



# Characterization of carbon fiber surfaces and their impact on the mechanical properties of short carbon fiber reinforced polypropylene composites



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## ABSTRACT

The aim of this paper is to evaluate the influence of carbon fibers (CF) surface properties and the amount of a coupling agent on the mechanical properties of injection molded CF reinforced polypropylene (PP) composites. Five types of CF, three sized, a de-sized and a de-sized and afterwards plasma-treated type, were characterized by X-ray photoelectron spectroscopy (XPS) and contact angle measurements. All fiber types were mixed with PP and various amounts of maleic anhydride grafted PP as coupling agent. Subsequently, all compounds were injection molded and characterized by measurement of flexural/tensile strength and modulus, notched/unnotched impact resistance, heat deflection temperature and fiber length. In addition fracture surfaces were analyzed by means of scanning electron microscopy (SEM).

Both, contact angle measurements and XPS, showed, in good agreement, key differences in surface properties between the five CF samples. Mechanical testing and SEM images of fracture surfaces proved that fiber surface properties and the amount of coupling agent have major impacts on fiber/matrix interaction, hence on mechanical composite performance.

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## 1. Introduction

Fiber reinforced polymer composites combine the high stiffness and strength of reinforcing fibers with the low weight of polymers. Due to their high strength-to-weight ratio they have been widely used in various application fields like aerospace, marine and automobile industries during the past few decades. Glass fibers are the traditional reinforcement fibers owing to their good performance at a low price. Nevertheless, many other fiber types provide some advantages compared to glass fibers [1]. Especially, carbon fibers (CF) gain more and more interest [2,3], as their high specific strength and stiffness offer the possibility for significant weight reduction [4–8]. However, the full potential of CF reinforced polymers has not yet been fully exploited. Due to their chemically inert surface and low surface energy, CF exhibit poor interfacial adhesion with matrix polymers, even with nonpolar polymers like PP [4,8]. Therefore, commercially available fibers are usually coated with a sizing that contains different functional groups. Common CF sizings are for use in polyamide (PA), polyurethane (PU) or

epoxy (EP) composites [1]. Numerous studies about CF functionalization, hence improved adhesion to various matrix polymers, by plasma treatment methods were published over the last two decades [3–5,7–11]. Furthermore, surface functionalities can be induced by electrochemical oxidation [12,13], chemical oxidation using nitric acid [14] or ozone treatment [15].

A polypropylene (PP) matrix, being completely nonpolar, shows poor adhesion to polar surfaces. For a strong interaction between PP and CF, the matrix polymer has to be modified, too. The most common method is the functionalization of PP with polar molecules, such as maleic anhydride. As polymer degradation, hence decrease of mechanical performance, occurs during functionalization, the use of functionalized polymers is limited to small amounts. Therefore, just a few wt.% of maleic anhydride grafted PP (MAPP) are usually added to the PP matrix as coupling agent between the nonpolar PP and polar fiber surfaces [1,2,8,16,17].

For determination of fiber surface composition and functionalities the most common method is X-ray photoelectron spectroscopy (XPS) [3,5,7–9,13,15,18–21]. Contact angle measurements are used for determination of surface energies [3,4,6,22]. Surface topography is usually examined using scanning electron microscopy (SEM) [6–10] or atomic force microscopy [6,18,20].

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Information on fiber/matrix interaction can be derived from micromechanical test methods, which allow for the calculation of the interfacial shear strength [6,8,9,12,15,18,22], or from macroscopic composite materials, either from mechanical performance [2,4,5,7] or from SEM images of fracture surfaces [2,4,8].

The aim of this paper is, to evaluate the influence of CF surface properties and the amount of MAPP on the mechanical performance of CF reinforced polypropylene composites. Five types of CF, three sized, a de-sized and a de-sized and afterwards plasma-treated type, were first characterized by XPS and contact angle measurements and subsequently processed to CF reinforced PP composites. Information on fiber/matrix interaction in dependence of CF surface properties and MAPP content was derived from mechanical composite performance and SEM images of fracture surfaces.

## 2. Experimental

### 2.1. Materials

Three commercially available types of CF were used in this study. All three types were identical in terms of strength, stiffness, length and diameter, but contained different sizings, namely, for use in PU, PA or PP. No further information on the surface properties were given by the supplier. All fibers had a diameter of 7  $\mu\text{m}$  and a cut length of 6 mm.

PP HD120MO by BOREALIS was used as matrix polymer for mechanical test samples. Scona TPPP 8112 FA, an MAPP grade by BYK KOMETRA, was added as coupling agent.

For contact angle measurements *n*-hexane, toluene, ethanol, ethylene glycol and deionized water were used.

### 2.2. CF surface modification

The sizings were removed by annealing at 500 °C in Ar atmosphere for 1 h. All three de-sized samples were analyzed by means of XPS. Only the annealed CF that originally contained a sizing for PU were subsequently used. For plasma treatment, the fibers were evenly spread on the trays of a DIENER Tetra 30 low-pressure plasma chamber. Surface modification was performed for 120 min using oxygen as process gas at a pressure of 0.2 mbar. The plasma chamber was operated at the maximum power of 500 W.

### 2.3. CF surface analysis

XPS measurements were performed using a THERMOFISHER Theta Probe XPS system and the acquired spectra assessed by means of the Avantage software package provided by the system manufacturer. Samples were irradiated with a monochromatic Al K $\alpha$  X-ray source (1486.6 eV) with a spot size of 400  $\mu\text{m}$  and a power of 100 W. The high resolution spectra were acquired with a pass energy of 20 eV and an energy step size of 0.05 eV. In order to neutralize the charge build-up on the analyzed surfaces, the XPS tool was equipped with a standard dual flood gun FG02 by THERMOFISHER, which provides simultaneously a beam of low energy electrons (−2 eV) and a beam of low energy Ar ions. Standard charge shift referencing of the spectra via a peak of adventitious carbon at 285.0 eV was applied. The qualitative and quantitative analysis was performed using the C1s, O1s and N1s photoelectron peaks with linear or Shirley background subtraction and normalization using Scofield sensitivity factors.

For contact angle measurements a capillary rise method [23–25] was used. Due to the relatively large sample size, this method is less susceptible to material inhomogeneities than other meth-

ods. The experiments were performed with a KRÜSS K100 tensiometer equipped with a fiber chamber. The contact angle  $\theta$  was derived from Eq. (1) [26], where  $m$  is the mass of absorbed liquid,  $t$  the absorption time,  $c$  is the capillary constant of the packed solid and  $\rho_L$ ,  $\sigma_L$  and  $\eta_L$  are the density, the surface energy and the dynamic viscosity of the test liquid, respectively.

$$\frac{m^2}{t} = \frac{c \cdot \rho_L^2 \cdot \sigma_L \cdot \cos \theta}{\eta_L} \quad (1)$$

Out of the 5 test liquids (*n*-hexane, toluene, ethanol, ethylene glycol and deionized water) the liquid with the best wetting behavior was used for determination of the capillary constant of a specific fiber type, while the other 4 liquids were used for determination of contact angles. From the derived contact angles, the surface energies of the fibers were calculated according to the Owens, Wendt, Rabel and Kaelble method [27,28] using Eq. (2), where  $\sigma_s^p$  and  $\sigma_s^d$  are the polar and disperse parts of the surface energy of the analyzed fiber, while  $\sigma_L^p$  and  $\sigma_L^d$  are the polar and disperse parts of the surface energy of the test liquid, respectively.

$$\frac{\sigma_L \cdot (\cos \theta + 1)}{2 \cdot \sqrt{\sigma_L^d}} = \sqrt{\sigma_s^p} \cdot \frac{\sqrt{\sigma_L^p}}{\sqrt{\sigma_L^d}} + \sqrt{\sigma_s^d} \quad (2)$$

### 2.4. Compounding and specimen preparation

All composites produced and characterized in this study contain a constant amount of CF (30 wt.%) and varied amounts of MAPP (0, 2 or 5 wt.%), with the rest being PP (70, 68 or 65 wt.%). Compounding was performed in a BRABENDER 350E mixer using Roller blades. The mixer was operated at 180 °C and 75 rpm. 200 g of each composite material was produced in one batch. PP (and MAPP when used) was filled in at first and melted for 2 min. Then the fibers were added and mixed for additional 5 min. All compounds were ground in a FRITSCH Universal Cutting Mill PULVERISETTE 19 using a 6 mm square perforation sieve. 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. An injection speed of 50 cm<sup>3</sup>/s was used for all specimens. The total cooling time was 30 s with a hold pressure of 80% of the resulting injection pressure being applied for the first 16 s.

Test specimens for flexural, impact and HDT-A testing were produced by cutting off the shoulders from tensile test specimens using a MUTRONIC Diadisc 4200 precision cut-off saw. This saw was further used to create a 2 mm notch in specimens for notched impact testing.

### 2.5. Composite analysis

Tensile testing was performed in accordance with EN ISO 527. The modulus was measured between 0.05% and 0.25% elongation and a test speed of 1 mm/min. Tensile strength was determined at a test speed of 5 mm/min.

Flexural testing was performed in accordance with EN ISO 178. Test speed was 2 mm/min, the modulus was measured between 0.05% and 0.25% elongation.

Charpy impact testing was performed in accordance with EN ISO 179/1eU and EN ISO 179/1eA.

The HDT-A testing was performed in accordance with EN ISO 75.

For determination of the length of fibers in the composite materials, the matrix was removed by annealing at 500 °C for 1 h in N<sub>2</sub> atmosphere. The recovered fibers were then suspended in water.

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