SURFACE PROPERTIES OF CARBON FIBERS: IMPACT ON THE MECHANICAL PERFORMANCE OF SHORT FIBER REINFORCED POLYPROPYLENE COMPOSITES

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ABSTRACT

Carbon fibers (CF) reinforced polymer composites are widely used in various application fields like aerospace, marine and automobile industries, as their high specific strength and stiffness offer the possibility for significant weight reduction. However, the full potential of CF reinforced polymers has not yet been fully exploited, as CF exhibit poor interfacial adhesion with matrix polymers. To overcome this shortage, CF are usually surface treated, in order to introduce functional groups that can interact with the polymer matrix or a coupling agent.

The aim of this study was to evaluate the influence of CF surface properties and the amount of coupling agent on the mechanical performance of injection molded CF reinforced PP composites. Therefore, sized, de-sized and plasma treated CF were first characterized by X-ray photoelectron spectroscopy (XPS) and contact angle measurements and subsequently processed to CF reinforced PP composites. Information on fiber/matrix interaction was derived from mechanical composite performance and scanning electron microscopy (SEM) images of fracture surfaces.

Contact angle measurements and XPS showed key differences in surface properties between the three CF samples. While for the sized fibers, highly polar surface energies and high amounts of surface functionalities were measured, the de-sized CF showed a mostly nonpolar character. Furthermore, low pressure plasma treatment could be used to induce functional groups on CF surfaces. 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. Composite performance was in accordance with the fiber surface properties, determined by XPS and contact angle measurements. The excellent performance of composites reinforced with de-sized CF is particularly remarkable, showing great potential for recycling of CF. The possibility to induce functional groups by low pressure plasma treatment further broadens the application spectrum of recycled CF.

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]. 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 study was to evaluate the influence of CF surface properties and the amount of MAPP on the mechanical performance of CF reinforced PP composites. Three types of CF, a sized, a de-sized and a 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

Materials
A commercially available CF type with a sizing for use in PU was used in this study. The sizing was also recommended for use in PP composites, but no further information was provided by the manufacturer. The fiber diameter was 7 µm and the cut length was 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.

CF surface modification
The sizing was removed by annealing at 500 °C in Ar atmosphere for 1 h. For plasma treatment, the de-sized fibers were evenly spread on the trays of a DIENER Tetra 30 low-pressure plasma chamber. Surface modification was performed for 120 minutes using oxygen as process gas at a pressure of 0.2 mbar. The plasma chamber was operated at the maximum power of 500 W.

CF surface analysis
XPS measurements were performed using a THERMOFISHER Theta Probe XPS system and the acquired spectra were assessed by means of the Avantage software package provided by the system manufacturer. Samples were irradiated with a monochromatic Al-Kα X-ray source (1486.6 eV) with a
spot size of 400 µm 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 inhomogeneity than other methods. The experiments were performed with a KRÜSS K100 tensiometer equipped with a fiber chamber. The contact angle \( \theta \) was derived from Equation 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.

\[
\frac{m^2}{t} = \frac{c \cdot \rho_L^3 \cdot \sigma_L \cdot \cos \theta}{\eta_L}
\]

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 Equation 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.

\[
\frac{\sigma_L \cdot (\cos \theta + 1)}{2 \cdot \sqrt{\sigma_L^d}} = \sqrt{\sigma_S^p} \cdot \sqrt{\frac{\sigma_L^p}{\sigma_L^d}} + \sqrt{\sigma_S^d}
\]

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 minutes. Then the fibers were added and mixed for additional 5 minutes. All compounds were ground in a FRITSCH Universal Cutting Mill PULVERISSETTE 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 cm³/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.

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$_2$ atmosphere. The recovered fibers were then suspended in water. The fiber length distributions were determined using a FASEP 3E-ECO system. The weighted average fiber length ($L_w$) was determined using Equation 3.

$$L_w = \frac{\sum_{i=1}^{n} L_i^2}{\sum_{i=1}^{n} L_i}$$

For SEM images of fracture surfaces after notched impact testing, a JEOL 6400 scanning electron microscope was used.

3 RESULTS AND DISCUSSION

CF surface analysis

Prior to compounding and further processing, the three CF samples were investigated by means of contact angle measurements and XPS, in order to determine the fiber surface energies and the elemental/chemical surface compositions, respectively. As can be seen in Table 1, the surface properties of CF can be significantly altered by plasma treatment or application of a sizing. Generally, the surface energy values calculated from measured contact angles are in good agreement with fiber surface compositions, obtained from XPS measurements.

<table>
<thead>
<tr>
<th>surface properties of CF</th>
<th>$\sigma_p$ [mN/m]</th>
<th>$\sigma_d$ [mN/m]</th>
<th>$\sigma$ [mN/m]</th>
<th>$\sigma_p/\sigma_d$ [-]</th>
<th>C [at-%]</th>
<th>O [at-%]</th>
<th>N [at-%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>de-sized</td>
<td>6.7</td>
<td>15.4</td>
<td>22.1</td>
<td>0.43</td>
<td>92.0</td>
<td>2.8</td>
<td>5.2</td>
</tr>
<tr>
<td>de-sized + plasma treated</td>
<td>12.2</td>
<td>12.5</td>
<td>24.7</td>
<td>0.97</td>
<td>86.3</td>
<td>9.1</td>
<td>4.6</td>
</tr>
<tr>
<td>sizing for PU</td>
<td>27.1</td>
<td>15.2</td>
<td>42.3</td>
<td>1.78</td>
<td>77.0</td>
<td>22.2</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 1: Surface properties of CF. Surface energies (polar, dispersive, total and ratio of polar to dispersive part) and fiber surface composition

For the sized CF, increased surface energies with much higher polar contents were determined compared to the de-sized fibers. These results hint at good interaction of the fiber surfaces with polar matrix polymers or the polar part of a coupling agent. Comparison of the de-sized samples showed, that low pressure plasma treatment can be used to introduce polar groups on carbon fiber surfaces. Even though the change of total surface energy was rather small, the ratio of polar to dispersive surface energy could be significantly increased by plasma treatment.

The performed qualitative and quantitative analysis of the acquired XPS survey spectra, shown in Figure 1 and Table 1, revealed the presence of carbon and oxygen as the main surface constituents of the sized CF. Annealing at 500 °C led to a significantly reduced relative content of oxygen, whereas, simultaneously, the relative amount of detected nitrogen increased. The depletion of oxygen is found to be in good agreement with the objective of the annealing treatment, confirming the removal of the original sizing. Nitrogen found in higher relative concentration compared to the sized CF most probably originates from the inner structure of CF. The analysis of the de-sized and afterwards plasma treated sample revealed an increased relative concentration of oxygen compared to the only de-sized sample, while the relative content of nitrogen kept almost constant.
In order to elucidate and discuss the differences/similarities among the investigated samples more in detail, the recorded high resolution spectra of the found elements were evaluated by means of the chemical shifts relative to the aliphatic C-C/C-H peak at 285.0 eV (taken also for charge shift referencing) [29-30]. The detailed chemical analysis of C1s spectra of the sized CF, given in Figure 2, demonstrated the presence of three additional peaks to the aliphatic C-C/C-H one, which can be attributed to C-O (286.4 – 286.6 eV), O-C-O (287.7 eV) and O=C-O (289.9 eV) functional groups, with the C-O group being the main constituent.

High resolution spectra of de-sized CF before and after plasma treatment were analyzed, too. These spectra, illustrated in Figure 3, could not be fitted in the same manner as the spectra of sized CF, because of the highly asymmetric shape of the main line (as a consequence of their electric
conductivity) and the presence of numerous features/satellites on the higher binding energy side, effects well known for amorphous as well as for graphite like carbon [31]. Therefore, no chemical functionalities could be identified in the spectra of de-sized and plasma treated CF, but the superimposed spectra indicate a potential presence of C=O groups on the surface of the plasma treated sample, due to the slightly increased intensity of the inelastic background on the higher binding energy side of the C1s peak (Figure 3a) with correspondingly higher amount of detected oxygen (Figure 3b).

![Figure 3: XPS high resolution spectra of carbon (a) and oxygen (b) of de-sized CF before and after plasma treatment](image)

**Composite analysis**

Analysis of the fiber length in the composite materials showed, that the length of all CF types is massively decreased during processing. However, no significant differences were found among the investigated samples, with \( L_w \) values being in a quite narrow range around 235 µm. Therefore, the differences in mechanical composites performance, given in Table 2 and Figure 4, can be attributed predominantly to the differences in fiber surface properties, hence fiber/matrix interaction.

<table>
<thead>
<tr>
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<tr>
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<td>11.8</td>
<td>145</td>
<td>139</td>
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<td>3.8</td>
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<tr>
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<td>12.5</td>
<td>146</td>
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<td>6.0</td>
<td>39.6</td>
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<td>2</td>
<td>de-sized + plasma treated</td>
<td>11.0</td>
<td>12.1</td>
<td>145</td>
<td>146</td>
<td>93</td>
<td>6.2</td>
<td>39.0</td>
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<td>9.8</td>
<td>131</td>
<td>100</td>
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<td>4.0</td>
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<td>12.8</td>
<td>146</td>
<td>150</td>
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<td>39.0</td>
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<td>5</td>
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<td>11.9</td>
<td>12.8</td>
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<td>142</td>
<td>137</td>
<td>92</td>
<td>7.2</td>
<td>44.9</td>
</tr>
</tbody>
</table>

Table 2: Mechanical properties of CF reinforced PP composites

The flexural modulus (FM) is almost unaffected by fiber surface properties and the amount of coupling agent. Only the values found for composites containing sized fibers are a little bit lower compared to composites containing de-sized fibers. This trend is more pronounced in tensile modulus (TM) values, where a significant dependence on MAPP content was found, too. Heat deflection temperature (HDT) values show a quite similar trend. The largest differences among the various
Composite materials were found in terms of strength values. Flexural strength (FS), tensile strength (TS) and impact strength, both notched (NIS) and unnotched (IS), are strongly affected by fiber surface properties and the amount of coupling agent, hence the fiber/matrix interaction. Figure 4 shows a comparison of NIS, IS as well as TS values for all composites investigated in this study. FS values are not included, as the trends are similar to those in terms of tensile strength.

The results are in good accordance with measured fiber surface properties. Use of sized fibers results in poor performance in composites without coupling agent, as the mostly polar fiber surfaces barely interact with the completely nonpolar PP matrix. Addition of MAPP leads to huge improvements, as the coupling agent can interact quite well with the polar functional groups, present on the fiber surfaces. Interestingly, the best mechanical performance without an addition of a coupling agent can be achieved by using de-sized fibers. For these fibers the lowest surface energy values with the smallest ratio of polar to dispersive content were measured. In accordance with fiber surface properties, but in contradiction to reports found in literature [4-5, 8], de-sized fibers show the best interaction with the nonpolar PP matrix. Due to the mostly nonpolar fiber surface, the addition of 2 wt-% MAPP yields just a slight improvement in composite performance, while no change can be measured, when the MAPP content is further increased. In comparison to the only de-sized CF, plasma treated fibers lead to poor composite performance, but, owing to their more polar surface, large improvements can be achieved by the addition of MAPP.

In order to visualize differences in fiber/matrix interaction, SEM images of fracture surfaces were recorded. Figure 5 shows images of composites containing sized as well as de-sized CF. Samples containing sized fibers show the expected results. In accordance with composite performance, poor fiber/matrix interaction can be seen in the composite without coupling agent (Figure 5a), while significantly better wetting of the fibers is visible in composites with MAPP added to the matrix polymer (Figure 5b). Surprisingly, the same behavior was found for composites containing de-sized fibers. Despite the excellent mechanical performance, fracture images of a composite containing de-sized fibers and no coupling agent show poor fiber/matrix interaction (Figure 5c). On the contrary, an improvement becomes apparent, when MAPP is added (Figure 5d), while only a small increase in mechanical performance can be measured.
As can be seen in Figure 5a, fibers pulled out from composites containing no coupling agent are very smooth, indicating that there are no remains of the PP matrix present on the fibers. Therefore, analysis of the sizing after processing is possible by means of XPS measurements on pull-out fibers. Table 3 shows that a massive change in fiber surface properties occurs during processing. While the total oxygen content as well as the contents of C-O and O-C-O groups decrease, formation of highly polar O=C-O groups seems to happen during processing.

<table>
<thead>
<tr>
<th>sample</th>
<th>carbon content [at-%]</th>
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<tr>
<td></td>
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<tr>
<td>before processing</td>
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<tr>
<td>after processing</td>
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</table>

Table 3: Surface composition of sized CF before and after processing

4 CONCLUSIONS

In good agreement, both, contact angle measurements and XPS, showed key differences in the surface properties among the three investigated CF samples. For the sized fibers, oxygen was found as the main constituent beside carbon. C-O, O-C-O and O=C-O functional groups were found on the surface of sized CF, leading to high surface energy values, with mostly polar content. Removal of the sizing led to almost complete depletion of oxygen on the fiber surfaces. Surprisingly, increased amounts of nitrogen, which most probably originates from the inner structure of the CF, were found in the de-sized sample. Low-pressure plasma treatment was found to increase the amount of oxygen present on the surface of the CF, leading to an increased ratio of polar to dispersive surface energy.
Mechanical testing of short fiber reinforced PP composites proved that fiber surface properties have a major impact on composite performance. As all other factors were kept constant, variations in the mechanical composite performance originate from differences in fiber/matrix interaction. Therefore, composite performance is, for the most part, in accordance with the fiber surface properties, determined by means of XPS and contact angle measurements. SEM images of fracture surfaces proved the assumption of a correlation between composite performance and fiber/matrix interaction. The only exception are composites containing de-sized CF and no coupling agent, where, despite excellent mechanical performance, poor wetting of the fibers is visible in SEM images.

Furthermore, XPS measurements on pull-out fibers showed that the surface properties of sized fibers, i.e. the chemical composition of sizings, massively change during processing. As this method is limited to samples with poor fiber/matrix interaction, no data on the change of sizing composition in the presence of a coupling agent, which can interact or chemically react with functional groups present in the sizing, is available. Nevertheless, XPS measurements on pull-out fibers seem to be a useful tool for characterization of the impact of processing on fiber surface properties or sizing composition.

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REFERENCES


