

Characterization of Electropolymerized Graphite Fiber-Polyacrylamide Composites

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SYNOPSIS

The synthesis of a series of graphite fiber-polyacrylamide composites was performed electrochemically in dilute sulfuric acid (0.125*M*)-acrylamide (2*M*) solution, 1 : 1 sulfuric acid (0.25*M*) : acetone-acrylamide (2*M*) solution, and 1 : 1 sulfuric acid (0.25*M*) : 2-propanol-acrylamide (2*M*) solution, respectively, using graphite fiber bundles as the working electrode. The graphite fiber-polyacrylamide composites, synthesized in a 1 : 1 2-propanol : sulfuric acid-acrylamide solution, were more easily characterized than those synthesized from the sulfuric acid-acrylamide solution that contained no alcohol. Composites that were synthesized in a dilute sulfuric acid solution were, however, more readily cross-linked. (Fourier transform infrared spectroscopy, FTIR, confirmed the formation of inter-chain and intrachain imide functional groups after the resin was cured at ~ 200°C.) Polymer weight gain analysis, coupled with surface morphology studies using scanning electron microscopy, showed that the thickness of the coatings, and hence the volume fraction of the resin in the composites, varied linearly with the time of electropolymerization. Scanning electron microscopy revealed an open and folded chain surface structure, which permitted unrestricted permeation of the monomer onto the electrode surface. Differential scanning calorimetry of the electropolymerized resins confirmed a glass transition temperature of between 180 and 207°C. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

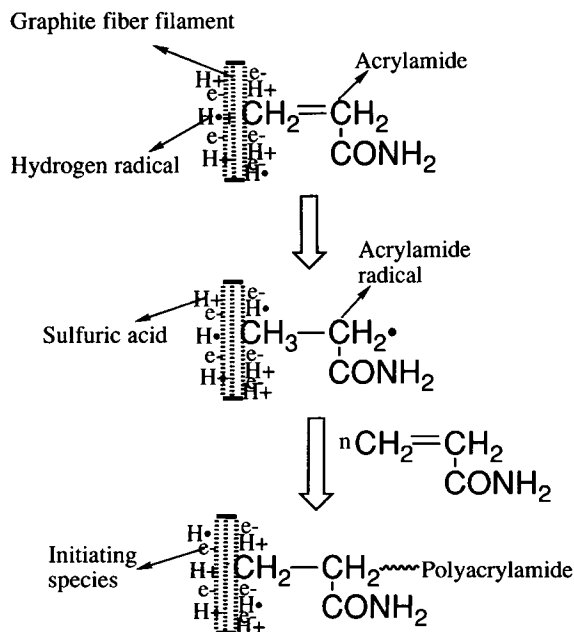
A variety of techniques are used to infiltrate graphite fiber preforms with polymeric resins. These techniques include solvent infiltration, solution coating, hot-melt infiltration, powder coating, and comingling of the reinforcing fibers with the polymeric matrix extruded as fibers. Some of these techniques are well suited for processing high melt viscosity thermoplastic matrix composites, while the others are used to process reactive thermosetting resin-graphite fiber composites. Although these techniques have been used for composite processing since the early 1970s, no significant innovation has been made. Problems associated with these traditional resin infiltration techniques include the inability to

adequately wet individual graphite fiber filaments contained in a graphite fiber bundle of about 3–12 K. Traditional resin infiltration techniques are also unable to control or monitor the volume fraction of the resin in the prepreg. Traditional resin infiltration techniques are slow, cumbersome, lack proper control, and cannot be effectively automated. The practice, whereby the volume fractions of the resin and the fibers are determined after the consolidation of the prepreg, and in some cases after the mechanical evaluation of the composite laminate, is inefficient and outdated. The difficulty in adequately controlling the coating process and coating uniformity add weight to the argument for alternative approaches to resin infiltration. In addition, new and innovative techniques of prepregging are needed in order to keep pace with the advancement in the other areas of composite technology.

The drawbacks of the traditional resin infiltration techniques can be overcome by applying the matrix directly onto graphite fibers, using an electrochem-

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ical technique. In the electrochemical technique, the resin is applied directly onto the graphite fiber preform from either an emulsion of the polymer salt, or from a solution of the monomer dissolved in an appropriate solvent-electrolyte system. The electrochemical technique allows for easy control of resin infiltration via the control and manipulation of the electrosynthetic parameters, such as the current density, monomer concentration, pH of the solution, electrolyte concentration, and reaction time. The properties of the resulting resin can be controlled by controlling the monomer functionality, via electrocopolymerization and/or electrocodeposition. Electropolymerization of a wide range of monomers on the surfaces of a variety of substrates has been reported.¹⁻¹⁰ Subramanian¹¹⁻¹³ and Bell et al.¹⁴⁻¹⁷ have pioneered a sustained effort in the area of electropolymerization onto graphite fibers. In their recent article, Bell et al.¹⁸ reported successful infiltration of AS-4 graphite fiber preforms with about 40 volume percent of thermoplastic matrix, poly[styrene-co-(3-carboxyphenyl) maleimide] by electrochemical polymerization.¹⁸ As noted previously,¹⁴⁻²⁰ this represents a significant advancement in composite processing technology. In the present article, we report the characterization of polyacrylamide-graphite fiber prepreps that are synthesized by electrochemical polymerization.



Scheme I Formation of polyacrylamide on graphite fiber surface from dilute sulfuric acid solution.

Table I Weight Gain of Fibers in 1 : 1 Acetone : Sulfuric Acid Solution (0.250M), 1 : 1 2-Propanol : Sulfuric Acid Solution (0.250M), and Pure Sulfuric Acid Solution (0.125M)^a

Time (sec)	Weight Gain (%)		
	Acetone (H ₂ SO ₄)	ROH (H ₂ SO ₄)	H ₂ SO ₄
30	11.2	—	—
60	—	43.9	39
150	—	89	71
300	94	174	89
600	178	246	146
1200	—	359	259
1500	288	—	—

^a A graphite fiber working electrode (~0.016 gm), 2.0 M acrylamide solution, and a current density of 100 mA/g of fibers were used.

EXPERIMENTAL

99% pure acrylamide was purchased from Aldrich Chemical Company and was used without further purification. Concentrated sulfuric acid, 18M, from May and Baker, was diluted with distilled water to 0.250M and was used as the supporting electrolyte. Surface oxidized AS-4 graphite fibers, from Hercules Inc., were wound onto an H-shaped 1.5 × 2.0 cm aluminum frame and were used as the working electrode. The counter electrodes were two 12.7 × 3.8

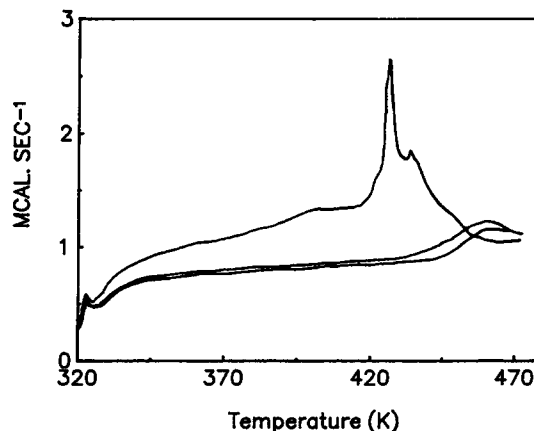


Figure 1 DSC thermogram (20 deg/min) of polyacrylamide (5.58 mg), synthesized in a 1 : 1 2-propanol : sulfuric acid solution (0.25M) [(M) = 2M, Cd = 100 mA/g, top curve = first trace, middle curve = second trace, bottom curve = third trace].

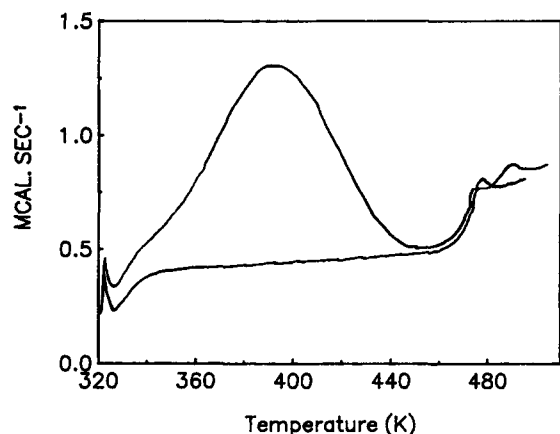


Figure 2 DSC thermogram (20 deg/min) of electro-polymerized polyacrylamide (5.66 mg), precipitated from the reaction solution (top curve = first trace, bottom curves = second and third traces).

× 0.15 cm rectangular stainless steel plates. A 3-compartment electrochemical cell¹⁸ was used in electropolymerization. The central compartment of the cell contained acrylamide (2.0M), dilute sulfuric acid solution (0.125M) and the graphite fiber working electrode. The supporting electrolyte-solvent system was composed of either 1 : 1 2-propanol : 0.25 M sulfuric acid solution or 1 : 1 acetone : 0.25M sulfuric acid solution. The two side compartments each contain the counter electrode and 0.125M sulfuric acid solution. For a 2-propanol-sulfuric acid

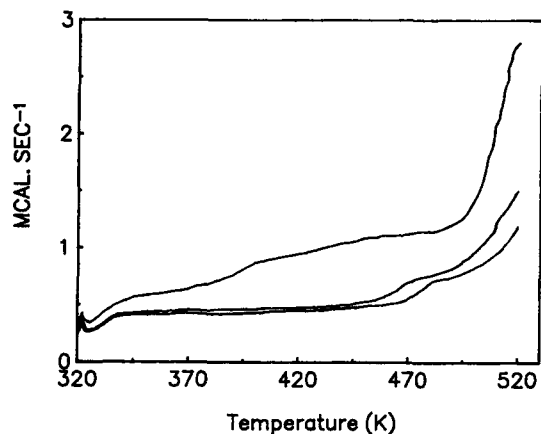


Figure 3 DSC thermogram (20 deg/min) of polyacrylamide (5.66 mg), synthesized in a 0.125M sulfuric acid solution [(M) = 2M, Cd = 100 mA/g (top curve = first trace, middle curve = second trace, bottom curve = third trace).

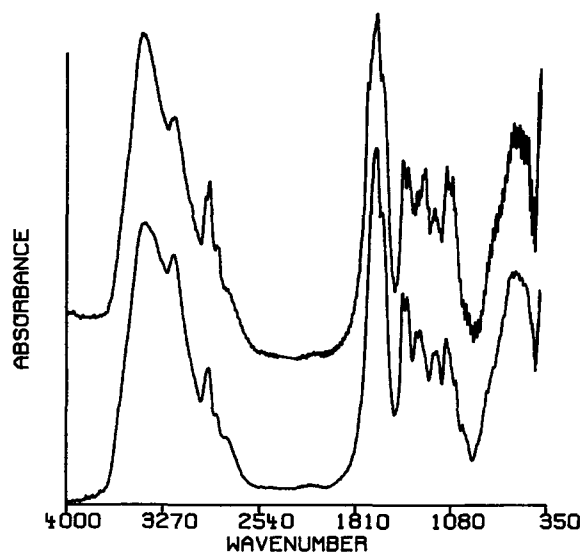


Figure 4 FTIR spectra for polyacrylamide, synthesized in 1 : 1 2-propanol : sulfuric acid solution (top curve = cured at 197°C, bottom curve = uncured).

or an acetone-sulfuric acid system, the side compartments each contain 1 : 1 2-propanol : dilute sulfuric acid solution or 1 : 1 acetone : dilute sulfuric acid solution, respectively, as well as the counter electrode. A Princeton Applied Research Potentiostat, model 363, was used as the source of direct current. The reaction solution was initially saturated

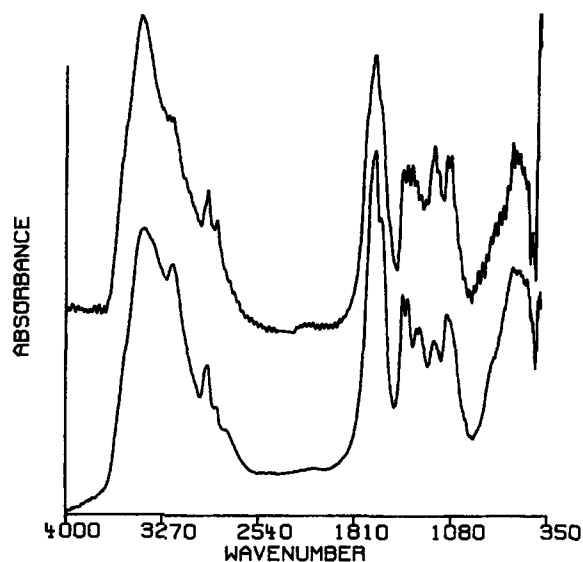


Figure 5 FTIR spectra for polyacrylamide, synthesized in 0.125M sulfuric acid solution (top curve = cured at 197°C, bottom curve = uncured).

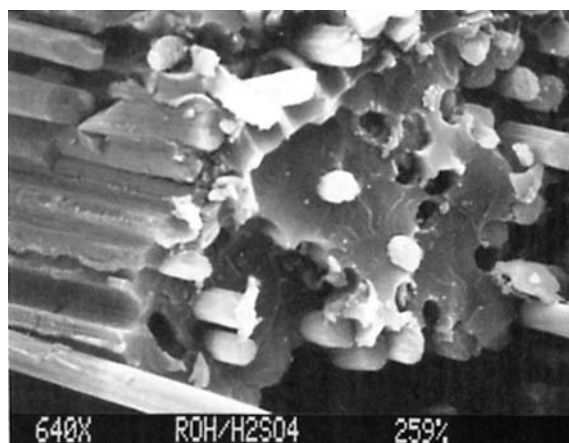
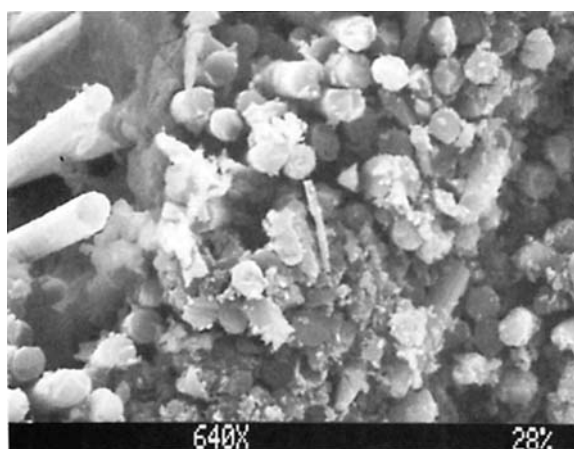
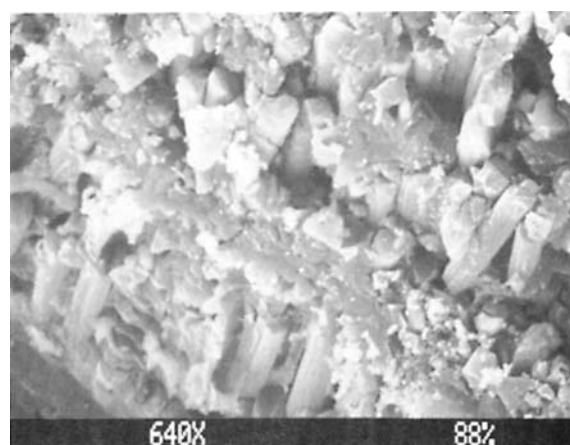
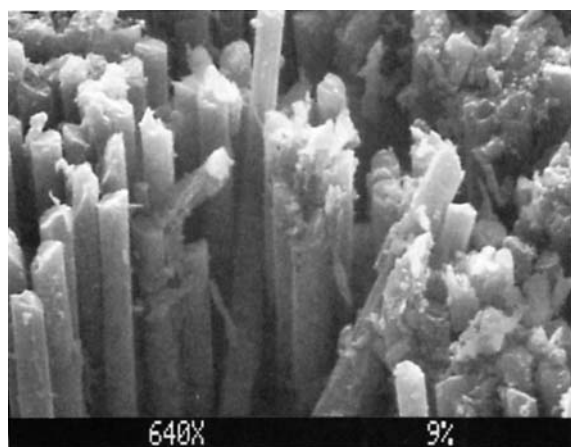


Figure 6 SEM micrographs of cross-sections of polyacrylamide-graphite fiber composites, synthesized after: 30 sec (top) and 60 sec (bottom) of electropolymerization, respectively.

with nitrogen before electropolymerization. The stainless steel counter electrodes and the graphite fiber working electrode were connected to the positive and the negative terminal of the potentiostat, respectively.

Initiation of electropolymerization was achieved by passing adequate current through the monomer-electrolyte-solvent system. The coated fibers were withdrawn from the reaction solution, were rinsed in methanol, and were dried initially at ambient temperature and were finally at 110°C to constant weight. Electropolymerization was interrupted at different electropolymerization times and the morphology of the resulting coatings was investigated.

Thermal analysis of the electropolymerized polyacrylamide coatings was performed with a Perkin-Elmer DSC 2, operated at 20°C per min under a nitrogen atmosphere. The differential scanning cal-

Figure 6 (continued) SEM micrographs of cross-sections of polyacrylamide-graphite fiber composites, synthesized after: 150 sec (top) and 1200 sec (bottom) of electropolymerization, respectively.

orimetry (DSC) was repeated several times until a steady, smooth thermogram was obtained. Functional group analysis of the coatings was performed, employing a Nicolet Fourier transform infrared spectrophotometer (FTIR), using KBr pellets. Scanning electron microscopy, SEM, was used to investigate the surface morphology of the electropolymerized coatings and the prepregs. The composites were scanned without further preparation, while the nonconducting polyacrylamide coatings were shadowed with gold to improve their conductivity.

RESULTS AND DISCUSSION

Scheme I shows the formation of polyacrylamide on the surface of a graphite fiber filament from dilute sulfuric acid solution. The initiating species are generated by the electric current. The typical re-

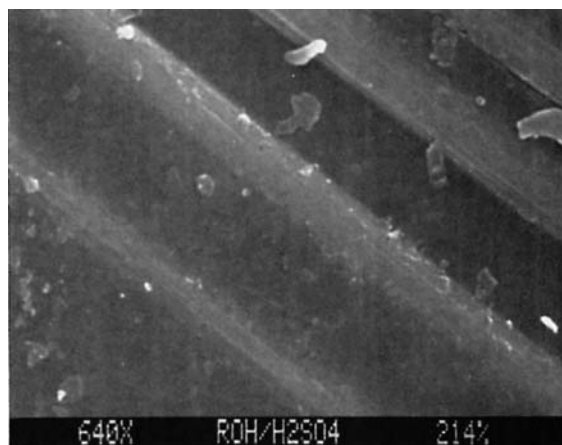
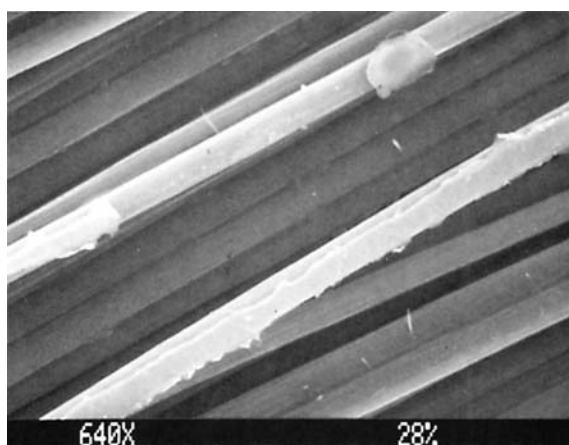
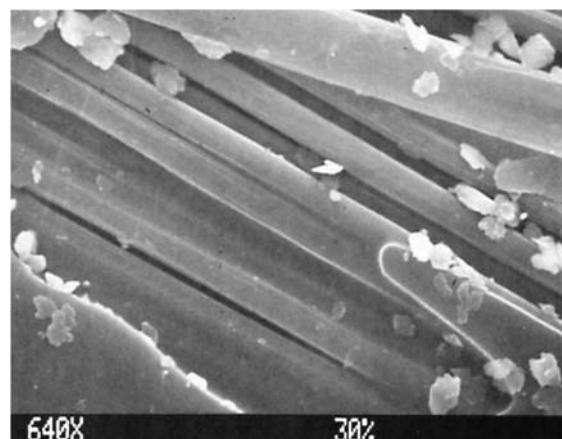
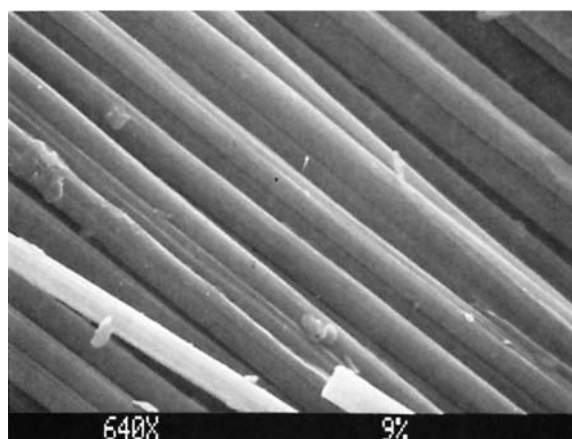


Figure 7 SEM micrographs showing the lateral view of the graphite fiber-polyacrylamide composites, containing: 8% (top) and 22% (bottom) by weight of the electrocoated resin, respectively.

Figure 7 (continued) SEM micrographs showing the lateral view of the graphite fiber-polyacrylamide composites, containing: 23% (top) and 68% (bottom) by weight of the electrocoated resin, respectively.

acting solution contains acrylamide monomer, growing chain radical, hydrogen radicals, hydrogen protons, and the polymer.

Electropolymerization of acrylamide onto a graphite fiber working electrode proceeded successfully in aqueous sulfuric acid solution. The presence of either 2-propanol or acetone did not inhibit the formation of polyacrylamide. However, polyacrylamide, formed in both a 2-propanol/sulfuric acid solution and an acetone/sulfuric acid solution, was more easily dissolved and was more processable. Preliminary dilute solution viscometry indicated that polyacrylamide, formed in 1 : 1 2-propanol : 0.125 M sulfuric acid solution, had a molecular weight slightly lower than that formed in 0.125 M sulfuric acid solution containing no alcohol.

For any given monomer concentration, current density, and sulfuric acid supporting electrolyte

concentration, the weight gain of fibers increased with electropolymerization time (Table I). The volume fraction of the electrocoated resin varied with the electropolymerization time, as was expected.

THERMAL ANALYSIS

Figure 1 shows the DSC thermogram of polyacrylamide synthesized from 1:1 propanol: sulfuric acid solution (0.250M). A glass transition temperature of 190°C was measured from the second and third DSC trace. The first DSC trace for polyacrylamide, precipitated from the reaction solution, showed a broad endothermic peak at about 100°C, due to the entrapped water (Fig. 2, trace 1). Trapped water and solvents are expelled by heating the samples above the glass transition temperature, T_g , and cooling rapidly to room temperature. Subsequent

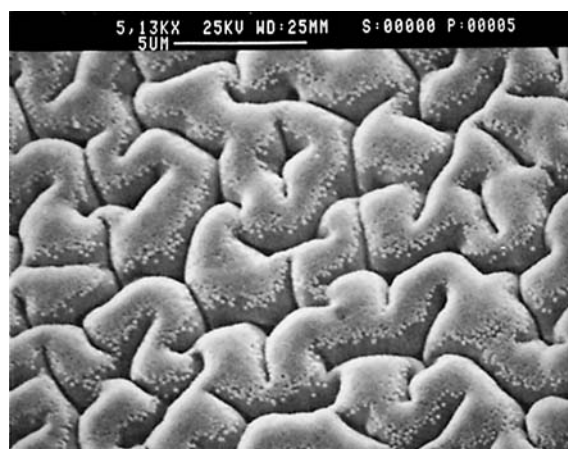
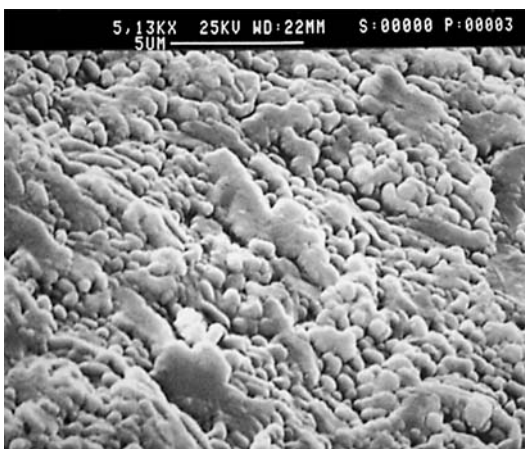
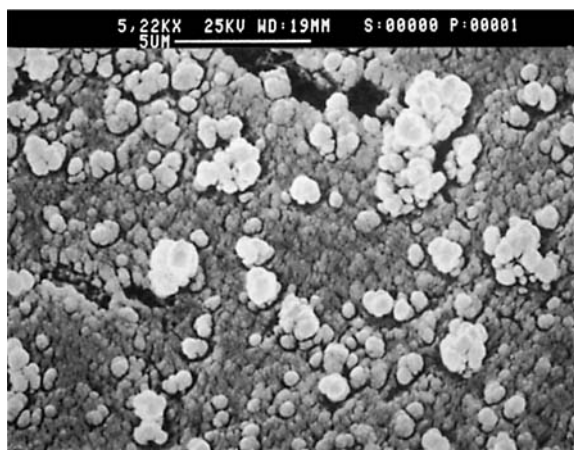


Figure 8 SEM micrographs showing polyacrylamide resin, synthesized using: 1 sec current pulse sequence (top) and 3 sec current pulse sequence (bottom).

Figure 8 (continued) SEM micrographs showing polyacrylamide resin, synthesized using continuous current at a magnification of: $\sim 500\times$ (top) and $\sim 500\text{ K}\times$ (bottom).

scans showed steady and smooth DSC traces (Fig. 2, traces 2 and 3). A sharp change in the baseline of the DSC trace occurred at T_g . A polyacrylamide sample, synthesized in 0.125 M sulfuric acid solution, showed a glass transition temperature of about 190°C (Fig. 3, second and third traces). The T_g of the coatings is in agreement with that reported by MacCallum and Mackerron.^{21,22}

FTIR SPECTROSCOPY

Figures 4(a) and (b) show the FTIR spectra for polyacrylamide, electropolymerized from a 1 : 1 2-propanol : sulfuric acid solution, with and without aging at 197°C , respectively. These spectra show a broad absorption peak between 2800 and 3500 cm^{-1} . The amide and hydroxy characteristic peak absorp-

tions also occur between 2800 – 3500 cm^{-1} . Unreacted vinyl double bond absorption occurs at about 3040 cm^{-1} , while the $-\text{CH}_2-$ peak absorption, characteristic of the polymer backbone, is observed at about 2929 cm^{-1} . The amide carbonyl absorption occurs at 1660 cm^{-1} . Curing eliminates water from the samples and forces the thermal polymerization of unreacted monomers. Consequently, the broad peak absorption at 3415 cm^{-1} became significantly sharpened, while the $-\text{CH}_2-$ absorption peak at 2929 cm^{-1} was intensified. Polyacrylamide, electropolymerized in sulfuric acid solution in the absence of 2-propanol, showed the same characteristic peaks [Figs. 5(a) and (b)]. Further inspection of Figures 4(b) and 5(b) reveals that polyacrylamide, cured at 197°C , formed an imide carbonyl with a characteristic absorption peak at 1771 cm^{-1} , as was earlier reported.¹⁹

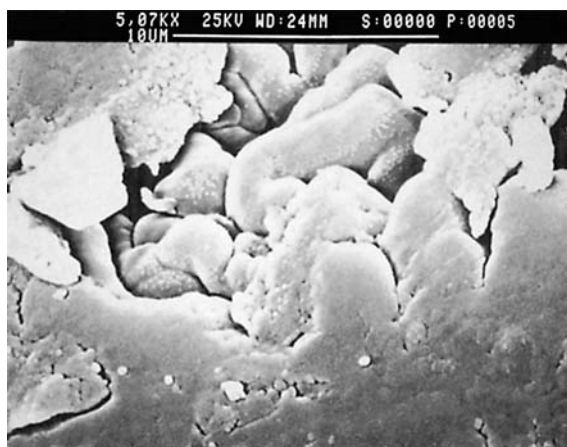
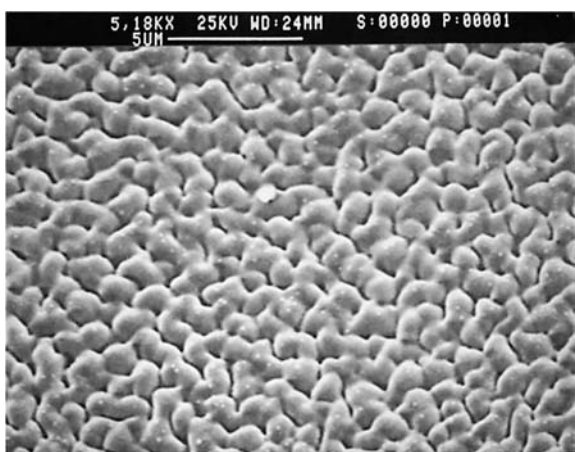


Figure 8 (continued) SEM micrographs showing polyacrylamide resin, synthesized using a 150-sec current pulse sequence at a magnification of: 513 K \times (top), and 513 K \times (bottom).

Figure 8 (continued) SEM micrographs showing polyacrylamide resin, synthesized using a 600-sec current pulse sequence at a magnification of: 518 \times (top) and 507 K \times (bottom).

COATING MORPHOLOGY

Figures 6(a)–(d) show the SEM micrographs of a cross-section of polyacrylamide–graphite fiber prepregs, produced after 30 sec, 60 sec, 150 sec, and 1200 sec of electropolymerization times, respectively. The weight gain of the fibers and, hence, the volume fraction of the resin increased with electropolymerization time. These micrographs show that the matrix became more continuous and homogeneous as the thickness of the coatings was increased. Figures 7(a)–(d) are the SEM micrographs showing the lateral view of the prepregs containing 9%, 28%, 30%, and 214% of polyacrylamide coatings. These pictures suggest that electropolymerization occurred on the surface of the individual fiber filaments and that, as the time of polymerization increased, the volume percent of the coatings increased, resulting

in the spreading of the coatings across the individual fiber ridges. The matrix, therefore, became more continuous as the volume fraction of the resin was increased.

Figures 8(a)–(h) show the SEM micrographs of the electropolymerized polyacrylamide resin dried to constant weight at 100°C. Figures 8(a) and (b) show the polymer resins formed by using 1 sec and 3 sec pulsed current sequences. These micrographs suggest that the coatings originated as polymer globules that conglomerate into one continuous mass. Figures 8(c) and (d) are the SEM pictures of the resin, formed by continuous current flow electropolymerization, at magnifications of 500 \times and 500K \times , respectively. The coatings show a regular surface folding pattern. The polymer surface foldings are separated by pores through which unreacted monomers permeate onto the surface of the working

electrode. Figures 8(e) and (f) show the SEM pictures of polymer resin, formed by a 150 sec pulse sequence, showing regular surface folding of the polymer and the separating discontinuous pores.

Figures 8(g) and (h) are the micrographs of the coatings formed using 600 sec current pulse sequences. These pictures show prepreg resin topologies (layers). We believe that these pictures confirm the reformation and propagation of new polymer chains at the end of each 600 sec current-off time. It was earlier reported that a 600 sec current pulse sequence allowed enough time for the termination of the growing chain during the current switch-off time and the initiation of new chains at the subsequent current-on period.²⁰ The radical lifetime of the polyacrylamide radical was earlier determined to be 5 sec.²⁰

CONCLUSIONS

Polyacrylamide-graphite fiber prepreps were successfully synthesized by electrochemical polymerization. The volume fraction of the polyacrylamide matrix varied with electropolymerization time; other reaction parameters maintained constant. Sufficiently cured resin had a glass transition temperature of 190°C. Functional group analysis confirms the formation of an imide linkage, resulting from either an interchain and/or intrachain condensation. SEM studies suggest an open and regularly folded surface morphology, which permits the unrestrained permeation of the unreacted monomer to the electrode surface for sustained electropolymerization.

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