AMMONIA PLASMA TREATMENT OF CARBON FIBERS: INFLUENCE ON INTERACTION BETWEEN FIBERS AND POLYMERIC SIZING

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Abstract

Surface activation of carbon fibers is an important production step to enhance surface energy and reactivity. This in turn improves the interaction between fiber and sizing and/or polymeric matrix in carbon fiber reinforced polymers. In the here presented work a low pressure ammonia plasma treatment is used for nitrogen functionalization of the surface of untreated carbon fibers, taken from the production process directly after carbonization. Compared to the untreated fibers an improved wetting behavior of the plasma treated fibers with respect to an aqueous epoxy based sizing dispersion is found, similar to that of carbon fibers activated by the standard process of anodic oxidation. Also the coverage of the ammonia plasma treated fibers by the dried sizing layer is improved, even though it is still less homogeneous than that of anodically oxidized fibers. In contrast, bonding between fiber and sizing is not improved by ammonia plasma treatment of the fibers. Here, only anodically oxidized fibers show improved properties.

1. Introduction

Commercial carbon fibers generally are equipped with a thin, polymeric sizing layer, which protects the fiber surface against damage during handling and textile processing. It also guarantees good wetting of the sized carbon fibers by the liquid resin during production of carbon fiber reinforced polymers (CFRP). Finally, the sizing can act as adhesion promoter, which supports high adhesion of the carbon fibers to the polymeric matrix in CFRP. The sizing layer must homogeneously cover the fiber surface, must form chemical and/or physical bonds with the functional groups of the fiber surface and must be chemically compatible to the polymeric matrix.

To comply with these needs, the inert surface of carbon fibers directly after the carbonization process generally is subjected to an activation treatment. In the industrial carbon fiber production process activation by electrolytic anodic oxidation is used, which results in the formation of oxygen containing functional groups [1–3]. It guarantees enhanced surface energy and reactivity of the carbon fibers, resulting in improved wetting by sizing dispersions and in enhanced fiber sizing bonding [4].
Alternatively, plasma treatment of carbon fiber surfaces is a promising method for surface activation, as it can realize a broader range of fiber surface chemistry [1, 5]. In a plasma the fiber surface interacts with ions, radicals, free electrons, atoms or molecules in excited states and neutral atoms or molecules. The resulting chemical and topographic properties of the surface depend on the chemistry of the plasma precursor gas and the parameters of the plasma process.
Plasma functionalization of carbon fiber surfaces often is performed by air or oxygen plasma treatments [1, 5–9], which result in the formation of oxygen containing surface functional groups similar to that formed by the industrial anodic oxidation process. An increase of surface energy and

improved wetting behavior are found [6, 7, 10, 11]. However, such a treatment is often accompanied by a decrease of fiber strength due to fiber damage due to the plasma treatment [8–11].
Alternatively, also the formation of nitrogen containing surface functional groups promises increased fiber sizing interaction. To form nitrogen containing functional groups on the carbon fiber surface, nitrogen [9, 12–14] and ammonia plasma [5, 9–11, 13–15] treatments are reported in literature. In particular ammonia represents a promising precursor gas, as it is assumed to form the highest concentration of amine and imine functionalities on the carbon fiber surface [13] and, at the same time, results in only negligible degradation of the fiber tensile strength [9–11, 15]. An increase of the surface nitrogen concentration is reported, which is correlated to an increase of surface energy and improved wetting properties [10, 11, 16].

In the here presented work an ammonia plasma was used for nitrogen functionalization of untreated 50k carbon fiber tows. Use of a low ammonia pressure batch process guarantees well defined process conditions and minimizes the influence of oxygen.
A comprehensive characterization of the interaction between the ammonia plasma treated carbon fibers and the sizing was performed. The wetting of the fibers by an aqueous epoxy-based sizing dispersion was investigated by tensiometry. The homogeneity of the dried sizing layer was investigated by atomic force microscopy (AFM). Finally, the bonding between sizing and fiber surface was investigated by desizing experiments in combination with x-ray photoelectron spectroscopy (XPS). All material properties of the ammonia plasma treated fibers were compared to that of untreated and anodically oxidized carbon fibers taken from an industrial process, to investigate the physical and chemical effects of the ammonia plasma treatment and its potential for composite applications.

2. Experimental

2.1 Types of carbon fibers

The carbon fibers used in this study are 50k tows of type SIGRAFIL® C30 T050 supplied by the SGL Carbon GmbH [17]. Untreated carbon fibers (UNT), which represent the starting material for ammonia plasma treatment, were taken from the production process directly after carbonization. As a reference, also anodically oxidized carbon fibers (STA) were supplied, which passed the standard activation treatment by electrolytic anodic oxidation.

2.2 Ammonia plasma treatment of carbon fibers

A low-pressure radio frequency (40kHz) plasma reactor from Diener Electronics was used to activate the untreated carbon fibers. Ammonia (NH_3) was used as precursor gas. The chamber was operated at a pressure of 0.5mbar, realized by an ammonia gas flow of about 20sccm. The power was set to 90W, which is 30% of the maximal power of the plasma generator. The reduced power was chosen to guarantee mild plasma conditions and to avoid damage to the fibers and a contamination due to an interaction of plasma and chamber.
An about 9cm long section of the untreated 50k carbon fiber tow was fixed at its two ends on a stainless steel frame. The distance of the fiber tow to the bottom of the frame amounts to about 1cm, allowing the plasma to completely surround the fiber tow. The frame was placed at the central position of the plasma chamber and was electrically grounded.
To minimize the oxygen concentration within the chamber during ammonia plasma treatment, the chamber was flushed three times before plasma ignition. For the flushing procedure, the chamber was evacuated to a pressure of 0.2mbar and then flushed by ammonia to a pressure of 0.5mbar.
Two different treatment times, namely 8min and 16min, were chosen. The corresponding fiber types are labelled PLA8 and PLA16, respectively.
After ammonia plasma treatment the samples were removed from the plasma chamber and stored under ambient conditions until further analysis. The maximal storage time amounts to about four

hours. As also CFRP is produced under ambient conditions, this storage represents realistic conditions of use.

2.3 Determination of contact angle by tensiometry

The contact angle between the different types of fibers and an aqueous sizing dispersion was determined by capillary rise experiments using a tensiometer DCAT 11 from DataPhysics. For the measurements, the carbon fiber tow was threaded into a cylindrical glass tube with an inner diameter of 3mm [4, 18]. The glass tube including the parallel aligned fibers was attached to the sensitive balance of the tensiometer. The end of the fiber bundle, extending for 2-3mm outside of the glass tube, was immersed into the sizing dispersion and the increase of mass during the absorption of the liquid by the fiber bundle was detected as function of time. Washburn's equation was applied to determine the contact angle between fiber and sizing dispersion [19]. Measurements using the test liquid n-hexadecane, which shows a contact angle of zero to the fibers, supply the geometric factor.

2.4 Nanoscale surface analysis by scanning force microscopy

Surface topography of the carbon fibers was analyzed by a Bruker Dimension Icon® scanning force microscope in tapping mode. Standard TESPA probes from Bruker with a tip radius of 8nm were used. Scan direction was chosen perpendicular to the fiber axis orientation. AFM height images of scan size 5µm x 5µm, scan rate 0.5Hz and 512 samples per line were recorded. From these images the average surface nano-roughness of the carbon fibers was calculated using the method of Jäger et al. [20]. A symmetric baseline, η=1 and a cut-off value of 0.7 were used. At least six AFM images per fiber type were analyzed for roughness analysis.

2.5 Analysis of surface chemistry by x-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy was performed using an Omicron XM 1000 monochromatized x-ray source with Al Kα radiation (1486.7eV) and an Omicron EA125 hemispherical electron analyzer. Survey scans were measured with a pass energy of 50eV. A Shirley background was used for background subtraction. Carbon fiber bundles were tightly fixed with a gold aperture on top of the grounded sample holder. At least three samples of each type of carbon fiber were analyzed and average values were determined. Elemental composition was determined by analysis of the XPS peak areas, corrected by the element and orbital specific sensitivity factors. The sum of the peak areas was normalized to 100%.

2.5 Sizing procedure

Sizing of the fibers was realized by a discontinuous dip coating process. To this end, fibers were fixed on a metal frame and dipped into the aqueous epoxy-based sizing dispersion (concentration 1 vol%) perpendicular to the liquid surface. Preparation of fibers for AFM investigation was realized by fixing single fibers on the frame. A minimum of 6 single filaments were prepared for each fiber type. Preparation of fibers for desizing and XPS investigation was realized by clamping the 50k fiber tow on the metal frame. The dipping velocity of 65mm/min and the immersion depth were controlled by the software of the dip-coater (KSV NIMA). The free clamping length of the fiber of 5cm was completely immersed in the liquid. Dip coating was followed by a drying process at 150°C for 5min (single fibers) or 15min (50k tow). The sized fiber types are labelled UNT-S, PLA8-S, PLA16-S, and STA-S.

2.6 Desizing procedure

Solvent extraction of the sized carbon fiber bundles was performed by Soxhlet treatment with MEK for 5h. Before drying at room temperature, the fibers were rinsed with distilled water. The desized fiber types are labelled UNT-D, PLA8-D, PLA16-D, and STA-D.

3. Results

In the following the interaction between the ammonia plasma treated carbon fibers and the epoxy-based sizing is investigated. The wetting behavior by the sizing dispersion, the homogeneity of the dried sizing layer, and the binding between fiber surface and dried sizing layer are addressed.

3.1 Wetting of ammonia plasma treated carbon fibers by the sizing dispersion

To investigate the wetting of the ammonia plasma treated carbon fibers by the aqueous epoxy-based sizing dispersion, contact angle measurements were performed by tensiometry. The results for the untreated fiber, the plasma treated fibers, and the anodically oxidized fiber are summarized in Figure 1 (see also Ref.[16]).

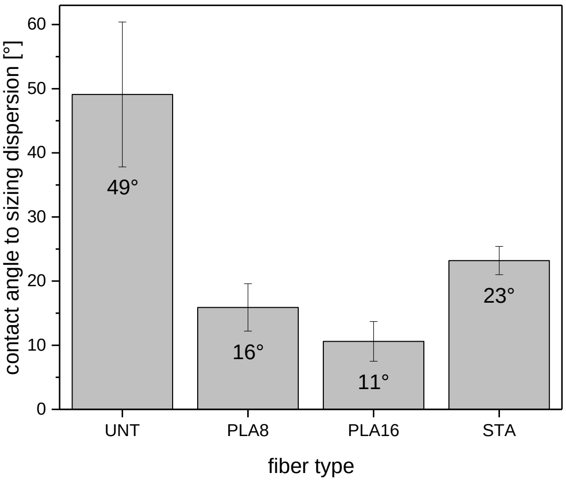

Figure 1 Contact angles between untreated carbon fibers, ammonia plasma treated fibers, and anodically oxidized fibers and sizing dispersion.

A contact angle of 49° is detected between the untreated fibers and the sizing dispersion. The relatively high value demonstrates the insufficient wetting of untreated carbon fibers by the polar sizing dispersion. Ammonia plasma treatment results in a significant decrease of the contact angle between fiber and the polar sizing dispersion, demonstrating the improved wetting behavior of these fibers. Plasma treatment even result in contact angles lower than that of the fiber STA, i.e. improved wetting behavior compared to the anodically oxidized fiber. The lowest contact angle of 11° is found after 16 minutes of plasma treatment.

3.2 Sizing behavior of ammonia plasma treated fibers

AFM imaging of the sized carbon fiber surface provides detailed information about the coverage of the carbon fiber surface by the polymeric sizing layer [20, 21]. Figure 2 shows background corrected AFM height images including on a color scale the nanoscale surface structure of different types of fibers. In the left column exemplary images of the unsized fibers, i.e. the untreated fiber, the ammonia plasma treated fibers, and the anodically oxidized fiber, are shown. In the right column exemplary images of the corresponding sized fibers after the dip coating process are shown.

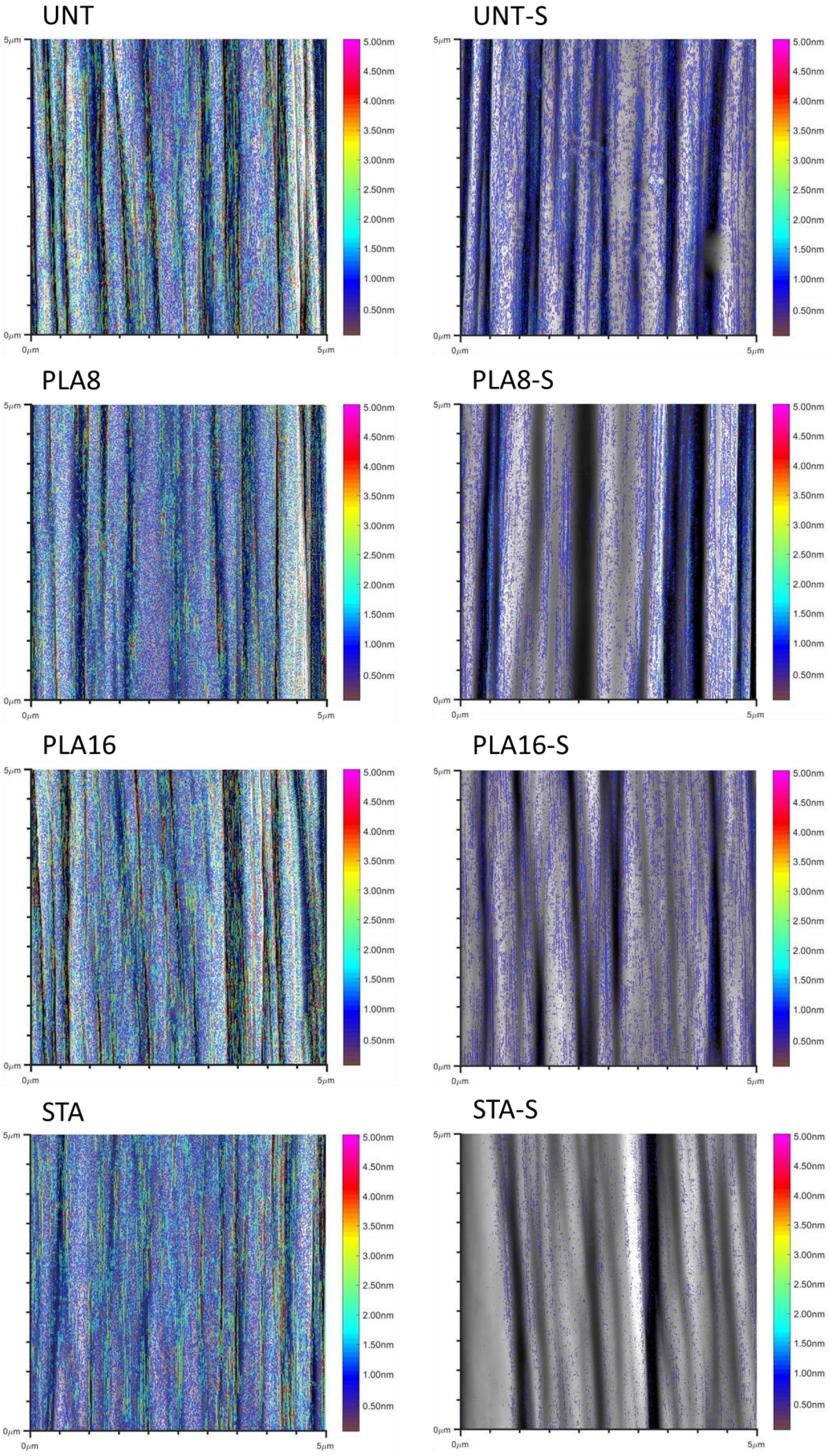

Figure 2 Background corrected AFM height images (gray) including nano-structures (color scale) of the surfaces of unsized and sized carbon fibers.

The unsized fibers are characterized by a very high number of nanostructures, which are homogeneously distributed over the surface. The nanostructures are typical for carbon fiber surfaces [20, 22]. No significant difference between the different types of unsized fibers are found, i.e. the ammonia plasma treatment does not influence the nanoscale surface structure.

In contrast, the sized fibers show a clearly reduced number of nanoscale structures. Here, the polymeric sizing layer covers the original fiber nanostructure. Depending on the activation type, the nanostructures are covered to different degrees. The image of fibers of type UNT-S still displays numerous nanostructures. This indicates incomplete coverage of the surface by the sizing layer. The ammonia plasma treated sized fibers (PLA8-S and PLA16-S) are characterized by a reduced number of nanostructures. Finally, the anodically oxidized sized fiber (STA-S) displays the lowest number of nanostructures. Here, the coverage of the fiber surface by the sizing layer is nearly complete.

In Figure 3 the corresponding nano-roughness values of the different types of unsized and sized fibers are shown.

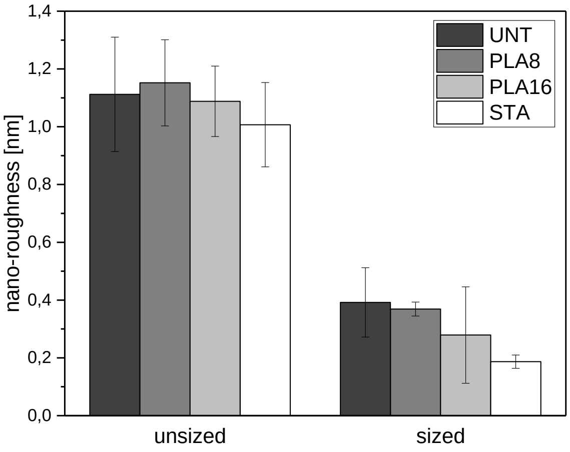

Figure 3 Nanoroughness of unsized and sized carbon fibers.

As already reported in a previous publication [16], all unsized fibers are characterized by a nano-roughness above 1nm. The values agree within the margins of error.
Sizing results in a significant decrease of the nano-roughness. As already indicated by Figure 2, the activation type determines the nanoroughness value of the sized fibers. Fiber UNT-S is characterized by the highest mean nano-roughness of 0.392nm ± 0.120nm, indicating incomplete coverage of the fiber surface by the sizing layer. Ammonia plasma treatment of the fibers reduces the nano-roughness of the sized fibers (PLA8-S and PLA16-S). Finally, the anodically oxidized fiber STA-S is characterized by the lowest nanoroughness of 0.187nm ± 0.023nm, which is about 50% of the value of fiber UNT-S.

The fiber surface nanostructure thus reflect the improved wetting behavior of the carbon fibers due to the activation treatment. However, even though the contact angles to the aqueous epoxy-based sizing dispersion of the ammonia plasma treated fibers PLA8 and PLA16 are below that of the anodically oxidized fiber STA (see Figure 1), the homogeneity of the dried sizing layer is higher for the sized fiber STA-S. This suggests further ordering processes during drying of the sizing layer, which do not depend on the wetting behavior alone.

3.3 Desizing behavior of ammonia plasma treated fibers

To investigate the interaction between fiber surface and the dried sizing layer, chemical desizing experiments were performed. Chemical extraction is able to open physical bonds between fiber and sizing. In contrast, sizing molecules chemically bound to the fiber surface cannot be removed. Investigation of the elemental composition of the fiber surface after chemical desizing thus presents information about the amount of dominantly chemically bound sizing molecules.
Table I summarizes the oxygen concentrations of all types of fibers in the unsized state, the sized state and the desized state. As the sizing layer is characterized by a high oxygen concentration, the oxygen concentration is a measure of the remaining sizing on the desized fibers. Additionally, the ratio of oxygen concentration of the desized fibers and the sized fibers is shown.

Table I Oxygen concentration of activated fibers, sized fibers and desized fibers together with the ratio of oxygen concentration of desized and sized fibers**.**

Type of fiber	Oxygen concentration [at%]			$O_{desized}$ / O_{sized} [%]
	Unsized fiber	Sized fiber (-S)	Desized fiber (-D)	
UNT	2.3 ± 0.6	19.8 ± 2.0	8.9 ± 0.8	45 ± 4
PLA8	4.0 ± 1.2	18.8 ± 2.1	9.5 ± 0.6	51 ± 3
PLA16	5.1 ± 0.8	19.5 ± 1.9	10.2 ± 1.8	52 ± 9
STA	8.0 ± 0.5	21.3 ± 0.5	14.2 ± 1.0	67 ± 5

The elemental composition of the unsized fibers is determined by their activation treatment, i.e. ammonia plasma treatment or anodic oxidation. It is described in detail in one of our previous publications [16].

Sizing of the fibers results in a significant increase of the oxygen concentration compared to the unsized fibers. The different types of sized fibers are characterized by similar oxygen concentrations of roughly 20at%. The slightly higher value of the fiber STA-S might results from nearly complete coverage of these fibers by the dried sizing layer.

Desizing results in a significant decrease of the oxygen concentration. About 50% of the oxygen concentration is removed by the desizing procedure. The remaining oxygen concentration is still clearly above that of the unsized fibers, indicating a residue of sizing on the fiber surface. The amount of remaining sizing coincides for the desized untreated fiber (UNT-D) and the desized plasma treated fibers (PLA8-D and PLA16-D) within the margins of error. Here, the activation treatment does not result in improved bonding between fiber and sizing. In contrast, the amount of remaining sizing is significantly higher for the desized anodically oxidized fiber STA-D, indicating a higher amount of chemically bound sizing molecules. As chemical bonding is significantly stronger than physical bonding, the increased concentration of chemically bound molecules promises enhanced adhesion between fiber and sizing. The results agree with our previous investigations on the desizing behavior of anodically oxidized fibers, where enhanced amounts of dominantly chemically bond sizing molecules were observed for fibers with high anodic oxidation degree [4].

4. Conclusions

Ammonia plasma treatment of carbon fibers was used to activate the surface of untreated carbon fibers. Enhanced wetting behavior of the plasma treated fibers by an aqueous epoxy-based sizing dispersion was found, which is even better than that of anodically oxidized fibers. Nanoscale microscopic analysis of the dried sizing layer also shows improved coverage of the surface of ammonia plasma treated fibers compared to untreated fibers. However, fibers show even better, nearly complete coverage after anodic oxidation. Desizing experiments reveal, that ammonia plasma treatment of the fibers does not enhance the amount of sizing material chemically bound to the fibers. In contrast, anodically oxidized fibers show enhanced chemical bonding between fiber and sizing. This might be expected since bonding between nitrogen surface functional groups and the epoxy groups of the sizing is less favorable than that between oxygen functional groups and epoxy groups [16].

We thus can summarize, that ammonia plasma treatment improves the wetting behavior of the carbon fibers. However, the interaction between the dried sizing layer and the fibers is not improved by the plasma treatment.

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