

# Chemical Treatment of Glass Fibers After Composite Recycling Process

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## EXECUTIVE SUMMARY

Glass fiber reinforced plastics (GFRP) are gaining a strategic relevance in many sectors because of their excellent properties such as high stiffness and strength combined with an extremely low density. Even if the environmental benefits offered by the use of GFRP are evident, their waste management remains a big issue. Until now no suitable disposal processes are accessible for end-of-life composites and in the future the waste related to the dismantling of products made of them will get of major importance. Considering the energy required for production of E-glass fibers (50 GJ/t) and epoxy resins (140 GJ/t) a reuse of the reinforcement is essential to reduce the environmental impact of GFRP waste. Today European legislation demands a waste hierarchy (directive 2008/98/EC) and, thus, landfill shows the lowest priority and has to be replaced at least by recovery (i.e. incineration) and recycling. The incineration process can only recover the caloric value of the matrix while the inorganic fraction is a zero sum game. In case of typically 70 % E-glass fiber and 30 % epoxy resin energy recovery would range below 8 % of the value already consumed for production. However, during combustion the fiber reinforcement is completely destroyed and, thus, no fiber recovery is possible. Although thermo-chemical processes for improving recycling the reinforcement phase have been developed the process temperature required to decompose the epoxy resins is too high and drastically reduces tensile strength. According to literature a recovery of fiber strength is possibly by etching processes based on a removal of surface flaws. In this study four different fiber materials have been thermally treated to induce a reduction of the mechanical properties. Subsequently the fibers were etched in order to determine the possible degree of recovery. It is demonstrated that all materials exhibited a dramatic loss of strength to about the half after the thermal treatment. However, only two fibers showed an increase after the etching process and, at least, about 80 % of the original strength could be reached. The possibility to recover fiber strength of thermally damaged inorganic reinforcement fibers offers great opportunities. However, it is not only necessary to develop an industrial viable process for fiber etching (i.e. recycling) but also to improve the technology of GFRP (i.e. eco-design).

## INTRODUCTION

Many and different sectors request lighter and stronger materials today. The most performing materials are composites made of plastics reinforced by fibers (FRP). Nowadays glass fiber reinforcement is typically prevailing. The most important advantage of glass fiber reinforced plastics (GFRP) is the strength and stiffness combined with a low density and low costs. In table 1, GFRP are compared with other materials like metals and plastics. GFRP are usually not isotropic materials and they exhibit a superlative longitudinal strength, far better as metals like steel and aluminum.

Table 1. Properties of selected materials to fiber reinforced epoxy resin (Anonymous, 1986, Nietzel, 2004, Moser 1992)

| Material                             | Density<br>[g/cm <sup>3</sup> ] | Strength<br>[MPa] | E-Modulus<br>[GPa] |
|--------------------------------------|---------------------------------|-------------------|--------------------|
| Steel (A36)                          | 7.8                             | 400–550           | 200                |
| Aluminum (2014-T6)                   | 2.8                             | 455               | 73                 |
| PP                                   | 0.9                             | 30-40             | 1.3-1.8            |
| PET                                  | 1.4                             | 55-80             | 2.8-3.5            |
| Epoxy resin                          | 1.2                             | 45-85             | 2.8-3.4            |
| Composite Epoxy/E-Glass longitudinal | 1.8                             | 1062              | 39                 |
| Composite Epoxy/E-Glass transversal  | 1.8                             | 31                | 8.3                |

GFRP are mostly used in structures where lightness is a determinant factor. In automotive applications GFRP cause reduction of fuel consumption due to the weight decrease. For example, 200 kg less weight for a 7.5 t truck offers 200 kg more payloads and, thus, 3.6 t less CO<sub>2</sub> emissions (considering 100.000 km) (Anonymous, 2008).

In wind power energy supply a huge amount of GFRP is used for the wind blades. The requirement of higher efficiency caused a rush scale-up of windmills because their power generation is proportional to their swept area. The global installed capacity of wind power had a yearly growth rate between 20 and 35 % (Larsen, 2009). In 2009 the global cumulative capacity installed was more than 158 GW doubling that of 2004 (GWEC, 2010). The biggest rotor already installed has a turbine blade diameter of 126 m and can generate a power of 5.000 kW. Each wind blade is made of 18 t of glass fiber reinforced plastics. According to literature, around 10 kg of GFRP are required for each kW capacity installed (Larsen 2009b). As a matter of fact the production of fiber reinforced materials has steadily grown during the last years. In Europe the annual production of GFRP is approximately 1 Mio. t. The glass fiber global production is growing according with the GFRP; in 2010 around the world capacity has been 4.7 Mio. t. (Anonymous, 2010).

Even if during its operating time, the wind blade is generating renewable energy, no practicable disposal or recycling processes has been developed up to now. GFR plastics contain between 50 and 70 % of inorganic reinforcements, the rest is a plastic fraction. The matrix and the reinforcement are not dissolved or blended into each other. The epoxy resin matrix has a very high chemical stability and can be separated from the reinforcement only by thermal decomposition. Considering the overall energy balance of GFR plastics from cradle to grave, the incineration process is not an environmentally sound choice because the calorific value is just between 15 and 8 MJ/kg (Pickering, 1991,

2006) and, as shown in figure 1, only 8% of the energy required for its production can be recovered (Pico, 2009).

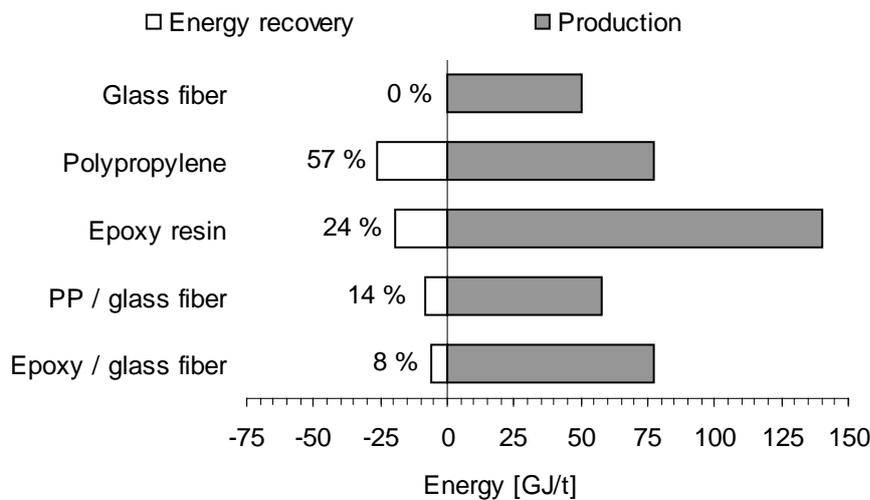


Figure 1. Energy balance of incineration (Pico, 2009)

Different recycling processes have already been developed to improve the reinforced plastic waste management. Pyrolysis process (Cunliffe, 2003), fluidized bed thermal process (Pickering, 2000), chemical treatment in near critical and supercritical water (Piñero-Hernanz, 2008) could offer a potential recovery of the reinforcement. However, the required process temperatures affect on the mechanical properties of the glass fibers and the fiber reuse remains the most difficult issue (Pico, 2009, Feih, 2009).

According to the literature (Bartenev, 1967,1969), the damages on the surface affect the mechanical properties of brittle materials like glass. Heat damages the fiber surface and causes surface flaws that significantly lower the reinforcement strength. A chemical process based on surface damages reduction (Sakka, 1957) was optimized and applied to different fiber reinforcements in order to recover their original strength. In detail, a superficial etching process has been employed to compare the recyclability of different materials.

## EXPERIMENTAL DETAILS

### Fiber Materials

For all experiments four amorphous fibers, E glass, Basalt, S2-glass and Advantex® have been selected. Their properties are summarized in table 2.

Table 2. Properties of fiber rowing used for the experiments.

| Sample    | Company       | Density                | Fiber diameter | Linear Density |
|-----------|---------------|------------------------|----------------|----------------|
| E-glass   | Saint Gobain  | 2.59 g/cm <sup>3</sup> | 9 μm           | 136 tex        |
| Basalt    | Kamenny Vek   | 2.80 g/cm <sup>3</sup> | 13 μm          | 1200 tex       |
| Advantex® | Owens Corning | 2.62 g/cm <sup>3</sup> | 16 μm          | 300 tex        |
| S2-glass  | Agy           | 2.48 g/cm <sup>3</sup> | 9 μm           | 406 tex        |

Table 3 shows the chemical composition of the fibers used for this investigation. It is clear that for all fiber samples SiO<sub>2</sub> is the main constituent. Basalt shows a more complex composition due to its natural origine, E-Glass, S2-Glass and Advantex® on the contrary

are obtained artificially by melting together 4 to 5 main components (high purity is required). In the following the most important facts of the selected samples are summarized:

- E-glass fibers are by far the most used inorganic fibers; they cover almost 99 % of the market. Due to the low costs and its wide range of applications E-Glass has become the benchmark for commercial continuous glass fibers.
- Basalt fibers are obtained by natural rocks; like the other samples the material is amorphous. It has a good temperature and chemical resistance coupled with a very cheap raw material but up to now it has not yet succeeded on the market.
- Advantex® fibers are boron-free E-CR glass that possesses significantly improved corrosion resistance against a wide range of aggressive acidic environments.
- S2-glass fibers are a product with very good strength, stiffness, resistance to high temperature and fatigue. However, due the high costs of S2-glass it could only succeed in niche markets.

Table 2. Chemical composition of samples used for the investigation (Wallenberger, 2000,).

| Element                        | E-glass | Basalt | Advantex®   | S2-glass |
|--------------------------------|---------|--------|-------------|----------|
| SiO <sub>2</sub>               | 52 - 56 | 49     | 59 - 61     | 65       |
| Al <sub>2</sub> O <sub>3</sub> | 12 - 16 | 16     | 13 - 14     | 25       |
| K <sub>2</sub> O               | -       | 1.5    | -           | -        |
| Na <sub>2</sub> O              | -       | 3.1    | -           | -        |
| Fe <sub>2</sub> O <sub>3</sub> | -       | 5.4    | -           | -        |
| FeO                            | -       | 6.4    | -           | -        |
| CaO                            | 16 - 26 | 9      | 21.5 - 22.5 | -        |
| MgO                            | 0 - 6   | 6      | 2.5 - 3.3   | 10       |
| TiO <sub>2</sub>               | -       | 1.4    | -           | -        |
| P <sub>2</sub> O <sub>5</sub>  | -       | 0.5    | -           | -        |
| MnO                            | -       | 0.3    | -           | -        |
| B <sub>2</sub> O <sub>3</sub>  | 5 - 10  | -      | -           | -        |

### Sample pretreatment

The fiber samples have been washed with ethanol (96 % vol) for 10 min in order to dissolve the sizing (i.e. coating) on the surface to exclude any possible influence. Furthermore, after the removal of the sizing a separation of single fibers from rovings is much easier. After the pretreatment the fibers have been dried at 110°C for 1 h and finally stored in a desiccator.

### Thermal treatment

In order to evaluate the change in mechanical properties of fiber materials during thermal processes (e.g. pyrolyzation) the samples have been exposed to a temperature of 400°C for 2 h. After the thermal treatment the samples were cut to a length of approximately 70 cm, were left at room temperature for at least 24 h.

## Chemical treatment

In order to eliminate the damages from the fibers, a chemical treatment was developed. In glass fibers, the main chemical compound is silicon dioxide. Starting from Sakka experiments (Sakka, 1957), an etching with hydrofluoric acid was developed for the fiber recovery process. The following procedure has been carried out as follow:

- 3 – 4 g fibers have been weighted
- Etching with 1% hydrofluoric acid
- Neutralization - 5 minutes in Hexafluorine
- Hexafluorine elimination - 5 minutes in deionized water and 10 minutes in ethanol
- Drying process - 1 hour at 110°C
- Finally the recovered samples have been weighted.

## Mechanical Properties

- Fineness  
It is quite common in the textile industry to use the fiber denier to characterize the fineness (DIN 60905, 1985, DIN 60910, 1985). It states the mass of a certain length of a filament, roving or yarn. In the case of the investigated fiber samples, which show a circular cross section, the diameter can be calculated according to equation 1.

$$d = \sqrt{\frac{4 \cdot 10^{-6} \cdot T_t}{\pi \cdot \rho}}$$

d Fiber diameter [ $\mu\text{m}$ ]  
T<sub>t</sub> Fiber denier [dtex]  
 $\rho$  Density [ $\text{kg/m}^3$ ]

Equation 1

The fiber denier of the fiber samples has been measured with a Vibroscope 400 by Lenzing Instruments. The measuring principle is based on a vibrational method. For each measurement a single filament is loaded with a pretension weight (table 3) and placed in the bracket. An electric impulse puts the sample in a vibrational state. The oscillation frequency is detected by an optical sensor which is processes to the fiber denier the data sent to a personal computer.

- Strength / Elongation  
Right from the Vibroscope 400 the fiber sample with fixed pretension weight is transferred to the Vibrodyn 400 by Lenzing Instruments. It is a small tensile test apparatus the fiber being fixed between two clamps (table 3). During measurement the lower clamp moves down indicating the elongation of the fiber. Simultaneously the upper clamp measures the resulting force. The test is carried out until breakage of the fiber. The data, a plot elongation versus force, is transferred to the personal computer which computes the force into a strength based on the prior determined titer.

Table 3. Parameters set for measurement with Lenzing Vibroskope 400 and Virbrodyn 400.

| Testing speed | Gauge length | Pretension weight |
|---------------|--------------|-------------------|
| 0.5 mm/min    | 20 mm        | 100 mg or 200 mg  |

## Data Analysis

The evaluation of the measured data has been made using statistical methods, calculating arithmetical average and standard deviation as well as the two Weibull parameters (Weibull, 1951, Feih, 2005). Weibull statistical function is widely used to describe the reliability of brittle materials. The probability of fiber breaking (PF) is expressed by a fracture probability function as shown in equation 2.

$$P_F = 1 - \exp\left(-\frac{L}{L_0}\left(\frac{\sigma}{\sigma_0}\right)^m\right)$$

|            |                              |            |
|------------|------------------------------|------------|
| $\sigma$   | breaking stress [GPa]        |            |
| $\sigma_0$ | Weibull size parameter [GPa] |            |
| $m$        | Weibull modulus [-]          | Equation 2 |
| $L$        | Actual gauge length [mm]     |            |
| $L_0$      | Reference gauge length [mm]  |            |

In case of the measurements of this investigation the volume size effects can be excluded since the length  $L_0$  was fixed by the measuring system ( $L = L_0$ ). Thus, the Weibull function is accessible by equation 3. The parameters have been determined by linear regression. The Weibull Modulus  $m$  is expressed by the slope and the  $\ln(\sigma_0)$  by the y-axis intercept.

$$\ln\left[\ln\left(\frac{1}{1-P_F(\sigma)}\right)\right] = m \cdot \ln(\sigma) - m \cdot \ln(\sigma_0)$$

Equation 3

The breaking stress data have been ranked from smallest to largest and put in order from 1 to N.  $P_F$  assigned to the experimental breaking stress is commonly expressed by the estimator given in equation 4.

$$P_F(\sigma_i) = \frac{i-0.5}{N} \quad i = 1 \dots N \quad N \text{ number of measured individuals} \quad \text{Equation 4}$$

The Weibull modulus  $m$  is used to indicate the distribution of the individual values. A large Weibull modulus means a low statistical distribution of the measured strengths and, thus, offers a reliable characterization method for brittle materials such as glass fibers.

## RESULTS

All the samples showed a significant loss of mechanical properties in terms of tenacity and elongation after thermal treatment. As sketched in figure 2 after 2 h at 400°C the original strength was reduced to 45 % for S2-glass, to 49 % for Basalt, 61 % and 60 % for E-glass and Advantex®. Even if S2-glass and Basalt fibers remained after thermal treatment stronger than E-glass and Advantex, their mechanical quality was strongly reduced.

The strength of the S2-glass-fibers (3.5 GPa) after the pretreatment is around twice as s the Advantex® (1.8 GPa) and the E-Glass (1.9 GPa). The most striking results were obtained after the chemical treatment. Both the E- as well as the S2-glass were too brittle to be measured. During the handling operations such as fixing of the pretension weight and fixing in the Vibroscope the fibers broke and a determination of strength was not possible at all. In contrast, the Basalt and Advantex® fibers after etching could be measured as usual and the original strength was partially recovered. In particular the Basalt fibers after etching showed a residual strength of about 1.87 GPa, which is the same strength measured for Advantex® and E-Glass after the pretreatment.

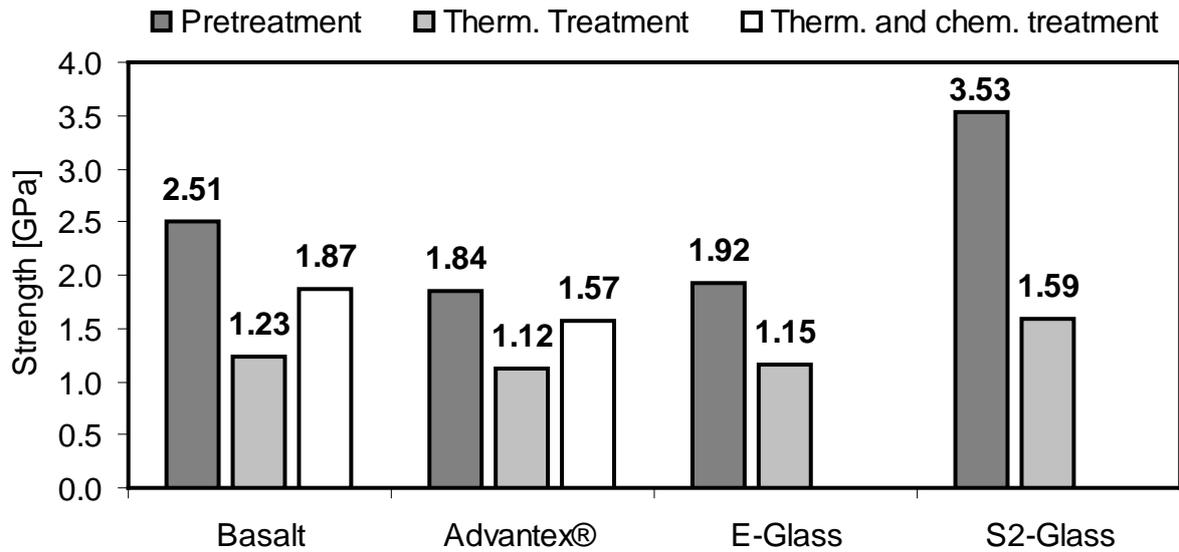


Figure 2. Strength against thermal and chemical treatment.

The E-modulus as well as the Weibull m-modulus did not significantly change during the thermal treatment as demonstrated in figure 3 and 4. The E-modulus of Basalt, Advantex® and E-Glass slightly increased during the thermal treatment at 400°C while for the S2 glass a slight decrease from 87 GPa (after pretreatment fiber) to 78 GPa (after thermal treatment) was determined. For the Basalt and Advantex® fibers the E-modulus was recovered after chemical treatment even if its fluctuations were too low and could even be an artifact due to the measuring system.

The figure 4 plots the m-modulus which is quite low as typical for brittle materials (Feih, 2009). No common trends are clearly deducible. Basalt exhibits a lower statistical distribution of the measured strengths compared with the other samples and, thus, a low reliable strength of the fibers. In particular, a reduction of m-modulus in Basalt and Advantex® fibers was found after chemical treatment.

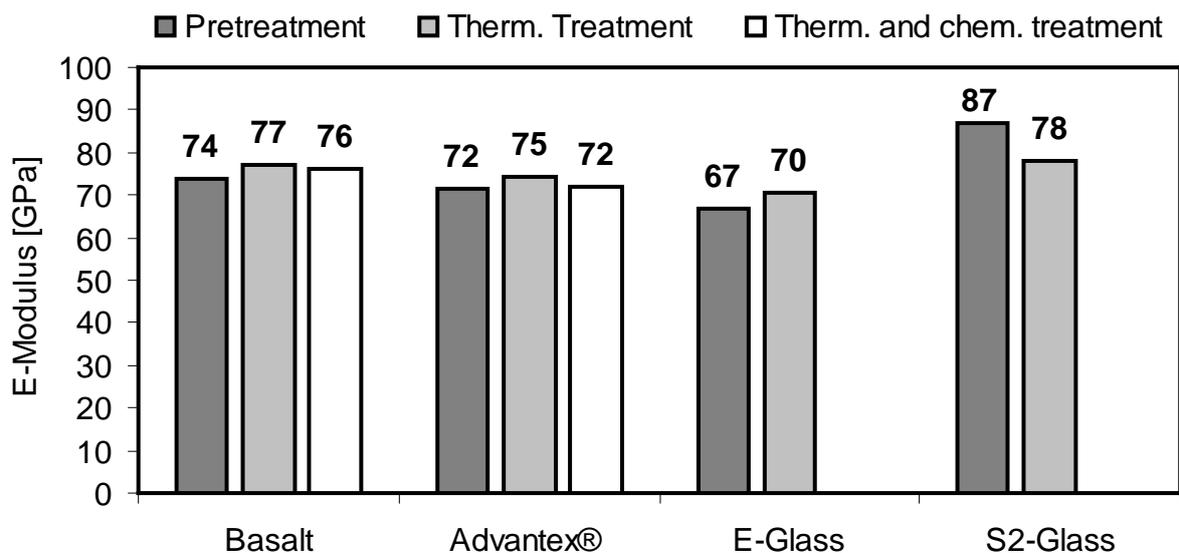


Figure 3. E-modulus against thermal and chemical treatment.

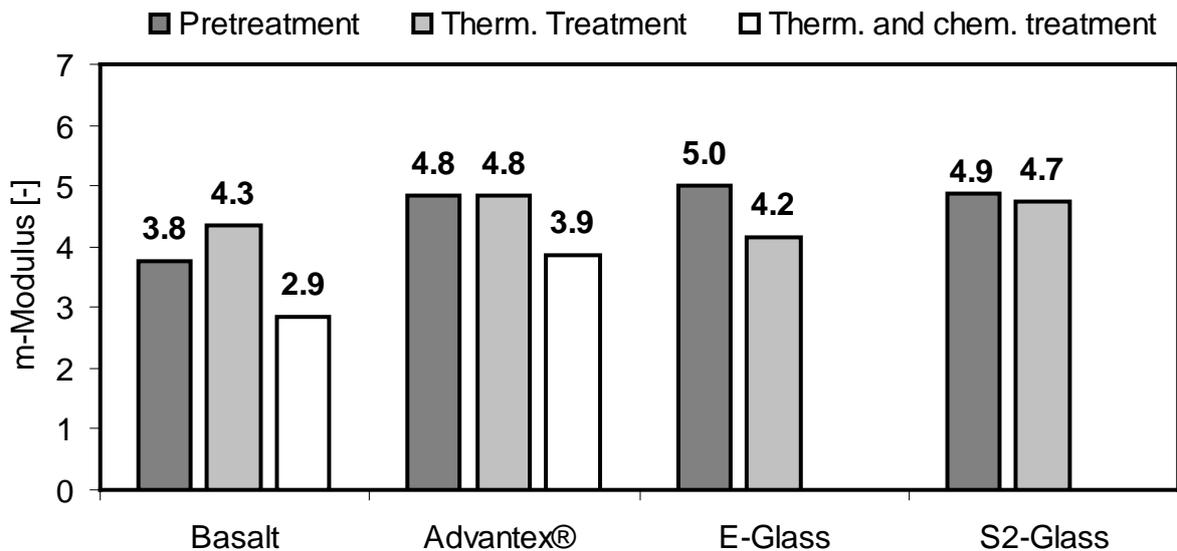


Figure 4. Weibull m-modulus against thermal and chemical treatment.

## CONCLUSIONS

The results show that an etching process can significantly recover the fiber strength of Basalt and Advantex® that has been previously damaged by an heat treatment. In regard of a recycling process for glass fiber reinforced plastics this procedure offers a great potential. In particular end-of-life composites from wind power rotor blades, commonly epoxy resin, could, thus, be treated by a pyrolysis process. On the one hand, the organic material will decompose and a synthesis gas can be produced. It offers the possibility of feedstock recycling. On the other hand the fiber fraction can be re-used. However, due to the temperatures prevailing during the pyrolysis process the mechanical properties are significantly reduced which hinders a direct re-use. Thus, the etching process could be a possibility to increase fiber properties and to improve the chance for a re-use. At least about 80 % of the original fiber strength can be regained.

Up to now the etching process is still far away from an industrial realization. On the one hand the most common glass fiber, E-glass, could not yet be recovered in regard of strength. It is currently under investigation whether the etching procedure can be further improved and be successfully applied to E-glass. On the other hand the use of hydrofluoric acid represents a great economic and ecologic burden. Alternative, less toxic solvents, would be desirable. Again, further experimental work is required.

The experiments offer a great potential for significantly improving the treatment of GFRP. Since the GFRP market has been grown higher-than-average within the last years and within the next years it is clear that in the future a large volume of end-of-life GFRP will arise. It seems, thus, to make sense to further develop the investigated recycling process.

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