Electrochemical process for preparing continuous graphite fibre–thermoplastic composites

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An electrochemical process for preparing thermoplastic matrix–graphite fibre composites has been developed. Graphite fibre–poly(maleimide-*co*-styrene) matrix composites were prepared using unsized AS-4 graphite fibre preforms as the working electrode. Copolymers of a wide range of N-substituted maleimides and styrene were formed directly on the surface of the graphite fibres. The rate of electrocopolymerization varied with the electrocopolymerization parameters, such as the comonomer concentration, current density, supporting electrolyte concentration, electropolymerization time, nature of the solvent, solvent/dilute sulfuric acid ratio and the structure of the maleimide. Graphite fibre preforms preimpregnated with the electropolymerized thermoplastic matrices were processed into unidirectional composite laminates. The electrosynthesized thermoplastic matrix composites showed excellent physical and mechanical properties.

(Keywords: matrix–fibre composites; electrochemical preparation; characterization)

INTRODUCTION

Electropolymerization is currently being investigated as a novel technique for applying uniform and controlled-thickness thermoplastic matrices directly onto conducting graphite fibre preforms. This technique represents a new route to preparing *in situ* thermoplastic matrix–graphite fibre composites[1,2]. The need for an innovative technique for processing thermoplastic matrix–graphite fibre composites is demonstrated by the difficulty of uniformly applying viscous thermoplastic melts onto individual fibre strands in a fibre bundle containing about three thousand or more filaments. Thermoplastic resins are not easily dissolved by low-boiling solvents. In fact, finding an appropriate solvent for moderate- to high-temperature-resistant and high-molecular-weight thermoplastics is difficult and laborious. Graphite fibre–thermoplastic matrix prepregs produced by the traditional solution or hot-melt impregnation processes have poor interfacial properties, owing to poor wettability of the fibres by the viscous thermoplastic melts. Poorly wetted fibres are weakly bonded to the matrix, resulting in weak adhesion and lowered efficiency of load transfer from the matrix to the reinforcements.

Thermoplastic resins possess positive attributes such as excellent toughness, very good hot/wet properties, excellent solvent resistance and long shelf-life. They can be reversibly processed and have a capacity for large-volume processing. Their disadvantage stems from the difficulty of producing uniform and void-free prepregs and the associated high processing cost. The merits of thermoplastic matrices over the traditional thermosetting resins provide the incentives for the development of innovative techniques of resin infiltration. Various authors have reported the application of thermoplastic matrices in the form of polymer powder onto graphite fibre preforms, as a new way of resin infiltration[3,4]. The polymer-powder-coated preforms were subsequently processed into prepregs by resistance fusion. The drawback of this technique includes the formation of voids ($\sim 5\%$). The resulting composites consequently have lowered mechanical properties. Investigation of *in situ* preimpregnation of the fibre preforms by bulk and solution polymerization is currently being initiated. The formation of the resin, however, does not occur exclusively on the surfaces of the fibres. Quantitative control of the coating thickness, very crucial in the production of *in situ* composites, cannot be easily achieved. Olefinic monomers are not suitable candidates for this process because of the associated Thrommsdoff's effect, which often occurs in chain polymerization. The applicability of this process is undoubtedly limited by the inability to coat the reinforcing fillers effectively and controllably, the occurrence of high void fraction

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and the concomitant poor mechanical properties of the composites. New and innovative approaches to processing thermoplastic matrix–graphite fibre composites are highly desired. One of the most promising of these techniques is the *in situ* electrochemical synthesis of the matrix directly onto graphite fibre preforms.

Electropolymerization in organic media has been investigated by authors such as Funt[5,6] and others[7,8]. These authors studied the nature and mechanism of olefinic electropolymerization. In these studies, it has been clearly demonstrated that the electropolymerization of vinyl monomers may occur via a radical or ionic mechanism depending on the nature of the electrolyte, solvent, co-reactants, catalyst and monomer. Subramanian[9] and Bell *et al.*[10] extended the realm of the electropolymerization technique into the area of surface treatment of conducting graphite fibres. Use of water as the primary reaction medium resulted in high-molecular-weight polymers and limited the polymerization to a free-radical mechanism[11]. Unsized graphite fibre reinforcement was adopted as the working electrode and placed in the monomer–electrolyte–solvent chamber of the electrolysis cell. Through the passage of a predetermined amount of electric current per unit surface area/weight of the reinforcement, the monomers were selectively electropolymerized. AS-4 graphite fibre preforms electrocoated with a 0.2 μm thick poly(glycidyl acrylate-*co*-methacrylate) interlayer and processed into graphite fibre–epoxy resin composites showed simultaneous improvement of more than 20% in both the impact and shear strength[12]. The improvement in the mechanical properties of the electrocoated fibre-reinforced epoxy resin was attributed to the ability of the ductile polymeric interlayer to absorb deformation energy and arrest crack propagation by crack bridging, crack blunting and crack energy dissipation mechanisms. Recently Iroh *et al.* employed the electropolymerization technique to prepare thick ($\sim$3.0 μm) *in situ* thermoplastic matrix–graphite fibre prepregs[13]. They also demonstrated direct electropolymerization of thick poly(maleimide-*co*-styrene) and poly(*N*-substituted maleimide-*co*-styrene) matrices onto the graphite fibre preforms. The graphite fibres, preimpregnated with the thermoplastic coatings (prepregs), were subsequently directly compression-moulded into graphite fibre–poly(*N*-substituted maleimide-*co*-styrene) composites. The composites showed excellent impact strength $\sim$220 kJ m^{-2} and moderate shear strength $\sim$60 MPa at about 40 vol% of the matrix. In this paper we report our investigation on the electrochemical synthesis, characterization and mechanical evaluation of selected electrocoated matrix–graphite fibre composites.

EXPERIMENTAL

Instrumentation

The Pratt & Witney Potentiostat/Galvanostat No. P&WA XA-596383 model No. 203 and the Princeton Applied Research Potentiostat No. 363 were used as the source of constant current. By placing the potentiostat in the galvanostatic mode, a predetermined amount of constant direct current was applied through the electrodes. A Hewlett-Packard Digital Multimeter No. 3438A was used to monitor the applied current and cell voltage (*Figure 1*). The potential difference between the working and the counter electrodes was monitored by connecting an SCE reference electrode in series with the working electrode.

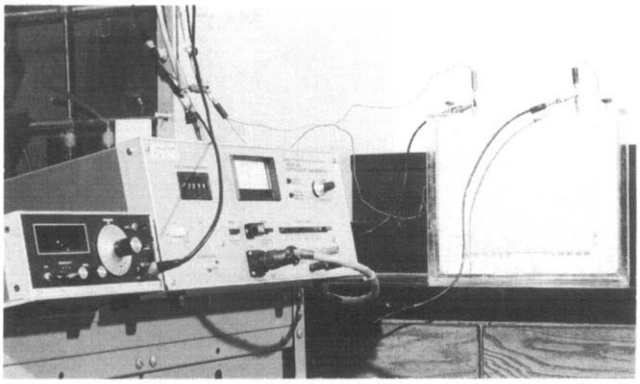


Figure 1 The Delrin tank electropolymerization set-up

Electropolymerization cell

A three-compartment electrochemical cell (*Figure 1*) was used. The cell was composed of a Delrin reaction tank placed inside a glass chromatographic tank ($29 \times 26 \times 9.5$ cm^3 (o.d.)). The Delrin tank is the middle electrolytic reaction chamber. It contains the monomer–electrolyte solution and the graphite fibre working electrode. The monomer chamber is separated from the anodic chambers by a 0.4 μm pore polypropylene membrane. The two anodic counter electrode compartments contain sulfuric acid supporting electrolyte (0.025 M), some solvent and stainless-steel counter electrode respectively.

Monomers

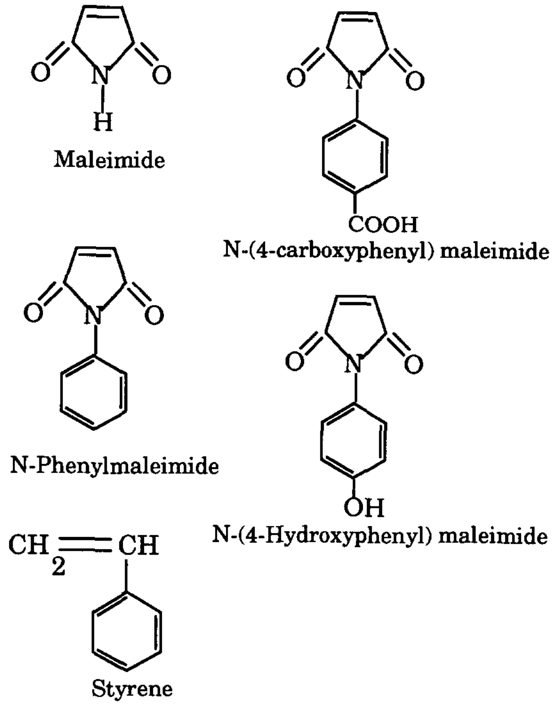
Maleimides, *N*-substituted maleimides and styrene were the comonomers used. Polymaleimides are suitable matrices for advanced polymeric composites because of their excellent rigidity, thermal stability and processability. Monomeric maleimides are expected to react strongly with electron-donor monomers like styrene. In this study, maleimides, *N*-phenylmaleimide (N-PMI), *N*-(4-hydroxyphenyl)maleimide (N-PHPMI) and *N*-(4-carboxyphenyl)maleimide (N-4CMI) were electrocopolymerized with styrene (*Scheme 1*). The maleimides were used as purchased, while styrene was extracted twice in 10% sodium hydroxide solution to remove inhibitors and subsequently washed twice in distilled water.

Electrodes

Stainless-steel plates $20 \times 20 \times 0.16$ cm^3 were used as the counter electrode. Transition-state metals like platinum, rhenium and titanium, which are unreactive in acid or alkaline solutions, are strongly recommended as counter electrode materials. The working electrode comprised continuous graphite fibre filaments would on an H-shaped aluminium frame.

Electropolymerization

The Delrin monomer chamber containing 500 ml maleimide (0.75 M), 500 ml styrene (0.75 M), 100 ml *N*-dimethylacetamide (DMAc) and 1000 ml sulfuric acid solution (0.025 M) was placed inside the large glass chromatographic tank. The working electrode was placed in the centre of the tank by a well designed adaptor. The two counter electrode compartments were filled with 1:1



Scheme 1 Monomers for electropolymerization

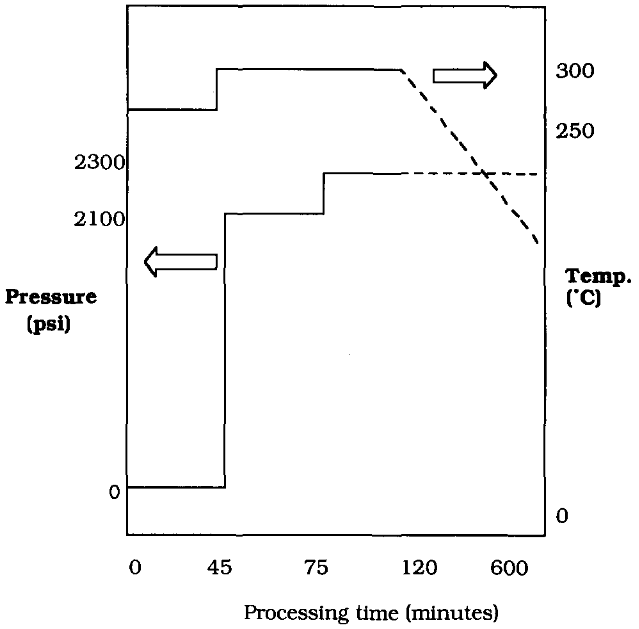


Figure 2 Variation of pressure and temperature with time during the consolidation of the prepregs

sulfuric acid solution (0.015 M):DMAc. A stainless-steel plate was placed centrally in each of the counter electrode chambers previously filled with the supporting electrolyte:DMAc (5:1). The stainless-steel plates (counter electrodes) were connected to the positive terminal (red) of the potentiostat, while the graphite fibre working electrode was connected to the negative terminal (green). The potentiostat was then switched into the galvanostatic mode by placing the potentiostat/galvanostat switch on the latter. This represents a very crucial step for constant-current electropolymerization because current control is achieved in this mode. A suitable current density in milliamperes per unit weight of graphite fibres was selected such that the effective density of the initiating current per unit weight of fibres is maintained constant. By so doing, properties of the resin that depend on the initiating current (initiator concentration), such as the molecular weight and molecular-weight distribution, are maintained constant. A current density of 25 mA/g fibre was used for most of the electropolymerization reactions reported in this paper. Electropolymerization was commenced when the cell on/off switch was switched on. The potentiostat mains power on/off switch is always on. If otherwise, the operator must wait at least 15 min after the power button was switched on, for the instrument to stabilize, before starting electropolymerization. Electropolymerization is terminated when the cell button is placed in the off position and the coated fibre was withdrawn from the cell.

Characterization

The glass transition temperature of the electropolymerized matrix was measured by a DuPont Thermomechanical Analyzer operated at 10°C min^{-1} in a nitrogen atmosphere.

Composite processing

The freshly coated fibres were rinsed in distilled water and dried at ambient temperature for about 10 h. They were subsequently dried under vacuum at 250°C for 6 h. The weight of the dried prepreg was determined and the weight of the coatings was obtained as the difference between the former and the weight of the uncoated fibres measured prior to electropolymerization. The prepregs were then cut to size, stacked into the stainless-steel mould cavity and placed in between the platens of a hot press, previously heated to 250°C. The moulding was maintained at the contact pressure for 45 min at 250°C. The moulding temperature and pressure were then raised to 300°C and 2100 psi (14.48 MPa) respectively. This moulding pressure was maintained for 30 min. It was then released to contact pressure for 1 min and finally raised to 2300 psi (15.86 MPa). The platen heaters were switched off 1 h after 2300 psi was applied to the moulding and the set-up was air cooled under pressure (*Figure 2*).

Mechanical testing

The *in situ* electropolymerized matrix–graphite fibre composites were mechanically tested by the notched Izod impact test, short-beam shear test and three-point flexure in accordance with the ASTM test procedures D256-76, D2344-86 and D790-86 respectively.

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.

RESULTS AND DISCUSSION

Electropolymerization

Electropolymerization was initiated when an electric current of about 25 mA/g fibre was passed through the electropolymerization cell assembly containing the electrodes, sufficient amount of comonomers ~0.2 M, solvent and supporting electrolyte ~0.013 M. Both the *N*-substituted and non-substituted maleimides electrocopolymerized with styrene. The amount of copolymer coatings formed during electropolymerization, weight gain of fibres, was measured as the difference between the weight of the high-temperature dried prepreg and the weight of the uncoated fibres. The weight gain of fibres is dependent on monomer concentration, weight of the graphite fibres, current density, supporting electrolyte concentration and electropolymerization time. The weight of the copolymer coatings formed on AS-4 graphite fibre surfaces after about 20 to 60 min of electropolymerization is presented on *Tables 1–3*. Graphite fibre weight gain of about 40% was obtained in about 30 min of electrocopolymerization. The glass temperatures T_g of the copolymers were measured by using a DuPont 9900 Thermal Mechanical Analyzer. T_g values of 250 and 205°C were obtained for the electropolymerized poly(*N*-(4-hydroxyphenyl)maleimide-*co*-styrene) and poly(*N*-phenylmaleimide-*co*-styrene) respectively (*Table 4*). The T_g of the copolymers was measured from the midpoint of the second and/or third t.m.a. trace (*Figures 3* and *4*). Previously Bell *et al.* reported d.s.c. glass transition temperatures of 230 and 250°C for electropolymerized poly(maleimide-*co*-styrene) and poly(*N*-(4-carboxyphenyl)maleimide-*co*-styrene) respectively[13]. The electrocopolymerized copolymers have glass transition temperatures comparable to those reported for the bulk polymerized analogue[14].

Table 1 Weight gain of fibres during the electropolymerization of N-PHPMI and styrene in a large Delrin cell ($C_d = 25$ mA/g, [M] = 0.75 M, $[H_2SO_4] = 0.0125$ M)

Reaction time (min)	Fibre bundle layers (number)	Weight of coatings (g)	Weight gain of fibres (%)
60	1 (12 000)	11.4	62
60	1 (12 000)	12.5	68
60	1 (12 000)	10.3	56
60	1 (12 000)	11.6	63
60	5 (3000)	13.5	43
60	5 (3000)	10.9	43

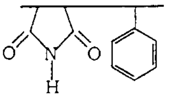
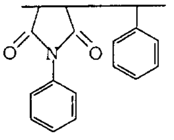
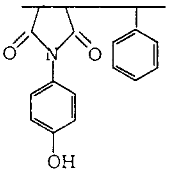
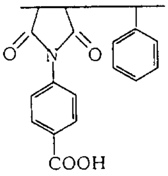
Table 2 Weight gain of fibres during the electropolymerization of N-PHPMI, N-PMI[a] and styrene respectively in the small polypropylene cell

Reaction time (min)	Weight of fibres (g)	Weight of coatings (g)	Weight gain of fibres (%)
60	2.3	1.5	63
28	2.3	1.0	45
30	2.3	0.7[a]	32[a]
60	2.4	1.3[a]	55[a]

Table 3 Reproducibility of the electropolymerization of maleimide and styrene in small polypropylene cell ($C_d = 10$ mA/g, $[H_2SO_4] = 0.0125$ M)

[M] (mol l^{-1})	Reaction time (min)	Weight of fibres (g)	Weight of coatings (g)
0.5	40	5.57	0.46
0.5	40	4.96	0.52
0.5	35	5.03	0.63
0.5	35	4.91	0.7
0.5	40	5.12	0.69
0.5	40	4.87	0.7

Table 4 Electropolymerized copolymers and their T_g values

Copolymer type	T_g (°C)	Polymerizability (%)
Poly(maleimide-*co*-styrene)  	232 (d.s.c.)	Good (>50%)
Poly(N-PMI-*co*-styrene)  	200 (t.m.a.)	Good (~60%)
Poly(N-PHPMI-*co*-styrene)  	250 (t.m.a.)	Good (>50%)
Poly(N-4CMI-*co*-styrene)  	250 (d.s.c.)	Very good (~100%)

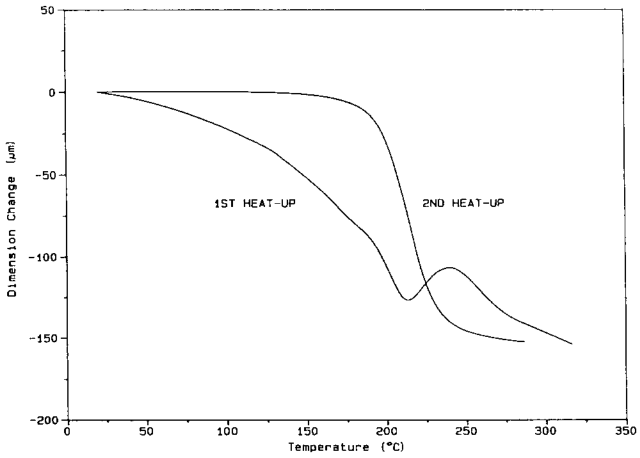


Figure 3 T.m.a. traces of electropolymerized poly(N-PMI-*co*-styrene)

Mechanical properties

The variation of the flexural strength of poly(*N*-(4-hydroxyphenyl)maleimide-*co*-styrene)–graphite fibre composites with the volume fraction of the resin is shown on *Figure 5*. The electropolymerized matrix composites showed excellent flexural strength ~2000 MPa at about 68 vol% of fibres. This represents about twice the value reported by Subramanian for electrocoated fibre-reinforced epoxy resin[9]. The electrosynthesized poly(*N*-(4-carboxyphenyl)maleimide-*co*-styrene) and poly(*N*-phenylmaleimide-*co*-styrene) matrix–graphite fibre composites, however, have comparable flexural strengths to those of graphite fibre-reinforced epoxy resin.

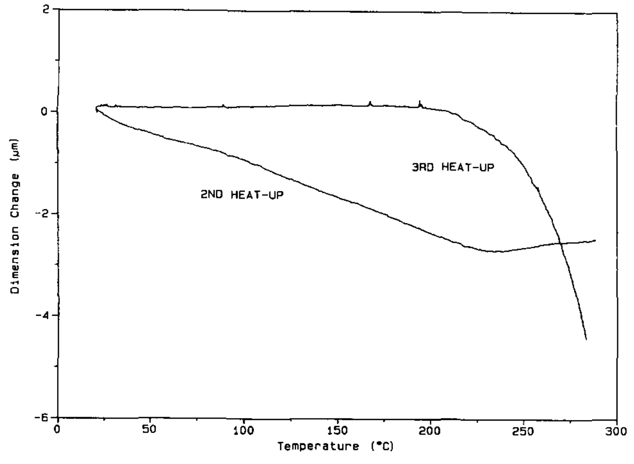


Figure 4 T.m.a. traces of electropolymerized poly(N-PHPMI-*co*-styrene)

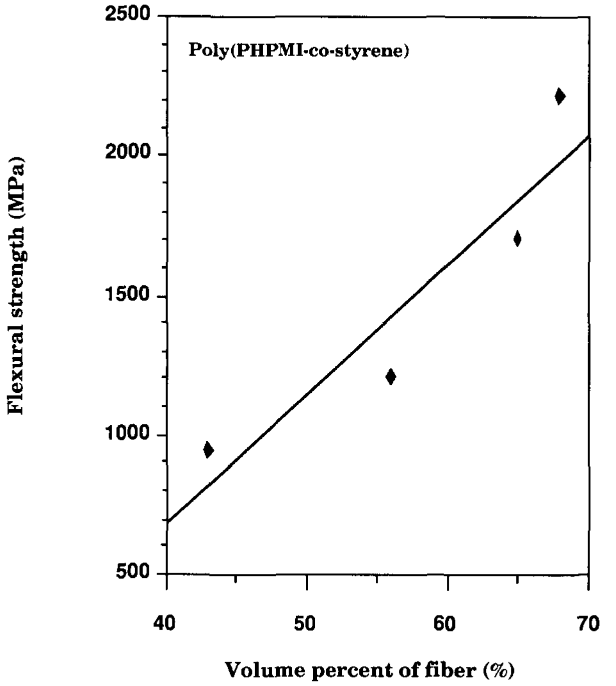


Figure 5 Dependence of the flexural strength of graphite fibre–poly(N-PHPMI-*co*-styrene) composites on the volume fraction of fibres

Figure 6 shows the impact strength of the electropolymerized poly(*N*-(4-hydroxyphenyl)maleimide-*co*-styrene)–graphite fibre composites as a function of the volume fraction of the resin. These composites had high impact strength, which predictably increased with decreased resin volume fraction. When compared with commercially treated graphite fibre–epoxy composites, the electropolymerized matrix composites showed about 75–100% improvement in the impact strength.

The dependence of the shear strength of the electrocoated poly(*N*-(4-hydroxyphenyl)maleimide-*co*-styrene) matrix–graphite fibre composites on the volume fraction of the electrocoated resin is shown on *Figure 7*. The shear strength of the composites remained slightly lower than those obtained for poly(glycidyl acrylate-*co*-methacrylate)-coated graphite fibre–epoxy composites[12]. They, however, compared favourably with poly(styrene-*co*-acrylonitrile)-coated graphite fibre–epoxy composites of the same volume fraction[8]. One cannot compare the performance of these composites directly with commercial epoxy samples where the interfacial properties have been optimized by years of research and study of fabrication procedures.

Figure 8 shows the SEM micrograph of electropolymerized poly((*N*-(3-carboxyphenyl)maleimide-*co*-styrene) matrix prepreg. The micrograph shows a smooth, uniform and continuous matrix coating. *Figure 9* is the SEM micrograph of the fracture surface of the electropolymerized composite. This micrograph suggests that the electropolymerized matrix composites fail by fibre pull-out and fibre delamination. The suggested failure mechanism accounts for the very high impact strength and moderate shear strength of the composites.

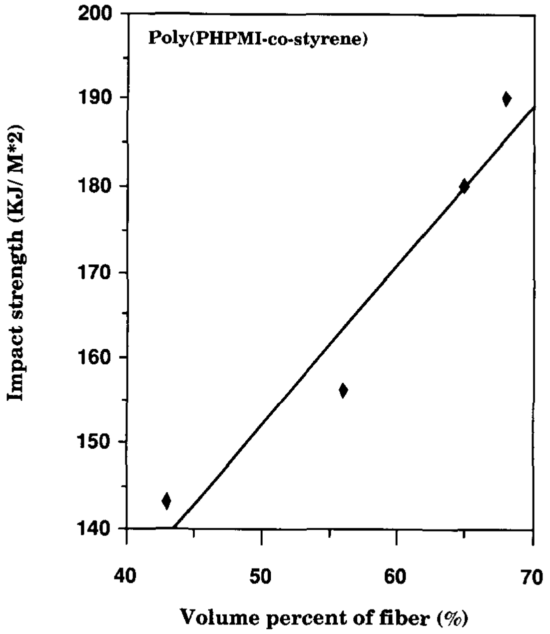


Figure 6 Dependence of the impact strength of poly(N-PHPMI-*co*-styrene)–graphite fibre composites on the volume fraction of fibres

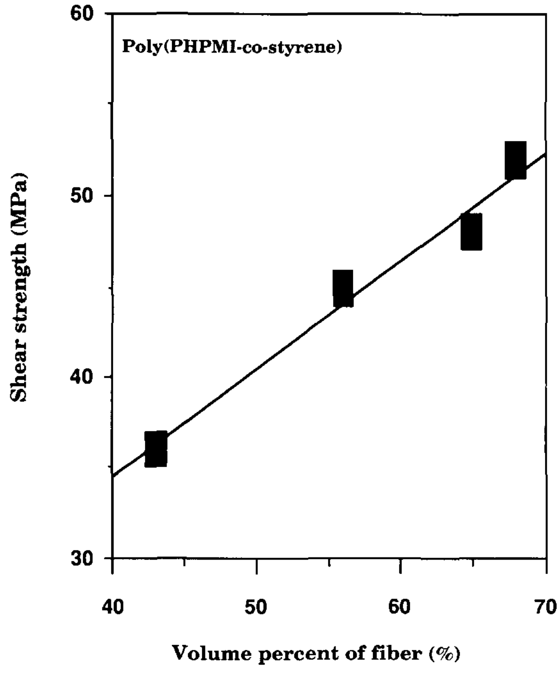


Figure 7 Dependence of the interlaminar shear strength of the graphite fibre–poly(N-PHPMI-*co*-styrene) composites on the volume fraction of fibres

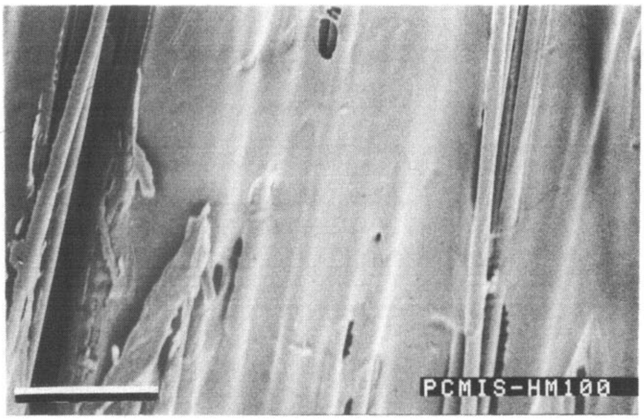


Figure 8 SEM micrograph of electropolymerized poly(N-3CMI-*co*-styrene)–graphite fibre prepreg (scale bar 50 μm)

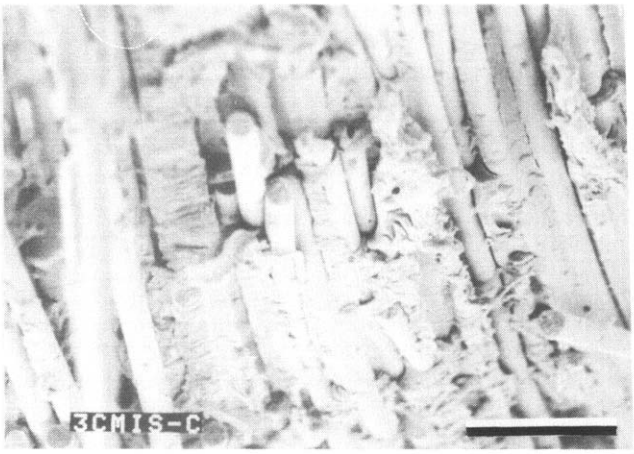


Figure 9 SEM micrograph of a fracture surface of electropolymerized matrix composite (scale bar 50 μm)

CONCLUSIONS

Electrochemical copolymerization has been used to impregnate continuous unidirectional graphite fibres with controlled volume fraction of poly(*N*-substituted maleimide-*co*-styrene) thermoplastic matrix. The volume fraction of the electropolymerized matrix composites varied with the electrocopolymerization time; all other reaction parameters were maintained constant. The electrocopolymerizability of the maleimides with styrene, defined as the percentage weight gain on fibres per half hour, varied with the substituent on the maleimide nitrogen in the following order: Ph(COOH) $\geqslant$ Ph(OH) $>$ Ph $>$ H $\geqslant$ R. The glass transition temperature of the electrocopolymerized matrix was also dependent on the nature of the substituent on the maleimide nitrogen.

The electropolymerized matrix composites containing about 60 vol% of fibres showed excellent impact strength $\sim$175 kJ m^{-2}, good flexural strength $\sim$1750 MPa and moderate interlaminar shear strength $\sim$50 MPa. Generally, the composites showed a dependence of mechanical properties on the volume fraction of the constituents as predicted by the rule of mixtures.

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