

## 탄소섬유 표면에서의 전기중합: 연속공정

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## Electropolymerization onto the Surface of Graphite Fibers: A Continuous Process

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**요 약:** Glycidyl acrylate와 methyl acrylate의 공중합체를 탄소섬유의 표면에 연속전기중합법을 이용하여 코팅하였다. 전기중합 개시반응 메커니즘을 규명하기 위해 단량체-용매-전해질 시스템에 대한 cyclic voltammetry 측정을 하였는데 수소이온의 환원만 관찰되었다. 공정 변수인 전류, 반응시간, 단량체 농도, 전해질 농도, 교반 속도의 영향에 대해 조사하였다. 무게 증가 속도는 전류와 단량체의 농도에 비례하였고 전류가 일정할 때 전해질 농도의 영향은 없었다. 일정량의 전류 이상에서는 무게 증가가 전류와 무관하였다. 코팅된 고분자의 분자량은 전류에 반비례하였다.

**ABSTRACT:** Copolymer of glycidyl acrylate and methyl acrylate was coated on the surface of graphite fibers by using continuous electropolymerization technique. Cyclic voltammetric study of monomer-solvent-electrolyte system was done to determine the initiation mechanism. Only reduction of hydrogen ions was observed. The processing parameters in terms of current, reaction time, concentration of comonomer, concentration of supporting electrolyte and agitation speed were investigated. The initial rate of weight gain was proportional to current and concentration of the comonomer, but concentration of the supporting electrolyte had no effect when current was controlled. Above a certain amount of current, the weight gain had no relation with the current. The molecular weight of coated polymer was inversely proportional to the current applied.

**Keywords:** electropolymerization, carbon fiber, weight gain.

## INTRODUCTION

The main advantage of graphite fiber composites is their high specific tensile strength and stiffness. It is primarily this reason that reinforced graphite fiber composites are replacing metals in applications where weight savings are important,

i. e., the aerospace and transportation industries. Novak,<sup>1</sup> Brewis,<sup>2</sup> and Herrik<sup>3</sup> observed that the impact strength and mode of failure of graphite fiber-epoxy resin composites were inversely related to their interlaminar shear strength (ILSS). Non-treated graphite fiber reinforced epoxy resin composites have low ILSS and tend to fail when

loaded in shear. As the ILSS increases with various surface treatments, the mode of failure changes to a combination of shear and tension. Hence, as the ILSS increases, failure becomes brittle, and the impact strength of the composite decreases.

Over the past decade, various attempts have been made to overcome this conflict in properties, including approaches such as toughening of the matrix,<sup>4,5</sup> hybridization of graphite composites,<sup>6-8</sup> and incorporation of a ductile polymer coating onto the graphite fibers.<sup>9-11</sup> Incorporation of a ductile polymer interlayer seems a very practical method to improve impact strength and shear strength of the resultant composite as well as maintaining the required optimum levels of other properties. A ductile interlayer can improve impact strength by plastic deformation of interlayer polymers<sup>12,13</sup> and reducing residual thermal stress.<sup>14</sup> It can also heal the fiber surface flaws, protect the fibers from breaking in the process and facilitate physical and chemical bonding between fiber and matrix.

Since graphite fibers are conductive, a thin polymeric interlayer can be applied by electropolymerization.<sup>9,15-23</sup> The advantages of electropolymerization are as follows: Easy wetting of fiber surfaces can be attained due to the better match of surface tension of the monomer relative to water. Good bonding between fiber and interlayer can be obtained because of the electrical attraction induced in electropolymerization and penetration of monomer into graphite pores. The reaction rate and molecular weight ( $M_w$ ) of the coated polymer can be controlled easily by the amount of the current flowing through the system. A uniform polymer interlayer can be obtained because the resistance of coated polymer encourages polymerization onto areas of lesser thickness.

In this study, copolymer of glycidyl acrylate (GA) and methyl acrylate (MA) was coated as a ductile interlayer by continuous electropoly-

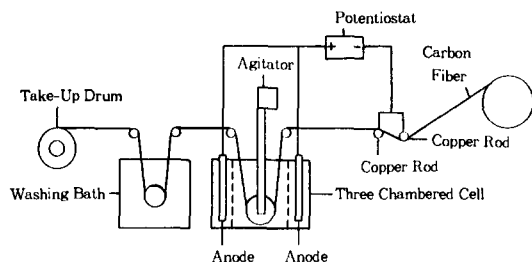
merization. Cyclic voltammetry (CV) study of monomer-solvent-electrolyte (M-S-E) system was done to determine the initiation mechanism and the processing parameters in terms of current, reaction time, concentration of comonomer, concentration of supporting electrolyte and agitation speed were investigated. The study for the parameters was done for a better understanding of continuous electropolymerization.

## EXPERIMENTAL

**Materials.** Methyl acrylate (Aldrich Chemical Co.) and glycidyl acrylate (Polyscience Co.) were distilled under reduced pressure. The middle fraction was collected and stored in a refrigerator under nitrogen. Sulfuric acid (J. T. Baker Co.) was used as purchased. Hercules AS-4 unsized graphite fibers were used without further treatment. AS-4 graphite fibers were supplied continuously, high strength, PAN based fibers, with 3K filaments per bundle. The fiber has been surface oxidized to provide the necessary functionality for chemical reactivity with the matrix and to enhance wetting properties.<sup>24</sup>

**Cyclic Voltammetry Study.** For an aqueous monomer-solvent-electrolyte system (GA/MA comonomer-water-sulfuric acid), a standard calomel electrode was used. For nonaqueous systems, acetonitrile and 50 mM of tetrabutyl ammonium perchlorate (TBAP) were used as solvent and supporting electrolyte respectively. A silver/silver nitrate (0.1 M) was used as a reference electrode. In both solvent systems, a graphite electrode was used as the working electrode and a platinum electrode was used as the counter electrode. The cathode sweeping rate was 100 mV/sec.

**Apparatus for Electropolymerization.** Fig. 1 shows a laboratory unit designed for the continuous coating of graphite fibers. A three chambered cell was made of thick glass plates. Each



**Figure 1.** Schematic diagram of an apparatus for continuous electropolymerization.

volume of the two anode chambers was 375 cc. The chambers were separated by a hydrophobic membrane (Celgard micro-porous polypropylene membrane 3501). In each anode compartment, a dimensionally stable anode (Eltech Systems Co., 4158-IT: titanium oxide coated with iridium oxide) was used and the size of the anode was 100 mm  $\times$  200 mm  $\times$  1.25 mm. In the cathode compartment, a single strand (3 K) of graphite fibers was continuously passed through the cell. The length of fibers immersed in the aqueous solution of monomers was 36 cm. The cell was covered to reduce the evaporation of the monomers, but several holes for the entrance and exit of fibers, for the flow of solution and for the agitator were necessary. Current was applied through the fibers via two copper rods. Fibers were pulled by the take up drum which was driven by a speed-controllable motor. A vertically oscillating agitator was attached to enhance the spreading of the fibers and to facilitate the removal of hydrogen gas which was generated on the surface of fibers. Current was controlled by a Potentiostat/Galvanostat (EG & G Princeton Applied Research Model 363) and the potential was recorded on a strip chart recorder in reference to a standard calomel reference electrode.

**Procedure for Electropolymerization.** After the solvent-electrolyte was degassed in a reservoir with nitrogen for 30 min, a comonomer was mixed with the solvent-electrolyte. The

comonomer-solvent-electrolyte system was added to the cell through the holes on top plate of the cell. The carbon fibers were immersed in the aqueous solution of comonomer and electrolyte in the central chamber of electropolymerization cell. Electropolymerization was initiated by passing constant current through the cell, and reaction time was varied by changing the speed of the take-up drum. After passing through the electropolymerization bath, the graphite fibers were rinsed in a water bath, wound on a pick-up drum driven by a gear motor and then dried in a vacuum oven overnight at room temperature. The weight gain on the surface of the graphite fibers was checked by thermal gravimetric analysis.

**Characterization.** A DuPont 900 thermogravimetric analyzer (TGA) was used to determine the weight gain of the graphite fibers in the electropolymerization. TGA was run under nitrogen atmosphere and temperature was scanned up to 700  $^{\circ}\text{C}$  at a programmed heating rate of 50  $^{\circ}\text{C}/\text{min}$ . IR spectra were obtained using a Mattson Cygnus FT-IR operated at 4  $\text{cm}^{-1}$  resolution and using a mercury cadmium telluride detector. A sixty degree germanium IRS element was used as the background for the spectra. Molecular weight determination was made on a Waters gel permeation chromatograph, Model 200, equipped with four Ultra-Styrigel columns with pore sizes of 100, 500, 1000 and 10000  $\text{\AA}$ . Tetrahydrofuran (THF) was used as a solvent at a flow rate of 1.0 mL/min at 23  $^{\circ}\text{C}$ . Only electropolymerized poly(methyl acrylate) (PMA), which was soluble in THF was examined. Polystyrene (PS) standards and a known molecular weight of PMA (Aldrich Chemical Co.,  $M_w=10000$ ) were used to construct the molecular weight calibration curve.

## RESULTS AND DISCUSSION

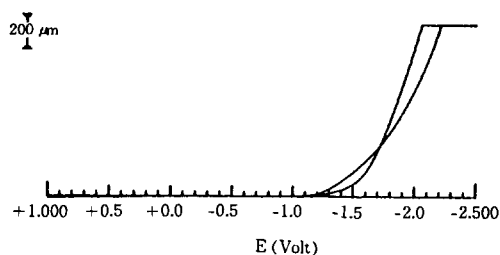
**Cyclic Voltammetry Study.** CV was used to

measure the reduction potential of the chemical species in the M-S-E system and to determine the initiation mechanism. The response of CV from an aqueous system which contains 0.025 M sulfuric acid as supporting electrolyte with comonomer (0.107 mol GA/0.416 mol MA) is shown in Fig. 2. These data are typical of the current-potential curve for an aqueous acidic solution.<sup>14</sup> Reduction of hydrogen ions dominated the voltammogram; no other electrode reaction was apparent.

In the nonaqueous system, acetonitrile and TBAP (50 mmol) were used as the solvent and the supporting electrolyte respectively. In Fig. 3, voltammograms of sulfuric acid, 0.05 N sulfuric acid, monomers and monomers in 0.05 N sulfuric acid are shown. When 1 drop of sulfuric acid was added to the 20 mL of background, there was a strong reduction peak; in the case of 1 drop of 0.05 N sulfuric acid, there was a minor reduction peak. As a result, it has been concluded that the strong reduction peak in an aqueous system is mainly due to hydrogen ions generated from the sulfuric acid. In Fig. 3 (d)-(g), there was no reduction peak when monomers alone were added to the background; the reduction peak observed was dependent only on the amount of sulfuric acid added. The hydrogen reduction peak corresponded to the only reaction observed.

From the CV study, it can be observed that the reduction potential of these monomers, under the above conditions, is much higher than that of hydrogen ions. It is suggested here that the initiation of electropolymerization is due to the reduction of hydrogen ions, whereby hydrogen free radicals will react with monomers to start the chain reaction in preference to recombination to form hydrogen gas. No monomer free radical anions will be formed to start the polymerization because the electrochemical reaction of the lowest potential dominates the overall electrode reaction.

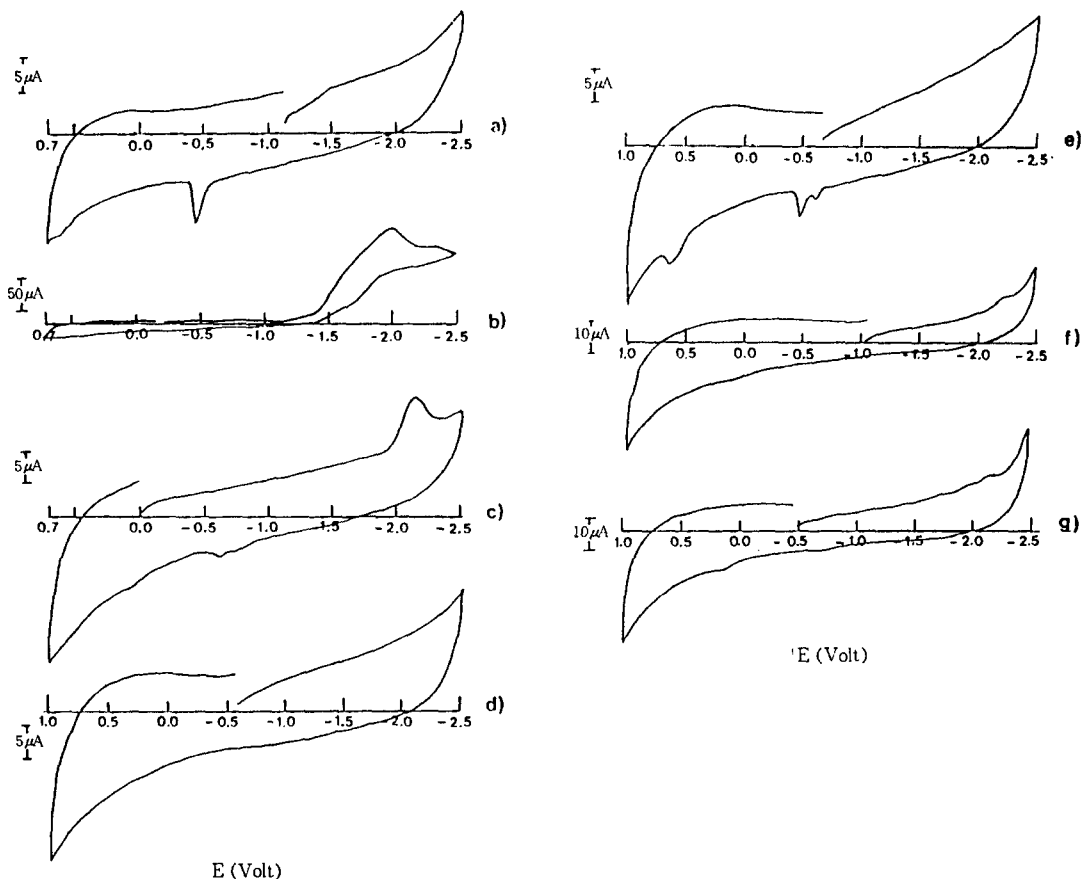
**Current and Reaction Time.** To study the



**Figure 2.** Cyclic voltammogram in an aqueous system: 0.025 M sulfuric acid and comonomer (0.0107 M GA/0.416 M MA).

effects of the variables on the continuous electropolymerization process, weight gain onto the surface of the graphite fibers was measured by changing each parameter, such as current, reaction time, concentration of comonomer, concentration of supporting electrolyte and agitation speed. In Fig. 4, weight gain was measured as a function of the current at various reaction time in 5 vol% of GA/MA (1:3) comonomer solution. At a reaction time of 0.486 min, there was no weight gain at low current up to 10 mA, but after this, the weight gain was relatively constant up to 300 mA current. At low current the accumulated active centers on the surface of the graphite fibers were very low in number because of the short residence time of fibers and the low current. As a result, there was no weight gain. It is supposed that there is a threshold in the numbers of active centers required for weight gain on the surface of the graphite fibers in this process. Between 20 mA and 50 mA current range, weight gain was proportional to the current, because increased current generates more hydrogen radicals, which can react with monomers. Above 50 mA current, initiation reaction was not enhanced even though more hydrogen radicals were generated as the current were raised. When the following two competing reactions are compared, reaction (1) was dominant.



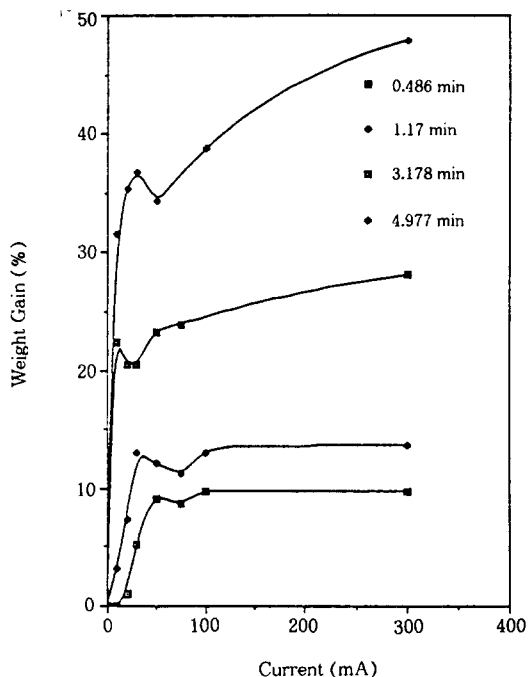


**Figure 3.** Cyclic voltammogram in a nonaqueous system: a) background; b) background with 1 drop of sulfuric acid; c) background with 1 drop of 0.05 N sulfuric acid; d) background with GA (120 mM); e) background with MA (180 mM); f) background with GA (120 mM), sulfuric acid (0.4 mM) and water (870 mM); g) background with MA (190 mM), sulfuric acid (0.4 mM) and water (879 mM).



This is due to the diffusion limit of hydrogen radicals to monomers through the thickness of coated polymers. At the reaction time of 1.17 min, the weight gain increased linearly up to 30 mA current, but beyond that current the weight gain was slightly reduced up to 75 mA current, and above 100 mA current weight gain became relatively constant. Up to 30 mA current, the accumulated active centers were enough to cause the growth of polymers onto the surface of graphite fibers

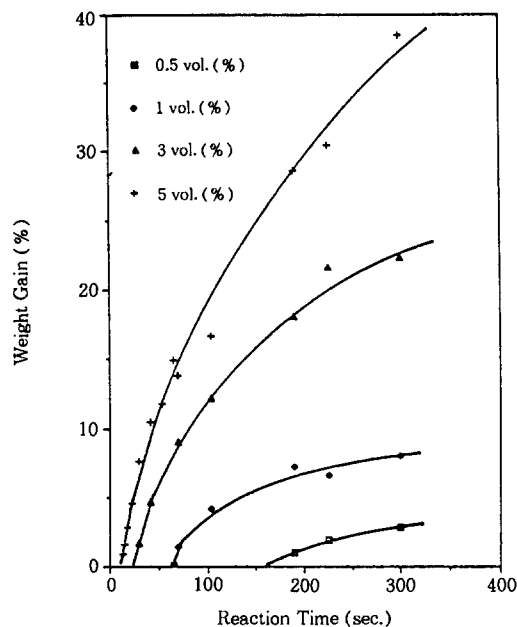
and reaction (2) was the major reaction; as a result, weight gain varied linearly with the current. Between 30 mA current and 75 mA current, recombination reaction (1) was enhanced on the surface of polymer coated graphite fibers. As a result, the evolution of hydrogen gas began to hinder the weight gain on the surface of the graphite fibers. Thereby, the weight gain was slightly reduced. Above 75 mA current, the weight gain leveled off for the same reason as presented in the previous reaction, i. e., 0.486 min of reaction time and above 50 mA of current range. At the reac-



**Figure 4.** Weight gain on the bare graphite fibers in 5 vol% comonomer solution.

tion times of 3.178 min and 4.977 min, the trend of weight gain was almost identical with that of a reaction time of 1.17 min. However the proportional current range was reduced due to the increased amount of current. For longer reaction times, the weight gain increased gradually with the current. It is believed that the increase in current creates more hydrogen radicals, thereby enhancing the diffusion of hydrogen radicals through the coated polymers to the monomers. Consequently, the weight gain will increase.

**Concentration of Comonomer.** Weight gain as a function of the reaction time at 50 mA current was measured at various comonomer concentration. The results are shown in Fig. 5. When concentration was increased, the weight gain increased and the time lag decreased. These are due to the higher concentration of comonomer and the consequent increase in the number of active centers accumulated on the surface of the graphite fi-



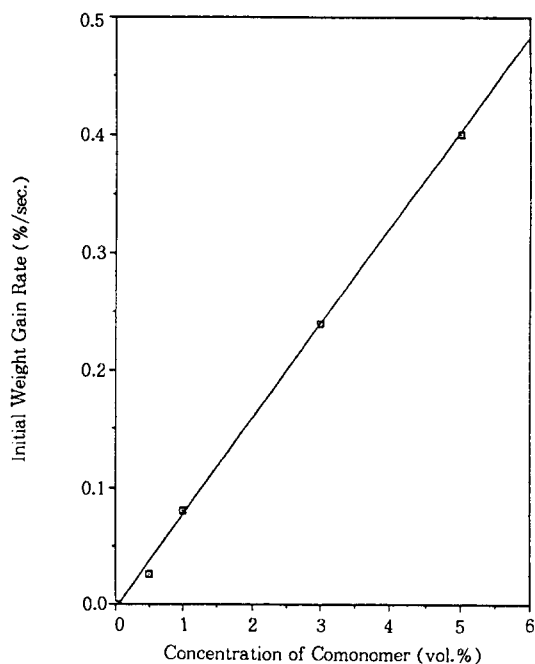
**Figure 5.** Weight gain as a function of the reaction time at various comonomer concentration.

bers so as to enhance the weight gain.

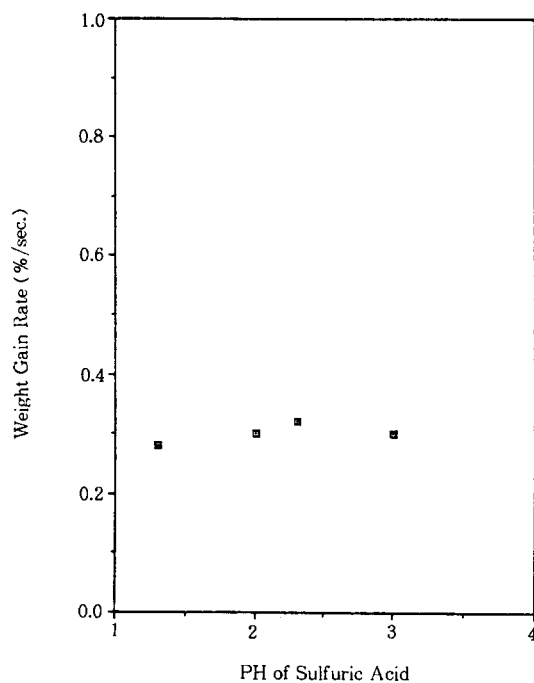
The initial rate of weight gain was measured at each concentration of comonomer. The results are shown in Fig. 6. At 50 mA current, the initial rate of weight gain was linearly proportional to the concentration of comonomer.

#### Concentration of Supporting Electrolyte.

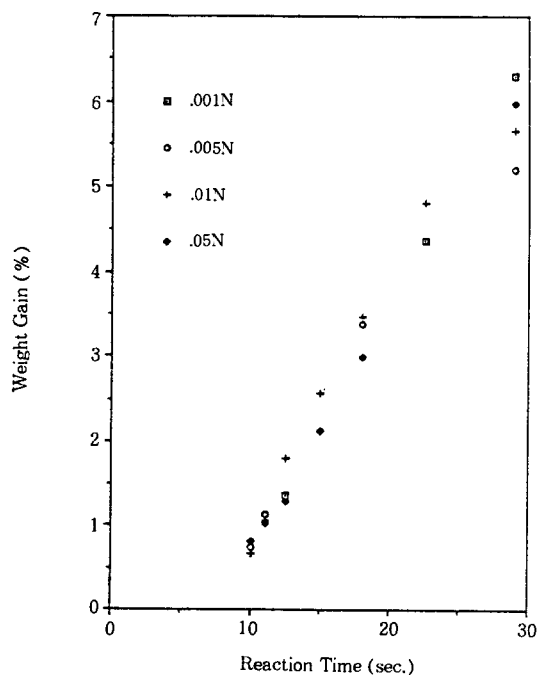
Weight gain in 3 vol% comonomer solution was measured for different concentrations of supporting electrolyte at 50 mA current. The results are shown in Fig. 7 and the rate of weight gain as a function of the concentration of supporting electrolyte is shown in Fig. 8. When current was controlled, i. e., a constant current of 50 mA was applied, the weight gain was almost same, regardless of the concentration of the supporting electrolyte. Fig. 8 shows that the rate of weight gain was independent of the concentration of the supporting electrolyte. In this experiment, there were sufficient hydrogen ions to react with electrons and, as a result, hydrogen radicals were generat-



**Figure 6.** Initial rate of weight gain as a function of the concentration of comonomer at 50 mA current.



**Figure 8.** Weight gain rate as a function of the concentration of supporting electrolyte: in 3 vol% comonomer solution at 50 mA current.



**Figure 7.** Weight gain as a function of reaction time at different concentration of supporting electrolyte.

ed in proportion to the amount of current applied. However, the potential difference in the cell is reduced as the concentration of supporting electrolyte is increased, at a constant current.

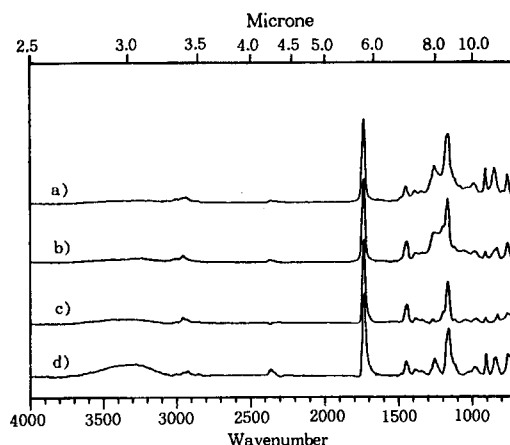
**Agitation Speed.** At 10 and 50 mA current, and 5, 1.17, and 0.486 min reaction time, the weight gain was checked as a function of the agitation speed. The results are shown in Table 1. In experiment A and C, the amount of current applied was too critical to start weight gain. Weight gain occurred as the agitation speed was reduced. It is clear that more current is needed to start weight gain as the agitation speed is increased, when a critical range of current is applied. In experiment B, weight gain occurred regardless of agitation speed. This means that a sufficient number of active centers to start weight gain accumulated on the surface of graphite fibers under such experimental conditions. It is clear from the study

**Table 1. Weight Gain as a Function of Agitation Speed**

experiment	reaction time (min)	current (mA)	agitation speed (cycles/min)			
			22	44	58	74
A	5.000	10	16.5	16.4	0.0	0.0
B	1.170	50	7.5	7.9	8.0	8.4
C	0.486	50	5.1	0.0	0.0	0.0

of agitation speed that a sufficient amount of current must be applied to obtain the weight gain.

**Characterization.** In Fig. 9, the FT-IR spectra of solution polymerized poly(glycidyl acrylate) (PGA) (a), solution polymerized GA/MA copolymer (b), electropolymerized GA/MA copolymer (c), and electropolymerized PGA (d) are shown. There are no apparent differences between spectrum (a) and (d) except at wave numbers of 3300 and 970  $\text{cm}^{-1}$ . In spectrum (d), there is a broad peak near 3300  $\text{cm}^{-1}$ . This indicates the presence of hydroxy functional groups, generated during the electropolymerization by the opening of epoxy rings. The peak ratio of the epoxy functional group to carbonyl functional group is 0.275 in spectrum (a), and 0.248 in spectrum (d). This means that approximately 10% of the epoxy rings were opened. This was also supported by Soxhlet extraction of the coated graphite fibers. Acetonitrile was used as a solvent and the extraction was conducted for 4 days. Forty six percent of the polymer coating was extracted from the coated fibers; the partially extracted fibers were stiffer than the unextracted fibers. This means that crosslinked polymers remained on the surface of the graphite fibers, but that the overall cross-linking density was quite low. In spectrum (c), the mole ratio of GA in the comonomer solution was 0.2, as a result, a small hydroxy peak presents and the peak ratio of epoxy to carbonyl functional group is found to be slightly less than spectrum (b). This follows for spectrum (a) and (d), for the same reason. The differences in these



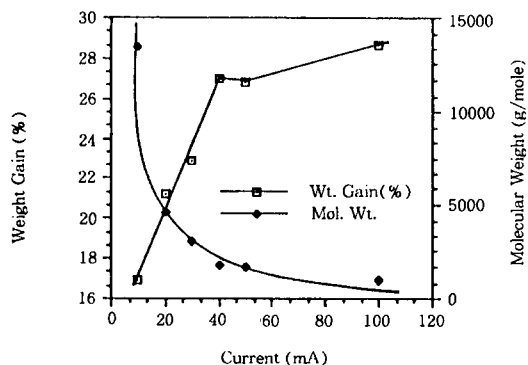
**Figure 9.** FT-IR spectra of polymers: (a) solution polymerized PGA; (b) solution polymerized GA/MA copolymer; (c) electropolymerized GA/MA copolymer; (d) electropolymerized PGA.

spectra are due to the opening of the epoxy rings, which is enhanced in acidic solution at long reaction times.

Electropolymerized PMA was used to determine the effect of current density and concentration of supporting electrolyte on the molecular weight of coated polymer. PMA homopolymer was used because the electropolymerized GA/MA copolymer, somewhat crosslinked, was insoluble in THF.

To study the effect of current density in electropolymerization, weight gain and molecular weight of PMA were measured by changing current density. The results are shown in Fig. 10. The weight gain was linearly proportional to current up to 40 mA and the rate of weight gain was rapid. This means that termination of chain growth is primarily the reaction of the growing centers and hydrogen radicals ( $\text{Mn}\cdot + \text{H}\cdot \rightarrow \text{polymer}$ ); after a certain amount of polymer was coated onto the surface of graphite fibers, the hydrogen radical recombination reaction ( $\text{H}\cdot + \text{H}\cdot \rightarrow \text{H}_2$ ) was enhanced due to reduced diffusion of monomers to the hydrogen radicals through the

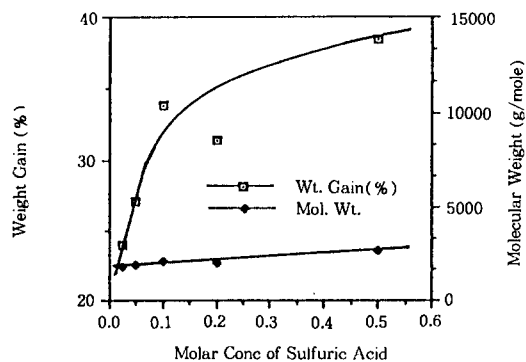




**Figure 10.** The effect of current on the MW and weight gain of PMA in 5 vol% MA solution.

coated polymer. The molecular weight was found to be inversely proportional to the current density. This means that the mechanism of chain growth is that of radical polymerization. In these data, the molecular weights are very low as approximately 1000–13000 g/mole. This is due to the high current density of the working electrode; in the continuous process, only a single strand of graphite fibers was used as cathode and 10–100 mA of current was applied for electropolymerization.

The effects of the supporting electrolyte upon weight gain and molecular weight are shown in Fig. 11. The molecular weight was almost constant, regardless of the concentration of the supporting electrolyte. This is due to the controlled current (50 mA) which was applied during the electropolymerization. But in this instance the weight gain was increased by increasing the concentration of supporting electrolyte. This can possibly be attributed by the following causes: When the reaction time was long, some polymers were already coated onto the surface of graphite fibers. If the concentration of hydrogen ions was increased, the production of hydrogen radical on the fiber surface through the coated polymers ( $H^+ + e \rightarrow H\cdot$ ) will increase. The increased hydrogen radical will in turn increase the initiation reaction ( $H\cdot + M \rightarrow HM\cdot$ ) and, as a result, the



**Figure 11.** The effect of the concentration of supporting electrolyte on the  $M_w$  and weight gain of PMA in 5 vol% MA solution.

weight gain will increase according to the concentration of the supporting electrolyte.

## CONCLUSIONS

Copolymer of GA and MA was coated on the surface of graphite fibers using electropolymerization. CV determined that only the reduction of hydrogen ions occurred. As a result, production of hydrogen radical ( $H^+ + e \rightarrow H\cdot$ ) is the dominant reaction on the surface of graphite fiber. The initial rate of weight gain was proportional to current and concentration of the comonomer, but concentration of the supporting electrolyte had no effect when current was controlled. Above a certain amount of current, the weight gain had no relation with the current. Weight gain was not linearly proportional to reaction time; this is due to the two competing reactions and resistance to diffusion through the polymer coatings. The molecular weight of coated polymer was inversely proportional to the applied current.

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