Electrochemical Grafting of 4-Phenoxybenzoic Acid Units onto Oxidized Carbon Fibers as a First Step for High Temperature Composites

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ABSTRACT: The electropolymerization of 4-phenoxybenzoic acid (4-PBA) onto carbon fibers (CFs) was studied as a way to synthesize coated CFs with grafted poly(para-phenyl ether ketone) (p-PEK) and enhance their wettability by matrices such as PEK or PEEK. Since the pristine CFs were not electrochemically active enough, a proper electrochemical oxidation treatment using sulfuric acid was applied, capable of creating oxygen-containing groups onto their surface. The groups formed in the oxidized CFs were electron acceptors and their amount was quasi-quantitatively evaluated based on their ability to absorb dye from aqueous solutions. The graft electropolymerization of 4-PBA onto the CFs electrode was achieved at anodic potentials using cyclic voltammetry (CV). The grafted coating had a thickness of up to 0.35 μm. The materials were characterized using FTIR, NMR, SEM, and TGA. A possible reaction mechanism is proposed, for the grafting of 4-PBA units onto the carboxyl groups of the treated CFs. The coated CFs were more thermally stable compared to the treated CFs without grafting. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 1466–1478, 2013

INTRODUCTION

Due to the considerable research and manufacturing efforts in the field of carbon fibers (CFs), these materials are now mature enough to be used not only in sophisticated applications but also in conventional ones.[1,2] Their success is due to the combination of properties that may provide a solution in complex problems of materials science and technology. The properties of the carbon fibers (and especially their high mechanical strength and stiffness) are mainly exploited through their composites (carbon fiber-reinforced composites, CFRCs), with the use of various matrices.[3] Some of the most important applications of them are in the sports and leisure industry with articles for many sports (tennis racquets, golf clubs, etc.), in the aerospace industry (the newest and largest commercial airplanes, Boeing 787 and Airbus A380, have a large part of their airframe built from CF composites) and for the blades used in wind turbines.[1,4–6]

Even though there are many materials proposed as matrix in CFRCs (mainly polymers), the most widely used matrices are epoxy resins. Nowadays, the technology to produce CFRCs has advanced to the point that resin transfer molding (RTM) processes are routinely applied to produce various articles, ranging from bike helmets to boat keels and for the whole range of production scale, starting from customized, bench-scale level up to

full production line.[4,7] Nevertheless, the full exploitation of the CF properties has not yet been achieved, mainly because their wettability by the matrices is rather poor. This can be attributed to the inherently inert and smooth surface of carbon fibers, which does not permit the anchoring of the matrix onto the surface of the fibers; thus, the fibers are not loaded with the stress that they can carry, but with a smaller load defined by the winkle out of the fibers from the matrix (pull out effect).[4]

One of the biggest challenges in the field of CFRCs is the use of thermoplastic matrices, especially high-temperature polymers [e.g., poly(ether ether ketone), PEEK and poly(ether ketone), PEK]; it is expected that with their use the production volume will increase, since generally the processes of thermoplastics are more time- and cost-effective. For example, PEEK reinforced with CFs has been proposed for use in tribological applications (bearings, mechanical seals, rollers, etc.).[8] However, due to the considerably higher viscosity of the thermoplastic melts, the conventional high-throughput thermoplastic processes (e.g., injection) cannot be easily applied, because the problem of poor wettability of CF is amplified and fiber impregnation becomes more demanding than in the case of thermosets.[9,10]

The aim of the present work is to electropolymerize 4-phenoxybenzoic acid (4-PBA) onto CF in order to coat their surface with grafted 4-phenoxybenzoic acid units. This is expected to

enhance the wettability of the CFs from thermoplastic matrixes (such as PEK or PEEK) and to permit the better exploitation of their properties in PEK-CF (or PEEK-CF) composites. Both pristine and electrochemically oxidized CFs will be examined. In order to achieve the electropolymerization, the electrolysis of 4-PBA solutions will be examined by varying the treatment conditions (e.g., voltage) and the mechanism of the reaction will be investigated. Moreover, the thermal stability of the coated CFs will be investigated by thermogravimetric analysis (TGA), to find out if they can withstand the high melting temperature of the matrix (above 350°C).

EXPERIMENTAL

Materials

The commercial carbon fibers (CFs) used were Torayca Type 300B 3K, consisting of an untwisted yarn with 3000 monofilaments. The commercial grade poly(para-phenyl ether ketone) (p-PEK) in the form of powder was from Victrex. Tetrabutylammonium tetrafluoroborate (TBABF$_4$, Merck) was dried at 110°C up to constant weight before use. Sulfuric acid (96 wt %, Merck), N,N'-dimethylsulfoxide (DMSO, Merck) and 4-phenoxybenzoic acid (4-PBA, Fluka, as powder) were used as received.

Electrochemical Treatment of CFs with Sulfuric Acid Solutions

A two-compartment cell was used, having the carbon fibers as working electrode and a Pt-plated Pt disk plate as counter electrode. A saturated calomel electrode (SCE) was used as reference electrode, separated from the rest of the cell by a Luggin capillary. An aqueous solution of sulfuric acid 5% w/w was made by proper dilution of concentrated 96 wt % H$_2$SO$_4$ and used for the treatment. After treatment, the fibers were rinsed with water and acetone and then dried at 105°C for 1 h. These fibers were used for further characterization.

Coating of CFs by Electrolysis of 4-Phenoxybenzoic acid (4-PBA) Solutions

All electrolysis experiments took place at room temperature, in an one-compartment electrochemical cell having a volume of 150 mL, using the three electrodes setup. The counter electrode was a square Pt-plated Pt plate, having a surface area of 9.0 cm^2 and the reference electrode was again SCE separated from the solution by a Luggin capillary. Different materials were used as working electrodes: pristine CFs, electrochemically treated CFs and a Pt-plated Pt square plate with surface area of 4.8 cm^2. The solutions consisted of the solvent (DMSO), the electrolyte TBABF$_4$ (in concentration of 0.1 M) and the monomer 4-PBA (in concentration of 0.1 M); before the beginning of the electrochemical treatment, the solutions were deaerated by bubbling nitrogen for 10 min. After the end of the electrochemical experiment, the working electrode was rinsed with DMSO, then washed with acetone and water to remove TBABF$_4$ residues and soluble oligomers and then were dried at 105°C up to constant weight. These fibers were used for further characterization.

For controlling the voltage applied and for measuring the current passing during both the electrochemical treatment and the electrolysis of 4-PBA solutions, a potentiostat Wenking POSS88 (Bank Elektronik) was connected to the respective cells.

Characterization of the Materials

Fourier-Transform Infrared (FTIR) spectra were recorded in a Perkin Elmer Spectrum GX spectrometer using KBr discs. Thermogravimetric Analysis (TGA) was carried out using a Mettler Toledo 815E thermobalance with aluminum pans, by heating the sample from 25 to 1000°C with a heating rate of 10°C/min, under nitrogen flow. The morphology of the fibers was examined using a FEI Quanta 200 Scanning Electron Microscope; measurements were performed on samples without any further treatment (using Low Field Detector—LFD) or coated with gold (with thickness 5 nm). Nuclear Magnetic Resonance (NMR) ^{1}H spectra were recorded in solutions, using a Varian Gemini 2000 NMR spectrometer having Oxford instrumentation magnet, with a resonance frequency of 300 MHz. The deposited coatings were washed out from the electrode surface using proper solvent (CDCl$_3$ or CCl$_4$). The dye adsorption was determined from solutions. Carbon fibers were added in a dye aqueous solution of methylene blue (0.032 g/L), with a ratio of 1.65 g/L. The color of the solution was determined optically at specific times by comparison with a colorimetrical calibration scale.

RESULTS AND DISCUSSION

Optimum Conditions for the Electrochemical Treatment of CF

Table I summarizes the conditions used for all these experimental procedures: the pristine CFs were electrochemically treated and then the treated CFs were used as working electrode to try electropolymerize 4-phenoxybenzoic acid (4-PBA). Furthermore, a Pt plate was used as working electrode to study the CVs of the 4-PBA solution (since is an electrochemically inert metal). In order to avoid confusion, the following terms will be used for the CFs: (1) pristine (or initial) CFs, for the commercial fibers before any treatment ("as received"), (2) treated CFs, for the CFs after the electrochemical oxidation with the H$_2$SO$_4$ solution and (3) coated CFs, for the treated CFs after the electrolysis of the 4-PBA solution: it remains to be proven whether (and under what conditions) 4-PBA can indeed electropolymerize and, if yes, whether the polymer is actually grafted onto the CFs.

For the electrochemical treatment of CFs, a sulfuric acid solution of 5% w/w was used, with multiple scans in the potential region from −3 V up to +3 V (scan rate 50 mV/s). These conditions have been proposed in the literature for commercial PAN-based CFs as an effective treatment method in order to create oxygen-containing groups with large surfacial concentration.[11,12] Figure 1 shows the cyclic voltamograms recorded during the treatment of the CF up to 20 cycles. In the first cycle only a reduction peak centered at −1.1 V can be seen. Beginning from the second cycle, there are one oxidation and one reduction region. Both of them are broad: the oxidation is between 0.8 and 1.5 V and the reduction region between −0.6 and −1.6 V. This indicates that both the peaks result from the overlapping of several electrochemical reactions. By increasing the number of cycles, the current of the peaks (both anodic and cathodic) generally increases; however, after the 10th cycle this increase was very small. A similar behavior has been already

Table I. Conditions for the Electrochemical Treatment of Carbon Fibers (CFs), and for the Electrochemical Coating with 4-Phenoxybenzoic acid (4-PBA) onto the Treated (oxidized) CFs or onto Pt

Code of the material	Electrochemical treatment conditions[a]	Coating conditions[b]		
		Electrode	Potential or region of potential (V vs. SCE)	Time or number of cycles
CF	–			
CF-2	2 sweeps			
CF-5	5 sweeps			
CF-10	10 sweeps			
CF-20	20 sweeps			
CF-10/A-10	10 sweeps	CF-10	A: −2.0 → +2.0 → −2.0	10
CF-10/A-20				20
CF-10/B-10			B: 0.0 → +3.0 → 0.0	10
CF-10/C-05			C: −3.0 → +3.0 → −3.0	5
CF-10/C-10				10
CF-10/C-20				20
CF-10/+2.5V	10 sweeps	CF-10	+2.5	10 min
CF-10/+2.8V			+2.8	10 min
CF-10/+3.0V			+3.0	10 min
Pt/A-10		Pt	A: −2 V → +2 V → −2 V	10
Pt/A-20				20
Pt/C-20			C: −3 V → +3 V → −3 V	20

[a] Solution: H_2SO_4 (5% w/w), potential region: −3 to +3 V, scan rate: 50 mV/s.

[b] Solution: DMSO, $TBABF_4$ (0.1 M), 4-phenoxybenzoic acid (4-PBA) (0.1 M), scan rate: 100 mV/s.

described in the literature during a similar treatment.[11] The broad oxidation peak has been attributed to the intercalation of carbon fibers by the sulfuric acid and the formation of graphite or "defect" oxides, i.e. oxygen containing groups in defect sites of the graphene structures that constitute the CFs. These oxides can be in the bulk or the surface of the CFs. Similarly, the
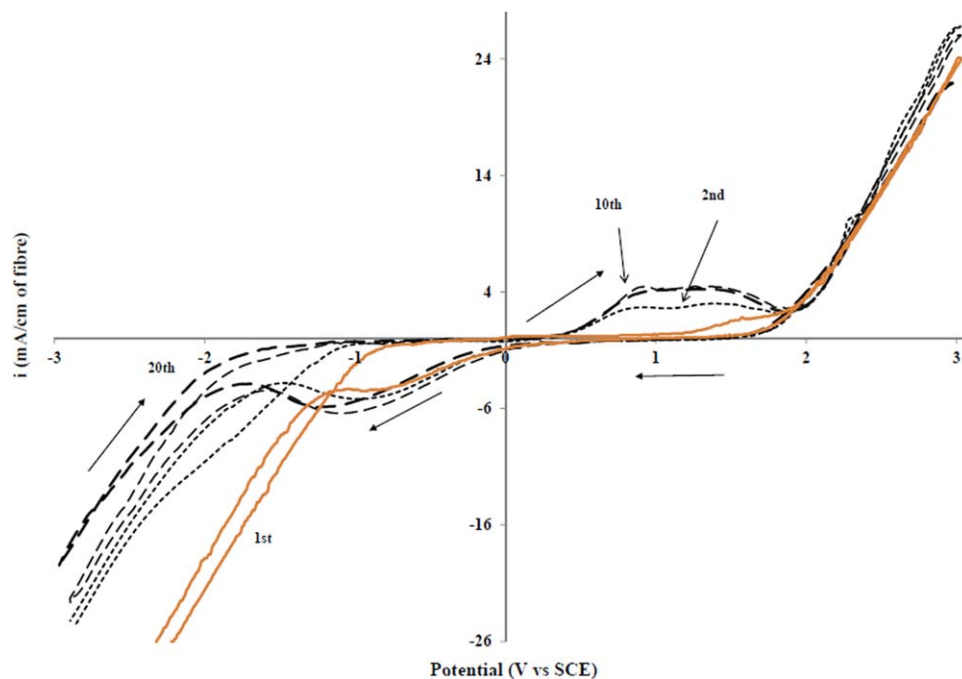

Figure 1. Cyclic voltammograms for the electrochemical treatment of pristine carbon fibers with 5% w/v H_2SO_4 solution for repetitive potential sweeps (scan rate 50 mV/s). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
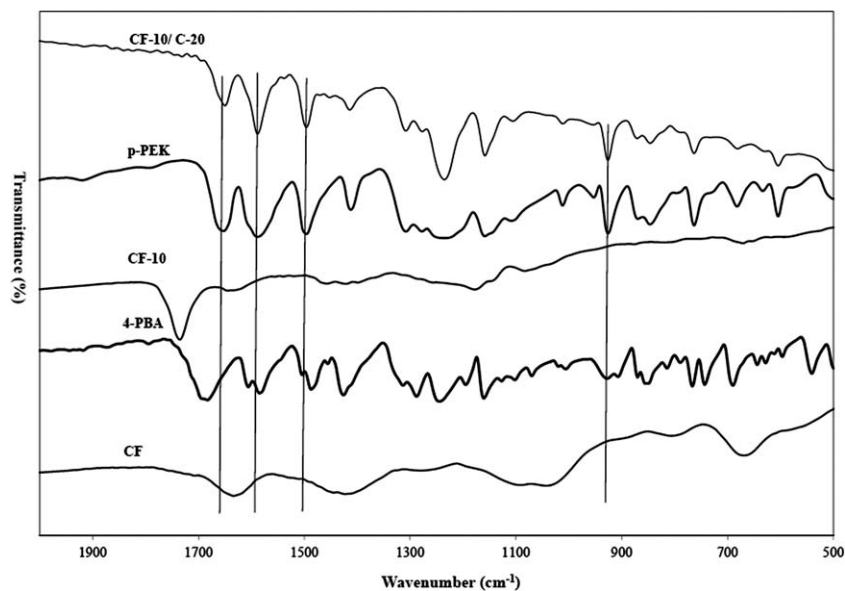
Figure 2. FTIR spectra of 4-phenoxybenzoic acid (4-PBA), poly(parA-phenyl ether ketone) (p-PEK) and pristine (CF), treated (CF-10) and coated carbon fibers (CF-10/C-20, for the codes see Table I).

reduction peak has been attributed to the partial reduction of these oxides, leaving oxygen-containing groups in the surface of the fibers.[11]

Figure 2 presents the FTIR spectra of the CFs before and after the above mentioned electrochemical treatment for 10 cycles. The spectrum of the pristine CFs exhibits peaks at 2940 (not seen in Figure 2), 1630, 1380, 1255, 1075, 1015, 850, 795, and 665 cm^{-1}, all attributed to carbon–carbon and carbon–hydrogen bonds.[13–15] After the electrochemical treatment two large peaks appear at 1740 and 1195 cm^{-1}; both of these peaks can be attributed to carbon–oxygen bonds, the former to carbonyl and carboxyl groups and the latter to hydroxyl and phenol groups.[15] The ability of this kind of electrochemical treatment to create oxygen-containing groups onto the surface of the carbon fibers has been documented in the literature: using X-ray Photoelectron Spectroscopy (XPS), it was found that the amount of oxygen on the surface of the fibers after this treatment was around 20 at %. Many oxygen-containing groups were detected (phenolic, carboxylic, ether, and lactonic), however, due to the inherent ambiguousness in deconvoluting the peaks of the spectra, the exact surfacial concentration of each group could not be quantifically determined.[11] Additionally, it has been reported that during linear sweep in sulfur acid solutions, graphite is gradually oxidized starting from alcohol, then to ketone and finally to carboxylic acid groups (before themselves undergoing Kolbe decarboxylation and releasing carbon to the solution).[12] The spectra of the other materials will be discussed below.

To find the optimum treatment conditions in terms of active groups formed on the fibers surface, the discoloration ability of the treated fibers from aqueous solutions was determined. This method is a proper and easy test that can determine the surface concentration of groups in carbonaceous materials in quasi-

quantifical level.[13–18] The dye used was methylene blue (MB), which contains electron donor groups.[16] Figure 3 shows the dye adsorption versus time of CFs treated under different conditions. As the potential region was fixed, the treatment time was varied by changing the number of potential sweeps. The dye adsorption of the treated CFs was considerably higher than that of the untreated CFs. As MB contains electron donor groups, the new oxygen-containing groups formed during the electrochemical treatment of the CFs are electron acceptors (i.e., carbonyls and/or carboxyls). Both dye adsorption amount and dye adsorption rate increased by increasing the number of sweeps, indicating a corresponding increase of the electron acceptor group concentration. However, comparing the treated carbon fibers coded CF-10 with those coded CF-20, the differences between them were rather small (i.e., the former reached a maximum dye adsorption value of 92.5% in about 1 h, the latter a value of 96.5% in the same time). Given that the latter were treated with double number of electrochemical cycles (i.e., 20 compared to 10 cycles), or, equivalently, that the treatment time of the latter was double that of the former, the differences of the dye adsorption were not large enough to justify such an increase of treatment time. Hence, the treated carbon fibers that will be used to study the electropolymerization of 4-PBA are the fibers treated for 10 cycles (coded CF-10).

Coated CFs: Effect of the Electrochemical Parameters on Achieving the Electropolymerization of 4-PBA

Preliminary experiments showed that, when pristine CFs were used as working electrode for electrolysis, the current passing through the cell was extremely low. Thus, it was concluded that these fibers have negligible electrochemical activity and are not proper for electropolymerizing 4-PBA onto them. As there are not any references in the literature about the electropolymerization of 4-PBA on CF (or any other substrate), potentiostatic
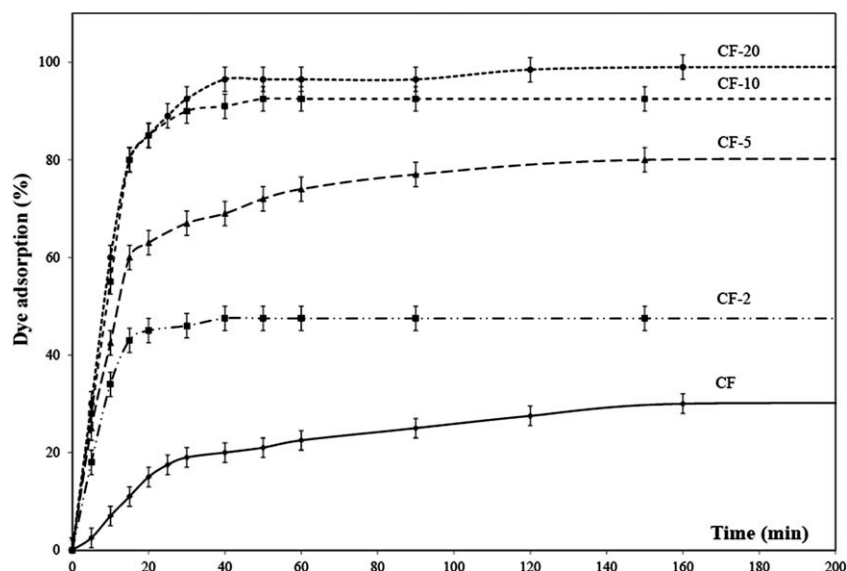
Figure 3. Discoloration ability of the pristine and the electrochemically treated carbon fibers from methylene blue solutions (for the codes see Table I).

conditions were initially tested. Preliminary experiments showed that cathodic conditions were not appropriate for achieving electropolymerization (the current dropped to zero very fast). The current versus time curves during the potentiostatic treatment of 4-PBA for anodic potentials (see also Table I) had the same shape, reaching a plateau value of current before 100 s. This could be explained by the fast formation of a thin, nonconducting coating, which insulated the surface of the conducting CFs, not permitting any further growth of it. Therefore, under potentiostatic conditions only very thin depositions were formed and no electropolymerization of 4-PBA could take place. This was also verified by comparing the FTIR spectra of the

treated CFs before and after the potentiostatic depositions, which showed not any differences.

As potentiostatic conditions were ruled out, potentiodynamic conditions (i.e., cyclic voltammetry) were used. Specifically, the electrolysis of 4-PBA was studied (using the aforementioned electrolytic solution), with treated CFs as working electrode, in three different potential regions, namely A: $-2-+2$ V, B: $0-+3$V, C: $-3-+3$ V, respectively (scan range 100 mV/s). In each case, a definite number of cycles were used, either 10 or 20. Figure 4 shows the cyclic voltammograms of the 4-PBA solution at the different potential ranges (see also Table I). In the range
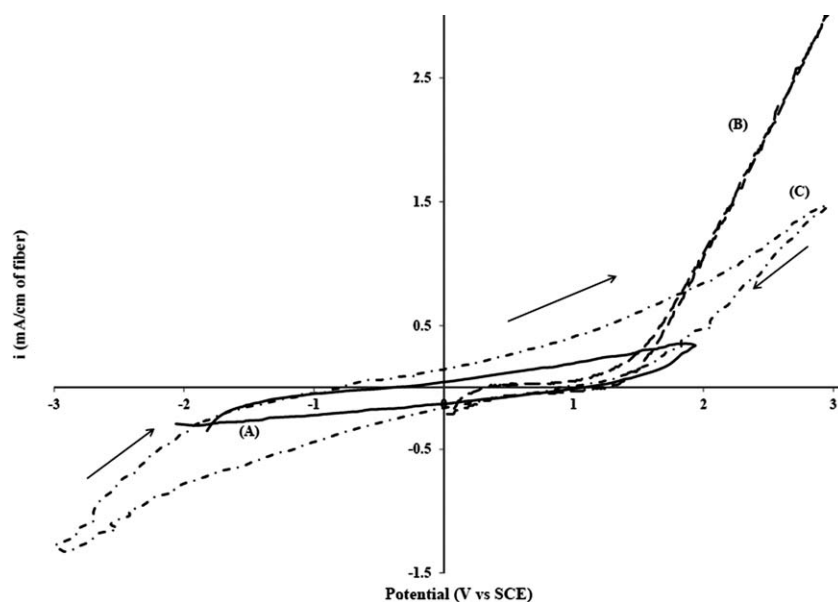

Figure 4. Comparative cyclic voltammograms during the electrolysis of 4-phenoxybenzoic acid (4-PBA) solution in different potential regions using treated carbon fibers as working electrode (CF-10, 20th sweep, scan rate 100 mV/s). Potential regions (A): from -2 to $+2$ V, (B): from 0 to $+3$ V, (C): from -3 to $+3$ V.
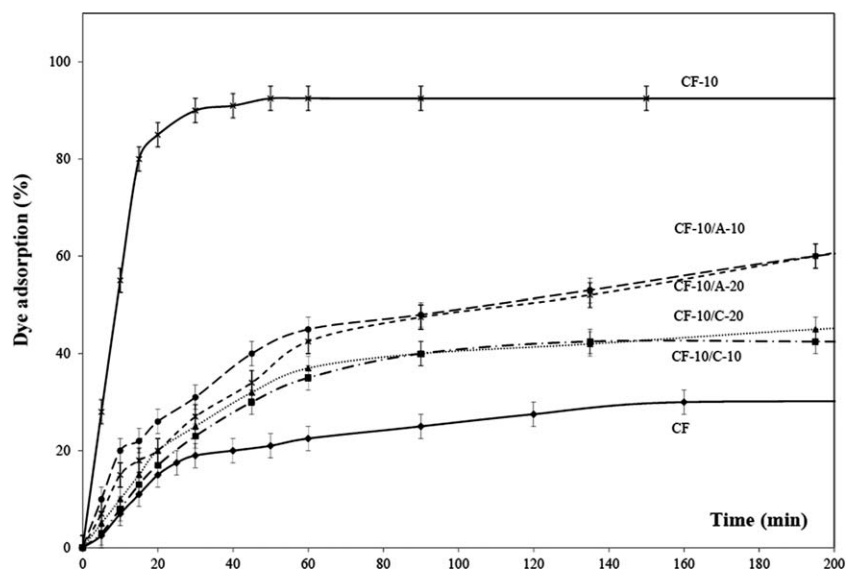
Figure 5. Discoloration ability of the coated CFs from methylene blue solutions (for the codes see Table I).

from −2 V to +2 V, the current that passed through the cell was very small, indicating that it is very unlikely to have any electrochemical phenomena (much more any electrochemical reactions) in this region. In the range from 0 to +3 V, the active current that passed during the first cycle was quite large (i.e., the surface enclosed by the CV was large enough), indicating that there was some kind of electrochemical activity. However, from the second cycle on, the active current decreased rapidly (i.e., the surface enclosed by the CV is almost nothing). This behavior can be possibly attributed to electrografting of 4-PBA onto the treated CFs during the initial scan, leading to the formation of a thin coating. This coating is an electronic insulator and nullifies the electrochemical activity of the coated CFs, not permitting any electropolymerization in the subsequent sweeps (similar to the case of potentiostatic conditions). In the literature, a similar behavior has been reported during electrolysis of acetonitrile solutions of various acid anions (e.g., 1-naphthalaneacetic acid), where (after the first potential sweep) no current passed due to grafting onto the carbon electrode surface.[19] Finally, in the range from −3 to +3 V, the active current that passed was large enough and, more importantly, it did not decrease during the repetitive scans. This is an indication that during every sweep at least some electrochemical reaction(s) were taking place, either in the solution or in the surface of the fibers (or even in both of them). However, the electrochemical mechanism of the reaction could not be analyzed, since the CVs did not have any clear oxidation/reduction peaks.

The FTIR spectra of the treated and the coated CFs (with 20 sweeps in region C), together with the spectra of the monomer (4-PBA) and the polymer (p-PEK) are presented in Figure 2. The spectrum of the 4-PBA had a multitude of peaks and was similar to that reported in the literature,[20,21] i.e. the material did not contain any additives. The more representative peaks in the FTIR spectrum of p-PEK are at 1655 cm^{-1} (attributed to C=O ketone carbonyl), at 1590 cm^{-1} (attributed to C=C in phenyl ring), at 1505 cm^{-1} (again attributed to C—C in phenyl

ring), at 1240 and 1165 cm^{-1} (both attributed to C—O—C ether link) and at 930 cm^{-1} (attributed to C—H in phenyl ring).[22,23] The most important difference between the FTIR spectra of 4-PBA and p-PEK was the peak at 1680 cm^{-1} (attributed to the acidic C—O), which in p-PEK was shifted at 1655 cm^{-1}; this shift has been used in the literature as a proof criterion for the successful grafting of p-PEK onto carbon nanotubes.[20] The main peaks in the FTIR spectrum of the coated CFs were at 1655, 1590, 1505, 1240, 1165, and 930 cm^{-1}. Comparing the FTIR spectra in Figure 2, the spectrum of the coated CFs was the same as that of p-PEK and completely different to those of the pristine and the treated CFs, as well as that of 4-PBA. More importantly, in the region of 1800–1600 cm^{-1} the coated CFs present the carbonyl-attributed peak as the p-PEK at 1655 cm^{-1}, without any peaks at 1740 (the most intense peak in the spectrum of the treated CFs) or at 1680 cm^{-1} (the representative peak in the spectrum of 4-PBA). This is a clear proof that 4-PBA was indeed successfully electropolymerized (i.e., grafted) onto the surface of the (electrochemically treated) CFs under the conditions used. Generally, electropolymerization or electrochemical grafting seems to be achieved quite easily (even though sometimes inadvently).[12,24]

To quantifically determine the efficiency of the electropolymerization, the dye adsorption of the coated CFs was also measured. Figure 5 presents the MB discoloration ability of the CFs after electropolymerization of 4-PBA under different conditions. The dye adsorption of the various coated CFs was considerably lower than that of the treated CFs (CF-10) which were not coated with 4-PBA. This is an indication that 4-PBA was grafted onto the electron acceptor groups on the surface of the treated CFs (which were created during the electrochemical treatment with H$_2$SO$_4$), and thus the concentration of the remaining groups decreased but they did not totally disappear. The latter is proven from the fact that the grafted CFs had higher dye adsorption than the pristine CFs. Consequently, the decrease of the dye adsorption of oxidized CFs indicates their effective

grafting with 4-PBA. CFs treated in the wider potential range (C, i.e., from −3 to +3 V) were more sufficiently grafted by 4-PBA compared to the CFs treated in the narrow potential range (A, i.e., from −2 to +2 V).

Further evidence for the electropolymerization of 4-PBA onto the treated CFs was provided from the SEM micrographs. Figure 6 presents the SEM micrographs of the initial, the treated and three coated CFs, with 5, 10, and 20 sweeps in region C. The initial CFs [Figure 6(a)] shows a smooth surface; after the electrochemical treatment with H_2SO_4, the outer surface of the CFs appears more rough [Figure 6(b)]. Furthermore, the SEM image of the cross section [Figure 6(c)] indicates that the treatment did not cause any damage on the backbone of the fibers. Even though there are not many reports in the literature, it is generally accepted that electrochemical oxidation treatments lead to a decrease of the CF diameter, due to the partial dissolution of the fibers' outer layers, without damaging their backbone.[11,25] The coated CFs [Figure 6(d–g)] had smoother surface than the treated CFs. More importantly, it is also clear that the thickness of the coating onto the CFs progressively increased by the number of electropolymerization sweeps. The coated CFs with 5 sweeps [Figure 6(d)] seems to cover only partially their rough surface, that with 10 sweeps [Figure 6(e)] totally cover the surface of the CFs starting to form bumps. Finally, the coated CFs with 20 sweeps [Figure 6(f,g) have an almost uniform coating around the fiber. Even though the CF cross section is kidney-like, by measuring at least 15 different monofilaments from at least three different photos of every fiber (with the same magnification and approximately the same direction), the mean monofilament diameter was calculated. That of the pristine CFs was 7.26 μm, that of the treated CFs was 7.07 μm and that of the coated CFs was 7.13 μm (with 5 sweeps), 7.41 μm (with 10 sweeps) and 7.75 μm (with 20 sweeps), with all the measurements having almost the same standard deviation (0.35–0.40 μm). Thus, the electrochemical treatment led to decrease of the CFs diameter (due to the partial dissolution of the outer layers) and the electropolymerization of 4-PBA led to increase of them (due to the coating of the fibers by the grafted 4-phenoxybenzoic acid units). Assuming uniform covering of the monofilaments, the thickness of the coating was calculated at about 0.05 μm (with 5 sweeps), 0.15 μm (with 10 sweeps) and 0.35 μm (with 20 sweeps). Even though these values cannot be used as exact, they are indicative that the coating grew progressively with every consecutive sweep.

Electrolysis of 4-PBA Solution Using Pt Working Electrode: Comparison with the Electrolysis with Treated CFs

The cyclic voltammograms during the deposition of 4-PBA onto treated CFs (i.e., Figure 4) do not present any features (e.g., peaks or knees). This can be attributed to one or more of the following reasons: (a) there were multiple electrochemical phenomena that overlap, (b) the reactions were very fast and cannot be detected,[26] (c) the surface of the treated CFs was not inert enough for the electrochemical phenomena to be clearly detected. As a result, the CVs were not very helpful for studying the electropolymerization mechanism. To elucidate the mechanism of the polymer formation, cyclic voltammograms were

measured with Pt as working electrodes, using the same 4-PBA/DMSO/TBABF₄ solution.

Figure 7 presents the comparative CVs of the 4-PBA solution in the region from −2 to +2 V (10th cycle) for the different working electrodes. In the case of the Pt, during the first cycle a large oxidation peak at −0.45 V was detected in the anodic sweep, followed by a smaller one at +1.10 V, whereas during the cathodic sweep only a moderate reduction peak at −0.57 V appeared. It seems that this reduction peak was related to the oxidation peak at −0.45 V; if it was such a case, then a partial reduction takes place. The current that passed from the Pt electrode was considerably larger than in the case of CF-10 electrode, indicating (as already mentioned) that the treated CFs were electrochemically inactive in this region. From the second cycle on, the main oxidation peak shifted to higher potential, the minor oxidation peak (at +1.10 V) almost disappeared and the reduction peak became progressively larger (i.e., the reduction turned from partial to complete) and shifted to lower potential. Thus, during the 10th cycle (Figure 7) the oxidation peak was at +0.15 V and the reduction peak at −0.89 V. Moreover, from the second cycle on, a new reduction peak appears during the cathodic sweep at +0.80 V, which too becomes progressively larger and sharper. This peak cannot be related to the other peaks and probably should be attributed to some kind of electrochemically driven desorption phenomena (electrodesorption).

Similarly to Figure 7, Figure 8 presents the comparative CVs in the region from −3 to +3 V (10th cycle) for the different working electrodes. The general features of the CVs with the Pt were similar to those described in the region from −2 to +2 V. The differences were that the couple of oxidation/reduction peaks of Pt shifted to higher/lower potential, respectively; moreover, the electrodesorption peak of Pt was even more prominent and sharp and shifted to +1.01 V. The current that passed through the CF-10 electrode in region (A) was low, but in region (C) it was clearly higher, comparable to that of Pt electrode (Figure 8). This indicates that in region (C) the treated CFs were electrochemically active, even though they did not present any discrete peaks in their CVs.

Structure of the Coating Deposited onto Pt Electrode

After the electrolysis of the 4-PBA solution with Pt as working electrode, it was detected that a thin coating was formed onto the Pt electrode. By testing with various solvents, it was found that the coatings were soluble in chloroform and CCl_4. Thus, proper solutions were made by dissolving the coatings in $CDCl_3$ or CCl_4 and the ^{1}H-NMR spectra of these materials were measured. For comparison, the NMR spectra of the monomer 4-PBA (solvent: CCl_4) and the p-PEK (solvent: DMSO-d_6) were also recorded. The results are summarized in Table II. The spectrum of the monomer 4-PBA is exactly the same as that reported in the literature[27] and has five peaks, assigned as presented in Scheme 1(a). By integrating the corresponding peaks and normalizing with respect to the (A) hydrogen (Table II, columns named "peak area"), the theoretically expected hydrogen ratios were found. In the spectrum of p-PEK two hydrogen peaks can be distinguished, with their assignment again presented in Table II and Scheme 1(b).[28] It is clear that both the
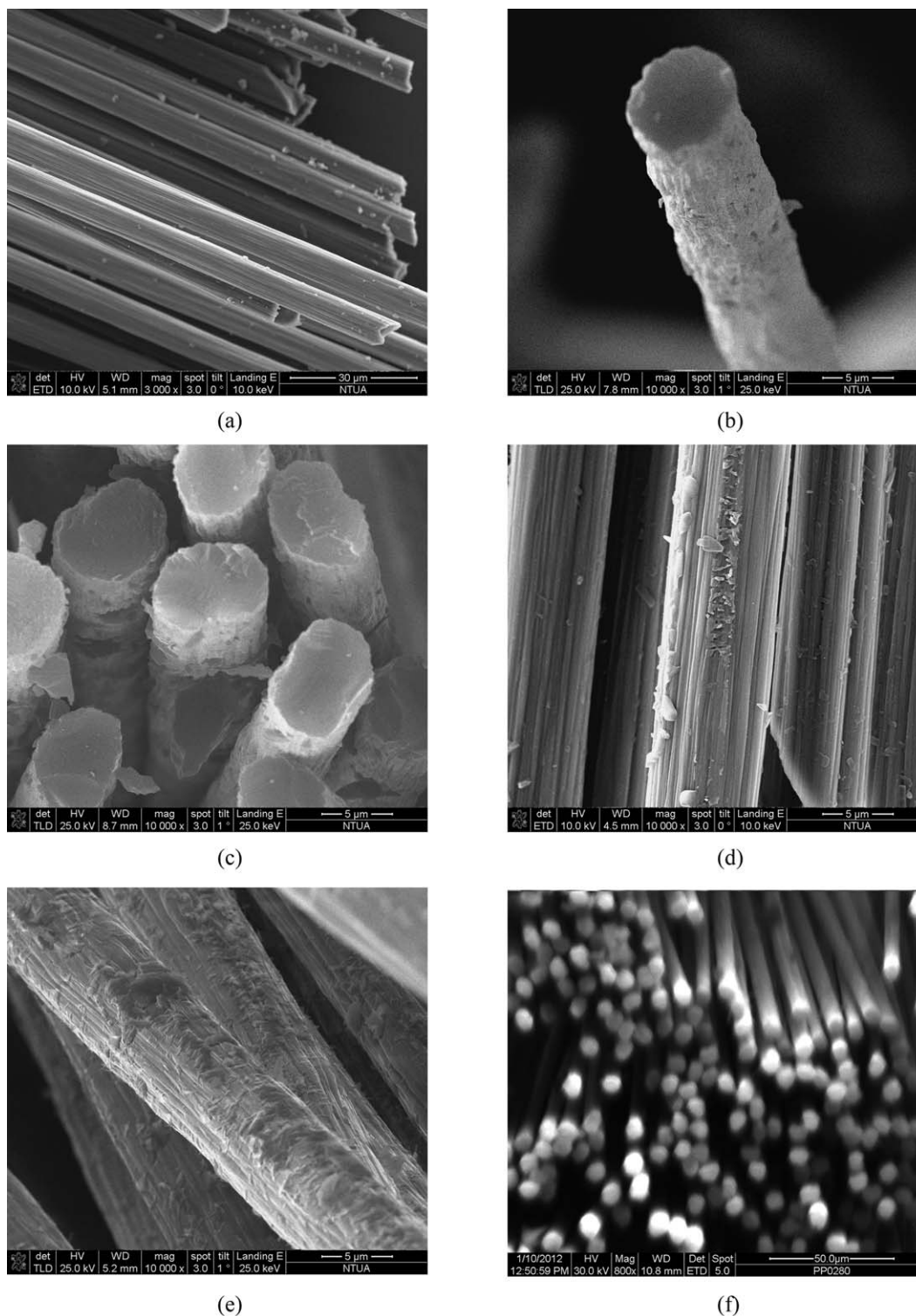
Figure 6. SEM micrographs of: (a) pristine carbon fibers (CF), (b), (c) treated CFs (CF-10), (d)–(f) various coated CFs (d: CF-10C/C-05, e: CF-10/C-10, f, g: CF-10/C-20, for the codes see Table I).

materials deposited onto Pt electrode were not p-PEK and resemble more to 4-PBA, exhibiting the same five hydrogen signals (with only a slight shift of 0.1 ppm or less). Furthermore, the peak area shows a notable decrease for the intensity of the edge hydrogen (symbolized as "C" in Scheme 1/a), without any

significant change of the other hydrogen peak areas. To quantify this decrease, the integrals ratio: "C/(A + B + D + E)" was calculated for 4-PBA and for the two coatings. This ratio for the monomer is near the theoretically expected value of 1/8, but for both the coatings it has a value of approx. 1/12. This is an
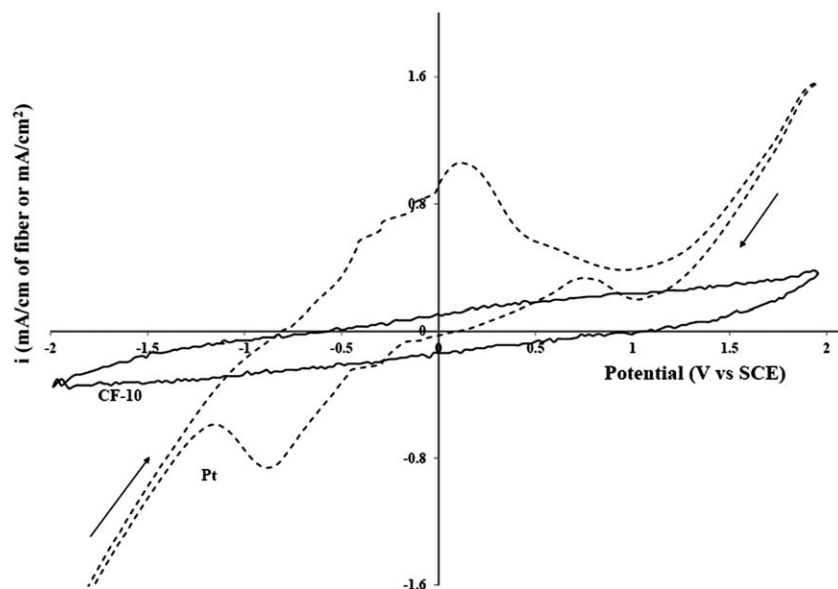
Figure 7. Comparative cyclic voltammograms during the electrolysis of 4-phenoxybenzoic acid (4-PBA) solution in the region from −2 to +2 V, using different working electrodes (CF-10 or Pt, 10th sweep, scan rate 100 mV/s).

indication of partial dimerization of 4-PBA during the electrolyisis using Pt as working electrode (if the material was a pure dimer, the value would have been near 1/16 and if it was composed of trimers or higher oligomers, the value would have been even lower).

Further comparison of the NMR results for 4-PBA with those for the coatings formed onto Pt, two more conclusions also aroused:

1. There are not any other new peaks in the NMR spectra of coatings formed onto Pt compared to 4-PBA, and

2. Apart from the edge ("C") hydrogen, the peak areas do not differ significantly from those of 4-PBA.

Taken all together, it can be assumed that the dimer is formed by the dehydration reaction of the edge "C" hydrogen with the hydroxyl group of the carboxyl moiety, following a reaction as presented in Scheme 2. The dehydration reaction that forms this ether-ketone dimer is probably the oxidation/reduction electrochemical reaction detected in the CVs with Pt as working electrode (Figures 7 and 8). However, it seems that in the case of Pt the dimer did not grow into polymer, because it was electrochemically desorbed from the
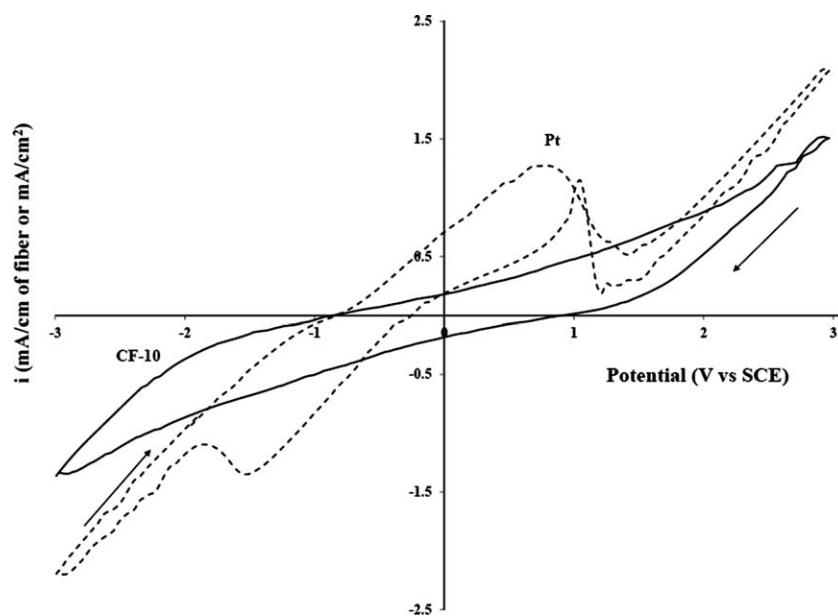

Figure 8. Comparative cyclic voltammograms during the electrolysis of the 4-PBA solution, with CF-10 or Pt as working electrode, in the region (C), from −3 to +3 V for the 10th cycle (scan rate 100 mV/s).

Table II. Analysis of the ^{1}H-NMR Spectra Measured (for the codes see Table I)

Code of assigned hydrogen (Scheme 1)	Material (solvent)									
	4-PBA (CDCl$_3$)[27]		4-PBA (CCl$_4$)		Pt/A-20 (CDCl$_3$)		Pt/ C-20 (CCl$_4$)		p-PEK (DMSO-d$_6$)	
	Shift (ppm)	Peak area	Shift (ppm)	Peak area	Shift (ppm)	Peak area	Shift (ppm)	Peak area	Shift (ppm)	Peak area
(A)	8.080	1.0	7.781 (d)[a]	1.00	8.066 (d)	1.00	7.938 (d)	1.00		
(A′)									7.828 (s)	1.00
(B)	7.405	1.0	7.164 (t)	0.94	7.404 (t)	1.00	7.408 (t)	0.86		
(C)	7.212	0.5	6.941 (t)	0.50	7.204 (t)	0.33	7.186 (t)	0.31		
(B′)									7.263 (s)	0.99
(D)	7.088	1.0	6.855 (d)	0.97	7.094 (d)	1.00	7.069 (d)	0.95		
(E)	7.030	1.0	6.780 (d)	0.97	7.02 (d)	0.95	6.990 (d)	0.75		

[a] Multiplicity of the peak: (s) singlet, (d) doublet, (t) triplet peak.

electrode surface during the cathodic sweep (corresponding to the peak at about 1.0 V).

Thermal Stability of the Coating Formed During Electropolymerization of 4-PBA onto Treated CF

The thermal stability of the coated CFs up to 1000°C in inert atmosphere was studied by TGA. Figure 9 presents the TGA measurements {i.e., [1 − (ΔG/G$_0$)] × 100, %} and the weight loss rate {i.e., the first derivative of the TGA measurements, $d[1 − (\Delta G/G_0)]/dT$, K^{-1}} for the electrochemically treated and the coated CFs with electropolymerized 4-PBA (coded CF-10 and CF-10/C-20, respectively).

The treated CFs started losing mass at around 150°C, reaching an almost steady rate of around 2.5×10^{-4} K^{-1} after 200°C. The weight loss rate had two small local minimums (i.e., negative peaks) centered at around 200 and 600°C, respectively. The first peak was very broad (ending at about 500°C) and it started

Scheme 1. Hydrogen assignments (according to the literature) for: (a) 4-phenoxybenzoic acid (4-PBA), (b) p-PEK.[26,27]

well above 100°C, so it cannot be attributed to removal of water. The peaks seem to be the result of overlapping (indicating that there were more than one decomposition reactions), but it should probably be correlated with decarboxylation reactions (leading mainly to evolution of CO$_2$). The second peak could again be related to the decomposition of more stable oxygen-containing groups, possibly carbonyl-type groups. The weight loss of the second peak is much smaller than the first, indicating that the decomposition reactions probably led to the evolution of CO (which has smaller molecular mass than CO$_2$). The accumulative weight loss up to 1000°C of CF-10 was around 20% of the initial mass, even though the amount of the oxygen in the treated CFs was not as high; however, when oxygen groups volatilize, they take some carbon atoms with them.

Compared to CF-10, the CF-10/C-20 fibers were generally more thermally stable: the onset of the weight loss for CF-10/C-20 fibers was at higher temperature (at around 200°C), their accumulative weight loss up to 1000°C was only 10% and their mean weight loss rate was around 1.5×10^{-4} K^{-1}. However, their weight loss rate curve showed two sharp negative peaks centered at around 320 and 430°C, respectively. As the initial decomposition temperature during pyrolysis of p-PEK was calculated at around 455°C,[29] the latter peak can be correlated to the onset of the decomposition of the polymer grafted onto the CFs. Furthermore, the weight loss rate of the coated CFs up to 280°C was almost the same as that of the treated CFs. This is an indication that part of the surface of the treated CFs was not covered during the electropolymerization by grafted monomer units (and it followed the same decarboxylation reaction kinetics as the treated CFs). Between 500 and 800°C, the weight loss rate of the coated CFs had almost stable value (around 1.0×10^{-4} K^{-1}) and above 800°C it increased with a small rate (reaching a value of around 1.5×10^{-4} K^{-1}).

On the Mechanism of 4-PBA Electropolymerization and the Grafting onto Treated CFs

4-PBA is a carboxylic acid. Generally, electrolysis of carboxylic acids is considered to lead to the formation of radicals (most times cations, but in other cases not charged) following some
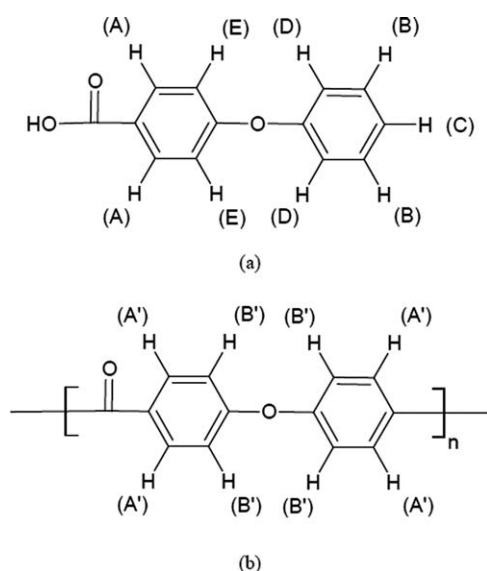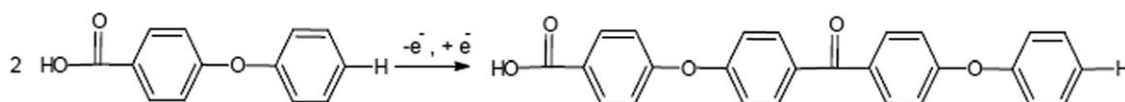
Scheme 2. Proposed electrochemical dimerization mechanism of 4-phenoxybenzoic acid (4-PBA) during electrolysis using Pt as working electrode.

kind of decarboxylation, either through a Kolbe[30,37] or a non-Kolbe reaction mechanism.[30,37] Depending on the specific conditions, these radicals can then recombine in the solution creating various new molecules,[33,34] or can be grafted onto the electrode surface,[30,34,36,38] or (in the case of dicarboxylic acids) they can even polymerize.[31,32,34] The H[1]-NMR spectra of the coatings deposited onto Pt indicate that in the current occasion, it is not likely for the reaction to proceed through a decarboxyliation mechanism. However, it should be noted that, in all the cases reported concerning decarboxylation, the acid is in the dissociated form of the anion (i.e., —COO[−]). Considering the current system, 4-PBA is a very weak acid and DMSO is an aprotic solvent, meaning that the equilibrium of the acid dissociation: —COOH = —COO[−] + H^{+} will be in favor of the left hand side of the reaction. As a matter of fact, when Kolbe decarboxylation was achieved in DMSO solutions, it was only by using extreme electrolysis conditions.[39] Thus, it can be assumed that other electrochemical reaction schemes (other than the decarboxylation) might be available.

Recently, the polymerization of 4-PBA into p-PEK was reported using polyphosphoric acid (PPA)/P$_2$O$_5$ as a reaction medium.[28] Even though the reaction mechanism was not analyzed, the polymerization most probably proceeded through an aromatic electrophilic substitution mechanism. According to such a mechanism, the first step would be the cation formation by dehydroxyliation of COOH to —C[+]=O (cf. Scheme 3).). This was achieved by the use of extremely dehydrating reaction medium (both PPA and P$_2$O$_5$ are dehydrating agents and their mixture is even more so). It seems that the use of

DMSO as a solvent (which is too a dehydrating agent) and the fact that 4-PBA was not in its anionic form, made it possible for the aromatic electrophilic substitution to take place (Scheme 2). This reaction mechanism can explain the deposition of the 4-PBA dimers when the electrolysis of the 4-PBA/DMSO solution was conducted using Pt as working electrode.

When treated CFs were used as working electrode (in order to produce the coated CFs), the electrolysis of the 4-PBA solutions led to the formation of grafted polymer onto their surface (as the results of FTIR showed). The possible reaction mechanism is presented in Scheme 3. Initially, during the anodic sweep the carboxyl groups onto the surface of the CFs are oxidized to carbonyl cations (—C[+]=O). During the cathodic sweep, these groups react with the hydrogen in the para-position (i.e., the "C" hydrogen in Scheme 1/a), creating the first monomer unit. Again, during the next anodic sweep the carboxyl groups of the grafted 4-PBA units are oxidized to carbonyl cations (with the same, as aforementioned, reaction) and the reaction continues, leading to the growth of the polymer chain. In the case of Pt working electrode, there are no —COOH groups onto the surface; thus, the 4-PBA units cannot be grafted on the surface (and grow into polymer). Instead, the monomers react with each other forming the dimer (according to Scheme 2), which is then electrochemically desorbed from the surface (and into the solution) during the cathodic sweep (at potential around +1.0 V). As a result, the film formed in the surface of Pt electrode contains only a mixture of 4-PBA monomer and dimer.
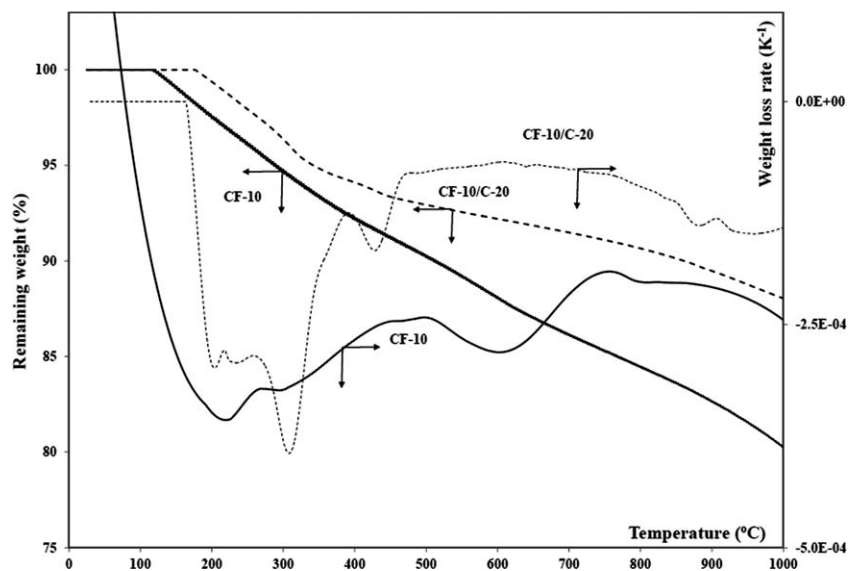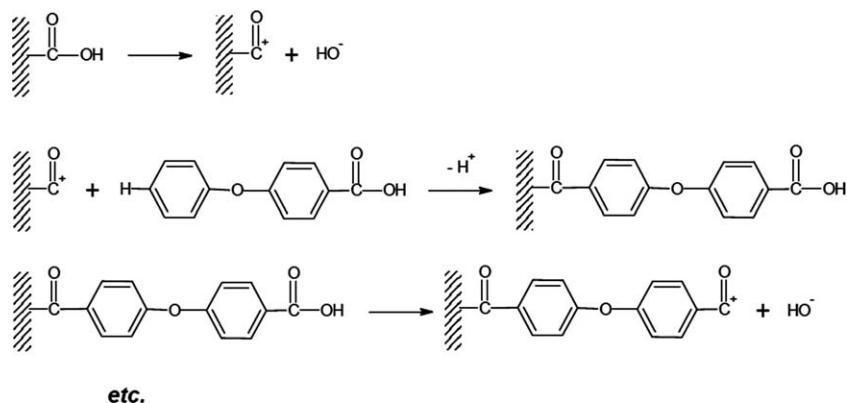

Figure 9. TGA curves of the electrochemically treated (CF-10) and the coated carbon fibers (CF-10/C-20, for the codes see Table I).

Scheme 3. Proposed electropolymerization mechanism of 4-phenoxybenzoic acid (4-PBA) during electrolysis using electrochemically treated carbon fibers as working electrode (CF-10, for the code see Table I).

The formation of the 4-PBA dehydrated dimers onto the Pt electrode agrees with such a mechanism. Moreover, the fact that the treated CFs contained —COOH permitted the grafting of the 4-PBA units onto the CFs surface and led to the formation of the poly(para-phenylene ether ketone) coating (Scheme 3), as the FTIR spectra clearly showed and the SEM photos (as well as the TGA measurements) affirmed. The carbon fibers with the grafting onto their surface had better thermal stability than the treated CFs. Furthermore, the coated CFs with the grafted polymer are expected to be more compatible with thermoplastic matrices such as PEK (or PEEK), due to chemical affinity of their surface. Therefore, there are good perspectives for the application of these fibers in manufacturing CF-PEK or CF-PEEK composites with improved properties.

CONCLUSIONS

The coating of carbon fibers (CFs) by graft electropolymerization of 4-phenoxybenzoic acid (4-PBA) was investigated, to enhance the wettability of the CFs by matrices such as PEK or PEEK. As the pristine CFs were not electrochemically active enough, a proper electrochemical oxidation treatment using sulfuric acid was proposed, capable of creating oxygen-containing groups onto their surface. Based on the dye adsorption ability from methylene blue (MB) solutions, the electron acceptor groups formed onto the surface of the oxidized CFs were quasi-quantifically estimated and the suitable oxidation conditions were chosen. The coating of the treated CFs was studied using DMSO/electrolyte/4-PBA electrolysis solution. It was proven that grafting of 4-PBA units could be achieved only under anodic conditions. Moreover, the FTIR spectra, the SEM micrographs and the MB adsorption measurements showed that electropolymerization was possible when cyclic voltammetry (CV) conditions were applied. The coating thickness was related to the number of the sweeps and polymer coatings up to 0.35 μm were synthesized. The current–voltage curves during the electropolymerization onto treated CFs did not show any features. To study the reaction mechanism, CV experiments with Pt working electrode were carried out and the H^1-NMR spectra of the depositions onto Pt electrode were measured. It is suggested that the electropolymerization reaction proceeds through an aromatic electrophilic substitution mechanism (following an electrochemical

oxidation/reduction cycle), leading to dehydration of 4-PBA to form ether- ketone dimer; in the case of the treated CFs, the 4-PBA units are grafted onto the carboxyl groups formed onto their surface during the electrochemical oxidation. The TGA measurements showed that the coated CFs with the grafted polymer had increased thermal stability during pyrolysis compared to the electrochemically treated CFs without grafting.

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