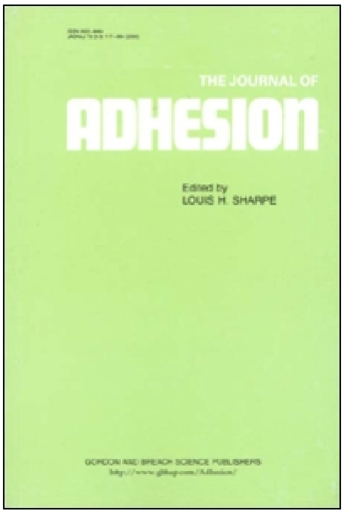

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BF_4^-, $^+N_2$-C_6H_4-$CH(CH_3)$-Br diazonium salt was electrochemically reduced in order to graft phenylethyl bromide groups to carbon fibers. The pretreated fibers (CF-Br) served as macroinitiators of atom transfer radical polymerization (ATRP) of vinylic monomers. This procedure combining a diazonium salt and ATRP permitted the polymerization of butyl, glycidyl and hydroxyethyl methacrylates at the surface of carbon fibers (CF) resulting in CF-PBMA, CF-PGMA, and CF-PHEMA hybrids, respectively. The surface chemistry and wettability of these hybrids were interrogated by XPS and water contact angles. The change in the wettability of carbon fibers reflects the chemical nature of the tethered polymer chains as the wettability decreases in the order CF-PHEMA > CF-PGMA > CF-PBMA > CF. Furthermore, CF-PHEMA was found to resist non-specific adsorption bovine serum albumin (BSA) compared with the more hydrophobic CF-PBMA system.

This work shows that the use of diazonium salt is a facile, new surface chemistry option for grafting initiator of ATRP to carbon fiber. This strategy ensures a good carbon fiber-polymer adhesion through covalent bonds.

Keywords: ATRP; Carbon fiber-polymer adhesion; Carbon fibers; Diazonium salts; Polymer brushes

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INTRODUCTION

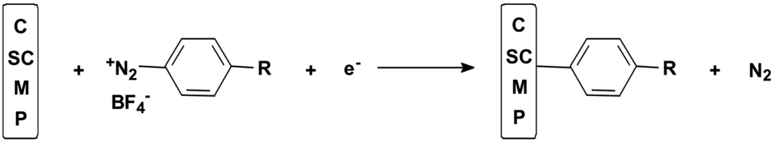
The integration of organic adlayers with conducting surfaces such as metals, carbon, semi-conductors, and diamond thin films imparts a wide panel of properties that encompasses adhesion, lubrication, optical response, chemical sensing, anti-fouling, and biocompatibility. In order to gain long-term stability, the development of new immobilization chemistries is required for the covalent attachment of organic layers to substrates.

One elegant way to modify conductive and semi-conductive surfaces is *via* the electrochemical reduction of aryl diazonium salts as depicted in Figure 1 [1].

The method is simple: a diazonium salt (BF_4^- $^+N_2$Ar-R) dissolved in an aprotic medium with a supporting electrolyte (acetonitrile ACN + 0.1 M NBu_4BF_4) or in acidic aqueous medium (for example H_2SO_4 0.1 M) is reduced at room temperature, using the surface to be modified as a cathode.

This electrochemical treatment has been achieved successfully on glassy carbon [2], highly oriented pyrographitic carbon (HOPG) [3], carbon fibers [4,5], carbon felts [6], carbon nanotubes [7], iron [8], noble and coinage metals [9], hydrogenated silicon [10], thin films of doped diamond [11], and reduced polymer surfaces [12]. The functional group R can be alkyl, perfluorinated chain, -OH, -COOH, halides, NO_2 groups, etc. [1].

The versatility and simplicity of this method attracted a large number of research teams working in the surface treatment, electrochemistry, catalysis, adhesion, and biomedical areas. For example, diazonium salts were found to be effective in immobilizing colloidal gold nanoparticles onto carbon surfaces [13] or in the preparation of a modified carbon electrode that exhibits a redox electroactivity that is due to 4-aminophenyl ferrocene grafted to the former electrode [14]. Polyoxometalates were attached as catalysts on the surface of carbon through coupling with diazonium salts [15]. In the biomedical



C : carbon, **SC** : semiconductor, **M** : metal, **P** : polymer

FIGURE 1 Modification of surfaces by electrochemical reduction of diazonium salts.

domain, diazonium salts were employed with a view to attaching glucose oxidase to conducting ultrananocrystalline diamond (UNCD) thin films *via* a covalent bond. The UNCD-glucose oxidase hybrid served as a robust biosensor given the properties of UNCD [16].

As far as polymer adhesion is concerned, Adenier *et al.* have attached polystyrene (PS) to an iron surface modified using a diazonium salt containing 4-benzoylphenyl moieties. Covalent bonding of PS to the substrate was achieved under irradiation [17]. Alternatively, carboxyphenyl groups were attached to the iron surface by reduction of the diazonium salt of 4-aminobenzoic acid, and the subsequent grafting of poly(1,2-propanediyl fumarate) to the phenylcarboxylate functions was achieved through ionic bonds with Mg^{2+} ions [17].

Since aryl diazonium salts are employed to form a conversion layer, it is important to mention how they bind to surfaces and if they form monolayers or multilayers. We have shown by XPS for the iron $-C_6H_4-COOH$ interface the existence of a carbide type C1s peak that accounts for C-Fe chemical bonding [18]. Moreover, Combellas *et al.* [19] have brought ToF-SIMS evidence for the formation of a polyphenylene-like layer which results from the attack of the first grafted aromatic groups by additional radicals. This surface polymerization may account for the high grafting density of aryl groups. In the case of Cu-Ar-I, the grafting density of the phenyl iodide groups reached 10^{-8} mol/cm^2; that is 60 Ar-I groups/nm^2 or about 10 monolayers [9].

Recently, we have tackled the *grafting from* method of attachment of polymers to surfaces instead of attaching preformed polymers to diazonium salt-treated substrates (the so-called *grafting onto* method). We have explored the propensity of the salts to graft initiators of atom transfer radical polymerization (ATRP). ATRP is the most investigated controlled radical polymerization technique [20] and can be confined to a large panel of materials surfaces [21].

The rationale for exploring the *grafting from* method is that the polymer grafting densities are much higher than those obtained with the *grafting onto* approach. Given the covalent link between the substrate and the aryl layer, together with the possibility to attach brominated groups which ensure the initiation of ATRP, we have designed BF_4^-, $^+N_2-C_6H_4-CH(CH_3)-Br$ (**D1**) [22,23]. Upon electrochemical reduction this salt produces grafted $-C_6H_4-CH(CH_3)-Br$ (**1**) moieties that are effective in surface-initiating ATRP (SI-ATRP) of vinylic monomers on iron [22–24], glassy carbon [25,26], and doped UNCD thin films [27].

In this paper we explore the possibilities offered by this unique "Diazo/ATRP" protocol to grow polymer chains on the surface of carbon fibers (CF). CFs are used in a variety of applications ranging from structural composites to various materials. Efficient surface modifications would enlarge further applications and/or improve their performances in various already known applications. The target polymers are poly(butyl methacrylate) (PBMA), poly(hydroxyethyl methacrylate) (PHEMA), and poly(glycidyl methacrylate) (PGMA). The corresponding CF-polymer hybrids were characterized by X-ray photoelectron spectroscopy (XPS) and water contact angle measurements to assess the surface chemical composition and the hydrophilic/hydrophobic characteristics, respectively. CF-PBMA and CF-PHEMA hybrids were further compared in terms of non-specific adsorption of bovine serum albumin (BSA) used as a biomacromolecular probe of the ultrathin polymer overlayers.

EXPERIMENTAL

Synthesis of the Diazonium Salt BF_4^-, $^+N_2$-C_6H_4-$CH(CH_3)$-Br (D1)

The synthesis of the starting diazonium salt **D1** was described in refs. [23,24]. ^1H NMR (200 MHz, $CDCl_3$), δ ppm : 3.67 (q, 1H), benzylic protons; 2.07 (d, 3H), methylic proton; 7.90 (d, 2H) and 8.50 (d, 2H), aromatic protons β to the diazonium function and to the benzylic carbon, respectively.

Preparation and Electrochemical Treatment of Carbon Fibers

Carbon fibers (7 µm diameter, Toho Tenax HTS 5631, Wuppertal, Germany) were subjected to a thorough pre-thermal treatment that consists of removing sizing (600°C, 20 min under argon and hydrogen mixture).

Electrochemical reduction of **D1** was achieved using an EGG Princeton Applied Research potentiostat (Oak Ridge, TN, USA) with sizing-free carbon fiber bundles acting as cathodes. The grafting reaction was performed in acetonitrile (Sigma-Aldrich, Steinheim, Germany) medium [ACN + 0.1 M of NBu_4BF_4 (a Fluka product, Buchs, Switzerland)] by chronoamperometry for 300 s, at a potential of 310 mV negative to the peak potential (measured on glassy carbon). The electrochemically pretreated carbon fiber samples (CF-Br) were then thoroughly rinsed under sonication in ethanol, dichloromethane, and acetone.

Surface-Initiated ATRP of Vinylic Monomers

The general procedure for *grafting* poly(alkyl methacrylate)s *from* the surface of carbon fibers modified by electrochemical reduction of **D1** is adapted from ref. [23]. Note that the surface-confined ATRP was performed in the absence of free initiator but in the presence of a sufficient amount of Cu^{++} which acts as a deactivator for the control of the process in terms of molecular weight distribution of the tethered chains [24,28]. Basically, the monomers n-butyl methacrylate, glycidyl methacrylate and hydroxyethyl methacrylate (BMA, GMA and HEMA, respectively, all Aldrich products, Steinheim, Germany) were purified by passing through an activated basic alumina column to remove the inhibitor and stored under nitrogen at −4°C before use. -*N,N,N′,N′,N′*-pentamethyldiethylenetriamine (PMDETA), CuCl, and $CuCl_2$ (Aldrich, Steinheim, Germany) were used as received. First, a 100-mL double-walled cylindrical tube (similar to a Schlenk flask) equipped with a magnetic stir bar and sealed with a rubber septum was deoxygenated under vacuum, followed by back-filling with nitrogen three times. The CuCl (45 mg, 4.5×10^{-4} mol) and $CuCl_2$ (6.8 mg, 5.05×10^{-5} mol) powders and the carbon fibers CF-Br were introduced into the cylindrical tube under a nitrogen flow. A mixture containing 0.1 mol of the monomer (BMA or HEMA), PMDETA (87 mg, 5.02×10^{-4} mol), and toluene (3 g) previously degassed, was added to the polymerization tube using a syringe (previously purged with nitrogen) under a nitrogen flow. The tube was placed in an oil bath at 90°C for 24 h. For GMA, we adapted the procedure published elsewhere [29]: GMA (1.9 mL,14 mmol), CuBr (10 mg, 0.07 mmol), $CuBr_2$ (3.9 mg, 0.0175 mmol), and bipyridine (27.5 mg, 0.175 mmol) were added to 4 mL of a mixed solvent [DMF:water, 2:1 (v/v), where DMF = dimethylformamide]. ATRP of GMA was performed at room temperature for 24 h. In the case of ATRP of HEMA, the solvent was distilled water and the polymerization took place at room temperature. For all CF-polymer hybrids, the polymerization was stopped by cooling and opening the tube in order to expose the catalyst to air. The CF-PBMA, CF-PGMA, and CF-PHEMA hybrids were taken out and rinsed successively, under sonication, with acetone/water, acetone, and dichloromethane.

Interaction of CF-PHEMA and Cf-PBMA with Bovine Serum Albumin

The CF-PHEMA and CF-PBMA hybrids (5 mg of fibers) were incubated, for 24 h at room temperature, in 10 mL of phosphate buffered saline (PBS) solution (pH 7.4) of bovine serum albumin (Sigma, 400 μg/ml, Steinheim, Germany). The fibers were then thoroughly rinsed with a 5% v/v aqueous solution of Tween 20® (Aldrich, Steinheim, Germany) to remove loosely bound protein, then with distilled water.

The CF-polymer-BSA specimens were analyzed by attenuated total reflection infrared spectroscopy.

XPS

The spectra were recorded using an ESCALAB 250 system (Thermo VG Scientific, East Grinstead, UK) fitted with a micro-focused, monochromatic Al Kα X-ray beam (1486.6 eV, 650 µm spot size). The *Avantage* software, version 3.51, was used for digital acquisition and data processing. The fibers were pressed against electrically conductive double-sided adhesive tapes. The pass energy was set at 150 and 40 eV for the survey and the narrow regions, respectively. Additional high resolution C1s spectra were recorded with pass energy of 15 eV. Spectral calibration was determined by setting the aliphatic C-C/C-H C1s component at 285 eV. The surface composition was determined using the integrated peak areas and the corresponding manufacturer's sensitivity factors.

Water Contact Angles

Water contact angles were examined with a Krüss DSA10 instrument (Hamburg, Germany), a drop shape analyzer. The DSA 10 traces the profile of a sessile or a pendent drop, from which the contact angle of, *e.g.*, a drop resting on a solid surface and the tension of a drop hanging from a tip may be computed. The fiber samples were mounted on a sample holder placed between a horizontal light source and a CCD video camera. Live video images of the samples are obtained by adjusting lighting and focus. The needle location was adjusted so it was visible in the image.

After loading water in the syringe, droplets were placed on the fiber surface under an optical vessel to minimize evaporation. The entire system was located in thermostated chamber at 25.0 ± 0.5°C Under these standard conditions, the focus was on the water drops gently placed on the fibers. The plunger of the syringe was operated by hand to get one single drop. (These standard observations are shown in Figure 7, left hand side.)

In this paper we also present a new qualitative approach to investigate the wettability of the fibers. To do so, the fiber bundles were inserted in the syringe needle and the latter was then assembled with the syringe which was already loaded with water. The syringe was maintainted vertically by a holder in a location so that its video image was in focus. The plunger was operated by hand until a drop was obtained which was appropriately imaged and brought in focus. (The images of this second approach are shown in Figure 7, right hand side.

ATR

Infrared ATR spectra were recorded on a Nicolet 860 Fourier transform infrared (FTIR) (Thermo Electron, Madison, WI, USA) spectrometer with a resolution of 4 cm^{-1} by adding 250 scans. ATR configuration was used with a 45° incidence $39 \times 15 \times 0.4\,mm^3$ silicon crystal (48 internal reflections on each face.) The crystals were cut from n-doped silicon wafers (Siltronix, Archamps, France; resistivity ~150 ohm · cm). Spectra were run in a sample compartment flushed for 20 min with dry air. They were referenced to a background spectrum previously recorded on the crystal without the carbon fibers and cleaned under the same conditions as the covered crystal. The fibers were dispersed in acetone before being widespread on the wafer. The solvent was evaporated at room temperature.

RESULTS AND DISCUSSION

There are three important steps in the "Diazonium salt/ATRP" protocol: (i) synthesis of the diazonium salt with initiating group, (ii) electrografting, and (iii) surface-confined ATRP. We shall describe these three steps in the case of the preparation of CF-polymer hybrids.

The starting diazonium salt **D1** was synthesized in one pot from the commercially available 1-(4-aminophenyl) ethanol as shown in Figure 2.

Once this salt is synthesized and purified it can be stored at −20°C for several months.

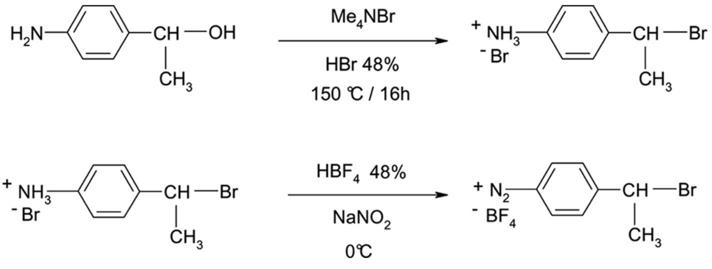


FIGURE 2 Method of synthesis of a brominated diazonium salt for surface-initiated ATRP.

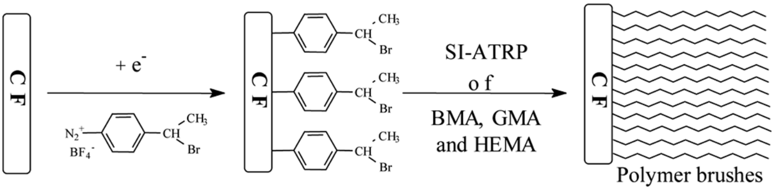
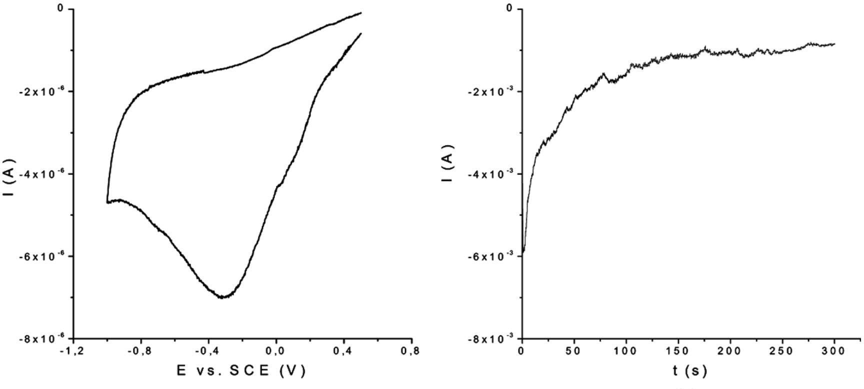


FIGURE 3 Growth of polymer brushes on carbon fibers modified by electrografted ATRP initiators based on parent aryl diazonium salts.

The “Diazonium salt/ATRP” protocol that we have established for the growth of polymer brushes on conductive and semi-conductive materials surfaces is depicted in Figure 3.

The non-commercial **D1** is readily electrochemically reduced on glassy carbon (GC) to yield attached -C_6H_4-$CH(CH_3)$-Br (**1**) groups for surface-initiated ATRP. Glassy carbon plates served for the determination of the electrochemical reduction potential (see Figure 4a). One can observe a broad, irreversible, monoelectronic wave at $Ep_c = -0.31$ V/SCE which corresponds to the reduction of the diazonium salt. The electron transfer is concerted with the cleavage of dinitrogen, giving an aryl radical which binds to the surface. As far as carbon fibers are concerned, grafting was achieved by chronoamperometry (Figure 4b) maintaining for 300 s at a potential of −700 mV, reference SCE. The very steep decrease of the current with



(a) (b)

FIGURE 4 Cyclic voltammogram (a) of a glassy carbon electrode grafted with 5 mM **D1** in ACN + 0.1 M NBu_4BF_4, $\nu = 0.2$ V/s. Reference SCE. Chronoamperometry (b) of a carbon fiber bundle grafted with 5 mM **D1** in ACN + 0.1 M NBu_4BF_4, 700 mV negative potential, t = 300 s, $\nu = 0.2$ V/s. Reference SCE.

time is characteristic of the formation of the organic layer which hampers the electron transfer from the electrode. The electrochemically treated CFs were then thoroughly rinsed under sonication in deaerated acetone. They served as macroinitiators for ATRP.

At this stage, it is important to stress that the attachment of aryl groups occurs in extremely mild conditions; that is, at room temperature and within a few minutes. This is particularly important when the substrate under test is a carbon material. Indeed, published literature indicated harsh and time-consuming classical conditions for the surface chemical modification of carbon nanotubes [30] and diamond nanoparticles [31], *i.e.*, boiling in strong acidic media for several hours followed by additional organic chemical reactions. These conditions are so aggressive that an increased roughness of the surface is observed. The alternative surface modification of carbon fibers by silane coupling agents [32] is also time-consuming and employs aggressive conditions.

The CF-polymer hybrids were characterized by XPS and water contact angle measurements. Figure 5 shows the survey scans of CF, CF-Br, CF-PBMA, CF-PGMA, and CF-PHEMA. The main peaks C1s and O1s are centered at 285 and 530 eV, respectively. One can also detect Br3d at 71 eV and Br3p at 183–190 eV from the initiator grafted to CF (CF-Br). These peaks were also detected at the surface of

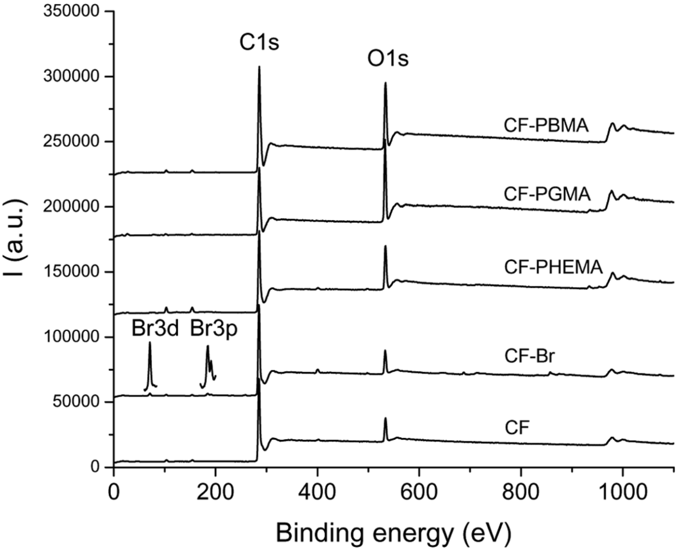


FIGURE 5 XPS spectra of CF-polymer hybrids and the reference materials CF and CF-Br.

CF-PHEMA and CF-PGMA; they correspond to the polymer chain ends. The detection of bromine after ATRP testifies for the living character of the ATRP process. For CF-PBMA the bromine peaks were too noisy. Formerly, bromine is in the -CH(CH_3)Br chemical environment after electrochemical reduction of the parent diazonium salt (see Figure 3). As the polymer chains grow, the bromine atoms are transferred from the grafted initiators to the macromolecules ends. When the ATRP process is stopped, the tethered polymer chains are terminated by bromine atoms. Note, in Figure 5, the presence of two minor peaks Si2p ($\sim$103 eV) and Si2s ($\sim$153 eV) due to a surface contamination of the fibers by silica leached from the glassy reactor where the fibers were modified. This type of contamination is frequently detected by sensitive XPS instruments.

Table 1 reports the surface elemental composition (in atomic ratios) as determined by XPS.

The surface O/C ratios increase as the carbon fibers are modified with polymethacrylates. These polymers have two (PBMA) or three oxygen atoms (PGMA, PHEMA) per repeat unit, hence the increase in O/C ratios. However, the thickness of the polymer overlayers is lower than or equal to the XPS sampling depth ($\sim$10–12 nm). Indeed, the O/C ratios determined for the CF-polymer hybrids reach 50, 84, and 90.4% of the corresponding pure PHEMA, PGMA, and PBMA, respectively. It follows that the fibers can be detected through the grafted polymer chains.

As far as Br/C ratios are concerned, they decrease on going from CF-Br to the CF-polymer hybrids. Indeed, the bromine atoms from the grafted aryl groups are displaced to the tethered chain ends, *i.e.*, away from the ATRP initiating sites. For this reason, and as the polymer chains get longer upon the progress of the ATRP process, the relative Br/C atomic ratios decrease. Although the grafted initiator groups -C_6H_4-CH(CH_3)Br have a limited efficiency in initiating ATRP, the detected bromine is mainly due to the end chains as we have discussed elsewhere. Indeed, we demonstrated that the

TABLE 1 Apparent Surface Chemical Compositions of Untreated and Modified Carbon Fibers as Determined by Xps

	O/C	Br/C
CF	0.093	0
CF-Br	0.089	5.94×10^{-3}
CF-PBMA	0.226	–
CF-PGMA	0.361	0.41×10^{-3}
CF-PHEMA	0.252	2.02×10^{-3}

non-reacted initiators have negligible intensity of their corresponding Br3d peaks [24]. If the bromine atoms are only due to non-reacted initiators grafted to CFs, there would be no ATRP process and, subsequently, no change in the surface composition.

The high resolution C1s regions from CF, CF-Br, and CF-polymer hybrids are displayed in Figure 6. CF and CF-Br exhibit complex

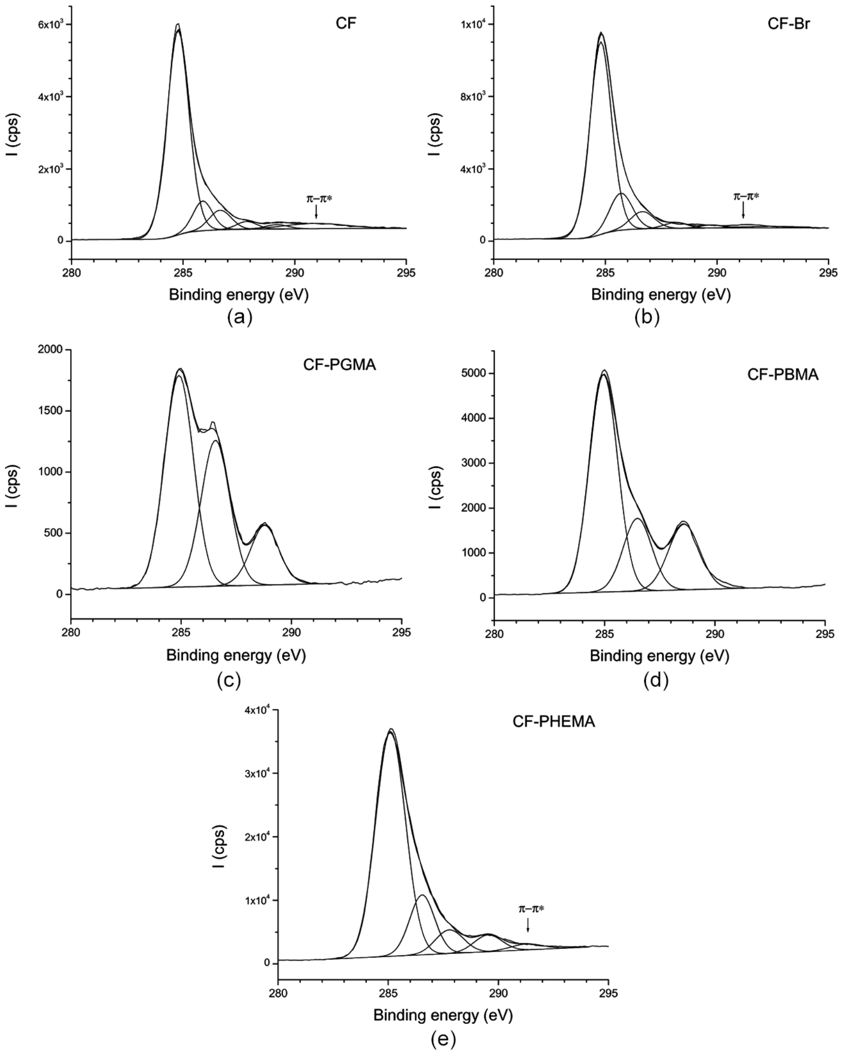


FIGURE 6 Peak-fitted C1s regions from CF, CF-Br, and CF-polymer hybrids.

C1s structures fitted with six components centered at 284.8 (sp2 carbon atoms), 285.8 ± 0.1 (C-N for CF and also C-Br for CF-Br), 286.7 (C-O), 288 ± 0.15 (C = O), 289.5 ± 0.2 (O-C=O), and 291–292.4 eV ($\pi \rightarrow \pi^*$ shake-up satellite from the graphitic carbon atoms of the fibers and electrografted aryl groups). The structure of C1s does not change significantly upon attachment of the aryl layer. Nevertheless, one can note that the shake-up satellite from the bare CF is slightly attenuated while a slight increase in the proportion of the component at 285.8 ± 0.1 eV, partially due to C-Br, is increased. After surface-initiated ATRP, the poly(alkyl methacrylates) induce a very typical C1s structure with three main components centered at 285, ~286.5 and ~289 eV corresponding to C-C/C-H, C-O and O-C=O chemical environments [33]. This occurs particularly for CF-PGMA and CF-PBMA, two hybrids with O/C ratios close to those of the pure reference polymers PGMA and PBMA, respectively. For CF-PHEMA, the fibers were less attenuated and therefore contributed to the C1s signal. For this reason, the C1s peak was fitted with two more components centered at 288 and 291.5 eV due to C=O bonds and the characteristic $\pi \rightarrow \pi^*$ shake-up satellite from the graphitic carbon atoms of the fibers, respectively [33].

The peak fittings provide the contributions of the characteristic O-C=O (C1s at ~289 eV) to the total C1s peaks from the CF-polymer hybrids. The contributions are 4.9, 14.3, and 19.9% for CF-PHEMA, CF-PGMA, and CF-PBMA, respectively. The CF-PHEMA is much less than the 16.7% calculated for pure PHEMA, which suggests a thin coating on CF. This confirms the low O/C atomic ratio reported in Table 1. For CF-PGMA, the contribution of the ester groups is 14.2% quasi equal to the 14.3% calculated from the chemical structure of PGMA. This result proves a thick and homogeneous coating of PGMA Finally, the CF-PBMA hybrid exhibits an ester contribution of 19.9%, higher than 12.5% expected for PBMA. Nevertheless, the shake-up satellite characteristic of carbon fibers is not detected, which is in favor of a compact PBMA coating in line with the O/C ratio reported in Table 1 for CF-PBMA.

The hydrophilic/hydrophobic character of the CF-polymer hybrids was examined by water contact angles in comparison with the behavior of CF and CF-Br. Usually, the determination of the contact angles or wettability on fibers is achieved by the Wilhelmy-gravitational method [34]. Alternatively, one can use another method which is based on the direct measurement from sessile drops [35]. In the present work, we would like to emphasize the evolution of the hydrophilic/hydrophobic character of the treated carbon fibers and have chosen to perform direct measurement of contact angles of sessile drops. In addition (as mentioned in the Experimental section), we explored another way to examine the water-fiber interactions by drawing the fiber bundles through the needle of a syringe and pressing the plunger to get a water drop to wet the fibers. This original, qualitative approach is particularly useful for a very hydrophobic fiber because it forces the contact of water with the fiber. Indeed, it is not always easy to put a water droplet in contact with a hydrophobic surface which naturally repels water.

Figure 7 shows digital photographs of water drops deposited onto the various fibers (left hand side) and those interacting with fiber

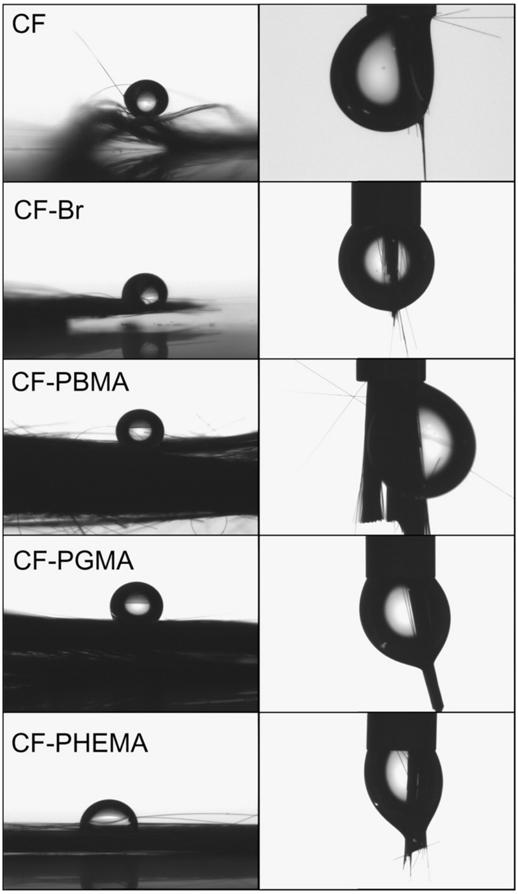


FIGURE 7 Interaction of water drops with untreated CF, CF-Br, and CF-polymer hybrids. The CF-PHEMA hybrid is the most hydrophilic material due to the grafted ultrathin layer of PHEMA.

bundles inserted through the needle (right hand side) Qualitatively, the water contact angle decreases in the order CF > CF-PBMA > CF-Br > CF-PGMA > CF-PHEMA.

On the right hand side of Figure 2, it is worth noting that the water drops are repelled by the CF and CF-PBMA fibers. Indeed, untreated carbon fibers are known to be hydrophobic as they are constituted of graphite. The substantial hydrophobic character of CF-PBMA is due to the butyl chains in the BMA repeat units. CF-PGMA is more hydrophilic due to the oxirane group and finally CF-PHEMA hybrid is the most hydrophilic due to the OH groups in the HEMA repeat units. PHEMA is well known to be a relatively hydrophilic polymer, a character that imparts a substantial resistance to non-specific protein adsorption [36].

It is clear that this qualitative study of the wettability of the fibers is in line with the chemical structure of the ultrathin polymer layers grown by ATRP. It is also strong supporting evidence that the organic polymer adlayers are uniform and behave as pure, thick films or sheets.

The hydrophilic/hydrophobic character of the fibers was further evaluated by BSA adsorption. Figure 8 displays the 2000–1200 cm^{-1}

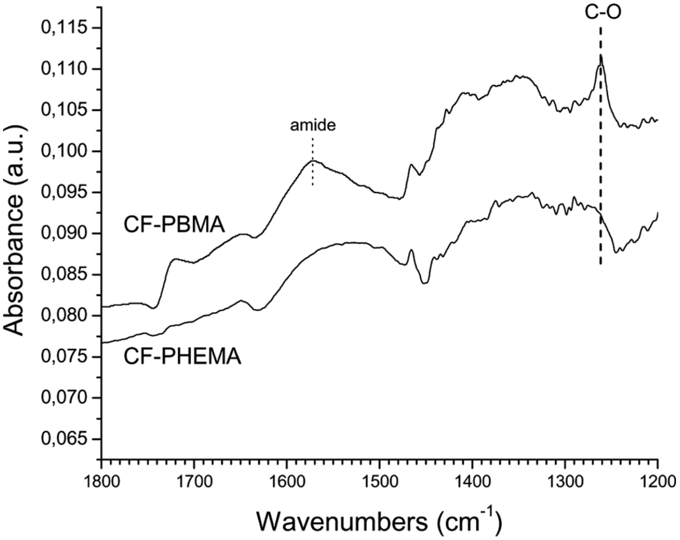


FIGURE 8 ATR-IR spectra of CF-PBMA and CF-PHEMA after interaction with BSA and rinsing with Tween and water. The former hybrid exhibits an intense and broad peak due to the amide groups from the adsorbed protein. Note that the C-O band at ~1260 cm^{-1}, ν_{as}(COO), is due to contamination by adsorbed carbonates (37).

region of ATR-IR spectra for CF-PBMA and CF-PHEMA after interaction with BSA. The CF-PBMA exhibits a broad peak due to the amide groups from BSA at 1571 cm^{-1}. At this position, no similar signal is observed for PHEMA. This difference in the spectra shows that BSA adsorption was more favorable on the hydrophobic CF-PBMA. In contrast, the CF-PHEMA hybrid decreases the protein adsorption, a result that is in line with the literature [36]. This result also shows that the ultrathin layers prepared by the "Diazonium salt/ATRP" protocol impart macroscopic properties to the fibers that would have been observed for pure PBMA and PHEMA.

FUTURE OUTLOOKS

Recent publications have reported on the spontaneous grafting of aryl groups by simply dipping substrates in diazonium salt solutions [38,39] or in solutions where the diazonium cations were in-situ generated [40]. This makes for simplicity of the diazonium salt surface chemistry. Particularly, for sp2 and sp3 carbon nanomaterials it is an important step since it is not possible to treat them electrochemically. Indeed, for powdered (nano)materials it is difficult to make a contact to such materials; therefore, electrografting is difficult if not impossible [41].

Moreover, several research teams spend a great deal of time and effort on nanomaterials for several fundamental and applied purposes. Combining a spontaneous grafting of aryl diazonium salts followed by growing polymer chains *via* surface-confined controlled radical polymerization would be a plus. In this regard, Wu *et al.* [42] have taken advantage of the spontaneous attachment of aryl groups for ATRP on carbon nanotubes. As far as we are concerned, we have recently bound ATRP initiator to nanodiamond (ND) *via* the spontaneous reduction of the diazonium salt **D1** in water at room temperature. We were able to attach poly(tert-butyl methacrylate) (PtBMA) chains. The resultant ND-PtBMA hybrids were further hydrolyzed in order to obtain ND-poly(methacrylic acid) nano-platforms for the covalent immobilization of proteins [43].

Whatever is the initial step for attaching polymerization initiators or monomers from diazonium salts, there are several points that still need to be addressed for this series of compounds:

- What are the grafting density, homogeneity, and thickness of the aryl layer (see, for example, ref. [24]?. The thickness of the polyaryl layers obtained by reduction of diazonium salts should be controlled. This means that for a given substrate and a given concentration of the diazonium salt, the potential and the duration of the electrografting reaction should be controlled, which amounts to controlling the charge passed in the experiment.

- What is the initiation efficiency of the grafted brominated aryl groups that are accessible to the monomers?
- Since the diazonium salts lead to a polyphenylene layer, it is likely that the tethered ATRP chains and the polyphenylene chains grafted from the salts form trees, with ATRP polymers constituting the side branches. This branched structure is likely to exist but is yet to be thoroughly examined by high resolution surface analytical techniques such as AFM.
- A systematic study needs to be performed to compare diazonium salts and classical coupling agents such as silanes and thiols under the same conditions that are for the same substrates and polymerization media. This comparison is needed for polymer adhesion either *via* the “grafting onto” or “grafting from” method.

CONCLUSION

Polymer chains were *grafted* by ATRP *from* the surface of carbon fibers modified by the electrochemical reduction of the brominated aryl diazonium salt $BF_4^-, ^+N_2\text{-}C_6H_4\text{-}CH(CH_3)\text{-}Br$ (**D1**). The grafted $\text{-}C_6H_4\text{-}CH(CH_3)\text{-}Br$ species were effective in initiating ATRP of n-butyl methacrylate, glycidyl methacrylate, and hydroxyethyl methacrylate at the surface of carbon fibers. The CF-PBMA, CF-PGMA and CF-PHEMA hybrids were characterized by XPS and water contact angles. XPS allowed the detection of elemental markers and characteristic functional groups from the underlying electrochemically pre-treated carbon fibers and from the grafted polymers.

Qualitative observations of water drops interacting with the untreated and polymer-coated fibers indicated wetting trends that are in line with the chemical structures of the tethered polymer chains; *i.e.,* CF-PHEMA being the most hydrophilic material despite a very thin polymer overlayer. Consequently, the CF-PHEMA hybrid was found to resist more to BSA non-specific adsorption compared with the more hydrophobic CF-PBMA system.

Combining ATRP and diazonium salts as a source of grafted initiators is a valuable approach, since grafting occurs in very mild conditions. It follows that the “Diazonium salt/ATRP” method fits extremely well with carbon fibers as they are amenable to electrochemical pretreatment.

From the above, these new strategies show conclusively that the chemistry toolbox of experts interested in carbon and other materials should contain aryl diazonium salts, given their versatility in forming active platforms. They permit the exploration of new chemistry options for surface treatments, particularly grafting ATRP initiators to carbon in very mild conditions. Although much is yet to be done to standardize the use of diazonium salts for surface treatment (particularly of sp2 and sp3 carbons), these chemical compounds can be considered as true and interesting new coupling agents for binding polymers and other materials to surfaces.

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