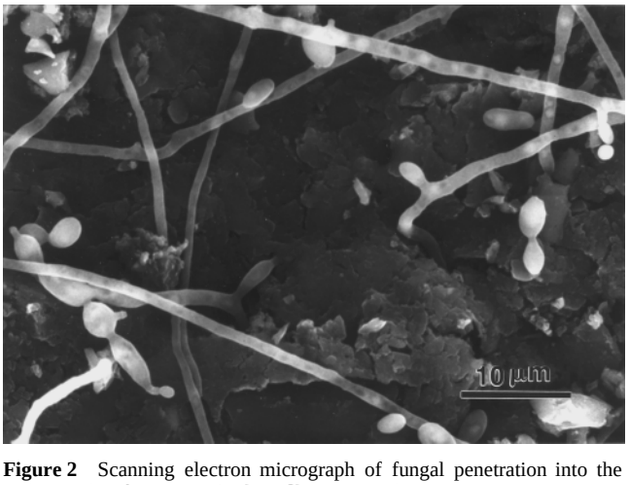

Figure 2 Scanning electron micrograph of fungal penetration into the resin matrix of an epoxy/carbon fiber composite.

autoclaved once to extract soluble organics and then removed. The composite extracts were inoculated with 100 μl of the fungal consortium. Culture aliquots for growth were measured spectrophotometrically at 600 nm. Triplicate samples were used in the experiment.

Sample preparation for scanning electron microscopy (SEM)

Samples of composites were prepared for SEM examination following the procedures of fixation in glutaraldehyde, washing with cacodylate buffer and refixing in osmium tetroxide, dehydration in a series of ethanol solutions, critical-point drying in liquid CO_2, and coating with gold-palladium as described elsewhere [10,11].

Electrochemical impedance spectroscopy (EIS)

Coupons of the composites were prepared for EIS monitoring. EIS cells were constructed by gluing a piece of FRPC onto a 316 stainless steel coupon (50.0 × 50.0 mm) with a conductive silver epoxy (SPI Instrumental, West Chester, PA, USA). The EIS cells have been described elsewhere [10,11]. On the composite surface, a 30-mm long acrylic tube (i.d. 34.9 mm; o.d. 38.1 mm) was attached to the polymer-stainless steel coupon by Epon 828 epoxy resin (Shell Chemical Co, Houston, TX, USA) cured with Amercoat 90 resin (Ameron, Protective Coatings Group, Brea, CA, USA) in a ratio of 1 : 4. After curing the adhesive, the internal surfaces of the tube and the composite directly exposed to the internal of the tube were thoroughly sterilized with 70% ethanol and dried in a laminar-flow sterile hood. Initially, a 15.0-ml volume of sterile 0.2 M NaCl solution and 1.0 ml of the salt medium (described above) were added to the acrylic tube of the EIS cell as a working electrode, and measurement of the impedance responses was made after equilibration of the system. The uniformity of all prepared EIS cells was evaluated by EIS spectra analyzed in magnitude, phase angle and Nyquist complex plane plots to determine the validity of using them in subsequent monitoring. Then, three of the prepared EIS cells were inoculated with 100 μl of the fungal consortium maintained on malt extract medium. Three additional EIS cells were kept as sterile controls. Aseptic procedures were used throughout the EIS measurement to avoid contamination and cross contamination of the EIS cells.

Our EIS system consists of a Schlumberger 1250 frequency response analyzer combined with a Schlumberger 1286 electrochemical interface (Schlumberger Technologies – Instruments Division, Billerica, MA, USA). Z-plot software (Scribner Associates, Charlottesville, VA, USA) was used to manipulate the system. During data acquisition, samples were potentiostatically held at their open circuit potential (OCP), and a sinusoidal perturbation of 20–50 mV was applied to the system. Impedance responses were measured over a range of frequencies from 65 kHz to 1 mHz and spectra were recorded as a function of immersion time at ambient temperature and pressure. OCPs were monitored *vs* a saturated calomel electrode as a reference electrode of the tri-electrode system. Platinum mesh was used in the EIS cell as a counter electrode, and the constructed EIS cell as a working electrode. Both Bode magnitude and phase angle plots as well as the Nyquist complex plane plots were used to provide information on increases in porosity, local defects and disbonding.

Interlaminar shear strength test

At the end of EIS monitoring, composites from the inoculated and control EIS cells were sectioned with a diamond-

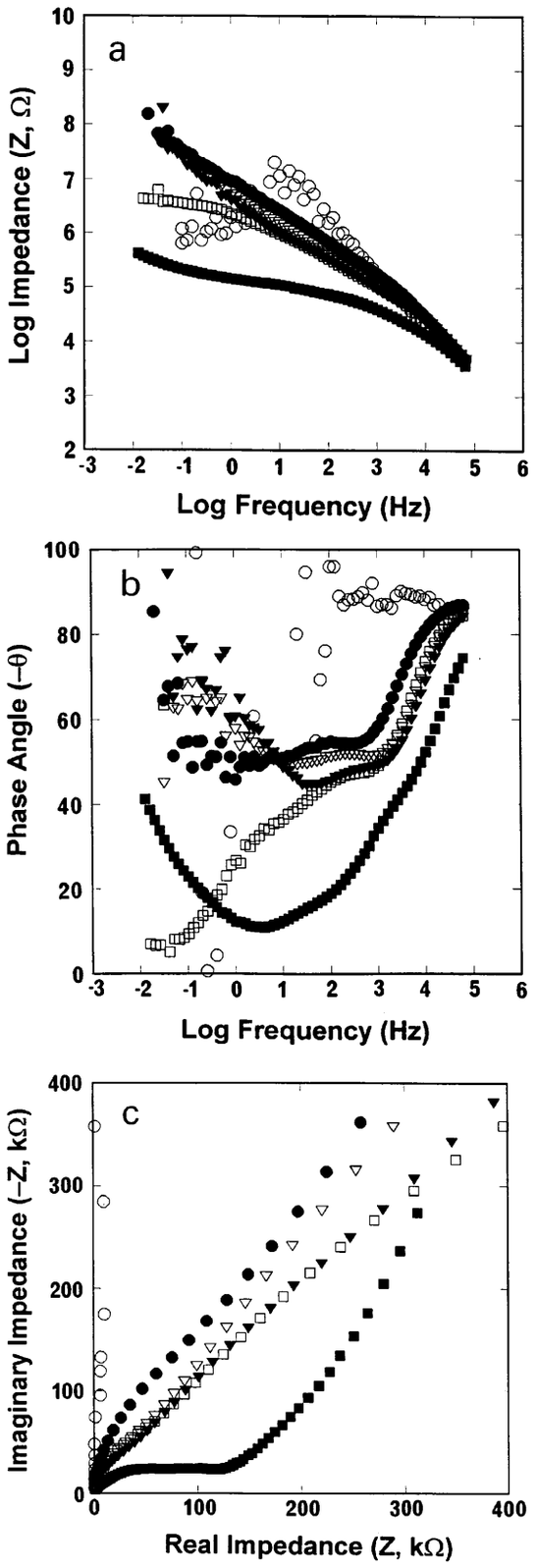

Figure 3 Electrochemical impedance spectroscopy diagrams of an epoxy/carbon fiber composite inoculated with a fungal consortium for 179 days. (a) Bode impedance plot; (b) phase angle plot; and (c) Nyquist complex plane plot. ○, Time 0; ●, 33 days; ▽, 53 days; ▼, 97 days; □, 136 days; ■, 179 days.

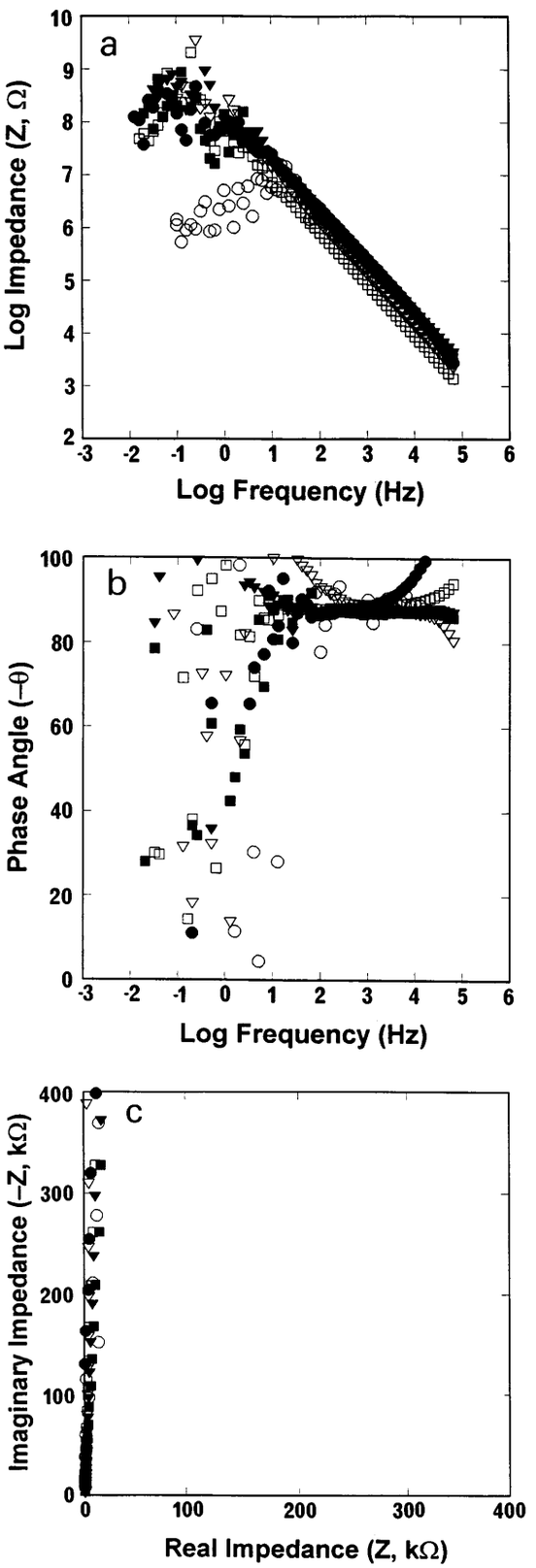

Figure 4 Electrochemical impedance spectroscopy diagrams of an epoxy/carbon fiber composite held under aseptic conditions for 179 days. (a) Bode impedance plot; (b) phase angle plot; and (c) Nyquist complex plane plot. ○, Time 0; ●, 33 days; ▽, 53 days; ▼, 97 days; □, 136 days; ■, 179 days.

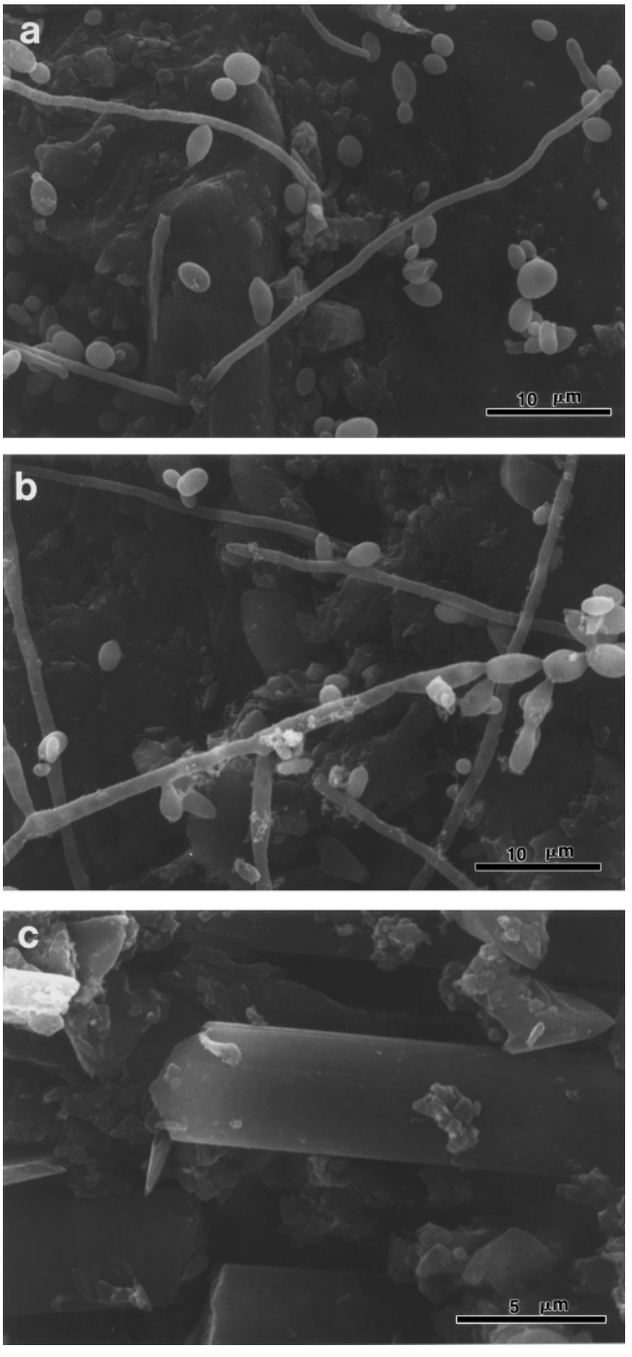

Figure 5 Scanning electron micrographs of (a) fungi colonizing composite surfaces; (b) fungal hyphae penetrating resin; and (c) fracture morphology of the fiber/resin interfaces after incubation with fungi for 179 days.

tipped wet saw blade to an approximate dimension of 38 mm × 1.3 mm for mechanical analysis. Specimens were tested in a three-point flexure with a span-to-depth ratio of 6 : 1 to promote interlaminar shear failure. Thin rubber pads were placed between the contact pins and the specimen to prevent premature surface damage at these locations. Failure modes were noted and interlaminar shear properties were observed with SEM.

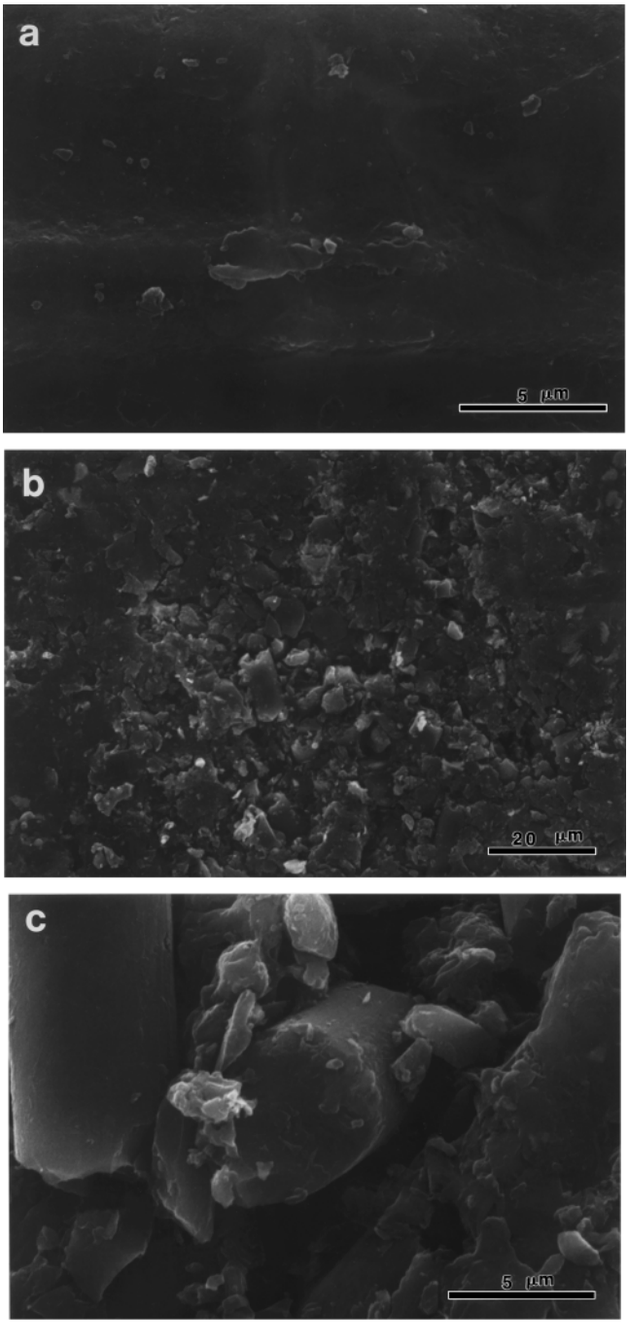

Figure 6 Scanning electron micrographs of (a) composite surfaces; (b) a cross section of the composite; and (c) fracture morphology of the control kept under aseptic conditions for 179 days.

Results and discussion

We previously observed that all five composite materials being studied were susceptible to attack by fungi [7,10,11]. SEM observation indicated fungal colonization of the composites and localized penetration of fungal hyphae into the interior of the composite resins, particularly for the material containing a fluorinated polyimide resin reinforced with glass fibers [11]. In another study, composite materials were also reported to be susceptible to a consortium of bacteria, including sulfate-reducing bacteria [22]. The differ-

ence between these two studies was that, in the former, a fungal consortium enriched from degraded polymeric materials was responsible for degradation, while in the latter, a constituted consortium of bacterial species was proposed to cause decomposition of the material. Microorganisms may also contaminate the materials during manufacture [19]. As a result, the biodeteriogens will grow when the environmental conditions become favorable.

In the current investigation, epoxy/graphite fiber composites were susceptible to colonization by fungi (Figure 1). Fungal penetration into the resin matrix was also observed after 30 days of incubation (Figure 2). It appears that the microorganisms utilize one or more of the chemical additives of the composite material as growth substrates [7,11].

Aqueous extracts of whole composite coupons significantly stimulated fungal growth (data not shown). These data support the hypothesis that organic carbon components of the composite materials provide essential nutrients for microbial growth. This is the first direct indication of the nutritional relationship between the FRPC deterioration and the growth of fungi. The data also confirm observations from an earlier study that composite fibers serve as carbon and energy sources for the growth of microorganisms [7,11]. Composites contain a range of chemicals to improve the material properties, including plasticizers, flame retardants, catalysts, and colorants [1,12,17]. Most of these additives are biodegradable, particularly polyesters under both aerobic and anaerobic conditions [5,6,8,9,15,20].

The success or failure of an FRPC is also governed by the degree of adhesion between the fiber surface and the resin matrix. Electrochemical impedance spectroscopy (EIS) has been used for assessment of failure of protective coatings [13,18], electronic packaging polyimides [3,10], and composites [4,21]. Localized weakening of the bonding between the reinforcing fibers and the resin matrix will result in fiber disbonding and delamination when the material is under stress. When this happens, a decrease of impedance is detected. To our knowledge, no investigation of microbial degradation of composites has been reported using EIS.

In our study, EIS spectra of composite coupons with fungal biofilms showed large deviations from the initial spectra. A decrease of impedance was observed at high frequency region with a bending point between 10^3 and 10^4 Hz within 179 days (Figure 3a). A phase angle plot showed correspondingly continuous bending away from the initial spectrum (Figure 3b), indicating a decrease of pore resistance of the composite matrix or an increase of pore size and pore numbers. The development and compression of the semicircles, indicated by curves bending away from those at the beginning of the experiment in the Nyquist complex plane plots (Figure 3c), also confirmed that the conductance of the composite increased over time of incubation as the composite matrix deteriorated progressively.

During the 179 days of monitoring, EIS spectra in the magnitude, Bode and Nyquist complex plane plots collectively demonstrated that there was a continuous deterioration of the composite matrix after inoculation. However, the composite held under aseptic conditions showed minimal changes of the impedance and phase angle (Figure 4a and b), and almost no change in the Nyquist complex plane plot (Figure 4c). The small deviation between measurements at different samplings can be explained by the variation in electrical noise and water permeation into the resin. The magnitude of impedance showed that the composite was intact in sterile controls after 179 days.

Composites from the inoculated EIS cells showed fungal hyphae and spores on surfaces of the composite (Figure 5a and b), while no microorganism was observed on surfaces of the control at the end of EIS monitoring (Figure 6a and b). No significant difference of interlaminar shear strength was detected between the inoculated and the control composites. The resultant fracture indicated that bonding strength between fibers and resins was weakened more after inoculation with the fungi compared to the control (Figures 5c and 6c). The inability of the mechanical test to detect any differences between inoculated and control may be due to the insensitivity of the technique to a small proportion of disbonding over the whole composite matrix. However, a fiber push-out test did not show any significant differences between the two treatments.

Since sizing chemicals, including starch derivatives, acetylated celluloses, and vinyl esters are biodegradable [5,6,8,9,21], delamination of fibers from resin matrices is likely to occur as a result of their microbial decomposition. These failures may be avoided by using a sizing that is resistant to microbial attack or by incorporating a biocide. Organics in resins which may support growth of microorganisms can be either eliminated or inactivated by incorporation of a biocide in the matrix. Elimination of microbial contamination in the composite manufacturing process would provide additional protection against biological deterioration.

Conclusions

Composite constituents such as matrix resins, additives and fibers are susceptible to microbial growth, resulting in potential damage to the resins and delamination of the fibers from resin matrices. Microorganisms may obtain energy from chemicals in resins and on the fiber surfaces. Fungi were shown to be responsible for the degradation of composite materials, and it appeared that sizing chemicals and resin constituents were readily degraded by fungi.

Acknowledgements

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