Grafted Carbon Fibers and Their Physicochemical Properties. I. Grafting of Methacrylic Acid onto Carbon Fibers

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ABSTRACT: A simple, reproducible method for grafting different carbon fibers (modified and unmodified, high-modulus, and high-tensile) with methacrylic acid is presented. The grafted carbon fibers were characterized by wetting measurements and electrokinetic studies. Scanning electron microscopy micrographs showed grafted polymer chains on all carbon fiber surfaces. The success of the grafting procedure depends on a suitable modification of the fiber surface. The amount and size of the grafted polymer chains on modified carbon fibers depend on the amount of initiator used. Contact angle measurements indicate an increase of the contact angle versus water and a decrease versus diiodomethane. The surface polarity calculated from the surface tensions obtained from contact angle values decreases for all systems under investigation. Zeta (ζ) potential measurements confirmed these results. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1175–1185, 1999

Key words: grafting reaction; carbon fiber; methacrylic acid; contact angle; zeta potential

INTRODUCTION

Carbon fiber containing polymeric composites with outstanding properties, such as high modulus and high tensile strength, low density, and a chemical inertness, have various applications in many advanced materials, for example, in the aircraft industry and sporting goods.¹ These mechanical properties of such composite materials are achieved only through optimal stress transfer from the matrix material to the fiber reinforcement. Therefore, it is, in many cases, necessary to modify the nonpolar carbon fiber surface. Various methods of surface modifications can be applied to carbon fibers, such as sizing and different oxidizing methods (that is, boiling in oxidizing acids, plasma modifications, and electrochemical oxidations).²⁻⁴ These surface oxidations improve the fiber matrix adhesion by forming covalent bonds between fiber and resins or by polar interactions between the components. Another method of achieving good stress transfer is mechanical interlocking between covalently bonded polymer on the carbon fiber surface and the matrix.⁵ Zeng and Bailing⁶ tried to graft Nylon 10.10 by *in situ* polymerization to the carbon fiber surface but obtained only poor composite properties. Others, that is, Koschinski and Reichert,⁷ described the preparation of carbon-fiber-reinforced poly(phenylene sulfide) (PPS) also by in situ polymerization. A high adhesion between grafted fibers and PPS resulted. Bhama and Stupp⁸ performed in situ polycondenzation of p-acetobenzoic acid, di-

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acetoxyhydroquinone, and pimelic acid in the presence of functionalized carbon fibers to produce grafted polymers on carbon fibers. The grafting took place at the carboxyl groups present on the carbon fiber surface. Poly(methyl methacrylate) was grafted onto carbon fiber surfaces by electron beam irradiation of methyl-methacrylate-soaked carbon fibers.⁹ Tsubokawa and Ueno¹⁰ modified thin carbon films through the introduction of azo-, acylperchlorate, or carboxyl surface groups. In a second reaction step, these groups were grafted with vinyl or epoxy monomers by radical-, cationic-, or anionic-initiated polymerization. Here, we describe a simple method to graft modified carbon fibers with methacrylic acid. Our investigations focused on zeta potential (ζ potential) and contact angle measurements to study the physicochemical properties of the grafted carbon fibers.

EXPERIMENTAL PART

Grafting Reactions

In order to optimize the parameters necessary to attach methacrylic acid to different carbon fiber surfaces, various preliminary experiments were performed. The amount of initiator azodiisobutyronitrile (AIBN) was varied between 1 and 10 mol %, and the results were studied by scanning electron microscopy (SEM) and contact angle measurements. We used unmodified polyacrylonitrile (PAN)-based carbon fibers [high tensile (HT) and high modulus (HM)] from SGL Carbon (Meitingen, Germany; Sigrafil C320.00A and HM48.00A) as well as fibers, treated 10 min in oxygen plasma (1.5 mbar; reactor power, 16.5 W; gas flow, 4.5 mL (STP)/min). The plasma reactor has already been described.¹¹

Fibers and initiator were placed in a reaction vessel, and the methacrylic acid was poured over the mixture. Then it was heated up to 75°C until the polymerization was completed. This took about 15 min. In order to remove any unreacted monomer, the samples were extracted with water for 7 days and dried at 50°C, 1 mbar, until a constant weight was reached.

Surface Morphology

All treated fibers were analyzed by SEM to show changes in the surface morphology. Fibers were investigated with a Hitachi S-2700 scanning electron microscope. Grafted fibers were sputtered with gold prior to microscopic analysis since the polymer is nonconducting.

Contact Angle Measurements

Since the contact angle, θ , of a test liquid on carbon fibers is not easily measured directly because of the small fiber diameters (about 7 μ m), we used a gravimetric method, the modified Wilhelmy technique, to estimate the contact angles to water (surface tension $\gamma = 72.8$ mN/m; polar component of the surface tension $\gamma^p = 50.7$ mN/m; and dispersive part of the surface tension γ^d = 22.1 mN/m; polarity $X^P = \gamma^P/\gamma = 0.7$) and to diiodomethane ($\gamma = 50.8$ mN/m; $\gamma^p = 6.7$ mN/m; and $\gamma^d = 44.1$ mN/m, $X^P = 0.13$).¹²

Because of the very small mass change during the measurement while using a monofilament, five fibers were put parallel to each other onto an aluminum carrier. The carrier was placed into a ultramicroelectrobalance (MP8, Sartorius, Göttingen, Germany; accuracy, 0.1 μ g; reproducibility, 0.2 μ g) so that the ends of the fibers were located over the test liquid surface. Weight recordings were obtained during fiber immersionemersion cycle at the stage velocity of 3 μ m/s. After immersion of the fibers into the liquid, for approximately 15 min, the same direction was kept, then the direction was changed until the end of emersion. The immersion and emersion was realized through a reversible elevator operated with a direct current motor. The direct current was taken from a constant current source (Philips Power Supply Unit PE1507).¹³

For the contact angle, θ , calculation, the effective fiber diameters, d, were estimated by scanning electron micrographs. Advancing θ_a and receding θ_r contact angles were calculated by the Wilhelmy equation from the mass changes Δm , which were detected during the immersion and emersion of the fibers into the test liquid, as follows:

$$\cos \theta = \frac{\Delta m \cdot g}{U \cdot \gamma} \tag{1}$$

where g is the acceleration of gravity, U is the fiber perimeter, and γ is the surface tension of the used test liquid.

Due to the very small fiber diameters, no buoyancy slope could be obtained. To check the reproducibility, all measurements were carried out ten times on fibers of the same sample. All contact angle values are average values, and the error values are standard errors. The contact angle measurements were performed in an air-conditioned room at a constant temperature of 20°C.

By use of the harmonic mean method introduced by Wu,¹¹ a combination of the harmonic mean equation, which is valid between low-energy materials,

$$\gamma_{sl} = \gamma_s + \gamma_{lv} - 4 \left(\frac{\gamma_{lv}^d \cdot \gamma_s^d}{\gamma_{lv}^d + \gamma_s^d} - \frac{\gamma_{lv}^p \cdot \gamma_s^p}{\gamma_{lv}^p + \gamma_s^p} \right)$$
(2)

and the Young equation,¹⁴

$$\gamma_{lv} \cdot \cos \theta = \gamma_s - \gamma_{sl} \tag{3}$$

which leads to the following term:

$$(1 + \cos \theta) \cdot \gamma_{lv} = 4 \cdot \left(\frac{\gamma_{lv}^d \cdot \gamma_s^d}{\gamma_{lv}^d + \gamma_s^d}\right) + \left(\frac{\gamma_{lv}^p \cdot \gamma_s^p}{\gamma_{lv}^p + \gamma_s^p}\right) \quad (4)$$

(Indices: s = solid; l = liquid; v = vapor)

We calculated from measured contact angle values between fibers and water and diiodomethane and the known surface tensions of this test liquids using the term above the solid surface tension. The solid surface tension is given by the following equation:

$$\gamma_s = \gamma_s^d + \gamma_s^p \tag{5}$$

and the polarity X^P of the solid surface.

$$X^{P} = \frac{\gamma_{s}^{P}}{\gamma_{s}} \tag{6}$$

The surface tensions for the used test liquids are known, as mentioned above.

Zeta (ζ) Potential Measurements

The ζ potentials were determined with the electrokinetic analyzer EKA (Anton Paar KG, Graz, Austria) based on the streaming potential method¹⁵ only for the grafted C320.00A carbon fibers. Details of the ζ potential measuring technique are reported elsewhere.^{16,17}

To measure the time dependence of the ζ potential, the analyzer was filled with a $1 \cdot 10^{-3}M$ KCl–electrolyte solution. After the preparation of the fiber-measuring cell with approximately 1.5 g fiber, the cell was connected with the analyzer, fast-rinsed with the KCl–electrolyte solution, and degassed; finally, the measurement started. The decrease of the ζ potential with time is caused by uptake from water, and this effect depends on the hydrophilic character of the solid.¹⁸ A reason of the decrease of the ζ potential is the swelling of the solid, which causes a transfer of the shear plane into the solid. The diffuse part of the electric double layer is excluded from the mechanical or electrical interaction. Another reason is the removal of surface adsorbed soluble components, which causes a decrease of the solid surface potential.

For the investigation of the dependence of the ζ potential upon concentration of the electrolyte, the analyzer was filled with bidistilled water and the fiber-measuring cell was rinsed. The conductivity in the measuring system is now under 300 μ S/cm. First, the water value of the ζ potential was measured; and, subsequently, the KCl concentration was raised (using a digital burette from Fa. Brand, Wertheim, Germany), and the system, including the fiber-measuring cell, were rinsed in either measuring directions. The concentration was raised up to 0.01M KCl. At high electrolyte concentrations, the correlation of the measuring values decreases in both directions of flow $(dU/dp) \approx 0$.²⁴

It is possible to obtain information from the concentration dependence of the ζ potential about the degree of interactions between the solid surface and the ions of the electrolyte solution, based on specific or electrostatic interactions. For most fiber materials, the ζ potential values show corre-



Figure 1 Schematic picture of $\zeta = f(pH)$ for Brønstedt acidic and alkaline surface functional groups and for complete hydrophobic surfaces.



(c)

Figure 2 SEM of untreated, methacrylic-acid-grafted HM48.00A: grafted with (a) 0.5, (b) 2.5, and (c) 10 mol % AIBN.

sponding to the Stern theory¹⁹ a parabolic-like curve trend; this is caused by the adsorption properties of the solid for potential determined ions, as well as specific adsorbated ions. The following two characteristic parameters can be derived from this parabolic trend: the maximal ζ potential ζ_{max} and the maximal concentration value c_{max} . The Stern theory makes no assumptions regarding to the kind of charge carriers close to the phase border, so it should be valid for solids, where the surface potential is determined through dissociation of surface groups or through the adsorption of ions. It is possible to calculate the adsorption potentials of ions on a solid surface from these two characteristic values with a combination of the following equations:

$$2RT \ln c_{\max} = \Phi_- + \Phi_+ \tag{7}$$

and

$$\Phi_{-} - \Phi_{+} = 2F\zeta_{\max} \tag{8}$$



Figure 3 SEM of oxygen-plasma-treated, methacrylic-acid-grafted HM48.00A: grafted with (a) 1.0 and (b) 5.0 mol % AIBN.

where R is the gas constant, F is the Faraday constant, and T is absolute temperature. To keep the ion strengths constant, the pH dependence of the ζ potential was determined in a $1 \cdot 10^{-3}M$ KCl–electrolyte solution. The pH value was varied in a range of pH 3 to 11 by adding drops of 0.1M HCl or KOH solution.

By measuring the pH dependence of the ζ potential, the acidity or basicity of solid surfaces can be determined qualitatively. If the assumption is valid that the formation of the electrical double layer is caused by the dissociation of acidic functional surface groups, a plateau area in the alkaline range (Fig. 1) for the pH dependence of the ζ potential is obtained, caused by the dissociation of this acidic surface groups. If there is a change of the sign of the ζ potential in the acidic range, this is, first of all, caused by repressing the dissociation of the acidic surface groups, and, secondly, by the adsorption of the currently potential determining ions. The analogous trend of the ζ potential is present (Fig. 1) if there are any alkaline surface groups. The isoelectric point (iep) is also a measure of the acidity or basicity of a solid surface, when the dissociation of surface groups is the dominate mechanism of the formation of the electrical double layer. If the iep has a low value, then the solid surface has an acidic character; if the iep is situated in the alkaline range, then basic surface groups are present.²⁰

RESULTS AND DISCUSSION

Grafting Reactions and SEM Investigations

Grafting reactions with methacrylic acid and unmodified HM48.00A carbon fibers were performed with 0.5, 2.5, and 10 mol % AIBN. Only the experiment with 10 mol % AIBN showed a relative high amount of short grafted polymer chains attached to the fiber surface (see Fig. 2). Only very small amounts of grafted polymer were found performing the polymerization with 0.5 and 2.5 mol % AIBN. The probability to graft polymer chains onto an unmodified fiber surface increases with increasing amount of growing polymer chains, and this is proportional to the initiator concentration. A completely different grafting behavior was found while performing the polymerization in the presence of oxygen-plasma-modified carbon fibers.

Using oxygen-plasma-modified HM48.00A fibers and varying the initiator content (1 and 5 mol %), the chain length behavior of the grafted polymers showed the dependence, expected from normal free radical polymerization kinetics. From SEM investigations, it can be seen that small amounts of AIBN gave long but few grafted polymer chains; larger amounts of initiator resulted in many small polymer chains grafted onto the fiber surface. This suggests a regular radical polymerization mechanism to be responsible for the



Figure 4 SEM of oxygen-plasma-treated, methacrylicacid-grafted C320.00A, grafted with 10 mol % AIBN.

formation of grafted polymers²¹ (see Fig. 3). Due to the long duration of the Soxhlet extraction, we assume that all polymers still present on the fiber are covalently bonded to the carbon fiber surface. All physisorbed molecules should have been removed through the extraction process. It was impossible to remove the grafted polymers from the surface without degrading it. A larger magnification was chosen for Figure 3(b) in order to show the influence of the oxygen plasma treatment on the surface morphology. Oxygen plasma treatment causes a disruption of the graphitic structure of carbon fiber surfaces.²²



Figure 5 Contact angle versus water of untreated, grafted HM48.00A.



Figure 6 Contact angle versus diiodomethane of untreated, grafted HM48.00A.

Additionally, 10-min oxygen-plasma-treated C320.00A fibers were also used to check the reproducibility of the grafting method. Here, initiator concentrations of 1, 5, and 10 mol % were applied (see Fig. 4). We found the same polymer length-initiator concentration dependence as for the modified HM48.00A fiber.

These results indicate a strong influence of the plasma modification of the carbon fibers prior to the polymerization. Without any modifications of the fibers, it is almost impossible to graft polar monomers (like methacrylic acid) to a nonpolar carbon surface. However, the higher the initiator concentration, the higher the probability that a radical attaches itself onto the carbon fiber surface.

Contact Angle Measurements

To estimate the fiber solid surface tension by the harmonic mean method introduced by Wu, the contact angles versus water and diiodomethane were measured. Using the modified Wilhelmy method, the following two reproducible contact angles were obtained: the advancing contact angle θ_a and the receding contact angle θ_r . θ_a should be characteristic for the low energy part of the fiber surface and θ_r for the high-energy part. We calculated the solid surface tensions from the θ_a values, which were determined by immersing the dry fibers into the test liquid.

 $\theta_a~{\rm for~methacrylic-acid-grafted~unmodified}$ HM48.00A fibers measured versus water (Fig. 5) diminishes to a relative constant value within the error range. The error became greater due to the



Figure 7 Contact angle versus water of oxygenplasma-treated, grafted HM48.00A.

relative nonuniform character of this modification. But the surprising aspect is that the contact angles do not decrease with increasing initiator content and, therefore, with a increasing amount of polar polymer chains grafted onto the fiber surface. θ_r remains constant; therefore, the contact angle hysteresis, defined as the difference between θ_a and θ_r , becomes smaller. This indicates that the fiber surface becomes more homogeneous. But more interesting is the fact that the contact angles determined versus diiodomethane (Fig. 6) decrease with increasing content of initiator. The contact angle hysteresis increases by a small value, which means that the surface becomes heterogeneous versus diiodomethane. The contact angle is a direct measure for wettability. So the grafted carbon fiber is better wettable by



Figure 8 Contact angle versus diiodomethane of oxygen-plasma-treated, grafted HM48.00A.



Figure 9 Contact angle versus water of plasmatreated, grafted C320.00A.

the nonpolar liquid diiodomethane, even though polymethacrylic acid is a polar, water-soluble polymer. This might be explained through molecular arrangements, where the polar groups attract each other by forming a quasi-micelle; thus, the nonpolar parts of the polymer chain are on the outside, which influence directly the contact angle versus the chosen test liquids. For oxygenplasma-treated HM48.00A, θ_a remains constant within the error range (Fig. 7), but the contact angles measured versus diiodomethane (Fig. 8) decrease. The hysteresis also increases from almost zero to a larger value.

For grafted, in oxygen-plasma-modified C320.00A carbon fibers, θ_a measured versus water (Fig. 9) even increase by 18 degrees for fibers grafted with 1 mol % initiator; but with an increasing initiator



Figure 10 Contact angle versus diiodomethane of oxygen-plasma-treated, grafted C320.00A.

MA-grafted HM48.00A ^a (mol % AIBN)	γ (mN/m)	γ^{p} (mN/m)	$\gamma^d \ (mN/m)$	X^P	
0	38.18 ± 1.31	17.12 ± 1.56	21.06 ± 0.88	0.45	
0.5	49.01 ± 3.70	21.27 ± 3.13	27.74 ± 1.97	0.43	
2.5	49.87 ± 3.08	21.31 ± 2.70	28.56 ± 1.48	0.43	
10	48.80 ± 2.75	18.51 ± 2.37	30.29 ± 1.39	0.38	

Table I Surface Tensions and Polarity of Unmodified, Grafted HM48.00A Fiber

^a MA is methacrylic acid.

amount, θ_a decreases again. Also surprising is that by the grafting of a water-soluble polymer, the contact angle increases. θ_r remains constant. The hysteresis increases, and, therefore, the fiber surface becomes more heterogeneous after grafting such a polymer. The contact angles estimated versus diiodomethane (Fig. 10) also decrease.

The fiber surface tensions calculated from this contact angle values are shown for all grafted carbon fibers in Tables I–III. For all grafted carbon fibers, the dispersive component of the surface tension γ^d increases by a large amount, while the polar part γ^p remains almost constant for untreated, but grafted HM48.00A. Therefore, the fiber surface tension increases to a greater value.

Oxygen-plasma-modified, grafted HM48.00A have the same surface tension within the error range, even though γ^p diminish nearly by the same amount as γ^d increases by grafting polar polymer chains onto the fiber surface. The surface polarity decreases drastically.

The fiber surface tension for oxygen-plasmatreated and grafted C320.00A fibers diminishes compared to the ungrafted fiber to a constant value; any variation of the initiator content in the grafting mixture (methacrylic acid and AIBN) does not affect the polar or dispersive part of the surface tension, and, therefore, the surface polarity also remains constant.

Zeta (ζ) Potential Measurements

The reproducibility of electrokinetic measurements depends strongly on the sample quality and preparation. This means that every measurement of the concentration- or pH-dependence needs a well-defined starting point, which is dependent on the time that the whole system needs for equilibration. It is fixed by a long time measurement. The time dependence of the ζ potential of the poly(methyl acrylic) acid-grafted carbon fibers indicates that the ζ potential remains constant during the measurement. An untreated carbon fiber needs only 50 min to equilibrate. But the negative ζ potential values decrease by 10 mV. Usually, carbon fiber do not swell, so the decrease of the ζ potential is caused by the cleaning process of the surface through rinsing in the measuring cell. The removal of water-soluble components of a solid surface generally shows an analogous time dependence.

For all investigated carbon fibers, the pH dependence of the ζ potential shows a striking plateau range in the alkaline part (Fig. 11). The dissociation of the acidic surface groups causes this plateau range. The ungrafted carbon fibers (C320.00A, treated 10 min in oxygen plasma) have the lowest plateau value of the negative ζ potential (see Table IV). Oxygen plasma treatment of carbon fibers leads to oxygen-containing surface groups, where the groups form acidic functional surface groups.²³ The decrease of the negative ζ potential is caused by the repression of the dissociation of the acidic surface functional groups. At lower pH values, the adsorption of protons, which are potential determining ions, is the predominant process, which leads to a change

Table II Surface Tensions and Polarity of Plasma-Modified, Grafted OP HM48.00A Fiber

MA-grafted 10-min OP ^a HM48.00A (mol % AIBN)	$\gamma (mN/m)$	$\gamma^p (mN/m)$	$\gamma^d (mN/m)$	X^P
0	55.32 ± 2.92	35.23 ± 2.64	20.09 ± 1.25	0.64
1	57.56 ± 3.64	32.47 ± 2.75	25.09 ± 2.39	0.56
5	55.34 ± 3.03	25.19 ± 2.69	30.15 ± 1.39	0.46

^a OP is oxygen plasma.

MA-grafted 10-min OP ^a C320.00A (mol % AIBN)	γ (mN/m)	$\gamma^p ({ m mN/m})$	$\gamma^d \; ({ m mN/m})$	X^P
0	53.35 ± 2.57	34.20 ± 2.45	19.15 ± 0.76	0.64
1	46.16 ± 4.90	18.74 ± 4.67	27.42 ± 1.49	0.41
5	50.26 ± 3.45	20.56 ± 1.75	29.70 ± 2.97	0.41
10	53.83 ± 3.90	24.90 ± 2.97	28.93 ± 2.53	0.46

Table III Surface Tensions and Polarity of Plasma-Modified, Grafted OP C320.00A Fiber

^a OP is oxygen plasma.

of the surface charge if the pH is increased over the iep. The iep also is a measure for the surface acidity, but this high acidic value could not be estimated due to the high surface functionalization. Those high acidic values are not measurable because the proton concentration is too low; a high ion strength of the electrolyte solution would cause a decrease of the negative ζ potential. The modification results in a plateau ranging from pH 5 to 9 at $\zeta_{\text{plateau}} = 26.4$ mV. The plateau values from the pH dependence and the shift of the iep towards more acidic values can be explained by a polarization effect.

A shift to higher negative ζ potential values was found for the grafted fibers. Fibers grafted with 1 mol % AIBN has the highest negative plateau value because it has the highest hydrophobia, that is, the highest contact angle versus water. ζ_{plateau} decreases with increasing initiator content, which leads to smaller and shorter polymer chains bonded to the carbon fiber surface.



Figure 11 pH dependence of ζ potential of oxygenplasma-treated, grafted C320.00A.

The peak appearing at pH \sim 10 is probably due to some effects caused by the reaction of the methacrylic acid groups with the alkaline solvent. If the polymer chains become longer, the peak takes more shape. The higher the initiator content, the higher the iep, which indicates a diminution of the acid character of the modified carbon fiber surfaces. The smaller the amount of initiator, the longer the polymer chains, and the fewer the number of grafted molecules to the carbon fibers. Therefore, more original acid surface, derived from the oxygen plasma treatment, remains.

Correction of surface conductance [Fig. 12(b)] does not affect the trends of the concentration dependence of the ζ potential [Fig. 12(a)]; only the values of the ζ potential were shifted to higher values. The adsorption potentials of K⁺ and Cl⁻ (Table V) show that Cl⁻ is preferably adsorbed on all modified carbon fibers as well as on the plasma-treated C320.00A. A modification of the plasma-treated C320.00A by grafting methacrylic acid onto the fiber surface enlarges the adsorption potentials for Cl⁻ but decreases for K⁺. Grafting of polymer chains onto the carbon fiber surface dramatically changes their morphology, which influences the formation of the electrochemical dou-

Table IV	$\zeta_{\rm plateau}$	Values	of Plasma-Modified
and Grafte	ed OP (C 320.00 A	A Fiber

Grafted 10-min OP ^a C320.00A (mol % AIBN)	$\zeta_{\mathrm{plateau}} \left(\mathrm{mV} \right)$	iep
0	-26.4	
1	-49.4	2.9
5	-41.1	3.1
10	-39.1	3.8

^a OP is oxygen plasma.



Figure 12 (a) Concentration dependence of ζ potential of oxygen-plasma-treated, grafted C320.00A. (b) Concentration dependence of ζ potential of oxygen-plasma-treated, grafted C320.00A (correction of surface conductance).

ble layer and, therefore, the ζ potential. A possible explanation for the decrease of K^+ ions adsorption potentials is the ion exchange of protons with

 K^+ , so K^+ is situated in the inner Helmholtz layer and is therefore not measurable by streaming potential measurements. The higher the amount of grafted polymer onto the fiber surface, the greater the amount of exchanged protons by K⁺ ions and, therefore, the smaller the K⁺ adsorption potentials. The higher the amount of K^+ in the inner Helmholtz layer, the more Cl⁻ ions can be adsorbed in the outer Helmholtz layer, and, therefore, the Cl⁻ adsorption potentials enlarges. But the results obtained from concentration dependence of the ζ potential are difficult to explain. Since the specific adsorption of ions occurs in concurrence with the adsorption of water, it is expected that hydrophobic surfaces have higher negative ζ potentials.²⁴ As indicated by the contact angle measurements versus water, the hydrophobic character of the methacrylic-acidgrafted surfaces increases and, therefore, the negative ζ potential.

For all carbon fibers characterized by ζ potential measurements, no differences for the ζ potential value, measured in bidistillated water, were detected. Changes of the water ζ potential value would indicate that a modification can cause differences in the concurrence mechanism between water adsorption and specific ion adsorption. The above postulated assumption that the grafted methacrylic acid polymer chains form a quasimicelle has been undetermined by these ζ potentials measurements $[\zeta = f(pH, c)]$. Both measurements indicate an increase of the surface hydrophobicity caused by the influence of the fewer, but bigger hydrophobic quasi-micelles. The negative ζ_{max} and $\zeta_{plateau}$ values and the ieps enlarged with decreasing initiator concentration, while this causes the iep values to decrease due to the increasing surface acidity due to relatively large amount of free, nongrafted, plasma-modified carbon fiber surface.

Table V C_{max} , ζ_{max} , and Adsorption Potentials of K⁺ (Φ_+) and Cl⁻ Ions (Φ_-) for Grafted OP C320.00A Fibers

Grafted 10 min OP ^a C320.00A (mol % AIBN)	$\begin{array}{c} Corrected \\ \zeta_{max} \ (mV) \end{array}$	$C_{\max} \; (\text{mol/L})$	Φ_{-} (kJ/mol)	Φ_+ (kJ/mol)
0	37.73 ± 0.50	0.003	-17.94 ± 0.19	-10.66 ± 0.10
1	-64.77 ± 0.97	0.003	-20.55 ± 0.33	-8.06 ± 0.14
5	-52.10 ± 0.99	0.003	-19.33 ± 0.33	-9.28 ± 0.14
10	-52.00 ± 1.70	0.003	-19.32 ± 0.54	-9.29 ± 0.21

^a OP is oxygen plasma.

We have shown that it is possible to graft methacrylic monomers onto carbon fiber surfaces by simple radically initiated bulk polymerization, which was proved by SEM investigations, wetting, and ζ potential measurements. Modified and unmodified carbon fibers differ strongly in their grafting behavior. For modified carbon fibers, the usual polymerization kinetics are found. The grafted polymers have a significant influence on the wetting behavior and the ζ potential estimated as a function of pH dependence and electrolyte concentration. Grafting of a water-soluble polymer onto carbon fibers worsens the wettability versus water and improves it towards the nonpolar liquid diiodomethane. The surface polarity determined from the calculated surface tensions decreases for all investigated systems. This has also been proved by measurements of the ζ potential.

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