Electrocoating of carbon fibres with polymers: 3. Electrocopolymerization of polyfunctional monomers

S. Shkolnik* and C. Barash
Department of Applied Chemistry, Soreq Nuclear Research Center, Yavne 70600, Israel
(*Received 28 November 1991; revised 4 November 1992*)

The electrocopolymerization of glycidyl methacrylate and methyl methacrylate is described. The compositions of the monomer–electrolyte solution and the parameters of the polymerization coating process that provide formation of thin, even coatings on carbon fibres were determined. The mole fraction of glycidyl methacrylate in the synthesized copolymers was calculated from glass transition temperature, Fourier-transform infra-red and nuclear magnetic resonance determinations. The mechanism of the electrochemical reaction, which leads to grafting of the copolymer onto the carbon fibre surface, is discussed. Composites from carbon fibres coated with the mentioned copolymers showed improved fracture energy during delamination (60–100%) and improved interlaminar shear strength (~20%) in comparison with specimens from uncoated fibres.

(Keywords: electrocopolymerization; carbon fibres; glycidyl methacrylate; methyl methacrylate; copolymers; grafting; strain-energy release rate)

INTRODUCTION

The electrochemical copolymerization of methyl methacrylate (MMA) and methyl acrylate (MA) on carbon fibres (CF) has been described elsewhere[1]. The compositions of the monomer–electrolyte solution and the parameters of the process that provide formation of thin, even coatings on CF were found. Composites from CF coated with poly(MMA-*co*-MA) showed improved strain-energy release rate (G_{Ic}) (40–200%) and improved interlaminar shear strength (*ILSS*) (10–20%). However, dichloromethane removed all copolymer present on the CF surface and the weight of the extracted fibres remained unchanged in comparison with the initial weight. It would be interesting to develop an interlayer that contains functional groups capable of reacting with one of the matrix components and very likely also with active groups on the CF surface, to form covalent bonds.

The surface grafting of polyesters, by the ring-opening copolymerization of glycidyl methacrylate (GMA) with phthalic anhydride, on carbon black containing COOK groups has been reported[2]. This reaction was initiated by carbon black and carried out at 120°C. A similar compound was obtained[3] by the electrochemical condensation of propylene oxide with phthalic anhydride in *N*,*N*-dimethylformamide (DMF) at 25°C. The electrochemical polymerization of GMA on the surface of CF was later also described[4]. In this case a crosslinked polymer layer was formed, and on the i.r. spectrum peaks at wavenumbers 1640 and 912 cm^{-1}, attributed to the unsaturated vinyl bonds and epoxy groups, were absent.

In the present work GMA and MMA were chosen as comonomers for preparation of a copolymeric interlayer. It was assumed that, at the cathode, copolymerization will take place by means of reduction of the monomers at the double bond on the CF surface[5] and, under certain conditions, some of the oxirane rings of GMA will be involved in the creation of strong bonds between the polymeric layer and the CF surface.

EXPERIMENTAL

Materials

Carbon fibres of type ACIF-XHT, made in Kibbutz Afikim, Israel, were used. The characteristics of these fibres were described previously[5]. The fibres were electrochemically oxidized and dip-coated with an epoxy resin by the manufacturer. The desized fibres were obtained by extraction of the CF in trichloroethane followed by drying at 50°C. Another desizing process, a thermal treatment at 400°C for different periods of time, was found to be inappropriate owing to the lack of coating in the cathodic electropolymerization on the fibres[5]. This phenomenon can be explained by the elimination of the strongly acidic groups, formed on the CF surface during their oxidation, by the heat treatment[6]. MMA (>99% with 25 ppm hydroquinone) was used as received; GMA (95%) was purified by distillation prior to use. Both monomers were from Fluka (Buchs, Switzerland). Lithium chloride (99.4%, Baker Analyzed) and *N*,*N*-dimethylformamide (>99.8%, Fluka) were used without further purification.

Preparative electrocopolymerization

The electrochemical copolymerization was performed in a three-compartment cell described in a previous paper[5]. The monomer–electrolyte solution was poured

---

*To whom correspondence should be addressed

0032-3861/93/142921–08

into the central (cathodic) chamber of the cell and stirred during the reaction. The two outer compartments were filled only with the aqueous solution of the electrolyte. The CFs, wetted in distilled water and stretched on a Teflon frame, were introduced into the cathodic chamber and coated in a controlled-current mode. The coated fibres were removed from the solution, rinsed with a mixture of water/DMF (1:1), and dried at 50°C to a constant weight.

The weight (W) and mole (F) fractions of the monomers in poly(MMA-*co*-GMA), as copolymeric interlayers with glass transition temperatures (T_g) of 60, 70 and 80°C, as well as the mole fractions (f) in the monomer feed, were calculated by the Fox relationship and Fineman–Ross equation, respectively. The data obtained are presented in *Table 1*. The values of the reactivity ratios of MMA and GMA used in the calculations were 0.75 and 0.94, respectively[7].

Voltammetric behaviour of the monomers

Cyclic voltammetry was used to measure the reduction potential of the monomers in working solutions at a CF electrode. The experiments were carried out in an undivided cell, using an AFRDE4 potentiostat (Pine Instrument Co., USA). Changes in current between the CF and a carbon rod, as counter-electrode, at a scan rate of 100 mV s^{-1}, were measured and plotted by a X–Y recorder (type WX1100, Graphtec Corp., Japan). Saturated calomel was used as reference electrode.

Polymer characterization

Samples of electropolymerized copolymers, for T_g determination and characterization by Fourier-transform infra-red (*FT*i.r.) and nuclear magnetic resonance (n.m.r.) spectroscopy, were collected from the CF surface in a Soxhlet apparatus by continuous extraction with dichloromethane and subsequently precipitated with petroleum ether.

Differential scanning calorimetry. The tests were carried out on a Mettler TA4000 thermal analysis system composed of a DSC25 differential calorimeter cell coupled to a TC11 TA processor. The calorimeter was calibrated using indium of high purity as standard. The samples were contained in sealed aluminium pans and scanned at a heating rate of 10°C min^{-1} up to a temperature 40°C higher than that of the expected T_g, in a dry nitrogen environment (50 ml min^{-1} flow rate). The midpoint of the baseline shift corresponded to the T_g.

Table 1 The calculated weight and mole fractions of monomers in copolymers with different T_g, and the corresponding mole fractions in feed[a]

		W		*F*		*f*	
No.	T_g (°C)	MMA	GMA	MMA	GMA	MMA	GMA
1	60	0.269	0.731	0.344	0.656	0.354	0.646
2	70	0.448	0.552	0.536	0.464	0.567	0.433
3	80	0.617	0.383	0.696	0.304	0.734	0.266

[a] MMA, methyl methacrylate; GMA, glycidyl methacrylate; T_g, glass transition temperature; W and F, weight and mole fractions, respectively, of the monomer in copolymer; f, mole fraction of the monomer in feed

FTi.r. spectroscopy. The dichloromethane-insoluble part of the polymer coating together with the fibres were pulverized in a mortar with a pestle. KBr pellets, which contained the soluble fraction of the copolymer or the insoluble one pulverized with the CF, were prepared and used for characterization, in an *FT*i.r. spectrophotometer (type 5DX, Nicolet Instrument Corp., USA). In parallel, the extracted fibres, coated with the insoluble part of the polymer, were examined by the attenuated total reflectance (a.t.r.) technique (KRS-5 crystal) on a spectrophotometer (type 60SXR, Nicolet). The wavenumber range scanned was 4600–400 cm^{-1}.

N.m.r. spectroscopy. The ^{1}H n.m.r. spectra of the copolymers, containing tetramethylsilane as an external standard reference, were recorded in deuterochloroform, using a Bruker CXP200 *FT*n.m.r. spectrometer. For the determination of the composition of the MMA/GMA copolymer, the integral ratio of the protons of the methoxy and glycidyl groups was taken into consideration.

Scanning electron microscopy. SEM was carried out on a JEOL JSM-1300 instrument at 25 kV. The scanning electron micrographs were used for morphology and homogeneity examination of the surface of the coated fibres.

Mechanical tests

The *ILSS* and mode I delamination tests were performed on composite specimens reinforced with copolymer-coated CFs. The *ILSS* was determined on flat specimens, in a three-point bending fixture, at a span/depth ratio of 5:1. The strain-energy release rate G_{Ic}, a crack propagation criterion, was evaluated from the experimental data of the mode I tests. Details of these measurements and calculations, as well as specimen preparation, have been described elsewhere[1].

RESULTS AND DISCUSSION

Electrocopolymerization of methyl methacrylate and glycidyl methacrylate

The electrocopolymerization of MMA and GMA was conducted in the cathodic compartment of a divided cell. Sulfuric acid could not be used as electrolyte, as in the case of the electrocopolymerization of MMA and MA[1], because it would have led to the opening of the epoxy ring in GMA. Nevertheless, several electrocoating runs were performed, using as a monomer–electrolyte solution 15% MMA and GMA in ethanol in the presence of 1.7 M H_2SO_4 and 1.15 M H_2O. The monomer composition No. 1 (*Table 1*) was used. The results showed that, even at relatively high current densities (0.75–1.0 mA cm^{-1}) and long reaction times (up to 100 min), the weight gain remained low (5–6%).

It was decided to change both the electrolyte and the solvent in the working solution. The following aprotic solvents were tried: acetonitrile (AN), γ-butyrolactone (BL), DMF, 1,3-dioxolane, ethylene glycol dimethyl ether, nitromethane and propylene carbonate. Copolymers of MMA and GMA, at different mole fractions of the monomers in the polymer, were soluble in all the above-mentioned solvents. Owing to the good solubility and rapid dissolution of LiCl – which was chosen as electrolyte – in DMF and BL, these solvents were selected for further tests.

The solubility of a monomer mixture (No 1, *Table 1*) in DMF or BL diluted with distilled water is depicted in *Figure 1*. It is seen that (a) dilution of the solvents with water reduces their ability to dissolve the monomers, and (b) BL is the better of the two solvents. In order to obtain a 10% solution of the monomer mixture, the monomer/water ratio had to be 0.7 and 0.9 for BL and DMF, respectively. The mixture of DMF and water at a ratio 1:1 was used in the electrocopolymerization reactions.

Figure 2 shows that, at relatively short electrocopolymerization times, the weight gain at 0.3 mA cm^{-1} was 1.2–1.6 times lower than when the current density was 0.5 mA cm^{-1}. However, from previous work[1] it is known that low current densities enable the formation of even coatings. Thus, all further electrochemical reactions were carried out at a current density of 0.3 mA cm^{-1}.

The data in *Figure 3* show that the copolymerization rates of all three monomer compositions are almost identical, and equal to approximately 1.25% weight gain per minute. However, for the same reaction duration, the increase of MMA in the monomer feed decreases the weight gain of the copolymer on the CF.

The influence of the content of the monomer mixture in the monomer feed on the weight gain at identical reaction times is presented in *Figure 4*. Linear relationships were found with deviations at longer reaction times. The best least-squares fitted line for the electropolymerization time of 20 min (*Figure 4* line 1) had a correlation coefficient of 0.996, which dropped to 0.814 when the reaction time reached 60 min (*Figure 4*, line 5).

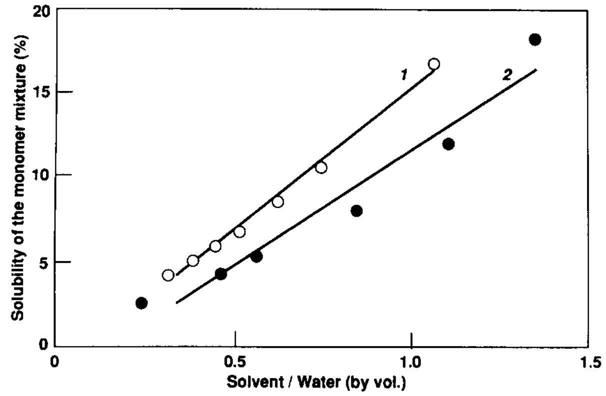


Figure 1 Variation of the solubility of the monomer mixture with solvent content in the monomer–electrolyte solution. Monomer mixture: MMA/GMA = 0.35:0.65 (mole fraction). Solvent: (1) γ-butyrolactone, (2) N,N-dimethylformamide

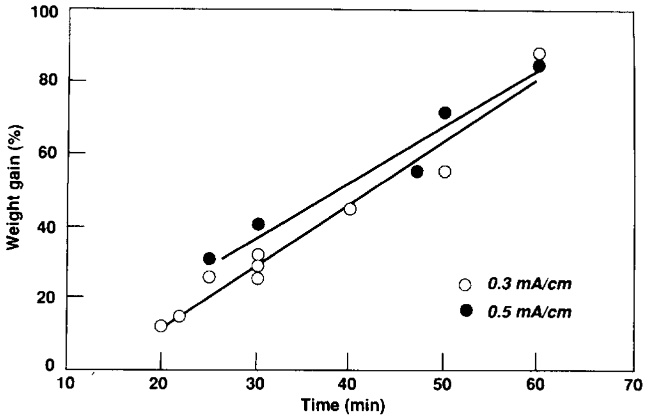


Figure 2 Variation of the weight gain with the duration of the electrocopolymerization of MMA with GMA: $DMF/H_2O = 1:1$ (by volume); MMA/GMA = 0.35:065 (mole fraction); content of monomer mixture and LiCl in the working solution, 10% (by volume) and 0.09 M, respectively

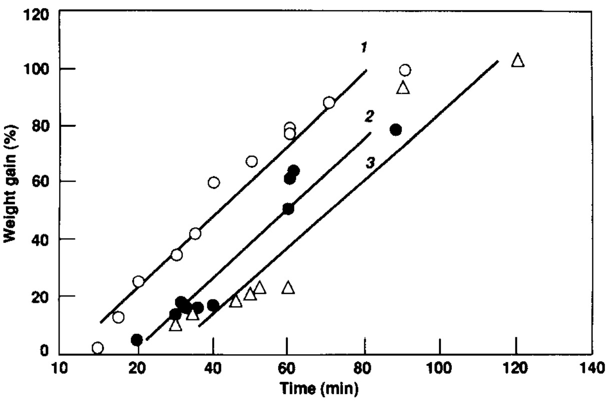


Figure 3 Variation of the weight gain with the duration of the electrocopolymerization of MMA with GMA: MMA/GMA (in mole fractions) for (1) 0:1, (2) 0.57:0.43 and (3) 0.73:0.27; monomer and LiCl concentrations as in *Figure 2*

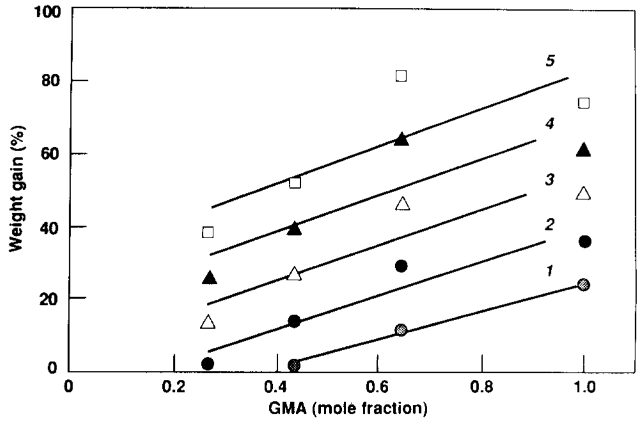


Figure 4 Variation of the weight gain with GMA content at different electrocopolymerization times: (1) 20, (2) 30, (3) 40, (4) 50 and (5) 60 min. Monomer and LiCl concentrations as in *Figure 2*

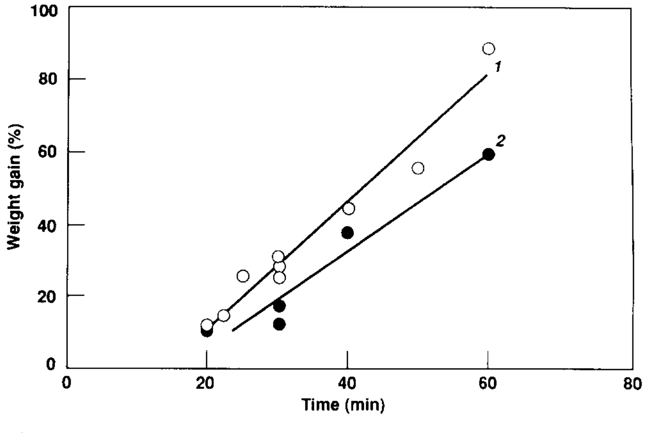


Figure 5 Variation of the weight gain with the duration of the electrocopolymerization of MMA with GMA at different electrolyte concentrations: (1) 0.09 M and (2) 0.06 M LiCl. Monomer and solvent content as in *Figure 2*

The dependence of polymerization yield on electrolyte concentration is presented in *Figure 5*. The polymerization rate was higher at higher electrolyte contents, and equalled 1.74 and 1.32%/min for concentrations of 0.09 and 0.06 M, respectively.

For spectroscopic characterization, samples of CF coated with copolymers of different compositions (see *Table 1*) were prepared. The conversion of the reactions did not exceed 5%.

It was expected that, at the cathode, the double bonds of MMA and GMA would be initiated by hydrogen radicals and react[5], and that the oxirane ring – the second functional group of GMA – would remain unchanged[5,6]. In fact, when the polymer-coated CFs were exposed to Soxhlet extraction with acetone or methylene chloride, only a fraction of the coating dissolved. The insoluble part of the copolymer was directly proportional to its GMA content (*Figure 6*): the increase of the GMA mole fraction in the monomer feed from 0.27 to 1.0 raised the insoluble fraction of the copolymer by a factor of 2.

The presence of the insoluble part of the copolymer can be explained either by its crosslinking with the assistance of the opened oxirane ring, or by grafting of the copolymer onto the active CF surface.

The solvent AN was also tested. As the solubility of GMA in AN is poorer than in DMF, the concentration of the monomer in the solvent mixture AN/H_2O = 2.2:1 was 7%. At current densities of 0.5–2.0 mA cm^{-1} and electropolymerization times up to 24 h, no coating on CF was obtained. This phenomenon is apparently connected with the different structures of the investigated solvents, AN and DMF. Evidently, AN is sorbed on the surface of the filaments, which leads to a deactivation of the grafting centres on the CF[8].

It was deemed of interest to clarify which of the components of the monomer–electrolyte (working) solution is responsible for the strong bonds between the polymeric layer and the CF surface.

As mentioned above, alkali-metal carboxylate groups (on carbon black) react with GMA and open its oxirane rings. The electrocopolymerization of GMA with MMA on the surface of CF is carried out in the presence of LiCl. Therefore, it was decided to replace LiCl by an electrolyte that does not contain metal ions (H_2SO_4 at low concentration) or by a salt with a lower dissociation constant ($AlCl_3$), and to test their influence on the solubility of the electrochemically obtained coatings.

Figure 7 shows that the kinetics of the reaction is almost independent of the type of electrolyte (cf. Nos 2, 3 and 4). Surprisingly, H_2SO_4, at a mole fraction ratio of GMA/MMA = 0.65:0.35, led to higher copolymerization rates (line 1 in *Figure 1*). It should be noted that all layers obtained on the surface of CF from reaction solutions with different types of electrolytes were only partly soluble in organic solvents (*Table 2*, Nos 2, 5–7). The soluble fraction content was inversely proportional to the amount of GMA in the monomer mixture. Again, the layers that were formed at unexpectedly high copolymerization rates (*Figure 7*, line 1) comprised increased insoluble polymer fractions (*Table 1*, No. 6).

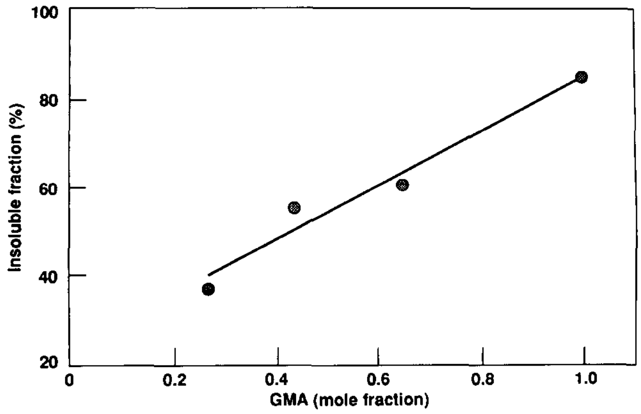


Figure 6 Variation of the insoluble fraction of the copolymer with GMA content in the monomer feed

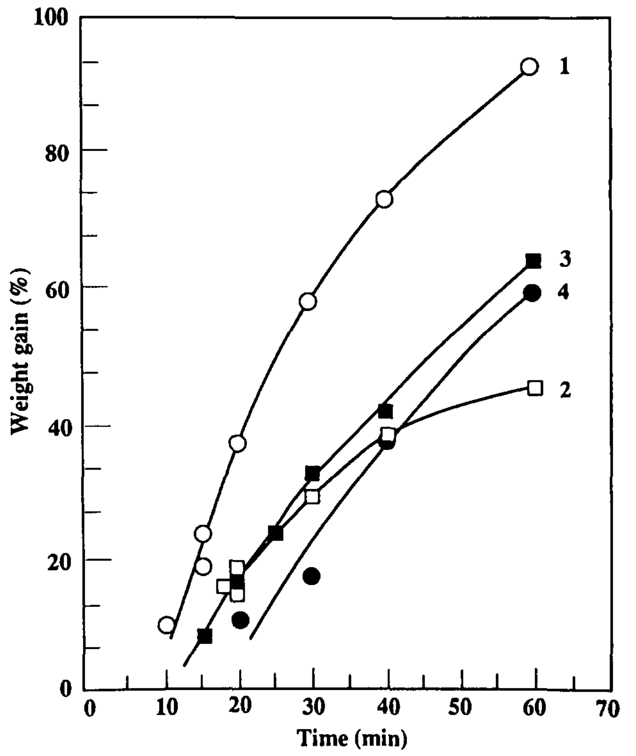


Figure 7 Variation of the weight gain with the type of electrolyte: (1) and (2) H_2SO_4, (3) $AlCl_3$ and (4) LiCl. Monomer and electrolyte concentration as in *Figure 2*; GMA/MMA (in mole fractions) for (1), (3), (4), 0.656:0.344; and (2) 0.206:0.794; the pH of working solutions 1, 2, 3 and 4 was 1.9, 1.9, 3.7 and 9.6, respectively

From these tests it can be concluded that the pH of the monomer–electrolyte solution and the degree of dissociation of the electrolyte do not influence the persistence of the copolymer on the CF after extraction by solvent.

It has been reported that methylene chloride removes all the poly(MMA-*co*-MA) present, which was obtained by electrochemical copolymerization of MMA with MA on CF, from their ethanol or water/ethanol solutions[1]. Therefore it was of interest to check the solubility of polyMMA synthesized under the same conditions as poly(MMA-*co*-GMA). At current densities of 0.5–1.4 mA cm^{-1} and a reaction time of approximately 24 h, a weight gain of 380% was obtained, which was entirely soluble in acetone and methylene chloride.

These experiments led us to the assumption that the oxirane ring of GMA is involved in the creation of the strong bonds between the polymeric layer and the surface of CF. To explain the nature of this link, *FT*i.r. and n.m.r. tests were conducted.

The *FT*i.r. analyses of the soluble fraction of the copolymer and of the insoluble part pulverized with CF were performed on dried potassium bromide pellets. The

Table 2 Characteristics of GMA/MMA copolymer coatings on carbon fibres[a]

	Mole fraction of GMA in copolymer		T_g (°C)				
No.	Calculated	Determined by n.m.r.	Expected	Determined by d.s.c.	Absorbance ratio A_{908}/A_{1731}	Type of electrolyte	Soluble copolymer fraction (%)
1	1.0	1.0	46	41	0.360	LiCl	16
2	0.656	0.67	60	62	0.195	LiCl	40
3	0.464	0.44	70	70	0.172	LiCl	45
4	0.304	0.33	80	81	0.152	LiCl	63
5	0.656	–	60	–	–	$AlCl_3$	35
6	0.656	–	60	–	–	H_2SO_4	10
7	0.206	–	87	–	–	H_2SO_4	82

[a] The content of the monomer–electrolyte solution: DMF/H_2O = 1:1 (by volume); monomer and electrolyte concentrations 10% and 0.06 M, respectively

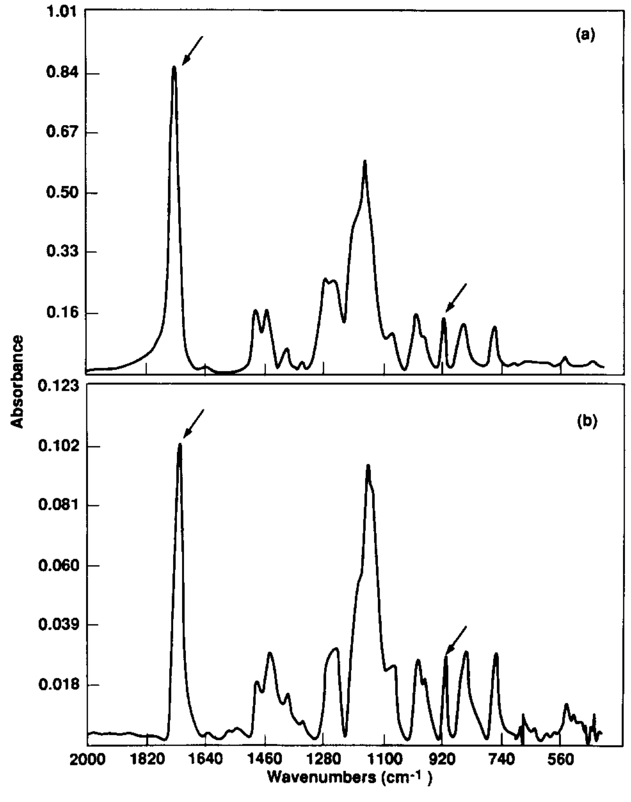


Figure 8 *FT*i.r. spectra of (a) dichloromethane-soluble fraction of poly(MMA-*co*-GMA) and (b) dichloromethane-extracted coated fibres examined by the a.t.r. technique. Polymer composition No. 1 (*Table 1*)

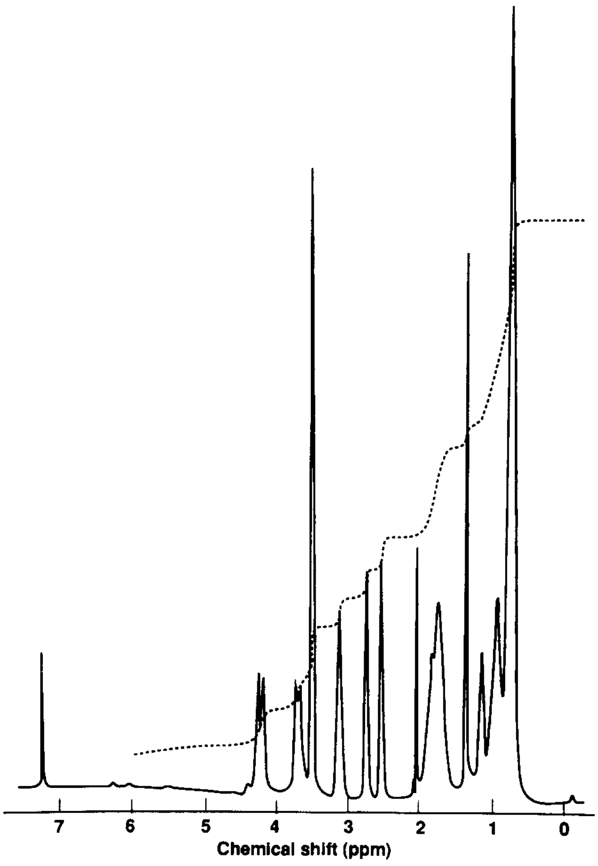


Figure 9 N.m.r. spectrum of the dichloromethane-soluble fraction of poly(MMA-*co*-GMA) in deuterochloroform at room temperature. Polymer composition as in *Figure 8*

extracted fibres with the insoluble part of the copolymer on their surface were also examined in reflected i.r. beams. The i.r. spectra in the wavenumber region from 2000 to 400 cm^{-1} of one of the GMA/MMA copolymers are presented in *Figure 8*. The peaks at the wavenumbers 908 and 1731 cm^{-1} were selected as the most suitable ones for the analysis of epoxy and carbonyl groups, respectively (*Figure 8a*). The peaks of the same groups, when measured in reflected i.r. beams, are shifted to the right (*Figure 8b*) and are equal to 905 and 1722 cm^{-1}, respectively.

The absorbance ratios $A_{epoxy}/A_{carbonyl}$ and the corresponding calculated GMA mole fractions in poly(GMA-*co*-MMA), as copolymeric interlayers with T_g values of 60, 70 and 80°C, are presented in *Table 2* (columns 6 and 2 respectively). As expected, the ratio of the absorbances diminishes with a decrease in the GMA content.

In order to determine whether the calculated mole fractions correspond to the real ones, n.m.r. tests of copolymers with different GMA content were carried out. One of the spectra obtained is presented in *Figure 9*. The average integral ratio of the five protons of the glycidyl group

to the three protons of the methoxy group CH_3–O gives a mole fraction content of GMA/MMA=0.67:0.33 (*Figure 9*). The n.m.r.-determined mole fractions, which are almost identical to the calculated ones, are presented in column 3 of *Table 2*.

The absorbance ratio of 908 cm^{-1} vs. 1731 cm^{-1} (column 6) is linearly related to the GMA content (column 3) in the copolymer and can be expressed by the following equation:

$$A_r = 0.308F_g + 0.033 \qquad (1)$$

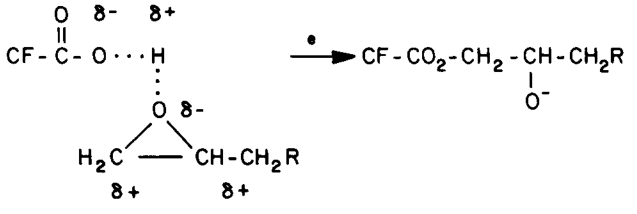
where A_r is the absorbance ratio of 908 and 1731 cm^{-1}, and F_g is the mole fraction of GMA, containing the epoxy group, in the copolymer. The intercept 0.033 is considered to be a correlation factor arising from the very weak absorption of polyMMA at wavenumbers near 908 cm^{-1} (ref. 9). This best least-squares fitted line has a correlation coefficient of 0.95.

The glass transition temperatures of the soluble part of the GMA/MMA copolymers determined by d.s.c., and the expected ones (columns 5 and 4, *Table 2*) from the calculated mole fractions, are almost equal.

From the instrumental measurements it can be concluded that the mole fraction of GMA in GMA/MMA copolymers can be calculated with high precision from T_g (see equation (1) in ref. 1) and n.m.r. determinations. The mole fraction can also be calculated with sufficient accuracy by introducing the *F*Ti.r. data into equation (1).

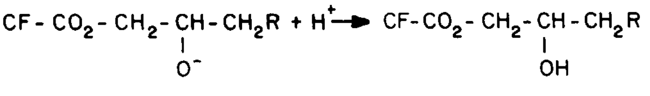
The *F*Ti.r. spectra of the coated fibres after extraction were approximately eight times less intense than those of the soluble fraction (cf. (a) and (b) in *Figure 8*). The absorbance ratio A_{905}/A_{1722} decreases with an increase in the MMA content. Thus, at calculated mole fractions of MMA of 0, 0.344, 0.536 and 0.696, the absorbance ratio was found to be 0.298, 0.272, 0.225 and 0.206, respectively. The presence of the epoxy group in a quantity surprisingly higher than in the soluble fraction (cf. the absorbance ratios of both copolymer fractions) is evidence that the oxirane group does not lead to a crosslinking of the copolymer.

It is known that anodic oxidation of graphitic materials in aqueous solutions creates surface oxides, consisting mainly of carboxylic and phenolic groups[6,10]. As mentioned above, the CF used were electrochemically oxidized by the manufacturer. Thus, the insolubility of a part of the GMA/MMA copolymer can be explained by a grafting reaction on the cathode between the carboxyl groups on the CF surface and the oxirane ring, as follows:



where R is $CH_2{=}C(CH_3){-}CO_2{-}$.

In a solvent mixture DMF/H_2O=1:1 there are sufficient cations H^+ at the cathode, which do not allow continuation of the ring-opening polymerization through the epoxy groups, and the process is terminated:



$$CF{-}CO_2{-}CH_2{-}\underset{O^-}{CH}{-}CH_2R + H^+ \longrightarrow CF{-}CO_2{-}CH_2{-}\underset{OH}{CH}{-}CH_2R$$

Thus, it may be assumed that the chemical bonding of the copolymer with the CF surface is carried out by the formed ester groups, which cannot be determined by the instrumental methods used.

The radical copolymerization of the monomers at the cathode occurs in accordance with a well established mechanism[5]. It includes electrochemical formation of an initiator on the electrode surface (the hydrogen radical in this case), followed by typical polymerization steps.

Cyclic voltammetry of GMA and MMA in aqueous and non-aqueous solutions was performed (*Figure 10*). At a potential of −3.0 V the current, which passed through the solution of the electrolyte in water, was 3.5 mA (curve 1). Replacement of water by DMF diminished the current 10-fold (cf. curves 2 and 1). Addition of water or GMA to solution 2 (*Figure 10*) almost did not change the current value (see curves 2, 3 and 4). A synergistic effect was observed when GMA was fed into a DMF/water mixture: at the same potential (−3.0 V) the developed current was approximately 10 times higher (cf. curves 5 and 3). Practically no current change took place when MMA was added to the DMF/water mixture (cf. curves 6 and 3 in *Figure 10*).

It should be noted that when the experiments were performed in the range of +1.0 to −2.5 V, peak currents were observed at −0.8 to −0.9 V (in aqueous solutions) and at −1.1 to −1.3 V (in non-aqueous solutions).

Morphology and micro-level homogeneity of the coatings

The morphology and homogeneity of the coatings were examined by SEM. *Figure 11a* indicates the texture of an uncoated CF: the surface is smooth but wavy. When the fibres were coated with a polyGMA homopolymer, the structure of the surface was globular (*Figure 11b*). On the micrograph with a magnification of 15000, globules varying in size between 100 and 600 nm can be distinguished (*Figure 11c*).

The surface of the coating from poly(MMA-*co*-GMA) with a mole fraction of 0.65 GMA in the copolymer (No. 1, *Table 1*) was still globular (*Figure 12a*). After extraction with methylene chloride, the surface became almost smooth (*Figure 12b*). The micrograph of the fibre coated with a copolymer having a mole ratio of MMA/GMA=0.7:0.3 shows that polymerization occurred along the fibre axis, forming structures that resemble the wavy texture of the uncoated fibres (*Figure 12c*). However, there are still rare hillocks, arising from the

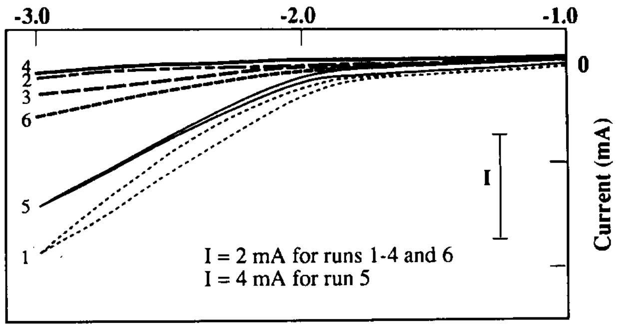


Figure 10 Cyclic voltammograms at a cathodic sweeping rate of 100 mV s^{-1} of: (1) LiCl in water; (2) LiCl in DMF; (3) LiCl in DMF/water (1:1); (4) GMA (10%) and LiCl in DMF; (5) GMA (10%) and LiCl in DMF/water (1:1); and (6) MMA (10%) and LiCl in DMF/water (1:1). The LiCl concentration in the above listed solutions was 0.06 M

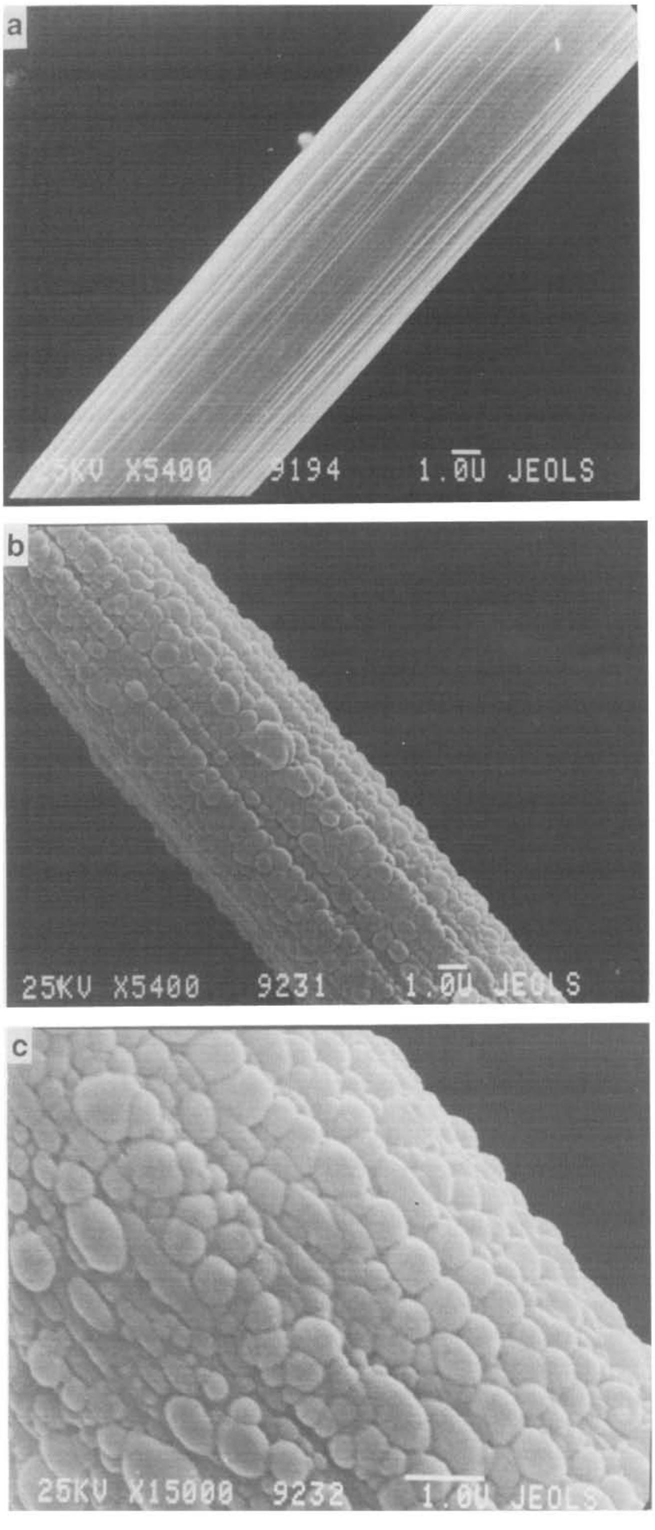


Figure 11 SEM micrographs of polyGMA on CF: (a) uncoated CF; (b) and (c) CF coated with 12.6% of polyGMA at different magnifications

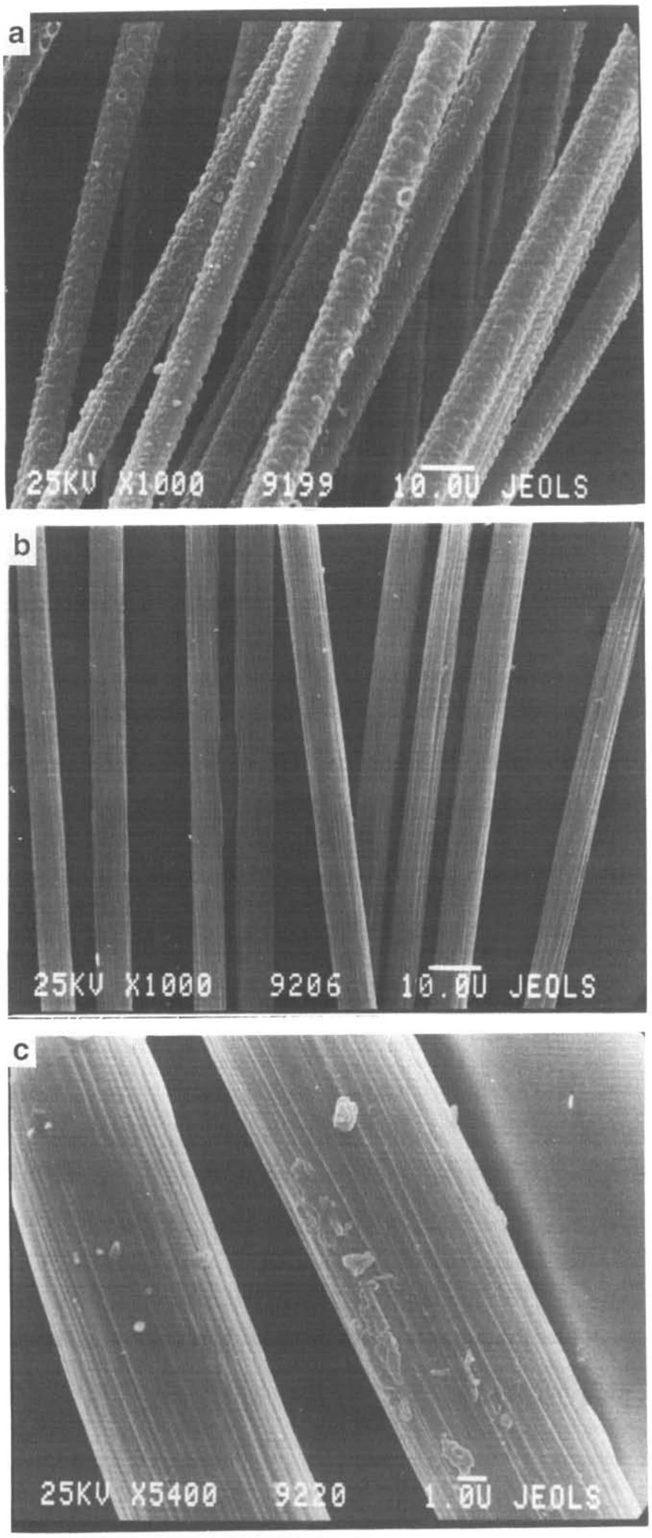


Figure 12 SEM micrographs of poly(MMA-*co*-GMA) on CF: (a) fibres coated with 11.9% of copolymer; (b) after extraction (25.2% coating before solvent treatment); (c) fibres coated with 9.8% of copolymer. In (a) and (b) the GMA content was 0.65, in (c) it was 0.3 (mole fraction)

fibre surface, which disappear after extraction in methylene chloride.

It should be noted that the coating of all samples examined by SEM (*Figures 11* and *12*) was performed in solutions that contained equal volume quantities of the solvent (DMF) and precipitant (H_2O) and 0.09 M of LiCl. The increase of DMF by a factor of 2 detrimentally altered the surface of the polymer coatings, on which growths appeared (*Figure 13a*). Decreasing the electrolyte concentration to 0.06 M slowed down the electrocopolymerization rate and promoted the formation of thin, even coatings (*Figure 13b*), using the monomer compositions listed in *Table 1*.

Mechanical tests

The samples were prepared according to the technique described in ref. 1, and the interlaminar shear strength

Table 3 Strain-energy release rate (G_{Ic}) and interlaminar shear strength (*ILSS*) of composites, reinforced with CF, uncoated or coated with poly(MMA-*co*-GMA)

No.	T_g of copolymer layer (°C)	Weight gain (%)	Layer thickness (calculated) (nm)	G_{Ic} (J m^{-2})	ΔG_{Ic} (%)	*ILSS* (MPa)	Δ*ILSS* (%)
1[a]	–	–	–	475	–	67	–
2	60	12.2	308	1025	116	74	10
3	80	13.2	332	770	62	80	20

[a] CF sized by manufacturer

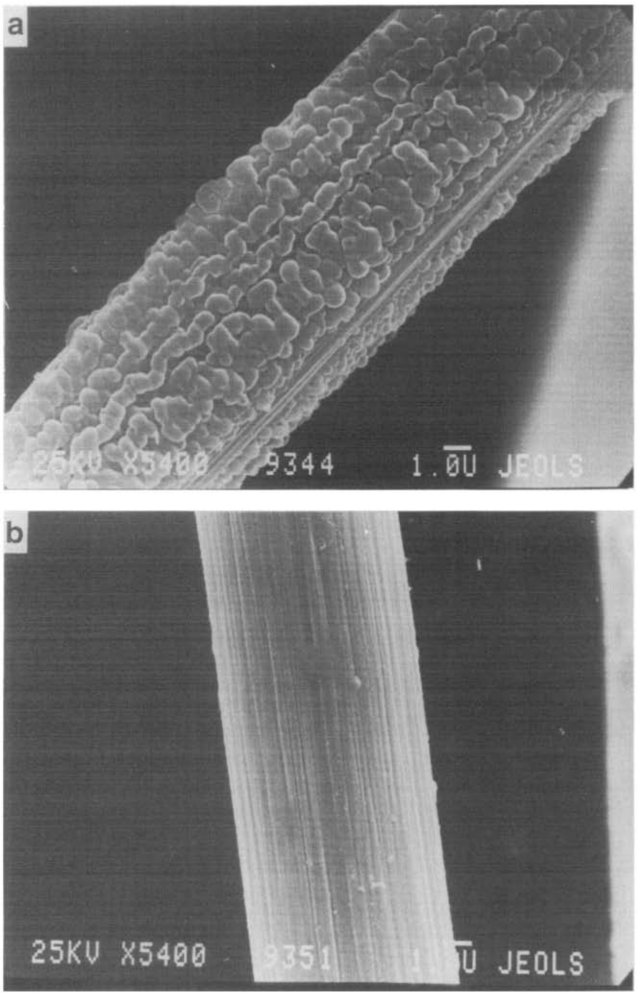


Figure 13 SEM micrographs of poly(MMA-*co*-GMA) on CF with coating carried out: (a) in a mixture of DMF/H_2O=2:1 and (b) in the presence of 0.06 M LiCl. MMA/GMA ratio as in *Figure 12a*

and the change of the fracture energy during delamination were tested.

The composition of the coating was the major parameter whose effect was investigated in the present study. *Table 3* presents the average G_{Ic} values of five tests for fibre contents of approximately 60%. In general, they show that all composites prepared from coated CF, independent of the T_g of the layer, demonstrate higher G_{Ic} (60–100%) and *ILSS* (10–20%) than do the specimens from untreated CF.

The ductility of the coatings influences the composite's G_{Ic}. The G_{Ic} of composite No. 2 (*Table 3*) is therefore higher than that of specimen No. 3, which differs from the first in T_g. The opposite trend was observed in the *ILSS* tests, evidence that the fracture energy during delamination is of the same order as the impact resistance.

CONCLUSIONS

The electrocopolymerization of GMA and MMA was investigated. Replacement of MA[1], in the electrochemical copolymerization coating process of CF, by GMA required qualitative and quantitative changes in the working solution. The latter contained the monomers and the electrolyte (LiCl) dissolved in a DMF/water mixture. At low current densities (<0.5 mA cm^{-1}), thin (submicrometre), even coatings of poly(GMA-*co*-MMA) on CF were obtained. The mole fraction of GMA in the synthesized copolymers was determined with high precision from T_g and n.m.r. analysis. It can also be calculated with sufficient accuracy by introducing the i.r. data into an empirically obtained equation. No difference between the calculated and determined monomer fractions in the copolymer was observed. This is evidence that the reactivity ratios of MMA and GMA used[7] also fit the electrochemically initiated reaction. The insolubility of the coatings is explained by the grafting reaction between the carboxyl groups on the surface of the CF and the oxirane rings.

Composite material specimens reinforced with poly(GMA-*co*-MMA) coated CFs (60% fibre content) showed an improved G_{Ic} (60–100%) in comparison with specimens from untreated CF. Electrocoating with the above-mentioned copolymer also increased the *ILSS*, by a factor of 1.2.

ACKNOWLEDGEMENTS

This research was supported by the Israeli–European Community Science Foundation. The authors wish to thank Professor H. Höcker for the n.m.r. analyses carried out at the Wollforschungsinstitut, Aachen, Germany.

REFERENCES

1 Shkolnik, S. and Höcker, H. *Polymer* 1992, **33**, 1669
2 Tsubokawa, N., Yamada, A. and Sone, Y. *Polym. Bull.* 1983, **10**, 63
3 Wallace, R. A. and Vijayaraghavan, N. V. *Polym. J.* 1973, **5**(1), 105
4 Matyushova, V. G., Lipatova, T. E. and Lipatov, Yu. S. *Dopov. Akad. Nauk Ukr. RSR* (*B*) 1986, **4**, 48
5 Zinger, B., Shkolnik, S. and Höcker, H. *Polymer* 1989, **30**, 628
6 Donnet, J. B. and Bansal, R. C. 'Carbon Fibers', Marcel Dekker, New York, 1990, p. 213
7 Brandrup, J. and Immergut, E. H. 'Polymer Handbook', Interscience, New York, 1966, p. II-209
8 Lipatova, T. E., Matyushova, V. C. and Narazhaiko, L. F. *Vysokomol. Soedin.* (*A*) 1986, **28**(10), 2043
9 Swaraj, P. and Bengt, R. *Anal. Chem.* 1975, **47**(8), 1428
10 Jannakoudakis, A. D., Jannakoudakis, P. D., Theodoridou, E. and Besenhard, J. O. *J. Appl. Electrochem.* 1990, **20**, 619