

# FUTURE DIRECTIONS IN THE RECYCLING OF COMPOSITE MATERIALS

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## ABSTRACT

Different technologies based on solvolysis were applied to degrade an epoxy resin model and a carbon fibre reinforced RTM6 epoxy resin representative of aerospace applications: CO<sub>2</sub>-expanded water and generally recognised as safe solvents used neat or in mixture with water. The most efficient solvolysis conditions were then selected to scale up the process and to recover carbon fibres, which were subsequently reused to make new materials.

## 1 INTRODUCTION

Environmental legislation is becoming more and more restrictive, and just the environmental impact of these materials disposed in landfills is accelerating the urgency to reach more industrial scale solutions to the recycling of composites. Three generic approaches have been identified for the recycling of thermoset and thermoplastic composites: mechanical, thermal and chemical recycling [1].

The material can be ground to a recyclate that can be used as charge or partial reinforcement in new products, however this leads to only a limited incorporation in such materials. This approach is suitable only for glass fibre reinforced plastics and not for carbon fibre composites. The thermal methods, such as pyrolysis or fluidised bed process, decompose the composite resin at temperatures between 400-700 °C, which are energy intensive and can lead to damage of carbon fibres. Chemical recycling (solvolysis) uses an appropriate solvent to depolymerise the resin and release the fibres and eventually, the fillers or inserts. This approach generally requires lower temperatures (ambient to 400 °C) enabling the recovery of monomers and other chemicals from the resin and high-quality fibres.

Nevertheless, elevated temperatures and pressures are usually necessary to degrade the resin sufficiently and release the fibres; quite often supercritical conditions, especially of water, are used. These conditions are energy consuming and reactor materials can be very expensive in order to withstand the severe conditions. The production of resins and carbon fibres requires raw materials from fossil-derived resources and is also energy intensive [1]. The recovery of valuable products from composite materials (fibres and organic compounds), for reuse in new materials, is therefore essential to improve resource efficiency, decrease the cost of composite re-manufacture and reduce the environmental impact. In light of this, our objective in the EXHUME project is to research and develop novel engineering technologies along with robust proven technologies to recycle composite materials. Three approaches based on solvolysis have been investigated using neat solvents generally recognised as safe (GRAS) or mixtures of solvents and CO<sub>2</sub>-expanded liquids. The results obtained on

a model epoxy resin led us to identify suitable conditions to deconstruct the resin and to solubilise the degradation products. In this paper, these conditions have been applied to a real composite material used in aeronautics and the most efficient conditions in terms of degradation rate were scaled up.

## 2 MATERIALS AND METHODS

### 2.1 Materials

The epoxy resin used was based on the diglycidyl ether of bisphenol A (DGEBA) prepolymer, Dow D.E.R. 332 from Sigma Aldrich cured with diamine 4,4'-diaminodiphenyl sulfone (DDS) also from Sigma Aldrich, in stoichiometric conditions. D.E.R 332 epoxy prepolymer has a high purity with an epoxy equivalent weight (EEW) of 171-175 g/eq. These products were chosen to manufacture samples due to their common use in composite materials and the relative simplicity of the resulting bond network. The mixture was first heated up to 120 °C and stirred until a clear solution was obtained. It was poured into an aluminium container, which was coated beforehand with release agent (PVA Mould Release Agent from Easy Composites). The system was cured over 5 hours at 250 °C with a heating ramp of 1 °C/min. The plates were left in the oven until the temperature reached about 25 °C. The resulting glass transition temperature measured by differential scanning calorimetry (DSC) was between 170 and 210 °C, which is comparable to commercial epoxy resins cross-linked with polyamines. This also indicates a degree of crosslinking above 0.8 [2]. Figure 1 shows the molecular structure of the obtained resin after curing.

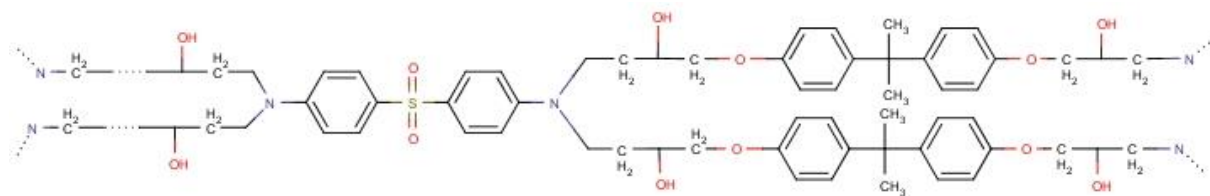


Figure 1: Structure of the epoxy model resin after polymerisation.

A composite material made of RTM6 epoxy resin and 20 plies of T700 carbon fibre woven fabric was then used. Its thickness was 6 mm and its fibre volume content was about 53%.

Acetone (analytical grade), ethanol (HPLC grade) and 2-propanol (specified laboratory reagent, extra pure) were purchased from Sigma Aldrich. Distilled water was produced in our laboratory. Carbon dioxide (CO<sub>2</sub>) was purchased from BOC Industrial Gases (purity 99.9% v/v).

### 2.2 Reactors and experimental methodology

Initial lab-scale experiments were realised in a 316 SS Parr Instrument batch reactor of about 115 ml. A resin sample was placed in the vessel with the appropriate solvent system at an initial loading rate (volume of solvent / reactor volume) of 0.5. The system was then heated to the desired temperature, which required between 24 minutes to reach 250 °C and about 53 minutes to reach 350 °C. After a desired time, the system was cooled down to ambient temperature by forced air convection and then by a water bath when the temperature was below 100 °C. The cooling phase required up to 80 minutes from 350 °C.

The liquid fractions were then recovered in glass bottles tightly closed and kept at 4 °C before being analysed. Acetone was used to flush the reactor and recover non-soluble products at ambient temperature. A phase separation in the liquid fractions was also observed after rest (from few minutes to several hours) and resulted in a deposit at the bottom of the bottles. The deposit could be dissolved only by acetone and were also subject to analysis.

For the experiments realised with CO<sub>2</sub>, the reactor was first pressurised with CO<sub>2</sub> to the desired initial pressure before heating. A blank test was first undertaken to measure the amount of gas injected.

Scale-up experiments were realized in a 5 L hastelloy batch reactor from Parr Instrument. The heating phase required about 75 min to reach 320 °C. Due to the weight of the reactor, it was not

possible to lift it out of the oven to cool, therefore the cooling phase required about 2 h for the temperature to decrease below 200 °C and about 20 h to reach 35 °C.

The organic residue on the fibres was measured by calcination at 500 °C until no mass change was observed. For each experiment, the degradation rate  $R\%$  was calculated using equation (1).

$$R\% = \frac{\text{initial mass} - \text{remaining mass}}{\text{initial mass}} \times 100 \quad (1)$$

### 3 RESULTS AND DISCUSSION

#### 3.1 Solvolysis of the model epoxy resin

Three methods were considered to degrade the resin: either pure solvent, two-solvent mixtures or CO<sub>2</sub>-expanded solvent. A total of 52 experiments were therefore realized, for which the main results are discussed here (experiments # 1-5 in Table 1 and # 8-10 in Table 2).

Exp. #	Sample	Gas and additives	Measured P <sub>0</sub> (bar)	Measured T (°C)	Measured P (bar)	t (min)	R% (± 1%)
1	Model resin	No	0	300	80	60	23
2				350	156	60	84 <sup>(*)</sup>
3				350	157	90	57
4		CO <sub>2</sub>	35	300	81	60	41
5				300	82	120	51
6	Composite	No		320	106	180	58
7		CO <sub>2</sub>	35	300	81	120	18

Table 1: Conditions and results of hydrolysis experiments with a resin concentration = 30 mg/mL and a solvent loading rate = 0.5. P<sub>0</sub> is the initial pressure. <sup>(\*)</sup> resin concentration = 10 mg/mL.

Exp. #	Sample	Measured T (°C)	Measured P (bar)	t (min)	R% (± 1%)
8	Model resin	300	137	90	-4
9		320	180	90	77
10		350	235	30	93
11	Composite	300	142	120	40
12				180	49
13		310	162	120	56
14				150	75
15				180	76
16		315	170	180	81
17		320	182	180	92

Table 2: Conditions and results of solvolysis in a mixture of water and 80 vol.% acetone, with a resin concentration = 30 mg/mL and a solvent loading rate = 0.5.

Experiments performed in neat water showed that about 1 h at 350 °C was necessary to almost fully degrade the epoxy model resin with a resin concentration of 10 mg/mL (experiment # 2 in Table 1). However the degradation reached only 57% at 350 °C during 90 min for a threefold increase in resin concentration (experiment # 3 in Table 1). The degradation could be increased by almost a factor of 4 by increasing the temperature by 50 °C (cf. experiments # 1 and 2 in Table 1). The maximum resin concentration appeared to be 30 mg/mL, from which the solvent is saturated and the resin degradation slowed down (Figure 2).

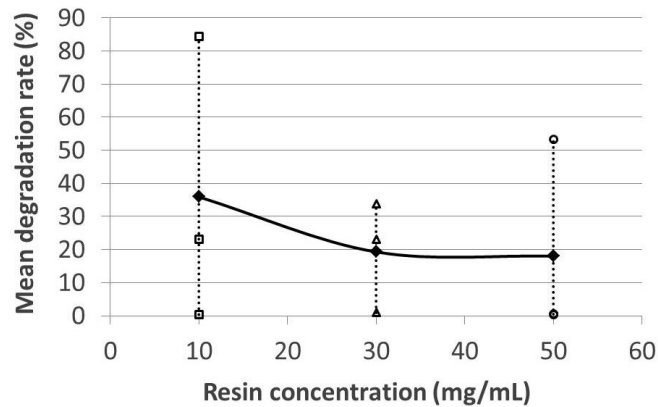


Figure 2: Effect of the resin concentration on the degradation rate in neat water (scatter results from different temperature and time range at each resin concentration value [3]).

Experiments in CO<sub>2</sub>-expanded water appeared to enhance the resin degradation compared to neat water at the same temperature. The degradation rate was almost doubled when CO<sub>2</sub> was added by pressurizing the reactor at 35 bar before starting the heating (experiments # 1 and 4 in Table 1).

Experiments in mixtures of water with another GRAS solvent, such as acetone, ethanol and 2-propanol, were realized at different mixture proportions [3]. The results indicated that the addition of one of these GRAS solvents led to a higher degradation rate at 350 °C compared to pure water. The best mixture appeared to be water and 80 vol.% acetone, leading to a degradation rate of 93% after 30 minutes at 350 °C and reaction products completely soluble even at room temperature in the presence of acetone. The reaction time could be decreased more than threefold compared to pure water (cf. experiments # 3 in Table 1 and # 10 in Table 2) at 350 °C. However the pressure reached 235 bar at 350 °C with 80 vol.% acetone. Lower temperatures were then tested. At 300 °C and 137 bar no resin degradation is measured after 90 min while 77% was obtained at 320 °C and 180 bar (cf. experiments # 8 and 9 in Table 2). This solvent mixture was then used to solvolyse virgin T700S carbon fibres alone, in order to measure the effect of the process conditions on their mechanical properties [4]. Fibre tows were exposed to 350 °C for 30 minutes in the mixture of water and 80 vol.% acetone. The tensile strength was decreased by less than 10%. Considering these promising results, the solvent mixture was applied to a composite material made with the same type of fibres and RTM6 epoxy resin.

### 3.2 Solvolysis of a real composite material

Samples of the T700 fibre reinforced RTM6 epoxy resin (Figure 3a) were exposed to different temperatures between 300 and 350 °C in either pure water, CO<sub>2</sub>-expanded water and mixture of water and 80 vol.% acetone. The conditions and the results are given in Tables 1 and 2.



Figure 3: a) Samples of T700 fibre reinforced RTM6 epoxy; b) Fibres recovered after solvolysis (experiment #17 in Table 2).

Compared to the model resin, the effect of CO<sub>2</sub> on the resin degradation is much lower (cf. experiments # 5 and 8 in Table 1) and led to a degradation rate of only 18% after 120 min at 300 °C.

On the other hand, it was about 1.6 times higher with the same mixture after 180 min at 320 °C compared to pure water (cf. experiments # 6 in Table 1 and # 17 in Table 2) and led to visually very clean fibres as shown in Figure 3b. Furthermore, the dissolution of the reaction products was significantly better, as shown by Figure 4, leading to less contaminated fibres.

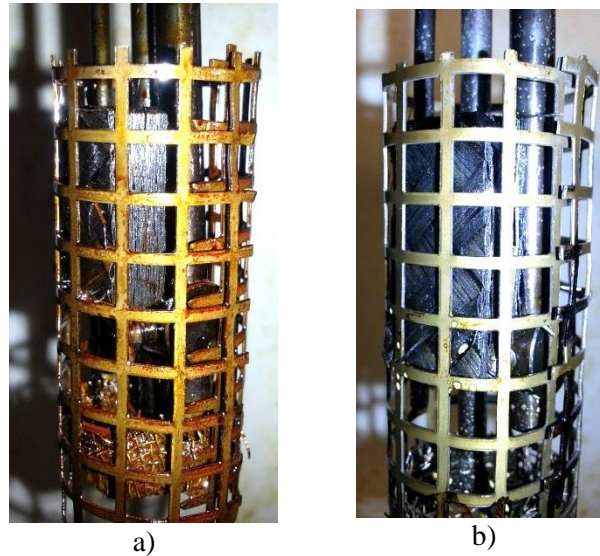


Figure 4: a) Basket and fibres coated by organic products after pure hydrolysis at 320 °C – 180 min (experiment # 6 in Table 1); b) Basket and fibres after solvolysis in the mixture of water and 80 vol.% acetone at 320 °C – 180 min (experiment # 17 in Table 2).

### 3.3 Scaling-up of the solvolysis process

The conditions of the experiment # 17 in Table 2 were used to solvolyse larger composite samples (50 x 50 mm<sup>2</sup> to 50 x 80 mm<sup>2</sup>) in a 5 L batch reactor (Figure 5a). In order to take into account the longer heating and cooling phases, the reaction time was set at 120 min instead of 180 min. About 100 g of fibres could be recovered after each experiment considering a resin concentration of 30 mg/mL and the experiment was repeated 6 times. The different plies were perfectly separated, not sticky and visually without any resin residue or organic contamination (Figures 5b and c). The woven architecture was also preserved. The amount of organic residue at the surface of the fibres was evaluated using a Soxhlet extraction method with acetone and led to a low value of 3 wt.% maximum. The fibres were analysed by scanning electron microscopy (SEM) and showed very clean surfaces without any washing (Figure 5d). No scale effects were observed and solvent diffusion and mass transfer did not seem to be affected by the size of the composite samples.

The recovered pieces of fabrics were then manually unwoven and the obtained carbon fibre tows were reused to manufacture a plate using random hand lay-up and manual impregnation with a commercial epoxy resin and vacuum moulding. The resulting plate gave a fibre content of about 50 wt.% and showed very encouraging results for further investigations (Figures 5e and f).

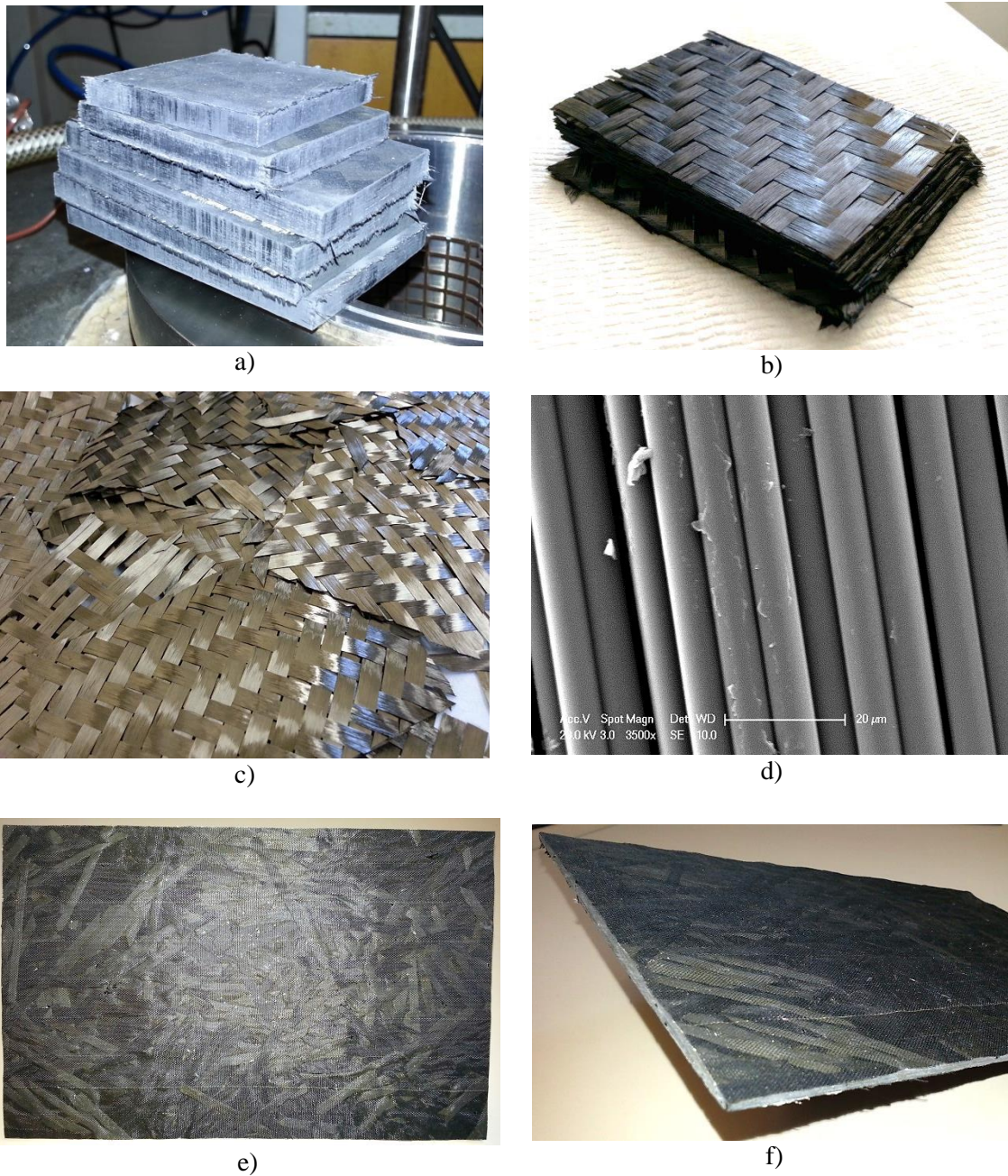


Figure 5: a) Samples of composite materials before treatment; b) One of the samples after the treatment; c) Carbon fibre plies after the treatment; d) SEM of unwashed carbon fibres recovered after the treatment; e) and f) Plate manufactured with recovered carbon fibre tows randomly distributed ( $265 \times 165 \times 3 \text{ mm}^3$ ).

#### 4 CONCLUSIONS

Different solvolysis technologies were applied to degrade a model epoxy resin. The results obtained led to the choice of suitable conditions in terms of efficiency while keeping the temperature and the pressure at reasonable values. These conditions, involving the mixture of water and acetone at 80 vol.%, were then applied to a commercial material typical of aeronautic applications. The good results enabled us to scale up the process to recover enough fibres for remanufacturing.

### ACKNOWLEDGEMENTS

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### REFERENCES

- [1] G. Oliveux, L. O. Dandy and G. A. Leeke, Current Status of Recycling of Fibre Reinforced Polymers: review of technologies, reuse and resulting properties, *Progress in Materials Science*, **72**, 2015, pp. 61-99 (doi: [10.1016/j.pmatsci.2015.01.004](https://doi.org/10.1016/j.pmatsci.2015.01.004)).
- [2] S. R. White, P. T. Mather and M. J. Smith, Characterization of the Cure-State of DGEBA-DDS Epoxy Using Ultrasonic, Dynamic Mechanical, and Thermal Probes, *Polymer Engineering and Science*, **42**, 2002, pp. 51-67 (doi: [10.1002/pen.10927](https://doi.org/10.1002/pen.10927)).
- [3] G. Oliveux, L. O. Dandy and G. A. Leeke, Degradation of a Model Epoxy Resin by Solvolysis Routes, *Polymer Degradation and Stability*, **In Press** (doi: [10.1016/j.polyimdegradstab.2015.04.016](https://doi.org/10.1016/j.polyimdegradstab.2015.04.016)).
- [4] G. Oliveux, L. O. Dandy and G. A. Leeke, A step change in the recycling of composite materials, *Proceedings of the 4<sup>th</sup> International Conference on Industrial and Hazardous Waste Management*, Chania, Crete, Greece, 2-5 September 2014.