



## Investigation on the thermo-oxidative stability of carbon fiber sizings for application in thermoplastic composites



Jiri Duchoslav<sup>a, b, \*</sup>, Christoph Unterweger<sup>b</sup>, Roland Steinberger<sup>a</sup>, Christian Fürst<sup>b</sup>, David Stifter<sup>a</sup>

<sup>a</sup> Christian Doppler Laboratory for Microscopic and Spectroscopic Material Characterization (CDL-MS-MACH), Center for Surface and Nanoanalytics (ZONA), Johannes Kepler University (JKU) Linz; Altenberger Straße 69, 4040 Linz, Austria

<sup>b</sup> Kompetenzzentrum Holz GmbH (Wood K plus), Division Wood Polymer Composites, Altenberger Straße 69, 4040 Linz, Austria

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### ABSTRACT

The stability of the surface chemical composition of different polymer sizings on carbon fibers, designed as a reinforcing material for thermoplastic composites, was investigated in detail under conditions closely related to the standard processing ones, *i.e.* high temperature, short periods of processing time and presence of an oxidative atmosphere. X-ray photoelectron spectroscopy and contact angle measurements were used to characterize the surface properties of the sizings in dependence of treatment time and temperature. The obtained results clearly show a rapid thermo-oxidative altering of the initial surface functionalities, in particular of the polyether based component, which was found to be the major surface constituent of all types of investigated sizing systems. Moreover, the observed degradation of surface functionalities leads to significant changes in the surface free energies of the sizings determined by contact angle measurements. Finally, the surface analysis of single fibers, which were pulled out during fracture of model composite specimens, confirmed that the revealed surface degradation of the sizing also takes place during a standard polymer composite manufacturing process.

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### 1. Introduction

Short carbon fibers (CFs) have been recognized as a promising reinforcing material for thermoplastic composites. When compared to glass fibers, which are the most commonly used reinforcing material in thermoplastic systems, CFs possess higher specific strength and stiffness and thus offer a promising potential for weight reduction and improvement of the mechanical performance of the polymer composites [1–6]. However, despite the excellent mechanical characteristics, bare CFs are known to suffer from poor wettability and adhesion to matrix polymers [3,7], most likely due to the chemical inertness and smoothness of the fiber surface exhibiting a low surface free energy [3,7–9]. In order to improve the interfacial adhesion between the bare CFs and the polymer matrix, which is essential for the great potential of CFs to

be fully exploited, different concepts can be used.

Frequently, the bare, inactive surface of the CFs is directly modified by means of various methods. Commonly used methods include *e.g.* different plasma treatments [7,9–14], oxidation using nitric acid [14–17], electrochemical oxidation [18], thermal treatment [19–21], treatment with liquid nitrogen [14], ozone treatment [22], liquid ammonia treatment [23] or a combination thereof. As a consequence, the surface free energy increases, different functional groups are introduced to the surface and often also an increase of the surface roughness is observed, which all together contributes to an improved adhesion to the polymer matrix.

Another efficient concept involves the use of an additional chemical component, a coupling or sizing agent, grafted onto the surface of CFs [2,6,8,24–30] or added directly into the fiber-polymer matrix system [3,6,31–33]. Similarly to the above mentioned surface modification, the functional groups introduced by the coupling or sizing agent provide an enhanced compatibility between the reinforcing and the matrix material. Moreover, application of a sizing may also improve the handling and composite processing characteristics of fibers. For example, reduced

\* Corresponding author. Christian Doppler Laboratory for Microscopic and Spectroscopic Material Characterization (CDL-MS-MACH), Center for Surface and Nanoanalytics (ZONA), Johannes Kepler University (JKU) Linz, Altenberger Straße 69, 4040 Linz, Austria.

E-mail address: [jiri.duchoslav@jku.at](mailto:jiri.duchoslav@jku.at) (J. Duchoslav).

fiber breakage due to fiber protection during processing, improved wear resistance and dosing properties are described [8,29]. For these reasons most of the commercially available CFs are already sized [2,6,25,34]. Simultaneously, with the increasing number of differently sized CFs released into the market, also a strong demand for a suitable methodology arises, which can identify the most compatible sized fibers for a chosen polymer matrix.

Although a good prediction of the sizing-matrix compatibility can be made by using parameters, like the surface free energies [35], this approach seems to be not fully reliable for all types of composites, as demonstrated for a number of differently sized fibers in polypropylene (PP) composites [6].

Owing to the manufacturing temperatures of thermoplastic composites, a potential problem may lie in the insufficient thermo-oxidative stability of fiber surface, a fact which is often simply ignored. Only a few studies have been carried out to date showing that the surface chemical composition of some sized glass fibers and ozone treated CFs may undergo significant changes during annealing at elevated temperatures of a few hundreds of °C under inert atmosphere [36–38]. Moreover, the processing of thermoplastic composites is usually performed under the oxidative atmosphere of air. As a consequence oxygen from the air can easily dissolve in the molten polymer system [39]. Thus it cannot be ruled out that the presence of oxygen, both in the surrounding as well as directly inside of the molten system, will intensify the alteration of the sizing chemistry.

In the current work, the stability of the surface chemical composition of three types of differently sized CFs were investigated in detail within model conditions approximating standard processing of PP composites. For this purpose, the sized CFs were annealed in air at temperatures of 190 and 240 °C, the lower and upper limits of a standard processing temperature window for PP composites [2], and for short periods of time in the range of 2–10 min. The surface chemistry of each type of the studied sizings was determined prior and after each annealing step using X-ray photoelectron spectroscopy (XPS) as a surface sensitive technique. Furthermore, the impact of the performed heat treatments was also evaluated by means of the surface free energies derived from contact angle measurements, a method less susceptible to material inhomogeneities on a lateral length scale. In order to prove the relevance of the obtained results for standard composite processing, the surface chemistry of correspondingly sized CFs, which were directly pulled out of fractured PP composite specimens, were analyzed, too.

## 2. Experimental section

### 2.1. Materials

Three types of commercially available short CFs containing different sizings on the surface and therefore being designed for different matrix systems of polyurethane (PU), polyamide (PA) and PP were investigated. All used fibers were supplied by the same manufacturer (Toho Tenax, JPN), had the same diameter of 7 µm and a length of 6 mm and differed only in the type of sizing. For contact angle measurements, standard solvents of *n*-hexane (99%, Roth, GER), toluene (99.5%, Roth, GER), ethanol (99.8%, Roth, GER), ethylene glycol (99.5%, Roth, GER), and deionized water were used. As a matrix polymer for composite specimens, PP HD120MO (Borealis, AUT) was used.

### 2.2. Thermo-oxidative stability tests

In order to assess the thermal stability of the different sizings, the pellets of the sized CFs were, at first, mounted on a standard

microscopic glass slide and fixed with conductive silver glue (G360Z, Christine Groepl, AUT). Prior to annealing, the mounted CFs were analyzed by means of XPS in order to gain information on their original surface elemental and chemical composition. Afterwards, the glass slides with the sample fibers were put into a laboratory oven, already preheated to a temperature of 190 °C, kept there for 2 min and then removed in order to be measured by XPS exactly in the same positions as before. The annealing was then repeated four more times, i.e. the samples were annealed in total for 10 min. In the same manner, but with newly prepared specimens, the experiment was repeated using a higher annealing temperature of 240 °C.

Due to the larger quantity of material needed to perform contact angle measurements of the thermally treated fibers, additional batches of 15 g from each fiber material were separately annealed for 10 min at both temperatures of 190 and 240 °C.

### 2.3. Composite specimen preparation

For the investigation of the impact of typical composite manufacturing conditions on the surface chemistry of CF sizings, test specimens containing 30 wt. % CFs in a PP matrix were produced. Compounding was performed in a Brabender 350E mixer using Roller blades. The mixer was operated at 180 °C and 75 rpm. In order to retain long fibers in the compounds, the fibers were added after melting of the polymer was complete. During the subsequent mixing time of 5 min the melt temperature increased to approximately 190 °C. All compounds were then cooled in air and ground using a cutting mill. From the milled compounds, tensile test specimens in accordance with EN ISO 3167 were produced using a Battenfeld HM 1300/350 injection molding machine. The injection and mold temperatures were 190 and 60 °C, respectively. Fracture surfaces, required for obtaining single pulled out fibers for XPS analysis, were obtained by notched impact testing of the test specimens in accordance with EN ISO 179/1eA.

### 2.4. Analytical methods

XPS measurements were performed using a Theta Probe XPS system (ThermoFisher, GBR) and the obtained spectra were evaluated using the Avantage software package provided by the system manufacturer. A monochromated Al-K<sub>α</sub> X-ray source (1486.6 eV) with the spot size of the X-ray beam being 400 µm in diameter was used. Only for the XPS analysis of single pulled out fibers a much smaller spot size of 20 µm was chosen. The hemispherical analyzer of the system was operated in the CAE-mode (constant analyzer energy) with a pass energy of 200 eV for survey spectra and 20 eV for the detailed (high resolution) spectra, which corresponds to a full width at half maximum of 2.52 eV and 0.63 eV for the Ag3d<sub>5/2</sub> reference peak, respectively. In order to neutralize the charge build-up on the analyzed surfaces, the XPS system was equipped with a standard dual flood gun (FG02, ThermoFisher, GBR) providing simultaneously a beam of low energy electrons (−2 eV) and a beam of low energy Ar-ions. Standard charge shift referencing via the C1s peak of an aliphatic carbon at 285.0 eV was applied. For data evaluation the background of the photoelectron peaks was subtracted by applying a Shirley-type background. For the calculation of the elemental composition of the investigated samples, the determined areas under the peaks were normalized by using the Scofield sensitivity factors.

Scanning electron micrographs of fractured surfaces of prepared composite specimens were taken using JAMP 9500F (JEOL, JPN). For that purpose no conductive coatings were applied on the investigated surfaces.

The contact angle measurements were performed by means of a

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