Biodegradation **9:** 39–45, 1998.

Microbial degradation of polymeric coatings measured by electrochemical impedance spectroscopy

Ji-Dong Gu[1], D.B. Mitton[2], T.E. Ford[3,*] & R. Mitchell[1]
[1] *Laboratory of Microbial Ecology, Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA;* [2] *Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA;* [3] *Department of Environmental Health, Harvard School of Public Health, 665 Huntington Avenue, Boston, MA 02115, USA*
*(*author for correspondence, e-mail: ford@endor.harvard.edu)*

Accepted 25 January 1998

Key words: biodegradation, biodeterioration, coatings, electrochemical impedance spectroscopy, fungi, polyimides

Abstract

This paper reports results of biodegradation studies of polyimide coatings exposed to a mixed fungal culture using electrochemical impedance spectroscopy (EIS). The fungal consortium was originally isolated from degraded polyimides and identified species include *Aspergillus versicolor*, *Cladosporium cladosporioides*, and a *Chaetomium* species. Actively growing fungi on polyimides yield distinctive EIS spectra through time, indicative of failure of the polymer integrity compared to the uninoculated controls. An initial decline in coating resistance was related to the partial ingress of water molecules and ionic species into the polymeric matrices. This was followed by further degradation of the polymers by activity of the fungi. The relationship between the changes in impedance spectra and microbial degradation of the coatings was further supported by scanning electron microscopy, showing extensive colonization of the polyimide surfaces by the fungi. Our data indicate that EIS can be a sensitive and informative technique for evaluating the biosusceptibility of polymers and coatings.

Introduction

Metals are known to be susceptible to corrosion in many environments, including moist air, freshwater, marine, and industrial conditions (e.g. heat exchangers and cooling towers). Many different groups of microorganisms have been implicated in corrosion reactions, both through the physical presence of a biofilm and as the result of specific metabolic activities (e.g., Ford & Mitchell 1990). In comparison, less information is available for nonmetallic materials. However, besides electrochemical protection, metals are often painted with inert polymeric materials to provide a barrier between substratum materials and the corrosive species.

Paints and coatings represent a world-wide business worth approximately $61 billion dollars in 1996 (Reisch 1996). In 1995, the total paint demand was 22 million tons and is projected to be 25 million tons by the year 2000. As a result of the Clean Air Act in 1990, volatile organic solvents, which were suppressants for potential microbial development in coatings, are now prohibited in the United States. There is therefore a trend towards increasing the use of biocides in coating materials to inhibit microbial contamination during the manufacturing processes and storage.

Polyimides are an important class of polymeric materials used in insulating layers of integrated circuits in computers (Lai 1989), thermosetting polymers, fiber-reinforced polymeric composites, and coatings. Polyimide coatings are also found in neural prosthesis implants (Leyden & Basiulis 1989). They are uniquely suited for these applications because of their high stability, processibility, and low dielectric constants (Jensen 1987). However, the polyimides in these systems are often in contact with aqueous media and possibly airborne microorganisms. Their surfaces may condense moisture, providing an opportunity for the development of microbial biofilms, and subsequent biodeterioration.

Polyimides have exceptional chemical, mechanical and thermal stability, but they respond to moisture, resulting in changes of their dielectric properties (Gu et al. 1996a; Lai 1989). Even very small changes in the transport properties of a coating may cause variations in its ability to resist electrochemical corrosion of the underlying metal. In addition to moisture adsorption into the polymeric matrix of polyimides, contamination by microorganisms, particularly fungi, has been reported to be a common problem during processing and in service (Thorp et al. 1994).

Microorganisms have been found to be capable of colonization of surfaces of magnetic tapes (McCain & Mirocha 1994), building materials (Ezeonu et al. 1994a; 1994b), glass and carbon fibers (Gu et al. 1994a), graphite sheets (Gu et al. 1994a), fiber-reinforced polymeric composites (Gu & Mitchell 1995; Gu et al. 1995c; 1995d; 1995e; 1995f; 1996b; 1996c; 1997a; 1997b), and polymeric coatings (Gu et al. 1996a; 1996b; 1998; Mitchell et al. 1996). Earlier results have shown that polyesters (e.g., poly(hydroxybutyrate) and cellulose acetates) (Gross et al. 1993; 1995; Gu et al. 1993a; 1993b; 1993c; 1994b) and polyethers (Kawai, 1987) are all susceptible to biodegradation by both aerobic and anaerobic microorganisms. Different methods for testing biodegradation and biodeterioration of polymers have been proposed (ASTM 1993a; 1993b; 1993c; Gross et al. 1993; 1995; Gu et al. 1993a; 1993b; 1993c; 1994b), but none is suitable for slow-degrading polymers such as paints and coatings. Earlier reports of tests for biodegradation of coating materials have failed to provide quantitative information on biodegradation and the processes and mechanisms involved (Seal & Shuttleworth 1986).

Recently, we reported that microbial degradation of electronic insulating polymers can be detected quantitatively with application of electrochemical impedance spectroscopy (EIS) (Ford et al. 1995; Gu & Mitchell, 1995; Gu et al. 1995a; 1995b; 1996a; 1997a; 1998; Mitton et al. 1993). Impedance can be measured directly in the frequency domain by applying a single-frequency voltage to the interface and measuring the phase shift and amplitude, or real and imaginary parts of the resulting current at the frequency. EIS is a useful technique in monitoring the integrity of oxide layers on metal surfaces and in studying electrical and electrochemical properties of dielectric materials. Polymeric coatings can be evaluated using this technique. Corrosion and separation of the coating from the underlying materials, water uptake by the coating polymers and interface delamination can also be determined with this method. Examples of EIS applications are mostly on corrosion and corrosion resistant coatings in electrolyte solution rather than under conditions of biological challenge (Macdonald, 1987; Mansfeld, 1995; Walter, 1986). The objective of this study was to demonstrate the use of EIS as a sensitive and informative technique for testing biosusceptibility of polymeric coatings.

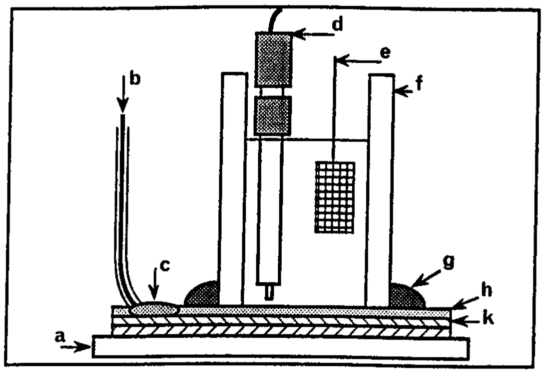


Figure 1. Schematic illustration of an electrochemical impedance cell used in the study of polyimide coating degradation. *a*, Plexiglass base; *b*, working electrode connection; *c*, silver loaded epoxy; *d*, standard calomel electrode; *e*, platinum counter electroder; *f*, Plexiglass cell to hold NaCl electrolyte; *g*, Amercoat; *h*, polymer; and *k*, metallic substratum.

Materials and methods

Electrochemical impedance spectroscopy (EIS)

Polyimide coatings used in this study were Kapton HN (pyromellitic dianhydride and 4, 4′-diaminodiphenyl ether) (E. I. Du Pont Co., Wilmington, Delaware, USA). The Kapton polyimides had a molecular weight of 2.5 × 10^5 (M_w) relative to polystyrene standards without further corrections.

EIS cells were constructed by the following method: polyimide resin was applied to one side of a 316 stainless steel coupon (50.0 × 50.0 mm) and cured at 200 °C for 48 hours. Once the polyimide coating was dry, a 30.0 mm long acrylic tube (I.D., 34.9 mm; O.D. 38.1 mm) was attached to the polymer-stainless steel coupon by a mixture of Amercoat 90 resin (Ameron, Protective Coatings Group, Brea, California, USA) and Epon 828 resin (Shell Chemical Co., Houston, Texas, USA) in a ratio of 4:1. A schematic diagram of the EIS cell used in our study is shown in Figure 1. After the sealants had cured, the internal and external surfaces of the EIS cells were sterilized with 70% ethanol and dried at room temperature in a laminar-flow sterile hood.

Our EIS analytic system consists of a Schlumberger 1250 frequency response analyzer combined with a Schlumberger 1286 electrochemical interface (Schlumberger Technologies - Instruments Division, Billerica, Massachusetts, USA). Z-plot software (Scribner Associates, Inc., Charlottesville, Virginia, USA) was used to control the system and analyze the data. During data acquisition, EIS cells were potentiostatically held at their open circuit potential (OCP), and a sinusoidal perturbation of 20 mV was applied. The impedance response was 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. A trielectrode system was used in this study; a saturated calomel electrode as a reference electrode, a platinum mesh as a counter-electrode, and the EIS cell itself as a working electrode. In all experiments, the surface areas of the working electrode were 38.3 cm^2. Bode magnitude and Nyquist complex plane plots were used to provide information on the coating stability.

At the initiation of the experiment, 15.0 mL of sterile 0.2 *M* NaCl solution was added to the acrylic tube of the working electrode, followed by 1.0 mL of a minimum salt solution. The salt solution consisted of (g L^{-1}): K_2HPO_4, 0.8 g; KH_2PO_4, 0.2g; $CaSO_4 \bullet 2H_2O$, 0.05; $MgSO_4 \bullet 7H_2O$, 0.5; $FeSO_4 \bullet 7H_2O$, 0.01; and $(NH_4)_2SO_4$, 1.0 g. Measurement of the impedance response was made immediately after a short equilibration time (approximately 30 minutes). Uniformity of all prepared EIS cells was evaluated to determine the validity of using them for replicate analyses and for random assignment as inoculated and sterile controls. One set of prepared EIS cells (three) was inoculated with 100 μL of the fungal consortium, maintained on a malt extract medium (Difco Lab., Detroit, Michigan, USA) and described earlier (Gu et al. 1995a; 1995b; 1996a). The consortium was previously obtained by enrichment from degraded polyimides. A second set of EIS cells was maintained under sterile conditions throughout the study as experimental controls. At regular time intervals, the impedance responses of all EIS cells were determined. Aseptic procedures were used throughout the determination to avoid contamination and cross contamination. At the conclusion of the study, polymer films from inoculated and sterile EIS cells were prepared for examination by SEM.

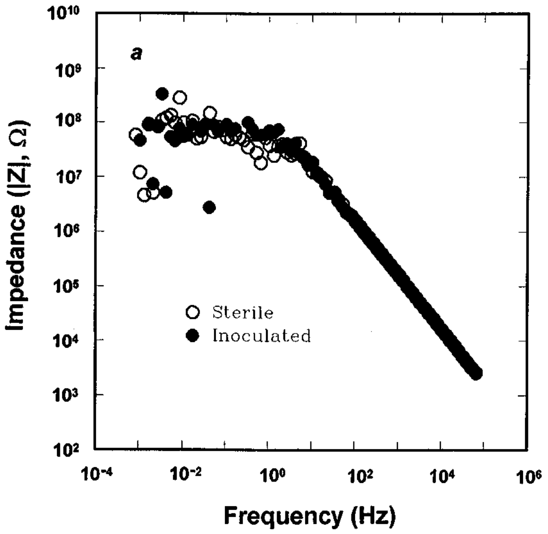
SEM sample preparation

Polyimide coated samples from the inoculated and sterile EIS cells were fixed in 3% glutaraldehyde buffered with 0.2 *M* sodium cacodylate for about 12 hours. The fixative was pre-filtered through a 0.2-μm-pore-size polycarbonate membrane filter (Gelman Science, Ann Arbor, MI). Samples were then washed with 0.2 *M* Na cacodylate three times, additionally fixed in 1% osmium tetroxide in 0.1 *M* Na cacodylate, and rinsed again with 0.2 *M* Na cacodylate followed by deionized water three times for each treatment. The samples were dehydrated in an ethanol-distilled water series of 40, 60, 70, 80, 85, 90, 95 and 100% ethanol. Samples were stored in 100% ethanol in air-tight sealed glass vials before critical point drying in liquid CO_2(Samdri PVT-3B, Tousimis Research Co., Rockville, MD). Immediately following drying, they were coated with gold-palladium and viewed under an AMR 1000 scanning electron microscope.

Results and discussion

EIS is considered one of the least destructive and most informative techniques of electrochemical analysis available for monitoring interfacial phenomena of polymeric coatings on metal surfaces (Ferraz et al. 1995; Kendig & Scully 1990; Mansfeld & Tsai 1991; Mansfeld 1995; Scully & Hensley 1994; Titz et al. 1990; Tsai & Mansfeld 1993; Walter 1986) and has enabled physical transport processes to be successfully studied with electrochemical and mathematical models (Macdonald, 1987; van der Weijde et al. 1994; van Westing et al. 1994a; 1994b). Recently, this technique has also been used effectively in the detection of microbial degradation of electronic insulation polymers (Ford et al. 1995; Gu & Mitchell 1995; Gu et al. 1994a; 1995a; 1995b; 1996a; Mitton et al. 1993), and fiber reinforced polymeric composites (Gu et al. 1995c; 1995d; 1995e; 1995f; 1996b; 1996c; 1997a; 1997b).

Analysis of impedance data is commonly carried out over a wide frequency range with the aid of Bode plots or Nyquist complex plane plots in order to determine the individual components of the equivalent electrical circuit model that represents the polymer/solution interface (Macdonald, 1987; Mansfeld,



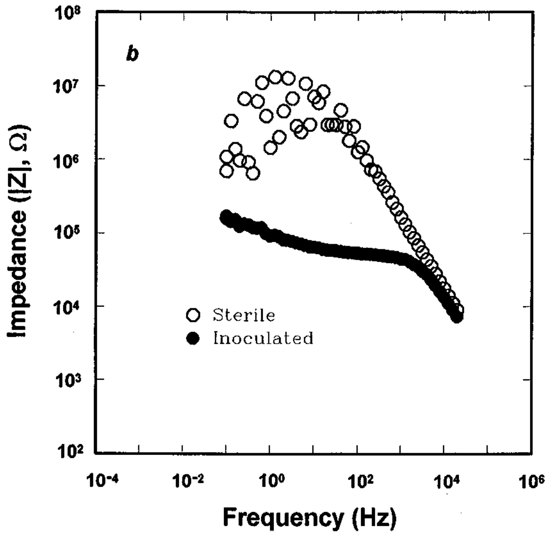


Figure 2. Bode magnitude plots of polyimides (*a*) at initiation of the study and (*b*) after 122 days of incubation.

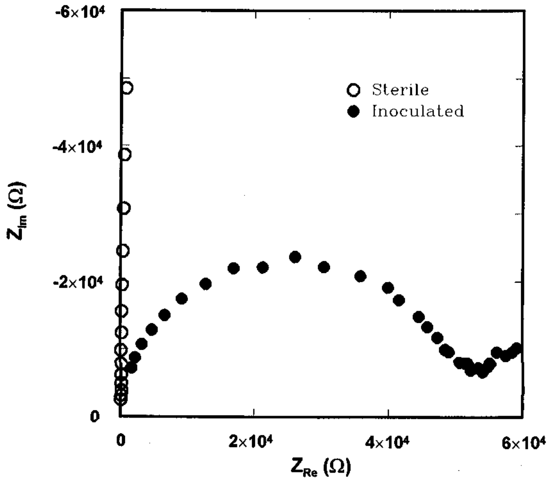


Figure 3. Nyquist complex plane plot of polyimide coatings after 122 days of incubation following inoculation and under sterile conditions.

1995; van der Weijde et al. 1994; van Westing et al. 1994a; 1994b; Walter, 1986). Several graphical presentations of impedance data are available over a wide frequency range. The most commonly applied are Bode plots and Nyquist plots. The Bode plot graphs the logarithm of the impedance modulus and phase angle versus the logarithm of frequency, and the Nyquist complex plane plot graphs the resistive versus the reactive components of impedance.

In the current study, polyimides were chosen as candidate materials to assess their properties as protective coatings. They were coated on one side of a conductive stainless steel coupon. Degradation of polyimides was monitored in the inoculated and sterile EIS cells containing a 0.2 *M* NaCl solution for 122 days at ambient temperature. No apparent difference in electrochemical response was observed between the inoculated and the sterile cells at the initiation of the experiment, indicating the uniformity and excellent resistivity (10^8 Ohms) of the polyimide coating (Figure 2a). However, after 122 days of exposure, a decrease of impedance in the lower frequency region (10 to 10^{-2} Hz) was detected in the inoculated EIS cells and to a lesser extent, the sterile EIS cells. In the higher frequency region (10^3 to 10^4), a large decrease in impedance was detected in inoculated EIS cells (Figure 2b). The decrease of pore resistance in the lower frequency region in the sterile EIS cells could be explained by the partial adsorption of moisture and ionic species into the polymer matrix resulting in a decrease in film resistivity. A decrease of impedance in the higher frequency region indicated that polymer was degraded. Exposure to the fungi is thought to have enhanced transport of water and ionic species into the polymer matrices, due to fungal penetration into, and destruction of, the polymer integrity (Gu et al. 1996a). Impedance decreases in the higher frequency region were only observed in EIS cells inoculated with the fungal culture, supporting the

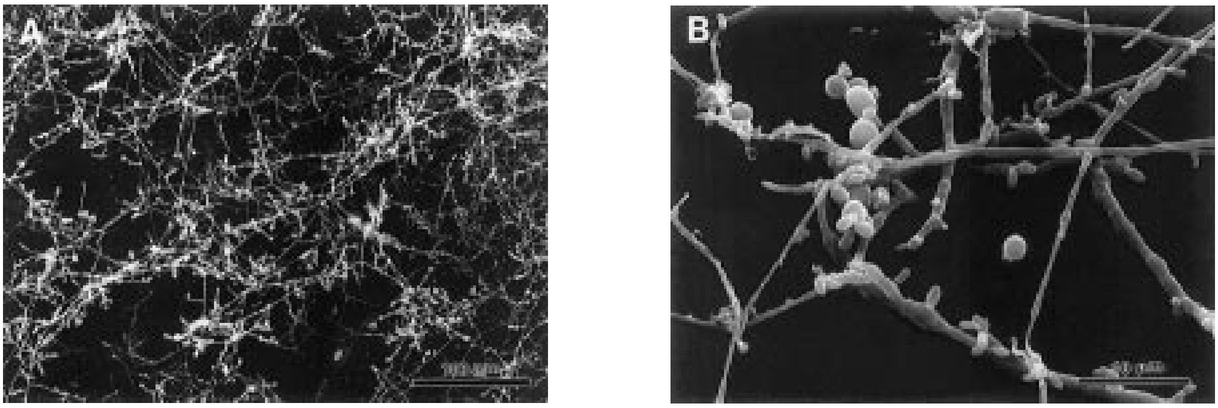


Figure 4. SEM micrographs of deteriorated polyimides from an inoculated EIS cell showing fungi growing on the polymer coating.

Figure 5. SEM micrograph of intact polyimides from sterile cells after 122 days of incubation.

hypothesis that fungal activity contributed directly to polymer degradation.

The decline in impedance, observed in the inoculated cells but not in the sterile control cells (Figure 2b), signifies a decrease in capacitance of the polymer coating. Impedance magnitude decreased from 10^8 at time zero to below 10^5 in the inoculated EIS cells within 122 days. During the same period of incubation, impedance of the sterile cells changed from 10^8 to 10^7 Ohms (Figure 2a) after partial adsorption of water and ionic species. A high impedance is considered a strong indicator that a coating is not defective ($> 10^7$ Ohms) (Mansfeld 1995). Therefore, the polyimide coating did not appear to degrade under sterile conditions, undergoing only limited adsorption of water and ionic species.

When data were plotted in the Nyquist plot, clear differences were observed between the inoculated and sterile controls. Degraded coatings showed progressive decreases in the radii of developed semicircles as the incubation time increased (Figure 3). At the same time, coatings maintained under sterile conditions showed almost no change throughout the incubation period. Polymer coating degradation in the presence of fungi had been previously modeled by physically creating a series of needle-sized holes in the polymeric film that had been shown by EIS to be previously intact (Gu et al. 1996a). A single needle-sized hole resulted in dramatic decreases in pore resistance. In response to an increasing number of holes in the polymer, impedance continued to decrease, but the difference between the intact and damaged film was much greater than that between the films with different numbers of holes. This creates a problem in the analysis in that the EIS technique may be too sensitive to detect small defects in a polymer or coating to allow effective determination of severe damage (Mansfeld 1995). Growth of the fungi is thought to result in severe deterioration of polymer with potentially disastrous consequences for coatings. EIS may only be useful in determining the initiation of fungal deterioration and cannot reliably be used to monitor time to coating failure.

Following our impedance studies, polyimide coatings from the inoculated and sterile EIS cells were examined by SEM in order to observe the extent of fungal colonization. SEM micrographs of polyimide from inoculated cells show extensive fungal growth (Figure 4). In contrast, SEM micrographs of polyimide from sterile cells show no fungal colonization (Figure 5). The species of fungi, *Aspergillus versicol-*

or, *Cladosporium cladosporioides*, and a *Chaetomium* species, were isolated and identified from a sample of the polyimide surface. All of these fungi are common in air and on surfaces (Ezeou et al. 1993a; 1993b) and can readily contaminate a coated surface. Similar microorganisms have been isolated from electronic components, including magnetic disks (McCain & Mirocha 1994).

In conclusion, EIS can be used in monitoring the initial steps of polymer degradation by microorganisms. This technique provides information which is indicative of specific mechanisms of the degradation process. Susceptibility of polymer coatings to fungal colonization and subsequent deterioration suggest that application of these coatings in specific environments, e.g., where any humidity is present, should be approached with caution. Addition of fungicides/biocides may be warranted for application of polymers in these environments, but only after extensive testing of efficacy, and appropriate considerations of coating integrity and potential human exposure to toxic substances.

Acknowledgments

This research was supported in part by grants #F49620-92-J-108 and #F49620-95-1-0151 from the U.S. Air Force Office of Scientific Research to Harvard University. We thank Mr. E. Seling for his expert assistance in SEM observation.

References

ASTM (American Society for Testing and Materials) (1993a) Standard test method for determining the aerobic biodegradability of degradable plastics by specific microorganisms. In: 1993 Annual Book of ASTM Standards, Volume 08.03, D5247-92 (pp 401–404). ASTM, Philadelphia, Pennsylvania, USA

— (1993b) Standard practice for determining resistance of synthetic polymeric materials to fungi. In: 1993 Annual Book of ASTM Standards, Volume 08.03, G21-90 (pp 527–529). ASTM, Philadelphia, Pennsylvania, USA

— (1993c) Standard practice for determining resistance of plastics to bacteria. In: 1993 Annual Book of ASTM Standards, Volume 08.03, G22-76 (pp 531–533). ASTM, Philadelphia, Pennsylvania, USA

Ezeonu IM, Noble JA, Simmons RB, Price DL, Crow SA & Ahearn DG (1994a) Effect of relative humidity on fungal colonization of fiberglass insulation. Appl. Environ. Microbiol. 60: 2149–2151

Ezeonu IM, Price DL, Simmons RB, Crow SA & Ahearn DG (1994b) Fungal production of volatiles during growth on fiberglass. Appl. Environ. Microbiol. 60: 4172–4173

Ferraz O, Cavalcanti E & Di Sarli AR (1995) The characterization of protective properties for some naval steel/polimeric coating/3% NaCl solution systems by EIS and visual assessment. Corrosion Sci. 37: 643–652

Ford T & Mitchell R (1990) The ecology of microbial corrosion. Adv. Microb. Ecol. 11: 231–261

Ford T, LaPointe E, Mitchell R & Mitton DB (1995) Role of microorganisms in failure of complex polymers and protective coatings. In: Biodeterioration and Biodegradation 9, the 9th International Biodeterioration and Biodegradation Symposium (pp 554–561). Institution of Chemical Engineers, Warwickshire, UK

Gross RA, Gu J-D, Eberiel D, Nelson M & McCarthy SP (1993) Cellulose acetate biodegradability in simulated aerobic composting and anaerobic bioreactors as well as by a bacterial isolate derived from compost. In: Kaplan D, Thomas E & Ching C (Eds) Fundamentals of Biodegradable Materials and Packaging (pp 257–279). Technomic Publishing Co., Lancaster, Pennsylvania, USA

Gross RA, Gu J-D, Eberiel D & McCarthy SP (1995) Laboratory scale composting test methods to determine polymer degradability: model studies on cellulose acetate. In: Albertsson A & Huang S (Eds) Degradable Polymers, Recycling and Plastics Waste Management (pp 21–36). Marcel Dekker, Inc., New York, USA

Gu J-D, Coulter S, Eberiel D, McCarthy SP & Gross RA (1993a) A respirometric method to measure mineralization of polymeric materials in a matured compost environment. J. Environ. Polym. Degr. 1: 293–299

Gu J-D, Eberiel DT, McCarthy SP & Gross RA (1993b) Cellulose acetate biodegradability upon exposure to simulated aerobic composting and anaerobic bioreactor environments. J. Environ. Polym. Degr. 1: 143–153

— (1993c) Degradation and mineralization of cellulose acetate in simulated thermophilic compost environments. J. Environ. Polym. Degr. 1: 281–291

Gu J-D, Ford TE, Thorp KEG & Mitchell R (1994a) Microbial degradation of polymeric materials. In: Naguy T (Ed) Proceedings of the Tri-Service Conference on Corrosion (pp 291–301), U.S. Government Printing Office, Washington DC, USA

Gu J-D, Yang S, Welton R, Eberiel D, McCarthy SP & Gross RA (1994b) Effects of environmental parameters on degradability of polymer films. J. Environ. Polym. Degr. 2: 129–135

Gu J-D & Mitchell R (1995) Microbiological influenced corrosion of metal, degradation and deterioration of polymeric materials of space application. Chinese J. Mat. Res. 9(Suppl.): 473–389

Gu J-D, Ford T & Mitchell R (1995a) Microbial degradation of electronic insulating polymers. In: Abstracts of the American Society for Microbiology Meeting (p 262), ASM, Washington DC, USA

Gu J-D, Ford TE, Mitton B & Mitchell R (1995b) Microbial degradation of complex polymeric materials used as insulation in electronic packaging materials. Corrosion/95, Paper No. 202, National Association of Corrosion Engineers, Houston, Texas, USA.

Gu J-D, Ford TE, Thorp KEG & Mitchell R (1995c) Microbial deterioration of fiber reinforced composite materials. In: Angell P, Borenstein SW, Buchanan RA, Dexter SC, Dowling NJE, Little BJ, Lundin CD, McNeil MB, Pope DH, Tatnall RE, White DC & Ziegenfuss HG (Eds) International Conference on Microbial Induced Corrosion (pp 25/1–25/7), NACE International, Houston, Texas, USA

— (1995d) Microbial deterioration of fiber reinforced polymeric materials. In: Scully JR (Ed) Corrosion/95 Research in Progress Symposium (pp 16–17), NACE International, Houston, Texas, USA

— (1995e) Effects of microorganisms on stability of fiber reinforced polymer composites. In: Hui D (Ed) 2nd Intern. Conf. Composite Eng. (pp 279–280), Univ. of New Orleans, Louisiana, USA

Gu, J-D, Thorp T, Crasto A & Mitchell R (1995f) Microbiological degradation of fiber-reinforced polymeric composites. Electrochemical Society Meeting Abstracts 96(1): 143–144

Gu J-D, Ford TE &. Mitchell R (1996a) Susceptibility of electronic insulating polyimides to microbial degradation. J. Appl. Polym. Sci. 62: 1029–1034

Gu J-D, Ford T, Thorp K & Mitchell R (1996b) Microbial growth on fiber reinforced composite materials. Internat. Biodeter. Biodegr. 37: 197–204

Gu J-D, Lu C, Thorp K, Crasto A & Mitchell R (1996c) Fungal degradation of fiber-reinforced composite materials. Corrosion/96, Paper No. 275, NACE International, Houston, Texas, USA

— (1997a) Fungal degradation of fiber-reinforced composite materials. Mat. Perform. 36: 37–42

— (1997b) Fiber-reinforced polymeric composites are susceptible to microbial degradation. J. Ind. Microbiol. Biotechnol. 18: 364–369

Gu J-D, Roman M, Esselman T & Mitchell R (1998) The role of microbial biofilms in deterioration of space station candidate materials. Internat. Biodeter. Biodegr. (in press)

Jensen, RJ (1987) Polyimides as interlayer dielectrics for high-performance interconnections of integrated circuits. In: Bowden MJ & Turner SR (Eds) Polymers for high technology-electronics and photonics, ACS Symposium Series 346 (pp 465–483). American Chemical Society, Washington, DC, USA

Kawai F (1987) The biochemistry of degradation of polyethers. CRC Crit. Rev. Biotechnol. 6: 273–307

Kendig M & Scully J (1990) Basic aspects of electrochemical impedance application for the life prediction of organic coatings on metals. Corrosion 46: 22–29

Lai JH (1989) Polymers for Electronic Applications, CRC Press, Inc., Boca Ralton, Florida, USA

Leyden RN & Basiulis DI (1989) Adhesion and electrical insulation of thin polymeric coatings under saline exposure. Mat. Res. Soc. Symp. Proc. 110: 627–633

Macdonald JR (1987) Impedance spectroscopy: emphasis solid materials and systems, John Wiley & Sons, New York, NY, USA

Mansfeld F (1995) Use of electrochemical impedance spectroscopy for the study of corrosion protection by polymer coatings. J. Appl. Electrochem. 25: 187–202

Mansfeld F & Tsai CH (1991) Determination of coating deterioration with EIS. I. basic relationships. Corrosion 47: 958–963

McCain JW & Mirocha CJ (1994) Screening computer diskette and other magnetic media for susceptibility to fungal colonization. Internat. Biodeter. Biodegr. 33: 255–268

Mitchell R, Gu J-D, Roman M & Soukup S (1996) Hazards to space missions from microbial biofilms. In: Sand W (Ed) DECHEMA Monographs: Biodeterioration and Biodegradation, Vol. 133 (pp 3–16). VCH, Frankfurt, Germany

Mitton B, Ford TE, LaPonite E & Mitchell R (1993) Biodegradation of complex polymeric materials. Corrosion/93, Paper No. 296, NACE International, Houston, Texas, USA

Reisch MS (1996) Paints and coatings. Chem. Eng. News 74: 44–60

Scully JR & Hensley ST (1994) Lifetime prediction for organic coatings on steel and a magnesium alloy using electrochemical impedance methods. Corrosion 50: 705–716

Seal KJ & Shuttleworth WA (1986) The biodeterioration of polyurethanes by fungi used as standard test organisms for evaluating the susceptibility of plastics. In: Barry S & Houghton DR (Eds), Biodeterioration 6 (pp. 643–648) CAB International Mycological Institute, Slough, UK

Thorp KEG, Crasto AS, Gu J-D & Mitchell R (1994) Biodegradation of composite materials. In: Naguy T (Ed) Proceedings of the Tri-Service Conference on Corrosion (pp 303–314). U.S. Government Printing Office, Washington DC, USA

Titz J, Wagner GH, Spähn H, Ebert M, Jüttner K & Lorenz WJ (1990) Characterization of organic coatings on metal substrates by electrochemical impedance spectroscopy. Corrosion 46: 221–229

Tsai CH & Mansfeld F (1993) Determination of coating deterioration with EIS. II. development of a method for field testing of protective coatings. Corrosion. 49: 726–737

van der Weijde DH, van westing EPM & de Wit JHW (1994) Electrochemical techniques for delamination studies. Corrosion Sci. 36: 643–652

van Westing EPM, Ferrari GM & de Wit JHW (1994a) The determination of coating performance with impedance measurements. II. water uptake of coatings. Corrosion Sci. 36: 957–977

— (1994b) The determination of coating performance with impedance measurements. III. *in situ* determination of loss of adhesion. Corrosion Sci. 36: 979–994

Walter GW (1986) A review of impedance plot methods used for corrosion performance analysis of painted metals. Corrosion Sci. 26: 681–703