

INVESTIGATION OF THE INTERACTION BETWEEN CARBON FIBERS AND EPOXY BASED SIZING USING POTENTIOMETRIC TITRATION AND ATOMIC FORCE MICROSCOPY

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Abstract

To shed light on the interaction between carbon fibers and epoxy-based polymer sizings, chemical desizing experiments by applying solvent extraction were performed on sized carbon fibers of different degrees of surface activation. The topography of the fibers was monitored before and after chemical desizing by atomic force microscopy and the amount of respective sizing on the fiber surface was determined by thermogravimetric analysis. Using potentiometric titration the epoxide reactivity of the carbon fibers was investigated. The results show that the formation of a dominantly chemically bonded layer of polymeric sizing on the carbon fiber surface, which can induce enhanced interfacial adhesion in the composite material, can be furthered by a suitable choice of surface activation of the fibers. A higher functionalization of the fiber surface promises improved fiber sizing bonding resulting in a more complete chemically bonded layer.

1. Introduction

For production and mechanical performance of carbon fiber reinforced polymers the coating of the reinforcing carbon fibers with a polymeric sizing film plays an important role. On the one hand, the sizing improves handling and textile processing properties of the fibers. On the other hand, it ensures an optimal wettability of the fibers by the liquid polymeric resin during composite production and can improve fiber matrix adhesion in the composite material [1–6]. Both, wettability and adhesion, can be tuned by the surface properties of the carbon fibers and the use of functional sizings specifically adapted to the properties of carbon fiber and resin. In case of epoxy based sizings the sizing film on the carbon fiber surface is assumed to consist of two parts: a chemically bonded layer, which bonds to the functional groups on the fiber surface, and a physisorbed layer [7, 8]. To realize a strong interfacial adhesion between fiber and polymeric matrix in the composite material, a distinct chemically bonded layer with a strong interaction to the fiber and the matrix polymer is assumed to be preferable.

During sizing application and drying, the reactive epoxide groups of the polymer sizing react with functional groups on the activated fiber surfaces to different degrees. Epoxide-specific titration permits quantitative investigations of the remaining reactive epoxide groups on the fiber surface, which are a measure for fiber sizing interaction [9]. The epoxy equivalent (EE) and the epoxy index (EI) can be determined [10, 11].

In the presented study the influence of fiber surface activation on the formation of the chemically bonded sublayer of the polymeric sizing is examined by using sized carbon fibers of different degree of anodic oxidation. To expose the chemically bonded layer, a chemical desizing procedure by means of solvent extraction in a Soxhlet apparatus permits the gentle removal of the physisorbed layer. First, the epoxy index of the sized carbon fibers is measured by potentiometric titration, then, the epoxy index of the chemically bonded sizing layer is investigated on the desized fibers. Also the nano-roughness of the carbon fiber surfaces, which is a measure of the degree of sizing removal [12] is determined before and after chemical desizing by atomic force microscopy (AFM). To obtain the mass of sizing present on the fibers, thermogravimetric analysis (TGA) is carried out on the sized and desized fibers.

2. Experimental

2.1. Materials

Three types of 50k polyacrylonitrile-based carbon fibers with different surface activation levels were used. The standard (STA) and highly (HIG) activated carbon fibers were functionalized by anodic oxidation in an aqueous ammonium bicarbonate solution using different charge densities, the acidic activated fiber (A) was functionalized by anodic oxidation in diluted sulfuric acid. The fibers were coated by a polymeric sizing layer by drawing the roving through a bath of an aqueous epoxy-based sizing dispersion followed by a drying process. An advanced functional sizing with a high reactivity due to an increased number of epoxide groups per molecule was used to coat the fibers. Thus six fiber samples were available, i.e. unsized (STA, HIG, A) and sized fibers (STA-sized, HIG-sized, A-sized) with three different activation levels.

2.2. Desizing procedure

Chemical desizing of the sized fibers was performed by solvent extraction using a Soxhlet apparatus. The fiber bundles were placed in the extraction chamber using a thimble permeable to fluid. As solvent for the desizing procedure methanol was used and the fibers remain in the extraction chamber for 6h with a reflux time of about 20min. After Soxhlet treatment, washing of the fibers was carried out with ethanol and distilled water. A drying process in an oven for 3h at a temperature of 80°C followed. The desized fibers are labelled STA-desized, HIG-desized and A-desized.

2.3. Atomic force microscopy

The unsized, sized and desized carbon fibers were examined by AFM (Bruker, Dimension ICON). The topography of the fibers was imaged in tapping mode with a scan size of 5µm x 5µm and 512 samples per line. The used standard tapping probes from Bruker measure a tip radius of 8µm. Following the procedure introduced by Ref. [13], the nano-roughness of the fiber surface was calculated from the height data by subtracting a suitable background. The nano-structures on the fiber surface were visualized using a color scale and are shown together with the background corrected microscale fiber surface topography in gray scale. At least 9 AFM images are evaluated for each fiber specimen.

2.4. Thermogravimetric analysis

To quantify the amount of sizing on the fiber surface, thermogravimetric analysis using a Netzsch STA 449 F3 Jupiter was performed. The carbon fibers were heated with a heating rate of 10 K/min up to 735°C under an inert nitrogen atmosphere to ensure complete sizing removal [14]. For each sample two measurements were performed, which provide the mass loss as function of temperature. The maximal mass loss reflects the original sizing content on the fibers.

2.5. Potentiometric titration

The potentiometric titration of the epoxide groups and the determination of the epoxy equivalent were performed according to Refs. [15, 16], i.e. a direct titration was performed with a standard solution of hydrogen bromide in glacial acetic acid. The fiber material was placed in a beaker with the test solution consisting of methylene chloride and tetraethylammonium bromide solved in glacial acetic acid. This test solution was titrated with 0.1 N perchloric acid reagent, which reacts with the bromine anion to hydrogen bromide, which in turn reacts with the epoxide groups in two steps (see Figure 1). The protonation of the epoxide group is followed by the addition of the bromine anion. For detecting the end point of titration, a glass / silver – silver chloride combination electrode measures the change in potential in the solution during the titration process. Due to a stoichiometric reaction of hydrogen bromide and epoxide groups to bromohydrins, the quantity of perchloric acid reflects the epoxy content of the sizing layer on the fibers. Equation 1 allows the calculation of the epoxy equivalent in grams per mole and of the epoxy index in moles per gram using the mass m of sizing in grams, the concentration of the perchloric acid solution c of usually 0,1 mol/l, and the volume V_0 and V_1 of perchloric acid solution in milliliters. V_0 was determined in a previous blank test and V_1 is the volume used in the experiment.

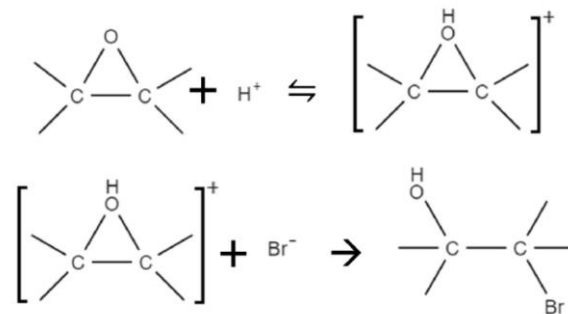


Figure 1. Reaction of hydrogen bromide and an epoxide group in two steps.

$$EE = 1000 m / (V_1 - V_0) c = 1 / EI. \quad (1)$$

3. Results and Discussion

3.1. Surface topography of the fibers

To investigate the micro- and nanoscale surface topography of the different types of fibers, AFM images were evaluated. Figure 2 shows typical background corrected AFM height images of fiber surfaces with nano-structures pictured in color scale. The surface of the unsized fiber (Figure 2a) is characterized by a high concentration of nano-structures. Sizing of the fibers (Figure 2b) covers the nanostructures by a smooth polymeric sizing film. After the desizing process (Figure 2c) the physisorbed sizing layer is removed and the nano-structures reappear. The reappearance of the nano-structures after desizing indicates that a possible remaining sizing layer must have a thickness in the sub-nanometer range.

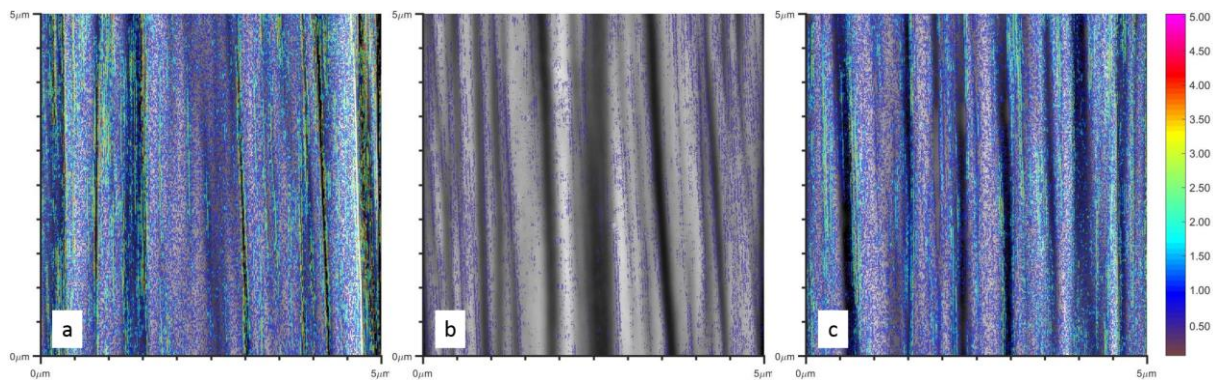


Figure 2. Background corrected atomic force microscopy height images (gray) of fiber surfaces including nano-structures (color scale) of an unsized (a), sized (b) and desized fiber (c).

Calculation of the nano-roughness values of the different fiber types (see Figure 3) gives further information about sizing coverage. The activated, unsized fibers are characterized by high nano-roughness values above 0.9nm. Sizing of the fibers results in a significantly lower nano-roughness with values below 0.4nm, which is independent of the activation of the fibers. After the desizing process, a high number of nano-structures reappears and the nano-roughness again increases to values above 0.7nm. Here, the nanostructures are assumed to be covered by a remaining chemically bonded sizing layer. The different values of the nano-roughness indicate a coverage of the nano-structures to different degrees. With increasing surface activation level of the fibers the nano-roughness of the desized fibers decreases, i.e. the coverage of the nanostructures by the chemically bonded sizing layer increases. We conclude that the formation of the chemically bonded sizing layer is more complete for higher functionalization of fiber surface. Consequently, the acid treated carbon fiber (A) promises best conditions for a stable bonding with the sizing.

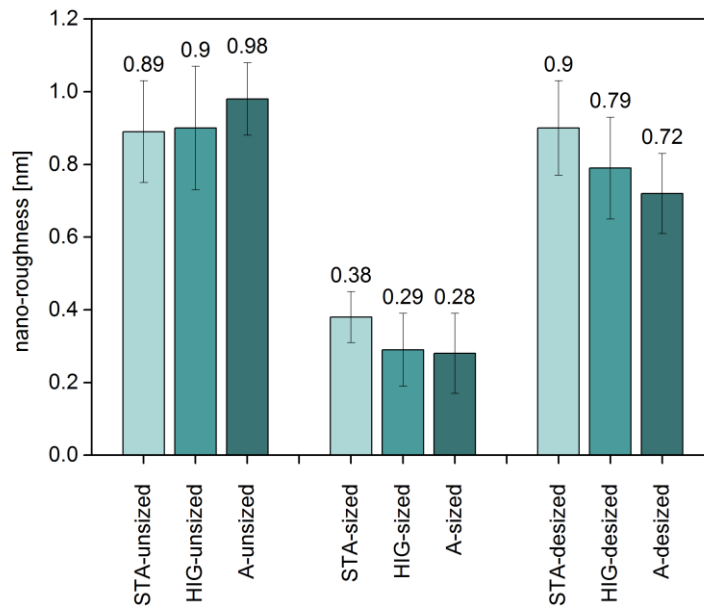


Figure 3. Nano-roughness of unsized, sized and desized carbon fibers.

3.2. Sizing content of the fibers

The sizing content of the sized and desized fibers was quantified by the mass loss of the samples during heat treatment as measured by TGA. Table 1 lists the sizing contents of the sized and desized fibers. For all sized fibers, the intended amount of sizing of about 1 wt% is found. The sizing content slightly decreases with increasing activation degree of the fibers. The reason could be, that the improved wetting behavior of the highly activated fibers results in thinner sizing layers [14]. In case of the desized fibers, mass loss is significantly lower than for sized fibers. As in the chemical desizing process the physisorbed sizing layer was removed, mass loss is assumed to result solely from the chemically bonded layer. With increasing activation level of the fibers, the mass loss of the desized fibers increases. This can be explained by the formation of a more distinct chemically bonded layer for increasing surface activation levels, as already suggested by the results of nano-roughness measurements.

Table 1. Mass loss after thermal treatment of sized and desized fibers.

Specimen Type	<i>sizing content</i> (wt%)
STA-sized	1.03 ± 0.02
HIG-sized	0.98 ± 0.01
A-sized	0.87 ± 0.01
STA-desized	0.14 ± 0.03
HIG-desized	0.18 ± 0.02
A-desized	0.28 ± 0.03

3.3. Surface chemistry of the fibers

The amount of reactive epoxide groups on the fiber surface was examined by potentiometric titration of the fibers before and after desizing. Figure 4 shows the epoxy indices as a measure of the residual epoxy reactivity of the sizing layer for all different types of fibers. In case of the sized fibers, we observe equal epoxy indices for the two fibers with lower activation degree (STA-sized and HIG-sized). This EI is interpreted as the intrinsic epoxy reactivity of the sizing. The decreased EI of the sized acid treated fiber (A-sized) may indicate a stronger chemical interaction of the sizing layer with the fiber. Here, a higher number of epoxide groups of the sizing layer might have reacted with the fiber surface and, thus, are no longer detectable by the titration. The lower EI can also be induced by the reduced amount of sizing on these fibers (see Table 1).

The values of the epoxy indices of the desized fibers is expected to represent the residual epoxy reactivity of the exposed chemically bonded sizing layer. We conclude that the decreasing EI of the higher activated fibers in combination with the increasing sizing amount (Table I) indicates a stronger chemical bonding between fiber and sizing. For the desized acidic treated fiber the lowest EI in combination with the most pronounced remaining sizing layer (see Figure 3 and Table 1) promises the formation of a complete chemically bonded layer.

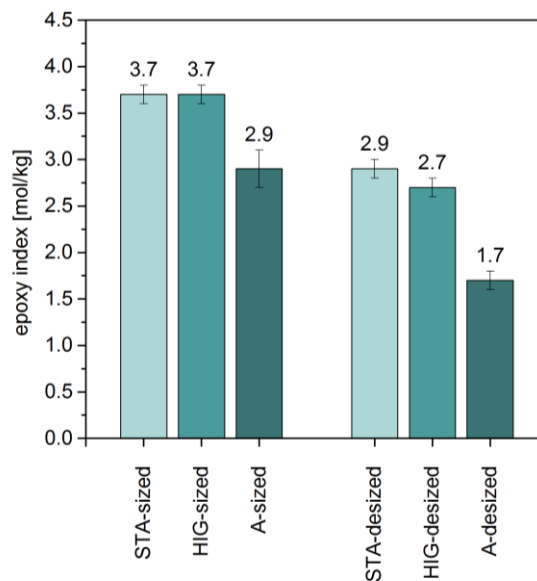


Figure 4. Epoxy index of the sizing layer on the titrated fibers.

4. Conclusions

Desizing experiments by solvent extraction were performed on three types of sized carbon fibers of varying degree of surface activation, to expose the chemically bonded parts of the sizing layer. On the desized fibers a decreasing nano-roughness and an increasing amount of remaining sizing were found with increasing surface activation degrees. This indicates an increasing formation of the dominantly chemically bonded sizing layer for higher activation degrees. Additionally, lower epoxy indices of desized higher activated fibers indicate an increased chemical bonding between fiber and sizing. The investigations illustrate the potential for an increase of the interfacial adhesion in fiber reinforced polymeric composite materials by improved chemical compatibility of fiber surface and polymeric sizing.

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