SURFACE AGING OF CARBON FIBERS ACTIVATED BY ANODIC OXIDATION: INFLUENCE ON SURFACE ENERGY AND SURFACE CHEMISTRY

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Abstract

An electrolytic anodic oxidation process is used to form oxygen containing functional groups at the fiber surface to increase its reactivity and surface energy. To examine the temporal stability of the surface properties, activated carbon fiber tows were aged under ambient conditions for defined time spans. Although the elemental composition as measured by x-ray photoelectron spectroscopy shows no significant changes as a function of time, the polar component of the surface energy analyzed by tensiometry decreases for aging times longer than 23 days. The results suggest that surface activation remains stable for a short exposure of anodically oxidized fibers to ambient conditions.

1. Introduction

During industrial carbon fiber production the carbon fiber surface is generally activated by an electrolytic oxidation process. This anodic oxidation forms reactive oxygen containing functional groups on the carbon fiber surface and increases the surface energy [1-3]. The increased surface energy assures good wetting of the fibers by a sizing dispersion. The sizing protects the fiber surface against damage during handling and textile processing. The functional groups formed by the activation enhance the bonding between carbon fiber, sizing and polymeric matrix in carbon fiber reinforced polymers (CFRP) [4-6]. To profit from the improved carbon fiber surface properties during CFRP production, a sufficient temporal stability must be guaranteed.

To investigate the stability of the surface properties, carbon fiber tows were treated by anodic oxidation and subsequently aged at ambient conditions for defined time spans up to 365 days. The polar and dispersive components of the surface energy of the fibers were investigated by tensiometry. X-ray photoelectron spectroscopy (XPS) was performed to analyze the elemental and functional composition of the fiber surface. The surface properties of the aged fibers were compared to that of fibers measured immediately after anodic oxidation treatment.

2. Experimental

2.1. Anodic oxidation

As starting material we used polyacrylonitrile-based 50k untreated carbon fibers (production line of SGL ACF in Moses Lake (USA)), which were taken from the production process directly after the carbonization step. The untreated carbon fiber tow was anodically oxidized in an experimental setup shown in Fig. 1 [7]. The fiber tow was guided through an aqueous electrolyte solution. As electrolyte ammonium bicarbonate (NH_4HCO_3) was used with a concentration of 3 wt%, which had an electric conductance of 30 mS/cm. The fibers were electrically contacted by graphitic guide rolls and acted as anode. In the electrolyte bath a graphite plate with a length of 70cm acted as cathode. The distance between fiber tow and cathode was 6 cm. The speed of the fiber tow through the electrolyte bath was motor controlled and ensured a treatment time of 20 s. The current density was fixed at 3.9 A/m². Calculation of the current density was based on the number of filaments (50.000), the diameter of the fibers (approx. 7 µm) and the assumption of a circular cross section of the fibers. After the electrochemical treatment the fiber tow was guided through a washing bath and recoiled on a grid spool. Finally, the carbon fibers were dried in a furnace for 2 h at 150 °C.

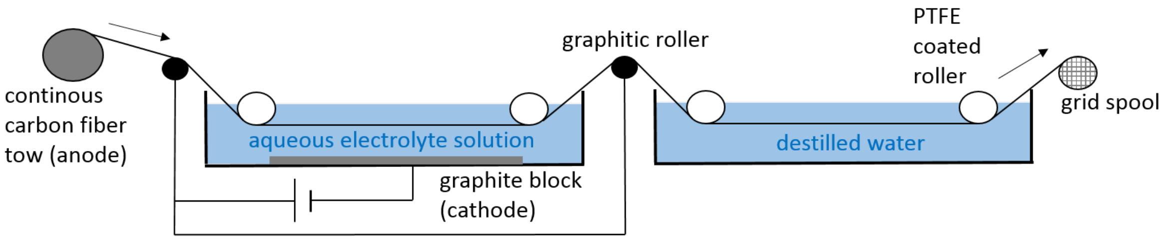

Figure 1. Experimental setup for dynamic anodic oxidation of the carbon fiber tow.

2.2. X-ray photoelectron spectroscopy

The investigation of the carbon fiber surface chemistry was performed by XPS using an Omicron XM 1000 monochromatized x-ray source with Al Kα radiation (1486.7 eV) and an Omicron EA125 hemispherical electron analyzer. Survey scans over the complete energy range were measured with 50 eV pass energy. Detailed spectra of the carbon 1s peak were measured with 17 eV pass energy. To avoid charging effects during the measurement the fiber tows were fixed on a grounded sample holder with a gold aperture. A Shirley background was substracted from the measured spectra. The elemental composition is given by the peak area of each element corrected by element and orbital sensitivity factors. The sum of the peaks of all elements is normalized to 100 %. Fitting of the carbon 1s peak reveals information about the functional composition of the carbon fiber surface [8, 9]. The carbon 1s region is fitted with six pseudo Voigt lines with the parameters peak area, peak position and full width at half maximum [10]. Identification of the functional surface groups is performed by the respective chemical shift. The area of the fit line is normalized to the total area of the carbon 1s peak to yield the ratio of the respective functional group.

2.3. Tensiometry

Determination of the surface energy of the carbon fibers was realized by capillary rise experiments using a DCAT 11 tensiometer from DataPhysics. The fiber tows were drawn in glass tubes with an inner diameter of 3 mm and neatly cutted. The prepared samples were attached to a sensitive balance and slowly dipped into the testing liquid (Fig. 2).

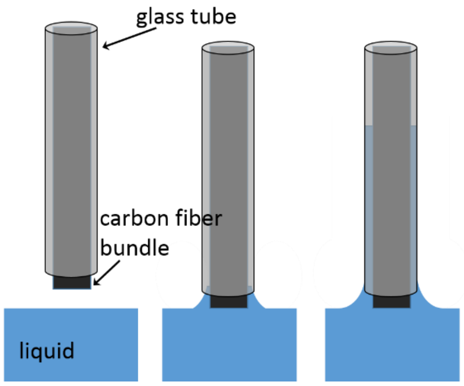

Figure 2. Principle of capillary rise experiments of carbon fiber tows.

The liquid is absorbed into the fiber sample and the increasing mass m during the absorption is measured as a function of time. The contact angle between fiber and liquid is provided by Washburn's equation (Eq. 1) (with surface tension σ_{Fl}, viscosity η and density ρ of the liquid) [11]:

$$\cos\theta = \frac{m^2}{t}\frac{\eta}{\rho^2 \sigma_{Fl} c} \tag{1}$$

The geometric factor c was determined using n-hexadecane as test liquid, which shows complete wetting of the fibers. Determination of the surface energy is performed using four test liquids with different polar and dispersive components. The method of Owens, Wendt, Rabel and Kaelble (OWRK) [12-14] provides the polar and dispersive components of the carbon fiber surface energy, based on Eq. 2 (Fig. 3).

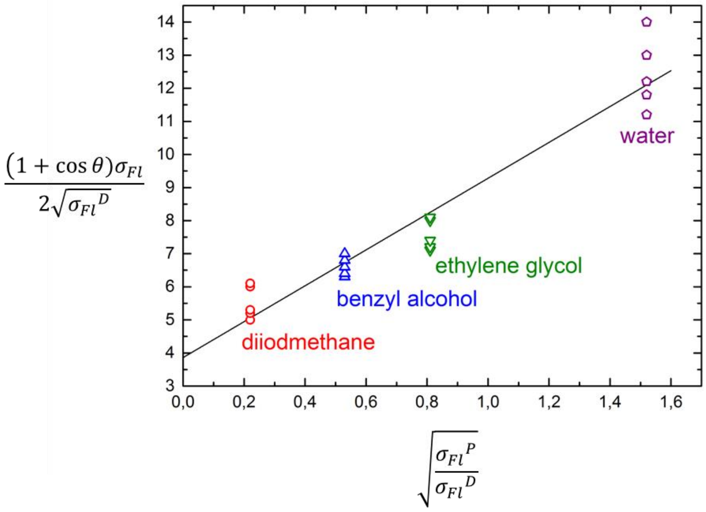

Figure 3. Method of OWRK to determine the surface energy of carbon fibers.

$$\frac{(1+\cos\theta)\sigma_{Fl}}{2\sqrt{\sigma_{Fl}{}^D}} = \sqrt{\sigma_s{}^P}\sqrt{\frac{\sigma_{Fl}{}^P}{\sigma_{Fl}{}^D}} + \sqrt{\sigma_s{}^D} \tag{2}$$

3. Results

To investigate the aging behavior of anodically oxidized fibers a comparison of surface energy, surface elemental composition and surface functionality of fibers directly after anodic oxidation treatment and of fibers aged for defined time spans was performed.

3.1. Surface chemistry and surface energy of untreated and of activated carbon fiber tows

The surface elemental composition of untreated carbon fibers as measured by XPS shows a high concentration of carbon and only low oxygen and nitrogen concentrations (Table 1). The carbon-carbon groups determined from the carbon 1s peak are aromatic and aliphatic structures, which represent the major part of functional groups, and $\pi \rightarrow \pi^*$ excitations. Additionally, smaller ratios of oxygen containing groups, i.e. COR, C=O and COOR groups, are identified (Table 2). The investigation of the untreated carbon fiber tows by tensiometry provides a surface energy of 33 mN/m (Table 3) with a very low polar component of 6% of the total surface energy.

Table 1. Elemental composition of untreated carbon fibers and carbon fibers activated by anodic oxidation.

Specimen	C [at%]	O [at%]	N [at%]
Untreated carbon fiber	97.2 ± 0.3	1.8 ± 0.3	0.9 ± 0.1
Activated carbon fiber	90.8 ± 0.7	6.7 ± 0.5	2.5 ± 0.3

Table 2. Functional composition of the carbon 1s peak of untreated carbon fibers and carbon fibers activated by anodic oxidation.

Functional group of the carbon 1s peak	Functional groups in [%]	
	Untreated carbon fiber	Activated carbon fiber
$C\text{-}C_{aromatic}$	73.5 ± 1.5	71.8 ± 1.4
$C\text{-}C_{aliphatic}$	13.0 ± 2.0	12.0 ± 1.1
C-OR	8.8 ± 1.5	8.7 ± 0.6
C=O	1.4 ± 0.3	2.9 ± 0.4
COOR	1.7 ± 0.2	2.9 ± 0.4
$\pi \rightarrow \pi^*$	1.6 ± 0.1	1.7 ± 0.2

After the activation of the carbon fiber tow by anodic oxidation the oxygen and nitrogen concentrations significantly increase by a factor of 4 and 3, respectively (Table 1). No change is found for the ratio of COR groups. In contrast, the ratios of C=O and COOR groups are increased by a factor of 2 (Table 2). The higher number of polar oxygen groups on the carbon fiber surface leads to a higher surface energy of 56 mN/m. The polar component significantly increases to about 70 % of the total surface energy (Table 3).
The surface chemistry of untreated carbon fibers and activated carbon fibers is comparable to literature [3, 15].

Table 3. Surface energy and its polar and dispersive components of untreated carbon fibers and carbon fibers activated by anodic oxidation.

Specimen	Surface energy σ [mN/m]	Polar component σ^p [mN/m]	Dispersive component σ^d [mN/m]
untreated carbon fiber	33 ± 1	2 ± 1	31 ± 1
activated carbon fiber	56 ± 2	39 ± 4	17 ± 3

3.2. Effect of aging on surface chemistry of activated carbon fiber tows

The elemental composition of the aged activated carbon fibers remains constant over the complete aging period (Fig. 4). The oxygen concentration has an average of 7.2 ± 0.7 at% over the complete time span. No significant change compared to the initial value of the activated carbon fiber is found. The same applies for the nitrogen concentration, which in average amounts to 2.9 ± 0.9 at% over the complete aging period. The oxygen containing functional groups behave similarily (Fig. 5). The ratios of the functional groups show no change over the complete aging time. The fit of the carbon 1s peak provides average ratios of 8.5 ± 1.0 %, 2.9 ± 0.4 % and 2.8 ± 0.4 % for the oxygen containing functional groups COR, C=O and COOR, respectively. This is in agreement with values obtained from the anodically oxidized fiber immediately after anodic oxidation.

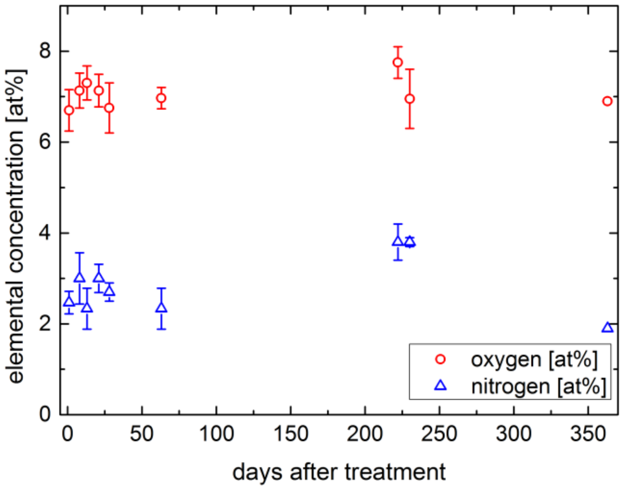

Figure 4. Oxygen and nitrogen concentration as function of aging time.

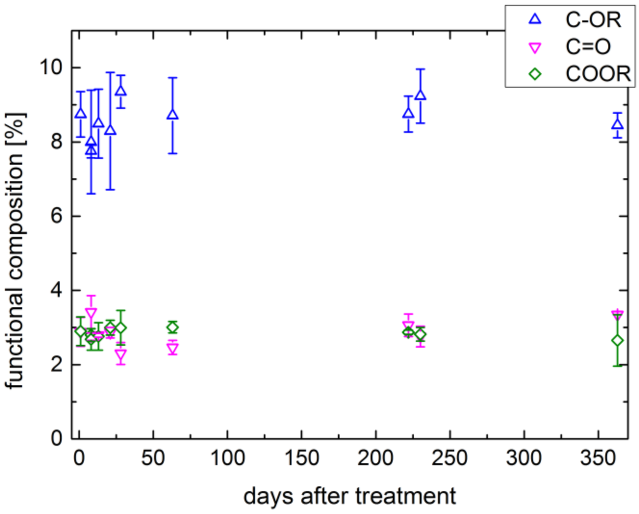

Figure 5. Ratios of oxygen containing functional groups as a function of aging time.

3.3. Effect of aging on surface energy of activated carbon fiber tows

The enhanced surface energy, i.e. the total surface energy and its polar and dispersive components, of the activated carbon fibers remains constant for about 23 days (Fig. 6). After this aging period a continuous decrease of the total surface energy and its polar component for about 57 days of aging takes place. At the same time the dispersive component increases. After more than 80 days of aging, constant values of the total surface energy (about 70 % of the starting value), the polar component (about 25 % of the starting value) and the dispersive component (about 180 % of the starting value) were found.

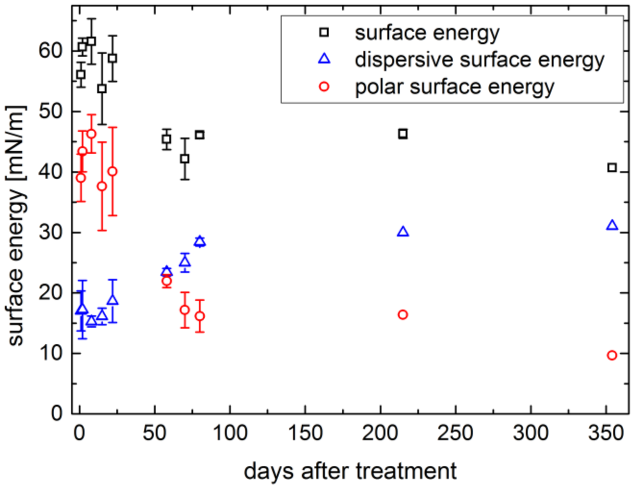

Figure 6. Total, polar and dispersive surface energy as function of aging time.

Although no change of the oxygen and nitrogen concentration and of the functional composition over time is observed, the total surface energy and the polar surface energy is significantly reduced.

The results can be explained by an adsorption of water on the activated carbon fiber surface. The adsorbed water molecules reduce the increased polarity of the activated fiber surface and thus decrease the surface energy. Under the ultra high vacuum conditions of the XPS measurement the water molecules probably desorb, resulting in unchanged elemental composition and functionality. This result is supported by the absence of the XPS signal related to water in the oxygen 1s peak.

4. Conclusions

The results demonstrate the influence of aging on the anodically oxidized carbon fiber surface. The total surface energy and its polar component remain stable for about 23 days. Afterwards, a significant decrease of surface energy due to storage at ambient conditions is observed, even though no changes of elemental composition and functionality were detected. The adsorbtion of water is probably responsible for the reduction of surface energy. This suggests, that long-time storage of the anodically oxidized fibers under ambient conditions should be avoided, to fully benefit from the improved surface properties realized by anodic oxidation. In contrast, the usually short time spans between fiber activation and sizing are not critical.

Acknowledgments

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