

Requirements for the chemical recycling of fibre reinforced polymers

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The increasing use of fiber reinforced polymers (FRP) in lightweight construction is presenting new fundamental challenges for the recycling industry. In Germany alone, approx. 225 kt of glass fibre reinforced plastic (GFRP) material was produced in 2019, compared to approx. 141 kt of carbon fibre reinforced plastic (CFRP) worldwide, which has to be recycled even after the end-of-life. Main focus is principally on epoxy resin and carbon fibers (used for example in wind power plants and in electro mobility). Apart from pyrolysis, which currently is the only industrially used process and is mainly applied to carbon fiber reinforced polymers, chemical processes are being researched for the recycling of reinforcing fibres and matrix. The ability to fully recover both fiber and matrix by using solvents at the same time is one of the main advantages of chemical solvent processes. The challenge in chemical recycling is the selectivity of the respective solvents when applied to the variety of material combinations as matrix or fiber reinforcement in composite materials.

Aim of this research work is the investigation and definition of requirements for a fiber recovery from the epoxy matrix with subcritical and supercritical water. In the chemical recycling of GFRP and CFRP waste, the epoxy resin is converted into a liquid phase, while the fibers remain as a solid residue. Due to the chemical stability of epoxy resins, their chemical recycling by solvolysis requires high temperatures and high pressures; the process conditions can be defined as subcritical or supercritical depending on the physical state of the solvent during the process. Especially the use of supercritical fluids is considered promising for the recycling of FRP. Supercritical fluids have low viscosity, a high mass transfer behaviour and, most important, a high diffusion coefficient, which leads to a high solvability. The typically used solvents water or alcohols are considered to be environmentally friendly. The results of the research show that the amount of resin remaining decreases with increasing temperature and processing time, while temperature having the greater influence on resin removal.

1. Introduction

The protection of resources is a task for society as a whole and is one of the major challenges industry is facing. Lightweight materials such as fiber-reinforced plastics, which are used in the aerospace and automotive industry, can provide a possible solution. In addition, by reusing or recycling the materials after their useful life, a large proportion of raw materials and energy can be recovered, thus conserving the limited resources available. The principle of resource conservation is the basis for this paper. Within the process of FRP recycling, a distinction must be made between thermoplastics and thermosets according to the polymer matrix used. Through heat application, thermoplastics can be converted into a formable state and remelted and thus recycled. (Martens, Goldmann 2016) In contrast, thermoset matrix systems cannot be melted due to their highly cross-linked macromolecular structure and are therefore a challenge for recycling. (Henning, Moeller 2020) Recycling processes for thermoset plastics can be differentiated according to three principles: mechanical, chemical and thermal recycling. Mechanical material recycling of FRP describes the shredding and thus the reduction of the particle size, whereby, in contrast to thermal and chemical recycling, the original material properties are retained. (Pickering 2006) In feedstock recycling, the macromolecules are degraded to low molecular weight compounds

by chemical or thermal processing (pyrolysis, gasification solvolysis, or hydrogenation). (Martens, Goldmann 2016) The pyrolysis of FRP for a separation of fiber and polymer matrix is already state of the art and is implemented on an industrial scale e.g. by the company CFK Valley Recycling GmbH & Co. KG and in the United Kingdom by ELG Carbon Fibre Ltd.. In pyrolysis, the plastic matrix is thermally decomposed and energetically utilized. Pyrolysis of GFRP requires higher temperatures that affect the mechanical properties of the glass fibers. (Pico, Bartl 2010) Moreover, the organic fraction from the pyrolysis process consists in a mix of hydrocarbons in solid, gas and liquid state that must be separated and processed in a refinery in order to find new applications. (Pico et al., 2014) In comparison to pyrolysis, in chemical processes, especially solvolytic processes, the matrix material is broken down into the respective monomers while the fibers stay intact. Solvolytic processes can be classified according to the type of solvent. A distinction is made between hydrolysis (water), glycolysis (glycol), alcoholysis (alcohol) and acid digestion (acid). (Oliveux et al., 2015)

In this paper, main focus lays on water as it is considered to be a more environmentally friendly reaction medium for separation of the polymer matrix and fiber material. The process of hydrolysis can be carried out in the subcritical or supercritical range. The critical point of water is 374°C and 221 bar; when this point is exceeded, the water is called supercritical and has special properties. The solubility of organic compounds increases in this range, whereas inorganic substances become insoluble and precipitate. The use of supercritical water is suitable for recycling GFRP and CFRP and is environmentally friendly compared to other solvents. In addition, evaporation or distillation can be used to separate the water or alcohol from the product. (Delvere et al., 2019) The aim of the experimental studies was to investigate the influence of the process parameters on the separation of the material composite of fibers and matrix.

2. State of the art

Chemical recycling of thermoset fibre-reinforced plastics offers the potential to recover the fibre and matrix component and is being increasingly researched in academia. (Delvere et al., 2019) However, a disadvantage is the strong dependence of the solvent on the chemical structure of the plastic. (Ma, Nutt, 2018) In addition, often solvents classified as hazardous or toxic are used and high temperatures or pressures are necessary for depolymerisation. Hydrolysis involves the dissolution of the plastic using water as an environmentally friendly reaction medium. Through the transition from atmospheric to supercritical conditions (see Figure 1), water fundamentally changes its character from an ionic solvent to a non-ionic solvent. Electrochemical properties, such as the dipole moment, decrease drastically, but water is still more polar than acetone in supercritical conditions. The pH value decreases by three units as much more hydroxonium ions are formed. In addition, water becomes completely mixable with gases such as oxygen, nitrogen, ammonia, carbon monoxide and dioxide. The solubility of inorganic compounds decreases drastically, but the solubility of organic compounds such as plastics increases strongly, up to complete solution. (Brunner 2009) The critical point of water is 374°C and 221 bar; when this point is exceeded, the water is called supercritical and has special properties.

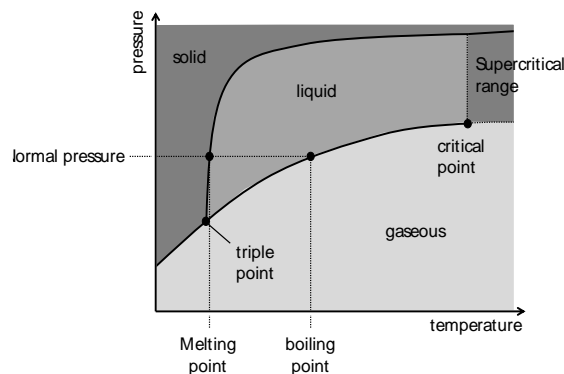


Figure 1 p-T-phase diagram

The depolymerisation with water can take place in the subcritical and supercritical area. For example, in the case of GF-reinforced unsaturated polyester resins, water is used to dissolve the reaction resin at temperatures of 250 – 325°C and with reaction times of 1 – 120 min. The mechanical properties of the fibres are partially retained. (Oliveux et al., 2012) In contrast, the recycling of carbon fibre-reinforced epoxy resin can be carried out using supercritical water as a solvent at 320°C, 180 bar for two hours. This dissolves the resin almost

completely (97 wt.-%), leaving fibres with good mechanical properties. (Oliveux et al., 2017) Special technology from the high-pressure sector is required to carry out the reactions in the supercritical range. In addition to the special technology, the necessary temperatures also mean a large energy consumption. Therefore, some publications follow the approach to decompose plastics with water in the subcritical state. Within these experimental set-ups catalyst (such as sulphuric acid) are used very often. But in contrary to the advantages of water, is not completely harmless. (Liu et al. 2009) Using an approach without catalysts, CFRP could be decomposed completely after 75 minutes at 290°C. Experiments were also carried out with additional 1 mol of sulphuric acid per ml of water. As a result, 100 % decomposition could be achieved after 90 minutes at 260°C. Although the addition of the catalyst reduced the reaction temperature even further, the process time was prolonged and the use of sulphuric acid poses a greater potential danger to both the environment and the processor than pure water. (Yuhan et al. 2009) In the present work, the hydrolysis of GFRP and CFRP under near-critical conditions was investigated without the use of catalysts.

3. Materials and Methods

For the hydrolysis in the near- and supercritical range, GFRP sheet material (2 mm thickness) was used made of glass-fibre reinforced epoxy resin and amine-based hardener with a fibre volume content of approx. 57 wt.% (+/- 1 %). The dimensions of the samples are given by the sizes of the test set-ups. For the experiments with near- and supercritical water, samples with a size of 80 x 80 mm were selected.

The experiments were carried out in an autoclave with a capacity of 2,000 ml. Considering the defined mixing ratio of 1 g cured FRP waste to 5 ml water, the sample weight of 40 g could finally be determined. The sample material is placed in a basket to keep it in the " steam phase " rather than in contact with the water. After closing the autoclave (with 190 Nm/screw), the measuring instruments for pressure and temperature were attached. The process begins with heating the reactor. As the temperature rises, the pressure in the reactor increases, creating the desired sub- or supercritical conditions. The test conditions were varied as listed in Table 1 in order to enable the definition of the Influencing parameter.

Table 1: Experimental parameter of hydrolysis

dwel time [h]	temperature (°C)	pressure (bar)
75-105-130	270-300-330	50-80-130

The reactor was heated and once the target temperature was reached the time measurement started. To ensure a constant pressure profile, the heating temperature of the reactor (T_{Reactor}) was down-regulated (T_{Reactor}) in stages. The pressure was set according to the selected temperature inside the reactor. An example is given in Table 2 for 300°C and 80 bar. After cooling down, the sample material, consisting of a solid and a liquid phase, was removed from the reactor and weighted.

Table 2: experimental data for the parameter-set 300°C und 80bar

T _{Reactor} [°C]	25	489	482	285	360	348	345	166	102
τ [h]	0	0	0	30	60	90	105	60	120
p [bar]	0	13	78	86	82	83	82	8	1
T _{inside} [°C]	25	194	300	300	300	300	300	300	300

In order to select a suitable post-solvolytic-treatment method for the fibre material, the solid residue was cleaned with acetone and analysed by gas chromatography and emission testing to determine the decomposition products. The emission tests were carried out according to VDA 278 / thermal desorption analysis. This method is used to determine the concentration and to identify the organic substances that can be outgassed from materials. The semi-quantitative VOC value is determined, which allows an estimation of the emissions of highly volatile substances. In thermo-desorption, a small amount of material (25 - 50 mg) is heated in a defined manner in a glass tube. The emitting substances are led into a cold trap by means of an inert gas flow and cryo-focused there. After completion of the heating phase, the cold trap is immediately heated up to 280°C to evaporate the focused substances. Figure 2 shows the chromatogram of a GRP sample after solvolysis (300°C, 85 bar, 40 g sample on 200 ml medium). The determined VOC value was 1625 µg/g. The evaluation of the chromatograms shows phenol and p-cumenol (isopropylphenol) as the main components at 30°C. Both substances are main decomposers. Both substances are main decomposition products of epoxy resins. In concentrations of <10 %, alkylated phenols such as cresols and thymols are also detectable. In the front

retention area, small amounts of acetic acid and glycol can be detected. The sample material was then washed with 60 °C hot water and acetone and dried in a drying oven at 60°C. After this pre-treatment, the sample material was found to be free of alkyl phenols. After this pre-treatment, no peak was detectable in the VOC value in the analyses, nor in the chromatogram at 30°C. The VOC value was not detected in the analyses. The non-dissolved matrix content still adhering to the fibre was determined by thermogravimetric analysis after homogenisation using a granulator.

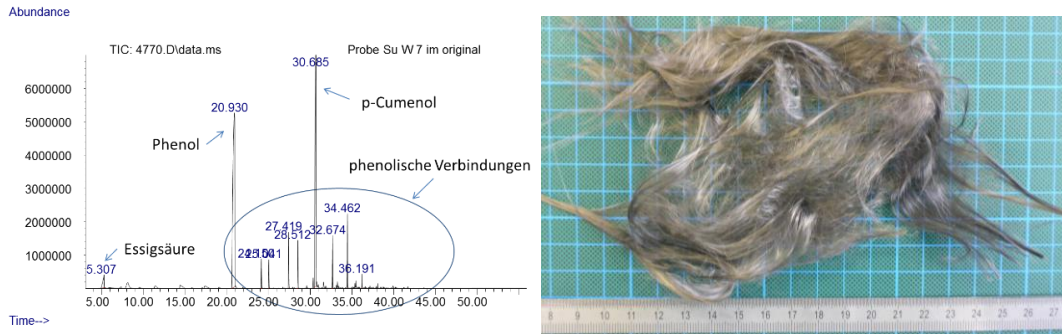


Figure 2: Chromatogram of the unwashed sample at TDS of 30°C (left) and CFRP sample material after pre-treatment (right)

4. Results

The process influence of temperature, pressure and residence time was evaluated with the help of the results from the thermogravimetric analysis (TGA) of the solid fibre residue. The organic components of a sample can be determined with the aid of TGA. The samples are annealed under oxygen exclusion in a muffle furnace in the temperature range of 25 -950° C at a heating rate of 10 K/min until the weight of the sample no longer changes. The resin volatilises as an organic component and the carbon fibres remain under inert gas conditions. The material is cooled down in a desiccator until the mass remains constant. The difference between the initial weight before and the final weight after annealing is the mass fraction of the resin.

The test conditions were still below the critical point of water (221 bar, 374°C) for all tests and are therefore referred to as sub- or near-critical water oxidation. In the following, the TGA results of the residue on the fibre material for the different materials are shown once as a function of temperature and residence time (Figure 3).

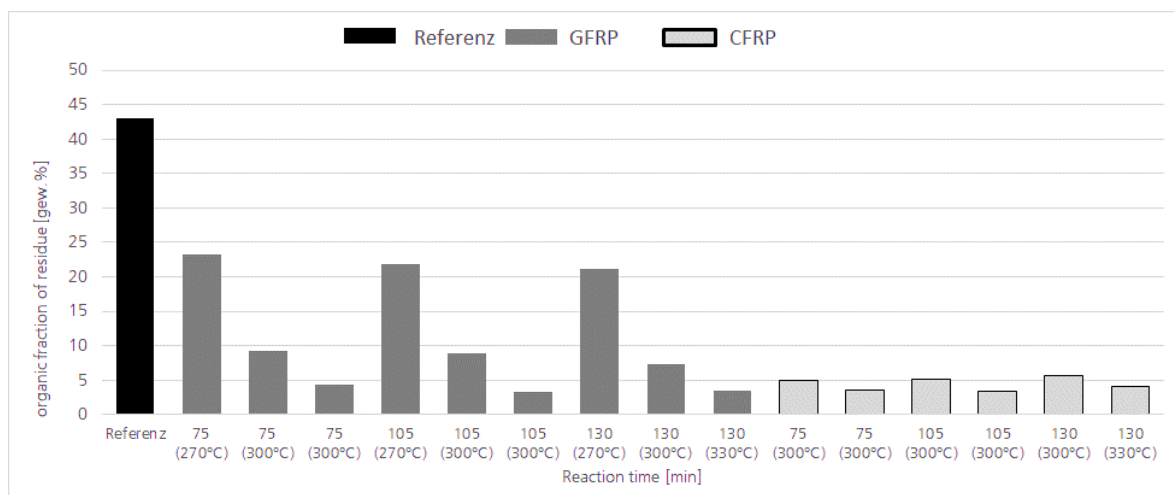


Figure 3: Resin content of the residue at different reaction temperatures for GFRP and CFRP material

The results show the great influence of the process temperature on the fibre-matrix separation of FRP. With GFRP and a reaction temperature of 270°C, there is a dissolution of the matrix of at least 46 % at 75 min and

51 % at 130 min. When the reaction temperature is increased to 300°C, only 7 % matrix remains on the fibre material at 130 min reaction time. At the test temperature of 330°C, the organic content of the fibre material is reduced to 3 %. The tests with the parameter of 300 °C and 330°C were also carried out with CFRP and an increase in solubility can be seen with an increase in temperature. At CFRP and a reaction temperature of 300 °C and 105 min, 88 % of the resin could be dissolved and at 330°C and 105 min up to 92 %. When comparing the results of GFRP and CFRP at 300°C, a difference in the undissolved resin content of approx. 8 % can be seen, irrespective of the reaction time. Instead, the values at a temperature of 330°C are in approximately the same range of 3.6 % of resin content in the fibre material.

The results for the dissolution of the matrix fraction of GFRP in the range from 270°C up to 330°C illustrates an increase in dissolved resin fraction by 43 % and thus a possible matrix solution of up to 91 %. When increasing the reaction time in the selected temperature range, only an increase of approx. 2 % for 270°C and 300°C can be seen for GFRP in all three selected temperature ranges. At 330 °C only an increase of 1 % can be seen. For CFRP material, the increase in solubility with an increase in the residence time at 300°C is only 1 % and even only 0.5 % at 330°C.

Based on the TGA analyses results on the variation of temperature and residence time, a reaction temperature of 330°C gives the most suitable parameters for effective fibre-matrix separation for both GFRP and CFRP. The residence time can vary in the range of 75-130 min and has a lower influence on the result, with the best results obtained for 105 min residence time for both samples. After drying, the fibre material was examined using a scanning electron microscope to detect possible damage to the fibres. The left picture in Figure 4 shows fibre material with a residual resin content of 23 %. In the illustration, the residual resin content is clearly visible, as well as the negative imprints of the fibres in the matrix and exposed fibres. The right picture in Figure 4 shows an SEM image of fibre material with a significantly lower resin content, which is due to the test conditions of 330 °C and 105 min dwell time.

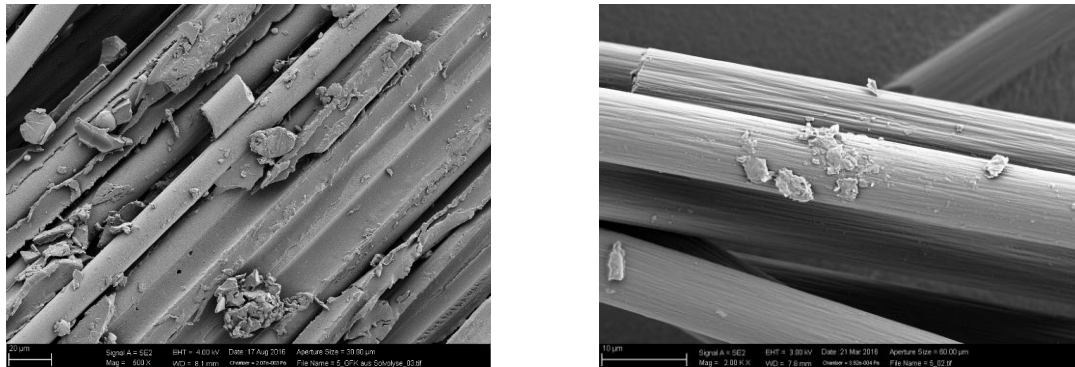
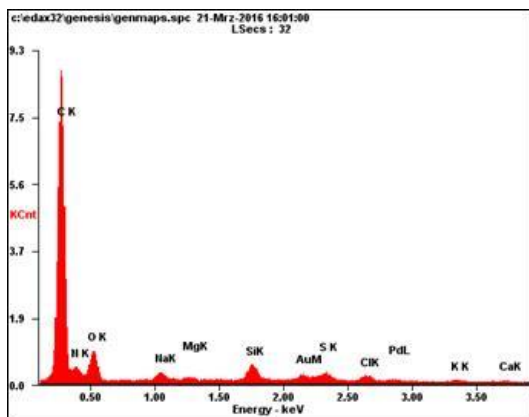


Figure 4: SEM image of fibre material after hydrolysis at 270°C and 75min (left) and at 330°C and 105min (right)

EDX images were taken of the material adhering to the fibre, which is presented in Figure 5 confirming that the adhering material to the fibre is resin.



Element	Wt%	At%
CK	67.35	72.75
NK	16.00	14.82
OK	13.59	11.02
NaK	00.81	00.46
MgK	00.21	00.11
SiK	00.94	00.43
SK	00.52	00.21
ClK	00.41	00.15
KK	00.11	00.04
CaK	00.07	00.02
Matrix	Correction	ZAF

Figure 5: EDX analyses of the material adhering to the fibre in Figure 4

5. Conclusion

The aim of this work was to investigate the parameter influence of temperature and residence time in the hydrolysis of FRP for effective fibre-matrix separation to expose the fibres for recycling. Due to the strong cross-linking, high strength and good chemical resistance, the chemical recycling of fibre-reinforced EP resins is a challenge. In the tests it could be shown that an increase in temperature from 270°C to 330°C and a dwell time of e.g. 105 min increases the degree of resin separation from the fibre in the case of GFRP from 51 % to 83 %. The dwell time, on the other hand, has only a minor influence. With an increase from 75 min to 130 min at a reaction temperature of 330°C, the degree of dissolution increased from 89.9 % to 92 %. For CFRP, the difference over all three residence times is small, in the range of 90-91.7 %. At a reaction temperature of 330°C and 105 min residence time, the highest possible resin separation was achieved for both materials, with 92 % degree of solution for GFRP and 91 % degree of solution for CFRP. It was also shown that the temperature has much higher influence on the resin separation compared to the residence time. A longer residence time does not give better results for both GFRP and CFRP. Therefore, the low residence time of 105 min will be necessary for energy-efficient recovery of FRP.

In the recycling challenge of future hybrid components with glass and carbon fibres, parameters could be determined (330°C and 105min) in which both GFRP and CFRP can be recycled. In further investigations, the optimisation of the process, e.g. by using a catalyst for 100 % separation, has to be examined. On the basis of the investigations, questions also arise for a transfer of the results to real waste materials with e.g. further additives such as chalk in the case of SMC components or also the economic consideration for an upscaling of the processes. Even if the process parameters are in the near- or subcritical range, the safe plant design places special demands on pressure safety. One possibility to make the process more effective and economical is the raw material utilisation of the liquid residues as basic chemical substances, which still needs to be investigated.

References

- Brunner G., 2009, Near and supercritical water. Part II: Oxidative processes, *The Journal of Supercritical Fluids*, 47, 382-390
- Delvere I.; Iltina M., Shanbayev M., Abildayeva A., Kuzhamerdieva S., Blumberga D., 2019, Evaluation of Polymer Matrix Composite Waste Recycling Methods, *Environmental and Climate Technologies*, 23, 168-187.
- G. Oliveux, J.L. Bailleul, E.L.G. La Salle, 2012, Chemical recycling of glass fiberreinforced composites using subcritical water, *Compos. A: Appl. Sci. Manuf.* 43, 1809–1818
- Henning F., Moeller E., 2020, *Handbuch Leichtbau – Methoden, Werkstoffe, Fertigung*, Carl Hanser Fachbuchverlag, München, D, ISBN 978-3-446-45638-9.
- Liu Y., Shan G.; Meng L., 2009, Recycling of carbon fibre reinforced composites using water in subcritical conditions, *Materials Science and Engineering A* 520, 179–183
- Ma Y., Nutt S., 2018, Chemical treatment for recycling of amine/epoxy composites at atmospheric pressure. *Polymer Degradation and Stability*, 153:307–317. doi:10.1016/j.polymdegradstab.2018.05.011
- Martens H., Goldmann D., 2016, *Recyclingtechnik – Fachbuch für Lehre und Praxis*, Springer Vieweg, Wiesbaden, D, DOI: 10.1007/978-3-658-02786-5.
- Oliveux G., Bailleul J.-L., Gillet A., Mantaux O.; Leeke, G. A., 2017, Recovery and reuse of discontinuous carbon fibres by solvolysis, *Composites Science and Technology*, 139, 99-108.
- Oliveux, G.; Dandy, L.; Lester, E., 2015, Current status of recycling of fibre reinforced polymers: Review of technologies, reuse and resulting properties. In: *Progress in Materials Science*. 72. Jg., 61–69
- Pickering S., 2006, Recycling technologies for thermoset composite – current status, In: *Composites Part A: Applied Science and Manufacturing*, 37; 1206-1215.
- Pico D., Bartl A., 2010, Chemical Treatment of Glass Fibers After Composite Recycling Process. In: " ISWA World Congress 2010 Papers and Proceedings S6
- Pico D., Seide G., Gries T., 2014, Thermo Chemical Processes: Potential Improvement of the Wind Blades Life Cycle, *Chemical Engineering Transactions*, 36, 211-216, DOI: 10.3303/CET1436036
- Witten E., Mathes V., 2019, Der Markt für Glasfaserverstärkte Kunststoffe (GFK), *Industrievereinigung Verstärkte Kunststoffe* www.avk-tv.de/files/20190911_avk_marktbericht_2019_final.pdf accessed 12.01.2021.
- Yuyan L., Guohuo S., Linghui M., 2009, Recycling of carbon fibre reinforced composites using water in subcritical conditions, *Materials Science and Engineering: A*, 520, 179-183.