



## Recycling of glass fibre reinforced composites using subcritical hydrolysis: Reaction mechanisms and kinetics, influence of the chemical structure of the resin

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### ABSTRACT

Hydrolysis in batch conditions was used to recycle composite materials reinforced with long glass fibres and made of unsaturated polyester resin cross-linked with styrene. Subcritical conditions of water (200 °C < temperature < 374 °C and pressure < 221 bars) were chosen regarding the involved chemistry for the case of simple esters. Experiments performed in light and heavy water confirmed the specific acid catalysis of the hydrolysis of ester bonds ( $k_{H_2O}/k_{D_2O} < 1$ ), indicating that it can be described by the A<sub>ac</sub>2 mechanism identified for simple esters. The hydrolysis kinetics was thus defined for three widespread commercial resins and showed a good fit to the experimental data. Secondary reactions like decarboxylation of carboxylic acid and dehydration of glycol were also described in terms of mechanisms and kinetics. They also showed a specific acid catalysis.

The obtained results enabled the definition of smooth conditions for the recovery of valuable products. They also showed that the chemical structure of the resin has an influence on the kinetics of hydrolysis but also on the kinetics of the main secondary reactions. However iso- and ortho-phthalic polyesters could be treated together.

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### 1. Introduction

The production of glass fibre reinforced composites (GFRP) reached about 1.2 million tons in 2007 in Europe, and about 1.6 million tons in the United States [1]. Environmental legislation like the EU-directives (99/31/EC, 2000/53/EC, 2002/96/EC and 2008/98/EC) causes increasing demand for recycling techniques that realise true material recycling [2].

Among the most studied techniques like thermolysis [3,4], grinding [5], and solvolysis [6–10], hydrolysis appears to be a potential technique as it enables the recovery of fibres and valuable products from the depolymerisation of the resin [11]. Furthermore water is inexpensive, ecological and easy to handle. Because its physico-chemical properties change with the operating conditions (temperature, pressure and volume), it is said to be an adjustable solvent [12]. Depending on the conditions, high-temperature water can support ionic, polar non-ionic or free-

radical reactions [13]. It appears then necessary to know the involved chemistry in order to define the appropriate reaction environment provided by high-temperature water.

The depolymerisation of unsaturated polyesters has been studied in different solvents and conditions [6,9,10,14,15], but without considering the chemistry involved during the process. Esters are known to be hydrolysable and it is generally believed that all ordinary esters hydrolyse by an A<sub>ac</sub>2 pathway [16]. This is actually the reverse reaction of esterification. The mechanism of hydrolysis has been studied on several simple esters, as model molecules, in near-critical water [17,18] and in supercritical and liquid subcritical water [19]. Krammer and Vogel [19] showed that in liquid subcritical conditions, hydrolysis of ethyl acetate followed an A<sub>ac</sub>2 mechanism, considering the obtained S-shaped curves for data measuring conversion versus time and the negative volume of activation obtained in the temperature range from 250 to 350 °C. Lesutis and co-workers [17] added the argument that the addition of electron-withdrawing substituents on benzoate ester did not affect reaction rate to confirm the A<sub>ac</sub>2 mechanism. The first step of this mechanism is the protonation of the ester by a hydronium ion to give a carbocation. A subsequent rate determining step consists of the attack of the protonated ester by two molecules of water, one

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acting as a nucleophile and the second assisting in dispersing the positive charge on oxygen in the transition state [16]. The objective of this work was to verify whether the hydrolysis of cross-linked unsaturated polyesters can be described by such a mechanism despite the size of the polyester chains, to define the kinetics and to observe the influence of the experimental conditions. As mentioned in a previous article [11], the products recovered from the polyester resin contain the monomers of the resin, indicating that ester bonds are broken. But secondary reactions also occur in parallel and lead to a degradation of those main products. The objective of this work was also to describe the mechanisms and the kinetics of the main secondary reactions, and to observe the influence of the experimental conditions.

Furthermore depending on the application, many different types of GFRC exist, in particular with different formulations of resins. Because of this wide variety, the recycling of GFRC can become even more complicated. In the case of hydrolysis at high temperature and pressure, the problem can come from different chemical mechanisms and kinetics. For this reason, mixture of composites made of different types of resin like epoxy, polyester or thermoplastic may not be possible. It will then be necessary to classify the resins according to their chemical mechanisms and kinetics of degradation. Among GFRC made of unsaturated polyester resin, orthophthalic polyesters are the most widespread but the use of isophthalic polyesters is not negligible, particularly in applications like swimming pools or boating industry. Hand layup processes are also more and more replaced by closed mould processes like resin-transfer moulding (RTM) and infusion, which use specific resins like dicyclopentadiene (DCPD)-based polyester for example.

The second objective of this work was thus to evaluate the possibility of mixing those most used unsaturated polyesters in a same batch for recycling by hydrolysis. Considering that they hydrolyse by the same mechanism, the hydrolysis kinetics was evaluated for three commercial polyester resins, as well as the kinetics of the main secondary reactions in order to determine the influence of the composition and the chemical structure.

## 2. Material and methods

### 2.1. Glass fibre reinforced composite material

The composite samples were taken from plates made by contact moulding. The plates were realised with 5 plies of Rovimat 500 T2/300 from Chomarat. Each ply is constituted of one layer of taffeta with a weight of 500 g/m<sup>2</sup> and one layer of mat with a weight of 300 g/m<sup>2</sup>. The plies were impregnated with three commercial pre-accelerated resins, giving three plates. The first resin, named resin A, contains an unsaturated polyester prepolymer made of propylene glycol (PG), phthalic anhydride (OPAA) and maleic anhydride (MAA), dissolved in 41 wt% styrene. The molecular mass of the prepolymer chains is 1384 g/mol. The theoretical structure of the prepolymer chains based on the initial monomers is shown on Figure A.1 in Appendix A. The second resin, named resin B, contains an unsaturated polyester prepolymer made of PG, isophthalic acid (IPA) and MAA, dissolved in 46 wt% styrene. The molecular mass of the prepolymer chains is 2322 g/mol. The theoretical structure of the prepolymer chains is shown on Figure A.2 in Appendix A. The third resin, named resin C, contains an unsaturated polyester prepolymer made of PG, diethylene glycol, OPAA, MAA and dicyclopentadiene (DCPD), dissolved in 37 wt% styrene. The molecular mass of the prepolymer chains is 906 g/mol. The theoretical structure of the prepolymer chains is shown on Figure A.3 in Appendix A.

For each resin, the cross-linking with styrene was realised at ambient conditions during 24 h, followed by a post-cure of 16 h à 40 °C. The initiator used was Luperox<sup>®</sup> K1. The resin content was evaluated for each plate by calcinations following the recommendations of the standard NF T 57 102. The plate thus contained (40.5 ± 0.3) wt% resin, the plate made of resin B (39.0 ± 0.5) wt% and the plate made of resin C (36.9 ± 1.4) wt%.

Data about the formulation of each resin (not detailed here because of confidentiality) enabled to calculate, for a given mass of resin, the number of moles of each monomer, the number of moles of ester bonds and the number of moles of chain ends. Those quantities were then used to study the reaction kinetics.

### 2.2. Subcritical hydrolysis treatment

The experiments were realised in a small batch reactor of about 28.8 mL. The latter was made up of a Swagelok<sup>®</sup> connector SS-16-VCR-6-DM and two Swagelok<sup>®</sup> caps SS-16-VCR-CP, each equipped with a stainless steel gasket SS-8-VCR-2. One of the two caps was instrumented with three K-Type thermocouples. This enabled the measurement of the temperature in the vapour phase, in the liquid phase and at an intermediate position depending on the initial volume of water. Distilled water from Labogros-Grosseron was used but also heavy water from Sigma–Aldrich. Once loaded with water and a composite sample, and closed, the reactor was immersed in a salt bath of sodium nitrate and potassium nitrate mixture. The regulation was made using the temperature of the bath, allowing a temperature inside the reactor at ±1 °C. The different temperatures were acquired using an Agilent unit 34970A with an acquisition card 34902A. The acquired values showed that the temperature was homogeneous in the reactor during the steady-state. At the end of the hydrolysis treatment, the reactor was cooled in a bath of cold water. The duration of the heating phase varied between 6 and 9 min, depending on the temperature to be reached. The duration of the cooling phase was around 3 min on average.

The experiments were performed in light and heavy water for composite samples made of resin A to evaluate the deuterium isotope effect on the reaction kinetics. Depending on the value of the ratio  $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$  and on the value of its inverse, it is possible to distinguish the reaction mechanism. They were performed in light water only for composite samples made of resin B or C.

The kinetics experiments were realised at 275 °C because it appeared to be the best compromise between the quality of the recovered fibres and the efficiency of the hydrolysis treatment [11,20]. The experiments at different temperatures were performed to complete the kinetics study and to evaluate the effect of the temperature on the kinetics. For all the experiments the reactor was filled with water at 50%, so that two-phase conditions were achieved and the volume occupied by composite samples did not affect the theoretical induced pressure. A ratio mass of resin on initial volume of water was defined so that the maximum potential quantity of recovered saturated carboxylic acid was not in excess compared to its limit of solubility in ambient conditions, and for each resin so that the concentrations of ester were approximately identical. Its value was 0.018 g/mL for samples with resin A, 0.022 g/mL for samples with resin B and 0.015 g/mL for samples with resin C.

### 2.3. Qualitative and quantitative analysis by gas chromatography–mass spectrometry (GC–MS)

After hydrolysis treatments, the organic fractions presented two phases when they rested in ambient conditions. They first showed an opaque homogeneous aspect with a yellow colour, then after

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