

# A STEP CHANGE IN THE RECYCLING OF COMPOSITE MATERIALS

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## Abstract

*Solvolysis was applied to carbon fibres and an epoxy resin separately. Neat water as well as acetone, ethanol and 2-propanol were used neat or in mixture with water; neat water was also used expanded with carbon dioxide and oxygen and finally solvolysis assisted with ultrasound was tested. The comparison of the results showed that mixtures with water were more efficient than neat water and the other neat solvents. The best combination was acetone/water in ratio 8:2 in volume. However this did not enable to decrease the operating temperature below 350 °C, nor expansion of water with carbon dioxide and oxygen, and the pressure could reach up to almost 330 bar. Nevertheless complementary experiments are necessary to really assess the interest of those conditions. The fibres could be significantly affected by the conditions, the mixture acetone/water in ratio 8:2 being a good compromise.*

## 1. Introduction

Composite materials have been increasingly used for the last 30 years. They advantageously replace metals in many applications. However they have a major drawback, their recycling, in particular thermosets as their resins are infusible once polymerised. New European waste directives on landfill and incineration will put mounting pressure on these traditional disposal routes for composite materials. In order to comply with the legislations, manufacturers of composite products will need to have products for which real recycling solutions exist [1]. Several methods have been tried from mechanical grinding to thermo-chemical degradation of resins. Grinding the material to a recyclate that can be used as charge or partial reinforcement in other products leads only to a limited incorporation in new materials. Furthermore this technique is more suitable for glass fibre reinforced composites (GFRC). The potential commercial value of recycled carbon fibres (rCFs) have led to the development of technologies enabling their recovery. Thus pyrolysis and solvolysis have been investigated for the last 20 years and even reached industrial scale and are commercially exploited [2]. Pyrolysis requires temperatures above 450-500 °C to degrade resins and release the fibres, even for unsaturated polyesters [5]. Recycling of composite materials by solvolysis has been studied at ambient conditions but at high temperatures and pressures as well, above 300 °C and 50 bar generally for carbon fibre reinforced composites (CFRCs) in particular. GFRCs require at least 275 °C for a reasonable treatment time [6]. Otherwise catalysts are necessary to enhance the reaction at lower temperatures [7]. However this is not always efficient enough to justify the use of catalysts [6] or strong alkaline or acidic conditions are necessary leading to fibre damages [9]. At ambient conditions, the recycling treatment was realized in very strong conditions, mostly acidic with solutions that can be dangerous in terms of safety and

environment [10]. Supercritical fluids have also been considered [14], however this can lead to high conditions, in particular with water which is supercritical from 374 °C and 221 bar. At industrial scale, the reactors able to withstand such conditions become very expensive and might be damaged by acidic or alkaline or oxidant conditions, that are even more detrimental in high temperatures and pressures [18]. Those processes can also be energy consuming. In light of this, it appears to be necessary to try to lower the solvolysis temperature and pressure to more reasonable level. Thus different approaches have been tried in the work presented here. Solvolysis in neat water was compared to solvolysis in other affordable generally recognised as safe (GRAS) solvents, such as acetone, ethanol and 2-propanol (which is cheaper than 1-propanol), neat or in mixture with water. Supercritical fluids were reported to achieve efficient and fast resin degradations thanks to enhanced diffusion and mass transport, as they present a combination of liquid-like solvent power and gas-like transport properties [19]. In order to achieve similar physical state, gas-expanded liquid (GXL) technologies have also been considered in our work. Finally a novel solvolysis technology has been tested.

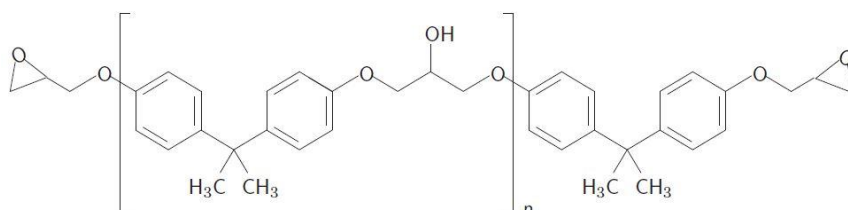
This paper thus presents significant results of experiments realised in the different conditions mentioned above. Our attention was first focused on carbon fibre/epoxy composites. Products of resin degradation were identified and recovered carbon fibres were characterised by mechanical testing.

## 2. Experimental

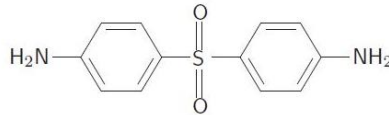
### 2.1. Materials

The epoxy resin used in the present work was based on diglycidyl ether of bisphenol A (DGEBA) prepolymer, Dow D.E.R. 332 from Sigma Aldrich (Figure 1), cured with the diamine 4,4'-diaminodiphenyl sulfone (DDS - Figure 2) also from Sigma Aldrich, in stoichiometric conditions. Those products were chosen to manufacture samples due to their common use in composite materials and the relative simplicity of the resulting network. D.E.R 332 epoxy prepolymer has a high purity with an epoxy equivalent weight (EEW) of 171-175 g/eq. The mixture was first heated up to 120 °C and stirred until a clear solution was obtained. Then it was poured into an aluminium container, which was beforehand coated with release agent (PVA Mould Release Agent from Easy Composites). The system was cured during 5 hours at 250 °C with a heating ramp of 1 °C/min. The samples 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 164 and 206 °C.

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. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) solution at 30wt.% was also produced in our laboratory and Carbon dioxide (CO<sub>2</sub>) was purchased from Air Liquid.



**Figure 1.** D.E.R. 332 DGEBA,  $n = 0.056$



**Figure 2.** DDS

The carbon fibres used were T700S from Torayca®. They were submitted separately to the same conditions as for the resin in order to avoid potential effect of composite manufacturing or post-processing.

## 2.2. Solvolysis experiments

The experiments were realised in a Parr Instrument batch reactor of about 115 mL. The resin or fibre sample was put in the vessel with the solvent at an initial loading rate of 0.5 (volume of solvent/reactor volume). The system was thus heated up to the desired temperature, which required about 24 min to reach 250 °C and about 53 min to reach 350 °C. After a chosen duration, the system was cooled down to ambient temperature by air convection and bath of tap water. The cooling phase required up to 80 min. Depending on the operating conditions, a residual pressure could be observed, indicating the production of gases during the solvolysis treatment. A first series of experiments was performed in neat water in different conditions as shown in Table 1 using a L9(3<sup>3</sup>) table. A second series of experiments was then realised with mixtures of water and GRAS solvents in the conditions of the Table 2 with the L9 table. Those were then completed to cover the whole range of mixture proportions for each solvent at 350 °C.

Levels	Temperature [°C]	Resin concentration [mg/mL]	Time [min]
1	250	10	0
2	300	30	30
3	350	50	60

**Table 1.** Conditions of solvolysis in neat water

Levels	Temperature [°C]	Solvent	Mixture [vol.%]
1	250	Acetone	0.20
2	300	Ethanol	0.50
3	350	2-propanol	0.80

**Table 2.** Conditions of solvolysis in mixtures of water and GRAS solvents, resin concentration = 30 mg/mL

Exploratory solvolysis in GXLs were realised with distilled water and either CO<sub>2</sub> or H<sub>2</sub>O<sub>2</sub>. For the experiments with CO<sub>2</sub>, the resin sample and water were loaded into the reactor and brought to the desired temperature. CO<sub>2</sub> was then injected at constant temperature causing a pressure increase only. For the experiments with oxygen, the resin sample, distilled water and H<sub>2</sub>O<sub>2</sub> were loaded into the reactor and brought to the desired temperature. The initial solvent loading rate was also 0.61. Three experiments were thus realised in the conditions described in Table 3. For those trials only, the system was stirred at 300 round/min.

Experiment	Temperature	Resin	Gas	Pressure
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#	[°C]	concentration [mg/mL]		[bar]
1	200	62.6	CO <sub>2</sub>	200
2	350	64.8	CO <sub>2</sub>	200
3	200	50.8	Oxygen	70

**Table 3.** Conditions of solvolysis in GXLs

### 2.3. Analysis of the recovered products

The liquid fractions recovered after solvolysis treatments were kept in fridge until their analysis by gas chromatography coupled with time-of-flight mass spectrometry (GC-TOF MS) in order to identify the products of the degradation reactions. Acetone was used to flush the reactor and recover products non-soluble at ambient temperature. A phase separation in the liquid fractions was also observed after a rest and left a deposit at the bottom. The deposit could be dissolved only by acetone. Those products were also analysed.

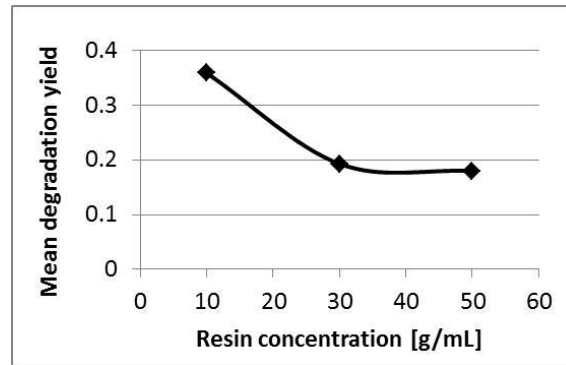
The tensile force of recovered carbon fibres was determined on fibre bundles by an own-developed method. Only conditions in which fibres could be released from the resin were considered.

## 3. Results and discussion

### 3.1. Comparison of the tested solvolysis systems

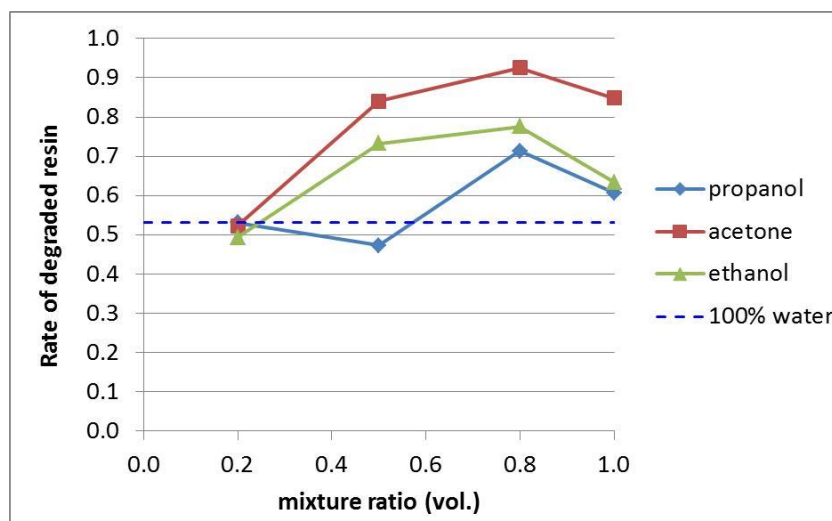
Solvolysis in GXLs was first compared to solvolysis in neat water in the same conditions (except the pressure which is induced by the solvent loading rate and the amount of gas injected or produced in-situ). Compared to those obtained with neat water, the results obtained with CO<sub>2</sub> at 350 °C did not show any positive effects. It was actually even worst as more partially degraded resin was found at the bottom of the reactor and coating the stirrer and the thermowell. Solid residues of resin were also found. The molar fraction of CO<sub>2</sub> was estimated to be about 0.07 [21]. At these temperature and pressure CO<sub>2</sub> was almost completely dissolved in water. Thus water was effectively expanded with CO<sub>2</sub>. At 200 °C in our conditions the molar fraction of CO<sub>2</sub> was about 0.83 and the solubility of water in CO<sub>2</sub> is less than 10% [21]. So water was actually not much expanded by CO<sub>2</sub>. The recovered resin sample did not seem to be degraded; no significant mass change was measured. Considering that the strong oxidant conditions might be detrimental to the reactor, oxygen-expanded water was tested only at 200 °C with a molar fraction of about 0.09 giving a pressure of 70 bar instead of 15 bar for neat water. The recovered resin sample did not show any mass change however its colour slightly changed on the surface indicating that it was a little oxidised. Nevertheless as the objective is to find low conditions to efficiently degrade an epoxy resin, those results do not show a significant improvement of the degradation thanks to expansion by gases. Further investigations with other solvents and gases are in progress in order to complete those preliminary experiments.

The influence of the resin concentration showed that the higher the concentration the less efficient the solvolysis (Figure 3). It might be due to a saturation of the medium. The limit value appeared to be 30 mg/mL. This value was then considered for the other experiments following. The influence of temperature showed that the degradation increased with increasing temperature. It also increased with increasing time at a given temperature until all the breakable bonds were broken.



**Figure 3:** Effect of resin concentration of the degradation yield.

The influence of the composition of the solvent finally showed that mixtures of water with a GRAS solvent were more efficient than neat water as well as neat GRAS solvent (Figure 4). The more efficient combination was water with 80 vol.% acetone in terms of degradation yield as well as in terms of dissolution of products. However this was true from 350 °C. At lower temperatures the degradation is not enhanced by mixtures. The mixtures from 50 vol.% were all supercritical at 350 °C with pressure of up to 330 bar and not lower than 200 bar. This state probably induced better solvent diffusion into the samples and mass transfers. However hydrolysis seemed to be the main solvolysis reaction and the more natural mechanism. The addition of a solvent to water did not allow the decreasing of the solvolysis conditions and could sometimes lead to a higher pressure than with neat water.



**Figure 4:** Effect of solvent composition on the rate of degraded resin at 350 °C during 30 min with a resin concentration of 30 mg/mL.

The GC-TOF MS analysis revealed that phenol is the major degradation products. Other products such as p-isopropylphenol, quinoline, anilines were also found. BPA was found in liquid fractions recovered from neat hydrolysis at temperatures lower than 350 °C. However in mixtures with GRAS solvents from 50 vol.% BPA produced by the reaction were more preserved and represented a major product. Thus a GRAS solvent as one of those used helps to limit secondary reactions. The analysis of the non-soluble residues led to identify the same products, indicating that the medium was saturated because of a lower solubility of those components at ambient conditions.

Results of experiments using the novel solvolysis method are presented during the conference.

### 3.2. Effect of the conditions on fibre properties

The results obtained for the fibres showed that below 350 °C no significant decrease of the strength was observed. However at 350 °C the fibres could be significantly affected, as shown on Figure 5. Mixture of ethanol with water at a volume ratio of 8:2 and neat 2-propanol were in particular very detrimental. If a composite made of the resin and the T700S fibres studied here is considered, the mixture acetone/water at a ratio of 8:2 seemed to offer a good compromise between resin degradation and fibre release and fibre integrity.

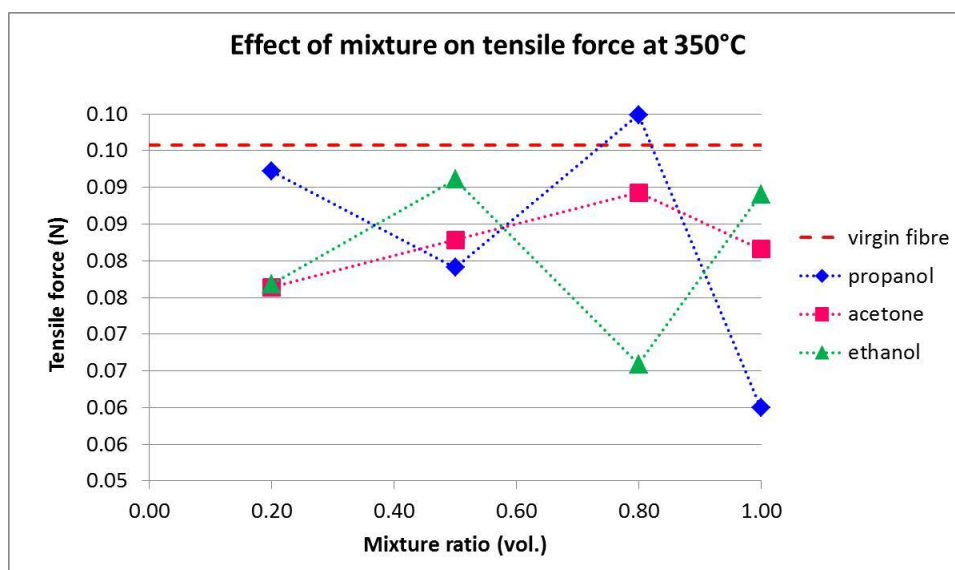


Figure 5: Tensile force measured on fibre bundles in different mixture conditions at 350 °C.

## 4. Conclusion

The recycling by solvolysis of carbon fibre reinforced epoxy resins has been studied by first considering the resin and the fibres separately. Different conditions using neat solvents or mixtures, with or without carbon dioxide or oxygen to expand the medium were considered. The results showed that it was not possible to lower the solvolysis conditions by adding a GRAS solvent to water. The enhancement of resin degradation by mixtures of water and GRAS solvents might be explained by the supercritical state induced by the mixture ratio. Thus it appears to be necessary to further investigate the gas expansion method as it could imitate the supercritical state inducing a better diffusion. The novel method showed very promising results. Thus a reactor integrating the new technology is currently tested and could

potentially significantly lower the solvolysis conditions, enabling thus a more cost-effective and greener process to recycling composites.

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