Formation of Graphite Fiber–Polyimide Prepregs by Electrodeposition

J. O. IROH* and W. YUAN

Department of Materials Science and Engineering, University of Cincinnati, Cincinnati, Ohio 45221-0012

SYNOPSIS

Nonaqueous electrodeposition of polyamic acid of pyromellitic dianhydride and 4,4'-diaminodiphenyl ether was carried out from an emulsion containing a solvent, precipitant, emulsifier, and the polyamic acid. The amount of polyamic acid deposited onto the graphite fibers was dependent on electrodeposition parameters such as the applied current, the amount of polyamic acid (solid content), precipitant/solvent (P/S) ratio, and the acid/base (COOH/TEA) mole ratio. The weight gain of fibers increased with increased current density, P/S ratio, solid content, and deposition time. A maximum weight gain of fibers of about 95% was obtained from an emulsion composed of 3 wt % solid content, P/S ratio of 3 : 1, and TEA/COOH ratio of 1 : 1. The electrodeposition of polyamic acid onto graphite fibers proceeded in accordance with the Faraday's law of electrolysis and a Coulombic efficiency of about 62.2 mg/C was attained. Thermal analysis shows that the cured polyimide coatings were thermally stable up to 500°C. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Graphite fibers are produced with surface treatments or sites designed to increase their chemical interaction and compatibility with the matrix. Fibers are coated with sizes immediately after manufacture to aid in subsequent handling, protect the fibers from damage, and improve the wetting of the fibers by the matrix.[1] Commonly used sizes include polyvinyl alcohol, epoxy, polyimide, and titanate coupling agents. Graphite fibers are sometimes coated with organic polymers, designed to provide flexible polymeric interphases. Subramanian and Crasto[2] successfully applied polymer interphases onto graphite fibers. The polymeric interphases are associated with the following property changes in a graphite fiber–polymer composite: improved interlaminar shear strength by providing strong bonds between the fibers and matrix; and improved fracture toughness by absorbing the energy of impact through deformation, and reducing stress concentration in the vi-

cinity of the surface. The strategy of choosing a polymer interphase is to use the interphasial properties to control the fiber/matrix adhesion. Other techniques such as solution dip coating,[3] plasma polymerization,[4-5] and electropolymerization,[6-9] have been used to apply polymer coatings on carbon fibers. Dip coating is the most commonly used method for impregnating carbon fibers with polymer matrices. However, the properties of the coatings obtained by this method are inconsistent.

Electrodeposition involves the migration of charged particles to an oppositely charged electrode under the influence of an applied electric field. It comprises three steps: electrophoresis, the transportion of the charged particles to the electrode surface; electrolysis, the gain or loss of electrons at the electrode; and electroendosmosis, the precipitation and squeezing out of the solvent from the film.[10] Both cathodic and anodic electrodeposition are prevalent today, but cathodic electrodeposition is believed to produce polymer films that are highly corrosion resistant. Electrodeposition can be carried out from aqueous or nonaqueous media. Aqueous electrodeposition has gained worldwide acceptance as a coating process for automotive, appliance, and

general purpose industrial coatings. The advantages of this process are the ease of automation, high efficiency of coating, low levels of pollution, and high throwing power, for example, the ability to coat the recessed portions of complex shaped products.[11] In the last 20 years, however, considerable interest in nonaqueous electrodeposition has emerged. One of the most important merits of nonaqueous electrodeposition is that water dispersibility is not required and a variety of polymers can be used. Several studies have been reported on the electrodeposition of polyamic acid from nonaqueous media.[12-16] Alvino et al.[12,13] and others[16] have studied the electrodeposition of polyamic acid from nonaqueous media. They found that the quantity and quality of the polyimide coatings were strongly dependent on a number of factors that were closely related to the nature of the emulsion. A systematic study was carried out by Uebner and Ng[14] to provide a more comprehensive and quantitative picture of electrodeposition from nonaqueous emulsions. Using a macroscopic model, they showed the significance of electroendosmosis on film formation. They also showed that the major cause of current decay during electrodeposition was the increased resistance of the adsorbed layer. An overview of nonaqueous electrodeposition of polyimide is given by Scala et al.[17] Their review covered the following areas: emulsion preparation, Faraday parameters (equivalent weight and Coulombic yield), nature of the emulsion particle (size, charge, composition, mobility), and nature of the deposited coating.

In this article, we report the electrodeposition of polyimide onto carbon fibers that was carried out from a nonaqueous emulsion. The effect of deposition parameters on the weight gain of carbon fibers was systematically investigated by varying a number of parameters while maintaining the others constant. These parameters include the solid content, precipitant/solvent (P/S) ratio, acid/amine mole ratio, current density, and deposition time. The polyimide coatings formed by electrodeposition were characterized by the dynamic contact angle analysis (DCA), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA).

EXPERIMENTAL

Unsized but surface oxidized Thornel T-650/35 and T-300 carbon fibers containing approximately

12,000 and 3000 filaments per bundle, respectively, were donated by Amoco Performance Products, Inc. in the form of continuous tows. The polyamic acid (PI2545) prepared from pyromellitic dianhydride (PMDA) and 4,4-oxydianiline (ODA), was obtained as a solution in N-methyl-2-pyrollidone at 13.4 wt % solids from Du Pont. Reagent grade dimethylformamide (DMF), triethylamine (TEA), and methanol were supplied by Fisher Scientific Co. and used as received.

The anode consisted of a bundle of the fibers approximately 50 mm long. The fibers were taped at both ends to an H-shaped polypropylene frame, which was covered by aluminum foil at one end to enhance conductivity. The frame was then inserted into the slots in the center of the side walls of the cell. The cathode was made up of two stainless steel plates ($153 \times 38 \times 1$ mm^3). They were placed into the slots on the wall of the cell, which were on the opposite sides of and at the same distance (2 cm) from the carbon fibers. A potentiostat/galvanostat (model-273A from EG&G Princeton Applied Research Co.) with a data collection and analysis station was used as a DC power source. Electrical contact was made through extension clips. A schematic illustration of the apparatus setup for electrodeposition is shown in Figure 1.

The polyamic acid solution was first diluted with DMF to a required solid content. A specified amount of TEA, which also served as a surfactant, needed for neutralization of the carboxyl groups present in the polyamic acid, was then added to this solution to form polyamic acid salt. The TEA/COOH mole ratio represents the quantitative relationship be-
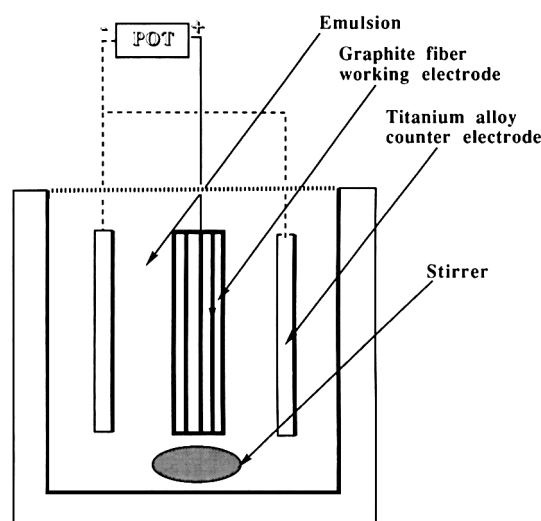

Figure 1   The electrochemical deposition cell.

tween the amino and carboxyl groups present in the TEA and polyamic acid, respectively. The polyamic acid salt solution was heated to 40°C with magnetic stirring and maintained at this temperature for 20 min to enhance the reaction between the polyamic acid and the TEA. The solution was then cooled down to room temperature for about 10 min, and the emulsion was formed by slowly dripping the precipitant (methanol) from a separating funnel into the vigorously stirred solution.

About 100 mL of the emulsion was placed in the cell. The electrodes were immersed in the emulsion and connected to the power source. Electrodeposition was performed by the constant current (chronopotentiometry) technique. The advantage of using this technique is that no feedback is required from the reference electrode to the control device. In addition, the applied constant current causes the electroactive species to be reduced or oxidized at a constant rate.[15] Electrodeposition was carried out by varying a number of parameters systematically while keeping the others constant. The P/S ratio was varied from 2.0/1 to 4.5/1 with an increment of 0.5 each time. The TEA/COOH mole ratio was varied from 0/1 to 2.0/1 with an increment of 0.5 each time, while the solid content was varied from 0.5 to 3.0 wt % with an increment of 0.5 wt % each time. The applied current density was varied from 50 to 300 mA in 50-mA increments. The deposition time was varied from 0.5 to 30 min with six increments. The coated fibers were immediately withdrawn from the emulsion after electrodeposition and left overnight in the hood to dry. The coated fibers were dried to constant weight in a vacuum oven at 100°C and 30 mm Hg. The weight gain of carbon fibers was determined gravimetrically as the difference between the coated and noncoated fibers.

Characterization

The uncoated fiber bundle was cut to a length of about 40 mm and weighed on an electroanalytical balance (XE-100A, Denver Instrument Co.). About 10 uncoated fiber bundle samples were randomly chosen and weighed. The average weight of these samples was taken as the weight of uncoated fiber bundle with a value of 0.0312 g/40 mm. The coated fiber bundle was cut to a length of 40 mm and weighed. Then it was annealed at 200°C for 1 h to complete the imidization of the coating. The weight difference between the coated fiber bundle after curing and the uncoated fiber bundle was then divided

by the weight of uncoated fiber bundle, and the result was taken as the weight gain of the carbon fibers.

SEM

The surface morphology of the coated and noncoated fibers was examined by using the scanning electron microscope (Stereoscan 90, Cambridge Inc.). The coated fibers were dried in the vacuum oven at 100°C for 1 h. All of the samples were coated with carbon or gold to enhance conductivity.

FTIR

The FTIR spectra were obtained by using a Perkin–Elmer 1800 FTIR spectrometer. The spectra were taken at a resolution of 4 cm^{-1} for 10 cycles from 4000 to 450 cm^{-1}. The FTIR samples were prepared by placing a polyamic acid solution (DMF as a solvent) directly on a KBr crystal disk (PKBr 25.0 × 4, OPTOVAC, EM Industries, Inc.), followed by drying in a vacuum oven between 80° and 85°C for 15 min to remove the solvent. The polyamic acid film was extracted in DMF for 24 h and the IR spectra were obtained by following the procedure described above. The cured polyimide samples were prepared first by placing polyamic acid solution on the KBr crystal disk as described above, followed by curing in an oven at about 200°C for 1 h.

RESULTS AND DISCUSSION

Effect of P/S Ratio

To determine the effect of the P/S ratio on the electrodeposition of the polyamic acid onto the graphite fibers, two sets of emulsions with a solid content of 1.0 wt % were prepared. One set of emulsion contained a TEA/COOH mole ratio of 0.5 : 1.0; the other set contained a TEA/COOH mole ratio of 1 : 1. Electrodeposition was performed by passing an electric current of 50 and 100 mA, respectively, through the electrochemical cell. Electrodeposition time was set at 1, 2.5, 5, 10, and 30 min. The control carbon fibers were immersed into the emulsions for 10 min with zero applied current. Table I shows the weight gain of the fibers. The control carbon fibers showed very little weight gain that remained nearly invariant with changing P/S ratio. Note that the emulsions used in this study had a solid content of 1.0 wt %. The relationship between the weight gain of fibers and the P/S ratio is shown in Figure 2.

The weight gain of carbon fibers due to the electro-deposition of polyamic acid increased as a function of the P/S ratios up to a maximum value at a P/S ratio of 3.5 : 1.0 and then leveled off. The explanation for this trend is that electrodeposition involves two processes: the deposition of polymer coatings onto the electrode surface, and the redissolution of the coatings by solvation. The precipitant used in the preparation of an emulsion acts as a coagulant and retards the dissolution of the coatings. If the electrodeposition parameters such as the solid content, amount of TEA, and the applied current are maintained constant, the deposition rate should also be constant. At lower P/S ratio, very little precipitant is present at the vicinity of the anode, resulting in a higher rate of dissolution with the concomitant reduction in the weight gain of fibers. As the P/S ratios was increased, the dissolution rate decreased, resulting in increased retention of the coatings (weight gain) on the fiber. When the P/S ratio was increased to a certain value where the dissolution rate became negligible relative to the deposition rate, the weight gain of fibers would become dependent on the other deposition parameters. To maximize the weight gain of fibers, the emulsion should have a P/S ratio above 3.5 : 1.0. It should be noted, however, that the higher the P/S ratio, the less the amount of solvent in the emulsion, the higher the viscosity of the medium, and the emulsion preparation becomes more difficult. Consequently it is preferable to work with an emulsion composed of a
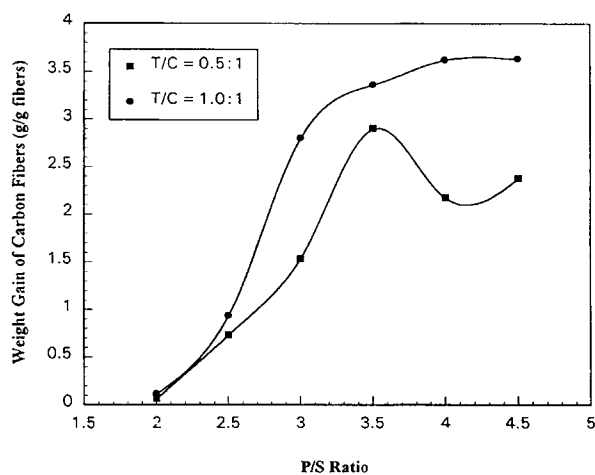

Figure 2 Dependence of the weight gain of fibers on the P/S ratio for TEA/COOH (T/C) ratios of 0.5 : 1.0 and 1 : 1.

P/S ratio of about 3.5 : 1.0. Significant variation in the weight gain of fibers occurred at a P/S ratio $\geq$ 3.5 : 1.0 and TEA/COOH mole ratio $\leq$ 1 : 1 (Fig. 2). An insufficient amount of TEA will lead to the instability of the emulsion and polymer particles will precipitate from the emulsion as a result of coagulation of the polymer. If the precipitated particles are deposited on the anode, a relatively higher weight gain of fibers will occur. If the precipitated particles are not deposited on the fibers, the decreased solid content in the emulsion will lead to a lower weight gain of fibers.

Table I   Effect of P/S Ratio on Weight Gain of Fibers

Deposition Parameters			Weight Gains (mg/mg Fiber) vs. P/S Ratio					
cd (mA)	dt (min)	t/c Ratio	2.0	2.5	3.0	3.5	4.0	4.5
0	10	0.5 : 1	0.04	0.02	0.01	0.02	0.01	0.01
50	5	0.5 : 1	0.06	0.48	0.58	1.08	0.95	1.05
50	10	0.5 : 1	0.08	0.78	1.07	2.13	1.74	1.82
50	30	0.5 : 1	0.07	2.05	2.19	4.41	3.37	3.27
100	5	0.5 : 1	0.05	0.33	0.94	1.70	1.57	1.94
100	10	0.5 : 1	0.06	0.73	1.53	2.90	2.17	2.37
100	30	0.5 : 1	0.08	3.47	3.44	4.28	3.55	3.19
50	1	1.0 : 1	0.11	—	0.16	0.18	0.18	0.19
50	2.5	1.0 : 1	0.12	—	0.40	0.42	0.44	0.44
50	5	1.0 : 1	0.11	0.44	0.82	0.84	0.93	0.93
50	10	1.0 : 1	0.14	0.86	1.60	1.88	1.86	1.86
100	2.5	1.0 : 1	0.10	—	0.69	0.75	0.76	0.82
100	5	1.0 : 1	0.13	0.54	1.57	1.76	1.97	1.98
100	10	1.0 : 1	0.11	0.93	2.80	3.36	3.62	3.63

Solid content = 1.0 wt %. P/S, precipitant/solvent; cd, current density; dt, deposition time; t/c ratio, TEA/COOH mole ratio.
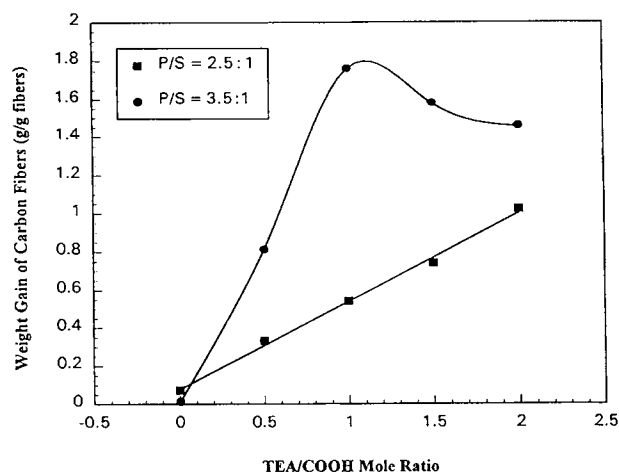
Figure 3 Dependence of the weight gain of fibers on the TEA/COOH mole ratio for precipitant/solvent (P/S) ratios of 2.5 : 1.0 and 3.5 : 1.0.

Effect of TEA/COOH Mole Ratio

Two sets of emulsions with solid content of 1.0 wt % were used to study the effect of TEA/COOH mole ratio on the weight gain of carbon fibers. One set of emulsion had a P/S ratio of 2.5 : 1.0 while the other had a P/S ratio of 3.5 : 1.0. Electrodeposition was performed by passing an electric current of 50 and 100 mA, respectively, through the electrochemical cell. Electrodeposition time was set at 1, 2.5, 5, 10, and 30 min. A control carbon fiber bundle was also immersed into the emulsions for 10 min without applying electric current. The dependence of the weight gain of carbon fibers on the TEA/COOH mole ratio is shown in Figure 3. At a P/S ratio of 2.5 : 1.0, the weight gain of fibers increased linearly with increased TEA/COOH mole ratio. When the P/S ratio was increased to 3.5 : 1.0, the weight gain of carbon fibers initially increased with increased TEA/COOH mole ratio until a TEA/COOH mole ratio of 1 : 1. Above this value, the weight gain of fibers decreased as the TEA/COOH mole ratio was increased. The weight gain of fibers is always higher at the P/S ratio of 3.5 : 1.0 than that at the P/S ratio of 2.5 : 1.0 for the same TEA/COOH mole ratio. These observations may be explained as follows. The TEA plays three roles in the electrodeposition of polyamic acid: it acts as an emulsifying agent; it also acts as a charge donating agent; and it enhances the conductivity of the emulsion. As discussed earlier, when the P/S ratio is 2.5 : 1.0, the redissolution rate of the coatings becomes significant. Further increase in the TEA/COOH mole ratio will result in increased deposition rate with the

concomitant increase in the weight gain of fibers. However, when P/S ratio is 3.5 : 1.0, the redissolution rate of the polymer becomes negligible. A further increase in the TEA concentrations will result in the formation of more stable and conductive emulsions, which will lead to an even higher deposition rate as shown in Figure 3. But when TEA/COOH mole ratio is greater than 1 : 1, the overdosed TEA will produce supersaturated salts resulting in a lower efficiency of deposition. To get maximum weight gain of carbon fibers, it is preferable to work with an emulsion with a TEA/COOH mole ratio of 1 : 1.

Effect of Solid Content

The effect of the solid content on the electrodeposition was determined by using emulsions containing varying solid content. These emulsions were composed of a P/S ratio of 3.5 : 1.0 and a TEA/COOH mole ratio of 1 : 1. Electrodeposition was performed by passing an electric current of 50 and 100 mA, respectively, through the cell. The weight gain increased only very slightly with increased solid content. The relationship between the weight gain of fibers and the solid content is shown in Figure 4. Only a slight change in the weight gain of fibers was observed over the solid content range studied. The gradual increase in the weight gain with an increase in the solid content is due to the increase in the number of charge carrying species and the consequent increase of the cell conductivity. Germant[18] suggested that the mobility of charge carrying species in an electric field is inversely proportional to
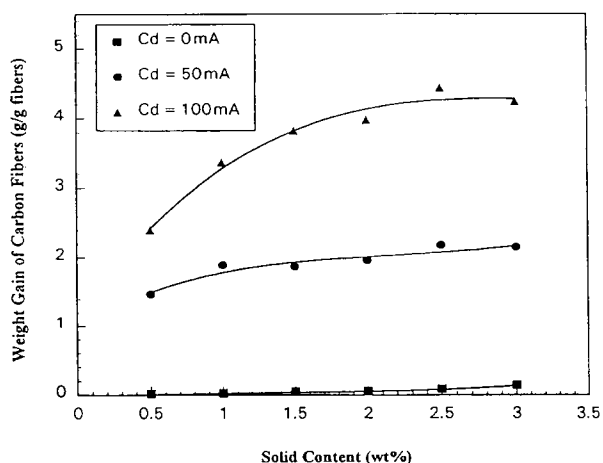

Figure 4 Dependence of the weight gain of fibers on the solid content for applied current (Cd) of 0, 50, and 100 mA.

their concentration. Hence, only a slight increase in the weight gain occurred with increased solid content. This illustrates why the applied current has a greater impact on the weight gain of fibers than the solid content. The weight gain of fibers increased significantly as the applied current was doubled from 50 to 100 mA (Fig. 4). The advantage of the slight change in the weight gain over the solid content range is the feasibility of a possible continuous process. Successive depositions from the same emulsion will lead to decreased solid content in the emulsion. If the change in the weight gain is large, successive deposition from the same emulsion will result in a decreased weight gain due to the depletion of the solid content. In that case, a continuous process will not be possible because the large changes in the weight gain will lead to nonuniform weight gain of the fibers.

Figure 5 Dependence of the weight gain of fibers on the applied current for deposition times (dt) of 1, 2.5, 5, and 10 min.

Effect of Applied Current

The effect of the applied current was determined by using two sets of emulsions with solid contents of 1.0 and 3.0 wt %, respectively. These emulsions were composed of a P/S ratio of 3.5 : 1.0 and a TEA : COOH mole ratio of 1 : 1. Deposition time was set at 1, 2.5, 5, and 10 min. The results of these experiments are shown in Table II. The relationship between the weight gain of carbon fibers and the current density is shown in Figure 5. The weight gain of fibers increased linearly with increased applied current. For a given emulsion composition, the amount of polymer deposited is directly proportional to the quantity of electricity passed. If the deposition time is constant, the amount of polymer deposited should be directly related to the electric current passed through the electrochemical cell in agreement
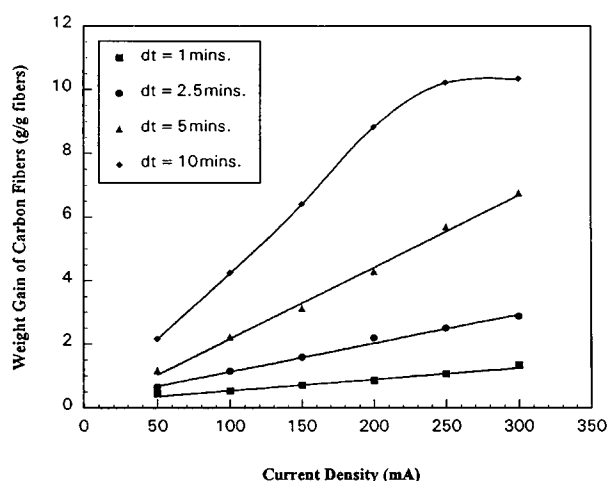
with the Faraday's law of electrolysis. At long deposition times and under high applied current, successive depositions from the same emulsion will deplete the polyamic acid, resulting in a lower weight gain of fibers. Also, as the polymer coating builds up on the electrode, it acts as an insulator and forms a high resistance path thereby slowing the rate of deposition. The longer the deposition time, the higher the charge passed, and the thicker the polymer film deposited. On the other hand, as the solid content is decreased, the conductivity of the emulsion will decrease. As a result, the cell voltage will increase to keep the current density constant. If the deposition time lasts too long or the current density is set too high, the cell voltage may be built up to the rupture voltage of the film. As indicated by Bosso and Zwack,[19] when the rupture voltage is reached,

Table II   Effect of Applied Current on Weight Gain of Fibers

Deposition Parameters		Weight Gains (mg/mg Fiber) vs. Current Density (mA)						
Solid Content (%)	dt (min)	0	50	100	150	200	250	300
1	1	—	0.18	0.36	0.43	—	0.63	0.99
1	2.5	—	0.42	0.75	1.12	1.34	1.62	1.87
1	5	—	0.84	1.76	2.67	3.48	4.04	5.15
1	10	0.02	1.88	3.36	5.03	5.62	7.17	7.45
3	1	—	0.43	0.51	0.69	0.84	1.04	1.32
3	2.5	—	0.64	1.13	1.57	2.16	2.47	2.85
3	5	—	1.15	2.20	3.10	4.28	5.67	6.73
3	10	0.13	2.14	4.23	6.39	8.82	10.21	10.32

P/S ratio = 3.5 : 1.0, TEA/COOH mole ratio = 1 : 1. P/S, precipitant/solvent; dt, deposition time.

the film is subjected to severe heating resulting in film rupture and delamination. During the electro-deposition of polyamic acid at an applied current ≥ 250 mA, severe gas bubbling occurred around both electrodes. Under higher applied current and longer deposition time, the intensity of the bubbling increased. At high applied current (≥ 250 mA) and long deposition times (≥ 30 min), the temperature of the cell may rise due to local heating. The temperature of the emulsion after 30 min of electrode-position using an applied current of 300 mA is higher than 40°C. The variation of the deposition rate with the applied current at a constant deposition time is shown in Figure 6. The rate of deposition increased linearly with the applied current. Deviation from linearity is probably due to the reasons discussed above. For the same emulsion composition, the deposition rate should be constant for the same applied current. But, because of the insulating nature of the deposited polymer film and the decreased conductivity of the emulsion, the deposition rate decreased with increased deposition time for the same current density.

Effect of Quantity of Charge

Figure 7 shows the relationship between the weight gain of carbon fibers and the charge passed through the electrochemical cell. The emulsion used in this study was composed of a solid content of 3.0 wt %, P/S ratio of 3.5 : 1.0, and TEA/COOH mole ratio of 1 : 1. It was found that when the charge passed through the electrochemical cell was low, electro-deposition proceeded in accordance with the Fara-
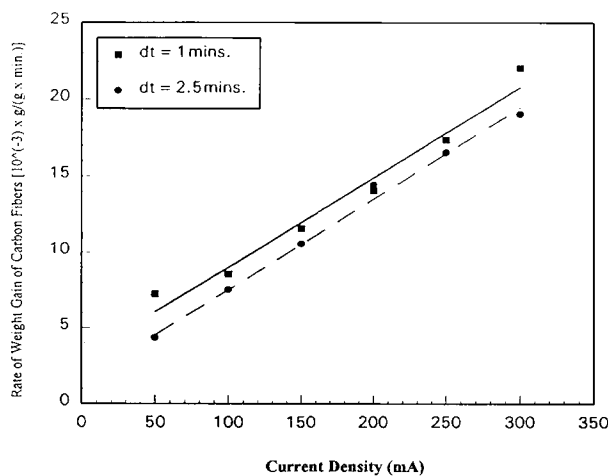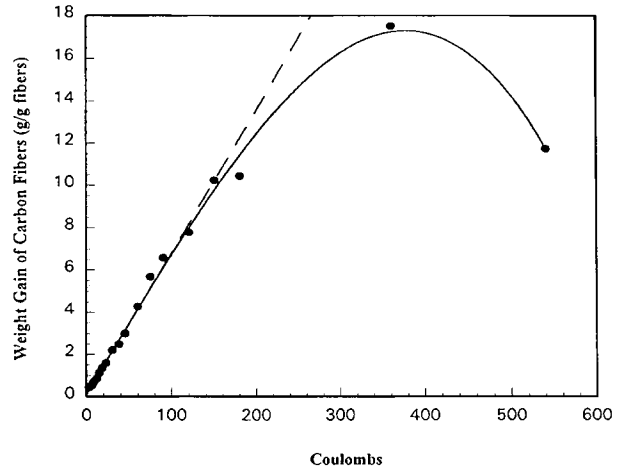

Figure 7 Dependence of the weight gain of fibers on the charge passed.

day's law of electrolysis. The weight gain of fibers is directly proportional to the charge passed. Deviation from linearity occurred when the charge passed through the electrochemical cell was very high and was attributed to the rupture and delamination of the polymer film. The linear portion of the curve shown in Figure 7 was used to calculate the value of Coulombic efficiency, C. The value of C is calculated to be 62.2 mg/C for the emulsion composed of a solid content of 3.0 wt %, P/S ratio of 3.5 : 1.0, and TEA/COOH mole ratio of 1 : 1. A similar curve was observed for the emulsion containing a solid content of 1.0 wt %, P/S ratio of 3.5 : 1.0, and TEA/COOH mole ratio of 1 : 1.
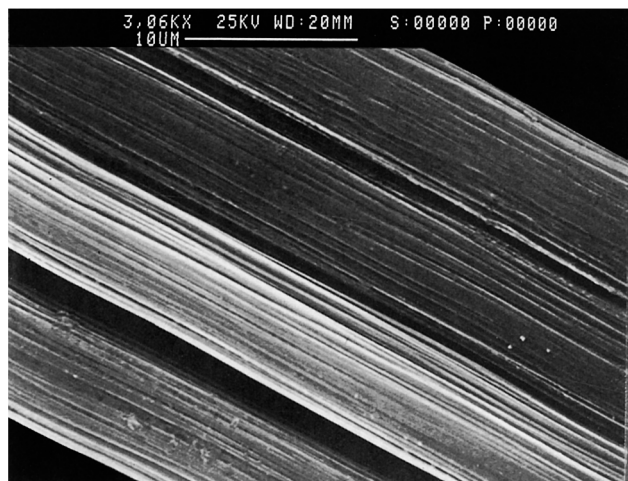

Figure 6 Dependence of the rate of deposition on the applied current for deposition times (dt) of 1 and 2.5 min.

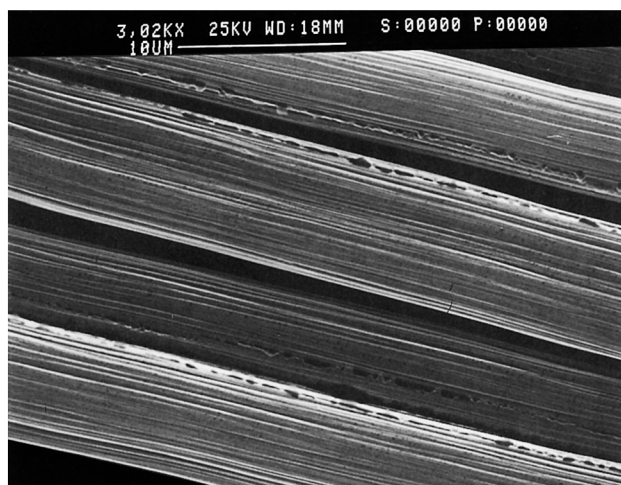**Figure 8** SEM micrograph for noncoated graphite fibers.

Figure 9 SEM micrograph for control fibers after immersion in an emulsion for 1 min at zero applied current.

SEM Microscopy

An SEM micrograph of the fibers before electrodeposition is shown in Figure 8. The surface of the fibers appears quite smooth, and only some longitudinal striations are visible. These striations probably occur during the spinning and surface treatments of the fibers. The SEM micrograph of the noncoated fibers after immersion in an emulsion composed of a P/S ratio of 3.5 : 1.0, TEA/COOH mole ratio of 1 : 1, and solid content of 1.0 wt %, for 1 min is shown in Figure 9. The longitudinal striations are still visible on the fibers, indicating that the weight gain of fibers, if any, was very small. The
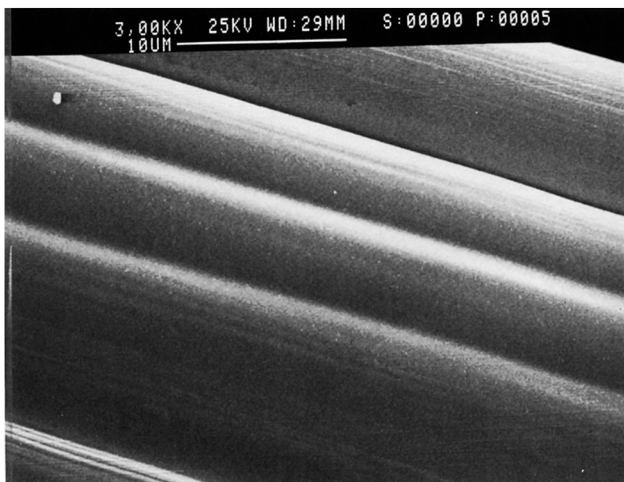

Figure 10 SEM micrograph for control fibers after immersion in an emulsion for 1 min at an applied current of 50 mA.
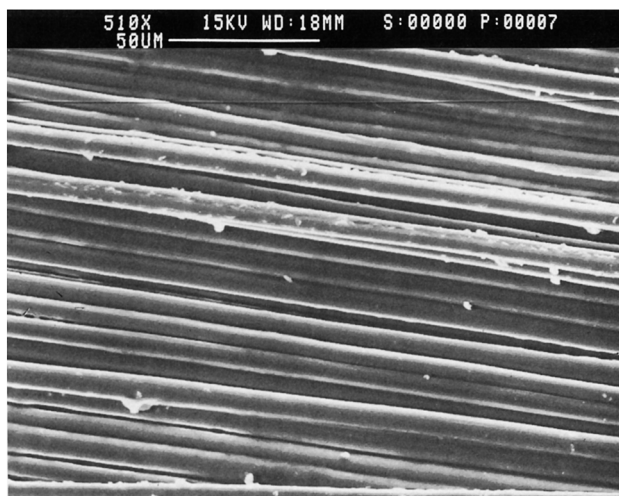

Figure 11 Dependence of the morphology of the coatings on the weight gain of fibers (top = 27.9 wt %; bottom = 54.5 wt %).

SEM micrograph of the fibers after electrodeposition using an applied current of 50 mA for 1 min is shown in Figure 10. The emulsion composition was the same as was used in the control experiment. Although some longitudinal striations are still visible, the fibers were covered by a uniform polymer film. This confirms that an applied electric field is the major driving force for the electrodeposition.

All the coatings are smooth and uniform, regardless of depositing conditions. As shown in Figure 11 (top) the fibers are completely covered by a thin uniform coating even at resin content of 27.9%. As the weight gain increases, the coating becomes

thicker and polymer film begins to form between adjacent fibers (Fig. 11). However, the single carbon fiber can still be distinguished when the resin content is below 45%. As the resin content increases beyond 45%, the whole fiber bundle starts to be covered by the polymer coating. Figure 11 (bottom) shows that when the resin content is ≥ 54.5%, the whole fiber bundle is covered by a smooth and uniform coating. It is very difficult to distinguish a single fiber filament. As the polymer film is formed, the increased electrical resistance of the coating directs further film formation to the uncoated areas that are more conducting, enabling a uniform film to be built up, free of pin holes. The freshly deposited film is also highly swollen, porous, and conductive and forces the film thickness to increase.

FTIR

FTIR spectra of the polyamic acid before and after electrodeposition are shown in the top part of Figure 12. The FTIR spectra of the cured polyimide are shown in the bottom section of Figure 12. The IR absorption bands occurring at 1720 and 1304 cm^{-1}
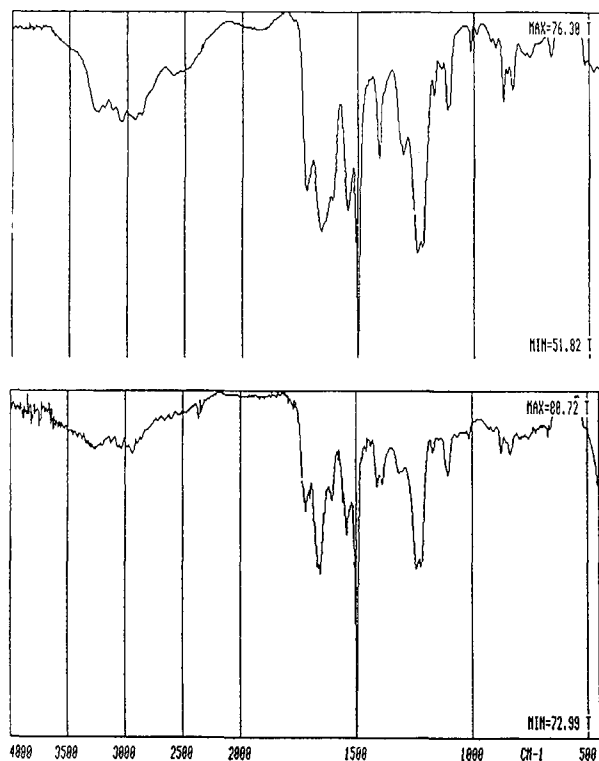

Figure 12   FTIR spectra of (top) bulk polyamic acid and (bottom) polyamic acid electrodeposited onto graphite fibers (extracted in DMF).
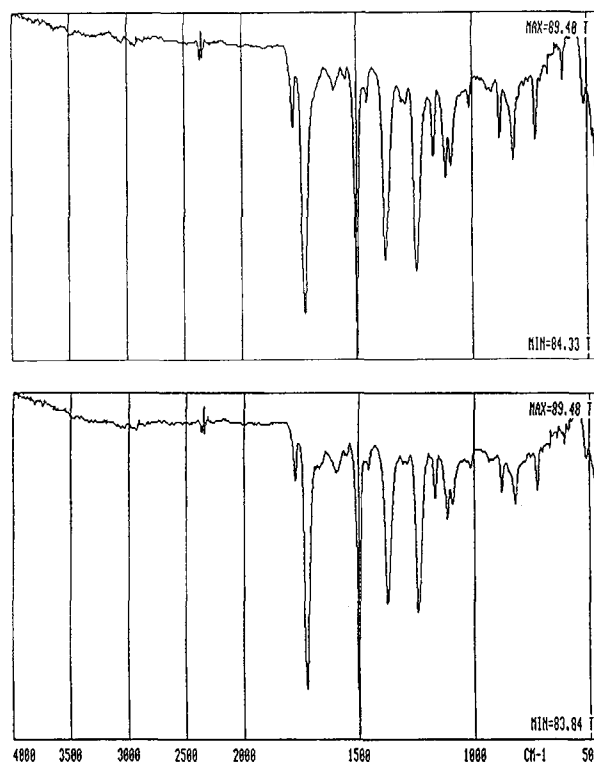

Figure 13   FTIR spectra of (top) polyimide cured from (bottom) bulk polyamic acid cured from the electrodeposited polyamic acid.

were assigned to the vibrational modes of carboxylic acid. The bands occurring at 1660, 1540, and 1406 cm^{-1} were assigned to the vibrational modes of the amide group. All these bands disappeared after curing. However, the characteristic absorption bands of the imide group near 1778, 1723, 1375, 1115, and 723 cm^{-1} were observed in the FTIR spectra of the cured samples (Fig. 13). As shown on Figures 12 and 13, the FTIR spectra of the film are similar to those of the bulk polymer. This indicates that electrodeposition does not alter the structure of the polymer.

Based on the FTIR results and Drzal et al.,[1] the possible mechanism of the electrodeposition process was suggested to be as shown in Figure 14. When the constant current was applied to the electrochemical cell, the polyamic acid salt in the emulsion dissociated to form negatively charged polycarboxylates and positively charged quaternary ammonium ion. The negatively charged polycarboxylates then, under the influence of the electric field, migrate to the anode. The soluble polycarboxylates accept protons to form the anode and precipitate as continuous polymer film. A similar mechanism of nonaqueous electrodeposition was also proposed by Yang and Chen.[16]
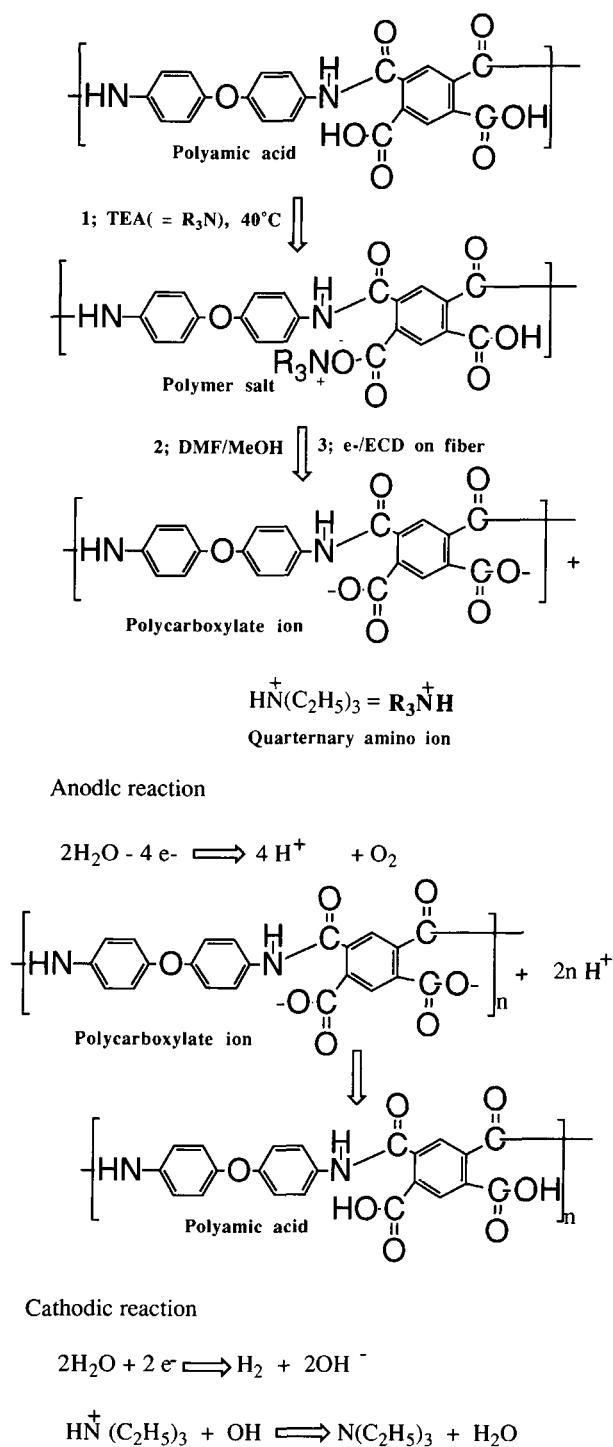
Polyamic acid

1; TEA(= R₃N), 40°C

Polymer salt

2; DMF/MeOH   3; e-/ECD on fiber

Polycarboxylate ion

$$\overset{+}{HN}(C_2H_5)_3 = R_3\overset{+}{N}H$$

Quarternary amino ion

Anodic reaction

$$2H_2O - 4\,e- \implies 4\,H^+ + O_2$$

Polycarboxylate ion $+\ 2n\,H^+$

Polyamic acid

Cathodic reaction

$$2H_2O + 2\,e^- \implies H_2 + 2OH^-$$

$$\overset{+}{HN}(C_2H_5)_3 + OH^- \implies N(C_2H_5)_3 + H_2O$$

Figure 14 Mechanism of electrodeposition of polyimide onto graphite fibers.

CONCLUSION

Electrodeposition of polyamic acid films onto carbon fibers has been studied with the objective to

modify the surface of carbon fibers. Electrodeposition was carried out from nonaqueous emulsions at constant current density. One of the most important advantages of nonaqueous electrodeposition is that water dispersibility is not required and a variety of polymer types can be electrodeposited. It was shown that an applied electric current is the major driving force of electrodeposition. No significant weight gain of the fibers was obtained without an applied current. However, the process is strongly dependent on the solid content, precipitant/solvent ratio, amount of surfactant, and preparation technique. The amount of surfactant, however, is critical to the emulsion stability. It was found that when the mole ratio of TEA and COOH groups in the polyamic acid is ≥ 1, the emulsion is clear and stable; when the mole ratio of TEA and COOH groups in the polyamic acid is < 1, the emulsion is milky, opaque, and also has some big particles precipitated out. The surfactant plays three roles in the electrodeposition process: acts as an emulsifying agent; acts as a neutralizing agent; and enhances the conductivity of the emulsion. But an overdose of surfactant will produce supersaturated salts with a concomitant lowered efficiency of the deposition process.

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