78 Chem. Mater. 1993, 5, 78–83

Mechanical Properties of Electropolymerized Matrix Composites

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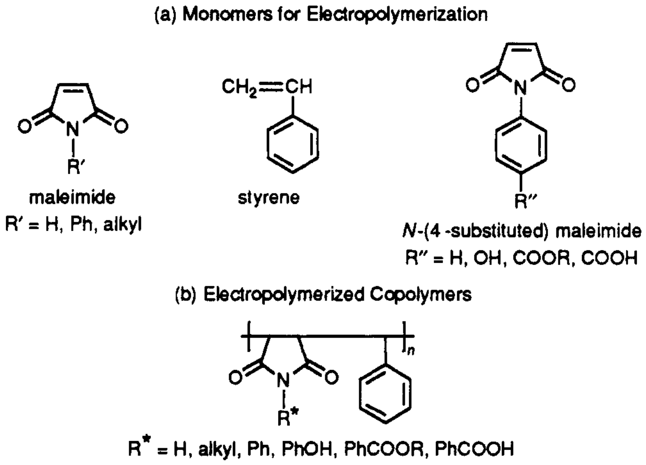
Received July 7, 1992. Revised Manuscript Received November 12, 1992

Electrochemically initiated polymerization has been used to apply thick matrix coatings of poly(styrene-*co*-*N*-((3-carboxyphenyl)maleimide)) onto unsized AS-4 graphite fiber preforms. Graphite fiber reinforcements preimpregnated with electropolymerized matrix coatings of the copolymer (about 3.0 μm thick) were consolidated by compression molding into continuous unidirectional composite tapes. The mechanical properties of the composites increased with increased volume fraction of the fibers as was expected but decreased with increased numbers of fiber bundle layers. The flexural strength, impact strength, and shear strength of the electropolymerized matrix composites ($v_f \sim 60\%$) remained relatively unchanged for composite matrices synthesized from varying feed composition of the comonomers.

Introduction

The mechanical properties of high-performance composites depend to some extent on the volume fraction of the fibers and the matrix as well as the nature of the interface between the reinforcement and the matrix.[1–4] The performance of a thermosetting matrix in composites is affected by the long cure times needed to form a completely reacted resin. An incompletely cured matrix continues to undergo further reaction after consolidation, resulting in poorer physical and mechanical properties of the composites.[5] Traditional thermosetting matrices have poor hot/wet properties and are susceptible to corrosion and brittle fracture. There is therefore a need for tough, high temperature and environmentally stable matrices. Thermoplastic matrices are generally very tough and are said to have fracture toughness of at least 1 order of magnitude higher than those of thermosets.[6,7] They also retain much of their mechanical properties in severe hot/wet conditions.[8–12] They therefore meet the requirements as resins for high-performance composites. Processing of thermoplastic matrix composites, however, is complicated by the high melt viscosity of the thermoplastic melts and the difficulty in dissolving thermoplastic resins in common low-boiling-point solvents.[13–14] Continuous fiber–thermoplastic matrix prepregs are therefore not easily produced by the traditional hot-melt impregnation or solution impregnation techniques. Currently powder impregnation and other novel processes are being investigated as alternative resin infiltration techniques.[13,15,16]

Scheme I



Electrochemical technique for applying in situ matrix coatings onto graphite fibers promises to be a valuable technique for preimpregnating graphite fiber preforms. In this paper, we report the mechanical properties of poly(*N*-(3-carboxyphenyl)maleimide-*co*-styrene)(*N*-(3-

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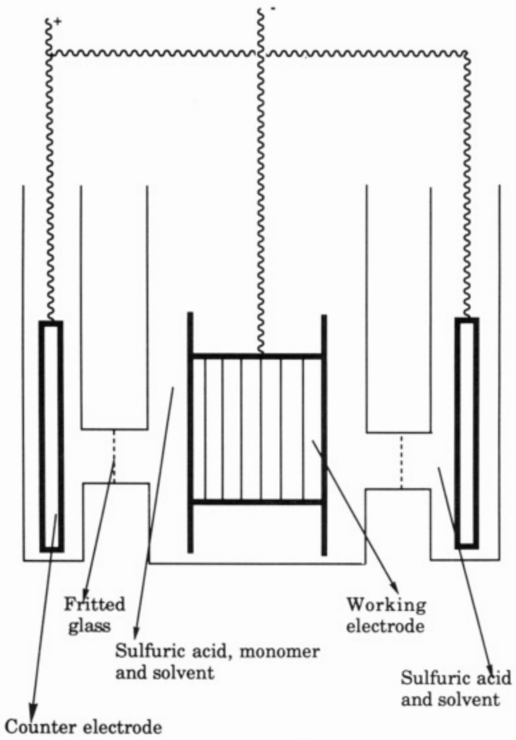

Figure 1. Electropolymerization cell.

CMI)) continuous graphite fiber composites produced by in situ electrochemical polymerization of the matrix directly onto graphite fibers and consolidation by compression molding.

Experimental Section

Electropolymerization. Electropolymerization was performed in a three-compartment electrochemical cell.[15,16] About 0.2 M solution of the comonomers (styrene and maleimide (Scheme I)) was prepared in a 1:1 DMAc:dilute sulfuric acid ~ 0.0125 M solution and placed in the middle chamber of the cell. The middle compartment also contain the graphite fiber working electrode. It was separated from each of the two side counter electrode chambers by means of a 0.04-μm pore size polypropylene membrane. Each counter electrode chamber contain dilute sulfuric acid (0.0125 M):DMAc (4:1) solution and stainless steel counter electrode. The counter electrodes and the graphite fiber working electrode was connected to the positive and negative terminals, respectively, of the potentiostat.[15,16] Electropolymerization was started when the cell's on/off button was switched on. A current density of about 25 mA/g of fiber was used to initiate electropolymerization. Termination of electropolymerization occurred when the cell's on/off switch was switched off and the coated fiber withdrawn from the cell. The weight gain of the fibers, represented by the difference between the weight of the high-temperature (250 °C) dried coated fibers and the weight of the uncoated fibers, was determined as a function of the electropolymerization time, other reaction parameters remaining constant.

Composite Fabrication. The graphite fiber preform was constructed by filament winding one to five layers of AS-4 graphite fiber bundles, each containing about 3000 individual filaments, onto an H-shaped aluminum frame. The preform was then placed in the central chamber of the electropolymerization cell containing 0.2 M comonomer solution, 0.0125 M sulfuric acid:DMAc (1:1) solution. The two side counter electrode chambers contain the stainless steel electrodes, and sulfuric acid (0.0125 M):DMAc solution (1:1) (Figure 1). The setup was connected to the source of direct current by means of alligator clips, and electropolymerization was commenced by passage of electric current. The preforms were electrocoated with thick copolymer coatings of varying volume fractions. Prepregs of the same volume fractions were produced consistently by using the same monomer–sulfuric acid concentration, current density, and electropolymerization time. High resin volume fraction prepregs were obtained at high comonomer concentrations, current density, and short electropolymerization times. Production of resin rich prepregs from a system containing low comonomer concentration and reacting at low current density, was accomplished at a relatively long electropolymerization time.

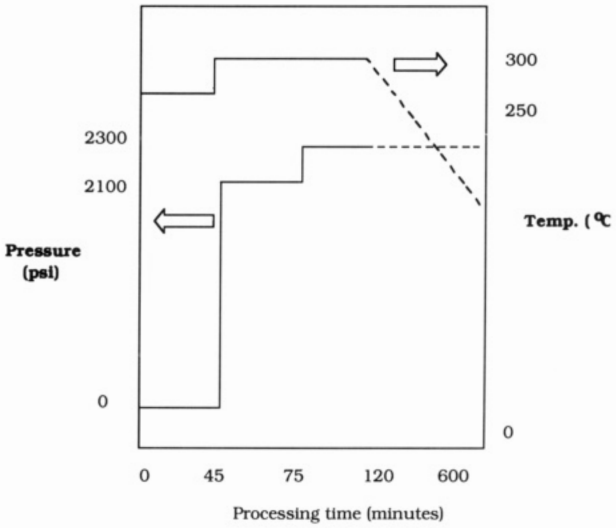

Figure 2. Processing of electropolymerized composites.

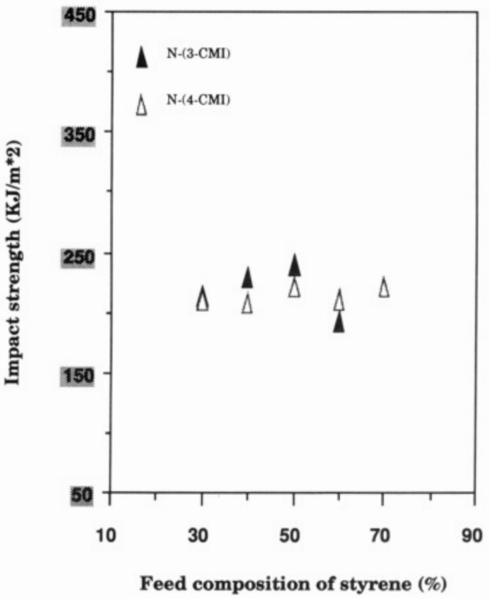

Figure 3. Dependence of impact strength on the comonomer composition.

Freshly coated prepregs were rinsed in distilled water and dried to constant weight at 230 °C under vacuum. The prepregs were cut into 16 cm × 15 cm mats and stacked together in a stainless steel mold cavity previously coated with Miller–Stephenson fluorocarbon release agent (MS-136). The mold containing the prepregs was placed between the compression molding press platens preheated at 250 °C. The molding temperature was raised to 300 °C and maintained at contact pressure for 45 min at this temperature. After the prepregs softened and relaxed, about 2100 psi pressure was applied. The molding temperature and pressure of 300 °C and 2100 psi, respectively, were maintained for 30 min and then released to contact pressure for 1 min and finally raised to 2300 psi. The platen heaters were then switched off, and the molding was air cooled under pressure (Figure 2).

Microscopy. The morphology of the prepregs and the fracture surface of composites were investigated by an AMR 1000 A scanning electron microscope. The SEM samples were shadowed with gold to enhance their conductivity. The distribution of

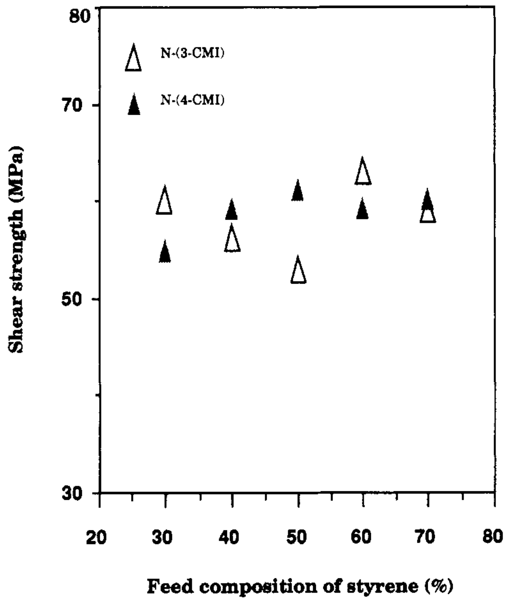

Figure 4. Dependence of shear strength on the comonomer feed composition.

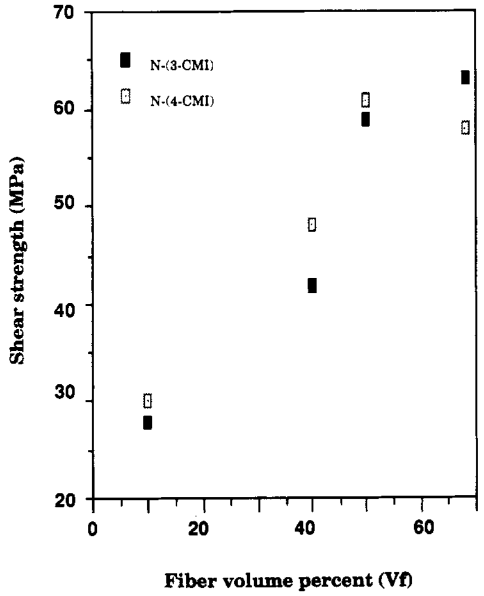

Figure 5. Dependence of the impact strength of poly(*N*-(4/3)-CMI-*co*-styrene) matrix composite on the volume fraction of fibers.

fibers in the prepreg was examined by Nikon optical microscope (SEM). The prepregs were embedded in an Epomet mounting material (provided by Buchler) for each handling and polishing. The assembly was polished using a 400 and 500 grit emery paper and in a vibrating Syntron LP 111 polisher.

Notched Izod Impact Test. The impact strength of the samples was determined by the notched Izod impact test in accordance with ASTM test procedure ASTM D 256. Test specimens 6.25 cm × 1.25 cm × 0.3 were notched, ~0.25 cm, and positioned in such a way that the notched side faced the hammer. Only one-half the specimen length from the center of the notched upward was exposed to the hammer. The five specimens used in each test had their dimensions measured prior to the test. The impact test was performed by the Izod Impact tester TMI Model, using a 5 ft-lb hammer operated by releasing the hook. The specimen is fractured during the downward free swing of the hammer. Corrections for pointer friction and windage were determined at the beginning and termination of the tests. The impact energy spent in the breakage of the specimen is read off from the scale and converted into impact strength after correcting for losses associated with free swing of the hammer.

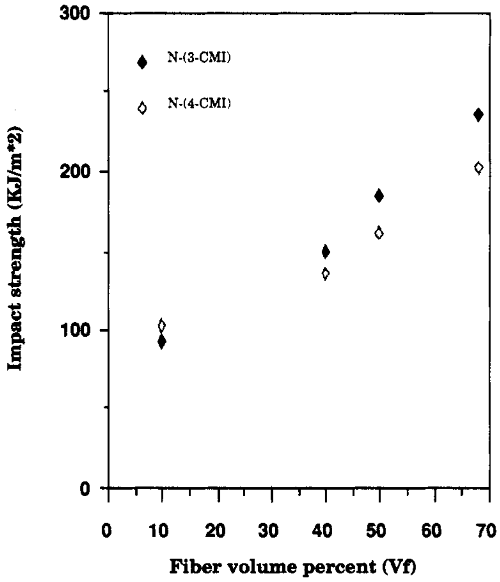

Figure 6. Dependence of the shear strength of poly(*N*-(4/3)-CMI-*co*-styrene) matrix composite on the volume fraction of fibers.

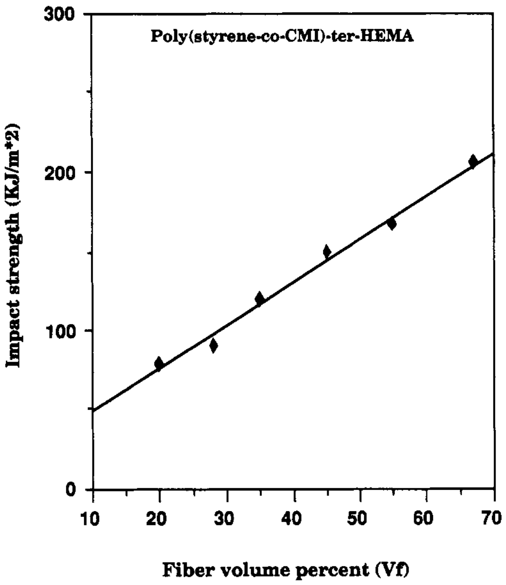

Figure 7. Dependence of the impact strength of poly((styrene-*co*-CMI)-ter-HEMA) matrix composite on the volume fraction of fibers.

Short Beam Shear Test. The interlaminar shear strength of the composites was determined by the short beam shear test according to ASTM test procedure ASTM D 3344. Instron universal mechanical tester Model F/CML operated at a strain rate of 0.1 cm/min and a chart speed of 1 cm/min was used for the test. About 10 specimens were used for each test.

Three-Point Flexural Test. The flexural strength of the composites was measured by the three-point flexural test for unidirectional composites in accordance with ASTM test procedure ASTM D 790-86. An Instron universal mechanical tester model F/CML was used. The test was done at a strain rate of 1 mm/min for specimen of length to thickness ratio (L/d) of 16. About 10 specimens were used in each test.

Results and Discussion

Mechanical Properties. *Effect of Comonomer Feed Composition.* Figure 3 shows the notched Izod impact strength of the electropolymerized matrix composites as a function of the feed composition of styrene. The

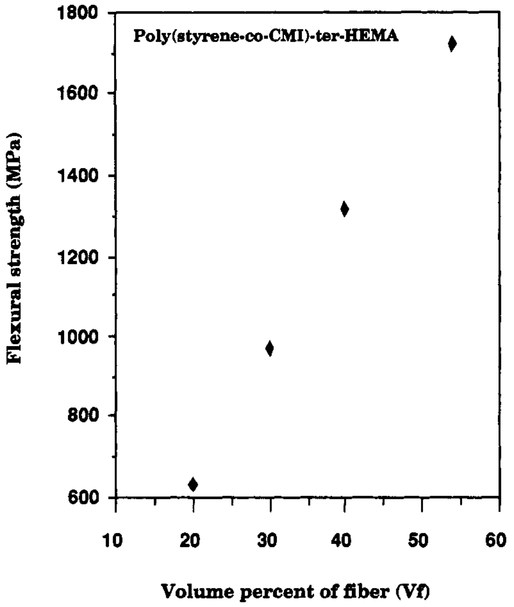

Figure 8. Dependence of the shear strength of poly((styrene-*co*-CMI)-ter-HEMA) matrix composite on the volume fraction of fibers.

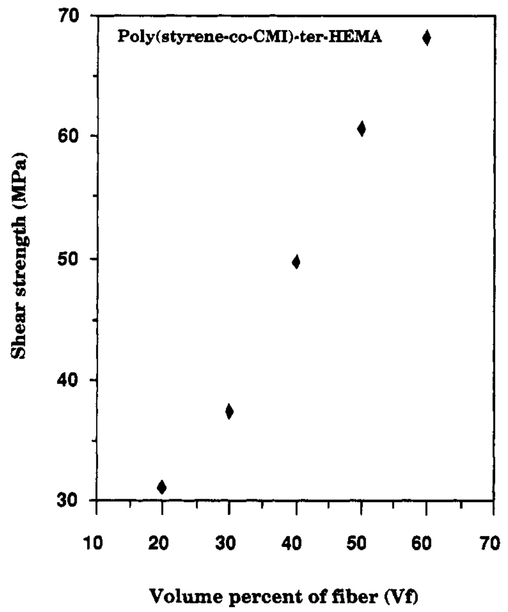

Figure 9. Dependence of the flexural strength of poly((styrene-*co*-CMI)-ter-HEMA) matrix composite on the volume fraction of fibers.

composite showed excellent impact strength of about 230 kJ/m^2. The impact strength of the composites remained relatively unchanged for prepregs produced from comonomer-sulfuric acid solution containing different styrene/N-(3-CMI) feed ratios. Copolymer compositional analysis performed by FTIR and nitrogen analysis confirmed a strong tendency toward alternation for the electropolymerized coatings.[15] Figure 4 shows the shear strength of the continuous poly(N-3-CMI)-*co*-styrene) graphite fiber composites as a function of the comonomer feed ratio. The composites showed moderate interlaminar shear strength ~60 MPa. The shear strength of the composites also remained relatively constant for composites produced from varying styrene/N-(3-CMI) feed composition.

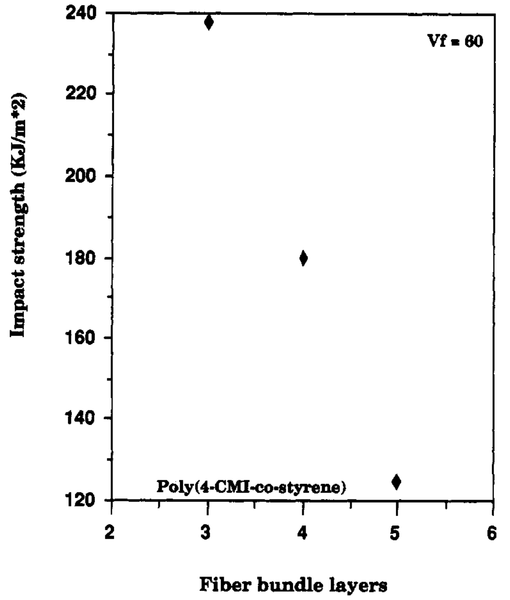

Figure 10. Variation of the impact strength of the composites with the number of fiber bundle layers.

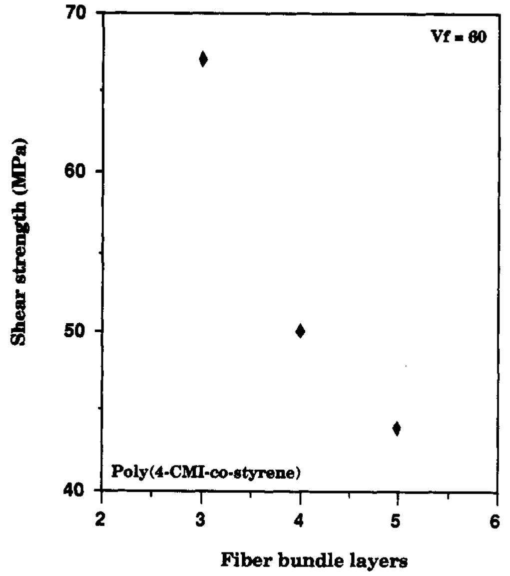

Figure 11. Variation of the shear strength of the composites with the number of fiber bundle layers.

Effect of Fiber Volume Fraction (V_f). The effect of matrix volume fractions on the mechanical properties of the composites show on Figures 5 and 6. Both the impact strength and shear strength of the composites increased with decreased volume fraction of matrix. Deviation from this trend occurred at very high resin volume fraction V_m > 80%. At very high resin contents, the distribution of the resin in the prepregs is nonuniform. There is also a tendency for the outermost section of the prepregs to be covered with layers of loosely bound copolymer coatings. These resin "rivers" further complicate the processing of the composites and often result in lowered mechanical properties.

Figures7–9 show the impact strength, shear strength, and flexural strength, respectively, of the electropolymerized poly(styrene-*co*-N-(3-CMI))–HEMA) matrix graphite fiber composites as a function of the volume fractions of the fibers and the resin. The mechanical properties of these composites increased with decreased volume fraction of the resin.

Functionalized polymers such as poly(hydroxyethyl methacrylate) (PHEMA) possess chemical functional groups capable of reacting with both the graphite fibers

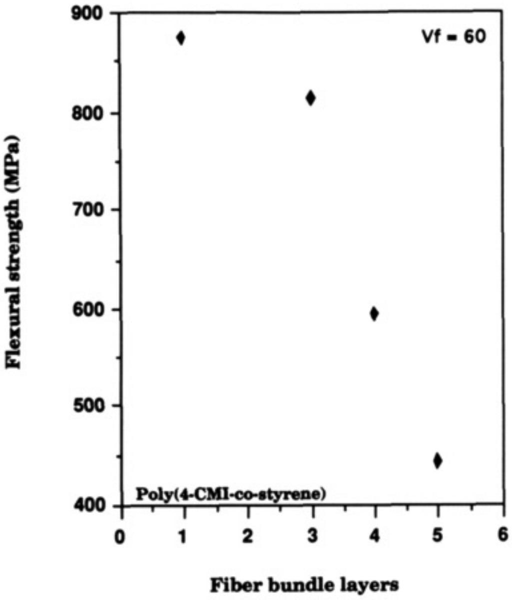

Figure 12. Variation of the flexural strength of the composites with the number of fiber bundle layers.

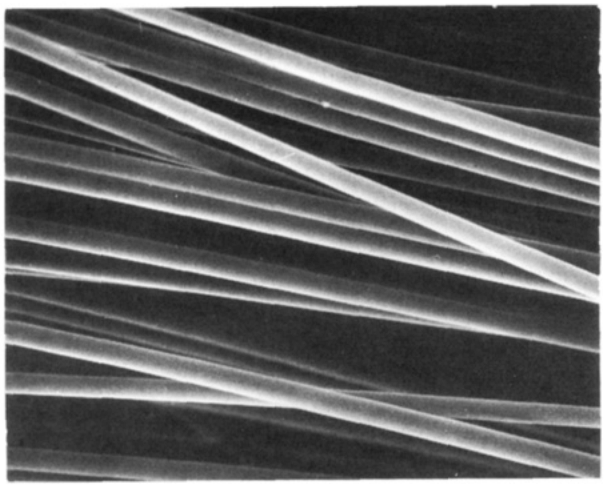

Figure 13. SEM micrograph of bare AS-4 graphite fibers × 530.

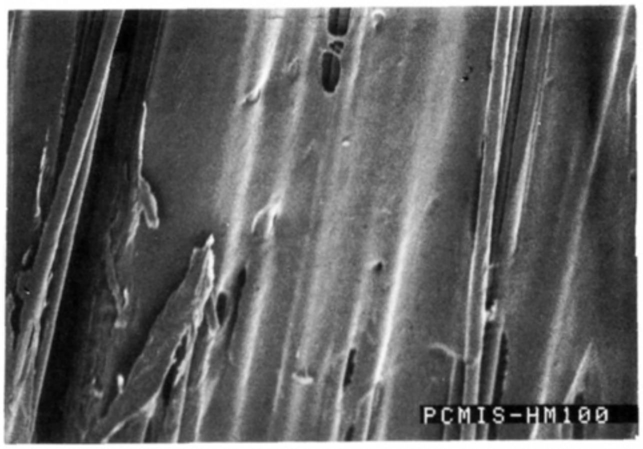

Figure 14. SEM micrograph of electropolymerized poly(*N*-(3-CMI)-*co*-styrene) graphite fiber prepreg × 530.

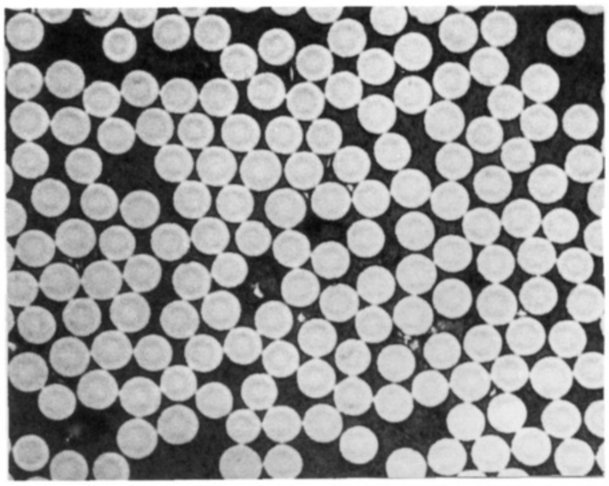

Figure 15. Optical micrograph of electropolymerized poly(*N*-3CMI)-*co*-styrene) graphite fiber prepreg × 1000.

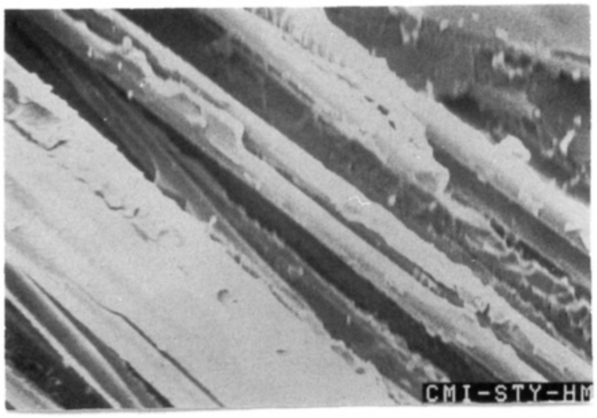

Figure 16. SEM micrograph of a fracture surface of electropolymerized matrix composite ×530.

and the copolymers. Improved adhesion between the reinforcements and the matrix should result in higher interlaminar shear strength of the composites. Further improvement in the mechanical properties of these composites can be achieved by further optimization of the technique. It is desirable that a three-dimensional cross-linked networks are formed in the final processing step.

Effect of Fiber Bundle Layers. Figure 10–12 show the effect of fiber bundle layers on the mechanical properties of poly(*N*-(4-CMI)-*co*-styrene) graphite fiber composites. The mechanical properties of these composites decreased sharply with increasing numbers of fiber bundle layers. Composite fabricated from prepregs composed of one fiber bundle–layer showed improved mechanical properties over composites produced from prepregs composed of five bundle–layers of graphite fibers. The normalized properties of the composites were used to correlate the mechanical properties with processing conditions; Normalized Properties = (Properties at V_f) × (0.60/V_f). The reduced mechanical properties measured for composites fabricated from prepregs composed of three or more fiber bundle-layers stems from the increasing difficulty of the comonomer-electrolyte solution, to penetrate into the fiber bundle layers and properly wet each individual fiber filament. Diffusion time much longer than the time scale of the present experiment is required to permeate each fiber bundle layer and properly wet the individual fiber filaments.

Microscopic Analysis. Figure 13 shows the SEM micrograph of the uncoated AS-4 graphite fibers. Unsized AS-4 graphite fibers are smooth and have rounded cross-section. Figure 14 shows the SEM micrograph of electropolymerized poly((carboxyphenyl)maleimide–styrene) matrix prepreg. The micrograph shows a smooth, uniform, and continuous matrix coating. The optical micrographs of the electropolymerized matrix-graphite fiber prepregs is shown on Figure 15. It shows a uniform copolymer coating distribution about the graphite fibers and the absence of voids in the samples. The absence of voids in the composites is one of the reasons for the improved mechanical properties of these composites. Figure 16 is the SEM micrograph of the fracture surface of the electropolymerized composite. This micrograph suggest that the electropolymerized matrix composites fail by fiber pull out and fiber delamination. The suggested failure mechanism accounts for the very high impact strength and moderate shear strength of the composites.

Conclusion

An electrochemical process for synthesizing in situ thermoplastic matrix graphite fiber composites has been developed. Graphite fiber reinforcements are well suited for this process because of their excellent electrical and thermal conductivity. Continuous glass fiber preforms coated with conducting carbon powder may also be used. Graphite fibers pre-impregnated with about 35 w/o to 40 w/o thermoplatic resins were used in composite fabrication. The electropolymerized matrix graphite fiber composites showed excellent flexural strength ~1800 MPa and impact strength ~230 kJ/m^2 at 40 volume fraction of the matrix. The mechanical performance of the electropolymerized composites compared favorably with the state-of-the-art advanced composites. The interlaminar shear strength of about 60 MPa suggest the possibility of further improvement in the shear strength. It is expected that prior surface treatment and functionalization of the graphite fiber surfaces should enhance further the adhesion between the reinforcements and the matrix. Reduction of the numbers of graphite fiber bundle layers in the preform from five to one, resulted in composites with improved flexural and impact strengths.

Acknowledgment. The authors acknowledge the support of a High Technology grant by the Connecticut Department of Higher Education for this research.