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# Recycling process for carbon fiber reinforced plastics with polyamide 6, polyurethane and epoxy matrix by gentle solvent treatment

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ABSTRACT

Due to the complex composition of carbon fiber reinforced plastics (CFRPs), a complete and useful recovery of such composite material is a real challenge. This paper presents studies on potential solvent-based recycling processes for three CFRP samples comprising polyamide 6 (PA6), polyurethane resin (PUR) and epoxy resin (EP) matrix. Different proprietary CreaSolv® Formulations were applied in laboratory scale and under thermodynamically subcritical conditions in order to dissolve the polymeric matrix and separate the inert carbon fibers. By variation of decisive process parameters, the influence of the temperature-time-load during solvent treatment and solvent recovery was observed carefully. A complete removal of the polymer matrix of all samples was achieved by means of multi-stage solvent extraction without reducing both the length and tensile strength of the recovered carbon fibers. The recovered PA6 matrix polymer revealed no significant decline of its initial average molecular weight. For the dissolved and extracted resin matrices, feedstock recycling was identified as suitable reprocessing. All of the solvent formulations tested were recycled successfully, keeping the initial dissolution properties and, thus, being applicable in a closed loop process design.



## 1. Introduction

Carbon fiber reinforced plastics (CFRPs) are increasingly used for various applications because they offer a great potential for lightweight construction (Witten et al., 2016). Associated therewith, the CFRP amount in circulation is growing steadily, while there exists no established recycling method for such composites at present. The urge to find suitable recycling processes is given, on the one hand, because the carbon fiber production is very energy intensive and requires non-renewable resources, while producing a considerable amount of $CO_2$ at the same time. On the other hand, at present, industry has no good alternative, since CFRPs cause short circuits in waste-to-energy plants (Limburg and Quicker, 2016). Furthermore, due to high organic content of CFRPs, landfilling is not allowed in Germany (German Federal Ministry of Justice and Consumer Protection, 2009).

Given this situation, different fiber-matrix separation methods have been investigated on an experimental scale (Asmatulu et al., 2014; Glöckner, 2015; Oliveux et al., 2015; Pimenta and Pinho, 2011). Basically, five types of recycling processes are potentially applicable: chemical (Hyde et al., 2006; Xu et al., 2013), thermal (Emmerich and Kuppinger, 2014; Lester et al., 2004; Oliveira Nunes et al., 2014; Pickering, 2006; Schneller et al., 2015), mechanical, electrical (Roux et al., 2015; Seifert et al., 2014), and biotechnological (Glöckner, 2015). The latter three are not widespread, whereas chemical and thermal processes are studied by numerous parties with thermal recycling being the prevalent technology applied in industry. Generally, all recycling technologies comprise a first crushing step of the CFRP material for handling purposes (Oliveux et al., 2015).

Biotechnological recycling of CFRPs is performed by the Hohenstein Institute, which uses microorganisms to decompose the polymer matrix (Glöckner, 2015). That has been shown successfully for CFRPs with epoxy matrix.

Electrodynamic fragmentation is another possible technology for the separation of fibers and matrices of CFRPs. This electrical recycling method comprises the application of high voltage pulses to composites placed in a liquid. Due to the short impulse duration, the dielectric strength of the composite is lower than that of the liquid. Therefore, the discharge goes through the composite, in particular, along the phase boundaries between fibers and matrix

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causing them to break apart (Roux et al., 2015; Seifert et al., 2014). Electrodynamic fragmentation requires lower energy expenses compared to thermal processes and allows a better separation than the one achievable by mechanical technologies. However, a clear-cut separation is not possible, the fibers are shortened with every impulse and the matrix fraction is a mix of different polymers if different CFRPs are recycled in the same batch.

CFRP recycling by mechanical means comprises a grinding step and subsequent classification by sieving. The products consist of a fiber-rich and a polymer-rich fraction, comprising high amounts of impurities. Due to this considerable 'downcycling', the reuse opportunities of the recovered materials are limited (Oliveux et al., 2015; Pimenta and Pinho, 2011).

Thermal recycling is based on the pyrolytic decomposition of the polymer matrix, while the fibers remain unharmed at the applied temperatures in inert atmosphere. Pyrolysis can also be carried out by adding steam (Oliveira Nunes et al., 2014). The heat supply can occur conventionally in an oven, via a fluidized bed (Pickering, 2006), microwaves (Emmerich and Kuppinger, 2014; Lester et al., 2004) or induction (Schneller et al., 2015). Typical process temperatures range from 450 to 700 °C, whereby the lower temperatures are adapted for polyester resin matrices, while epoxy resins and some thermoplastics like polyether ether ketone (PEEK) require higher temperatures (Oliveux et al., 2015). Pyrolysis of the matrix generates coke which remains on the fibers. Thus, small amounts of oxygen are allowed or the pyrolyzed composites are submitted to subsequent oxidation processes aiming to remove coke residues for improved bonding to a new matrix. In order to prevent a decrease of the fiber tensile strength, the maximum temperature in oxidative conditions is said to be limited to 550–600 °C depending on the fiber type (Oliveux et al., 2015). Using pyrolytic processes, high tensile strengths of the recycled fibers can be reached. Even in a fluidized bed process, it was possible to gain fibers with a tensile strength only 20% lower than the virgin fiber strength and no change in stiffness. This is despite the fact that the additional fiber abrasion by the bed material generally harms the fibers more than conventional pyrolysis processes (Pickering, 2006). The reduction of oxygen on the fiber surface, which is relevant for the bonding to the matrix, was in an acceptable range. The sizing is removed (Pimenta and Pinho, 2011) and - from a process point of view - the fiber length can remain constant. Drawbacks of pyrolytic processes are the relatively high process temperatures and especially the impossibility of material recycling of the matrix polymer. The latter is decomposed to oil and gas products and can therefore only be used for energy or possibly feedstock recovery. Nevertheless, it can be advantageous to establish a self-sustaining process by using the matrix products as energy source.

Chemical recycling of CFRPs is done by breaking the matrix polymer bondings using a suitable solvent at appropriate temperature and pressure. The process parameters are generally lower than for pyrolytic processes. The chemical processes can be divided into solvolytic processes, which imply the breakage of primary (intramolecular) bonds, and solvent-based processes, whereby only secondary (intermolecular) bonds are dissolved without harming the macromolecules. Usually the processes are carried out at ambient atmosphere, but also nitrogen purging is possible in order to prevent the decomposition of specific solvents.

Solvolysis can be conducted at sub- or supercritical conditions. At supercritical conditions, fluids possess special characteristics. A good diffusivity allows them to penetrate porous solids like vapor would do. The dissolving power is high and the removal of the products is guaranteed due to the increased mass transfer coefficient compared to a liquid (Hyde et al., 2006). Another advantage of supercritical processes is the usage of solvents which are not harmful at normal conditions (Schneller et al., 2016). In research, the most commonly used solvent is water, sometimes in combination with an alcohol, phenol or amine, but also organic solvents like benzyl-alcohols, methanol, ethanol, propanol, acetone or glycols are investigated, usually in alkaline conditions (Oliveux et al., 2015; Pimenta and Pinho, 2011). A drawback of supercritical processes are the high temperatures of more than 400 °C and pressures of more than 600 bar, which cause a high energy consumption and require robust equipment. On the contrary, solvolysis processes at subcritical conditions often need aggressive solvents, like nitric, sulfuric, or acidic acid, which are harmful to people and the environment. For the dissolution of epoxy resin, e.g., nitric acid has been applied for 8 min at 90 °C (Asmatulu et al., 2014), or a mixture of hydrogen peroxide and N,N-dimethylformamid has been used at 90 °C for 30 min (Xu et al., 2013), whereas both substances are corrosive or toxic to reproduction. The solvolytic depolymerization process of polyurethane to its monomers is also reported (Emmerich and Kuppinger, 2014).

The fibers gained from chemical processes, despite supercritical or aggressive conditions, show little loss in mechanical properties compared to virgin fibers. The sizing is removed as in the pyrolytic processes, but after certain processes the fibers exhibited a solvent wetting. If the conditions are not oxidant, the oxygen content of the surface of the recycled fibers is lower than for virgin fibers. Under oxidant conditions the opposite is the case, even though, the fiber tensile strength is considerably lower (Oliveux et al., 2015). From the polymer matrix, valuable products are gained which can be used for the synthesis of the original polymer, other polymers, or as fuel. Which products are generated depends on the polymer as well as the used solvent. Products from supercritical solvolysis of epoxy resin comprise phenol as main degradation product, as well as phenolic compounds like isopropyl phenol, cresol, or if the curing agent was an amine, aniline (Oliveux et al., 2015). Epoxy degradation products, including polymers, oligomers and monomers, have been successfully re-linked with curing agents based on isocyanate to various polymers with different characteristics. Examples include foamed or viscous materials or glues with lap shear strength comparable to virgin epoxy or polyurethane based glues (Polaczek and Stowasser, 2007). Besides the liquid products, also gases can arise (Oliveux et al., 2015).

Apart from the mentioned interesting developments regarding chemical recycling processes, there are still considerable challenges. These challenges can be resolved by the CreaSolv® Process (CreaSolv® is a registered trademark of CreaCycle GmbH), which has been developed and patented by the Fraunhofer Institute for Process Engineering and Packaging IVV (Fig. 1). The process uses proprietary CreaSolv® Formulations with the lowest risk potential for users and environment, ideally not to be classified according to Globally Harmonised System (GHS) criteria. These selective solvent preparations extract the target polymers and potential other valuable raw-materials from heterogeneous waste input streams at thermodynamic subcritical conditions. The polymer solution is separated from undissolved components or harmful and/or banned pollutants, such as plasticizers or halogenic flame retardants (Schlummer et al., 2017). At the end of the process, the solvents are recovered in order to ensure closed-loop circulation and to keep the process economically viable. The recycled polymer (product) is solvent free, meets properties of virgin material, and is suitable as a substitute material in production processes (Arends et al., 2012; Schlummer et al., 2006; Marwede et al., 2013; Mäurer and Schlummer, 2004). The CreaSolv® Process is also successfully used to recycle composite materials like metallized plastics or metal parts which are overmolded by a thermoplastic polymer. The plastic matrix is dissolved while the metal stays inert. After separation, the polymer solution is dried, the solvent is recovered and both materials (polymer and metal) are ready for reuse (Knappich et al., 2017; Knappich et al., 2018).

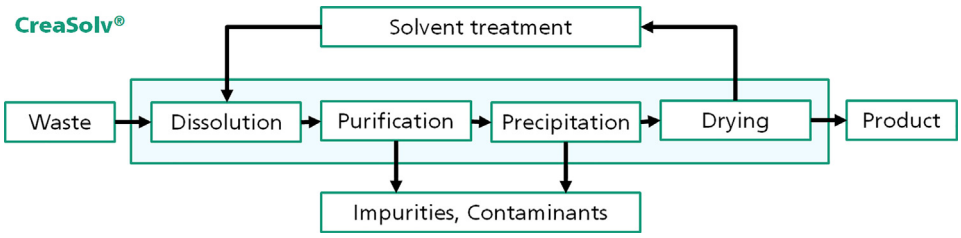


**Fig. 1.** Schematic presentation of the CreaSolv® process.

The presented work reports about finding suitable solvent preparations and process parameters for subcritical solvent-based recycling of CFRPs with PA6, PUR resin and EP resin matrices. The choice of those matrix materials was based on their relevance. Resins make up more than two thirds of all polymer matrix materials (Witten et al., 2016), whereby about 90% of the resins used for advanced composites are epoxy resins (Morgan, 2005). On the contrary, thermoplastic matrix materials are gaining increasing importance, due to several advantageous properties. The material is formable and weldable and does not need to be cured which allows shorter process times for production (Witten et al., 2016). To that end, the CreaSolv® Formulations were applied to dissolve the matrix material. For the assessment of the different process configurations, the process effectivity (fraction of matrix material removed in a specific process), the tensile strength of the recycled fibers as well as the average molecular weight of the recycled PA6 have been determined. Furthermore, the recyclability of the applied solvents has been investigated in laboratory scale.

## 2. Materials and methods

### 2.1. CFRP samples

Three different CFRPs have been investigated, one with thermoplastic (PA6) matrix and two with thermoset (PUR and EP) matrices. The specific carbon fiber type and matrix polymer used for each sample, as well as the respective manufacturing methods are listed in Table 1. Geometrically, the samples were unidirectionally reinforced plates with a thickness of 2.5 mm which implied 14 tape layers for CF-PA6, 110 rovings (50 k) for CF-PUR and 7 fiber layers for CF-EP. The plates have been cut to pieces of approximately $80 \times 15\ mm^2$, with the longer side parallel to the fiber direction, used as test specimen.

### 2.2. Applied solvents

As stated above, all nine of the solvent preparations tested were developed by CreaCycle GmbH, Grevenbroich. The selection of these CreaSolv® Formulations was based on solubility parameters according to Hansen (Hansen, 2007). Other factors included commercial availability of the ingredients, risk to users and environment, and the biological degradability. The exact chemical compositions of the formulations are proprietary and so they are named herein using the terms "CreaSolv® CFRP1", "CreaSolv® CFRP2", ..., "CreaSolv® CFRP9". The mixtures 1–9 were composed of different types of solvents in order to examine their individual functionality and effectiveness. Table 2 shows the properties of the applied CreaSolv® Formulations.

Additionally, sample preparation for analytical issues was done using hexafluoroisopropanol (HFIP), potassium trifluoroacetic acid and acetone, all of them purchased from Merck KgaA, Darmstadt.

### 2.3. Experimental setup

#### 2.3.1. Identification of suitable solvents

In order to investigate the dissolving capacity for the CFRP matrices, all of the named CreaSolv® Formulations have been applied to pieces of 1 g of each CFRP or respective mere matrix polymer. The mixture is heated up stepwise but not higher than the solvent's boiling temperature at ambient pressure until reaching a complete and homogenous solution. By variation of the temperature, the dissolution behavior and time were observed in order to identify the CreaSolv® Formulation with the best performance.

#### 2.3.2. Determination of the optimum process parameters

Based on the preliminary results from chapter 2.3.1, the dissolution behavior of the CFRP samples was examined more closely. The experiments were carried out on a heating plate with a beaker containing the solvent and a perforated stainless-steel basket. Within this basket the test specimens were fixed using a steel wire in order to allow stirring beneath without contacting or moving the samples. The matrix polymer concentration in the solvent was kept approximately constant with an amount of 6 equally sized CFRP pieces having an average total weight of 18 g and an average amount of solvent of 200 g in every process. The experiments were

**Table 2**
Overview of the applied CreaSolv® Formulations.

| Solvent | Properties |
|---|---|
| CreaSolv® CFRP1 | Polar protic |
| CreaSolv® CFRP2 | Polar protic |
| CreaSolv® CFRP3 | Non-polar |
| CreaSolv® CFRP4 | Non-polar aprotic |
| CreaSolv® CFRP5 | Polar aprotic |
| CreaSolv® CFRP6 | Polar aprotic |
| CreaSolv® CFRP7 | Polar protic |
| CreaSolv® CFRP8 | Polar protic |
| CreaSolv® CFRP9 | Polar aprotic |

**Table 1**
Sample materials and manufacturing.

| Sample | Fibers | Matrix | Manufacturing process |
|---|---|---|---|
| CF-EP | SGL Kümpers HPT®-320-C0 | Ebalta AH 140 resin/TC 90-1 hardener | Vacuum assisted resin infusion (VARI) |
| CF-PUR | Zoltek Panex® 35 | Huntsman RIMLINE® SK 97,007 polyol/SUPRASEC® 9706 isocyanate | Pultrusion |
| CF-PA6 | Celanese | Celstran® CFT-TP PA6-CF60 | Automated tape laying (ATL) |

done at three appropriate temperatures for each polymer-solvent system with 3 h duration. Subsequently, a dissolution step with 1.5 h duration was applied to the samples in order to remove the polymer matrix completely from the fibers. Based on the dry matter values of the resulting polymer solutions, the amount of removed polymer matrix in each step was calculated. Every solution of the performed test series for the PA6 matrix was split into three equal parts. One part was not further treated in order to determine the influence of the sole dissolution process on the polymer. The other two parts were dried independently by means of a vacuum drying oven at a pressure of 40 mbar and a temperature of 140 and 160 °C, respectively, for 4 h each. This is in order to investigate the impact of the drying process on the polymer properties and residual solvent content. A maximum temperature of 160 °C was selected at which long term resistance is guaranteed according to the polymer's datasheet. Based on the results from the described experiments regarding process effectivity, matrix and fiber properties, we defined the process parameters for an additional series of 4 dissolution process steps at a larger scale. Therefore, 1400 g solvent have been applied to 135 g of CF-PA6, using a double-walled glass vessel for heating. The process durations were 1.5 h for the first dissolution and 0.5 h for the subsequent dissolutions.

For the CFRPs with thermoset matrices, for each sample two temperatures have been investigated. The CFRP concentration was kept constant for all materials. Same as for CF-PA6, we performed a first extraction with appropriate duration and up to four subsequent dissolution steps with 0.5 h duration each. The dry matter values of the resin solutions from every solvent extraction have been measured in order to determine the effectivity of the regarded dissolution step. Since it cannot be ruled out that the solvents chemically interact with the resin matrices, the dry matter of these samples potentially does not only contain chains derived from the polymer, but may also contain chain parts from the solvent linked to the dissolved polymer parts. Apart from the mass balance regarding yield and solvent recovery, the resin products have not been further investigated. The recycled (polymer-free) fibers of all samples (PA6, PUR, EP) have been dried in a vacuum oven prior to be analyzed.

#### 2.3.3. Solvent recovery

In order to investigate the solvent recovery performance of the three tested solvent-polymer systems, the extracted polymer solutions have been dried in a vacuum drying oven as described above. The solutions of CF-PUR and CF-EP have been evaporated and distilled at ambient pressure. The recovered solvents have been mass balanced and qualitatively tested regarding their dissolution properties, applying them again to CFRP sample material.

### 2.4. Analytical methods

The dry matter values of the process solutions have been measured by applying the gravimetrical system Sartorius Moisture Analyzer MA35. Based on those values, the process effectivity of the single extraction steps has been calculated.

For evaluating the quality of the recovered PA6, a gel permeation chromatography according to (Sandler et al., 1998) has been performed in order to get the weight average molecular weight and the polydispersity of the samples. As sample preparation, from the solutions which had not undergone a previous drying process, the solvent was extracted by use of acetone. For the dried samples, no additional preparation was required. Sample conditioning consisted in dissolving the polymer in HFIP with 0.02 mol/L potassium trifluoroacetic acid at a concentration of 2500 ppm and filtering the resulting solution with a 0.20 μm filter. The column type was PPS PFG Linear XL, 7μ, 300 × 8 mm.

The recycled fibers have been subjected to single fiber tensile test applying FAVIMAT+ from Textechno according to ASTM D3822. For every sample, 20 single fibers have been tested. A clamping length of 25 mm was applied; the test speed was 0.5 mm/min. The fiber diameter was determined by the testing device over the vibration method according to ASTM D1577, gaining the linear density by detection of the resonance frequency.

To optically evaluate the matrix removal and fiber surface, SEM images of the recycled fibers have been taken at a voltage between 3 and 5 kV using ISI ABT Scanning Electron Microscope ABT-550.

## 3. Results and discussion

### 3.1. Process development and conditions

In order to obtain the best combination of solvent formulation, polymer material, dissolution kinetics and dissolution effectivity, we evaluated several test series as described in chapter 2.3.2 and presented in Table 3.

For CF-PA6 we only could identify two CreaSolv® Formulations as suitable solvents (CreaSolv® CFRP1 and CreaSolv® CFRP2). Regarding the process characteristics, the dissolution times for the samples with a mass of 1 g were considered. Fig. 2 shows the dependance of the dissolution time on the applied temperature. We selected 140, 160 and 180 °C as dissolution temperatures for both PA6-solvent systems. For the CFRPs with thermoset matrices, in each case only one suitable solvent could be identified during the preliminary trials: CreaSolv® CFRP2 for CF-PU and CreaSolv® CFRP7 for CF-EP. For each sample three temperatures have been investigated. Lower temperatures (180 °C for CF-PUR and 240 °C for CF-EP) turned out to require disproportionately long process duration (>4 h). For all polymer-solvent-systems the dissolution time decreased with higher temperature. This is due to the fact that higher temperatures in turn lead to increased diffusion and permeation rates as well as larger solubility parameter spheres (Hansen, 2007). Comparing the two solvent formulations for the PA6 material, CreaSolv® CFRP2 shows a higher performance than CreaSolv® CFRP1 in terms of dissolution kinetics.

Considering the effectivity (removed matrix material related to the total initial amount of matrix material) of the single dissolution step, we compared different temperatures but with constant process duration of 3 h. For CF-PA6, the effectivity of the two candidate solvent formulations increased with temperature. This increase was higher from 140 to 160 °C than from 160 to 180 °C.

**Table 3**
Overview of the performed test series.

| | CF-PA6/ CreaSolv® CFRP1 | | | CF-PA6/ CreaSolv® CFRP2 | | | | CF-PUR/ CreaSolv® CFRP2 | | CF-EP/ CreaSolv®CFRP7 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 140 °C | 160 °C | 180 °C | 140 °C | 160 °C | 160 °C[a] | 180 °C | 190 °C | 200 °C | 260 °C | 280 °C |
| 1st extraction | 3.0 h | 3.0 h | 3.0 h | 3.0 h | 3.0 h | 1.5 h[a] | 3.0 h | 1.0 h | 1.0 h | 2.0 h | 2.0 h |
| 2nd extraction | 1.5 h | 1.5 h | 1.5 h | 1.5 h | 1.5 h | 0.5 h[a] | 1.5 h | 0.5 h | 0.5 h | 0.5 h | 0.5 h |
| 3rd extraction | – | – | – | – | – | 0.5 h[a] | – | 0.5 h | 0.5 h | 0.5 h | 0.5 h |
| 4th extraction | – | – | – | – | – | 0.5 h[a] | – | 0.5 h | 0.5 h | 0.5 h | 0.5 h |

[a] Test series performed at increased scale.

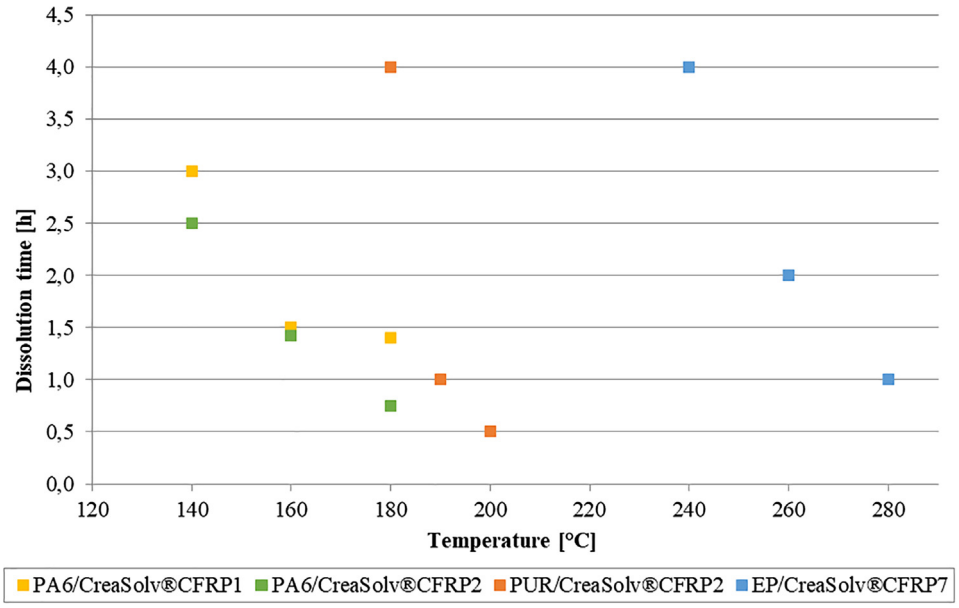


**Fig. 2.** Dissolution time of all investigated polymer-solvent-systems at different temperatures.

Thus, the temperature of 160 °C has been chosen for the larger-scale process series with CF-PA6. We also found that CreaSolv® CFRP2 presented higher numbers for the effectivity than for CreaSolv® CFRP1. At 140 °C this difference in dissolving performance was slight but the gap widened at 160 and 180 °C. In the latter case, the ratio of the effectivity to the dissolution time was 95 wt% to 45 min (CreaSolv® CFRP2) versus 70 wt% to 84 min (CreaSolv® CFRP1). Therefore, we decided to exclude CreaSolv® CFRP1 and to focus only on CreaSolv® CFRP2 as solvent for PA6 in subsequent test series for the reinforced polymer material. For CF-PUR, the same trend of an increase of the effectivity with the process temperature for constant process duration of 60 min has been observed. We chose 200 °C as suitable dissolution temperature for this matrix material. For CF-EP, the share of removed matrix material is similar at 260 and 280 °C by halving the process duration.

Fig. 3 shows the effectivity of the subsequent solvent extractions for one selected test series for each of the three CFRP systems. The target was to remove the matrix material completely within three extraction stages and with lowest possible temperature-time-load. According to the definition of the effectivity the highest amount of matrix material was always removed in the first step.

Based on the process series with CF-PA6 at increased scale, the average concentration of matrix polymer in the solvent has been calculated to 2.6 wt%. Since the saturation point of the solvent was by far not reached, a possible slight concentration variation over the single processes is not likely to have had an influence on the results. The fairly poor polymer concentration which was reached in the presented test series indicates that for CFRP dissolution processes a larger amount of solvent is needed than for polymer dissolution processes focusing on other input materials (typical values are between 5 and 30 wt%) (Knappich et al., 2017; Papaspyrides and Kartalis, 2000; Poulakis et al., 1997). The fibers of the investigated CF-PA6 pieces had a length of 80 mm which was not shortened by the recycling processes. According to (Thomason and Vlug, 1996, 1997; Thomason et al., 1996) glass fiber reinforced polypropylene with 10 mm fiber pieces show characteristics similar to those of composites made with endless fibers.

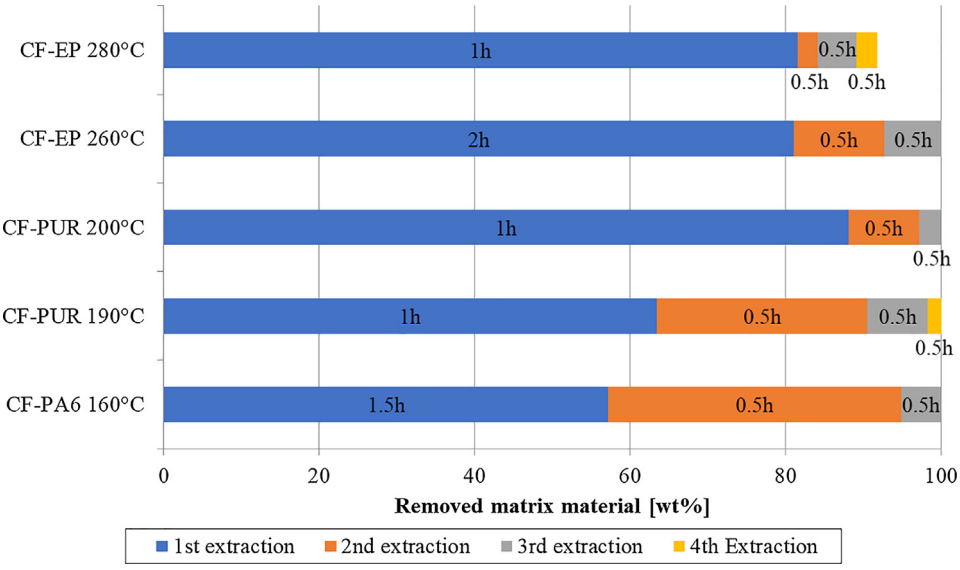


**Fig. 3.** Effectivity of the single steps of a series of 4 subsequent solvent extractions at a selected temperature for each of the investigated materials.

Thus, a further fragmentation of the CFRP pieces might be suitable, which would simplify the wetting of the matrix resulting in a lower overall solvent demand.

### 3.2. Quality of the recovered solvents, fibers and polymers

All of the used solvents were successfully recovered in large part for every material. For both CF-PA6/CreaSolv® CFRP1 and CF-PUR/CreaSolv® CFRP2, it was possible to recover 99.8 and 96.6 wt%, respectively, of the applied solvent. For the CF-EP/CreaSolv® CFRP7 system, 93.9 wt% of the solvent could be recovered. All of the recovered solvents were still in possession of their dissolution properties.

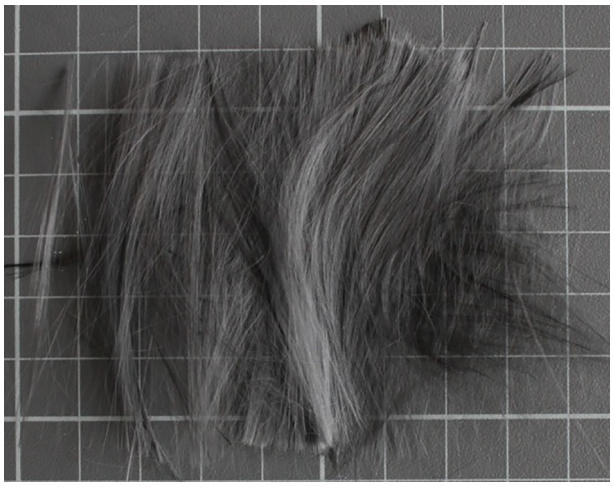

**Fig. 4.** Example for the recovered fibers after the 4th extraction of the process series at 240 °C with CFRP-PUR and CreaSolv® CFRP2 (the displayed squares have a size of 10 mm).

Fig. 4 shows the recovered fibers after four solvent extraction steps exemplary for CF-PUR. The fiber surface in detail of the CF-PA6 material after different stages of a process series is shown in the SEM images from Fig. 5. Both the optical impression and high magnification images show that the fiber surface is completely clean from matrix material after repeated extraction.

The tensile strength of the recycled fibers from process series in which it was possible to completely remove the matrix material, is shown as a box plot in Fig. 6. Only for the fibers recovered from CF-PA6 the tensile strength seems to decrease in comparison to the virgin fiber strength. Besides the rather high standard deviation, it should be noted, that the value for the virgin fiber strength in this case is a manufacturer specification. Since the starting material for the ATL manufacturing process are fiber-matrix tapes, no single virgin fiber sample was available for testing. Therefore, the value for the tensile strength of the CF-PA6 virgin fibers might be lower when determined with the same test method as used for the other samples. Another indication for the fact that the process does not harm the fibers is that there was no significant change in fiber strength when varying the number of solvent extraction steps, process duration, or dissolution temperature. For both thermosetting resin samples, the original virgin fibers were available for measuring their initial tensile strength values with the same test method. A comparison shows, that the values for the tensile strength of the CF-PUR fibers consistently increased during the dissolution processes. The numbers reached from 104% of the virgin fiber strength after the 1st dissolution at 200 °C to 118% after the 4th dissolution and for the dissolution series at 190 °C from 98%

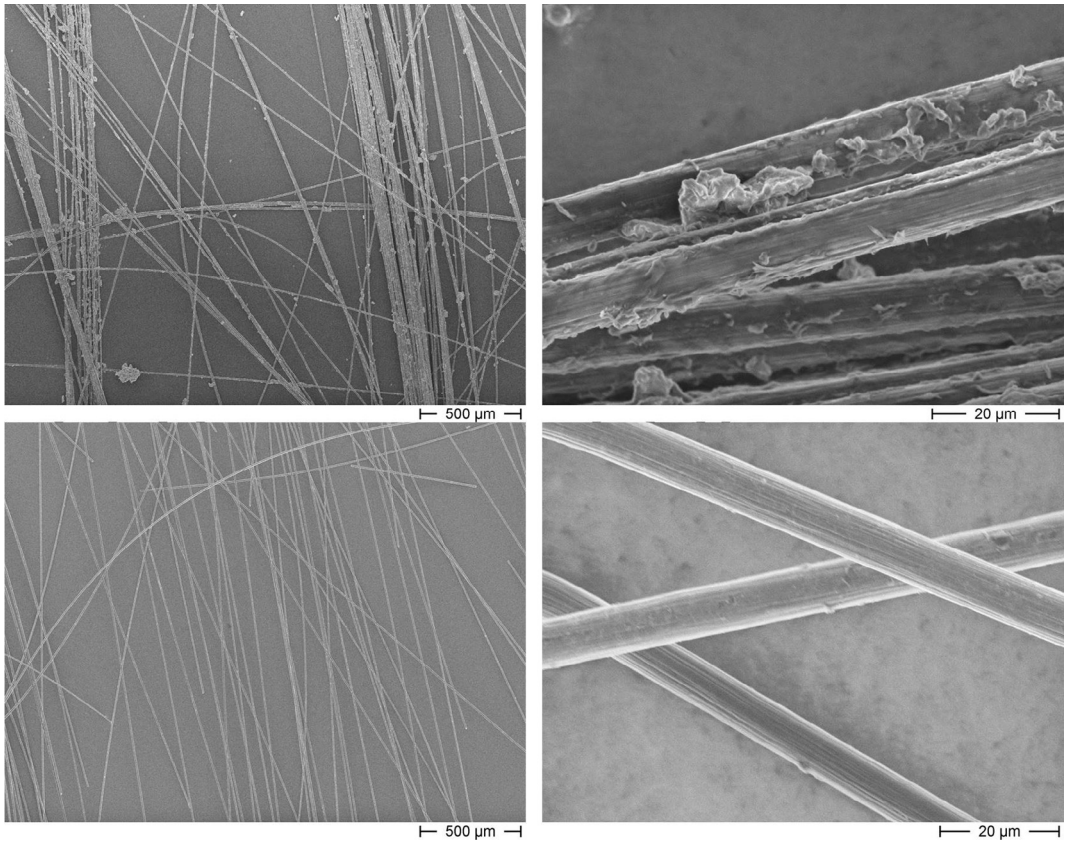


**Fig. 5.** SEM images of the carbon fibers from CF-PA6 after the 1st (top) and 2nd solvent extraction (bottom) of the small-scale recycling process using CreaSolv® CFRP2 at 160 °C.

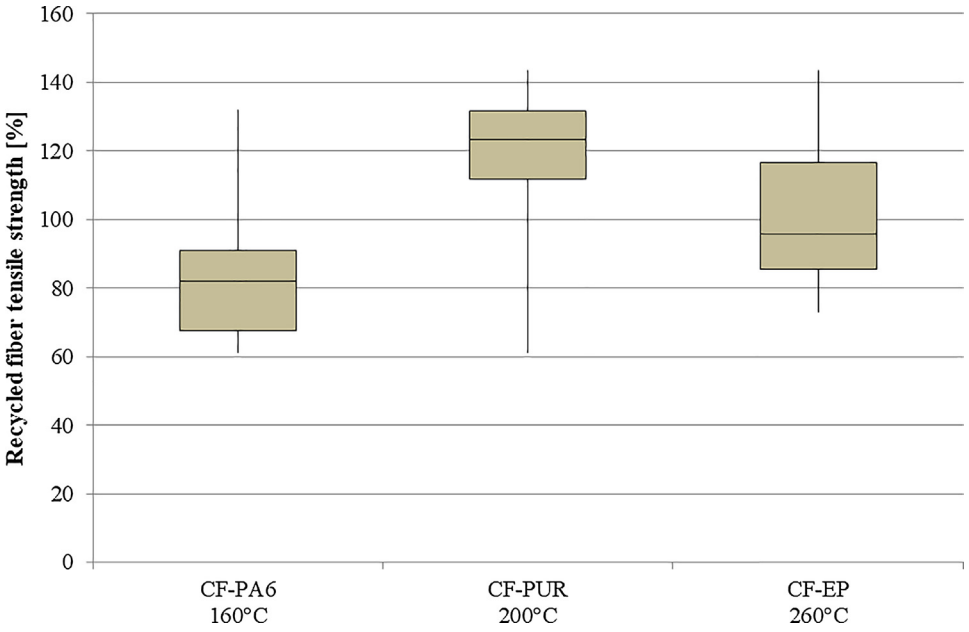


**Fig. 6.** Box plot of the tensile strength of recovered fiber samples from one selected process series comprising four solvent extraction steps for each CFRP (in total 3 h for CFRP-PA6, 2.5h for CFRP-PUR and 3.5h for CFRP-EP). 100% corresponds to the virgin fiber strength.

after the 1st to 123% after the 4th solvent extraction. The same trend was observed for the maximum absolute force measured in the tensile test. The evaluation of the recovered fibers from CF-EP material reveals no change in fiber tensile strength as well. Again, since the 100 percent mark is in between of the whiskers of the box plot for all of the three samples, it can be assumed that none of the recovered fibers are harmed by thermal or mechanical stress during the developed recycling process. In addition, due to the moderate temperature-time-load, all of the recovered fibers did not undergo any change in terms of tensile modulus (data not shown).

The recovered matrix polymer from CF-PA6 showed an average molecular weight less than 10% below the initial value for the two lower process temperatures applying CreaSolv® CFRP1 and slightly lower for CreaSolv® CFRP2 (Fig. 7). A PA6 sample taken from the hot press used for CF-PA6 sample manufacturing served as reference, since the manufacturing process itself can already potentially harm the polymer. Additionally, it was found that when increasing the process duration from 1.5 h to 3 h at a temperature of 160 °C, the average molecular weight decreased only from 95 to 90% of the initial value for CreaSolv® CFRP1 or from 87 to 84% for CreaSolv® CFRP2, respectively. For reasons of clarity, Fig. 7 only shows the results from the 3h-trials. This implies that the duration of the elevated temperature exposure is not the decisive parameter for polymer degradation but rather the process temperature level. Drying

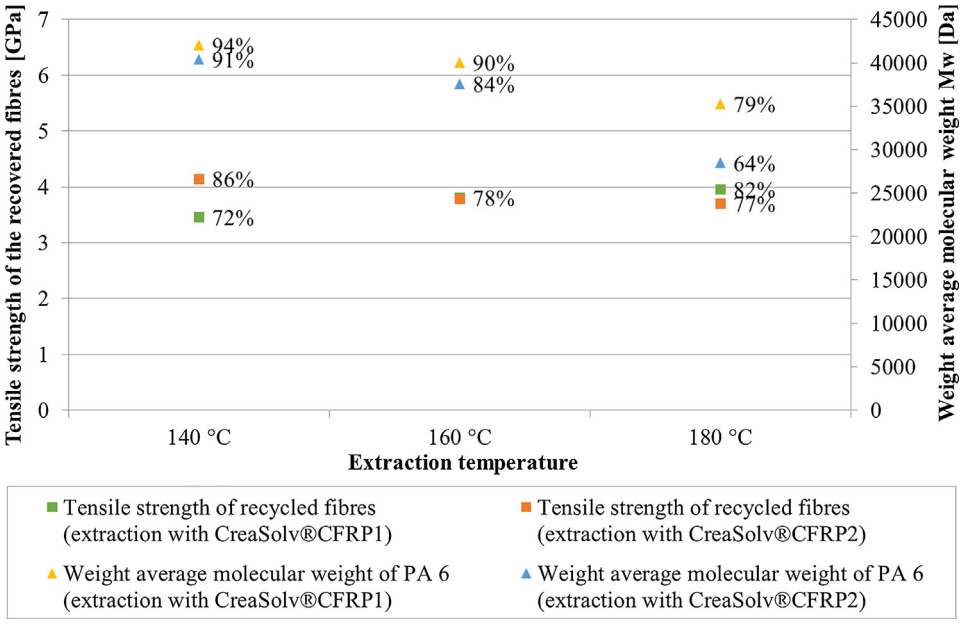


**Fig. 7.** Tensile strength of the carbon fibers and weight average molecular weight of PA6 after dissolution processes with a duration of 3 h at different temperatures for both applied CreaSolv® Formulations. The percent values present the comparison to the virgin fiber strength and weight average molecular weight, respectively, before the extraction.

at 140 as well as 160 °C did not lead to a decrease of the average molecular weight. Depending on the used solvent, the PA6 seemed to dry either as powder when using CreaSolv® CFRP1 or as melt with CreaSolv® CFRP2. From the process engineering point of view, it is possible to handle both types of intermediate properly but a liquid/pumpable material basically has the advantage of a better heat transfer, resulting in a higher efficiency of the drying process. Furthermore, a polymer melt is easier to be transported to the downstream residual degassing extruder.

## 4. Conclusion

Summing up, for all investigated CFRP materials it was possible to remove the polymeric matrix material from the fibers completely without or with only slight decrease in fiber's tensile strength by treatment with proprietary CreaSolv® Formulations. In none of the performed test series, the length of the recovered fibers was affected. The polymer matrix materials have been recovered in two different conditions. The polymer chains of the thermoplastic PA6 remain largely intact revealing a decrease of the average molecular weight of less than 20% for the configuration that allowed a complete removal of the matrix material (160 °C for 1.5 + 0.5 + 0.5 h). For both thermosets, PUR and EP, dissolved solvolysis products were obtained. All of the applied CreaSolv® Formulations were recovered successfully by means of vacuum distillation to more than 96% while maintaining the initial dissolving properties. Based on our experiences, a small-technical scale application (100–200 L) of the CreaSolv® Process usually achieves a solvent recovery of up to 99%. It can be assumed that the recovery rate will further increase with the scale of the process. To conclude, all of tested CFRP-samples could be successfully recovered with high product quality and in a form suitable for reuse.

Nevertheless, a deeper investigation of the recovered products and the influencing parameters might be necessary in order to optimize the presented recycling process. The content of a further study could comprise the examination of the state of the fiber surface in more detail regarding the sizing, presence of chemical groups and oxygen content which are relevant for successful bonding to a new matrix. Also, the drying behavior of the PA6 should be investigated more in detail, as well as the question whether the resins and respective solvents are modified by the dissolution processes or not. The development of an improved flow configuration in larger scale setup for proper matrix wetting might be useful. Therefore, a counter-flow arrangement for enhancing the process efficiency seems to be suitable since for all materials the largest matrix share has been removed in the first process stage of each test series.

In a further study, the solvent-based recycling processes described herein have been compared to the most common CFRP recycling method, the pyrolytic recycling, considering the same materials as used for the present work. The outcomes will be published separately, namely a comparison between the products from both process types, as well as the process characteristics including temperature level, process duration, and flow configuration.

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## Conflicts of interest

The authors declare no conflict of interest.

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