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Degradation of a model epoxy resin by solvolysis routes

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ABSTRACT

Different technologies based on hydrolysis were applied to degrade an epoxy resin model: CO_2-expanded water and generally recognised as safe solvents used neat or in mixture with water. The results showed that the degradation reaction can be enhanced thanks to the injection of CO_2 or the addition of a solvent generally recognised as safe, enabling supercritical fluids or enhanced fluidity liquids (resembling supercritical fluids) at lower temperature and pressure than for supercritical water.

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1. Introduction

Fibre reinforced thermoset composites are reported to be non-recyclable as they are infusible once they are polymerised. Currently, these materials are mainly landfilled, however this solution will become more expansive and is exacerbated by their environmental impact as these materials are not biodegradable. Raw materials to produce the resins and the fibres derive from fossil-derived resources. The production of these raw materials is also energy intensive as shown in Table 1. The recovery of valuable products from composite materials (fibres and organic compounds), for re-use 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, thermochemical methods have been considered to separate the fibres from the resin, which have largely focussed on pyrolysis [2—9] and solvolysis [9—44]. In pyrolysis, composite materials are heated up to 450—600 °C (depending on the nature of the resin) in absence or in presence of oxygen. The resin degradation produces oil, gases and chars that can lead to contamination of the remaining solid fractions (fibres and fillers if they are initially present in the material). The oil and gas products are mainly considered for energy recovery, the lowest level of the recycling hierarchy. The oil fraction contains valuable products with a composition that is too complex to cost-effectively separate them. The priority therefore in this method is to recover the fibres. In light of this, pyrolysis has been more applied to carbon fibre reinforced composites to reclaim carbon fibres that could compete with virgin fibres at a significantly lower price. The price of virgin carbon fibre is between 33 and 66 $/kg, whereas for pyrolytically recycled carbon fibre it is between 13 and 19 $/kg [45]. In the solvolysis method, a solvent medium is used to break the resin into low molecular weight products, and ideally into the monomers initially used to manufacture the resin [13—15,27,30,32,33,39,41,44]. According to the operating conditions (e.g. solvent selection, catalysts, temperature and pressure), it is possible to adjust the physicochemical properties of the medium and therefore to manage the involved chemistry to some extent. The system is heated to accelerate the reaction with the temperature reaching up to 450 °C depending on the resin to recycle, inducing a pressure of up to 250 bar. These conditions were achieved with water and alcohols to bring them in their supercritical state to enhance the diffusion and mass transfer [13—15,18,23,24,28,29,33,34,36]. However the reactors able to withstand such high conditions become very expensive due to the use of specialist steel alloy. The energy consumption at such high temperatures is high. Nevertheless, using solvolysis, it is potentially possible to decrease the treatment temperature in comparison to pyrolysis, and as a consequence the energy consumption. A classical way to reduce the reaction temperature is through the use of catalysts. Sodium or potassium hydroxide and hydrogen peroxide have been the most used catalysts to degrade more easily strong resins, such as epoxides [11,15,23,33,36,40]. An even more resistant resin, poly(etheretherketone) (PEEK), requires very harsh conditions

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Table 1
Energy intensity for the production of fibres and resins [1].

Material		Energy intensity for production (MJ/kg)
Resins	Polyester	63–78
	Epoxy	76–80
	PP	72–112
Fibres	GF	13–32
	CF	183–286
	Flax fibre	6.5
Metals	Aluminium	196–257
	Stainless steel	110–210
	Steel	30–60

typically using supercritical water (with temperature higher than 400 °C) [15], otherwise strongly acidic or alkaline conditions are necessary. On the other hand, polyester resins for example can be treated at less severe conditions [10,17,21,22,25,27,32,41] but the economic balance for the recycling of composites made with this type of resin is not satisfactory, as these materials are generally reinforced with glass fibres. Glass fibres recovered by these recycling routes are currently more expensive than virgin glass fibres [46]. On the other hand, virgin carbon fibres are valuable and therefore justify the application of solvolysis methods to recover them. The cost of their recovery can become very competitive to that achieved by pyrolysis, as it is largely dependent on the energy consumption, and as a consequence on the process temperature [47].

In light of this, the objective of the work in this article is to propose new approaches based on solvolysis technologies to recycle thermoset composite materials with improved environmental and economic impact. Chemical reagents generally recognised as safe (GRAS) have been selected to deconstruct different resins. The results obtained for mixtures of solvents and gas-expanded liquids (GXLs) are presented and compared to the reference solvolysis process based on water. In order to separate the problems and to ease the understanding of the involved chemistry, a model epoxy resin was studied as the formulation of commercially available resins is not readily disclosed, and without reinforcement (no fibre effect).

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 (Fig. 1), cured with diamine 4,4′-diamonodiphenyl sulfone (DDS – Fig. 2) 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
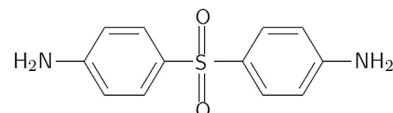

Fig. 2. DDS.

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 h 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 [48]. Fig. 3 shows the molecular structure of the obtained resin after curing.

A composite was manufactured with seven plies of carbon fibre fabrics made of Grafil Inc. Pyrofil™ TR30S 3K and EL2 epoxy resin cured with AT30 hardener from Easy Composites. The resin is a mixture of bisphenol-A and bisphenol-F. The hardener is based on diamines and bisphenol-A.

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_2) was purchased from BOC Industrial Gases (purity 99.9% v/v). Phenol (crystalline solid, ReagentPlus®, purity ≥ 99%) was purchased from Sigma Aldrich.

2.2. Reactor and experimental methodology

The 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 min to reach 250 °C and about 53 min to reach 350 °C. After a desired time, the system was cooled down to ambient temperature by
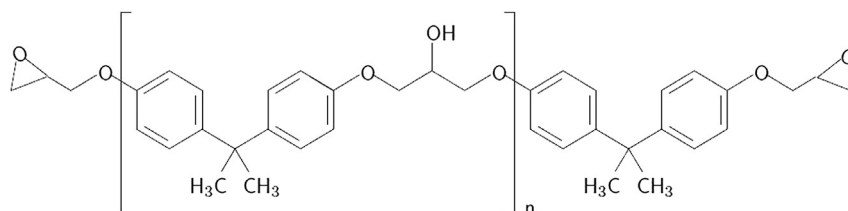

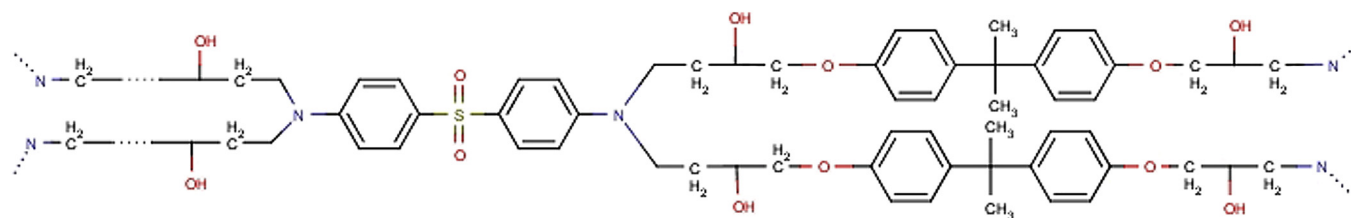**Fig. 1.** D.E.R 332 DGEBA, n = 0.056.

Fig. 3. Structure of the resin after polymerisation.

forced air convection and then by a water bath when the temperature was below 100 °C. The cooling phase required up to 80 min from 350 °C. Depending on the operating conditions, a residual pressure could be observed, indicating the production of gases during the solvolysis treatment. 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_2, the reactor was first pressurised with CO_2 to the desired initial pressure before heating. A blank test was first undertaken to measure the amount of gas injected.

2.3. Analysis

The liquid fractions recovered after solvolysis were analysed by a Waters Corporation gas chromatography coupled with time-of-flight mass spectrometry (GC-TOF MS, model Waters Micromass GCT Premier) with either an HP-5MS or a ZB-WAX column in order to identify the products of the degradation reactions using the library software *NIST MS Search 2.0*. Deposition of the non-soluble reaction products at room temperature or those that exceeded their solubility limit were dissolved in acetone before being subjected to the same analysis.

$$mean\ R\% = \frac{R\%\left(10\frac{mg}{mL}, 0\ min\right) + R\%\left(30\frac{mg}{mL}, 30\ min\right) + R\%\left(50\frac{mg}{mL}, 60\ min\right)}{3} \tag{2}$$

2.4. Solvolysis operating conditions

Three different solvolysis methods were used to degrade the epoxy resins: either pure solvent, two-solvent mixtures or CO_2-expanded solvent using the conditions shown in Table 2. The reference solvent was water, of which the efficiency was compared to the other systems. A first series of experiments was performed in water, using a $L_9(3^3)$ orthogonal array, at the conditions shown in Table 3 (experiments # 1–9). A few additional experiments were realised according to the conditions given in Table 3. A second series of experiments, using a $L_9(3^3)$ orthogonal array, was then realised with mixtures of water and a GRAS solvent, such as acetone, ethanol and 2-propanol; the mixture proportions and the solvolysis conditions are given in Table 4 (experiments # 31–39). Water and mixtures of water and acetone at 80 vol.% expanded by CO_2 were also considered.

A total of 52 experiments were realised. For each experiment, the degradation rate R% was determined using Equation (1). Only those presenting significant results are given in Tables 3 and 4.

$$R\% = \frac{initial\ mass - remaining\ mass}{initial\ mass} \times 100 \tag{1}$$

3. Results and discussion

3.1. Water experiments: effect of the temperature, time and resin concentration

The effects of temperature, time and resin concentration were determined in water alone. For this purpose, the results of the first series of experiments (experiments # 1 to 9 in Table 3) were treated with the statistical analysis software *Minitab 16.2.2* to evaluate the influence of the parameters on the response "mean degradation rate". The mean degradation rate R% is calculated at each parameter level with the other parameters varying as illustrated by the Equation (2) for the temperature at a level of 250 °C.

The results are shown in Fig. 4. They indicate that the degradation rate increased for both increasing temperature and time and decreased with increasing resin concentration. This might be due to a saturation of the solvent medium with degradation products. The maximum resin concentration of 30 mg/mL was therefore considered for all the other experiments.

In water alone, the model epoxy resin is almost completely degraded after 1 h at 350 °C for a resin concentration of 10 mg/mL, whereas at 300 °C the solvolysis rate reached only 23% after 1 h for a resin concentration of 30 mg/mL (experiments # 5 and 7 in

Table 2
Conditions of solvolysis.

|	Pure water	Mixtures water + GRAS solvent	CO_2 expanded liquids
Temperature (°C)	250, 300, 350	250, 300, 350	200, 250, 300
Time (min)	0, 30, 60	30	30
Resin concentration (mg/mL)	10, 30, 50	30	30
Mixture proportions	0	0.2, 0.5, 0.8, 1	0
Initial pressure	0	0	35 or 50 bar

Table 3
Conditions and results of hydrolysis experiments.

Exp. #	Gas and additives	Measured P_0 (bar)	Measured T (°C)	Measured P (bar)	t (min)	[Resin] (mg/mL)	R% (±1%)
1	No	0	250	35	0	10	0
2					30	30	1
3					60	50	1
4			300	80	30	10	23
5					60	30	23
6					0	50	0
7			350	155	60	10	84
8					0	30	34
9					30	50	53
10			325	114	120	50	43 (stirring)
11			325	115	120	50	52 (no stirring)
12	CO_2	35	300	81	30	30	Model resin: 39
							Composite: 65
13		35		82	30		20
14		50		90	30		14
15		35		81	60		41
16		35		81	60		27
17		35		82	120		51
18	Phenol 1 g/L	0	300	81	30	30	14
19	CO_2 Phenol 1 g/L	35		82			11
20	Phenol 10 g/L	0		81			11
21	CO_2 Phenol 10 g/L	35		83			18

Table 4
Conditions and results for experiments realised with GRAS solvent mixtures, time = 30 min and resin concentration = 30 mg/mL.

Exp. #	Solvent	Proportion (vol.%)	Measured T (°C)	Measured P (bar)	R% (±1%)
31	Acetone	0.5	250	114	−6
32		0.8	300	145	−6
33		0.2	350	156	52
34	Ethanol	0.8	250	82	−5
35		0.2	300	90	6
36		0.5	350	81	73
37	2-propanol	0.5	250	82	−1
38		0.8	300	81	3
39		0.2	350	83	72
40	Acetone	0.8	350	235	93
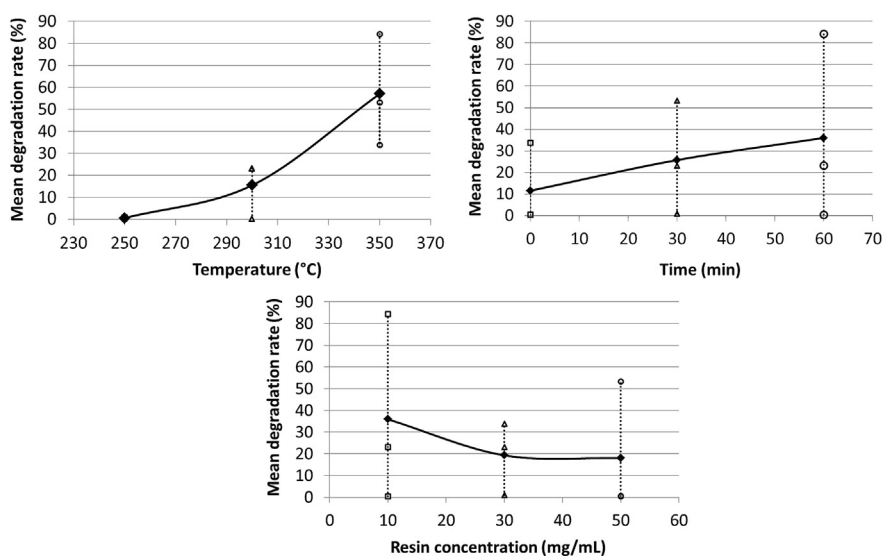
Fig. 4. Effects of temperature, time and resin concentration on the degradation rate.
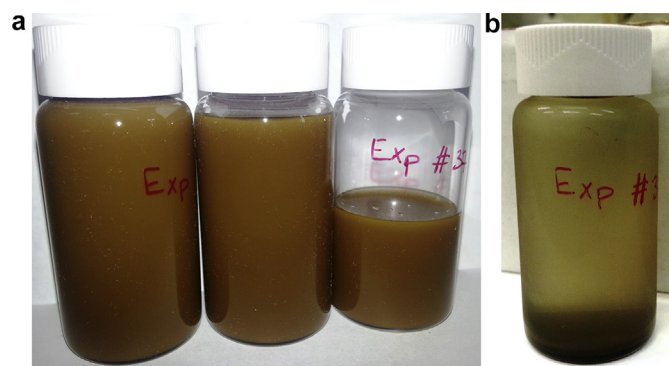
Fig. 5. Liquid fractions recovered after the experiment # 7 (conditions given in Table 3): a) right after the experiment; b) 20 days after the experiment.

Table 3). Furthermore, the solvolysis rate reached about 53% at 350 °C after 30 min with a resin concentration of 50 mg/mL (experiment # 9 in Table 3). A good compromise between time and temperature in water is apparent therefore in the range of 350 °C and 1–2 h with a resin concentration of 30 mg/mL. When the system is cooled after reaction, the solubility of some reaction products in water decreases, resulting in a dark sticky substance that would coat the fibres if an actual composite sample was used. A post-treatment step would be necessary to wash and recover the fibres.

The effect of the stirring was measured at 325 °C (experiments # 10 and 11 in Table 3) and showed that the stirring of the medium is detrimental to the resin degradation. The small molecules produced by bond breaking in the resin structure transfer towards the medium. When the medium is not stirred the local concentration of these molecules (around and into the sample) is high and creates a potential gradient, which tends to establish a constant out-of-equilibrium state at the solid/liquid interface. This gradient is the driving force of the mass transfer. When the medium is stirred, the concentration of the molecules transferred into the medium is uniformed and becomes constant at every points of the medium but evolves according to time. Therefore no gradient is observed at the solid/liquid interface and the mass transfer is not enhanced.

Table 5
Products identified by GC-TOF MS in the organic fractions recovered by hydrolysis at 350 °C, 156 bar during 60 min (experiment# 7 in Table 3 and Fig. 6) and by hydrolysis in the presence of CO_2 at 300 °C, 82 bar during 30 min (experiment # 13 in Table 3 and Fig. 7).

Peak #	Product name
1	Aniline
2	Quinoline
3	Phenol
4	Phenol, 4-(1-methylethyl)-
5	Phenol, 4-ethyl
6	Phenol, 3-(1-methylethyl)-
7	2H-1-benzopyran-3-ol, 3,4-dihydro-
8, 15	Amine derivatives
9	1,2-propanediol, 3-phenoxy
10	p-hydroxybiphenyl
11	Phenyl amine derivative
12	Phenol derivative
13	2-propanol, 1-phenoxy-3-(phenylamino)-
14	1H-indole, 2,5-dimethyl

At the end of the hydrolysis experiment, a residual pressure could be observed depending on the reaction conditions. The smell of the released gas was characteristic of hydrogen sulphide, indicating that the SO_2 bonds in the resin were hydrolysed (Fig. 3). The recovered liquid fraction had a yellow-orange colour and was more or less opaque depending on the reaction conditions (Fig. 5a). After some rest days, a deposit was observed at the bottom of the bottles (Fig. 5b), which is thought to be due to a combination of the insolubility of some reaction products at room temperature and to saturation of water with soluble products. The analysis of the chemical composition of both fractions (liquid and deposit) identified, apart from hydrogen sulphide, mainly two families of products: phenolic compounds, produced by the degradation of the epoxy pre-polymer, and amine compounds, produced by the degradation of the curing agent (Fig. 6 and Table 5). Bisphenol-A (BPA) can be recovered at lower temperature (250 and 300 °C) but it was completely degraded after 60 min at 350 °C. BPA is toxic and eco-toxic however, and might not be a desirable reaction product as it would be hard to reuse directly in new resin.
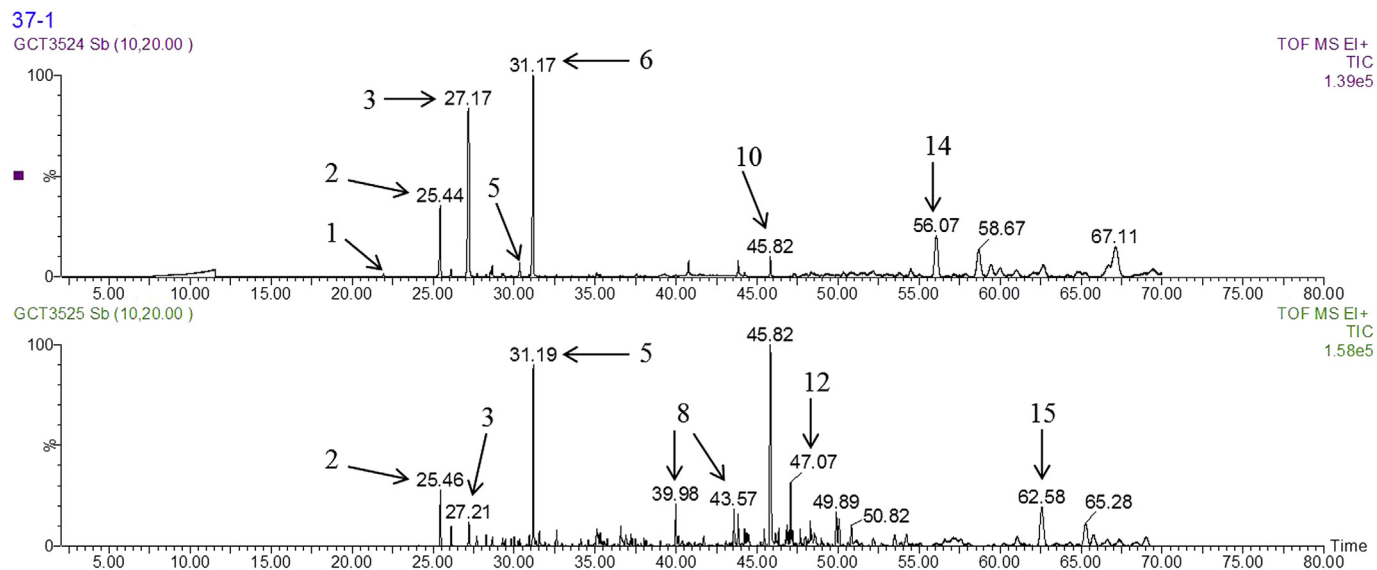

Fig. 6. Chromatograms of the liquid (top image) and deposit (bottom image) fractions recovered from experiment # 7 (conditions shown in Table 3). The relating product names are given in Table 5.
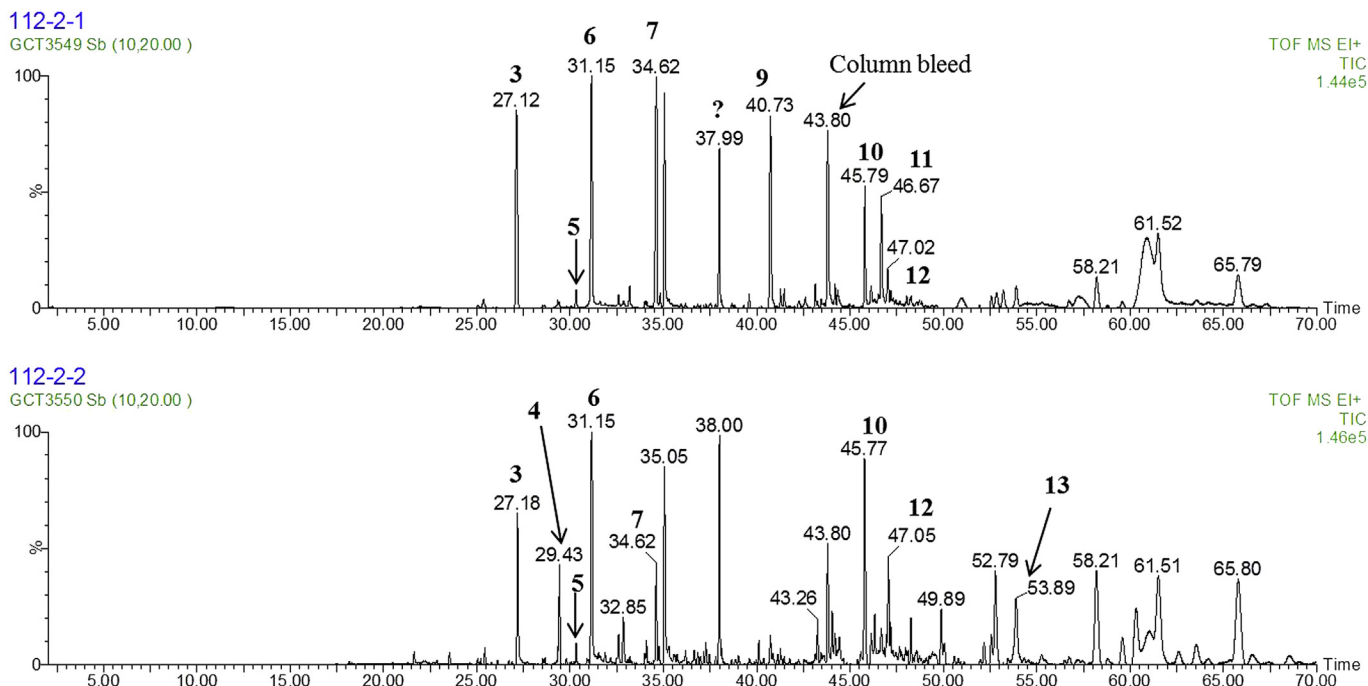
Fig. 7. Chromatograms of the liquid (top image) and deposit (bottom image) fractions recovered from experiment # 13 (conditions shown in Table 3). The relating product names are given in Table 5.

3.2. Efficiency of CO2-expanded water

The water-CO_2 system is considered as an enhanced fluidity liquid rather than a gas-expanded liquid due to the high temperature and pressure used in the present work [49]. It resembles a supercritical fluid and therefore shows similar properties (low viscosity, high diffusion and mass transfer). This solvent system was chosen because it could create supercritical-like water at significantly lower temperatures and pressures thanks to the low critical point of CO_2 (31 °C, 74 bar and 467.6 kg/m^3). The results show that the injection of CO_2 enhanced the resin degradation compared to neat water solvolysis at the same temperature (experiments # 5 and 15 in Table 3). On the other hand, it seems that increasing the amount of CO_2 decreases the degradation rate (experiments # 13 and 14 in Table 3). The chromatograms of the liquid fraction and of the deposit dissolved in acetone indicate that the composition is similar to that obtained for the fractions recovered after neat hydrolysis, although more complex (Figs. 6 and 7).

Following an experiment realised on the model epoxy resin and the composite made with the commercial epoxy resin EL2-AT30 and Pyrofil™ TR30S carbon fibres together (experiment # 12 in Table 3, the overall resin concentration kept at 30 mg/mL), a higher degradation rate of the model epoxy resin was observed compared to the model resin alone. A higher phenol production was also obtained possibly caused by a combined catalytic effect with phenol. This was evaluated by measuring the effect of CO_2 and phenol separately and combined (experiments # 13, 14, 18, 19, 20 and 21 in Table 3). The degradation rates indicate that a combined effect exists between CO_2 and phenol as shown by Fig. 8. The resin degradation was almost doubled when the phenol concentration was increased from 1 to 10 g/L in the presence of CO_2. As phenol is produced during the reaction, the liquid fraction recovered after experiment # 15 was reused to solvolyse a new resin sample under the same experimental conditions (experiment # 16). The results in Table 3 indicate that the resin degradation was significantly lowered despite the presence of phenol in the reused liquid fraction.

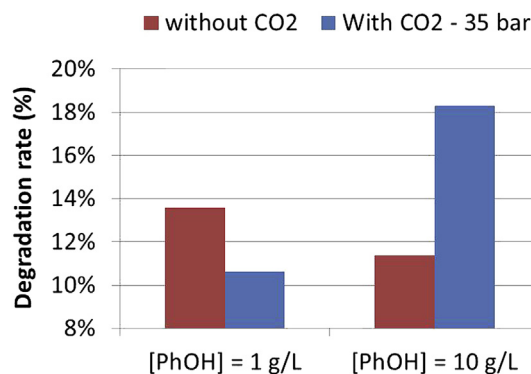**Fig. 8.** Interaction effect between CO_2 and phenol during hydrolysis at 300 °C for 30 min with a resin concentration of 30 mg/mL (experiments # 18 to 21 in Table 3).
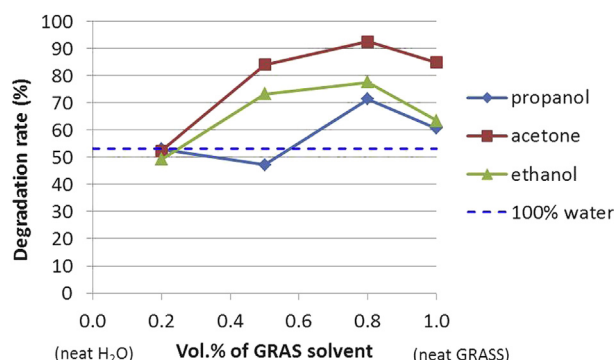

Fig. 9. Effect of the mixture proportion on the degradation rate at 350 °C.
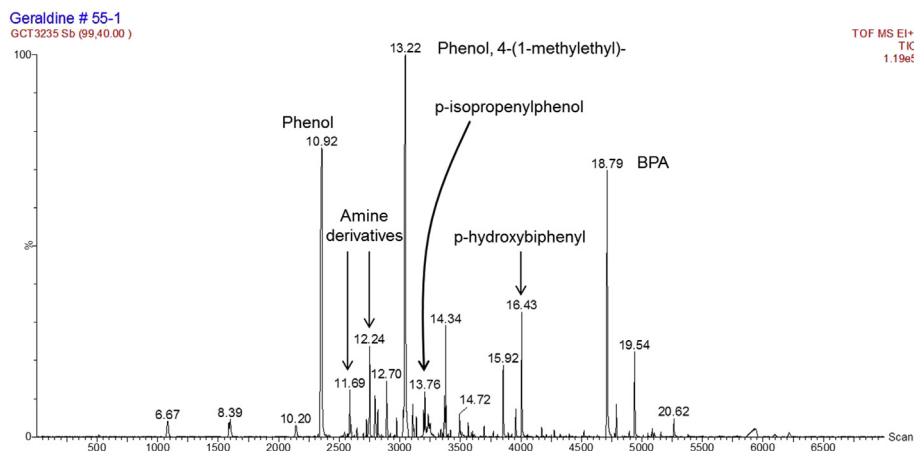
Fig. 10. Chromatogram of the liquid fractions recovered from experiment # 40.

This might be due to its saturation with the various reaction products. Furthermore the liquid fraction recovered after experiment # 15 still contained some dissolved CO_2 and was then enriched by more CO_2 to realise experiment # 16. This may also explain the negative effect on the degradation rate, considering the results obtained for experiments # 13 and 14 in Table 3.

Instead of adding phenol to the solvent system, it might be of interest to solvolyse phenolic and epoxy resins together in order to benefit from the combined effect between injected CO_2 and phenol produced by the degradation of the phenolic resin.

The CO_2-expanded water system seems therefore to be a promising technology to recycle composite materials more efficiently than with neat water at low CO_2 initial pressure.

3.3. Solvent mixture experiments

A comparison of the results obtained for pure hydrolysis and for solvolysis in mixtures of H_2O-GRAS solvents (Tables 3 and 4) shows that the addition of a GRAS solvent led to a higher solvolysis rate at 350 °C, when the added solvent was ethanol or 2-propanol. This was further investigated by undertaking a series of experiments in different solvent mixtures over a range of solvent volume proportion at 350 °C. The results shown in Fig. 9 indicate that the best mixture is water and acetone at 80 vol.%, leading to a degradation rate of 93% after 30 min at 350 °C. This means that the treatment time can be halved in comparison to neat water. A second advantage is that the reaction products are completely soluble in the mixture, even at room temperature, due to the presence of acetone.

The addition of a GRAS solvent did not to seem to accelerate the reaction, however it helps to lower the critical point of the solvent system compared to pure water. Values found in the literature [50] indicate that all the mixtures were supercritical at 350 °C and that all the mixtures at 80 vol.% were supercritical at 300 °C. The increased resin degradation of these systems compared to pure water is assumed to come from the enhanced diffusion and mass transfer from the supercritical state of the fluids. However, it can be observed that, when pure GRAS solvents were used, the degradation rate decreased compared to the mixtures at 80 vol.%. This would infer that the preferred reaction pathway is hydrolysis. Molecules of water and its ions are smaller than that of the GRAS solvents used and would therefore diffuse more easily in the resin.

Negative degradation rate were observed after a treatment at 250 and 300 °C, the samples were therefore heavier after solvolysis. As the final mass of the samples were measured after drying at 70 °C until no mass change was observed, this mass uptake can be explained by solvent molecules chemically bonded to the resin chemical structure.

The GRAS solvents used are assumed to be co-reactants as the resin degradation occurs in pure GRAS solvent as well. Further investigations are needed to understand the chemistry involved in presence of these GRAS solvents, and acetone in particular.

The liquid fraction recovered from experiment # 30 with 80 vol.% of acetone, at 350 °C, 30 min and a resin concentration of 30 mg/mL (Table 4) was analysed by GC-TOF MS and gave the chromatogram shown in Fig. 10. Similar products were recovered as with neat water, except that BPA can be recovered at 350 °C when acetone is added. Secondary reactions degrading BPA into other phenolic compounds seem therefore to be limited due to the presence of acetone. Similar observations were obtained with the two other GRAS solvents (ethanol and 2-propanol).

4. Conclusion

Different solvolysis technologies were applied to degrade a model epoxy resin. The results from the different GRAS solvents and their mixtures were compared to those solely obtained by reference neat water solvolysis. They indicated that CO_2-expanded water and a mixture of 80 vol.% acetone and water, in particular, were promising solutions to enhance resin degradation. The addition of either CO_2 or GRAS solvent to water produces either an enhanced fluidity liquid (similar to supercritical fluids) or a supercritical fluid by lowering the critical point of the solvent medium respectively, therefore improving diffusion and mass transfer compared to subcritical water. Furthermore, it seems that CO_2 acts as a catalyst in combination with the phenol produced by the resin degradation. On the other hand, GRAS solvents seem to act more as co-reactants and improve the solubilisation of the reaction products. Recovered fibres would therefore be less contaminated by resin residue. The analysis of the composition of the liquid fractions indicated that valuable products, such as phenol, can be recovered. Hydrolysis appeared to be the more obvious reaction pathway. Further investigations are in progress to understand better the chemistry involved in the degradation of epoxy resins, as well as experiments on real composite materials to assess the fibre integrity.

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