THERMO-OXIDATIVE DEGRADATION OF CARBON FIBER SIZINGS AND ITS IMPACT ON THE MECHANICAL PERFORMANCE OF CARBON FIBER REINFORCED POLYPROPYLENE COMPOSITES

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Abstract
The present work focuses in detail on the surface analysis of commercially available carbon fiber (CF) sizings subjected to model treatment conditions closely related to thermoplastic composite processing (190 and 240 °C, 2 – 10 min, oxidative atmosphere). Our experimental results revealed pronounced altering of the surface chemical composition of the investigated sizings in dependence of treatment time and temperature. Despite pronounced degradation of all three types, still significant differences in the thermo-oxidative stability were found among the investigated sizings. Using a novel approach, namely, XPS analysis of single CF pulled out of fractured PP composite specimens, we further demonstrated that the observed thermo-oxidative degradation also takes place during real composite processing. In accordance with these findings, mechanical testing of PP/CF composites revealed that variation of processing temperatures leads to significant altering of the mechanical performance of PP/CF composites. These changes differ among the three types of investigated sizings, reflecting the differences in thermo-oxidative degradation of the sizings during composite processing.

1. Introduction

Carbon fibers (CF), when compared to other reinforcing materials like glass or natural fibers, possess higher specific strength and stiffness and thus offer potential for significant weight reduction and improvement of the mechanical performance of polymer composites [1-6]. However, the full potential of CF reinforced polymers has not yet been fully exploited, as CF, due to their chemically inert surface and low surface energy, exhibit poor interfacial adhesion with matrix polymers [3, 7-9]. Therefore, commercially available fibers are usually coated with a sizing containing different functional groups that can interact with the polymer matrix or a coupling agent. Simultaneously, with the increasing number of differently sized fibers 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. A good prediction of the sizing/matrix compatibility can be made by using parameters, like the surface free energies [10], although this approach seems to be not fully reliable for all types of composites [6]. Owing to the manufacturing temperatures of thermoplastic composites, a potential problem may lie in

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the insufficient thermo-oxidative stability of the sizing, causing changes of the fiber surface properties during processing, a fact which is often simply ignored.
Therefore, the present work focuses, for the first time, in detail on the surface investigation of commercially available CF sizings subjected to different model treatment conditions closely related to thermoplastic composite processing (190 and 240 °C, 2 – 10 min, oxidative atmosphere). Using a novel approach, namely, XPS analysis of single CF pulled out of fractured composite specimens, we further investigated the thermo-oxidative degradation of the CF sizings after composite processing. Finally, composite specimens were prepared at different processing temperatures in order to evaluate the influence of thermo-oxidative degradation of sizings on the mechanical performance of CF composites.

2. Experimental section

2.1. Materials

Three types of commercially available short CF containing different sizings on the surface and therefore being designed for different matrix systems of polyurethane (PU), polyamide (PA) and polypropylene (PP) were used. All fibers were identical in length and diameter as well as mechanical properties and differed only in the type of sizing. As matrix polymer for composite specimens, Borealis PP HD120MO was used. Maleic anhydride grafted PP Scona TPPP 8112 FA by Byk was used as coupling agent in PP/CF composites.

2.2. Thermo-oxidative stability tests

In order to assess the thermal stability of the different sizings, the sized CF were, at first, mounted on a standard microscopic glass slide and fixed with conductive silver glue. Prior to annealing, the mounted CF 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 samples, the experiment was repeated using a higher annealing temperature of 240 °C.

2.3. Composite specimen preparation

Test specimens containing 20 wt. % CF in a PP matrix were produced. Compounding was performed in a Brabender 350E mixer using Roller blades operated at 75 rpm. In order to retain long fibers in the compounds, the fibers were added after melting of the polymer was complete. All compounds were then cooled in air and ground using a cutting mill. From the milled compounds, tensile test specimens were produced using a Battenfeld HM 1300/350 injection molding machine. Two series of experiments were performed, with differing processing temperatures (identical for both compounding and injection molding) of 190 and 240 °C.

2.4. Analytical methods

XPS measurements were performed using a Thermofisher Theta Probe XPS system and the obtained spectra were evaluated using the Avantage software package provided by the system manufacturer. The analyzed samples included virgin and heat treated CF (as described above) as well as pull-out

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fibers from fractured PP/CF specimens. A detailed description of the applied method is given elsewhere [11].

Tensile testing was performed in accordance with EN ISO 527.

For determination of fiber length distributions in the composite materials, the matrix was removed by annealing at 500 °C for 1 h in nitrogen atmosphere. The recovered fibers were then suspended in water. Fiber length distributions were determined using a FASEP 3E-ECO system.

3. Results and Discussion

3.1 Surface composition of untreated sizings

Prior to assessing the thermal stability, the initial surface elemental and chemical compositions of the three sizings were investigated by means of XPS. For all three samples, carbon and oxygen were the main surface constituents. Nitrogen was found on PU and PA sizings, but only in small concentrations of approximately 1 at. %. Then, high resolution spectra of the identified elements were recorded, which were subjected to a detailed chemical analysis. Table 1 shows that, contrary to the overall elemental composition, hinting at a similar nature of the PU and the PA sizing, the fitted high resolution spectra of C1s and O1s peaks revealed differences in the chemistry among all three types of sizings. Overall, all three sizings appeared to be composed mainly of polyether based components.

Table 1. Surface elemental composition of the three types of investigated sizings.

Sample	Elemental concentration (at. %)					
	C	O	N	C-C / C-H	C-O	O=C-O
PU	74.9	24.3	0.8	30,5	43,0	1,5
PA	74.9	24.0	1.1	28,7	46,2	0,0
PP	84.6	15.4	0.0	59,2	25,4	0,0

3.2 Thermo-oxidative stability of the sizings

At first, the thermo-oxidative stability of each type of investigated sizing was assessed by analyzing the XPS spectra acquired after each annealing step for both experimental temperatures (190 and 240 °C). A complete overview of the relative concentrations of the identified carbon functional groups together with oxygen and nitrogen is given in Figure 1. It can be seen that the chemical compositions of the sizings experienced thermal degradation, which was more pronounced at the higher temperature. All sizings show decreasing C-O contents and an increase in other oxygen containing functional groups. These functionalities, at least to some degree, result from oxidation of the C-O groups. However, there might be a second reason for the enrichment of different minor functionalities on the heat treated surfaces. Assuming that a sizing comprises of a copolymer or a mixture of different species, then a partial removal of one component due to preferential degradation would lead to an enrichment of the second one. The stated assumption might be found reasonable since it has been demonstrated that polyether based copolymers experience a preferential degradation at the polyether part [12].

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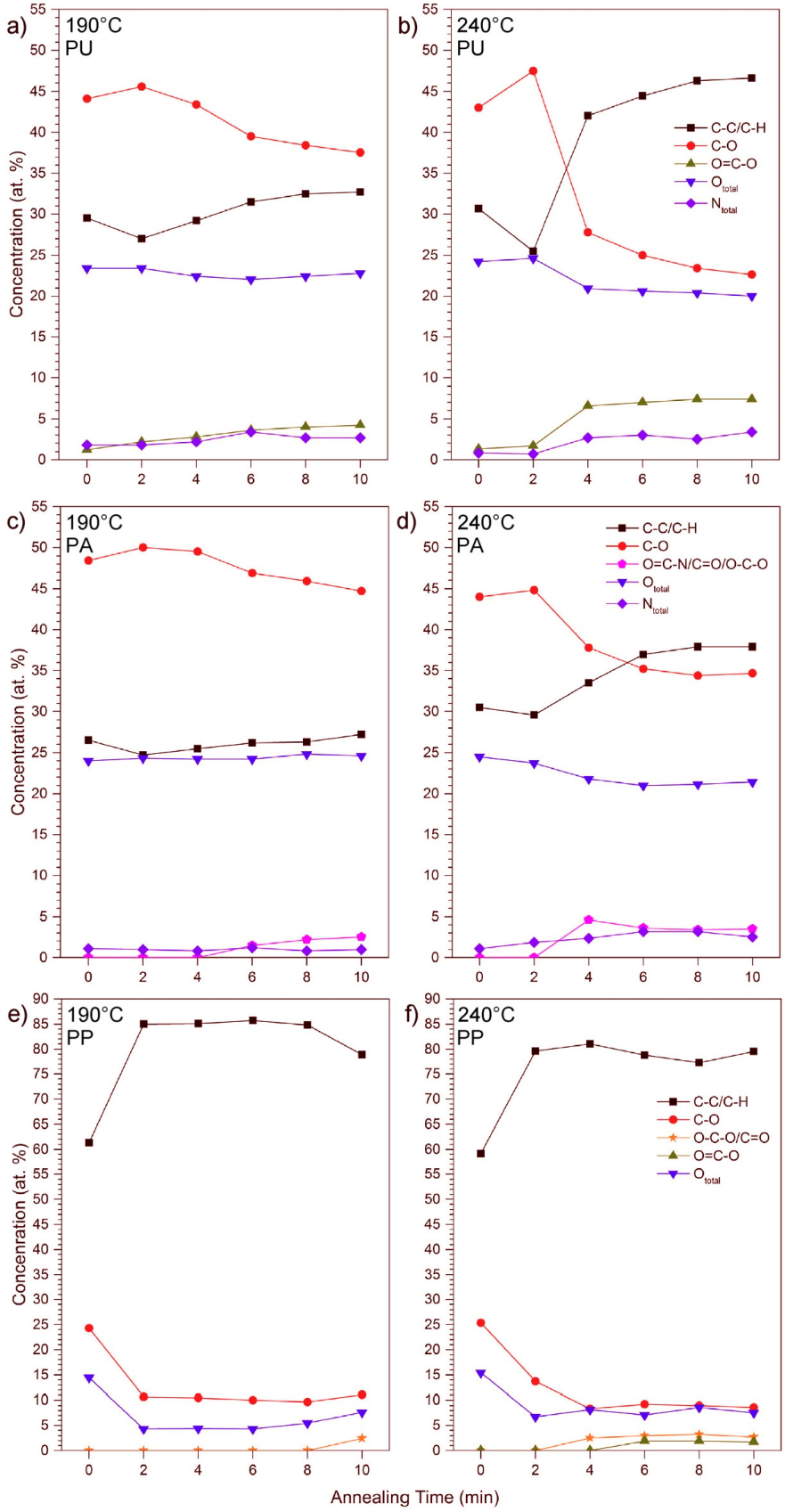

Figure 1. Evolution of relative content of oxygen, nitrogen and different functional groups of carbon on the surface of sized CF during annealing over time.

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3.3 Analysis of single CF pulled out of a PP matrix

Although all of the experiments demonstrated a rapid, more or less pronounced thermo-oxidative degradation for all three types of sizings, an important question arises concerning the factual impact of these findings on the behavior of sized CF in composite materials. In order to elucidate this issue, XPS analysis was performed on fibers pulled out of PP/CF specimen processed at 190 °C. Figure 2 shows a comparison of XPS spectra of pulled out, heat treated and untreated fibers for all three types of sizings. It can be seen that, although the spectra differ somehow, during heat treatment experiments and actual composite processing, similar effects take place at the fiber surfaces.

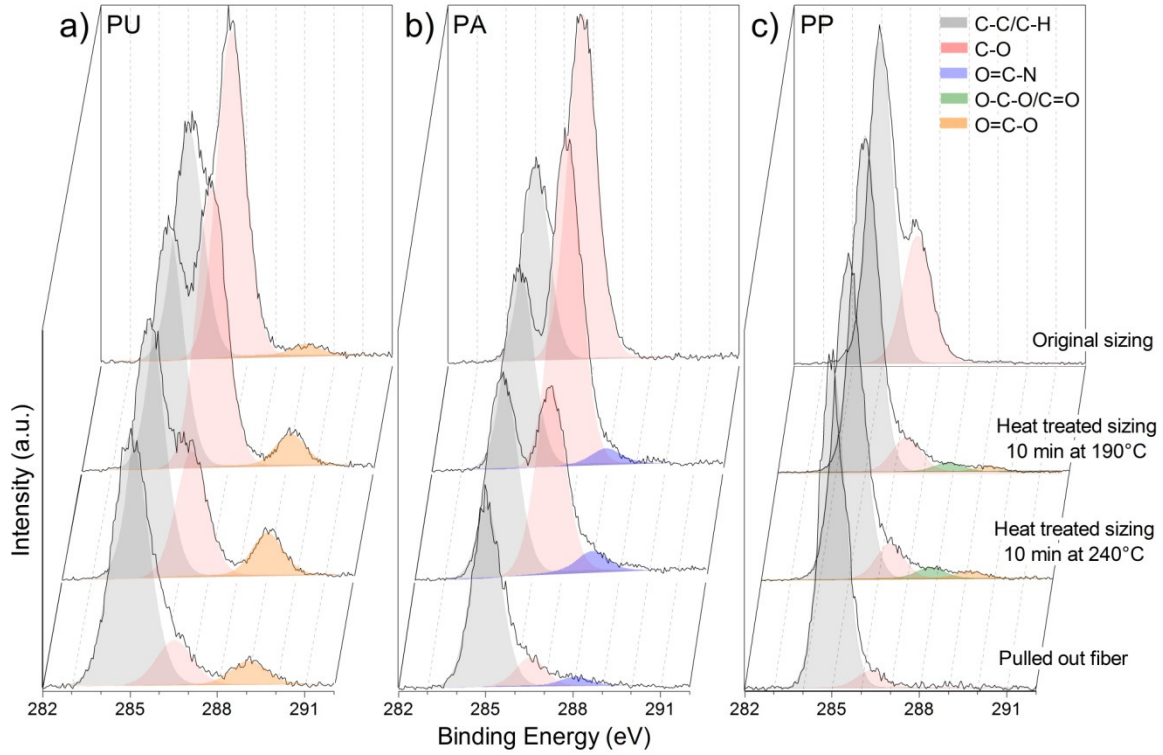

Figure 2. Comparison of the evaluated C1s spectra recorded on the surfaces of pulled out fibers, heat treated and original PU (a), PA (b) and PP (c) sizings.

3.4 Mechanical properties of PP/CF composites

Furthermore, mechanical properties of PP/CF composites in dependence of sizing and processing temperature were determined. First of all, it must be mentioned that, in addition to the changes in the fiber surface properties, significant variations of the fiber length in the composite materials occurred, when the processing temperature was changed. The length average fiber length increased from 327 to 405 µm when the processing temperature was changed from 190 to 240 °C. Therefore, increased mechanical performance might be expected for composites processed at 240 °C. In fact, only tensile modulus values increased with increasing processing temperature, while tensile strength values, which usually display a stronger dependency on the fiber/matrix interaction, show different trends. For composites containing PU sized CF the tensile strength is reduced for both, composites without and with coupling agent, when the processing temperature is increased from 190 to 240 °C, reflecting the strong degradation of the sizing at 240 °C. PP sized CF start to degrade almost immediately at 190 °C, but do not exhibit further degradation at higher temperature. Therefore, the strength of their composites is almost unaffected by the increase of the processing temperature (see Figures 1 and 3).

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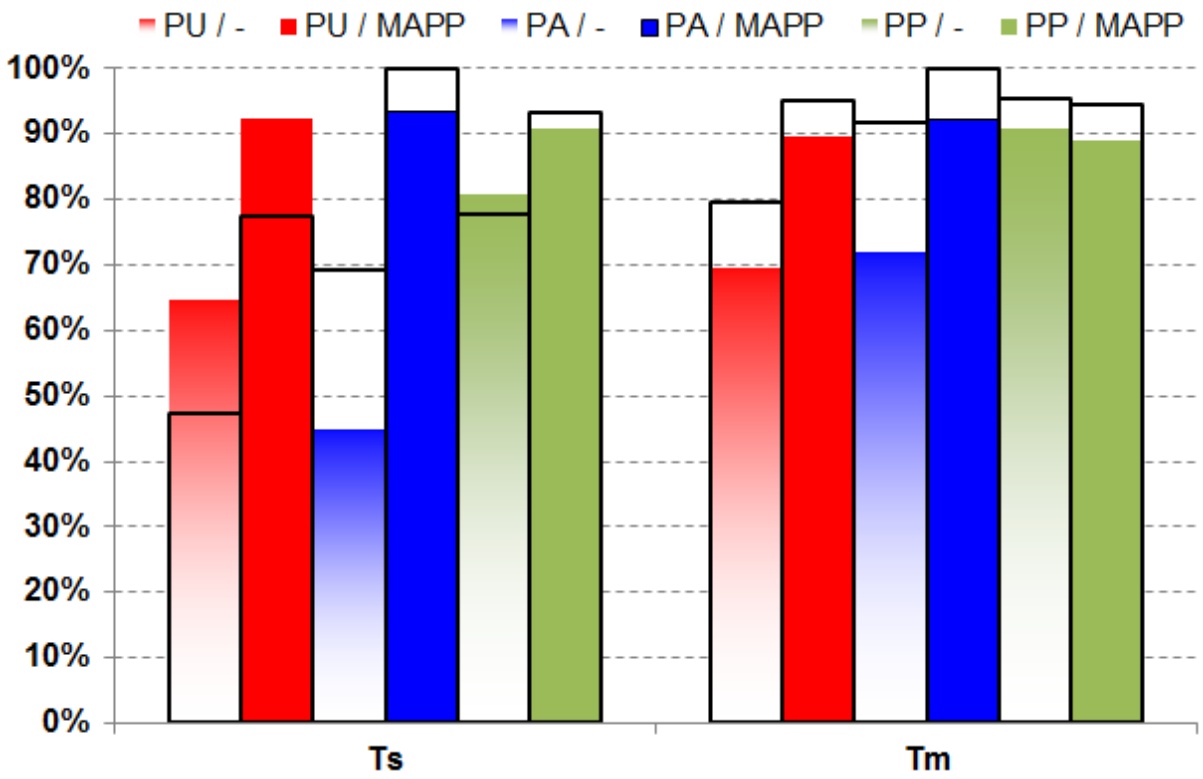

Figure 3. Tensile strength and tensile modulus of PP/CF in dependence of sizing and processing temperature. Colored bars = 190 °C, black frames = 240 °C

4. Conclusions

The thermo-oxidative stability of the surface chemical composition of three types of differently sized CF was investigated by XPS. The obtained experimental data showed for all three types of sizings a clear thermo-oxidative degradation of the surface, which was also found to take place also during PP composite processing, as confirmed by XPS analysis of single fibers pulled out of fractured composite specimens. Furthermore, alike the thermo-oxidative stability of the investigated sizings, the mechanical properties of PP/CF composites also displayed a dependency on the processing temperature, thus, reflecting the changes occurring at the fiber surface and the fiber/matrix interface. However, to fully understand the reactions taking place on the fiber/matrix interface during processing, additional analyses of composite and fiber surface properties is required.

Acknowledgments

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