Functionalization of carbon fibers by anodic oxidation: Surface analysis by X-ray photoelectron spectroscopy

Matthias Bauer[1,2], Fabian Schubert[1], Judith Moosburger-Will[2] and Siegfried Horn[1,2]

[1]Institute of Physics, Experimental Physics II, University of Augsburg, 86135 Augsburg, Germany
[2]Institute of Materials Resource Management, University of Augsburg, 86135 Augsburg, Germany
Email: Matthias.Bauer@physik.uni-augsburg.de, Web Page: http://www.uni-augsburg.de/exp2

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Abstract

In this work we investigate the influence of the parameters of the anodic oxidation process on the carbon fiber surface chemistry by x-ray photoelectron spectroscopy. To this end we vary different parameters of the anodic oxidation process, i.e. treatment time, electric current density, and concentration of the electrolyte. The surface of the anodically oxidized carbon fibers shows increasing oxygen and nitrogen contencentration with increasing treatment times and electric current densities. The same effect is achieved by decreasing the electrolyte concentration. An increase of the amount of COR, C=O and COOR groups is found after anodic oxidation compared to the untreated fiber. With increase of electrical current density and treatment time a significant increase of C=O and COOR groups is observed, while the number of COR groups only slightly increases or even decreases. Obviously, the oxidation process continues and higher oxidation states of the carbon atoms are created. Both COR and COOR groups, in particular COH and COOH, further chemical bonding to epoxy resins, which are frequently used as matrix systems for carbon fiber reinforced polymers. The results demonstrate the significant influence of the process parameters of anodic oxidation on the surface chemical composition and functionality of the carbon fiber surface and shows the possibility to design the carbon fiber surface chemistry.

1. Introduction

The adhesion between carbon fiber and polymer matrix in carbon fiber reinforced polymers (CFRP) has high influence on the interface dominated mechanical properties [1, 2]. To achieve good bonding a surface activation of the turbostratic carbon structure is necessary, which produces reactive functional groups on the fiber surface. For this purpose several methods are known, e.g. electrolytic oxidation, gas phase oxidation, plasma treatment or ozone treatment [3]. A widely used technique is the electrolytic anodic oxidation process [4, 5]. The fiber, which acts as the anode, runs through an electrolyte bath. The oxygen containing ions produced between anode and cathode are transported to the fiber and oxidate its surface. In principal, different electrolytes can be used [6, 7]. In our study we use ammonium bicarbonate, which is commonly used for industrial anodic oxidation of carbon fibers [8]. To study the relevant parameters of the anodic oxidation process, we vary treatment time, electric current density and concentration of the electrolyte. After the anodic oxidation process x-ray photoelectron spectroscopy (XPS) is used to characterize the chemical changes of the surface of the carbon fiber. This method is very surface sensitive and allows for determination of the surface chemical composition and functionality [9].

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2. Experimental

2.1. Fiber surface treatment

Untreated 50k Sigrafil® C30 T050 polyacrylnitril-based carbon fibers, in the following called UNT, were used. These fibers were treated in our experimental setup (see Figure 1) by static anodic oxidation (Ox), i.e. the fiber was not moved during oxidation. Current densities varied from 0.5A/m² to 4.2A/m² and treatment times from 10s to 50s. The fiber acts as the anode and is routed over teflon bars through the electrolyte bath and is electrically contacted via clamps. The cathode is realized by a flat graphite plate. As electrolyte we used ammonium bicarbonate with a concentration of the electrolyte bath of 3% and 8%. After treatment the fibers were washed in destilled water and dried for 1h at 150°C. The distance between cathode and anode (carbon fiber) is 6cm.

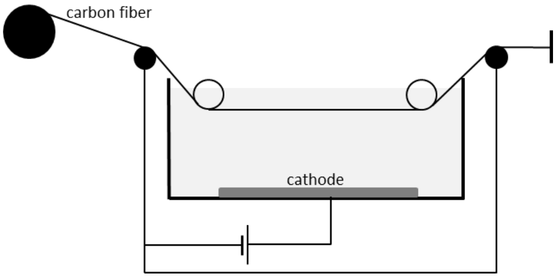

Figure 1. Design of the experimental setup for static anodic oxidation.

2.2. Fiber surface analysis by photoelectron spectroscopy

For chemical analysis of the carbon fiber surfaces we used x-ray photoelectron spectroscopy (XPS). This method is very surface sensitive and allows for determination of the surface chemical composition and functionality. An Omicron XM 1000 monochromatized X-ray source with Al Kα radiation (1486.7eV) was used. The survey scan was measured at 50eV pass energy and the highly resolved C1s spectrum was taken at 17eV pass energy. A Shirley background is subtracted. Samples measured consisted of carbon fiber bundles tightly fixed to the top of a grounded sample holder by a gold aperture. Surface elemental composition is determined by analysis of the respective XPS peak areas, corrected by the element and orbital specific sensitivity factors. The sum of the peak areas is normalized to 100%. The functional surface groups are investigated by fitting the highly resolved C1s spectrum by a suitable number of lines. The spectrum of the C1s region is fitted by six pseudo Voigt lines with the parameters peak position, full width at half maximum and peak area. Each type of chemical group is characterized by a specific chemical shift of the C1s signal [9-11].

3. Results

To study the influence of the anodic oxidation process on the fiber surface chemical composition and functionality, anodic oxidation treatment period, electric current density and electrolyte concentration are varied and the resulting carbon fibers are analyzed by XPS.

3.1. Influence of anodic oxidation period

XPS analysis of the untreated carbon fiber surface reveals only a low concentration of oxygen and nitrogen (see Table 1). During the oxidation process the surface chemical composition changes. After 10s of anodic oxidation (electrolyte concentration 3%, current density 3.2A/m²) the oxygen concentration rises to 9.7at% until it reaches its maximum of 17.2at% at the highest treatment time of

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50s. The same trend is observed for the nitrogen concentration. It rises to maximal 5.6at% for longer oxidation periods.

Table 1. Surface elemental composition of carbon fiber surface after different anodic oxidation treatment periods (electrolyte concentration 3%, current density 3.2A/m²).

	C [at%]	O [at%]	N [at%]
UNT	97.2	1.9	0.9
Ox, 10s	87.8	9.7	2.4
Ox, 20s	87.4	10.0	2.7
Ox, 30s	83.7	12.9	3.5
Ox, 40s	83.4	13.1	3.5
Ox, 50s	77.3	17.2	5.6

In Figure 2 the corresponding high resolution XPS spectra of the C1s peak are shown. In agreement with literature [9-11] the carbon main peak is positioned at a binding energy of 284.4eV and accounts for aromatic carbon structures. Aliphatic carbon is found at slightly higher binding energies of around 285.3eV. Alcohol and ether groups are located at a binding energy of 286.1eV. Carbonyl and carboxyl groups are found at 287.4eV and 288.7eV, respectively. The position of the fitted peak lines varies by maximal ± 0.2eV. The full width at half maximum (FWHM) of the graphitic peaks is 1.0 ± 0.2eV. The COR, C=O and COOR peaks have FWHMs of 1.2eV, 1.4eV and 1.4eV. All FWHMs vary by maximal ± 0.1eV. The conducting behavior of the carbon fiber leads to a π→π* excitation at a binding energy of 290.4 ± 0.2eV with FWHM of 2.2 ± 0.6eV.

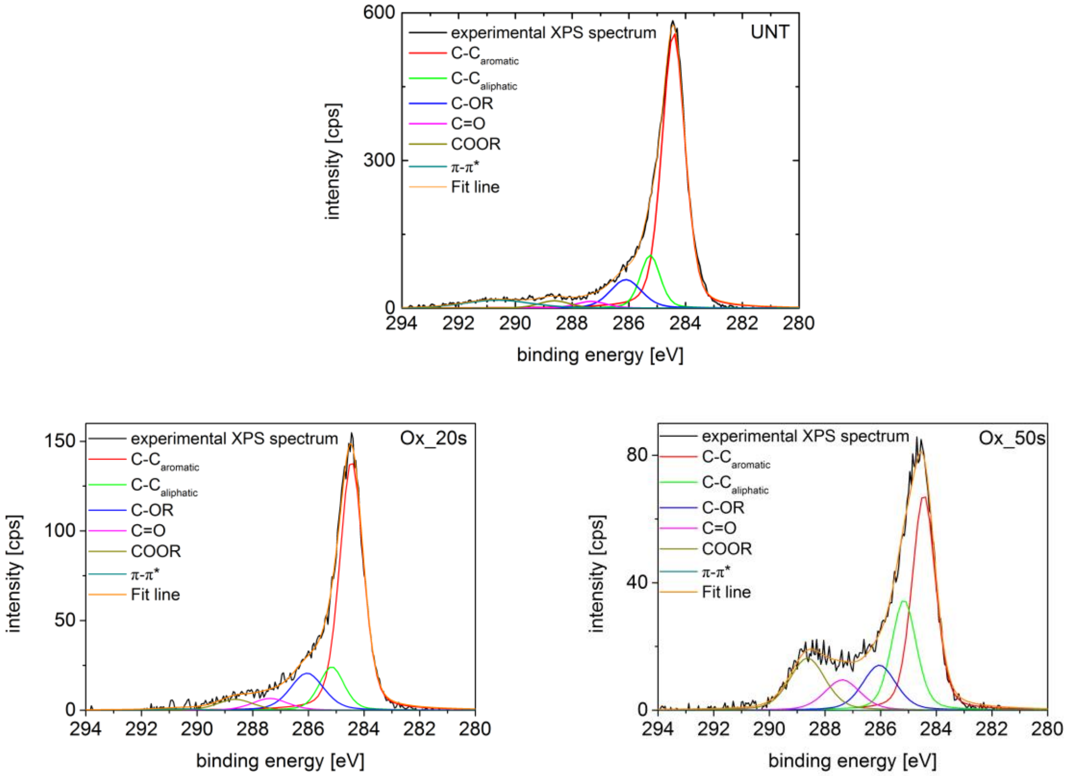

Figure 2. C1s spectra of the UNT sample and the anodically oxidized carbon fibers treated for 20 and 50s (electrolyte concentration 3%, current density 3.2A/m²).

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With increasing anodic oxidation the high binding energy tail of the C1s signal increases. This is due to an increase of C=O and COOR functionalities on the fiber surface. The COR groups, the chemical shift of which is lower, show only minor changes. The $\pi \rightarrow \pi^*$ peak can be identified only for the UNT fiber. After the oxidation process it has nearly vanished.

Table 2 summarizes the contributions of the chemical groups derived from the C1s spectrum. Additionally, the evolution of the oxygen containing groups is plotted in Figure 3a. The UNT fiber exhibits mainly COR groups. Small treatment times lead first to an increase of the COR groups and for long treatment times (more than 30s) to a slight decrease. In contrast, the ratio of the C=O and COOR groups is rising continuously. After 50s the highest oxidation state of the carbon atoms is created and COOR groups represent the highest part of the oxygen containing groups on the carbon fiber surface. The result is in good agreement with literature, where an increasing oxidation of the carbon atoms of the surface is described. According to [4] C-H groups first are converted into C-OH groups and, after longer treatment times, to C=O and COOR groups. If the treatment time is too long, CO_2 gas is formed.

Table 2. Functional composition of the C1s Peak of the carbon fibers treated by anodic oxidation for different treatment times (electrolyte concentration 3%,current density 3.2A/m²).

	$C\text{-}C_{arom.}$ [%]	$C\text{-}C_{aliph.}$ [%]	C-OR [%]	C=O [%]	COOR [%]	$\pi \rightarrow \pi^*$ [%]
UNT	72.6	14.0	7.5	1.8	2.0	2.1
Ox 10s	72.6	10.4	9.4	3.3	3.7	0.6
Ox 20s	70.5	12.3	10.4	3.3	3.1	0.4
Ox 30s	62.7	14.1	11.3	5.3	5.4	1.2
Ox 40s	62.8	13.4	11.0	6.1	6.2	0.5
Ox 50s	47.6	24.3	9.9	6.7	11.5	0.0

3.2. Influence of current density

For fixed oxidation time (20s) and electrolyte concentration (3%) next a variation of the electric current density is performed. For small current densities up to 2.1A/m² the oxidized fibers exhibit only small changes of the oxygen concentration (see Table 3). At higher current densities the increase of the oxygen concentration speeds up. The nitrogen content is continuously rising to 2.9at% at the highest current density. For all current densities the concentration of oxygen containing functional groups cleary exceeds that of nitrogen containing groups.

Table 3. Surface elemental compositon of carbon fiber surface after treatment with different anodic oxidation current densities (electrolyte concentration 3%, treatment time 20s).

	C [at%]	O [at%]	N [at%]
UNT	97.2	1.9	0.9
Ox, 0.5 A/m²	94.0	4.8	1.2
Ox, 1.3 A/m²	93.2	5.1	1.7
Ox, 2.1 A/m²	92.8	5.4	1.8
Ox, 3.2 A/m²	87.4	10.0	2.7
Ox, 4.2 A/m²	83.9	13.2	2.9

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Compared to the UNT sample, for small current densities the concentration of COR groups changes only slightly (see Table 4). In good agreement with the evolution of the oxygen concentration (see Table 3), the COR group concentration is rising significantly at higher current densities of more than 2.1A/m² up to a level of 10.8%. C=O and COOR groups show a similar trend. At a current density of 4.2A/m² the highest concentration of 5.3% for both types of groups is found.

In Figure 3b the concentrations of the oxygen containing groups derived from the C1s peak is shown as a function of current density. A clear increase of the C=O and COOR parts for high current densities is observed. The same trend is found in Figure 3a for high treatment times.

Table 4. Functional composition of the C1s Peak of the carbon fibers treated by anodic oxidation with different current densities (electrolyte concentration 3%, treatment time 20s).

	C-C$_{arom.}$ [%]	C-C$_{aliph.}$ [%]	C-OR [%]	C=O [%]	COOR [%]	π→π* [%]
UNT	72.6	14.0	7.5	1.8	2.0	2.1
Ox 0.5 A/m²	70.2	16.1	8.1	2.1	2.2	1.3
Ox 1.3 A/m²	65.3	20.0	8.7	2.3	2.4	1.3
Ox 2.1 A/m²	68.7	16.2	7.9	3.1	2.9	1.2
Ox 3.2 A/m²	70.5	12.3	10.4	3.3	3.1	0.4
Ox 4.2 A/m²	60.5	17.8	10.8	5.3	5.3	0.3

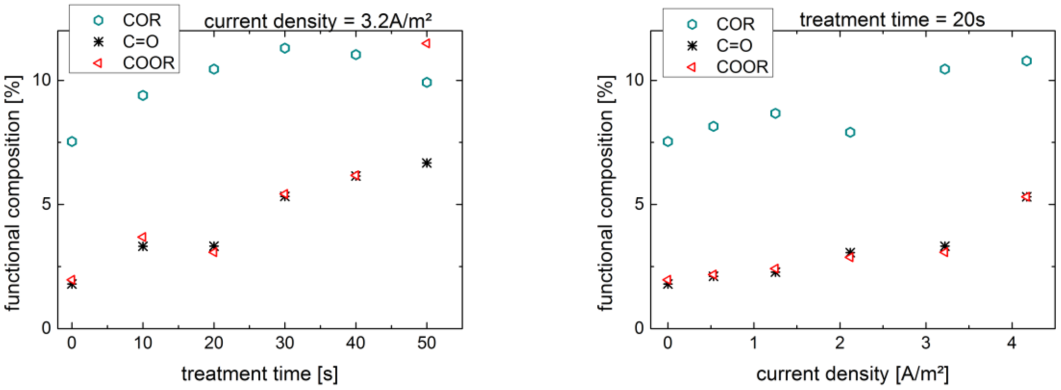

Figure 3. Change of concentration of the oxygen groups with anodic oxidation treatment (electrolyte concentration 3%) a) for different treatment times and b) for different current densities.

3.3. Anodic oxidation at different electrolyte concentrations

To investigate the influence of the electrolyte concentration of the bath, we increase the electrolyte concentration from 3% to 8%. All fibers are treated at the same current density of 3.3 ± 0.1A/m² for 40s. Table 5 summarizes the surface elemental composition of the two fiber types. As expected, both fibers show higher oxygen und nitrogen concentrations compared to the UNT fiber. However, it is interesting to note, that the lower electrolyte concentration results in a higher oxygen concentration (13.1at%) than the higher electrolyte concentration (7.1at%). We attribute this to the lower conductivity and therefore the higher resistance of the electrolyte bath with low concentration. Therefore, the voltage between fiber and electrode in the bath is higher. More oxygen can be attached to the carbon fiber surface due to the stronger oxidation process. Concerning the amount of nitrogen on the carbon fiber surface we find no significant change.

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Table 5. Surface elemetal composition of carbon fibers anodically oxidized with different electrolyte concentrations (treatment time 40s,current density 3.3A/m²).

	C [at%]	O [at%]	N [at%]
UNT	97.1	1.9	0.9
Ox, conc. 3%	83.4	13.1	3.5
Ox, conc. 8%	89.6	7.1	3.3

The fit results, shown in Table 6, reveal identical concentrations of COR groups. In contrast, the lower electrolyte concentration of 3% leads to an increase of C=O and COOR groups by a factor of 2. Again, an increasing oxidation of the surface carbon atoms is observed.

Table 6. Chemical composition of the C1s Peak of carbon fibers anodically oxidized with different electrolyte concentrations (treatment time 40s,current density 3.3A/m²).

	C-C$_{\text{arom.}}$ [%]	C-C$_{\text{aliph.}}$ [%]	C-OR [%]	C=O [%]	COOR [%]	π→π* [%]
Ox, conc. 3%	59.9	17.4	9.4	6.7	5.8	0.8
Ox, conc. 8%	66.8	17.5	9.4	2.8	3.0	0.5

3. Conclusions

We have shown that the process of anodic oxidation leads to an increase of oxygen und nitrogen concentration on the carbon fiber surface. Longer treatment periods or higher electric current densities lead to higher amounts of oxygen and nitrogen. Furthermore the concentration of the functional groups changes. For short treatment periods mainly COR groups are found on the carbon fiber surface. For longer treatment times an increase of C=O and COOR groups is detected. The same effect on the functional groups can be generated by a lower electrolyte concentration or higher current densities. Both COR and COOR groups, in particular COH and COOH, further chemical bonding to epoxy resins, which are frequently used as matrix systems for carbon fiber reinforced polymers [12].

Acknowledgments

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