

RECYCLING OF CARBON FIBERS FROM CARBON FIBER REINFORCED THERMOSET POLYMERS BY USE OF SUB- AND SUPERCRITICAL FLUIDS

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Abstract

The recycling process chain of carbon fiber reinforced polymers (CFRP) recycling consists of the preparation of the recyclables, the fiber-matrix separation, the textile processing of the recycled carbon fibers (rCF) and the re-infiltration of the rCF-semi-finished product. In the present study, the separation step is investigated since it has major impact on the mechanical properties, surface properties and the processability of the rCF as well as on the energy balance of the CF recycling process. The investigated separation process is based on the solvolysis of a thermoset matrix material by two different sub- and supercritical fluids (SCF). Pure water and a water/ethanol-mixture are used as solvents. Treatment time and temperature, which have major impact on the efficiency of the process, were varied. The rCF were examined by Scanning-Electron-Microscopy (SEM) and Atomic-Force-Microscopy (AFM) for matrix residues and possible degradations of the fiber surfaces. The chemical composition of the rCF surfaces is characterized via X-ray-Photoelectron-Spectroscopy (XPS) and compared to an electrochemically oxidized unsized virgin carbon fiber (vCF). The mechanical properties of the rCF were characterized via single-fiber-tensile-tests. The study shows that the rCF properties depend on the solvent composition and treatment conditions. For optimized parameters rCF with properties comparable to vCF were obtained.

1. Introduction

Lightweight construction is a key technology for the sustainable use of resources within the field of passenger and goods transportation (e.g. automotive, aerospace) and renewable energies (e.g. wind turbines). CFRP are suitable for this purpose because they are lightweight and simultaneously show high tenacity and high modulus caused by the reinforcing properties of the CF. High material and processing costs as well as the absence of ecological and economical viable recycling processes hinder the large scale application of CFRP. Regarding the conservation of resources and the currently rising market trend of CFRP applications it is necessary to create a sustainable and closed life cycle for these materials containing a value preserving recycling process. Solvolysis offers a large field of applications due to the possibility to vary the solvents, the temperature, the pressure and the dissolving power by adding different catalysts. This aspect also depicts a possible disadvantage of the recycling via solvolysis which arises from the high selectivity for the type of bond which is breakable by the solvents and their inherent properties [1]. This study presents a chemical recycling process with sub- and supercritical water and a

mixture of water and ethanol. It can be seen that the supercritical solvolysis is a promising method to create an efficient fiber-matrix separation process. Main advantages of supercritical fluids are the low viscosity which contributes to a high mass transport coefficient combined with a high diffusivity. The dissolving power of the SCF is pressure dependent [2]. Additionally, solvolysis with supercritical water is promising because it has economical and ecological advantages over other processes and is easy to handle [3, 4]. Another advantage related to the energy- and cost-efficiency is the possibility to regain the solvent fluids after the separation process and reuse it for subsequent recycling processes [5]. One specific characteristic of supercritical water is its ability to support ionic, polar non-ionic and also free-radical reactions due to the higher ion product at higher temperatures coupled with a lower dielectric constant [6]. The recycling via supercritical water has been studied for several years for example by Okajima et al. [7], Piñero-Hernanz et al. [8] and Liu et al. [9]. Supercritical alcohols for solvolysis are used by Jiang et al. [10] and Piñero-Hernanz [11]. All of these studies offer rCF with mechanical as well as surface properties comparable to vCF. As the SCF process is highly adjustable in terms of selectivity, there might be the option to regain rCF with chemical surface composition even comparable to vCF which have undergone an additional surface activation treatment by an electrochemical oxidation. For that reason, in this study the chemical composition of the rCF surfaces is compared to that of both, desized vCF and unsized electrochemically oxidized vCF.

2. Materials and Methods

2.1. Carbon fiber reinforced composite (CFRP) - material

The samples used for the recycling via sub- and supercritical fluids consist of twelve plies of plain weave fabric layers of Hexcel 48192 C 1270 ST sized carbon fibers [12] infiltrated via the vacuum assisted resin infusion (VARI) process. The thermoset matrix material is a tetra-functional epoxy resin named HexFlow®RTM6 [13]. Starting material consists of the resin and the hardeners 4,4'-methylenebis(2-isopropyl-6-methylaniline) and 4,4'-methylenebis(2,6-diethylaniline). The curing cycle was executed as specified in the data sheet [13] of the matrix material. The CFRP-samples were cut into 20 mm x 50 mm plates limited by the dimensions of the continuous flow-reactor used. Reference specimen for the performed investigations are thermally desized vCF. A temperature treatment of 1100°C for 1 h under a constant nitrogen flow was chosen for removing the sizing agent from the fiber surface. The second reference fiber is an electrochemical oxidized unsized vCF from the standard industrial process of anodic oxidation.

2.2. Experimental setup and conditions

The fiber matrix separation process was executed in a continuous flow-reactor based on the presented principle of Morin et al. [3]. A continuous flow of the fluid is important to prevent the dissolved resin from a re-condensation on the CF after leaving the sub- or supercritical conditions at the end of the separation process. For the presented investigation eight experiments with different process parameters were conducted. The pressure (25 MPa) was the same for all experiments. To gain information about the temperature dependence of the process, three different temperatures (350°C, 375°C and 400°C) were used. The influence of the treatment time was studied using two different treatment durations (60 min and 120 min) at constant temperatures for two different fluids, i.e. water and a mixture of water and ethanol (50% volume mixture).

2.3. Examination of the recycled carbon fiber surface properties

Scanning-Electron-Microscopy was used to check the effectiveness of resin removal. SEM micrographs of the reference vCF and all rCF were taken using a LEO DSM982 GEMINI. The fiber samples were fixed on a twin sided carbon tape and coated with a thin Au film. The SE-Inlens mode and a 1 kV acceleration voltage was selected to obtain the images. For a more detailed investigation of the influence of the solvolysis process on the rCF surfaces AFM measurements were conducted. Roughness measurement on the length scale of the fibrils can be used as an indicator for possible surface contamination and degradation. The AFM measurements (Dimension Icon®(Bruker)) were performed in tapping mode using a measuring tip with a tip radius of about 8 nm. For each investigated fiber sample three different fibers were measured at three different positions. Scan direction for the (5 x 5) μm sized micrographs was perpendicular to fiber axis with a scan rate of 0.5 Hz. For the mathematical evaluation of the fibril-roughness Matlab®R2012b was used to subtract a background from the raw data according to [14]. XPS-analysis shows the influence of the separation process on the surface functionality of the rCF surfaces. The XPS measurements were executed applying monochromatic Al-x-ray radiation (1486.7 eV). The photoelectrons were collected by an Omicron EA125 electron analyzer. To determine the elemental composition of the fiber surface a scan was taken over a binding energy range of 1386.7 eV to 0 eV with an applied pass energy of 50 eV and a step width of 0.5 eV. To identify the functional groups on the fiber surface a high-resolution scan of the C1s spectrum was taken over an energy range of 280 eV - 300 eV. The applied pass energy was 17 eV with a step width of 0.05 eV. For a quantitative analysis of the functional groups on the fiber surface the C1s spectra were fitted using Pseudo-Voigt shaped lines and a Shirley type background [15–17]. We chose the following energy ranges for the respective functional groups: C-C_{aromatic}: 284.4 eV - 285.0 eV; C-C_{aliphatic}: 285.0 eV; C-OR: 286.0 eV - 286.6 eV; C=O: 287.4 eV - 288.1 eV; COOR: 288.6 eV - 289.4 eV; satellite peak ($\pi - \pi^*$).

2.4. Examination of the recycled carbon fiber mechanical properties

The mechanical properties of the rCF were investigated by single-fiber-tensile-tests. For each sample twenty measurements were taken on a *Favimat+* (Textechno). The diameter of each measured fiber was determined via an acoustic stimulated oscillation (ASTM D 1577) of the fibers to get the fiber coarseness known as the titre of the CF. From the titre and the fiber density the diameter of each measured CF was estimated under the assumption of a circular cross section. The tensile tests, starting with a pretension of 1.0 cN/tex, were performed with a constant displacement rate of 0.5 mm/min. To determine the tensile modulus the range of 0.25% - 0.5% elongation was used.

3. Results and Discussion

Figure 1 shows a picture of the rCF after the separation process. The textile structure of the plain weave fabric is maintained during the process which is different to some other recycling techniques resulting in an unordered hairball-like fiber structure (cf.[8, 9, 18]).



Figure 1. Recycled carbon fibers after the fiber-matrix separation process.

3.1. Influence of the experimental conditions on the rCF surface properties

Figure 2 a) - c) shows the SEM pictures of the separated rCF using water for different treatment temperatures. It can be seen that most of the resin could be removed for all solvolysis parameters applied, but even at the highest temperature and for the longest treatment time some resin particles still remain on the rCF surfaces. For the water/ethanol mixture treatment (Figure 2 d) - f)) a similar behavior is observed, although an improvement of the resin removal occurs for all temperatures and treatment times. For both fluids an increased temperature and treatment time results in a more complete removal of matrix material.

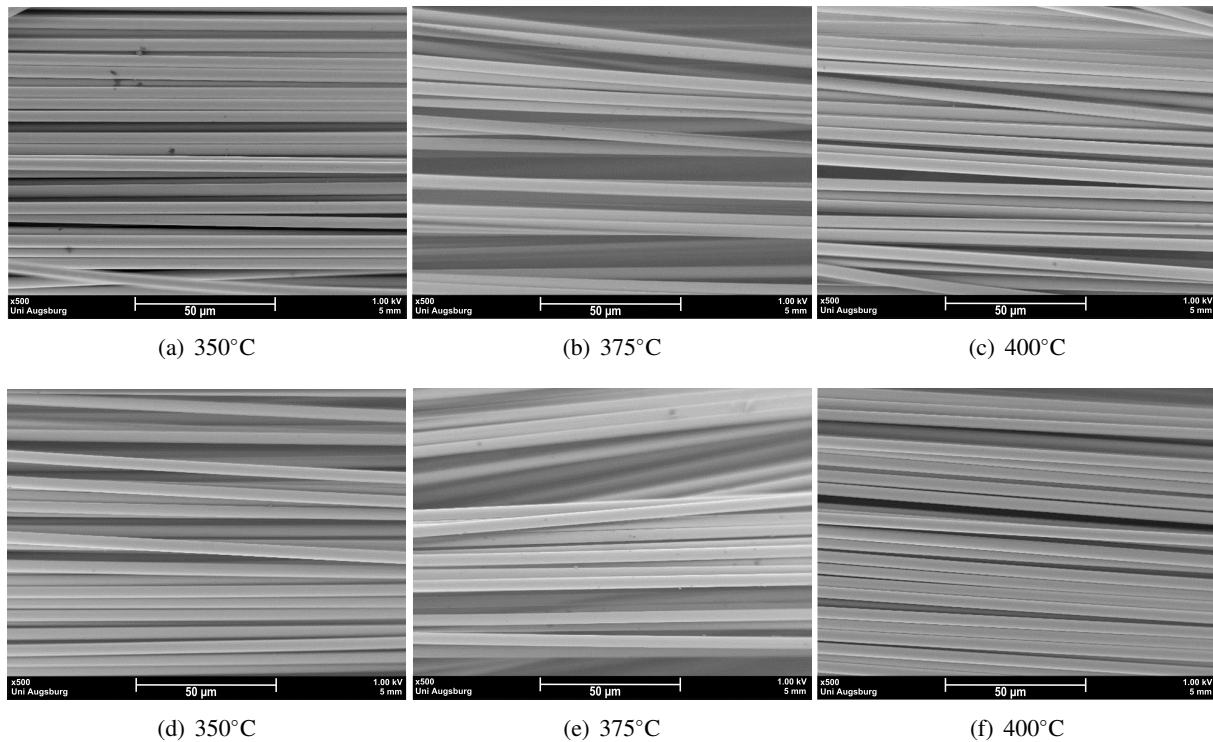


Figure 2. SEM pictures of rCF using water (a - c) and a water/ethanol mixture (d - f) as solvent and different treatment temperatures for 120 min.

Possible surface degradations of the rCF surfaces were examined by AFM measurements. Figure 3 shows the topography of the desized vCF and of the rCF, each separated by the two different fluids at 375°C and 25 MPa for 120 min. The measured values and the corresponding standard deviations for the fibril-roughness of the rCF and desized vCF are depicted in Figure 4. For both media, the fibril-roughness tends to be lower for the rCF than for the desized vCF. With increasing treatment time and treatment temperature the measured fibril-roughness decreases. We attribute the decrease of the fibril-roughness for the rCF compared to the vCF to a smoothing of the plain CF surface, while the decrease of the roughness with increasing treatment time and temperature is attributed to a more complete removal of the matrix. The latter interpretation is in accordance with the SEM images. For the water/ethanol treated carbon fibers (Figure 4 b)) the results for the fibril-roughness are also in good agreement with the SEM images. The effectiveness of the resin removal of the water/ethanol mixture is comparable to this of water at higher temperatures and for long treatment time. Consequently the fiber-matrix separation process by the method described allows for an almost complete removal of the matrix material from the fiber surfaces without major surface degradations.

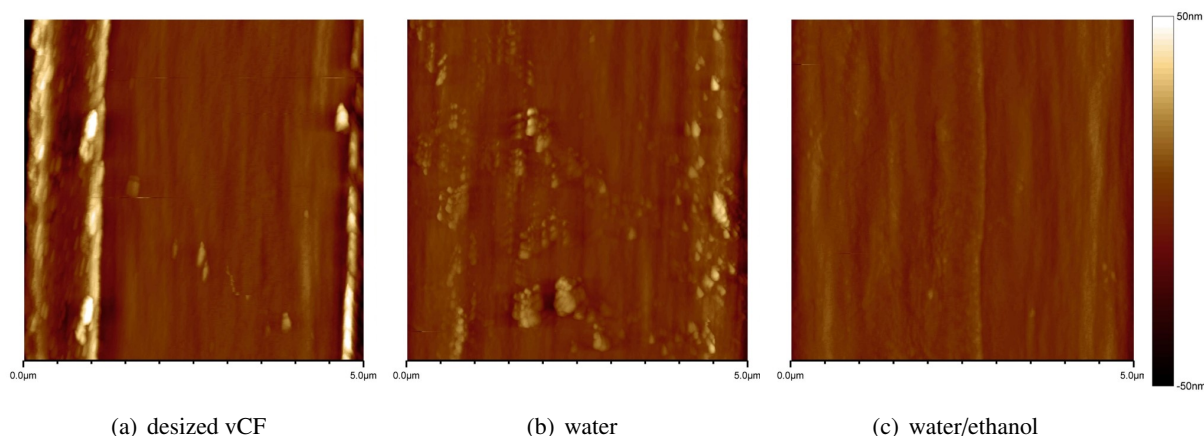


Figure 3. Topography of the desized vCF compared to separated rCF.

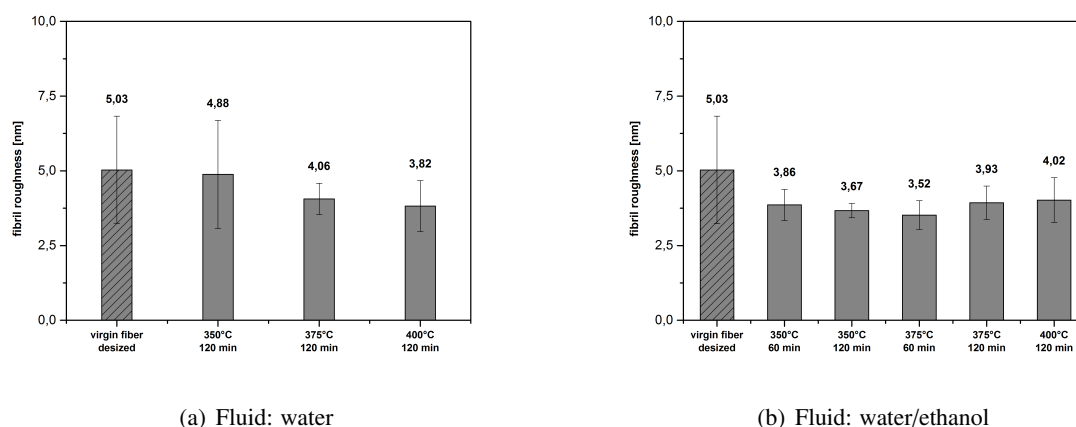


Figure 4. Fibril-roughness of the recycled carbon fibers compared to virgin desized carbon fibers.

3.2. Influence of the experimental conditions on the chemical composition of the rCF surfaces

In Figure 5 the relative concentration of carbon (C), oxygen (O) and nitrogen (N) on the rCF surfaces is compared to that of the desized vCF and an electrochemically oxidized fiber. Carbon and oxygen were detected on all surfaces. Nitrogen was detected on all fiber surfaces except for those treated by water/ethanol at 350°C for 120 min and 375°C for 60 min. The oxygen content for all rCF is lower than for the thermally desized fibers. The rCF show a higher nitrogen concentration than the desized vCF except for two treatment conditions. We attribute the increased nitrogen concentration to resin residues on the rCF. This interpretation is confirmed by the SEM images as well as the AFM-analysis. With regard to further processing of the rCF it is a promising fact that the elemental composition of almost all rCF is remarkably similar to that of electrochemically oxidized fibers. The results of the fitting procedure are depicted in Figure 6. C-C* represents both aromatic and aliphatic C-C bonds. The composition of functional groups of all rCF is similar to those of thermally desized and electrochemically oxidized vCF. The only significant difference is the higher amount of COOR-groups on the electrochemically oxidized fiber surface.

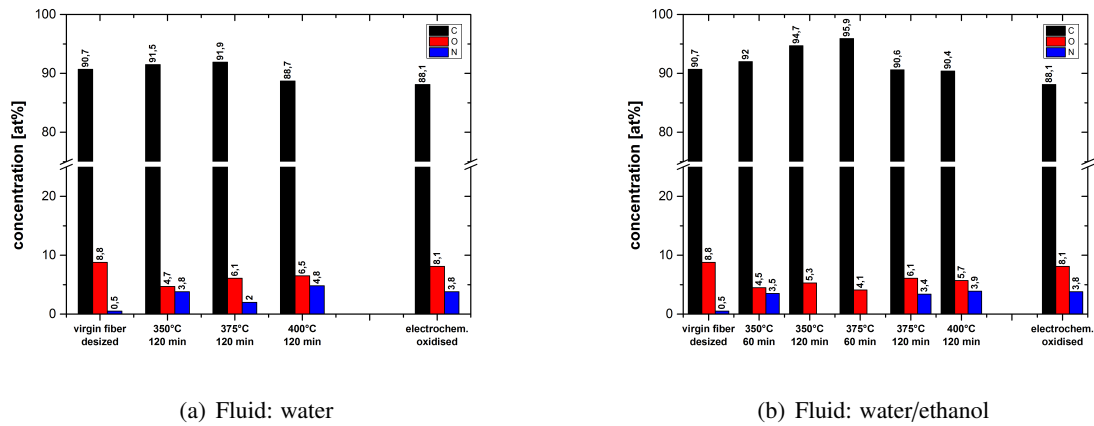


Figure 5. Elemental composition on the rCF-, vCF- and electrochemically oxidized CF-surfaces.

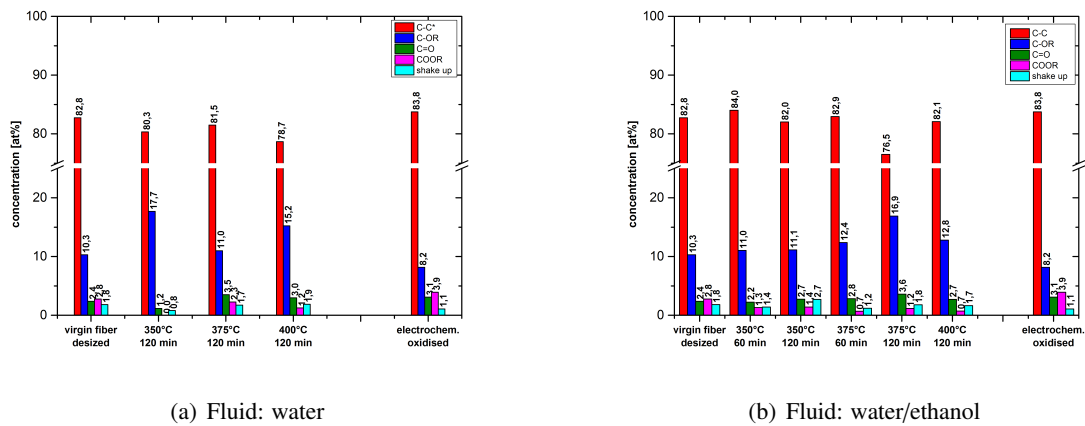


Figure 6. Functional groups on the rCF-, vCF- and electrochemically oxidized CF-surfaces.

3.3. Influence of the experimental conditions on the mechanical properties of the rCF

Another important point for an evaluation of the separation process is its influence on the mechanical properties of the rCF. Table 1 shows the results for the measured diameter, the tensile modulus and the tensile strength of the rCF compared to those of the desized vCF. Within the standard deviation no influence of the separation process on the specific values of the rCF compared to the desized vCF can be identified. Some fluctuation of the tensile strength as function of the treatment parameters is observed. It is not clear whether this is a real effect caused by the different treatment conditions. Therefore, it can be said that the fiber-matrix separation process conducted with the denoted parameters preserves the mechanical properties of the rCF to the greatest possible extent.

4. Conclusion

The presented fiber-matrix separation process provides recycled carbon fiber surfaces nearly free from resin residues and without major surface degradation. Moreover, the chemical composition of the rCF

Table 1. Diameter, Tensile modulus and Tensile strength of the rCF compared to desized vCF.

Experiment	Diameter [μm]		Tensile modulus [GPa]		Tensile strength [GPa]	
	H ₂ O	H ₂ O/C ₂ H ₆ O	H ₂ O	H ₂ O/C ₂ H ₆ O	H ₂ O	H ₂ O/C ₂ H ₆ O
desized vCF	6,59 \pm 0,25		220 \pm 6		3,95 \pm 1,29	
350°C, 60 min	–	6,68 \pm 0,19	–	216 \pm 5	–	4,55 \pm 1,06
350°C, 120 min	6,95 \pm 0,40	6,79 \pm 0,25	206 \pm 10	213 \pm 6	3,14 \pm 0,54	4,31 \pm 1,57
375°C, 60 min	–	6,80 \pm 0,29	–	209 \pm 6	–	4,71 \pm 1,05
375°C, 120 min	6,63 \pm 0,16	7,02 \pm 0,32	215 \pm 4	207 \pm 7	5,16 \pm 1,09	4,66 \pm 1,22
400°C, 120 min	6,77 \pm 0,39	6,73 \pm 0,25	210 \pm 9	209 \pm 5	3,64 \pm 1,02	4,05 \pm 0,88

surface is comparable to that of an electrochemically oxidized carbon fiber. This suggests that a further oxidizing surface treatment after this recycling process might be not necessary. This may contribute, beside the use of water as an inexpensive and easy to handle fluid as solvent, to an economical and ecological advantage of this recycling process. Furthermore, the mechanical properties of the rCF are comparable to these of the vCF and the textile structure can be maintained during the fiber-matrix separation process. This opens the possibility for a more effective reuse of the rCF in CFRP structures of second generation with enhanced mechanical properties.

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