INVESTIGATION OF THE SIZING BEHAVIOR OF CARBON FIBERS BY SINGLE FIBER DIP COATING EXPERIMENTS

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Abstract
In order to optimize the positive effects of fiber surface treatments on the interfacial adhesion between carbon fiber and polymer matrix in composite materials, the polymeric sizing has to be adapted according to the amount and wetting properties. To gain insight into the interaction between fibers and sizing solution, the results of single fiber dip coating experiments are monitored by scanning electron and atomic force microscopy. The nano-roughness as measured by atomic force microscopy reflects the sizing distribution and thickness. In the present work the investigation of the sizing behavior of carbon fibers is performed on fibers with variable degrees of surface activation using two different epoxy based sizings. The surface energies of the unsized fibers are determined by tensiometry and increase with increasing activation. Accordingly, the wettability with the epoxy sizing increases for the higher activated fibers. The resulting homogeneous sizing distribution is reflected by lower values of nano-roughness of the sized filaments. Additionally, the chemical compositition of the sizing has high impact on the wetting behavior. The results indicate the potential of the single fiber sizing experiments for a basic understanding of the sizing process and confirm the nano-roughness as a suitable quantity to evaluate the sizing behavior.

1. Introduction

The interface dominated mechanical properties of carbon fiber reinforced polymer composites are determined by the interfacial adhesion between the constituents. A successful adaption of fiber and matrix results in an increased performance of the composite [1, 2]. Numerous investigations have been performed concerning the possibilities of surface modification of carbon fibers, e.g. anodic oxidation or plasma activation, to improve the adhesion of fiber and matrix material [3, 4]. The selection of a suitable sizing and the sizing process is of equal importance.

The coating of reinforcing carbon fibers with a polymeric sizing improves handling and textile processing. In addition, a better wettability and enhanced interfacial adhesion between fiber and matrix material can be achieved [5, 6]. The amount and the distribution of sizing on the fiber surface is an important factor for both aspects of composite production. A deviation from ideal coating may result in a degradation of the mechanical properties of the composite. Therefore, comprehension of the basic principles of the sizing process and the interaction between activated fiber and sizing solution is crucial.

In the case at hand, single fiber sizing experiments are conducted using a dip coater. Carbon fibers of varying surface activation levels are coated applying two different epoxy sizing solutions. After a

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drying process, the sized filaments are investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The nano-roughness of the fiber surface is determined and permits an evaluation of the sizing behavior. In addition, the surface energies of the unsized fibers are measured by tensiometry.

2. Experimental

2.1 Materials

Three types of carbon fibers, differing in their electrochemical activation, are used. The medium activated carbon fibers were activated by anodic oxidation in an aqueous ammonium bicarbonate (NH_4HCO_3) solution, the highly activated fiber was functionalized by a diluted sulfuric acid (H_2SO_4). An untreated carbon fiber serves as reference. Two water based epoxy sizing solutions, Epoxy1 with a lower reactivity and Epoxy2 with a higher reactivity, are used for the dip coating experiments.

2.2. Tensiometry

Contact angle measurements are realized with a tensiometer (DCAT 11, DataPhysics) to determine the surface energies of the unsized carbon fibers. The 50k fiber rovings are threaded in cylindrical glass tubes to perform capillary rise experiments. Here, the tensiometer detects the increase of mass during the absorption of a test liquid by the fiber bundle over time. In order to calculate the contact angle between fiber and liquid, Washburn's equation is applied [7]. The necessary geometric factor is determined by measurements with a completely wetting liquid, in our case n-hexadecane. Furthermore, four test liquids with different magnitudes of polar and dispersive components of surface energy are selected: ethylene glycol, benzyl alcohol, diiodomethane and water. For each combination of test liquid and fiber at least 5 samples are measured. Using the approach of Owens, Wendt, Rabel and Kaelble (OWRK) the polar and dispersive components of the surface energies of the fibers are separated [8-10].

2.3. Dip coating of single carbon fibers

Single carbon fibers are fixed in a metallic frame and dipped into the epoxy sizing solution perpendicular to the liquid surface. Dipping velocity and immersion depth are controlled by the software of the dip coater (KSV NIMA). The fiber is completely immersed in the sizing bath using a free clamping length of 5cm. A sizing film is deposited when the filament is withdrawn with a constant velocity from the sizing bath. The dip coating is followed by a drying process at 150°C. For the following investigations, a minimum of 6 single filaments are prepared for each set of parameters.

2.4. Scanning electron microscopy and atomic force microscopy

The unsized and sized filaments are examined by SEM (Zeiss, DSM 982 Gemini) and AFM (Bruker, Dimension ICON). For SEM analysis, the fibers are fixed on a carbon tape and sputtered with a thin gold layer to guarantee electrical conductivity of the fiber surface. By atomic force microscopy the topography of the sized fibers is imaged in tapping mode with a scan size of 5µm x 5µm and 512 samples per line. According to the procedure introduced by Ref. [11], the nano-roughness of the carbon fiber surface is calculated from the height data by subtracting an appropriate background. The method enables visualization of the nano-structures on the fiber surface using a color scale. The computation of the nano-roughness is carried out with Matlab R2014b. For each specimen at least 9 AFM images are evaluated.

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3. Results and Discussion

3.1. Surface energies of unsized carbon fibers

The surface energies of the unsized carbon fibers with different degrees of surface activation are investigated by tensiometry. Table 1 lists the measured total surface energies, as well as polar and dispersive components. As expected, the surface energy of the carbon fibers increases with higher level of activation. The increasing polar character reflects the higher surface oxygen concentration of the activated fibers [12], which is advantageous for wetting with predominant polar liquids like water based epoxy solutions.

Table 1. Surface energies of the unsized carbon fibers with different degree of anodic oxidation.

Specimen	*Surface Energie* (mN/m)	*Dispersive component* (mN/m)	*Polar component* (mN/m)
untreated carbon fiber	34	32	2
medium activated carbon fiber	45	15	30
highly activated carbon fiber	69	15	54

3.2. Sizing behavior of the carbon fibers

Figure 1 shows differently sized carbon fibers, i. e. an industrially sized fiber (Figure 1b), a dip coated fiber with thin sizing layer (Figure 1c) and a dip coated fiber with thick sizing layer (Figure 1d). Additionally, an unsized fiber (Figure 1a) is shown as reference. The unsized fiber shows a pronounced fibrillar structure which is mostly preserved on the industrially sized fibers. Coating the fiber with a thin sizing layer in our experiment results in a similar surface morphology to that of the industrially sized fiber. In the case of a thick sizing layer, the fibrils are completely covered. For further processing of the fiber a thin, completely closed sizing layer appears to be favorable. The variation of dip parameters allows for identification of suitable sizing conditions to reach a thin sizing layer for the activated fibers. Dip coating at room temperature with a velocity of 67mm/min and a bath concentration of 2vol% (Epoxy1) and 0,25vol% (Epoxy2) results in thin closed sizing layers and, therefore, these parameters are used in the following for the sizing of the fibers with different degrees of activation.

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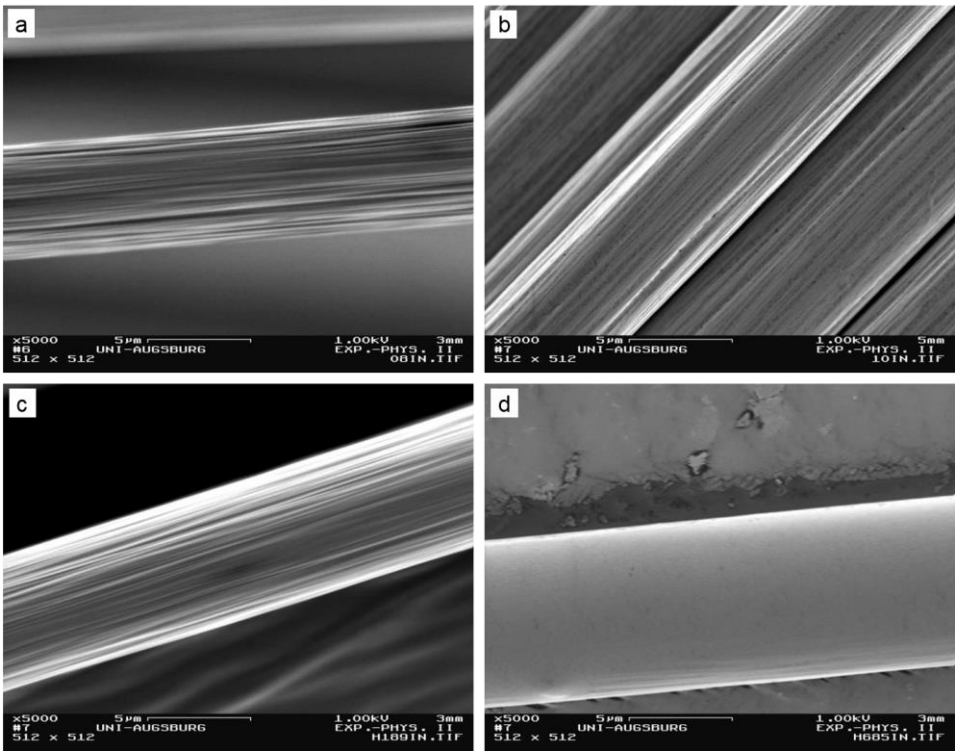

Figure 1. Exemplary SEM images of carbon fibers which are a) uncoated, b) industrially sized, c) dip coated with thin sizing layer, d) dip coated with thick sizing layer.

Evaluation of the AFM images provides detailed information about the sizing behavior. Figure 2 shows background corrected AFM height images with a colored nanoscale surface structure of a standard activated carbon fiber before and after industrial sizing. The unsized carbon fiber (Figure 2a) shows a high number of nanoscale structures homogeneously distributed over the surface. The nano-roughness amounts to 0,64nm. The sized fiber shows a low number of nano-structures (see Figure 2b) and a decrease of nano-roughness of the fiber surface down to 0,16nm.

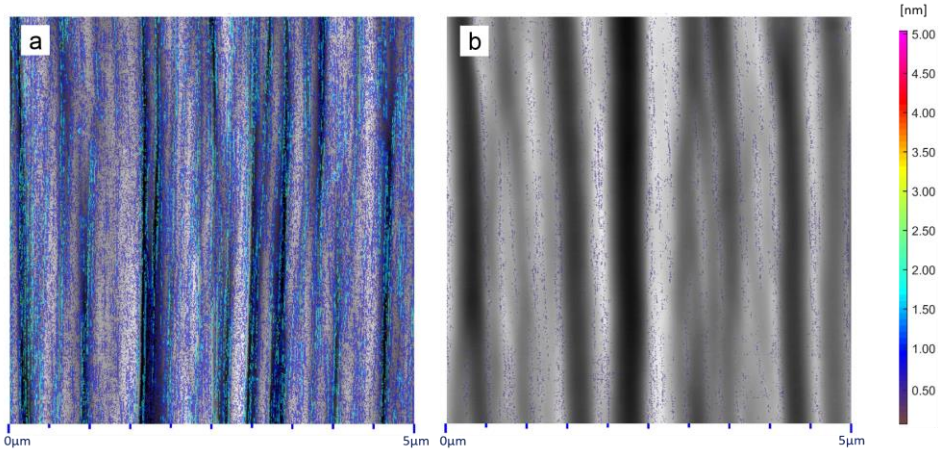

Figure 2. Background corrected AFM height images (gray) of fiber surfaces including nano-structures (color scale) of an unsized fiber (a) and an industrially sized fiber (b).

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Figure 3 shows AFM images of the carbon fibers from the dip coating experiments. Each set of parameters (degree of surface activation, type of sizing) is represented by one exemplary image. The nano-structures on the surfaces of all three types of uncoated fibers are well pronounced. In case of the sized fibers, the nano-structures are covered by the sizing to different degrees. The image of the untreated carbon fiber sized with Epoxy1 still displays numerous nano-structures. This indicates incomplete coverage of the surface with sizing and thus incomplete wetting between fiber and sizing solution. In contrast, both activated fibers show a very high degree of coverage of the nano-structures. For sizing Epoxy2 the coverage is almost complete. For all sized fibers the fibrillar structure is still visible. In spite of a lower concentration, the sizing Epoxy2 results in a smoother topography on nanoscale possibly due to a thicker sizing layer. These observations might be explained by the higher reactivity of the sizing solution Epoxy2.

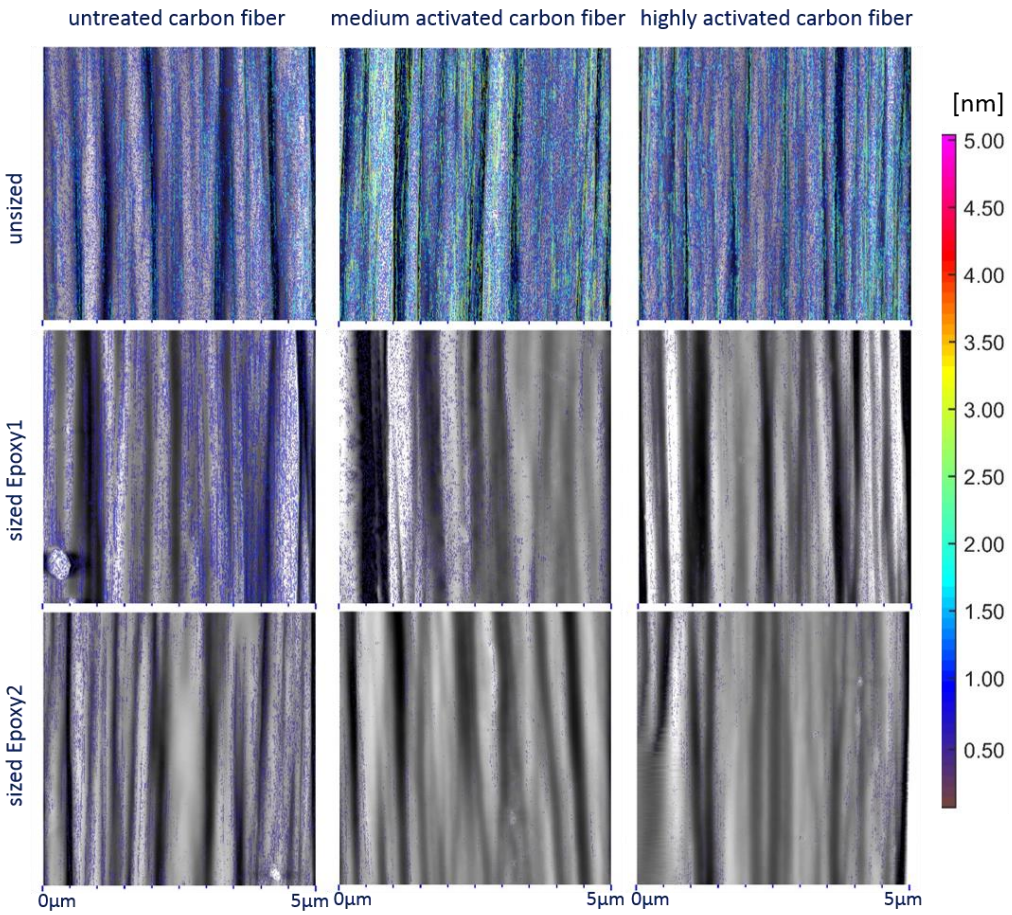

Figure 3. AFM height images of the examined carbon fibers.

The values of the nano-roughness of all fibers are plotted in Figure 4. Generally, there is a decrease of nano-roughness due to the sizing process, as also found for the industrially sized fiber. Among the sized fibers, the nano-roughness decreases with increasing activation for both kinds of sizing. For the same degree of fiber activation the nano-roughness of fibers sized with sizing Epoxy2 is lower than that of fibers sized with Epoxy1. We conclude that the activated fibers due to their increased surface energy show a better wettability for both sizings. In addition, sizing Epoxy2 shows a better wettability than Epoxy1, probably due to the higher reactivity.

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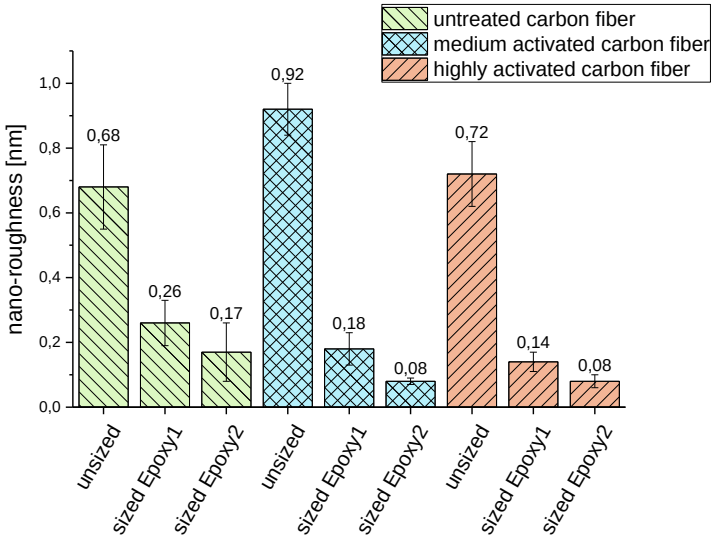

Figure 4. Nano-roughness of unsized and sized carbon fibers.

4. Conclusion

Single filament sizing experiments were performed using three types of fibers, differing in their surface activation level, and two different epoxy sizing solutions with varying reactivity. The wettability of the fibers increases with increasing activation level and increasing reactivity of the sizing. This behavior is attributed to the stronger attractive polar-polar interactions between fiber surface and sizing solution.

The investigations shed light on the dependence of sizing behavior of carbon fibers on different parameters, opening the possibility for an adaption of industrial processes based on small scale investigations.

Acknowledgments

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References

[1] L.G. Tang and J.L. Kardos. A review of methods for improving the interfacial adhesion between carbon fiber and polymer matrix. *Polymer composites*, 18:100-113, 1997.

[2] D.A. Jesson and J.F. Watts. The interface and interphase in polymer matrix composites: Effect on mechanical properties and methods for identification. *Polymer Reviews*, 52:321-354, 2012.

[3] J. Gulyás, E. Földes, A. Lázár and B. Pukánszky. Electrochemical oxidation of carbon fibres: surface chemistry and adhesion. *Composites Part A: Applied Science and Manufacturing*, 32:353-360, 2001.

[4] N. Dilsiz, N.K. Erinc and E. Bayramli. Surface energy and mechanical properties of plasma-modified carbon fibers. *Carbon*, 33:853-858, 1995.

[5] C.L. Weitzsacker, M. Bellamy and P.M.A. Sherwood. Studies of the effect of size on carbon fiber surfaces. *Journal of Vacuum Science & Technology A*, 12:2392-2397, 1994.

Excerpt from ISBN 978-3-00-053387-7

[6] B. Fernandez, A. Arbelaiz, A. Valea, F. Mujika and I. Mondragon. A comparative study on the influence of epoxy sizings on the mechanical performance of woven carbon fiber-epoxy composites. *Polymer composites,* 25:319-330, 2004.

[7] E.W. Washburn. The dynamics of capillary flow. *Physical review,* 17:273, 1921.

[8] D.K. Owens and R.C. Wendt. Estimation of the Surface Free Energie of Polymers. *Journal of Applied Polymer Science,* 13:1741-1747, 1969.

[9] W. Rabel. Einige Aspekte der Benetzungstheorie und ihre Anwendung auf die Untersuchung und Veränderung der Oberflächeneigenschaften von Polymeren. *Farbe und Lack*, 77:997-1006, 1971.

[10] D.H. Kaelble. Dispersion-polar surface tension properties of organic solids. *Journal of Adhesion*, 2:66-81, 1970.

[11] J. Jäger, J. Moosburger-Will and S. Horn. Determination of nano-roughness of carbon fibers by atomic force microscopy. *Journal of Materials Science*, 48:6803-6810, 2013.

[12] M. Bauer, J. Moosburger-Will and S. Horn. Functionalization of carbon fibers by anodic oxidation: Surface analysis by X-ray photoelectron spectroscopy. *Submitted Proceeding of the 17th European Conference on Composite Materials ECCM-17 in Munich, Germany,* June 26-30 2016.

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