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Full Length Article

Adhesion of carbon fibers to amine hardened epoxy resin: Influence of ammonia plasma functionalization of carbon fibers

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ABSTRACT

The modification of carbon fiber surface properties represents a powerful tool to improve the adhesion between fibers and polymeric matrix in carbon fiber reinforced polymers. In the presented work the surface of untreated carbon fibers, taken from the production process directly after carbonization, is functionalized by a low pressure ammonia plasma treatment. Compared to the untreated fibers an enhanced concentration of surface nitrogen functionalities and an increased surface energy are observed. This leads to an improved wetting behavior, similar to that of carbon fibers activated by anodic oxidation. No changes of the fiber surface topography on micro- and on nanoscale are induced by the plasma treatment. Compared to the untreated fiber no increase of interfacial fracture toughness between the plasma treated fibers and an amine hardened epoxy resin is detected by single fiber push-out tests. Anodically oxidized fibers, in contrast, show a significant increase of interfacial fracture toughness. The results suggest, that adhesion of carbon fibers to an amine hardened epoxy resin is dominantly enhanced by interactions between surface oxygen functionalities and the components of the resin. In contrast, nitrogen surface functionalities appear to be of minor importance for fiber matrix adhesion in carbon fiber reinforced amine hardened epoxy resin.

1. Introduction

In the industrial carbon fiber production process an electrolytic surface activation of the fibers is performed subsequent to stabilization and carbonization. This anodic oxidation process is necessary to enhance the surface reactivity of the carbon fibers and results in the formation of oxygen containing surface functional groups [1–3]. It improves the wetting properties and facilitates application of a polymeric sizing, which is necessary for further textile processing of the fibers. Bonding between the fiber surface, the sizing, and the polymeric matrix of a carbon fiber reinforced polymer (CFRP) is improved [3].

Anodic oxidation of carbon fiber surfaces is a cost efficient and easy to handle process. However, it is restricted to the formation of oxygen containing surface functional groups. In contrast, the concept of plasma treatment of carbon fibers allows for a broader range of fiber surface functionalization [3,4]. In a plasma the fiber surface interacts with ions, radicals, free electrons, atoms or molecules in excited states and neutral atoms or molecules. The surface is modified by etching, activation (formation of dangling bonds), functionalization (application of surface functional groups) or layer deposition. 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. In this paper we focus on plasma functionalization of carbon fiber surfaces.

Plasma functionalization of the carbon fiber surface is expected to improve the interaction with a polymeric matrix in CFRP. To further bonding to an epoxy matrix, functionalization often is performed by an air or oxygen plasma [3–9]. This results in a surface oxidation of the carbon fibers and the formation of oxygen containing functional groups similar to that of the industrial anodic oxidation process. Of particular interest are alcohol and carboxyl groups, which are expected to chemically react with the epoxy groups of the resin. If amine hardening epoxy resins are used, also carbonyl groups on the carbon fiber surface are of interest, which show a high reactivity towards the amine groups of the hardener [10]. After air or oxygen plasma functionalization an increase of adhesion between carbon fibers and epoxy matrices is observed [5,7–9]. However, such a treatment is often accompanied by a decrease of fiber strength due to fiber damage due to the plasma treatment [7,8,11,12].

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Alternatively, also the formation of nitrogen containing surface functional groups appears promising for improved bonding to an epoxy resin. A chemical reactivity of the epoxy groups of the resin in particular towards primary and secondary amine functionalities on the fiber surface is expected [10]. To form nitrogen containing functional groups on the carbon fiber surface, nitrogen [8,13–15] and ammonia plasma [4,8,11,12,14–16] treatments are described in literature. In particular ammonia represents a promising precursor gas for nitrogen functionalization, as it is assumed to form the highest ratio of amine and imine functionalities on the carbon fiber surface [14] and, at the same time, results in only negligible degradation of the fiber tensile strength [8,11,12,16]. An increase of interfacial adhesion of fibers, originally untreated and then treated by ammonia plasma, to bismaleimide resin is reported [8,11]. To the best of our knowledge, the adhesion of ammonia plasma treated carbon fibers to epoxy matrices is not addressed in literature so far, even though epoxy matrices represent one of the most frequently used polymers for CFRP production.

In the here presented work an ammonia plasma was used for nitrogen functionalization of untreated carbon fiber tows composed out of 50,000 single fibers, so called 50 k tows. Use of a low pressure batch process guarantees well defined process conditions and minimizes the influence of oxygen.

An extensive characterization of the properties of the ammonia plasma treated carbon fibers was performed. Surface chemistry was analyzed by x-ray photoelectron spectroscopy (XPS) and nanoscale topography by high resolution scanning force microscopy (AFM) and gas adsorption measurements (use of BET method). The surface energy and the wetting of the fibers by an aqueous epoxy-based sizing dispersion were investigated by tensiometry. The fiber mechanical properties were determined by single fiber tensile tests.

Additionally, for the first time, the adhesion of ammonia plasma treated carbon fibers to an amine hardened epoxy matrix was investigated. To this end, micromechanical cyclic single fiber push-out tests on specifically prepared model composites were performed, which allow to determine the interfacial fracture toughness of the carbon fiber epoxy system.

All material properties of the ammonia plasma treated fibers and their composites were compared to that of untreated and anodically oxidized carbon fibers from an industrial process, to elucidate the physical and chemical implications of the ammonia plasma treatment and its potential for composite applications.

2. Experimental

2.1. Types of carbon fibers

All carbon fibers used in this study are 50 k tows of type SIGRAFIL® C30 T050 and were 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. They passed the standard activation treatment by electrolytic anodic oxidation.

2.2. Ammonia plasma treatment on carbon fibers

The untreated carbon fibers were treated in a low-pressure radio frequency (40 kHz) plasma reactor from Diener Electronics. As precursor gas ammonia (NH_3) was used. The chamber was operated at a pressure of 0.5 mbar, realized by an ammonia gas flow of about 20 sccm. The power was set to 90 W, which is about 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 9 cm long section of the untreated 50 k carbon fiber tow was clamped at its two ends on a stainless steel frame. The distance of the fiber tow to the bottom of the frame amounts to about 1 cm, 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 0.2 mbar and then flushed by ammonia to a pressure of 0.5 mbar.

Four different treatment times, namely 2 min, 4 min, 8 min, and 16 min, were chosen. The corresponding fiber types are labelled PLA2, PLA4, 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 composite materials are produced under ambient conditions, this storage represents realistic conditions of use.

2.3. Analysis of surface chemistry by x-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy was performed with an Omicron XM 1000 monochromatized x-ray source with Al Kα radiation (1486.7 eV) and an Omicron EA125 hemispherical electron analyzer. Survey scans were measured with a pass energy of 50 eV, detailed scans with a pass energy of 17 eV. 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.

Chemical 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%. The functionality of the surface carbon atoms was investigated by fitting the C1s detail spectra with a suitable number of different lines. The respective chemical shifts allow for identification of the type of bonded functional groups. The spectra were fitted with pseudo Voigt lines with the parameters of peak area, full width at half maximum and peak position. The relative intensity of the respective functional groups, from now on referred to as ratio of peak areas, was determined by normalizing their peak areas to the total area of the C1s Peak.

2.4. Single fiber tensile testing

Tensile strength, tensile modulus and effective diameter of the fibers were determined by a Textechno Favimat+ . 20 measurements of each fiber type were performed. The effective diameter of each tested carbon fiber was determined by vibroscopic linear density tests (ISO 1973) with a free clamping length of 25 mm and a pretension of 0.7 cN/tex. The effective diameter of the carbon fibers was calculated from the fiber density and the assumption of a circular cross section. A constant testing speed of 0.5 mm/min was used for tensile testing, starting from a pretension of 1.0 cN/-tex. The elongation range between 0.25% and 0.5% was used to determine the tensile modulus.

2.5. 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. Two probe types, i.e. standard TESPA probes from Bruker with a tip radius of 8 nm and super sharp EBD-SSS NCHR AFM probes