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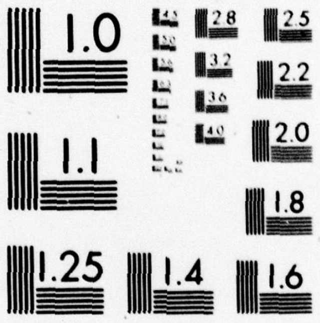
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An electrodepostion technique has been developed for interface tailoring in graphite fiber composites. Graphite fibers running continuously as the anode through an electrolytic cell were coated with a variety of copolymers carrying carboxyl functional groups. Fortafil CG-3 fiber, free of commercial surface treatments, was used in these experiments. The copolymers employed were a series of styrene-co-maleic anhydride, α-olefin-co-maleic anhydride, methyl

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ELECTRODEPOSITION OF POLYMERS ON GRAPHITE FIBERS: EFFECTS ON COMPOSITE PROPERTIES

by

R.V. SUBRAMANIAN, V. SUNDARAM
and A.K. PATEL*

ABSTRACT

An electrodeposition technique has been developed for interface tailoring in graphite fiber composites. Graphite fibers running continuously as the anode through an electrolytic cell were coated with a variety of copolymers carrying carboxyl functional groups. Fortafil CG-3 fiber, free of commercial surface treatments, was used in these experiments. The copolymers employed were a series of styrene-co-maleic anhydride, α-olefin-co-maleic anhydride, methyl vinyl ether-co-maleic anhydride, and ethylene-co-acrylic acid polymers. Unidirectional composite specimens were prepared by embedding the coated fibers in an epoxy matrix, and the effect of the interphase polymer was studied through variations in their impact, interlaminar shear, and flexural strengths in comparison to those of composites fabricated from commercially treated and untreated fibers. It is found that the introduction of the polymer interphase results in significant improvements in composite properties and that the extent of improvement is controlled by the nature of the polymer interphase. The molecular weight, chemical composition, and crosslinking of the interphase polymer are some of the molecular parameters modifying the effects observed. It is concluded that the electrodeposition of polymers on graphite fibers provides an effective method of optimizing composite strength and toughness through the introduction of an interlayer of variable properties.

INTRODUCTION

The remarkable strength enhancement and resistance to fracture that is achieved by the incorporation of strong fibers in low-strength, low-modulus resin is determined to a great extent by the existence of several polymer-fiber interfaces. Compatibility between the fiber and the polymer matrix is one of the most important considerations in developing useful composites. Adequate bonding between matrix and fiber is essential to permit the fiber to be loaded to its maximum strength. However, the preferential failure of the interface of a composite may increase fracture toughness by deflecting cracks perpendicular to the direction of the fiber alignment. Thus, there exists a dual requirement in the properties required of the interface.

Applications involving graphite fibers have made significant advancement in recent years in view of the fibers being readily available at a realistic price. A major initial drawback in their application for the reinforcement of polymers was the low interlaminar shear strengths that resulted. Work in the area of interfacial relationships in reinforced polymers has lead to the development of various surface modification techniques that result in improved compatibility between the fiber and the polymer and lead to improved interlaminar shear strengths (1-3). The disadvantage of these surface modification techniques is that the strength improvements are attained at the expense of the impact strength.

Research on asbestos and glass fiber composites has shown that the introduction of a polymer interlayer between the fiber and the polymer matrix leads to significant alterations in the mechanical properties of composites (4-8). A comprehensive program of research has been initiated in our laboratories to investigate the applicability of electrochemical processes for the formation of such a polymer layer on carbon fibers through electropolymerization and electrodeposition, since carbon is an electrically conducting material. Electropolymerization involves the polymerization of monomers in an electrolytic cell. Electrodeposition utilizes the migration of preformed polymers carrying ionized groups to the oppositely charged electrode under an applied voltage. The major advantage of utilizing these electrodic processes is that a uniform layer of controlled thickness and variable polymer structure and properties can be expected to be formed.

The results to date of our investigation along these lines have amply confirmed the expectations based on the concepts mentioned above (9, 10). The studies of electroinitiated polymerization on graphite fibers and the properties of composites prepared from the coated fibers have been reported elsewhere (11). In the present investigation, the effect on composites properties of introducing on carbon fibers an interlayer of polymer by electrodeposition has been studied.

In discussing interface tailoring, it is useful to recognize that the fiber and matrix are not bridged in the composite by a fine interface but by an interphase polymer. The properties of the interphase polymer can be significantly different from the bulk polymer properties. When a polymer coating is formed on the fiber by electrodeposition, the properties of the interphase are further modified by the polymer coating.

The primary concern of this investigation was the selection of copolymers which, when applied at the interface between the fiber and the matrix, will perform the dual function of retaining the toughness of the composite and at the same time result in the improvement in the interlaminar shear strength. The first objective was, therefore, the development of an electrodeposition technique for the formation of polymer coatings on carbon fibers. The second objective was the study of the effect of the interfacial polymer on the impact, and interlaminar shear strength of composites fabricated with the coated fibers, in comparison to those of composites fabricated using the commercially treated and untreated fibers.

In principle, both anodic and cathodic deposition of polymers should be possible. In anodic deposition, the electrode to be coated is suspended as the anode of an electrical circuit in a bath containing the polymer. In the current study, electrodeposition has been conducted using graphite fiber as the anode.

The polymer used for anodic deposition has free acid or acid anhydride groups attached to the polymer chain. At this stage, the polymer is usually hydrophobic. The hydrophobic-hydrophilic character of a resin can be varied to some extent by the chemical groups incorporated into the backbone of the polymer chain. The acid groups used for these materials are generally organic carboxyl groups. When the acid groups are neutralized with a base, a salt of the polymer is formed which can ionize in water to form positively and negatively charged ions. This polymer salt can be water soluble or at least water dispersible. When dispersed in water, the particle sizes are on the borderline between solution and colloids.

An electrodeposition polymer can be visualized as a suspension of polymer particles with the ionized carboxyl groups sticking out of the surface so that the particle carries a negative charge. The repulsion between like charges keeps the polymer dispersed in water. These charges also enable the particles to migrate towards the positively charged anode during electrodeposition. The efficiency of polymer deposition depends on the ratio of the molecular weight of the polymer to the number of free acid groups.

A wide variety of polymers with anionic, carboxyl functional

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groups were selected for electrodeposition. The molecular parameters that were varied in these polymers were (i) the molecular weight, (ii) the chemical composition, (iii) length of side chains, and (iv) crosslinking. The reactivity of the carboxyl functions with epoxy groups prompted the choice of epoxy resin as the matrix polymer. It was expected that the carboxyl groups of the electrodeposited polymer will react with the epoxy matrix to form a strong interfacial bond. The various factors pertaining to the effect of interphase polymers on composite mechanical properties have been studied by the introduction of an appropriate range of copolymers at the interface.

EXPERIMENTAL METHODS.

Materials.

Fortafil CG-3 graphite fiber tows (Great Lakes Carbon Corporation, Modulus 30 million psi) were used in all experiments. The tow used for electrodeposition was free of any surface treatment. The composite specimens for comparison were obtained from the untreated, uncoated, and also from the commercially treated CG-3 fibers. The polymers used for electrodeposition were a series of copolymers of maleic anhydride. Styrene-maleic anhydride copolymers, SMA-1000, SMA-2000, SMA-3000 of average molecular weight about 1600 were obtained from ARCO. The ratio of styrene to maleic anhydride in these copolymers was 1:1, 2:1 and 3:1 respectively. Other copolymers used were PA-6, PA-10 and PA-18 (Gulf) which are 1:1 low molecular weight copolymers of maleic anhydride with hexene, decene and octadecene respectively, and *Gantrez AN 119, AN 139 and AN 169 (GAF) which are similar 1:1* copolymers of maleic anhydride and methyl vinyl ether, with increasing molecular weights, 500,000, 750,000 and 1,250,000.

Electrodeposition.

Two methods were developed and evaluated for the electrodeposition of polymers on fibers: (a) batch process and (b) continuous process. In the batch process, the fibers are mounted on rectangular polymer frames which are then placed in a cell having two stainless steel plates as cathodes. The fibers form the anode of the circuit. The main disadvantage of the batch process was the difficulty encountered in alignment of fibers when fabricating the prepregs at a later stage. In the equipment built for the continuous process, the fiber tow from the spool was passed over guide rolls and through the electrolytic cell before being wound on a receiving drum covered by a mylar or teflon sleeve.

Figure 1 shows a simple setup that was initially designed for the continuous coating and alignment of carbon fibers. The electrolytic cell is shown in Figure 2. The important design feature of this setup was that it was feasible to align the coated fiber as it came out of the deposition bath. As is seen in Figure 1, the drum on which the fibers are being wound pulls the fibers through the bath. Thus, the residence time in the bath can be adjusted by varying the speed of the drum. The electrolytic cell consisted of a tank with two metallic plates on the sides. These plates were kept at a fixed distance from one another by two teflon rollers that were attached to the base of the electrodes. These rollers not only held the electrodes apart, but also acted as guides for the fibers running through the bath. The fiber on entry into the cell came into contact with a metallic sheet which transferred the charge onto the fibers. In the cell, the fibers ran through as the anode and the metal plates formed the cathode.

The applied voltage was controlled by a DC power supply. Electrodepositions were carried out from a 2.5 percent solution of the polymer at 10 volts, for a period of 1 minute. After polymer deposition, the fibers were wound onto the drum which was covered by a mylar sleeve sprayed with release agent (Freekote 33). The fibers were then washed for 5 minutes in the solvent medium to remove loosely adhering excess polymer and then dried in an oven at 120°C for one hour. The residual weight of the compact deposits of polymer on the fiber was in the range of 3-5 percent. The coated fibers were then used in the preparation of prepreg sheets.

Preparation of Composite Specimens

The diglycidyl ether of bisphenol-A (Araldite 6004, Ciba or Shell Epon 828) was used as the matrix polymer. Curing agent metaphenylenediamine (MPDA) was melted and dissolved in the epoxy resin at about 80°C and the solution was applied to the graphite fibers, which had been electrocoated, untreated or commercially treated as the case may be. The impregnated fiber tapes on mylar backing were precured in an oven at 80°C till they *became nontacky and semi-rigid. Strips of the appropriate sizes were* then cut from the prepreg sheets and placed in molds for compression molding into test specimens or bars from which interlaminar shear and impact test specimens were subsequently cut. The molding pressure was 165 psi at 300°F.

Mechanical testing of Composites

The volume fraction of fibers and void content of test specimens were determined before testing the specimens.

The fiber content was determined by digestion of weighed pieces of the composite, with boiling concentrated nitric acid for ½ hour to remove the matrix resin (ASTM D3173). In the determination of void content, specimens ½" x ¼" were weighed in air and reweighed when totally immersed in water. The specific gravity of the specimen (AD) was calculated from the apparent weight loss between the two weighings. The void content was then calculated from (TD-AD) */AD where TD is the theoretical density calculated from the fiber* content. The void contents were mostly less than 1% but ranged up to 1.5%.

The impact strength was determined on a Tinius Olsen Plastic Impact Tester in accordance with Method A,Izod of ASTM D256-73. Specimens 2.5" x 0.25" x 0.5" with 45° notches, were cut from rectangular bars of fabricated composite. The energy required for fracturing the specimen was read directly on the instrument. At least four determinations were made for each composite and arithmetic averages are reported.

The interlaminar shear tests were conducted according to ASTM D2344-76 on an Instron Model TTCML tensile tester utilizing a center loading flexure fixture, Instron Model 1000, at a crosshead speed of 0.1 cm/min. Flat beam test specimens 0.25" width were used. The thickness of the specimens was kept between 0.2" to 0.25"; the span-to-depth ratio was 4:1 and the length-to-depth 6:1. *The fiber orientation was parallel to the length of the specimen.* Eight specimens were tested for each sample.

Flexure tests were conducted according to ASTM D790, in the same Instron machine at a span-to-depth ratio of 16:1 and leng-to-depth ratio of 20:1 using specimens 0.08" thick and 0.5" wide. The crosshead speed was 0.1 cm/min. The strength values reported are averages of at least 5 determinations.

Experimental approach.

The general procedure consisted of electrodeposition of the selected copolymers on graphite fibers from aqueous ammonium hydroxide, the carboxyls of the copolymers being neutralized to 50 percent by the ammonium hydroxide. The coated fibers were washed *in the solvent medium used for electrodeposition,* dried, and then embedded in an epoxy matrix. The fabricated composites were tested for flexural, impact and interlaminar shear strengths.

RESULTS AND DISCUSSION

Electrodeposition.

Preliminary experiments conducted to standardize the operating conditions of the electrolytic cell showed that measurable deposits were formed on graphite fibers from solutions of 2.5 to 10.0 percent solids content at 10-50 volts in 1-10 minutes. The weight of the deposit tends to be high at high voltages and bath concentrations; as much as 15 percent based on the weight of the fiber could be electrodeposited easily. However, washing the fibers resulted in a dramatic reduction of the weight of the deposit. These values, however, tended to reach an approximately constant level after 5 minutes of washing, and were unchanged even after 30 minutes of washing. The residual layer of polymer thus seems to be more tightly held and is more difficult to dissolve away than the exterior layers of electrodeposited polymer. Therefore, using the time of washing as an additional parameter, the operating conditions were selected as: 10 volts, 2.5 percent solids content in bath, 1 minute deposition time and a washing period of 5 minutes in the initial solvent medium.

SEM pictures of electrocoated graphite fibers are shown in Figures 3 and 4. The unwashed fiber in Figure 3a carries lumps of polymer of uneven thickness in "sheesh-kebab" fashion; the cross-section through a thinly coated section of the fiber is seen in Figure 3b, and through layers of a thinly coated section in Figure 3c. On the other hand, the uniformity of coating after washing is seen in the picture shown in Figure 4a. This coating of an 1:1 hexene-maleic anhydride copolymer, PA 6, is much smoother than that of a higher molecular weight copolymer, AN 169 (methyl vinyl ether-co-maleic anhydride) shown in Figure 4b.

From a perusal of the many studies that have been made on the mechanism of carboxylate stabilized systems (12, 13), it is seen that the following reactions can contribute to the formation of a polymer film on the graphite fiber anode:

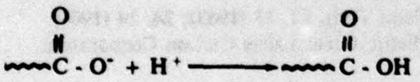
(1) Electrolysis of water

a) $H_2O \rightarrow OH^{\cdot} + H^{+} + e^{-}$

b) $2\ OH\cdot \rightarrow H_2O + O.$

c) $2\ O\cdot \rightarrow O_2$

(2) Reaction of the Carboxylate ion with H +



$$\sim\sim\overset{\overset{O}{\|}}{C}-O^{-} + H^{+} \longrightarrow \sim\sim\overset{\overset{O}{\|}}{C}-OH$$

Thus the protonation of the soluble polycarboxylates results in the precipitation at the anode of the insoluble acid. Furthermore, concentration coagulation could also occur at the electrode (14). However, the initially precipitated and deposited polymer layer would be "compacted" on the fiber surface and will be present as the insoluble acid film while the exterior layers including those resulting from concentration coagulation would be more easily solubilized by the basic solvent medium.

Anodic oxidation of the carboxylate by a Kolbe reaction is another possible reaction in anodic deposition (13):

$$\sim\sim COO^{-} \xrightarrow{-e^{-}} \sim\sim COO\cdot$$

$$\sim\sim COO\cdot \longrightarrow \sim\sim\cdot + CO_2$$

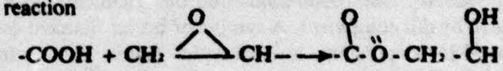
The polymer radicals produced thus can recombine to form crosslinked polymer or interact with the graphite anode to form a graft polymer. Both types of reaction would lead to the formation of an insoluble polymer layer strongly bonded to the fiber surface. Further detailed investigations of the behavior of the electrodeposited polymer in long term extraction and determination of changes in molecular weight are required to elucidate the nature of the various reactions occurring at the electrode surface.

Composite Properties.

The results of shear and impact tests are illustrated in Figure 5 and 6, respectively. It is evident that the electrodeposition of different copolymers on graphite fibers causes significant improvements in shear strengths of the composites. The data for untreated and commercially treated fibers are also plotted for comparison. An examination of shear test specimens after failure revealed that the failure was largely in shear. An example is shown in Figure 7.

The observed improvement in interlaminar shear strength can be taken as a measure of the increased adhesion between the carbon fiber and the epoxy matrix resin. At least two factors can be recognized in the electrocoating process that could have contributed to better adhesion. One is the efficiency of the deposition of charged polymers on the fiber surface to produce a uniform coating that adheres well. The scanning electron micrographs (Fig. 4) do attest to the uniformity of the polymer coating obtained. As an incipient polymer layer is formed, the increased electrical resistance of the coating directs further coating to uncoated areas which are more conducting. A uniform coating free of pin holes is thus formed on the fibers. The observation of better adhesion also indicates that the washing process did not materially deteriorate the uniformity or completeness of the polymer coating.

The polymer coating on the surface of carbon fibers makes the fibers compatible with the organic polymer matrix. In this case, where an epoxy resin is used, the possibility of chemical interaction between the carboxyl functional groups on the copolymer coating and the epoxy functional group of matrix resin must be taken into account. At the temperatures used in preparing the composite specimens, the esterification of -COOH by the epoxy group is a facile reaction



$$-COOH + CH_2\overset{O}{\triangle}CH- \longrightarrow -\overset{\overset{O}{|}}{C}-\ddot{O}-CH_2-\overset{\overset{OH}{|}}{C}H-$$

The carbon fiber epoxy matrix interface is thus bridged by a well adhering copolymer layer which is also chemically bonded to the epoxy matrix. The consequences of electrodeposition are improved adhesion and increased interlaminar shear strength.

The basic mechanism described here suggests the possibility of using polymers with appropriate functional groups which can interact with the matrix polymer after electrodeposition. Amino functional groups, for example, can be reacted with epoxy polymers. Electrodeposition of cationic amino polymers on carbon fiber cathodes can produce such coatings. Or, anodic electrodeposition of a butadiene-maleic anhydride copolymer can leave the unsaturation on the backbone of the copolymer to react with a polyester matrix. Such extensions of the electrocoating process are part of our continuing investigations.

Results for composite specimens containing 50 percent volume fraction of fiber were read from plots such as those illustrated in Figures 5 and 6, and are summarized in Table I for a number of systems. The most striking feature of the results is the general improvement in shear, impact and flexure strengths caused by the incorporation of an electrodeposited polymer interphase. Thus, increase in shear strengths is not accompanied by a corresponding loss in impact strength as is generally observed in various methods of surface treatment. Since the various steps in this new technique have not been optimized, it is the relative improvements in strength values determined in this study which are of significance. The results are similar to those noted in other studies of the effect of the interfacial layer on toughness and impact strength of glass and asbestos reinforced composites (4,6,8). In these studies also, encapsulating the filler or fiber reinforcement by a band of resin capable of high energy absorption was indicated to be highly desirable.

For polymers of the same chemical composition, a number of molecular features of the interphase polymer seem to have varying effects on composite properties. Undoubtedly these variations are related in turn to the physical and mechanical properties of the polymer interlayer. In the SMA copolymer series, the ratio of sytrene to maleic anhydride is varied from 1:1 to 2:1 to 3:1 in SMA 1000, SMA 2000 and SMA 3000 respectively. The comonomers in PA 6 and PA 18 are hexene-1 and octadecene-1 respectively; thus, while the backbone has the same structural unit in both these a-olefin copolymers of maleic anhydride, the side chains are very much longer in PA 18 than in PA 6. In the case of the methyl vinyl ether-maleic anhydride copolymers, the molecular weights increase progressively from 500,000 in AN 119 to 750,000 in AN 139 to

1,250,000 in AN 169. A wide range of controlling parameters is thus available in modifying the electrodeposited polymer film properties. It is conceivable that an independent evaluation of the properties of the polymer film on graphite fiber can be conducted which could then be correlated with corresponding changes observed in composite properties. Such a study of the coated fibers by torsional braid analysis has been initiated.

A comparison of the shear strength for the composite prepared from 60 percent commercial CG-3 fiber (~60 MPa, Fig. 5) with the value 75 MPa reported by the manufacturers (15) points to the need for optimization in experimental techniques used in this study. The observed flexural strength 1250 MPa, tensile strength 950 MPa at $V_f = 60\%$ are however comparable to the reported values of 1200 MPa and 1050 MPa respectively (15). In continuing efforts along these lines, the electrodeposition equipment has been modified as shown in Figure 8. Guide rolls and a rinse tank are introduced in this set-up. Power is supplied to the guide roll situated just before the drum by a 0.5 HP variable speed motor. All the other guide rolls and the speed of the drum are synchronized through a set of pulleys and rubber belts. The fiber tow is aligned as it emerges from the wash tank. It has been found that continuous boron filaments can be electrocoated by this equipment. A sample of boron filament coated thus with SMA copolymer is shown in Figure 9. A similar investigation of boron composites looks promising and is in progress.

CONCLUSIONS.

The introduction of a polymer interphase by electrodeposition of ionizable polymers on graphite fibers results in significant improvements in composite strength and toughness when the coated fibers are incorporated in an epoxy matrix. The molecular features of the interphase polymer offer a range of controlling parameters that influence the extent of improvement achieved. This novel technique can be extended to boron fibers.

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Table 1. Effect of Electrodeposited Polymer on Graphite Fiber Composite Properties (V_f:50%)[a]

Electrodeposited Polymer[b]	Interlaminar Shear Strength, MPa	Impact Strength, ~~MPa~~ kJ/m²	Flexural Strength, MPa
SMA 1000	68	57	110
SMA 2000	59	72	110
SMA 3000	62	56	100
PA 6	61	42[e]	100
PA 18	52	44[e]	91
AN 119	48	86	90
AN 139	59	130	95
AN 169	54	140	86
None (CG-3)[c]	34	63	78
None (CG-3)[d]	52	43	96

a) Fortafil fiber, (25 x 10^6 psi modulus); epoxy (DGEBA-MPDA) matrix

b) Copolymers of maleic anhydride with styrene (SMA), hexene (PA 6), octadecene (PA 18), and methylvinyl ether (AN); fully described in text.

c) Untreated, Fortafil CG-3 fiber

d) Surface treated, Fortafil CG-3 fiber.

e) Fibers electrocoated in modified apparatus.

Figure 1. Electrodeposition equipment

Figure 2. Electrolytic cell

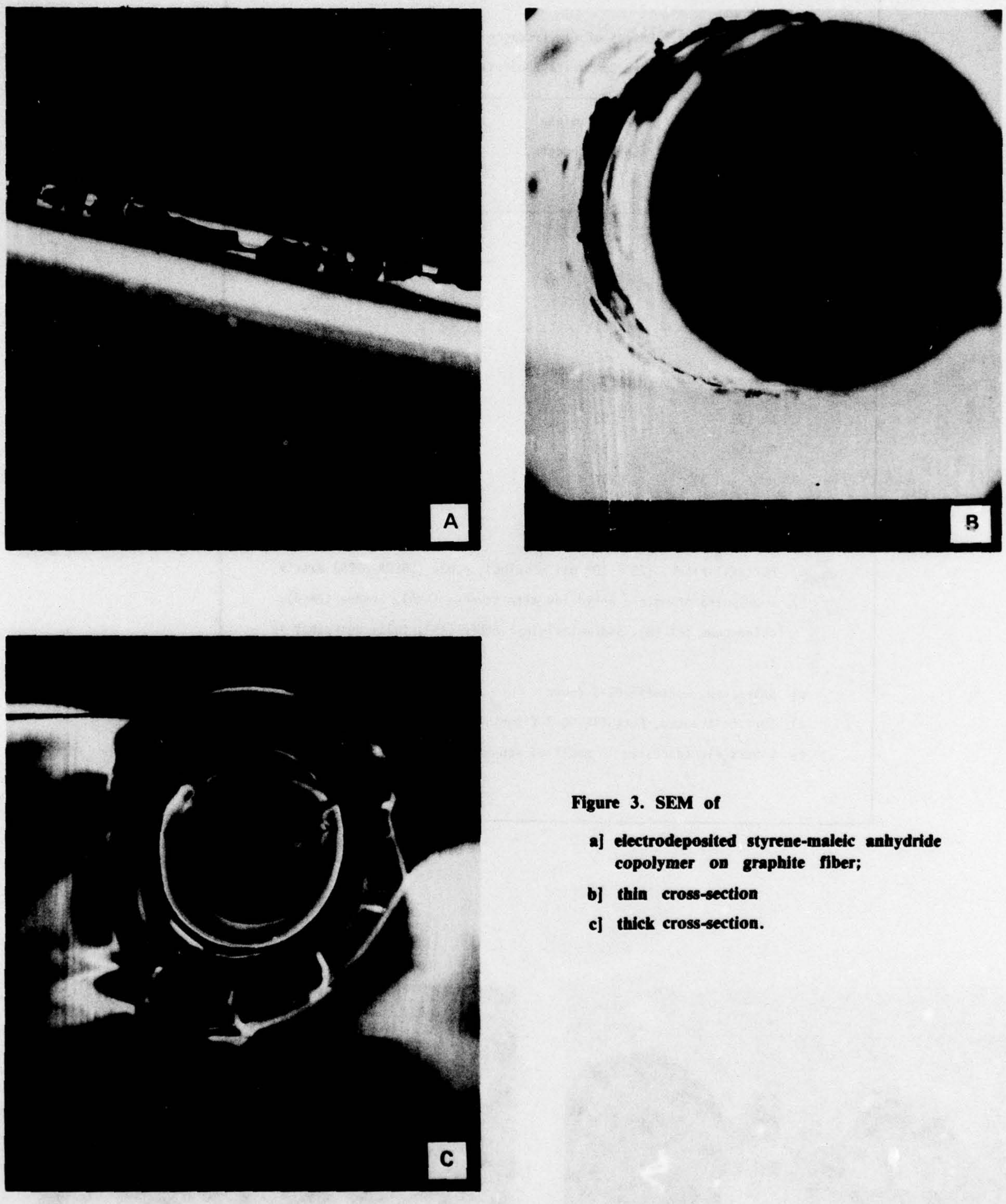

Figure 3. SEM of

a] electrodeposited styrene-maleic anhydride copolymer on graphite fiber;

b] thin cross-section

c] thick cross-section.

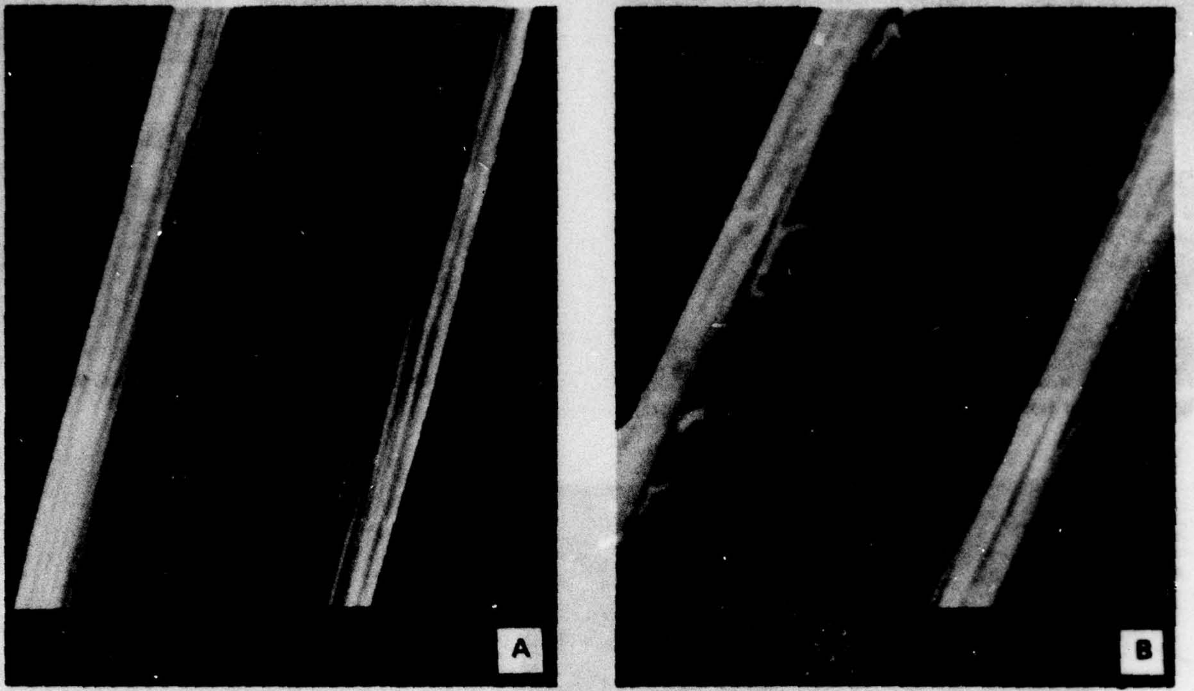

Figure 4. SEM of maleic anhydride copolymers electrodeposited on graphite fiber: a] PA 6 b] AN 169.

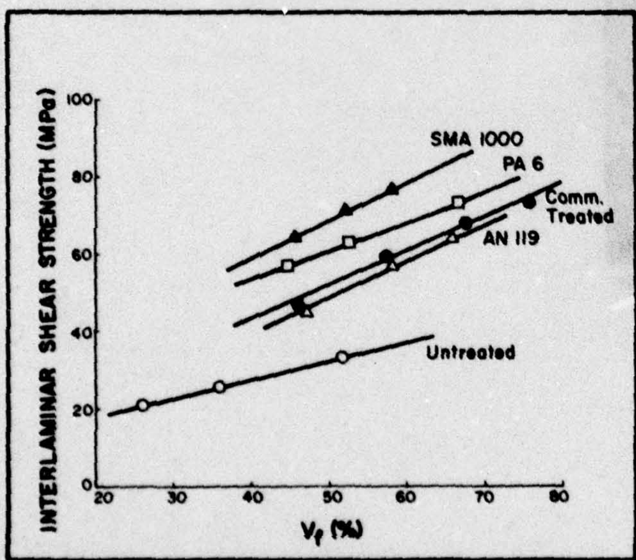

Figure 5. Interlaminar shear strengths of composites prepared from CG-3 graphite fibers electrocoated by the indicated copolymers.

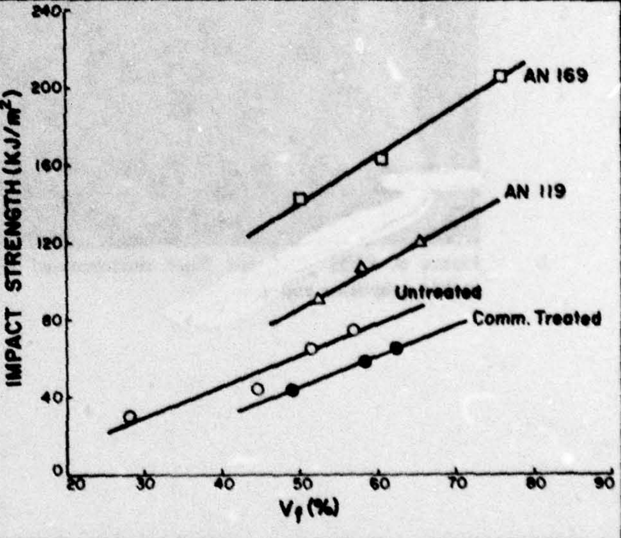

Figure 6. Impact strengths of composites prepared from CG-3 graphite fibers electrocoated by the indicated copolymers.

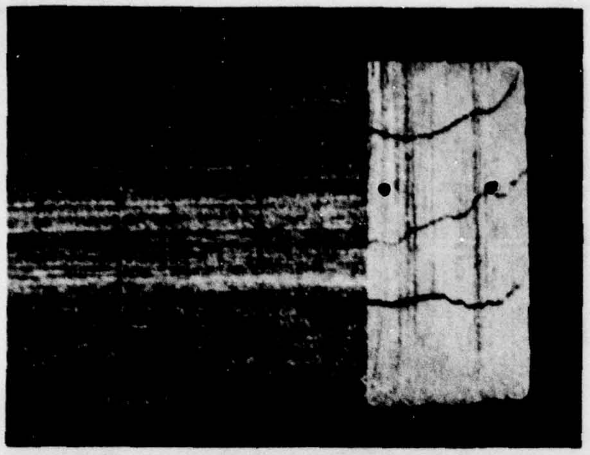

Figure 7. Shear test specimen showing random shear failure.

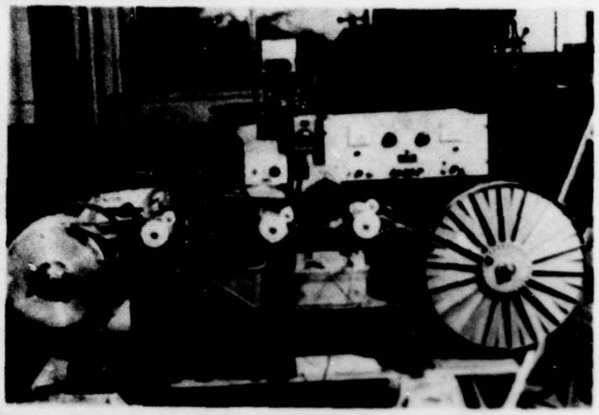

Figure 8. Modified electrodeposition equipment.

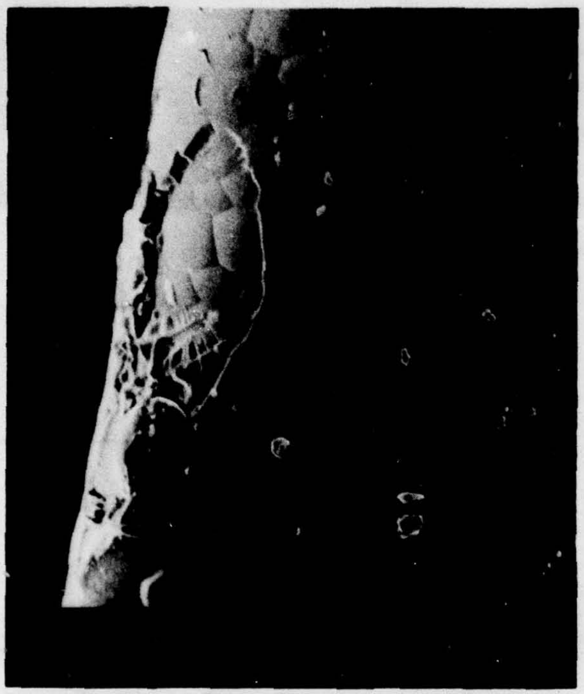

Figure 9. SEM of Boron fiber electrocoated by styrene-meleic anhydride copolymer.