

RECYCLING OF AERONAUTICAL COMPOSITES BY SUPERCRITICAL SOLVOLYSIS

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ABSTRACT

Due to European legislation, recycling of composites is a true challenge that is faced by companies. Some results of thermochemical recycling of epoxy based composites from the aeronautical field, using a solvolysis process in water, are described in this paper. Experimental design was made in order to describe the significant process parameters, including temperature, time, and catalyst. Experiments were performed in a batch-type reactor avoiding any mechanical steering. The carbon fibers and other products were recovered. The results from the Scanning Electron Microscopy (SEM) and thermal analysis measurements showed that the fibers may be obtained clean. A comparative study of the appearance of carbon fibers recovered from solvolysis done in supercritical water and in subcritical water was conducted.

INTRODUCTION

Different technologies have so far been investigated for recycling thermoset composites and obtaining carbon fibers from scrap polymer composites. The main recycling strategy is to decompose the polymeric matrix by various methods, obtaining clean carbon fibers. The technologies currently studied can be sorted into 3 main categories. First, mechanical recycling [1], the aim of which is to reduce the size of the processed parts by grinding and reusing the crushed materials in other resins and concretes. Unfortunately, a significant drop in mechanical properties is often observed. So it is not seen as a viable recycling technology. Furthermore, other problems caused by grinding such as dust and its impact on the machinery and personnel health are also factors which need to be considered [2-3]. The second recycling route relies on thermal processes: In this case, several methods are used to separate resins from fibers at different temperatures, reaching 700 ° C, with different oxygen concentration, like pyrolysis, combustion, gasification, from neutral atmosphere to highly oxidative ones [4-7]. Allred *et al.* [8] have developed processes which allow pyrolysis to convert catalytically, at low temperature, a variety of polymers and composites used in automotive, electronics and aerospace in particular, so obtaining hydrocarbons of low molecular weight. These can then be used as chemicals or fuels. The other components, metal, fibers, fillers, are separated. The reactors are closed systems and therefore non-polluting: during the reaction, gaseous products are emitted, and condensed by condensers. The remaining gas can be used as a heat source for other reactors. Pickering *et al.* [9–10] studied a continuous thermal oxidative process using fluidized bed reactor which was developed to recycle carbon fiber/epoxy resin composites. The epoxy resin matrix was partially oxidized into gas products such as CO₂, CO, H₂, light aliphatic hydrocarbons and small amounts of aromatic hydrocarbons at using a very short residence time at 550°C [11]. Clean carbon fibers were then elutriated from the fluidized bed reactor. The obtained fibers showed about 80% of the original strength and their modulus

was not changed. Gasification [12] is a thermal conversion of the solid in a fuel material in the presence of a gas reactive element: air, CO₂, water vapor...to obtain fuel gas products composed mainly of carbon monoxide, hydrogen and nitrogen mixed with tar and ashes. This process takes place at temperatures from 900 to 1100 ° C with air and from 1000 to 1400 ° C with oxygen enriched air. The gasification process is a common and economic technique, emitting a relatively poor gas containing up to 60% nitrogen and showing a heat power of 4-6 MJ / m³.

The third type of recycling technology is the solvolysis process. Solvolysis is a process for which the solvent plays the role of reagent [13] which breaks the chemical bounds of the resin.

Low temperature solvolysis: In studies performed by Tersac *et al.* [14-15], on epoxy resins hardened by anhydrides, solvolysis was effective for many resins at 200 and 250°C under atmospheric pressure, but the reaction time was very long and expensive organic reagents limited the use of this technique for polymer recycling.

Under or sub critical Solvolysis: it is made below the supercritical conditions of the solvent used. Futamura [16] studied this method to process epoxy and ABS polymers containing flame retardants, which can be converted entirely into oil.

Supercritical solvolysis: In these conditions, water has characteristics very different from those experienced at room temperature, its dielectric constant decreases and its ion product increases three times, which leads to an improved solubility of organic compounds [17]. Hernanz *et al.* [18] used supercritical water to recycle carbon fibers/epoxy resin composites. The recycling was conducted at a temperature of 250–400°C, a pressure of 4–27.0 MPa and a reaction time of 1–30 minutes. The removal of epoxy was about 75%. With the addition of some alkali catalysts, about 95% of the epoxy resin could be removed. However, the tensile strength of the recycled fiber was reduced to 90–98% of the virgin one. It may be due to the effect of alkali catalyst at high pressure and temperature.

The AERDECO project aims at developing a new course to recycle aeronautical composites by solvolysis.

The objective of our work is to evaluate the recycled carbon fibers and to analyze the liquid phase obtained using sub and supercritical water solvolysis.

MATERIALS AND METHODS



Figure 1 : picture of the composite samples

The reactor is an autoclave of 587 ml in 316L stainless steel; its maximal temperature and operating pressure are 510 ° C and 275 bars. It is equipped with a vacuum pump, a hydraulic circuit for the injection of fluids. It is heated by electrical induction and cooled by air flow.

The composite studied is showed in Figure 1. It is composed of carbon fibers, fabric, metal grid and an epoxy resin, Hexplay 914TM, which is a mixture of two epoxy monomers: TGMDA (tetraglycidylmethylenedianiline) and TGPAP (triglycidyl-p-aminophenol) known for their mechanical performances, which explains their use in aeronautics. The efficiency of the reaction is evaluated using A200S-*F1 balance from Sartorius, the sensitivity of which is 10⁻⁴ g.

EXPERIMENTAL DESIGN

To get a first description of the process and according to the literature, we chose to study, on subcritical conditions, 3 factors on a two levels optimized experimental design: temperature, time of solvolysis and catalyst. The response studied is the percentage of degraded resin.

Table 1: Design of experiments: experimental factors

Factors	-1	+1
Temperature (°C)	300	340
Time (min)	8	15
Catalyst (NaOH, 0.01mol/l)	0	1

Based upon this first set of experiments, some other runs were performed to allow a kinetic description and a first comparison between sub and supercritical operating conditions. The conditions used are given in table 2.

Table 2: experimental conditions of the supercritical test

Temperature (°C)	Time (min)	Solvents	Catalyst (mol/l)	Y % Mass Degraded resin	Pressure (MPa)
380	8	H2O	0	37	225

RESULTS

1 On the first set of experiments

The experiments described in table 1 led to a pressure of 9MPa at 300°C and 15.5MPa at 340°C. They showed that:

-no loss of mass was observed when the temperature was 300°C and that no catalyst was used.

-the macroscopic aspect of the recovered fibers depends on the experimental conditions.

2 Comparison between sub and supercritical conditions

The pictures in Figure 2 show the recovered fibers in subcritical, when the solvolysis had been efficient, and supercritical conditions before and after being rinsed. With subcritical conditions the fibers are well separated while with supercritical conditions, the fibers stick together as small blocks showing the original layers of reinforcing fibers.



Figure 2: pictures of fibers in different conditions before and after rinsing, a) subcritical, typical aspect after an efficient resin solvolysis b)supercritical

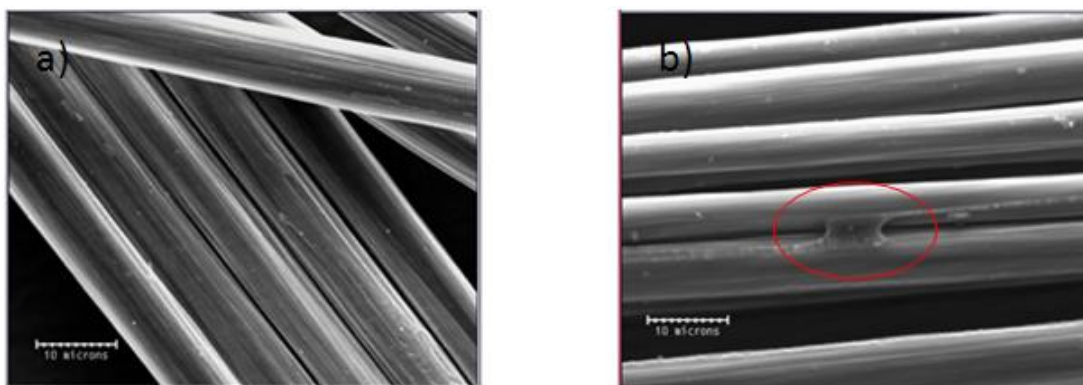


Figure 3: SEM micrographs of fibers obtained after solvolysis in: a) subcritical water, b) supercritical water. (CTTM le Mans)

Figure 4 shows the physical state of water during the two manipulations: we clearly see that in the experiment done under subcritical conditions, Figure 4-a), the composite always remains immersed in water with the presence of a small amount of steam. On the way to reach supercritical conditions, Figure 4-b), the water is in the vapor state only (brown line) for some time. The difference of state obtained using the two surrounding media in the two experiments is at the origin of the observed differences. The fibers can be separated or stacked together.

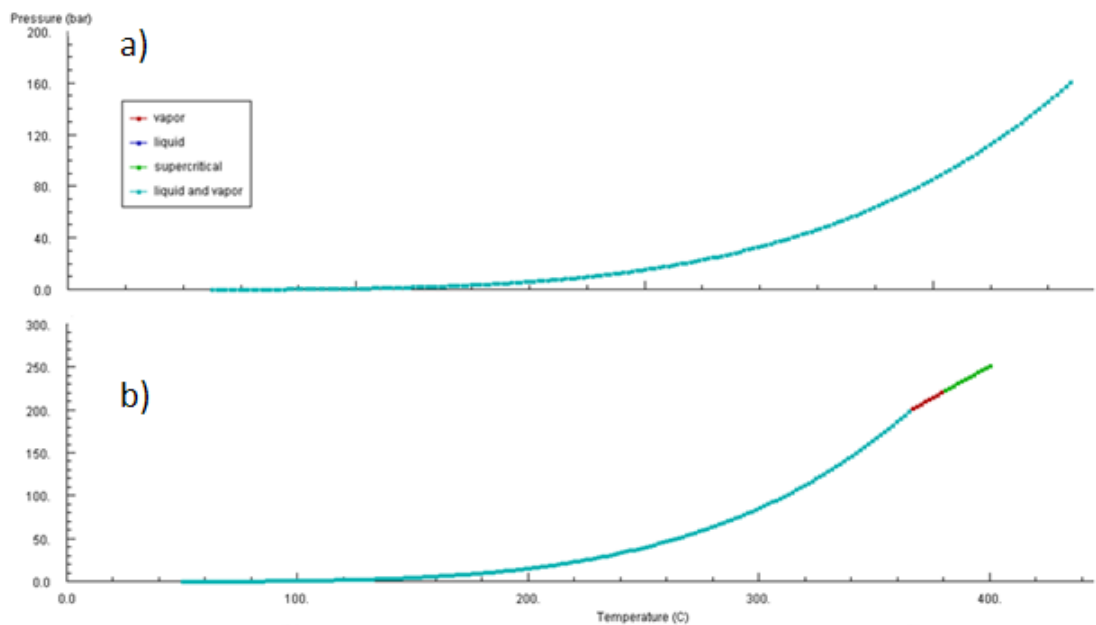


Figure 4: description of the physical state of water for both subcritical and supercritical manipulations (NIST national institute of standards and technology; CSTL chemical science and technology laboratory)

The fibers show different aspects depending on the conditions of reactive environments. Indeed, the AFM analysis micrographs on the surface of fibers, Figure 5, are a good tool to bring some information. The main difference is obvious in the phase images which show that the solvolysed fibers display a great phase lag, almost the same for the two processing conditions, and the virgin fiber a small phase lag. At this time, it is too early to know about the chemical or physical origin of this difference.

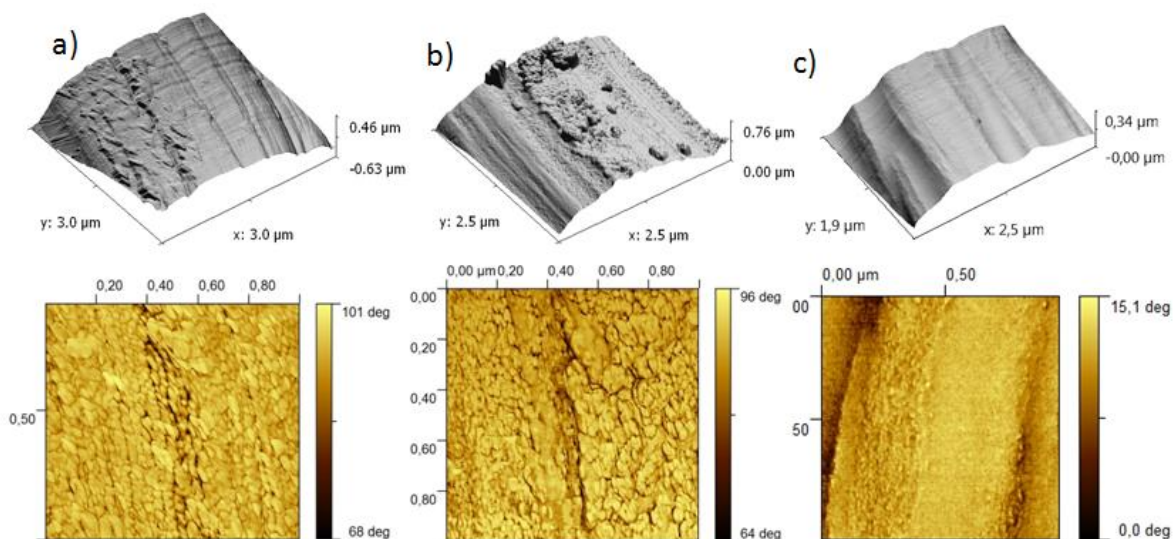


Figure 5: AFM micrographs analysis of fibers of subcritical solvolysis a), b) fibers of supercritical solvolysis, and the surface of virgin fibres c. (LPEC from Université du Maine and CTTM le Mans)

3 first approach of overall kinetic

The degradation of the resin occurs at the surface of the resin which binds the carbon fibers together.

The high temperature and high pressure degrade the resin in low molecular weight molecules which become soluble in water or form an organic phase insoluble in water.

A chromatographic analysis of the obtained organic products was performed. The results will be described in a further coming paper.

The kinetic depends, as usual, on temperature and time. We shall try to modelize it using a classical model.

The kinetic study is performed on a set of 17 experiments conducted on the range described in table 1.

Using a classical model, equation (1), to describe the observed results.

$$dW/dt = -k W^n \quad (1)$$

W is the percentage of remaining resin, k rate coefficient, n is the order of the reaction.

Integrating this equation for $n > 1$ and using an Arrhenian thermal dependence of rate of the reaction

$$W^{n-1} = W_0^{n-1}/1 - W_0^{n-1}.k.t \quad (2)$$

$$k = k_0 \exp(-Ea/RT) \quad (3)$$

Where k_0 is the pre-exponential factor, Ea is energy of activation, $W_0 = 1$ is the initial resin.

$$\ln W = (-1/n-1) * \ln(1 - k_0 \cdot \exp(-Ea/RT) \cdot t) \quad (4)$$

The figure 6 shows the results of fitting, with a nonlinear regression algorithm between $\ln W$ and the two independent variables, temperature and time.

The model suggests an energy of activation equal to 11826 (kJ/mol) and a pre-exponential factor equal to $-5.82 \cdot 10^{15}$. $a = -1/n-1$ is equal to -0.19, which gives an order of reaction of 6.26. The asymptotic errors are very small, likely due to the correlation between the parameters, see below, table 3.

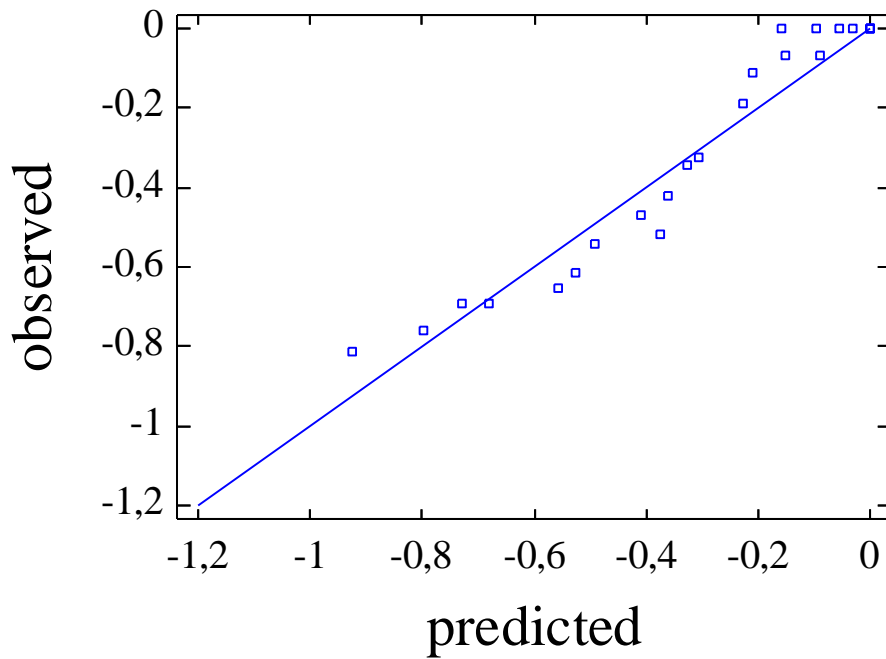


Figure6: fitting of a nonlinear regression model $\text{LnW} = f(\text{time}, \text{Temperature})$ (Eq(4)) , $R^2=93.8$

The table 3 shows estimated correlations between the coefficients in the fitted model.

Table 3: correlation matrix for coefficient estimates

	a	k	E
a	1.00	-2.79	-2.68
k	2.79	1.00	0.99
E	2.68	0.99	1.00

The numerical coefficients are highly correlated, so, the numerical values must not be considered as absolute measurements.

A further analysis of the residuals show that they are not randomly distributed, so the model can be improved or another model should be thought of to improve the description.

CONCLUSION

The main conclusion of this study is as follows: recycling of carbon fibers reinforced epoxy resin composites is feasible using subcritical conditions in water. An increase in temperature may lead to unseparated fibers, especially with the low amount of solvent needed to achieve the supercritical state. Work is still underway to identify and subsequently separate and recover different molecules obtained from solvolysis.

Kinetic and thermodynamic studies will be made to understand the behavior of this material and thermal exchanges occurring during the thermochemical reaction.

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