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Full Length Article

Interaction between carbon fibers and polymer sizing: Influence of fiber surface chemistry and sizing reactivity

Judith Moosburger-Will [a,*], Matthias Bauer [b], Eva Laukmanis [b], Robert Horny [b], Denise Wetjen [c], Tamara Manske [c], Felix Schmidt-Stein [c], Jochen Töpker [c], Siegfried Horn [a,b]

[a] Institute of Materials Resource Management, University of Augsburg, 86135 Augsburg, Germany
[b] Experimental Physics II, Institute of Physics, University of Augsburg, 86135 Augsburg, Germany
[c] BMW Group, Technical Integration, Ohmstraße 2, 84030 Landshut, Germany

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ABSTRACT

Different aspects of the interaction of carbon fibers and epoxy-based polymer sizings are investigated, e.g. the wetting behavior, the strength of adhesion between fiber and sizing, and the thermal stability of the sizing layer. The influence of carbon fiber surface chemistry and sizing reactivity is investigated using fibers of different degree of anodic oxidation and sizings with different number of reactive epoxy groups per molecule. Wetting of the carbon fibers by the sizing dispersion is found to be specified by both, the degree of fiber activation and the sizing reactivity. In contrast, adhesion strength between fibers and sizing is dominated by the surface chemistry of the carbon fibers. Here, the number of surface oxygen groups seems to be the limiting factor. We also find that the sizing and the additional functionalities induced by anodic oxidation are removed by thermal treatment at 600 °C, leaving the carbon fiber in its original state after carbonization.

1. Introduction

Commercial carbon fibers are generally equipped with a thin layer of polymeric sizing. It protects the fiber surface against damage during handling and textile processing. Additionally, it assures 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 supporting high adhesion of the carbon fibers to the polymeric matrix in CFRP. Strong fiber matrix adhesion, in turn, is closely related to the mechanical properties of the composite material [1–5]. The sizing layer must homogeneously cover the fiber surface, must chemically and/or physically bound to the fiber surface functional groups and must be chemically compatible to the matrix polymer.

To comply with these requirements, commercial carbon fibers are subjected to an electrolytic surface activation after carbonization [1,6–8]. Then, a sizing is applied by drawing the carbon fiber roving through a bath of sizing emulsion or dispersion. Moderate heat treatment results in drying of the sizing layer [5,7]. The anodic oxidation process enhances the surface energy and surface reactivity of the carbon fibers forming oxygen containing functional groups. This in turn improves wetting of the fibers by the sizing dispersion. The use of sizing dispersions which interact strongly with both, the fiber surface functional groups and the functional groups of the matrix, furthers bonding between the components [5]. Often sizing dispersions of the same chemical class as the polymer matrix are used to guarantee chemical compatibility. Also sized carbon fibers exhibit a sufficiently high surface energy, resulting in good wetting of the fibers with the liquid composite resin [2,3].

An understanding of fiber sizing interaction will further the improvement of fiber matrix adhesion and the correlated mechanical parameters of CFRP. To influence fiber sizing interaction, investigation of type and strength of fiber sizing bonding and identification of the decisive parameters of the activation and sizing steps are essential. Despite the high relevance of fiber sizing interaction for composite properties, only few publications focus on this topic. The surface energy of activated carbon fibers [2,3,8] and the contact angle between fiber and sizing dispersion [9] were investigated, the latter in one of our previous publications. Solvent extraction or thermal treatment followed by chemical analysis of the resulting carbon fiber surfaces, e.g. by photoelectron spectroscopy (XPS) or epoxy weight titration, provide information

* Corresponding author.
E-mail address: judith.will@physik.uni-augsburg.de (J. Moosburger-Will).

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about the degree of desizing and the bonding of the remaining sizing molecules [10–12]. Investigations of the sizing abrasion resistance are reported, which is also correlated to the fiber sizing adhesion [13].

Our manuscript expands the methods to investigate fiber sizing interaction by thermogravimetric analysis (TGA). TGA of sized fibers provides information about the thermal stability of the sizing layer and the total amount of sizing present on the fiber surface by removing such material by thermal desorption. TGA of chemically desized fibers analyzes the efficiency of the solvent extraction process, which only removes sizing material bonded by physical interactions. It thus provides information on the amount of remaining sizing material dominantly bound by chemical bonding.

Additionally, elemental composition and functionality of chemically or thermally desized fiber surfaces were analyzed by photoelectron spectroscopy. The latter provides information about the thermal stability of surface functional groups and bonded sizing molecules. Finally, surface energies and contact angles between fibers and sizing dispersion characterize the wetting behavior.

The influence of fiber surface chemistry on fiber sizing interaction is addressed by systematically investigating carbon fibers with different degrees of surface activation, resulting from anodic oxidation treatment using different charge densities and different electrolytes. These fibers are equipped with two types of epoxy based sizings with different chemical reactivity, to elucidate the influence of the sizing chemistry on fiber sizing interaction.

2. Experimental

2.1. Materials

Four types of 50 k polyacrylonitrile-based carbon fiber rovings with different levels of surface activation were used. The untreated carbon fibers (UNT), supplied by the production line of SGL ACF in Moses Lake, USA, is taken from the carbon fiber production process directly after carbonization. Electrochemical activation of these fibers and application of sizing were performed in a dynamic process at a pilot line of the BMW Group in Landshut, Germany. The standard (STA) and highly (HIG) activated fibers were treated by anodic oxidation in an aqueous ammonium bicarbonate solution using different charge densities. The acidic activated (A) fiber was anodically oxidized in dilute sulfuric acid. To size the four fiber types two different aqueous epoxy-based sizing dispersions were used, i.e. a standard epoxy sizing (EP1) and a functional epoxy sizing with an increased reactivity due to a higher number of epoxide groups per molecule (EP2) [11]. The two types of sizing dispersion are characterized by very similar densities, viscosities and surface tensions. All fiber types were sized applying the reactive sizing EP2 (UNT-EP2, STA-EP2, HIG-EP2, A-EP2), whereas for comparison only two fiber types were sized applying the standard sizing EP1 (STA-EP1, HIG-EP1). After application of the sizing dispersion the fibers were dried at a temperature of 160 °C, resulting in about 1wt% of dried sizing on all fibers.

2.2. Desizing procedure

Solvent extraction of the sized carbon fibers was performed by first stirring a fiber bundle in methyl ethyl ketone (MEK) for 1.5 h. Afterwards, Soxhlet treatment with MEK for 1.5 h was performed. Before drying at room temperature, the fibers were rinsed with ethanol and distilled water.

For thermal desizing, a bundle of carbon fibers was heated to a temperature of 600 °C (heating rate 10 K/min) under nitrogen atmosphere.

2.3. Analysis of contact angle and surface energy by tensiometry

Capillary rise experiments were performed with a tensiometer (DCAT 11, DataPhysics). To this end, the carbon fiber rovings were threaded into cylindrical glass tubes with an inner diameter of 3 mm. 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 2–3 mm outside of the glass tube, was immersed into a test liquid 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 test liquid [14]. Measurements using the test liquid n-hexadecane (zero contact angle) supply the geometric factor.

The surface energy of the activated fibers was determined by contact angle measurements with four test liquids of different polar and dispersive components of surface tension, namely diiodomethane, benzyl alcohol, ethylene glycol and high-purity water. The approach of Owens, Wendt, Rabel and Kaelble (OWRK) provides the polar and dispersive components of the surface energies of the fibers [15,16].

For each combination of fiber type and test liquid five measurements were performed.

2.4. 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 of the C1s peak 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. Two fiber bundles of each type of carbon fiber were analyzed, taken from different positions along the carbon fiber tow.

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 atoms was investigated by fitting the C1s detail spectra by six different lines. The respective chemical shifts allow the 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 ratio of the respective functional groups was determined by normalizing the respective peak area to the total peak area.

2.5. Thermal analysis

Thermogravimetric analysis of the carbon fibers was performed with a Netzsch STA 449 F3 Jupiter. The fiber sample was heated under nitrogen atmosphere at a rate of 10 K/min to a final temperature of 735 °C, while the mass loss was measured. Two measurements for each fiber type were performed.

3. Results and discussion

In the following the interaction of the four types of carbon fibers with the two types of sizing dispersions is investigated. The work focuses on the wetting behavior of the carbon fibers with the sizing dispersion, the thermal stability of the sizing layer and the fiber sizing bonding.