Electrocoating of carbon fibres with polyaniline and poly(hydroxyalkyl methacrylates)

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The electropolymerization of two kinds of polymer on carbon fibres is described. These coatings were selected owing to their potential to increase the interaction between the epoxy matrix and the reinforcing carbon fibres. Cathodic and anodic polymerizations were carried out to provide submicrometre coatings of poly(hydroxyalkyl methacrylates) and polyaniline, respectively. The formation of conductive polyaniline was traced using common electrochemical techniques, and its electrochemical behaviour was investigated. In a non-continuous process, the uniformity of the coatings depended on the surface properties of the carbon fibres, namely the existence of a thin sizing coating, and on the nature of the new polymer layer. Modification of the grip of the tows during the electrochemical process enables the formation of a uniform coating, which is essential from the practical point of view.

(Keywords: electropolymerization; carbon fibres; poly(hydroxyalkyl methacrylates); polyaniline)

INTRODUCTION

Carbon fibres (CF) are among the most promising of high-modulus, high-strength filamentary materials currently used in making plastic composites. Their reduced cost, good performance, low specific weight and outstanding chemical properties have vastly increased their use in aircraft and space applications, and are extending their applications to fields such as sports goods, medical prostheses, body armour, etc.

A serious problem concerning the utilization of CF as a reinforcement for epoxy resins is the low interlaminar shear strength of the resultant composites. In order to improve this, surface modifications (chemical, electrochemical or thermal) are performed on-line in the manufacture of CF. These treatments roughen the surface of the fibres, add functional groups and, consequently, increase the fibre–matrix interactions. A severe drawback of surface treatments is that they invariably lower the impact strength of the composite. It was found, both experimentally[1–3] and theoretically[4], that a submicrometre polymer interlayer introduced between the fibre and the matrix acts as a 'shock absorber' at the interface[5] and thus lowers the probability of crack formation.

Electrochemical techniques are widely used for producing the polymers[6]. Interface tailoring on CF, which seems to be the most promising approach to maximizing the mechanical properties, can be performed by an electrochemical method[7–9]. In this method, monomers are electrochemically polymerized on CF, functioning as an electrode in the process. Electrocoating of CF has the following advantages: (1) polymerization takes place mainly on the surface; (2) film thickness and homogeneity are easily controlled by the applied current or voltage; (3) wetting of the surface by the monomer will provide a uniform film on the porous surface; (4) the chemical and physical properties of the film can be controlled by proper choice of monomer(s) and reaction conditions; (5) the electrochemical process is simple and rather inexpensive, and therefore can be extended from laboratory to continuous semi-industrial scale without radical technological changes.

In spite of the potential advantages inherent to the electrocoating procedure, only a few examples have appeared in the literature[7–9]. In these publications, however, the details of the electrochemical process were seldom reported. In this communication the electropolymerization of poly(hydroxyalkyl methacrylates) and polyaniline on CF will be described. Cathodic and anodic polymerizations will be utilized to obtain uniform layers on CF, having different surface properties.

EXPERIMENTAL

Materials and electrochemical set-up

Hydroxyethyl methacrylate (HEMA; Merck, Darmstadt, FRG), hydroxypropyl methacrylate (HPMA; SP^2, New York) and aniline (Fluka) were distilled under reduced pressure and kept cold. Ultra-pure water (with resistivity of 17.5 MΩ) was used. Hydroquinone monomethyl ether (Fluka) was used as inhibitor without further purification.

ACIF-XHT™ carbon fibres were from ACF kibbutz, Afikim, Israel. They are extra-high-strength polyacrylonitrile- (PAN-) based fibres manufactured in tows of 6000 and 12 000 filaments. The diameter of a single filament is 7 μm. During their manufacture the filaments are dip-coated with an epoxy resin, the so-called sizing step, in order to improve their handling properties. The

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original sized CF (denoted CF_s) and unsized CF (denoted CF_{us}) were used. The unsized fibres were obtained by extraction of CF_s in trichloroethane for 15 h and drying for 12 h at 70°C. The weight loss of the fibres during this process was 1.5–2.2%. Another unsizing 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 of the fibres. Hence, only the extraction process was employed to obtain CF_{us} for coating purposes.

Two kinds of electrochemical cells were used:

(1) *Three-compartment cell.* The central chamber contained the solution (electrolyte and monomer), the working electrode (namely the CF) and a reference electrode. The two outer compartments, which contain only the electrolyte, were separated from the central one by porous sinters on which a salt bridge was layered. The salt bridges maintain a physical barrier against diffusion of monomer from the central compartment, and the sinters assure electrical communication between the solutions in the compartments.

(2) *Undivided cell.* This one-compartment cell contains the CF as a working electrode, surrounded by a cylindrical counter-electrode. Nitrogen was bubbled in all the compartments of these cells in order to maintain an inert atmosphere throughout the experiments.

The working electrode was constructed of CF, wrapped around an inert rectangular Teflon frame. It was connected to a metallic holder and kept in the centre between the two counter-electrodes. The symmetrical structure of the cell with respect to the carbon fibres induces a homogeneous electrical field, so that a uniform coating around the fibre is obtained. The counter-electrodes were carbon cloth, reinforced by a bag made of polypropylene web. They were pressed against the salt bridge in order to decrease the distance to the working CF electrode and thus to minimize the total resistivity of the cell. Two kinds of reference electrodes were used, according to the electrolyte of the solution: mercury sulphate electrode (MSE) and saturated calomel electrode (SCE), in sulphuric acid or hydrochloric acid, respectively.

Preparative electropolymerization

After assembling the electrochemical cell, the system was purged with nitrogen and the coating was carried out in a stirred solution. The reaction was controlled by applying constant current or voltage, which was either the total voltage (working – counter-electrodes) or the relative potential (working – reference electrodes). During the reaction the total voltage, relative potential and current were monitored. The electropolymerization of hydroxyalkyl methacrylates was carried out in a controlled current mode, while a potentiostatic mode was used for the polymerization of aniline. At the end of the electrolysis, the CF were removed from the solution, rinsed thoroughly with water and dried at 50°C to a constant weight (45 min). The edges of the tow were cut, the weight gain was measured and reported as a percentage with respect to the initial weight of the tow.

Voltammetric behaviour of polyaniline

Cyclic voltammetry, chronoamperometry and chronopotentiometry were carried out in an undivided cell, in which a carbon rod and calomel (SCE) were used as counter- and reference electrodes, respectively. An RDE 3 bipotentiostat (Pine Instruments, Grove City, PA) in conjunction with a Yokagawa 3086 *X–Y* recorder were used in the voltammetric experiments. The experiments were carried out under argon atmosphere in unstirred solution.

Scanning electron microscopy

SEM was performed on a JEOL JSM-1300 instrument at 25 kV.

RESULTS AND DISCUSSION

The criteria for selecting poly(hydroxyalkyl methacrylates) and polyaniline as coatings on CF were: (a) the feasible interactions between the functional groups of these polymer layers and the components of the epoxy matrix in the composites; (b) the solubility of these monomers, to a reasonable extent, in the reaction medium, whereas the resultant polymers are insoluble and hence deposited on the electrode (the CF). In the electropolymerization of hydroxyalkyl methacrylates, hydroquinone monomethyl ether was used as inhibitor. The inhibitor assists in the production of a uniform coating on the fibres by preventing the formation of homopolymer in the solution for a long period of time.

Polymerization of HEMA

The electropolymerization of HEMA was carried out in the cathodic compartment of a divided cell. Acidic solution (0.1 M H_2SO_4) was used as electrolyte. The polymerization mechanism of acrylic and methacrylic monomers in a cathodic process is well established[6], and can be described as an *indirect electropolymerization* process. It includes electrochemical formation of initiator on the electrode surface (hydrogen radical in this case), followed by typical polymerization steps. Addition of hydrogen radical to the double bond yields a monomer radical, and the latter starts the propagation step by subsequent addition to the double bond of another monomer. Termination of chain growth occurs through coupling with existing radicals. The mechanism of this radical polymerization process is as follows:

$$\begin{array}{llll} H_3O^+ + e^- & \rightarrow H^\cdot + H_2O & (E) & \\ H^\cdot + M & \rightarrow MH^\cdot & (C) & \text{Initiation} \\ MH^\cdot + nM & \rightarrow (M)_nMH^\cdot & (C) & \text{Propagation} \\ (M)_nMH^\cdot + MH^\cdot & \rightarrow H(M)_{n+2}H & (C) & \\ \text{or} & & & \text{Termination} \\ (M)_nMH^\cdot + H^\cdot & \rightarrow H(M)_{n+1}H & (C) & \end{array}$$

Parallel reactions

$$\begin{array}{lll} 2H^\cdot & \rightarrow H_2 & \text{Evolution of hydrogen} \\ MH^\cdot + H^\cdot & \rightarrow MH_2 & \text{Reduction of the monomer} \end{array}$$

Here E represents an electrochemical step, C a chemical step, and M is monomer.

During the reaction, hydrogen evolution was observed from the CF, the rate of which was dependent on the applied potential/current. The variation of the weight gain with the parameters of the reaction is presented in *Table 1*.

From *Table 1* the following conclusions can be drawn: (1) the weight gain is scaled up linearly with the increase of the total voltage; (2) when constant current density is

Table 1 Variation of weight gain with reaction parameters in the electropolymerization of HEMA on CF_s[a]

Total voltage (V)	Relative potential (V)[b]	Current density ($mA\,cm^{-1}$)[c]	Time (min)	Length of fibres (cm)	Weight gain (%)
4	1.98	13.3	20	3	31
5	2.20	26.6	20	3	41
6	2.25	38.3	20	3	46
		11.4	25	3.5	22
		11.4	25	10	25
		11.4	25	15	22
3.96	2.03	13.3	5	30	2
3.88	2.07	13.3	10	30	6.5
4.01	2.03	13.3	15	30	14
4.06	2.04	13.3	20	30	31.5
4.2	2.03	13.3	25	30	37.5

[a] The electrolyte was 0.1 M H_2SO_4; the concentration of HEMA was 4%; hydroquinone monomethyl ether (1.25% relative to the monomer) was used as inhibitor

[b] Potential relative to mercury sulphate reference electrode

[c] Current per cm length of the tow

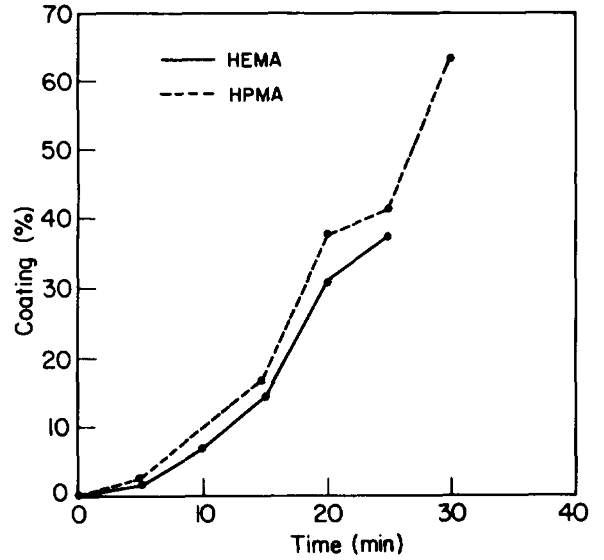

Figure 1 Variation of the weight gain with the duration of the electropolymerization of HEMA and HPMA on CF_s. Experimental conditions defined in *Table 1*

applied during the reaction the weight gain is constant regardless of the length of the CF; (3) the dependence of the weight gain on the duration of the reaction is not linear (*Figure 1*); (4) the relative potential in the polymerization is constant, regardless of its duration, whereas the total voltage increases at long reaction times. In addition it was found that decrease of the monomer concentration from ~4% to 2% caused a decrease in weight gain from 20–33% to 7–15%.

When the coating exceeded ~15–20% the CF were whitened, lost their flexibility and the filaments were bound together.

The best conditions to obtain weight gain of 20–30% were: current density (current per length of the tow) of 3 mA cm^{-1} for 15–20 min in a solution containing 4% of the monomer and 1.25% of the inhibitor (relative to the monomer). Under these conditions about 12 polymerizations were possible in the same monomer solution.

Polymerization of HPMA

The experimental system used for the coating of CF with poly(HPMA) (PHPMA) was identical to that of HEMA. The results are summarized in *Table 2*.

The effect of the current density and duration of reaction are very similar to their effect in the polymerization of HEMA: the weight gain increases linearly with increase of the current density (*Figure 2*), but non-linear increase in weight gain was observed at longer times (*Figure 1*). A similar dependence of the relative and total potentials on the duration of the reaction was observed: the potential with respect to the reference electrode was hardly altered, but the voltage between the working and counter-electrodes increased during the polymerization. In comparison to the polymerization of HEMA, *low current density* is required to form PHPMA. Thus, the best conditions to obtain weight gain of 15–20% were: current density of 1 mA cm^{-1} for 15–20 min in a solution containing 4% monomer. The relative potential under these conditions was 1.9 V (vs. MSE). The concentration of the monomer has the expected effect

Table 2 Variation of weight gain with reaction parameters in the electropolymerization of HPMA on CF_s[a]

Total voltage (V)	Relative potential (V)	Current density ($mA\,cm^{-1}$)	Time (min)	Weight gain (%)
3.05	1.80	0.5	5	2.35
3.25	1.80	0.5	10	7.05
3.46	1.82	0.5	15	17.06
3.39	1.89	0.5	20	37.18
3.21	1.75	0.5	25	41.42
3.58	1.87	0.5	30	63.3
3.80	1.85	0.5	10	10.60
3.88	1.84	0.75	10	13.76
3.90	2.02	1.0	10	21.54
4.06	2.25	1.5	10	29.4
4.20	2.38	2.0	10	41.81

[a] The electrolyte was 0.1 M H_2SO_4; the concentration of HPMA was 4%; hydroquinone monomethyl ether (3.0% relative to the monomer) was used as inhibitor; 30 cm tow length was coated

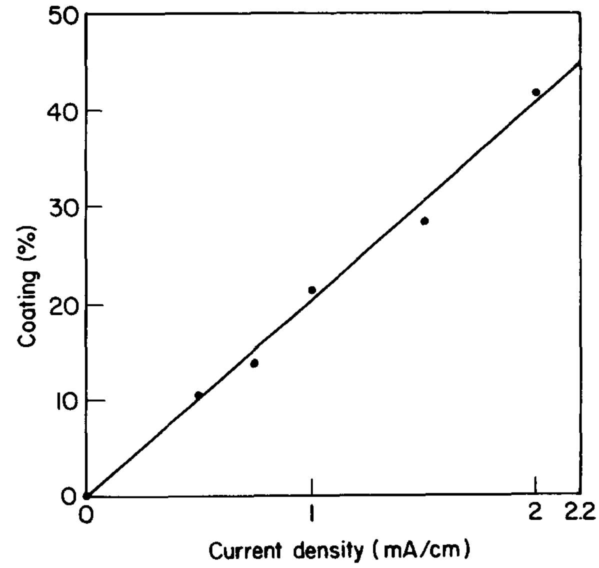

Figure 2 Variation of the weight gain with the current density applied in the electropolymerization of 30 cm CF_s with HPMA

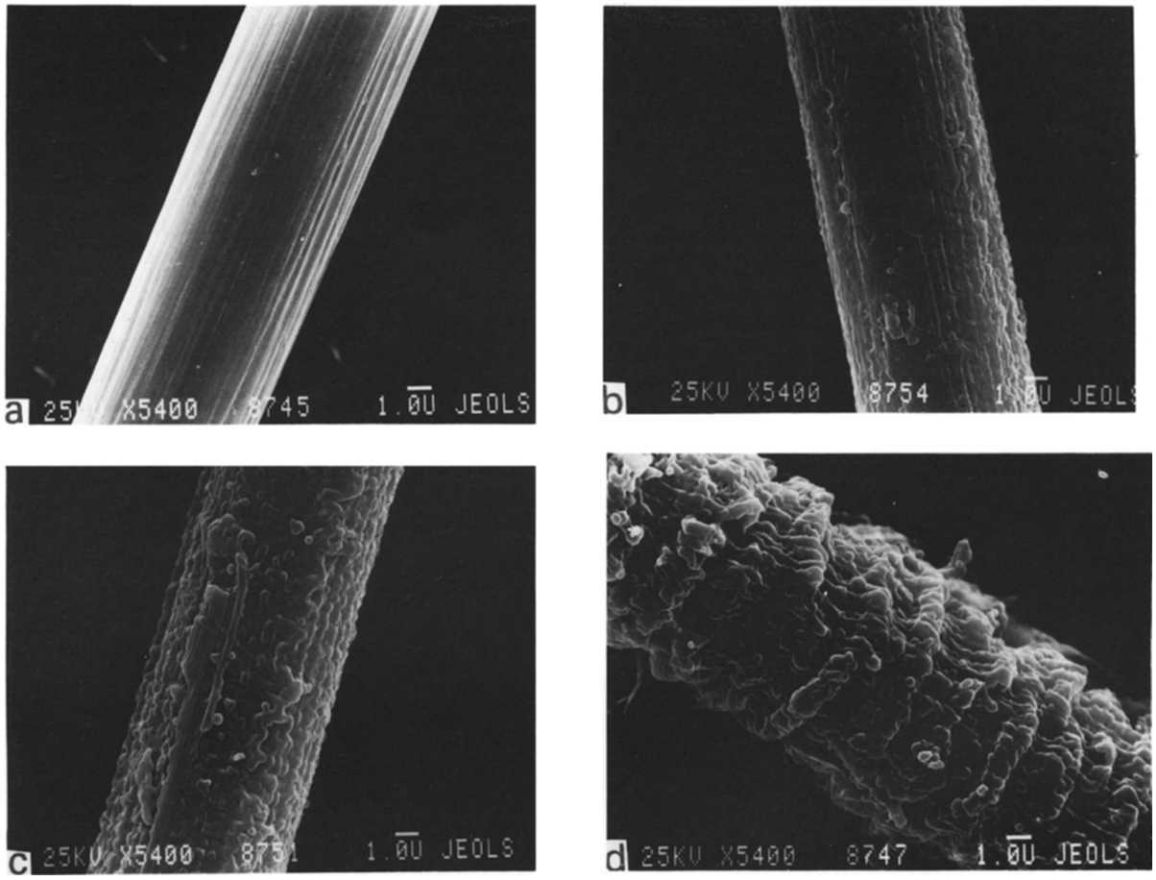

Figure 3 SEM micrographs of PHPMA on CF: (a) uncoated fibre; (b)–(d) fibres coated with 7.5, 17.5 and 32% of PHPMA, respectively

on the weight gain, e.g. when 2% monomer was used, the time required to obtain the same weight gain was doubled.

The CF/PHPMA are white coloured when coated with more than ~15%. Unlike the CF/PHEMA, the tows are *flexible* as the uncoated fibres and the filaments are not bound together.

The macro-level homogeneity of the coating is very important when utilization of the CF as reinforcing material for composite materials is considered. The homogeneity of the coating along the fibres was examined as follows: 30 cm tows coated with different percentages of HPMA were cut into 12 pieces (2.5 cm length each) and the pieces were weighed. The results show that at coatings of less than 20% the fibres are uniformly covered (e.g. 16.2 ± 2.9%), but as the weight gain increases the homogeneity decreases (e.g. 62.4 ± 13.0%). These findings were confirmed when the fibres were observed under the microscope.

A problem of inhomogeneity along the coated CF_{us} was noted. When the deposition was carried out on unsized CF, the weight gain decreased along the tow, from its connection to the metallic holder down. For example, the first and the last 5 cm of a 30 cm CF_{us} were 18 and 2% respectively. This phenomenon is interpreted as follows: one of the roles of CF sizing is to improve their handling (by increasing the interactions between the filaments). Hence, the tow can be represented as a conductor with a large cross-section, and therefore low resistivity, which is hardly affected by the length of the two*. When the sizing is removed, the tow is acting as a group of many *individual* conductors each having a very small cross-section and, therefore, the length of the filament has greater effect on their resistivity. As a result, the potential (IR) drop increases along the tow and, hence the weight gain decreases. To overcome this problem and to improve the homogeneity, the two edges of the tow were connected to the metallic holder. Thus, uniform 35 cm coated tows were obtained.

The morphology and the micro-level homogeneity of the coating were examined by scanning electron microscopy (SEM). *Figure 3a* indicates the texture of an uncoated fibre: the surface is smooth but wavy. The macro-level homogeneity of the coated CF was confirmed by the SEM studies. A change in the PHPMA morphology as a function of weight gain was observed. At low coverage the polymerization took place along the fibre axis, forming a structure that resembles the wavy texture of the uncoated fibre (*Figure 3b*). However, at high weight gains, strips of polymer (~1 μm width) perpendicular to the fibre axis were found, forming a ring-shape texture (*Figure 3d*).

Discussion

The thickness of the coating layer can be calculated from the weight gain. So, for instance, taking into account

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* In a bundle of sized fibres there is a good probability that a few fibres are bound together with the sizing layer, owing to non-ideal industrial coating process

the densities of CF and PHPMA, weight increases of 3.6, 18.9 and 40.3% correspond to thicknesses of 0.1, 0.5 and 1.0 μm, respectively.

The proposed mechanism for the electropolymerization of acrylates on the surface of CF implies that modification of the electrochemical parameters directly affects only the charge-transfer step (namely, the concentration of the hydrogen radical), which further affects the kinetics of polymerization. Thus, increase of the current density raises the concentration of the hydrogen radical. The linear relation between weight gain and current density indicates first-order kinetics of the polymerization with respect to concentration of initiator. The non-linear increase of weight gain (which corresponds to the yield of the reaction) with duration of the reaction may imply that the distribution of the products changes during the reaction. Four kinds of products should be considered: polymer coating the CF, soluble short-chain polymer fractions, hydrogen and reduced monomer (see the polymerization mechanism above). It is reasonable to assume that, at the beginning of the process, mainly soluble polymer fractions are formed and hence the yield of the insoluble polymer is low. As the reaction proceeds the soluble/insoluble product ratio changes in favour of the latter and leads to a non-linear increase of the weight gain.

Increase of the voltage between the working and counter-electrodes with longer reaction times was observed when a constant current was applied throughout the process. This phenomenon can be attributed to the increase of the resistivity of the fibres owing to the non-conducting coating that is being formed on their surface. The relative potential, a thermodynamic parameter, is unaffected by the duration of the reaction. The results in *Tables 1* and *2* show that, within the same time interval, a similar increase in weight gain caused the same increase in the total voltage.

The difference in the yield of HEMA and HPMA, at given reaction conditions, must be interpreted in terms of their intrinsic polymerization kinetics, because the concentration of the hydrogen radical should have the same effect on the two reactions. It is known that electron-donating substituents facilitate radical addition to a double bond. In HPMA the hydroxyl is separated by a carboxy and three methylene groups from the reaction centre, whereas in HEMA it is only two methylene groups. Therefore, in HEMA the electron-withdrawing effect is more pronounced. The same reasoning can account for the difference in the reactivity of the monomer radical. Accumulation of these effects during the propagation stage, where radical addition is the core process, may cause such differences in the monomer reactivity.

The deposition of poly(hydroxyalkyl methacrylates), which are insulating layers, must require that the layers are porous on either micro- or macroscale. If not, the cell impedance would increase rapidly and polymerization would cease. The cell voltage, namely the potential difference between the working and counter-electrodes, was constant during galvanostatic electrocoating of CF with even thick films (2–3 μm).

Polymerization of aniline

Polyaniline (PAn) is a conducting polymer which is different from the previously described polymers in terms of structure and mechanism of formation. This electroactive polymer can be prepared from acidic aqueous solution by the *direct oxidation* of aniline on the electrode under mild conditions. Thus, the mechanism of aniline polymerization is completely different from that of hydroxyalkyl methacrylates, where the electrochemical step is required to initiate the process. Recently, the electrochemical behaviour of PAn film on noble electrodes (e.g. platinum or gold) was investigated intensively owing to its potential applications as electrode material in storage batteries[10], coloured displays[11] and sensors[12]. A thin layer of PAn may also be adequate as the interlayer in composites reinforced with CF. Therefore, the electropolymerization of PAn on CF was investigated.

PAn was polymerized on CF in unstirred 1 M HCl solution, containing 2% of aniline, by applying a constant potential (0.8 V vs. SCE) or a constant current (2–10 mA). The duration of the reactions varied from 10 to 300 s in the voltammetric experiments, and was 15–60 min for thicker coatings. In the voltammetric runs CF tows (12 000 filaments, 1 cm length) were used as the anode in the polymerization. The coated fibres were then removed from the solution, rinsed with water and transferred to 1 M HCl solution, where cyclic voltammetry was carried out.

The potentiostatic growth of PAn film was followed during 30 min of polymerization. Complex chronoamperometric curves were observed (*Figure 4*). These curves are characteristic of nucleation-and-growth kinetics: the sharp drop of the current, observed after the positive step, can be ascribed primarily to the double-layer charging current. The current then increases, and this rising transient is followed by a steady-state current. This behaviour results from the time required to nucleate the film. During this period, mainly the propagation step takes place in a thin reaction layer near the electrode. Nucleation of oligomers and film growth on the electrode surface proceeds, and the current increases. In addition the increase of current can be attributed to the auto-catalysed production of PAn on surfaces already coated with a thin layer of PAn[13,14], and to the increase of the

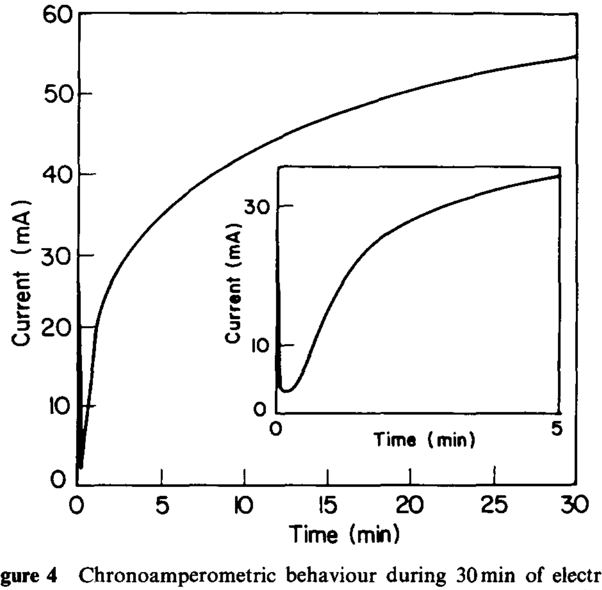


Figure 4 Chronoamperometric behaviour during 30 min of electropolymerization of aniline. Applied potential is 0.8 V vs. SCE. 2% aniline in 1 M HCl. 1 cm CF_s were used. Enlarged *i–t* curve during the first 5 min is inserted

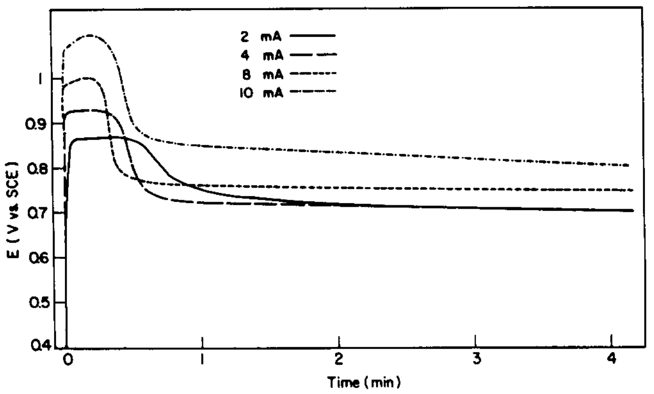
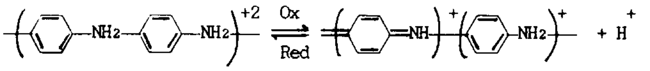


Figure 5 Potential–time curve of galvanostatic polymerization of aniline. Currents are shown in the figure. Other conditions as in *Figure 4*

electroactive area due to the formation of the conducting coating (see below).

The nucleation-and-growth mechanism was further confirmed in galvanostatic experiments (*Figure 5*). The initial potential ($V_{t=0}$) increased with the applied current: $V_{t=0}=0.87$, 0.925, 0.98 and 1.06 V at 2, 4, 8 and 10 mA, respectively. At short times ('induction time') after the current step, the potential increases. The rate of increase of potential depends on the applied current: at low currents the rise of the potential is hardly noticed, and the induction times were relatively long; whereas a notable rate of potential increase is observed at high currents. After the induction period, a rapid and then moderate decrease of potential is observed. These findings can be interpreted as follows: at short times a thin layer of PAn, the resistivity of which is greater than that of the electrode, is formed and, hence, the potential increases. The reasons for the subsequent potential decrease is the increasing of the electroactive area of the electrode because of the porosity of the PAn film, and the faster rate of aniline reacting on the CF/PAn electrode in comparison to the initial rate on uncoated CF (autocatalysis).

The cyclic voltammetry of CF/PAn is shown in *Figure 6*. Generally, the voltammetric behaviour is very similar to that reported on noble electrodes[11–14]. Between −0.2 and 0.7 V, two redox waves are observed, the larger located at 0.125 V and the smaller at ~0.5 V. The former wave is assigned to oxidation–reduction of PAn intraconversion of the benzenoid- and quinone-like structures, as shown below[11,15]:



The equation shows only the protonated structures because they are relevant to the solution conditions that were used. The peak at 0.5 V is due to the electrochemical response of the hydrolysis product and other by-products which are formed when the applied potential exceeds 0.75 V during the formation of PAn[16]. Recently this redox couple was correlated to the electrochemical response of phenazine, which is formed through crosslinked PAn chains yielding a two-dimensional structure[17]. The peak heights scale linearly with the scan rate, as expected from a thin electroactive coating. The anodic and cathodic waves are widely separated, and the peak separation (δE_p) increases with the scan rate. The dependence of δE_p on the scan rate was not observed on Pt/PAn electrode, when mild conditions were kept during the formation of the film[16,18].

Thick coatings of PAn were obtained mainly by applying a constant potential of 0.8 V between the CF and SCE in single- or multi-compartment cells. Flexible, fluffy coated tows were obtained, even from CF_s, regardless of the thickness of the coatings. The quality of these coated CF is advantageous when their utilization as reinforcement for composite materials is considered. However, inhomogeneity in the coating along the tows was observed, when both *sized and unsized* fibres were coated. For example, the first and the last 5 cm of a 30 cm long CF_s were 11.7 and 0.0%, respectively. The CF_{us} showed similar inhomogeneity: when a 30 cm coated tow was cut into two 15 cm units, 7.2 and 2.3% were obtained. As before, in CF_{us}/PHPMA, this phenomenon is attributed to the formation of individual coated filaments. The PAn, when forming a very thin layer, causes separation of the filaments in the tow (which initially were bound by the sizing). PAn is positively charged when formed in acidic solution, and repulsion between the single filaments may be the reason for the open structure of the tow, in contradiction to the CF coated with poly(hydroxyalkyl methacrylates). The transfer of the bound tow to many separated single filaments brings about an increase in the resistivity along the filament and thus the percentage decrease along the tow.

A non-uniform coating is unacceptable from a practical point of view. This problem was solved by connecting the two edges of the tow to the metallic holder, in order to reduce the voltage drop along the fibres. The results of the tow two-sided grip were satisfactory: uniform coatings were achieved. For example, when 30 cm tows

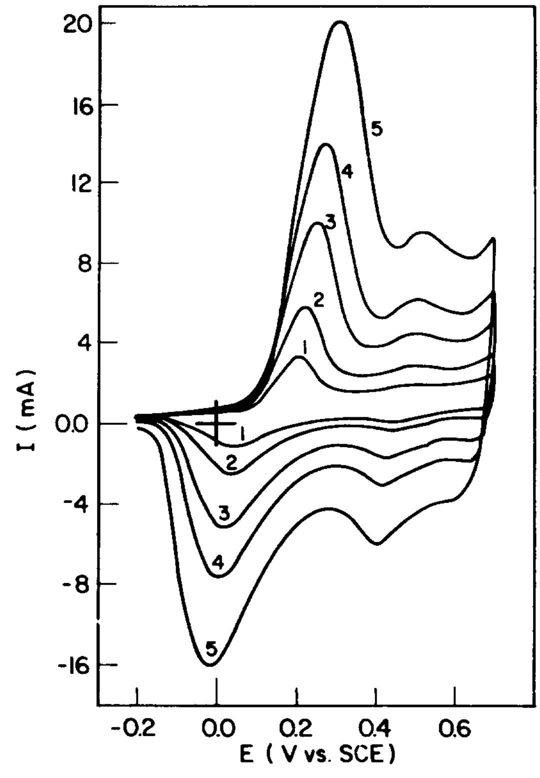


Figure 6 Cyclic voltammetry of CF_s/PAn in 1 M HCl. The fibres were coated potentiostatically for 1 min at 0.8 V. The scan rates are (1), 5, (2) 10, (3) 20, (4) 30 and (5) 50 mV s^{-1}

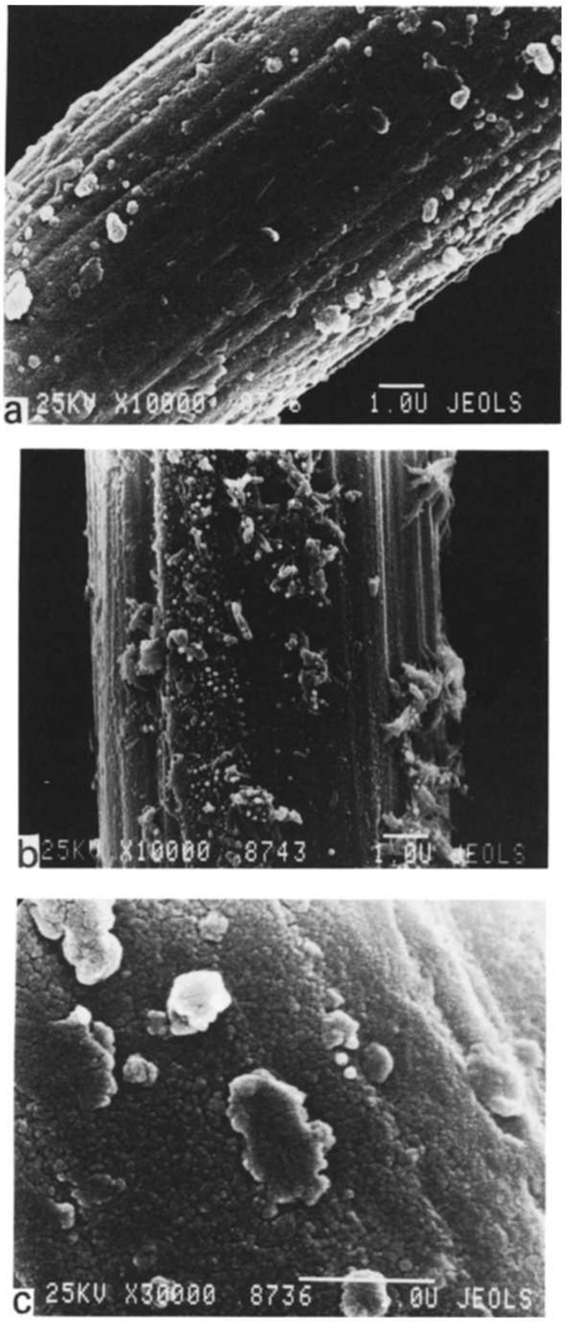


Figure 7 SEM micrographs of PAn on CF: (a), (b) fibres coated with 3.0 and 7.5% PAn (magnification × 10000); (c) as in (a) but magnification × 30000 (photographs reduced to ~60% in printing)

were coated, 5.2 ± 1.2% and 3.6 ± 0.7% for CF_{us} and CF_s were obtained, respectively.

Unlike the coating with hydroxyalkyl methacrylates, where the weight gain could be controllably scaled up, the percentage coating with PAn was limited to 6–8%. During the process the fibres were heavily coated with powdery material that could easily be washed away with water, after which green-blue coated fibres were obtained. The solution became coloured gradually and contaminated with small particles that fell off the deposited material. In spite of the obvious change in the composition of the solution, it could be used for several days and yielded reproducible coating percentages. It is suggested that, beyond a certain coating thickness, the PAn is deposited in a powder form which does not adhere to the CF, and thus limited thickness of the filmy coating is obtained.

The morphology of the PAn coating on CF was investigated using SEM. Single filaments coated with 3.0 and 7.5% of PAn are shown in *Figures 7a* and *7b*, respectively. CF/PAn exhibits two kinds of morphology: a thin layer, which covers perfectly the entire fibre, and spots of material dendritic growth. The thickness of the layer adjacent to the fibre surface can be estimated from the electron micrograph: the thickness is ~400 nm regardless of the percentage weight gain. At 3% coating the average diameter of the grain dendrite is ~0.5 μm (*Figure 7a*). Longer polymerization times give rise to higher weight gain (up to the limit of ~8%, as already mentioned), but the dendritic growth can account for the increase in the weight gain; the thickness of the polymeric layer does not change (compare *Figures 7a* and *7b*). Careful inspection of the layer beneath the dendrites reveals that the continuous layer is scratched with small cracks, the average width of which is 20 nm (*Figure 7c*). Similar cracked structure was recently reported for CF covered with polyindole film[19]. These electron micrographs support the findings concerning the limited weight gain that is obtained in the preparative coating of CF with PAn. Initially, a uniform polymeric layer covers the fibres. It is followed by dendritic growth that is still attached to the coated fibres. Finally, weakly bonded PAn dendrites are formed, and turn to powdery material which does not adhere to the CF.

CONCLUSIONS

In view of utilizing coated CF as reinforcement for composite materials, the electropolymerization of two kinds of polymers on CF was investigated. The polymerization of hydroxyalkyl methacrylates took place via electrochemical reduction of protons, which initiates the formation of the film. The conditions of the process were optimized in order to achieve uniform coatings of different thicknesses. Polyaniline was layered onto CF in a direct anodic process, which yields open and accessible structures. The deposition of PAn was traced using SEM and available electrochemical techniques, and the nucleation-and-growth mechanism was verified. The weight gain of CF/PAn could be controlled up to the limit of 8%. The two kinds of polymers were coated on sized and unsized CF. A difference in their surface activity with respect to the uniformity of the coating was observed. However, modification of the experimental set-up enables the production of long, uniformly coated carbon fibres. The success in forming controllably uniform, homogeneous and continuous coatings on CF encourages their utilization as reinforcing fibres for composite materials with improved mechanical properties. Such investigations are currently being carried out in our laboratory.

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