STATIC ANODIC OXIDATION OF CARBON FIBERS WITH DIFFERENT ELECTROLYTES AND SUBSEQUENT CHEMICAL ANALYSIS OF THE CARBON FIBER SURFACE

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Keywords: carbon fiber, anodic oxidation, XPS

ABSTRACT

X-ray photoelectron spectroscopy has been used to investigate the influence of different electrolyte solutions in the electrolytic anodic oxidation process on the carbon fiber surface chemistry. The carbon fiber surfaces oxidized with the common electrolyte, an aqueous ammonium bicarbonate solution (NH₄HCO₃), show an increasing oxygen concentration for longer treatment times and higher current densities. In comparison to this, the fibers treated with the alternative electrolyte dilute sulfuric acid (H₂SO₄) show a significantly higher oxygen concentration. Furthermore, the H₂SO₄ treatment leads to a higher amount of COOR and COR groups on the carbon fiber surface compared to NH₄HCO₃ treatment using the same parameters. The results show the high influence of the type of electrolyte in the anodic oxidation process on the chemical composition and functionality of the carbon fiber surface and demonstrate the potential of the anodic oxidation process for creation of adapted surface chemistry of the carbon fibers.

1 INTRODUCTION

In the common industrial carbon fiber production process the carbon fiber surfaces are activated through an electrolytic anodic oxidation process which creates oxygen containing functional groups on the carbon fiber surface [1]. This functionalization of the carbon fiber surface is very important to realize good bonding between fiber and polymer matrix in carbon fiber reinforced polymers [2]. As electrolyte often ammonium bicarbonate in aqueous solution is used [3,4]. The advantages of this basic electrolyte solution are the easy availability and the non-toxic behavior. To improve the effectiveness of the anodic oxidation process new electrolytes are under investigation. Acid electrolytes have shown to apply more oxygen groups, in particular more COOR groups, to the carbon fiber surface [5]. As for epoxy resin systems these acid groups further the bonding between the carbon fiber and the polymeric matrix [6,7], the use of acid electrolytes is promising for improved composite properties.

In this work the anodic oxidation behavior of the widely used electrolyte ammonium bicarbonate is compared to that of dilute sulfuric acid as an alternative electrolyte. To this end, anodic oxidation treatment with the two different electrolyte solutions under variation of the anodic oxidation treatment time and electric current density as well as the concentration of the electrolyte solutions was performed. The surface elemental composition of the resulting carbon fibers was analyzed by x-ray photoelectron spectroscopy. Curve fitting of the carbon 1s peak gives further information about the functional composition of the carbon fiber surface.

2 EXPERIMENTAL

2.1 Anodic oxidation setup

For anodic oxidation treatment untreated polyacrylonitril 50k carbon fibers were used, which were supplied by the production line of SGL ACF in Moses Lake, USA. They are taken from the production process directly after the carbonization process. The fibers were anodically oxidized in a static process. The corresponding experimental setup with a bundle of untreated carbon fibers spatially fixed...
within the electrolyte bath is shown below (Fig. 1). On both sites of the electrolyte bath the fibers are clamped. Via these clamps the fiber is electrically connected and works as anode. In the electrolyte bath a graphite block with a length of 15cm works as cathode. After anodic oxidation the fibers were washed in beakers of distilled water and dried in a furnace for 2h at 150°C. In the anodic oxidation process different parameters were adjusted. Current density was varied from 1.2A/m² to 5.8A/m² and the treatment time was changed between 5 and 80s. The calculation of the current density includes treated fiber length (15cm), filament number (50000 filaments) and diameter of the fiber (approx. 7µm). As electrolyte we used ammonium bicarbonate (NH₄HCO₃) and sulfuric acid (H₂SO₄) in aqueous solution. For the ammonium bicarbonate solutions two concentrations of 3wt% and 8wt% were used, for the sulfuric acid solutions four different concentrations of 0.3wt%, 0.7wt%, 1.6wt% and 3.6wt% are chosen. The distance between graphite block and carbon fiber was 6cm.

In previous studies we proved the comparability of our static surface treatment to dynamic anodic oxidation [8].

![Figure 1: Experimental setup for static anodic oxidation.](image)

2.2 X-ray photoelectron spectroscopy (XPS)

The carbon fiber surface was analyzed by XPS using an Omicron XM 1000 monochromatized X-ray source with Al Kα radiation (1486.7eV). Survey scans were measured with 50eV pass energy and the C1s-Peak for detailed information with a pass energy of 17eV. A Shirley background was subtracted. The carbon fiber bundles are fixed to a grounded sample holder to avoid charging during XPS measurements. Elemental composition of the carbon fiber surface is done by analysis of XPS spectra considering peak areas, corrected by the element and orbital sensitivity factors. The sum of all peak areas is normalized to 100%. Fitting of the highly resolved C1s region by a suitable number of lines reveals information about the functional composition of the carbon fiber surface. Therefore, the C1s spectrum is fitted by six pseudo Voigt lines with the parameters peak area, peak position and full width at half maximum. The respective chemical shifts allow to identify the different functional groups [9,10]

3 RESULTS

To understand the influence of the used electrolyte on the anodic oxidation process untreated carbon fibers are treated with the two different electrolyte solutions under variation of current density, treatment time and electrolyte concentration. After the surface treatment XPS is used to investigate the carbon fibers surface chemistry.

3.1 Influence of the treatment time on oxygen concentration

The untreated carbon fiber shows elemental concentrations of 2.0at% oxygen and 0.9at% nitrogen and is used as reference.

After anodic oxidation at a constant current density of 3.5A/m² (Fig. 2, left) the carbon fiber surfaces show continuous increase of oxygen concentration with increasing treatment times for both types of electrolyte. However, the sample treated in NH₄HCO₃ solution shows only slight increase of the oxygen concentration at low treatment times and reaches maximal values around 9at% for long treatment times of more than 60s. In comparison to that, the oxygen concentrations of carbon fibers treated in H₂SO₄ solution increase much faster and reach maximal values around 18at% for the longest
treatment time of 60s.
Anodic oxidation under variation of the treatment time with a higher current density of 5.7A/m² (Fig. 2, right) reveals a faster increase of the oxygen concentration for both electrolytes. However, only a slight increase of the maximal oxygen concentration compared to the lower current density is found. The NH₄HCO₃ treated sample reaches a maximal oxygen concentration of 10.7at%. On the H₂SO₄ treated carbon fiber surface values over 20at% are achieved.

Figure 2: Oxygen concentration as function of treatment time of carbon fibers treated with both electrolytes in the anodic oxidation process. Left: current density of 3.5A/m², Right: current density of 5.7A/m²

3.2 Influence of the treatment time on the functional groups
Analysis of functional groups on the carbon fiber surface was done by fitting the carbon 1s peak as described above. From the carbon 1s peak we can identify aromatic and aliphatic carbon structures. The more relevant groups for the adhesion to the matrix are the oxygen containing functional groups COR, C=O and COOR. The reason for the π→π* excitation at higher binding energies is the conducting nature of carbon fibers. The binding energies and the corresponding full width at half maximum (FWHM) values of the lines used in our fit are shown together with the corresponding functional groups (Table 1).

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Binding energy in eV</th>
<th>FWHM in eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C aromatic</td>
<td>284.3 ± 0.1</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>C-C aliphatic</td>
<td>285.3 ± 0.1</td>
<td>1.0 ± 0.2</td>
</tr>
<tr>
<td>COR</td>
<td>286.1 ± 0.1</td>
<td>1.3 ± 0.1</td>
</tr>
<tr>
<td>C=O</td>
<td>287.5 ± 0.2</td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td>COOR</td>
<td>288.8 ± 0.3</td>
<td>1.6 ± 0.2</td>
</tr>
<tr>
<td>π→π*</td>
<td>290.7 ± 0.3</td>
<td>2.1 ± 0.4</td>
</tr>
</tbody>
</table>

Table 1: Position and FWHM of the lines fitted in the carbon 1s peak and corresponding functional groups.

The untreated carbon fiber is characterized by 8.6% of COR groups, 1.3% of C=O groups and 1.8% of COOR groups.
For carbon fibers treated at a constant current density of 3.5A/m² with increasing treatment time the development of oxygen functional groups on the carbon fiber surface is observed (Fig. 3). The graph on the left side shows the results for the NH₄HCO₃ treated fibers. For increasing treatment times, the ratio of COR groups is slightly increasing by a factor of 1.3 and saturates for higher treatment times at a value of around 11%. Also the C=O and COOR groups are rising compared to the untreated fiber. However, here more significant increases by factors of 4 and 2, respectively, are found. The results are in good accordance with our previous studies [11]. According to literature for low treatment times first
C-H groups are oxidized to C-OH groups. With increasing treatment time, the carbon atoms are oxidized to higher oxidation levels and C=O and COOR groups are formed at the expense of the C-OH groups [12].

The results for H₂SO₄ treated samples (Fig. 3, right side) show similar trends. An increase of all oxygen containing functional groups is observed. However, the increase of the COR groups by a factor of 1.6 is higher than for the treatment in ammonium bicarbonate solution. Also the increase of the COOR groups by a factor of 4 is more significant. In contrast, the C=O groups only increase by a factor of 3. This could be explained by the stronger and faster oxidation process observed for the acid solution. Higher oxidations states like COOR are achieved to a greater extent. Furthermore, the oxidation progress seems to be strong enough to not only form higher oxidation states but also to form new COR groups. This leads also to an increase of the COR groups for the longer treatment times.

The same trends for both electrolytes are found at a higher current density of 5.7A/m². The NH₄HCO₃ treated carbon fibers reveal an increase of C=O and COOR groups both by a factor of 2, while the part of COR remains nearly constant (Fig. 4, left side). H₂SO₄ treated fibers (Fig. 4, right side) show increasing C=O and COOR groups by factors of 3 and 5, respectively. Here, the oxidation process is strong enough to nearly double the part of COR groups.

Figure 3: Oxygen containing functional groups as function of treatment time of carbon fibers treated with NH₄HCO₃ solution (left) and H₂SO₄ solution (right) in the anodic oxidation process at current density of 3.5A/m²

Figure 4: Oxygen containing functional groups as function of treatment time of carbon fibers treated with NH₄HCO₃ solution (left) and H₂SO₄ solution (right) in the anodic oxidation process at current density of 5.7A/m²
Using H$_2$SO$_4$ as electrolyte in the anodic oxidation process leads to a higher concentration of COOR groups, compared to NH$_4$HCO$_3$ treated carbon fibers (Fig. 3 and Fig. 4). This is in good agreement with literature where H$_2$SO$_4$ treated samples show higher concentration of acidic groups than basic electrolytes [5, 13].

3.3 Variation of the current density at treatment times of 10 and 40s

Anodic oxidation treatment as function of current density for both electrolytes was done for treatment times of 10 and 40s. The corresponding oxygen concentrations are shown below (Fig. 5). Continuous increase of oxygen concentration due to the proceeding oxidation process is found for both treatment times. The carbon fiber treated in H$_2$SO$_4$ solution for a time of 40s reaches maximal values of about 20at% oxygen for the highest current density of 5.7A/m$^2$. This is a factor of 10 compared to the oxygen concentration of the untreated sample. In contrast, the NH$_4$HCO$_3$ treated carbon fibers only reaches oxygen concentrations of about 10at%, which is only a factor of 5 compared to the untreated sample. The results for 10s show the same trend.

For both treatment times, the anodic oxidation process for H$_2$SO$_4$ compared to NH$_4$HCO$_3$ is clearly stronger.

3.4 Effect of the electrolyte concentration on the oxygen concentration of the fiber surface

Also the influence of the electrolyte concentration, which is directly correlated to the electric conductivity of the electrolyte solution, on the surface chemical composition of the carbon fibers was analysed for both types of electrolyte. For the ammonium bicarbonate solutions two concentrations of 3wt% and 8wt% were used, which result in electric conductivities of 30mS/cm and 70mS/cm. For the sulfuric acid solutions four different concentrations of 0.3wt%, 0.7wt%, 1.6wt% and 3.6wt% are chosen. They result in the electric conductivities 15mS/cm, 30mS/cm, 70mS/cm and 150mS/cm, respectively. A treatment time of 25s was used while a variation of the current density was performed. All results are summarized below (Fig. 6). As expected, for both electrolytes and all concentrations of electrolyte an increasing oxygen concentration with increasing current densities is found. Carbon fibers treated in H$_2$SO$_4$ solution show the highest oxygen concentration of more than 19at% for the lowest conductivity of 15mS/cm. The highest conductivity of 150mS/cm only results in an oxygen concentration of 15at%. The NH$_4$HCO$_3$ treated carbon fibers show similar trends. Again the lower conductivity of 30mS/cm lead to higher surface oxygen concentrations compared to the higher conductivity of 70mS/cm. Both electrolytes show the same trend, but in the case of H$_2$SO$_4$ treatment the effect seems to be slightly smaller as the oxygen difference between 30mS/cm and 70mS/cm is less than 1at% oxygen.
Figure 6: Oxygen concentration as function of current density of carbon fibers treated with both electrolytes and varying electrolyte concentrations.

3.5 Oxygen concentration as a function of charge density

Plotting the graphs as a function of current density or treatment time gives important information about promising values for these parameters in the anodic oxidation process. The product of current density and treatment time is the charge density. It is the charge exchanged per surface area between fiber surface and electrolyte in the anodic oxidation process. A direct correlation between oxygen concentration at the carbon fiber surface and charge density is expected, as shown before [8].

As shown below (Fig. 7) the oxygen concentration of the H$_2$SO$_4$ treated fibers shows an exponential recovery curve for increasing charge density. The oxygen concentration saturates at a value of about 20at%. In principal, NH$_4$HCO$_3$ treated carbon fibers shows the same trend, but a significantly weaker increase of the oxygen concentration for higher charge densities is observed. Saturation is found at an oxygen concentration around 10at%; this is by a factor of 2 lower than for the H$_2$SO$_4$ treatment with comparable parameters.

This confirms the results from the chapters before in a very clear and distinct graphical presentation.

Figure 7: Oxygen concentration on the carbon fiber surface as a function of the charge density

3.6 Nitrogen and sulfur concentration as a function of charge density

The nitrogen concentration as a function of the charge density is also investigated (Fig. 8, left graph). With increasing charge densities, the nitrogen concentration is increasing, until there seems to be a kind of saturation at a nitrogen concentration of around 3at%. In the case of NH$_4$HCO$_3$ as electrolyte the increasing nitrogen concentration can be explained by nitrogen which is naturally present within the electrolyte. During anodic oxidation it can react with functional groups of the fiber surface and result in nitrogen containing functionalities [14,15]. For the H$_2$SO$_4$ treatment the nitrogen
found at the carbon fiber surface is more difficult to understand. Firstly, the untreated carbon fiber already contains nitrogen, as the starting product is a polyacrylonitrile (PAN) fiber. Possibly the acidic anodic oxidation process results in a certain etching of the fiber surface, exposing lower lying layers with slightly enhanced nitrogen concentration. Furthermore, some nitrogen might result from ammonium bicarbonate leavings on the anodic oxidation equipment, even though a cleaning procedure was performed.

The concentration of sulfur on the anodically oxidized fiber surfaces is shown below (Fig. 8, right graph). Higher charge densities lead to a slow increase of the sulfur concentration if we use H₂SO₄ as electrolyte. No sulfur is found for the NH₄HCO₃ treatment.

![Figure 8: Nitrogen (left) and sulfur (right) concentration on the carbon fiber surface as a function of the charge density](image)

5 CONCLUSION

The effects of the widely used electrolyte aqueous ammonia bicarbonate (NH₄HCO₃) and of dilute sulfuric acid (H₂SO₄) as an alternative electrolyte on the anodic oxidation process of carbon fibers have been analyzed. Both electrolytes showed increasing oxygen concentrations on the carbon fiber surface for increasing treatment times and current densities. For H₂SO₄ treatment the oxidation process in all cases proceeded significantly stronger and faster, which underlines the high efficiency of anodic oxidation treatment with this acid electrolyte. Furthermore, H₂SO₄ treatment led to a higher amount of COOR and COR groups on the carbon fiber surface compared to NH₄HCO₃ treatment using the same parameters. These groups are important for the bonding between fiber and epoxy matrices, which shows the potential of sulfuric acid as electrolyte. Finally, we also showed a strong correlation between oxygen concentration and anodic oxidation charge density, which can be described by an exponential recovery curve.

The results demonstrate the high influence of type and concentration of the electrolyte solution of the anodic oxidation process on the surface chemistry of anodically oxidized carbon fibers. They underline the possibilities of anodic oxidation treatment for defined adaption of surface chemistry of carbon fibers.

ACKNOWLEDGEMENTS

We acknowledge support of the BMBF through the Leading-Edge cluster MAI Carbon.
REFERENCES


