Polymer Degradation and Stability 98 (2013) 785–800

Contents lists available at SciVerse ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

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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ARTICLE INFO

Article history:
Received 15 October 2012
Received in revised form
10 December 2012
Accepted 12 December 2012
Available online 19 December 2012

Keywords:
Glass fibres
Polymer-matrix composites
Unsaturated polyester
Chemical structure
Recycling
Kinetics

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 ($200\ ^\circ C <$ temperature $< 374\ ^\circ C$ 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 $A_{ac}2$ 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.

1. Introduction

The production of glass fibre reinforced composites (GFRC) 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 $A_{ac}2$ 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 $A_{ac}2$ 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 $A_{ac}2$ 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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http://dx.doi.org/10.1016/j.polymdegradstab.2012.12.010

acting as a nucleophile and the second assisting in dispersing the positive charge on oxygen in the transition sate [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^2 and one layer of mat with a weight of 300 g/m^2. 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® 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® connector SS-16-VCR-6-DM and two Swagelok® 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 $k_{\mathrm{H_2O}}/k_{\mathrm{D_2O}}$ 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 rest, a transparent aqueous phase and a non soluble organic substance at the bottom of the bottles.

The identification and the quantification of the products from the degradation of the resin, present in the aqueous phase, were realised with a gas chromatograph HP6890N fitted with an HP-5MS 30 m length, diameter 0.25 mm and a film thickness of 0.25 μm, coupled with a mass spectrometer HP5973N. The carrier gas used was hydrogen with a flow of 2.5 L/min. The mass acquisition was realised at constant flow and in a scan mode ($30 < m/z < 200$). The other acquisition conditions are given in Table 1. The liquid fraction samples were injected without solvent extraction. The column used was dedicated to the analysis of this work. In order to avoid contaminations, a blank run was systematically realised between each analytical run. The quantification was realised using a method of internal standard calibration. Among the recovered products, only propylene glycol and phthalic acid as original monomers and their secondary products were quantified. Propylene glycol-d8 (PG d8) was used as standard of propylene glycol. Phthalic anhydride-d4 (OPAA d4) was used as standard of phthalic anhydride or acid and benzoic acid. Acetone-d6 was used as standard of propanal and 2-propen-1-ol.

The evaluation of reproducibility of the measurements led to the estimation of the uncertainty of the measured values to be about ±10%.

3. Theory: modelling of the reaction kinetics

3.1. Kinetics of hydrolysis

Based on the assumption that the hydrolysis follows an $A_{ac}2$ mechanism, the reaction scheme can be described as on Scheme 1 [19], based on the resin A.

When an ester bond of a macromolecule of polyester is hydrolysed, a half-diacid and a half-diol are produced. Furthermore, the presence of chain ends must be considered. The proportion of acid or alcohol functions at chain ends is noted γ. So $(1-\gamma)$ diacids are produced by hydrolysis of two ester bonds and γ diacids are produced by hydrolysis of only one ester bond. It is the same for the diol. So the reactions 1–5 on Scheme 1 can actually be written as following:

1) $\frac{1}{2}\,\text{diacid} \rightarrow \frac{1}{2}\text{diacid}^- + H^+$

2) $\text{Ester} + H^+ \Leftrightarrow \text{Ester}^+$

3) $\text{Ester}^+ + 2H_2O \rightarrow [\text{Ester} - {}^+OH_2 - - - OH_2]$

4) $[\text{Ester} - {}^+OH_2 - - - OH_2] \rightarrow \text{Ester} - OH + H_3O^+$

5) $\text{Ester} - OH \rightarrow ((1+\gamma)/2)\text{diacid} + ((1+\gamma)/2)\text{diol}$

Table 1
Conditions of GC–MS.

Injector:	280 °C
Interface:	280 °C
Oven:	45 °C – 7 min, 20 °C/min, 300 °C–20 min
Injection:	1 μL with 1/50 division in SPLIT mode

The reaction kinetics is followed by the evolution of the total quantity of ester functions, which contains the non-protonated ester functions and the protonated ester functions [21]. Among all the ester functions, only the protonated ones can be attacked by molecules of water. The reaction scheme thus leads to the equation (1) for the rate of the hydrolysis reaction:

$$-\frac{d[\text{ester}]}{dt} = -\frac{d\left([\text{ester}]' + [\text{ester}^+]\right)}{dt} \equiv -\frac{d[\text{ester}^+]}{dt} = k_3\left[\text{ester}^+\right][H_2O]^2 \tag{1}$$

with [ester] the total concentration of ester and [ester]′ the concentration of protonated esters. The protonation reaction 2 gives rise to equation (2):

$$\left[\text{ester}^+\right] = K_2[\text{ester}]\left[H^+\right] \tag{2}$$

The rate of hydrolysis is finally written by the relation (3):

$$-\frac{d[\text{ester}]}{dt} = k_3K_2[\text{ester}]\left[H^+\right][H_2O]^2 \tag{3}$$

The catalyst H^+ can come from the dissociation of the acid functions (iso- or ortho-phthalic and succinic – maleic anhydride gives a derivative of succinic acid after cross-linking with styrene) and from the dissociation of water. Furthermore iso- and ortho-phthalic acid are known to decarboxylate giving benzoic acid. The latter dissociates in water and also produces protons. The carbon dioxide, formed by decarboxylation of carboxylic acids, dissolves in water forming carbonic acid. The latter can also produce a significant amount of protons. The dissociation constants of each acids present in the reaction medium and of water were then determined. For phthalic, succinic and carbonic acids, the temperature-dependent models proposed by Goldberg et al. [22] were considered. For the resin B, IPA was totally soluble in water in the conditions used [23]. Having no information on the dissociation constant of IPA in the conditions of hydrolysis, and considering their close chemical structures and dissociation constants in ambient conditions (Table 2), the same temperature-dependent relation as for OPA was used. For benzoic acid, the model proposed by Read [24] was used. The ionic product of water was determined using the model of Marshall and Franck [25]. The value of each dissociation constant at the reaction temperature of 275 °C is given in Table 3. Considering the excess of water, the concentrations of H^+ coming from water and from phthalic acid were calculated. The results are given in Table 4. The values in Tables 3 and 4 indicate that the majority of protons are provided by iso- or orhto-phthalic acid. Given the low value of its second dissociation constant, phthalic acid was considered to have only one dissociated acid function. The dissociation constant K_{a1} of phthalic acid allows to write the equation (4):

$$\left[H^+\right] = \sqrt{K_{a1}[\text{OPA}]_{\text{total}}} \tag{4}$$

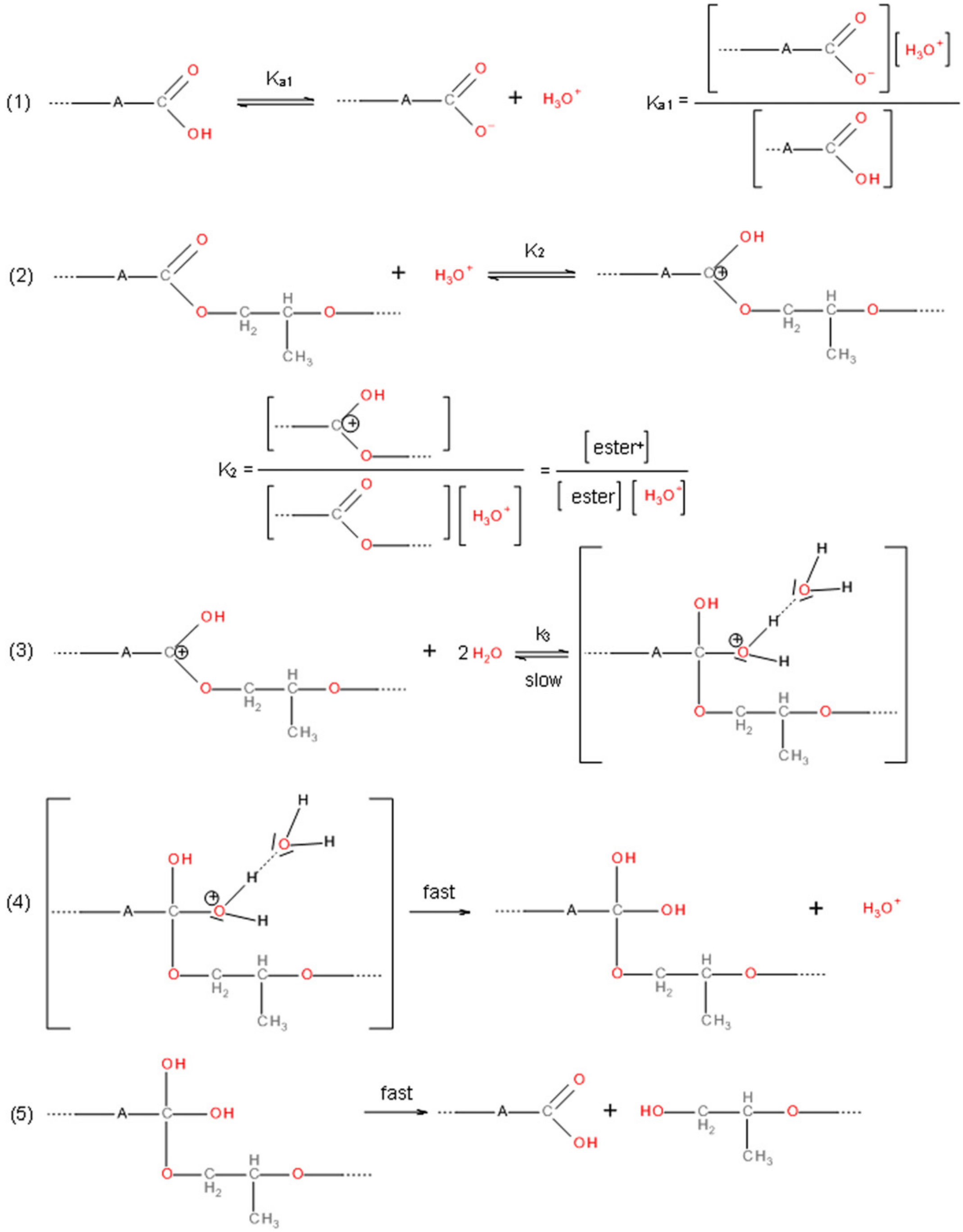
However in the equation (4), the concentration of H^+ is defined with the total concentration of OPA, instead of its instantaneous concentration. This consideration was made because the system of equations cannot be solved analytically if the instantaneous concentration of OPA is used.

The stoichiometry of reactions 2–5 leads to the relation (5):

$$[\text{OPA}]_{\text{total}} = \alpha\frac{1+\gamma}{2}\left([\text{ester}]_0 - [\text{ester}]\right) \tag{5}$$

with α the proportion of phthalic acid among the diacids constituting the resin A. The combination of equations (4) and (5) gives the relation (6):

$$\left[H^+\right] = \sqrt{K_{a1}}\sqrt{\alpha\frac{1+\gamma}{2}\left([\text{ester}]_0 - [\text{ester}]\right)} \tag{6}$$



Scheme 1. $A_{ac}2$ mechanism of the hydrolysis of an ester bond of a polyester resin.

By combining equations (3) and (6), the rate of hydrolysis can thus be written by the relation (7):

$$-\frac{d[ester]}{dt} = A[\mathrm{ester}]\sqrt{\alpha\frac{1+\gamma}{2}}([\mathrm{ester}]_0 - [\mathrm{ester}]) \quad (7)$$

with:

$$A = k_3K_2\sqrt{K_{a1}}[\mathrm{H_2O}]^2 \quad (8)$$

The solution of the differential equation (7) leads then to the expression of the rate of conversion ξ given by the equation (10).

$$\xi(t) = [\mathrm{ester}]_0 - [\mathrm{ester}] \quad (9)$$

$$\xi(t) = [\mathrm{ester}]_0\left(\tanh\left(\frac{A}{2}\sqrt{\alpha\frac{1+\gamma}{2}}[\mathrm{ester}]_0\cdot t\right)\right)^2 \quad (10)$$

Table 2
pK_a of phthalic and isophthalic acids in ambient conditions.

pK_a at 25 °C	OPA	IPA
pK_{a1}	2.95	3.62
pK_{a2}	5.41	4.60

Table 3
Dissociation constants (mol/kg) of the carboxylic acids and water at 275 °C on the saturation curve.

	K_{a1}	K_{a2}	K_{a1}/K_{a2}	K_{a1} of phthalic acid
Phthalic acid	1.27·10 − 04	1.14·10 − 08	1.12·10 + 04	–
Benzoic acid	1.81·10 − 06	–	–	1.42·10 − 02
Carbonic acid	2.55·10 − 09	7.10·10 − 12	3.59·10 + 02	2.01·10 − 05
Succinic acid	1.17·10 − 05	3.90·10 − 08	2.99·10 + 02	9.16·10 − 02
Water ($K_w^* = K_w/(\text{mol/kg})^2$ [25])	5.75·10 − 12	–	–	4.52·10 − 08

However it is not directly the evolution of concentration of esters which was followed, but the evolution of concentrations of OPA and PG and of their secondary products. Taking thus into account the reactions 2–5 and the equations (5) and (9), the evolution of the total concentrations of OPA and PG is modelled by the relations (11) and (12) respectively.

$$[\text{OPA}]_{\text{total}} = \alpha\frac{1+\gamma}{2}\xi(t) \tag{11}$$

$$[\text{PG}]_{\text{total}} = \frac{1+\gamma}{2}\xi(t) \tag{12}$$

Diffusion aspects were considered included in the hydrolysis rate constant. It is thus considered in this paper that if a limitation due to mass transfers exists, the global constant of hydrolysis rate k_3K_2 will be affected. Furthermore the hydrolysis reaction was considered to occur mainly at the interface between water and the resin of the composite sample. Inside the composite sample, pockets of water may exist in which hydrolysis reaction was considered to occur at the interface between water and the resin. A specific study will be necessary to define the diffusion and mass transfer's processes and to take into account the heterogeneity of the reaction system.

For the resin A, the kinetics of hydrolysis was then followed by the evolution of the total concentration of PG (with $[\text{PG}]_{\text{total}} = [\text{PG}] + [P_1] + [P_2]$) modelled by the equation (13), and by the evolution of the total concentration of OPA ($[\text{OPA}]_{\text{total}} = [\text{OPA}] + [\text{BA}]$) modelled by the equation (14). The parameter γ_A represents the proportion of ester bonds at chain ends and the parameter α_A represents the proportion of OPA among the diacids constituting the resin.

$$[\text{PG}]_{\text{total}} = \frac{1+\gamma_A}{2}\xi_A(t) \tag{13}$$

$$[\text{OPA}]_{\text{total}} = \alpha_A\frac{1+\gamma_A}{2}\xi_A(t) \tag{14}$$

$$\xi_A(t) = [\text{ester}]_0\left(\tanh\left(\frac{A}{2}\sqrt{\alpha_A\frac{1+\gamma_A}{2}[\text{ester}]_0\cdot t}\right)\right)^2 \tag{15}$$

Table 4
Concentrations of H^+ coming from the dissociation of phthalic acid and of water for the resin A at 275 °C.

	Ratio $[H^+]$ from phthalic acid/$[H^+]$ from water	
Resin A	1041	At the highest possible concentration
	393	At the end of the heating phase
Resin C	499	At the highest possible concentration
	217	After 10 min at 275 °C

For the resin B, the kinetics of hydrolysis was followed by the evolution of the total concentration of PG modelled by the equation (13) with its specific parameter γ_B and α_B.

Finally for the resin C, the chemical structure of the polyester macromolecules is more complex than for the resins A and B. Almost all the ester bonds are also of different natures in a same macromolecule (Figure A.3 in appendix A). As deuterated PG did not appear to be a good standard to quantify EG, 1,4-dioxane and DEG, their concentration could not be determined with sufficient accuracy. Without the appropriate standard, DCPD was also not quantified. The kinetics of hydrolysis could then be followed only by the evolution of the total concentration of PG modelled by the equation (16), and by the evolution of the concentration of OPA modelled by the equation (17). The parameters α'_C and α_C represent respectively the proportion of PG among the glycols and the proportion of OPA among the diacids in the resin.

$$[\text{PG}]_{\text{total}} = \frac{\alpha'_C}{2}\xi_C(t) \tag{16}$$

$$[\text{OPA}]_{\text{total}} = \frac{\alpha_C}{2}\xi_C(t) \tag{17}$$

$$\xi_C(t) = [\text{ester}]_0\left(\tanh\left(\frac{A}{2}\sqrt{\frac{\alpha_C}{2}[\text{ester}]_0\cdot t}\right)\right)^2 \tag{18}$$

Considering equations (13)–(18), the reaction kinetics was then defined for each resin by mathematical fitting of the parameter A to the measured values of total concentrations of PG and OPA. The fitting was realised with the Levenberg–Marquardt algorithm using the software *Mathematica*© *8.0*. The global rate constant of hydrolysis k_3K_2 was then calculated, but not k_3 alone because there is no information available about the equilibrium constant K_2 under the reaction conditions used. For that purpose, the concentration of water (H_2O and D_2O) in the reaction conditions was determined using the steam table from the NIST [26].

3.2. Kinetics of decarboxylation

Decarboxylation is said to be acid-catalysed [27]. The produced carbon dioxide would dissolve in water to give a carboxylate anion and a hydronium ion which then attacks the carboxylic acid [28]. But as seen previously in Table 3, hydronium ions coming from CO_2 dissolved in water are far from being in majority. The acid catalysis may more probably be due to the hydronium ions coming from the dissociation of phthalic acid in our case. The reaction is described on Scheme 2 and its rate can be modelled by the equation (19):

$$-\frac{\mathrm{d}[\text{OPA}]}{\mathrm{d}t} = k_6[\text{OPA}]\left[H^+\right] \tag{19}$$

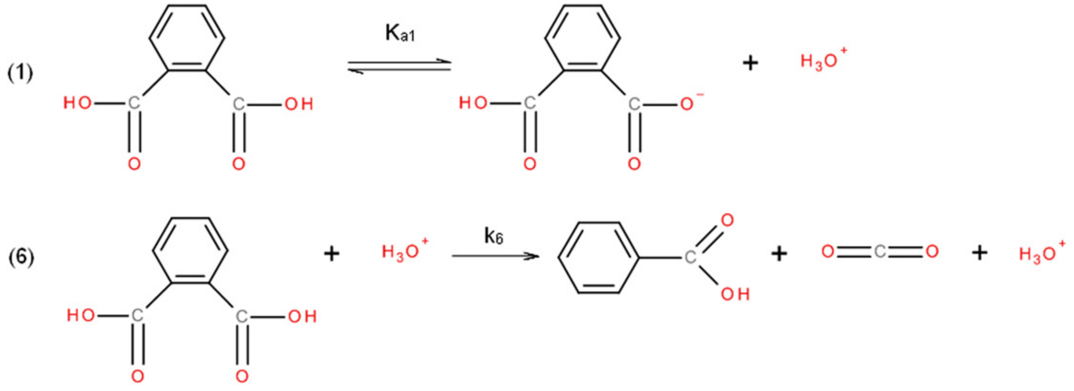
The evolution of the concentration of OPA is thus given by the differential equation (20):

$$\frac{\mathrm{d}[\text{OPA}]}{\mathrm{d}t} = \alpha\frac{1+\gamma}{2}\frac{\mathrm{d}\xi(t)}{\mathrm{d}t} - k_6[\text{OPA}]\left[H^+\right] \tag{20}$$

For the resin A, this differential equation becomes the relation (21) with the specific coefficients α_A and γ_A:

$$\frac{\mathrm{d}[\text{OPA}]}{\mathrm{d}t} = \alpha_A\frac{1+\gamma_A}{2}\frac{\mathrm{d}\xi_A(t)}{\mathrm{d}t} - k_6[\text{OPA}]\left[H^+\right] \tag{21}$$

Then the solution of this equation gives the model describing the evolution of the concentration of OPA during the hydrolysis of the polyester resin A and given by the relation (22), corresponding



Scheme 2. Considered mechanism of decarboxylation of OPA.

to the total concentration of OPA minus the proportion that decarboxylates:

$$[\mathrm{OPA}] = \alpha_A \frac{1+\gamma}{2}\xi_A(t) - \alpha_A \frac{1+\gamma_A}{2} k_6 \sqrt{K_{a1}}[\mathrm{ester}]_0 \left(x_{1,A}(t) - y_{1,A}(t)\right) \tag{22}$$

with:

$$x_{1,A}(t) = \frac{1}{\left(2-k_6\sqrt{K_{a1}}\right)\left(\cosh\left(\frac{A}{2}t\sqrt{\alpha_A\frac{1+\gamma_A}{2}[\mathrm{ester}]_0}\right)\right)^2} + \frac{1}{k_6\sqrt{K_{a1}}}$$

$$y_{1,A}(t) = \left(\frac{1}{\left(2-k_6\sqrt{K_{a1}}\right)} + \frac{1}{k_6\sqrt{K_{a1}}}\right) \times \left(\cosh\left(\frac{A}{2}t\sqrt{\alpha_A\frac{1+\gamma_A}{2}[\mathrm{ester}]_0}\right)\right)^{-k_6\sqrt{K_{a1}}}$$

The second term then represents the model of the kinetics of decarboxylation.

For the resin C, the evolution of the concentration of OPA is given by the equation (23):

$$[\mathrm{OPA}] = \frac{\alpha_C}{2}\xi_C(t) - \frac{\alpha_C}{2} k_6 \sqrt{K_{a1}}[\mathrm{ester}]_0 \left(x_{1,C}(t) - y_{1,C}(t)\right) \tag{23}$$

with:

$$x_{1,C}(t) = \frac{1}{\left(2-k_6\sqrt{K_{a1}}\right)\left(\cosh\left(\frac{A}{2}t\sqrt{\frac{\alpha_C}{2}[\mathrm{ester}]_0}\right)\right)^2} + \frac{1}{k_6\sqrt{K_{a1}}}$$

$$y_{1,C}(t) = \left(\frac{1}{\left(2-k_6\sqrt{K_{a1}}\right)} + \frac{1}{k_6\sqrt{K_{a1}}}\right) \times \left(\cosh\left(\frac{A}{2}t\sqrt{\frac{\alpha_C}{2}[\mathrm{ester}]_0}\right)\right)^{-k_6\sqrt{K_{a1}}}$$

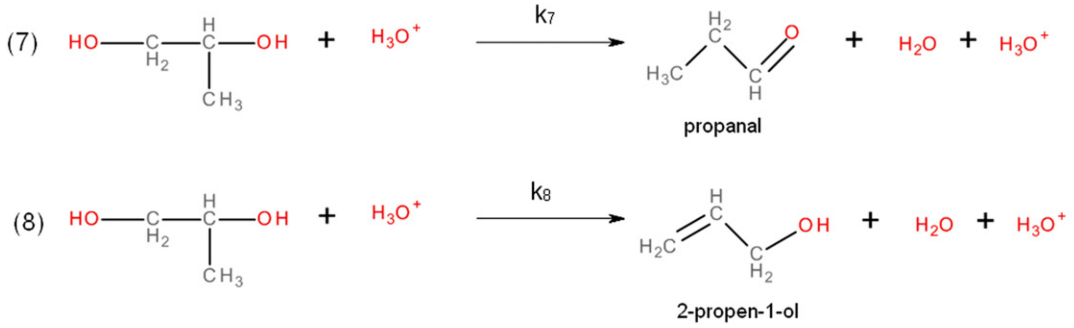
Knowing the values of the parameter A for both resins A and C, the dissociation constant K_{a1}, α_A and γ_A for the resin A, and α_C for the resin C, the reaction kinetics was then defined by mathematical fitting of the reaction rate k_6 in the equation (22) for the resin A and in the equation (23) for the resins C to the measured values of concentrations of OPA. The fitting was realised with the Levenberg–Marquardt algorithm using the software *Mathematica*© *8.0*.

3.3. Kinetics of dehydration

Dehydration of alcohols is known to be acid-catalysed [13]. The catalysis can here also be assigned to hydronium ions coming from the dissociation of OPA produced by hydrolysis of ester bonds. By dehydration, PG produces propanal and 2-propen-1-ol. The rate of dehydration described on Scheme 3 can thus be modelled by the equation (24):

$$-\frac{\mathrm{d}[PG]}{\mathrm{d}t} = (k_7 + k_8)[\mathrm{PG}]\left[\mathrm{H}^+\right] \tag{24}$$

The rate of gross production of PG during the hydrolysis of the polyester resins A and B is described by the equation (25):



Scheme 3. Considered mechanism of dehydration of PG.

$$\frac{\mathrm{d}[\mathrm{PG}]}{\mathrm{d}t} = \frac{1+\gamma}{2}\frac{\mathrm{d}\xi(t)}{\mathrm{d}t} - (k_7+k_8)[\mathrm{PG}]\left[\mathrm{H}^+\right] \quad (25)$$

with k_7 the rate of dehydration producing propanal k_8 the rate of dehydration producing 2-propen-1-ol, $\gamma = \gamma_A$ or γ_B for the resin A or B respectively, and $\alpha = \alpha_A$ or α_B for the resin A or B respectively.

The solution of this equation gives then the model describing the evolution of the concentration of PG during the hydrolysis of the polyester resins A and B and given by the relation (26), corresponding to the total concentration of PG minus the proportion that dehydrates:

$$[\mathrm{PG}] = \frac{1+\gamma}{2}\xi(t) - \frac{1+\gamma}{2}(k_7+k_8)\sqrt{K_{a1}}[\mathrm{ester}]_0(x_2(t) - y_2(t)) \quad (26)$$

with:

$$x_2(t) = \frac{1}{\left(2-(k_7+K_8)\sqrt{K_{a1}}\right)\left(\cosh\left(\frac{A}{2}t\sqrt{\alpha_A\frac{1+\gamma}{2}[\mathrm{ester}]_0}\right)\right)^2 + \frac{1}{(k_7+K_8)\sqrt{K_{a1}}}}$$

$$y_2(t) = \left(\frac{1}{\left(2-(k_7+k_8)\sqrt{K_{a1}}\right)} + \frac{1}{(k_7+k_8)\sqrt{K_{a1}}}\right) \times \left(\cosh\left(\frac{A}{2}t\sqrt{\alpha\frac{1+\gamma}{2}[\mathrm{ester}]_0}\right)\right)^{-(k_7+k_8)\sqrt{K_{a1}}}$$

The second term then represents the model of the kinetics of dehydration.

For the resin C, the evolution of the concentration of PG is given by the equation (27):

$$[\mathrm{PG}] = \frac{\alpha'_C}{2}\xi_C(t) - \frac{\alpha'_C}{2}(k_7+k_8)\sqrt{K_{a1}}[\mathrm{ester}]_0\left(x_{2,C}(t) - y_{2,C}(t)\right) \quad (27)$$

with:

$$x_{2,C}(t) = \frac{1}{\left(2-(k_7+k_8)\sqrt{K_{a1}}\right)\left(\cosh\left(\frac{A}{2}t\sqrt{\alpha_A\frac{1+\gamma}{2}[\mathrm{ester}]_0}\right)\right)^2 + \frac{1}{(k_7+K_8)\sqrt{K_{a1}}}}$$

$$y_{2,C}(t) = \left(\frac{1}{\left(2-(k_7+k_8)\sqrt{K_{a1}}\right)} + \frac{1}{(k_7+k_8)\sqrt{K_{a1}}}\right) \times \left(\cosh\left(\frac{A}{2}t\sqrt{\frac{\alpha_C}{2}[\mathrm{ester}]_0}\right)\right)^{-(k_7+k_8)\sqrt{K_{a1}}}$$

Similarly, knowing the values of the parameter A, the dissociation constant K_{a1}, the parameters α and γ specific to each resin, the reaction kinetics of decarboxylation was then defined by mathematical fitting of the reaction rate ($k_7 + k_8$) in the equations (26) and (27) to the measured values of concentrations of PG for the three resins.

4. Results and discussion

4.1. Products recovered from the resins

The analysis by GC–MS of the liquid phase of each sample led to the identification of the products. Monomers of the resins were recovered, particularly glycols and ortho- or iso-phthalic acid (OPA or IPA). For the resin C, DCPD was also recovered, indicating that chain ends were hydrolysed despite the close presence of styrene chains (Figure A.3 in appendix A) and the complexity of the DCPD molecule. For the three resins, PG dehydrated to give propanal and 2-propen-1-ol [13,29]. For the resin A, a tertiary product appeared from a time of 90 min at 275 °C and from a temperature of 325 °C after 10 min: 2-methyl-2-pentenal, which is produced by an aldol condensation of propanal followed by dehydration [30]. For the resins A and C, OPA produced benzoic acid by decarboxylation [13,28]. For the resin B, IPA was produced, but not detected because it is not soluble in water in ambient conditions, and did not decarboxylate. It was observed by Dunn and al. [28] that IPA is stable until at least 300 °C in water. Benzoic acid was observed in the liquid phase recovered from the resins B after the experiment at 325 °C during 10 min.

No styrene, maleic or succinic acid or styrene-succinic acid molecules were found for the three resins. Some traces of acetic acid were found at 275 °C. The origin of this product is attributed to maleic acid that would not be linked to styrene. A first step of decarboxylation giving acrylic acid followed by an oxidation to give acetic acid is proposed [31]. Traces of benzaldehyde, benzene acetaldehyde, α-methyl-benzenemethanol and acetophenone were detected. We showed that they could be attributed to styrene monomers [11].

A styrene-succinic acid copolymer should remain after hydrolysis of the ester bonds. Its structure depends on the relative proportion of monomers for each resin and on the relative proportions of maleic anhydride and styrene monomers.

Hydrolysis, dehydration and decarboxylation kinetics were then studied by following the evolution of the concentration of PG for the three resins, the evolution of the concentration of OPA for the resins A and C, and the evolution of the concentration of their secondary products. The measured values in mol/L were considered using density values of pure water under the reactions conditions [26].

4.2. Modelling of the reaction kinetics

4.2.1. Kinetics of hydrolysis and solvent isotope effect

The fitting of the adjustment parameter A to the measured values of total concentrations of PG and OPA is given in Table 5 for the hydrolysis of the resin A in light and heavy water. The evolution of the measured values and the associated theoretical curves as a function of time is given on Figs. 1 and 2. The molar ratio is defined by the measured concentration of a product divided by its initial concentration in the resin (in mol/L of water). The global constants of hydrolysis rate and their ratio $(k_3K_2)_{\mathrm{H_2O}}/(k_3K_2)_{\mathrm{D_2O}}$ are given in Tables 5 and 6 respectively.

The results of the product k_3K_2 calculated for H_2O and D_2O indicate that the ratio $(k_3K_2)_{\mathrm{H_2O}}/(k_3K_2)_{\mathrm{D_2O}}$ is less than 1 (Table 6). This confirms the specific acid catalysis of the hydrolysis, and that the hydrolysis mechanism begins with a fast protonation of ester bonds followed by the rate determining step of the protonated esters [32]. At this point the hypothesis of an $\mathrm{A_{ac}2}$ mechanism seems to be confirmed. However another mechanism may also apply: the unimolecular $\mathrm{A_{ac}1}$ decomposition. But if the ratio $(k_3K_2)_{\mathrm{D_2O}}/(k_3K_2)_{\mathrm{H_2O}}$ is considered, the obtained values are less

Table 5
Values of the global constant of hydrolysis rate at 275 °C–60 bars for the resin A.

Resin A:		A ($L^{0.5}/mol^{0.5}.s$)	k_3K_2 for $A_{ac}2$ ($L^3/mol^3.s$)	R^2
H_2O	PG	$9.9 \cdot 10^{-3}$	$5.7 \cdot 10^{-4}$	0.988
	OPA	$15.5 \cdot 10^{-3}$	$8.8 \cdot 10^{-4}$	0.922
D_2O	PG	$10.3 \cdot 10^{-3}$	$9.8 \cdot 10^{-4}$	0.916
	OPA	$10.3 \cdot 10^{-3}$	$9.8 \cdot 10^{-4}$	0.994

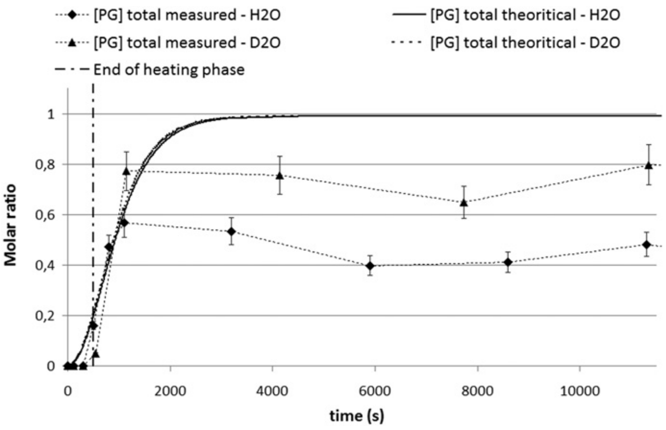


Fig. 1. Evolution of the total concentrations of PG for hydrolysis in H_2O and in D_2O of the resin A.

Table 6
Ratio of the global constants of hydrolysis rate in H_2O and in D_2O for the resin A.

	k_{H_2O}/k_{D_2O}	k_{D_2O}/k_{H_2O}
PG	0.6	1.8
OPA	0.9	1.1

than 2. An $A_{ac}1$ mechanism would give values of ratio $(k_3K_2)_{D_2O}/(k_3K_2)_{H_2O}$ of 2 or greater [33].

It can also be noted that the rate of hydrolysis in H_2O is higher when it is calculated using the measured concentration of OPA than with the measured concentration of PG (Table 5). This can be explained by the different nature of the ester bonds. PG can be bonded to one OPA and one succinic acid or to two OPA, or even to only one OPA or one succinic acid when it is placed at a chain end, while OPA is bonded only to PG on both sides. So the lowest rate of hydrolysis observed for the evolution of the concentration of PG may be due to bonds between PG and succinic acid more difficult to break [34]. The presence of styrene chains bonded to succinic acid may create steric hindrance so that protonation of the ester bond and then nucleophilic attack by water are more difficult. The hydrophobic character of styrene can be added to the steric hindrance. This was observed on esters of benzoic acid: branched butyl benzoate hydrolyses more slowly than the linear butyl benzoate [17]. Furthermore, in light water, the total recovery rate of OPA achieved 100% (Fig. 2), while PG was recovered only in part (Fig. 1). Knowing the formulation of the resin, the total recovery rate of PG suggests that only PG bonded to two OPA or placed at chain ends were released. If a coefficient taking into account the proportion of PG bonded to two OPA or placed at chain ends is applied to equation (14), the obtained value for the parameter A is $15.9 \cdot 10^{-3}$ $L^{0.5}/mol^{0.5}.s$, which gives a rate of hydrolysis very close to the one calculated using the measured concentrations of OPA. The theoretical curve thus obtained is represented on Fig. 3. Furthermore, all the ester bonds in the resin A are realised with PG but not always with OPA (succinic acid also contributes to a part of them). So PG appears to be the most representative of the evolution of the concentration of esters during hydrolysis. If PG was bonded only to OPA, same values of rate constant would have been obtained. Then the product k_3K_2 calculated using the evolution of the total concentration of PG can be considered as a global rate constant of hydrolysis for this resin, whereas the one calculated using the evolution of the total concentration of OPA is specific to bonds PG–OPA.

Moreover the rate constant of hydrolysis of isobutyl benzoate was $1.86 \cdot 10^{-3}$ $L^2/mol^2.s$ at 250 °C in two-phase conditions, which gives $4.2 \cdot 10^{-5}$ $L^3/mol^3.s$ if the mechanism is considered to involve two molecules of water instead of one as done by the authors [17]. The results obtained by those last authors enabled to evaluate a rate constant of $5.4 \cdot 10^{-3}$ $L^2/mol^2.s$ at 275 °C in two-phase conditions, so $1.3 \cdot 10^{-4}$ $L^3/mol^3.s$ if two molecules of water instead of one are considered in the rate determining step. Thus compared to that last value, our values of rate constant (Table 5) do not reflect important limitations due to diffusions and mass transfers.

Finally, hydrolysis achieved its maximum very fast: if all the ester bonds were broken, the reaction would produce more than 95% of the total quantity of the monomers PG and OPA initially

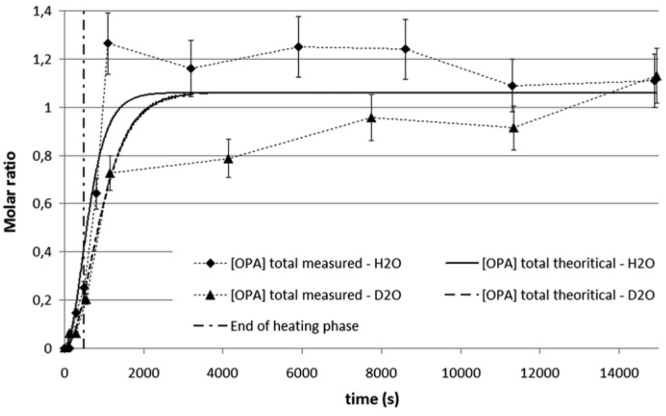


Fig. 2. Evolution of the total concentrations of OPA for hydrolysis in H_2O and in D_2O of the resin A.

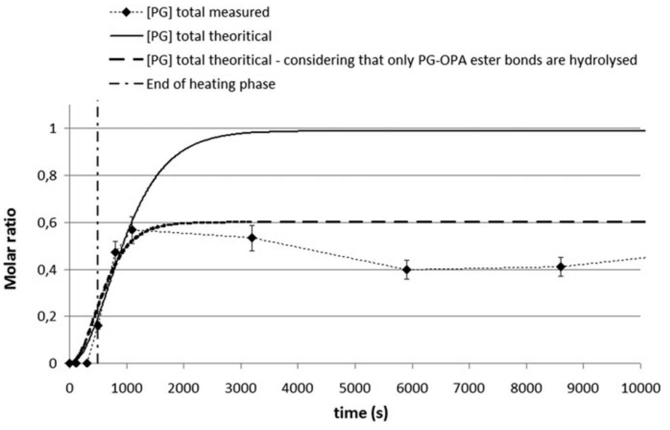


Fig. 3. Evolution of the total concentration of PG for hydrolysis of the resin A in H_2O considering the proportion of PG bonded to two OPA or placed at chain ends.

present in the resin in less than 40 min (duration of the heating phase included, so 2400 s on Figs. 1 and 2). A higher time did not enable to hydrolyse the non-hydrolysable ester bonds (those between PG and succinic acid), only secondary reactions occurred as shown in the following Section 4.2.4. However, despite this "maximum" hydrolysis, the composite sample was still solid and compact until a time between 135 and 180 min at 275 °C (Fig. 4). If all the hydrolysable ester bonds were broken after 40 min, a polymer made of styrene chains bonded to esters of succinic acid and PG would remain. This would be the polymer that maintained the solid state of the composite sample. The polyester prepolymer was dissolved in 41 wt% styrene monomers. So the resin contains only 59 wt% polyester. After 45 min at 275 °C, the loss of mass of resin achieved about 50%, which is in fact in fact consistent with the fact that almost all the ester bonds were broken. After 240 min, the loss of mass achieved 64% so if the ester bonds PG-succinic acid were not hydrolysed, this suggests that the styrene chains began to be degraded and/or extracted by dissolution in the aqueous medium. In the conditions used here, the relative dielectric constant ε of water was about 23. Water behaved then like an organic solvent between ethanol ($\varepsilon = 24$ at 25 °C) and acetone ($\varepsilon = 21$ at 25 °C). Acetone was able to dissolve the polymer remaining in the composite sample to release the fibres.

Table 7
Values of the constants of hydrolysis rate for each resin.

		Resin A (orthophthalic)	Resin B (isophthalic)	Resin C (orthophthalic – DCPD)
$[\text{ester}]_0$ (mol/L)		0.1003	0.1109	0.0736
$[\text{PG}]_{\text{total}}$	A ($L^{0.5}/mol^{0.5}.s$)	$9.9 \cdot 10^{-3}$	$7.3 \cdot 10^{-3}$	$26.4 \cdot 10^{-3}$
	R^2	0.988	0.992	0.987
	k_3K_2 ($L^3/mol^3.s$)	$5.7 \cdot 10^{-4}$	$4.2 \cdot 10^{-4}$	$15.0 \cdot 10^{-4}$
	Ratio/$(k_3K_2)_A$		0.7	2.6
$[\text{OPA}]_{\text{total}}$	A ($L^{0.5}/mol^{0.5}.s$)	$15.5 \cdot 10^{-3}$	n/a	$9.9 \cdot 10^{-3}$
	R^2	0.922	n/a	0.956
	k_3K_2 ($L^3/mol^3.s$)	$8.8 \cdot 10^{-4}$	n/a	$5.7 \cdot 10^{-4}$
	Ratio/$(k_3K_2)_A$		n/a	0.6

4.2.2. *Influence of the chemical structure of the resin on the kinetics of hydrolysis*

The values of the fitting parameter *A* and of the product k_3K_2 for each resin are given in Table 7. Fig. 5 shows the measured and theoretical curves for the evolution of the total concentration of PG for the resins B and C, in comparison with the curves obtained for the resin A. Fig. 6 shows the measured and theoretical curves for the evolution of the total concentration of OPA for the resin C (theoretical curve with the parameter A calculated using the evolution of the total concentration of OPA) in comparison with the curves obtained for the resin A.

For similar reasons as for the resin A, the product k_3K_2 calculated for the resin B using the evolution of the total concentration of PG can represent a global rate constant of hydrolysis. Considering that, the comparison of the values obtained for each resin (Table 7) indicates that hydrolysis is faster for the resin A than for the resin B. This can be explained by the different nature of the ester bonds in the resin B (PG—IPA) and in the resin A (PG—OPA).

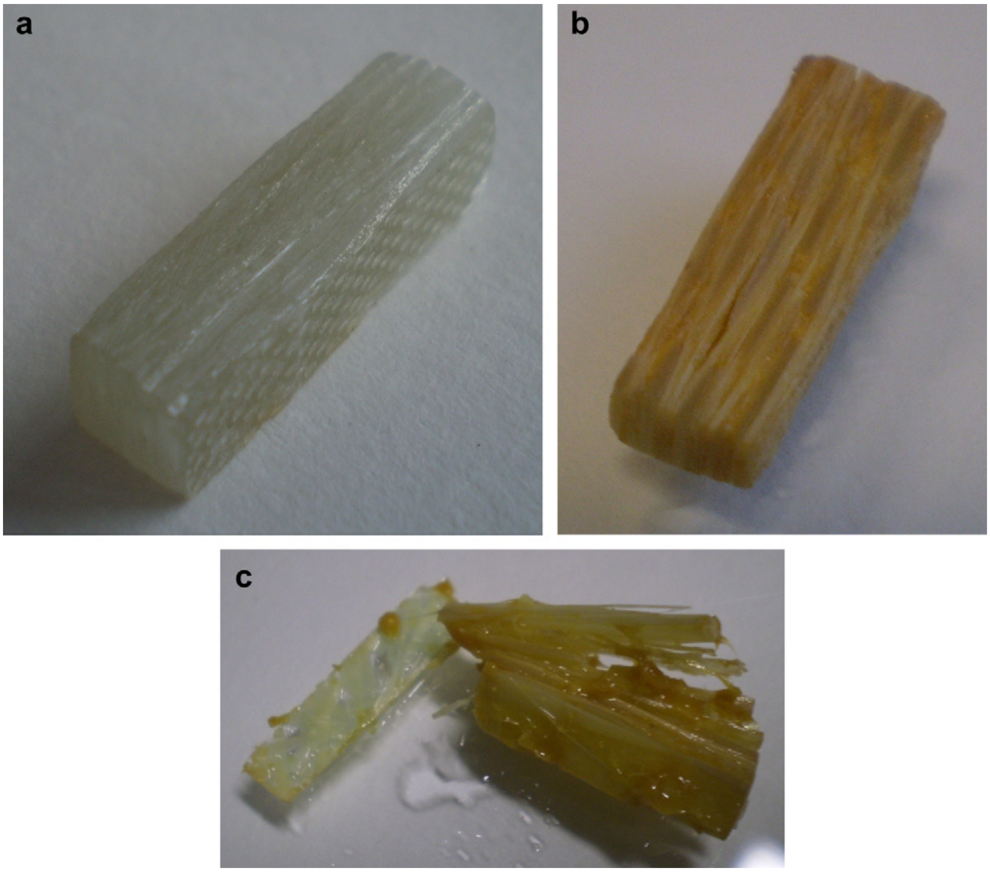


Fig. 4. Composite samples made of resin A (a) before hydrolysis, (b) after 135 min at 275 °C (8598 s including heating phase), (c) after 180 min at 275 °C (11,298 s including heating phase).

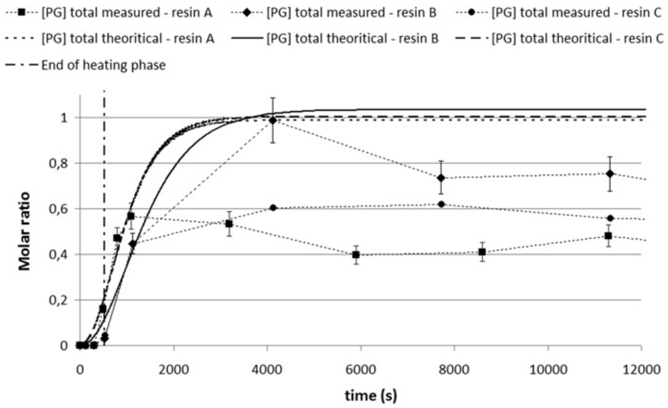


Fig. 5. Evolution of the total concentrations of PG for hydrolysis of resins A, B and C.

Isophthalates are known to be more resistant to hydrolysis than orthophthalates [34]. The ester bond PG—IPA is harder to break maybe because the two ester bonds around the aromatic cycle are further from each other than in the case of PG—OPA. The double bond C=O is very polar and this polarity may be increased when two bonds C=O are close from each other. As a consequence, protons are even more attracted since the polarity is greater. Longer polyester chains of the resin B may also explain the lower rate constant of hydrolysis.

However, although hydrolysis of the resin B is slower, the recovery rate of PG is higher for the resin B (about 75–80%) than for the resin A (about 60%) (Fig. 5). The ester bonds between PG and succinic acid of the resin A (fumarates give substituted succinates after cross-linking with styrene) did not seem to be hydrolysed. This was explained by the steric hindrance produced by the styrene chains and their hydrophobic character. However ester bonds between PG and succinic acid of the resin B seem to be hydrolysed. Styrene chains in the resin B are thought to be shorter than the ones in the resin A. Ester bonds between two polyester chains would thus be closer from each other in the resin B (Fig. 7). This greater closeness between two ester groups of two polyester chains separated by shorter styrene chains in the resin B might create a greater polarity. That would make the ester bonds between PG and succinic acid more attractive for protons. However this suggestion has to be verified. Considering a same ratio of styrene to polyester unsaturation for both resins (3.71 for the resin A and 3.75 for the resin B), shorter styrene chains in the resin may be due to a higher amount of catalyst systems (initiator and accelerator), added for the cross-linking, in the resin B than in the resin A. The higher recovery rate of PG for the resin B can also be explained by an amount of unreacted fumarates or maleates in the resin B higher than the one in the resin A.

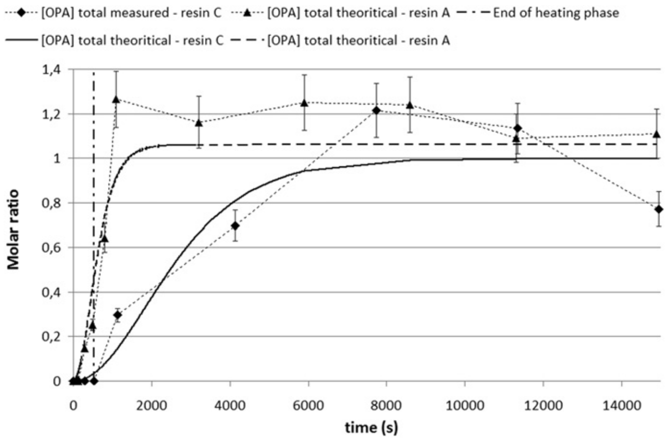


Fig. 6. Evolution of the total concentrations of OPA for hydrolysis of composites made of resins A and C.

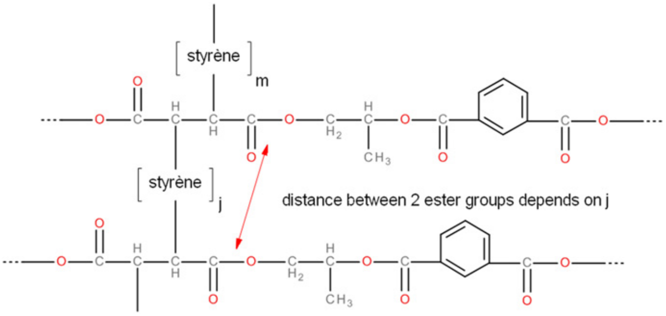


Fig. 7. Distance between two polyester chains induced by styrene chains.

It has to be noted that the first dissociation constant of IPA was considered equal to the one of OPA in the conditions used, while it is lower at 25 °C. If this ratio is the same in the conditions of hydrolysis used, this leads to constant rates k_3K_2 almost equal for the resins A and B. But instead of considering the product k_3K_2 to describe the global mechanism of hydrolysis, the latter can be more completely described by the more global constant rate $k_3K_2\sqrt{K_{a1}}$. In that case the ratio $(k_3K_2\sqrt{K_{a1}})_B/(k_3K_2\sqrt{K_{a1}})_A$ gives the same value as in Table 7. This confirms the slower hydrolysis of the resin B.

Finally the hydrolysis reaction enabled to break almost 80% ester bonds after about 60 min (including the heating phase). However, as for the composite sample made of resin A (Fig. 4), the composite sample made of resin B was still solid until 180 min (11,322 s including the heating phase), even if the plies began to separate as shown on Fig. 8. After 60 min at 275 °C, the yield of eliminated resin achieved about 42% and about 50% after 180 min. The resin B contains 48% by weight polyester. So this confirms that almost all the ester bonds were broken after 60 min. Thus a longer time may only lead to the degradation and/or dissolution of the remaining polymer styrene-succinic acid.

For the resin C, the ester bonds are almost all different, except at chain ends (Figure A.3 in appendix A). So it is not possible to define a global constant rate of hydrolysis. Only a global constant rate relative to each type of monomer can be calculated. So here, only the global constant rate relative to PG and OPA could be defined. The results given in Table 7 indicate a higher value for the constant relative to PG for the resin C than for the resin A, whereas a lower value for the constant relative to OPA is obtained. The results are difficult to interpret because of the complexity of the molecular structure of the resin. Its formulation makes it difficult to be described by a theoretical chemical structure. However the polyester macromolecules are on average much shorter than the ones of the resin A (906 g/mol against 1384 g/mol respectively). Globally, the double bonds C=C, so the styrene chains, are mainly at the chain ends of the polyester macromolecules. Furthermore chain ends are constituted of DCPD. It was shown that DCPD at chain ends does limit the hydrolysis rate even if it does not reduce the loss of mass [35]. It cannot be confirmed here as DCPD was not quantified. But considering that, it may mean that hydrolysis first breaks ester bonds in the middle of the chains where there are no styrene chains so no steric hindrance. Though it can be noticed that only about 60%

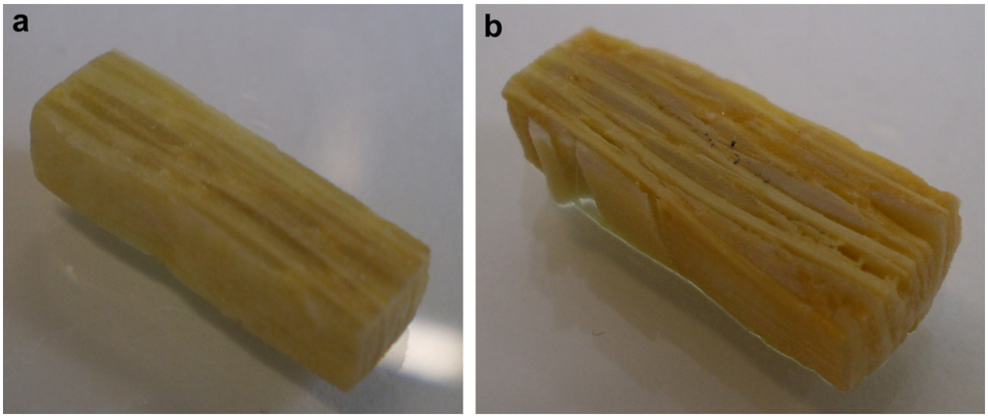


Fig. 8. Composite sample made of resin B (a) after 60 min at 275 °C (4122 s including heating phase), (b) after 180 min at 275 °C (11,322 s including heating phase).

PG are recovered and only about 50 min are necessary to achieve this maximum, whereas all the OPA are recovered in about 145 min. It might indicate different reaction mechanism. Ester bonds involved in the middle of the chains, potentially the first site of break, might be hydrolysed via an $A_{ac}1$ mechanism. This could explain the higher rate constant obtained relatively to PG. But this has to be verified.

A more intensive study of this resin is necessary. However it can already be said that this type of resin will require a specific hydrolysis treatment to be recycled even if the conditions are the same. Especially since the organic phases recovered after hydrolysis will contain more different species of monomers and their secondary products. Finally a specific brown colouration of the resin C was observed during hydrolysis (Fig. 9). However tar-like substance was not recovered after hydrolysis of this resin, whereas it was found for another DCPD-based polyester from DSM [36].

Fig. 9. Composite sample made of resin C after 240 min at 275 °C (14,937 s including heating phase).

The diffusion processes were here considered to be included in the rate constant of hydrolysis. They might play a role on the differences observed on the rate constants of hydrolysis for the three resins. This point will necessitate a dedicated study to characterise the involved types of diffusion process.

4.2.3. Temperature dependence of hydrolysis

The estimation of the temperature dependence of the ester hydrolysis in subcritical water was realised for the resins A and B. The law of mass action for the equilibrium constant of the protonation reaction 2 (Scheme 1) leads to the relation (28):

$$\ln(K_2) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{28}$$

with ΔH^0 the standard enthalpy and ΔS^0 the standard entropy of reaction.

Moreover if the reaction constant k_3 is considered to follow an Arrhenius Law, its expression as a function of the temperature T (in Kelvin) is given by the relation (29):

$$k_3 = A_S e^{-\frac{E_a}{RT}} \tag{29}$$

with E_a the activation energy of the reaction 3 (Scheme 1) and A_S a constant which takes into account the collision frequency and the steric effects. The logarithm of k_3 gives the relation (30):

$$\ln(k_3) = \ln(A_S) - \frac{E_a}{RT} \tag{30}$$

The combination of the equations (28) and (30) leads then to the expression (31) for the logarithm of the product k_3K_2:

$$\ln(k_3K_2) = -\frac{E_a + \Delta H^0}{RT} + \frac{\Delta S^0}{R} + \ln(A_S) \tag{31}$$

Using the measured data obtained for the evolution of the total concentration of PG at different temperatures, a so-called "apparent activation energy" ($E_a + \Delta H^0$) was determined using the plot of ln (k_3K_2) against $1/T$. A so-called "apparent activation entropy" ($\Delta S^0 + R\ln(A_S)$) was also calculated. Fig. 10 shows the dependence of ln (k_3K_2) against $1/T$ for the resins A and B. The

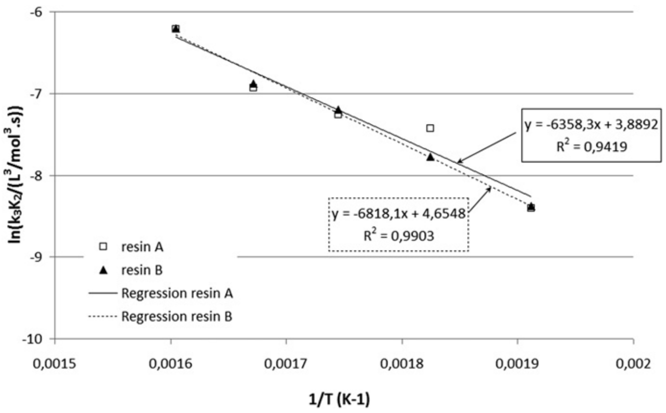


Fig. 10. Temperature dependence of the rate constant of hydrolysis of composite made of resins A and B.

results obtained for the “apparent activation energy” and the “apparent activation entropy” are given for resins A and B in Table 8.

The values obtained for both resins are not very different. The ester bonds are globally more difficult to break for the resin B given the apparent activation energy slightly higher than for the resin A. This may be explained by the ester bond PG—IPA stronger than the ester bond PG—OPA. However, globally an effect of the nature of ester bonds and of the molecular structure is not observed. Those both resins can thus be hydrolysed in the same conditions and together in a same batch. The hydrolysis rate of the isophthalic resin could thus be increased thanks to a higher concentration of catalyst H^+ as the dissociation constant of OPA is higher than that of IPA.

4.2.4. *Kinetics of the main secondary reactions and solvent isotope effect*

The evolution of the concentrations of OPA and PG as a function of time is represented on Figs. 11 and 12 for the experiments on the resin A in H_2O respectively. The fittings of the parameter k_6 for the decarboxylation of OPA and of the parameter $(k_7 + k_8)$ for the dehydration of PG were realised using the global constant of hydrolysis calculated from the evolution of the total concentration of PG, as it appears to be the most representative of the evolution of hydrolysis.

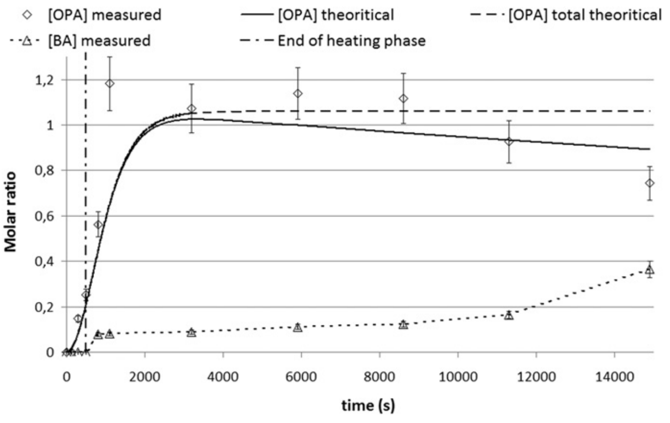


Fig. 11. Evolution of the concentration of OPA for hydrolysis of composite made of resin A.

Table 8
Apparent activation energy and entropy of the hydrolysis reaction of the orthophthalic and isophthalic polyester resins (values ±1).

	Resin A	Resin B
$E_a + \Delta H^0$ (kJ/mol)	53	56
ΔS^0 + constante (J/K.mol)	32	39

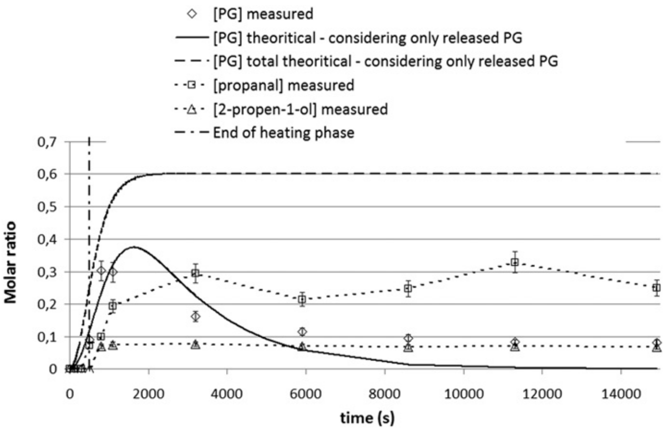


Fig. 12. Evolution of the concentration of PG for hydrolysis of composite made of resin A.

The values for the rate constants k_6 and $(k_7 + k_8)$ obtained from the experiments done in H_2O and in D_2O are given in Table 9. The ratios of the constants of rate in H_2O and in D_2O are less than 1, which indicates a specific acid catalysis of both secondary reactions. This confirms the mechanisms proposed for decarboxylation (Scheme 2 and equation (22)) and for dehydration (Scheme 3 and equation (26)).

Table 9
Rate constants of decarboxylation and dehydration for experiments in H_2O and in D_2O for the resin A.

	Decarboxylation k_6 (L/mol.s)	R^2	Dehydration $k_7 + k_8$ (L/mol.s)	R^2
H_2O	1.3	0.945	54.4	0.869
D_2O	12.4	0.967	62.9	0.852
Ratio k_{H_2O}/k_{D_2O}	0.1		0.9	

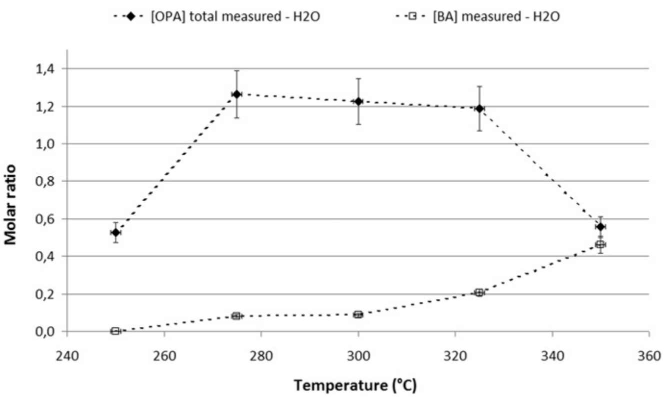


Fig. 13. Evolution of the total concentrations of OPA and BA at different temperature for a duration of 10 min in H_2O for the resin A.

The models of evolution of the concentrations of OPA (Fig. 11) and PG (Fig. 12) enable a satisfying representation of the measurements, although the models were defined with the consideration of a concentration of the catalyst H^+ calculated with the total concentration of OPA (equation (4)) instead of its instantaneous concentration. The theoretical curves thus obtained differ from the real theoretical curve essentially in a faster convergence to zero. Fig. 11 shows that the conversion of OPA in BA is quite slow. The consideration of the concentration of H^+ calculated with the total concentration of OPA is thus not so far from the reality.

The evolution of the concentrations of OPA and BA as a function of the temperature (Fig. 13) shows that 275 °C is the temperature which leads to the highest recovery rate of OPA while limiting the reaction of decarboxylation. Above 300 °C, the recovery rate of OPA decreases with the temperature and the rate of decarboxylation strongly increases. A dissociation constant of OPA decreasing with the temperature, according to the model of Goldberg et al. [22], may explain the decreasing recovery rate of OPA, despite a rate constant of hydrolysis increasing with the temperature. So hydrolysis is accelerated more probably thanks to a thermal effect. The increasing rate of decarboxylation with the temperature is also more probably due to a thermal effect than to an acid catalysis.

The evolution of the concentration of PG released by hydrolysis (Fig. 12) shows a maximum around 27 min (1600 s). About 60% of PG released by hydrolysis was still present (the theoretical curve indicates a molar ratio of 0.4 but relatively to the initial concentration of PG. This gives 60% relatively to the concentration of PG released by hydrolysis). After 45 min, only 25% of released PG remained. Dehydration is thus fast and important. A semi-continuous process could limit that secondary reaction by limiting the residence time of released PG in the reactor. The evolution of the concentrations of PG and its secondary products is represented on Fig. 14 as a function of the temperature. It shows that 275 °C is also the temperature which leads to the highest recovery rate of PG. The conversion into propanal and 2-propen-1-ol increases with the temperature, particularly propanal. The total recovery of PG decreases with the temperature for the same reason as for OPA. However above 325 °C, it increases with the temperature. This can be explained by the fact that ester bonds between PG and succinic acid were broken but probably more thanks to a thermal effect. The increasing rate of dehydration is also more probably due to a thermal effect.

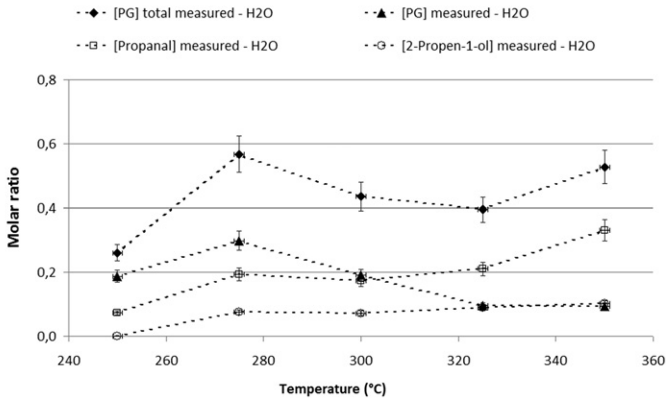


Fig. 14. Evolution of the total and instantaneous concentrations of PG and of the concentrations of propanal and 2-propen-1-ol at different temperature for a duration of 10 min in H_2O for the resin A.

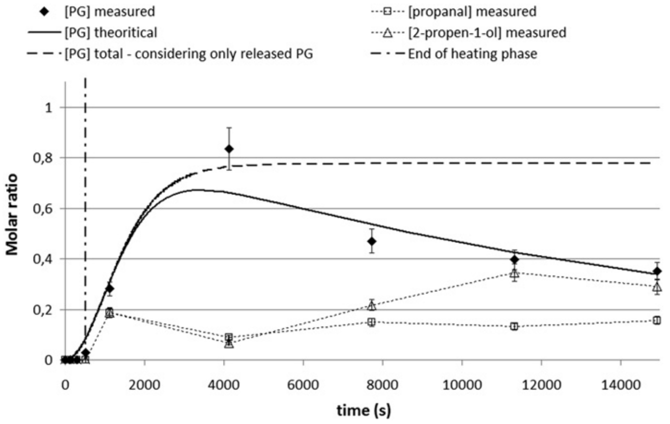


Fig. 15. Evolution of the concentration of PG for hydrolysis of composite made of resin B.

4.2.5. *Influence of the chemical structure on the kinetics of the main secondary reactions*

The evolution of the concentrations of PG as a function of time is represented for resins B and C on Figs. 15 and 16 respectively. The evolution of the concentration of OPA for the resin C is presented on Fig. 17. The fittings of the parameter $(k_7 + k_8)$ for the dehydration of PG were realised for the resin B using the global constant of hydrolysis calculated from the evolution of the total concentration of PG. For the resin C, the parameter k_6 was fitted using the rate constant calculated from the evolution of the total concentration of OPA, and the parameter $(k_7 + k_8)$ was fitted using the rate constant calculated from the evolution of the total concentration of PG. The results are grouped in Table 10.

For both resins B and C, dehydration of PG is considerably slower than for the resin A (Table 10). For the resin B, it can be explained by a lower production of H^+ provided by the dissociation of IPA than by the dissociation of OPA present in the resin A. For the resin C, the slower dehydration can be explained by the fast disappearance of OPA by decarboxylation. On the contrary, a slow decarboxylation and a fast dehydration are observed for the resin A (Table 10). The involved diffusion processes might also play a role in the kinetics of those secondary reactions.

If the resins A and B are hydrolysed in a same batch, dehydration of PG released from the resin B could be accelerated because of the production of H^+ from the dissociation of OPA released from the resin A. A semi-continuous process would allow a limitation of those secondary

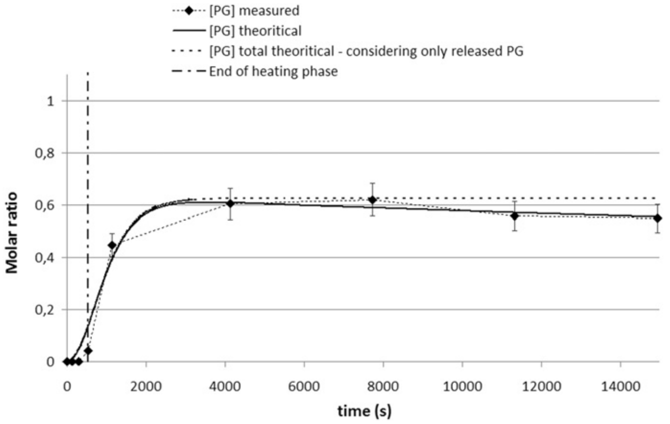


Fig. 16. Evolution of the concentration of PG for hydrolysis of composite made of resin C.

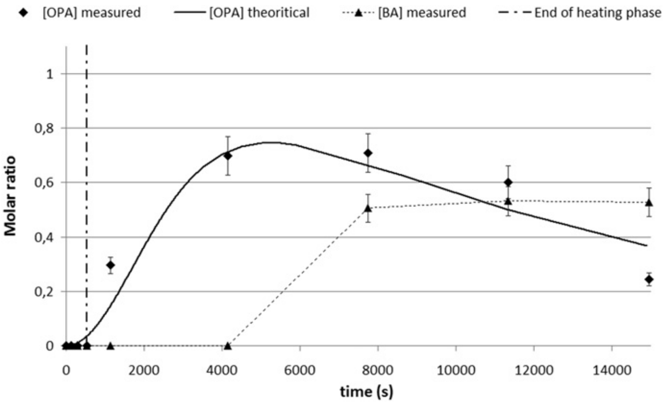


Fig. 17. Evolution of the concentration of OPA for hydrolysis of composite made of resin C.

Table 10
Rate constants of decarboxylation and dehydration for each resin.

	Decarboxylation k_6 (L/mol.s)	R^2	Dehydration $(k_7 + k_8)$ (L/mol.s)	R^2
Resin A	1.3	0.945	54.4	0.869
Resin B	n/a		9.8	0.969
Resin C	24.9	0.966	0.9	0.991

reactions. However the renewal of the aqueous medium would maintain a quite neutral pH. This can change the reaction mechanisms.

5. Conclusions

The study of the deuterium isotope effect indicates that the hydrolysis in subcritical conditions of unsaturated polyester cross-linked with styrene is acid-catalysed and that an $A_{ac}2$ mechanism is the most probable. Only hydronium ions can catalyse the reaction, so it depends on the pH. However the proposed model does not take into account the heterogeneity of the system and the diffusion processes. The presence of the fibres and their orientation may also influence the diffusion processes. Furthermore the ester bonds do not present the same reactivity and each ester group does not behave independently of its environment and especially of the surrounding ester groups [35]. That is partially observed in the present results as the global constant of hydrolysis is different if it is calculated relative to PG or to OPA. Ester bonds between PG and succinic acid also do not seem to be hydrolysable in the conditions used, certainly because of the steric hindrance and the hydrophobic character induced by the styrene chains bonded to succinic acid.

In less than 40 min at 275 °C, all the hydrolysable ester bonds are broken. PG and OPA, monomers of the studied resin, are produced but are also subjected to secondary reactions. Particularly PG dehydrates very rapidly in propanal. OPA decarboxylates but this reaction is quite slow. A semi-continuous process would allow a limitation of those secondary reactions. However the renewal of the aqueous medium would maintain a quite neutral pH. The mechanism of hydrolysis could then be different from the proposed $A_{ac}2$ mechanism and be considerably slower. Mass transfer improvement by the continuous renewal of the solvent could compensate the latter phenomenon. When hydrolysis achieves its maximum, the fibres of the composite material are still maintained by a copolymer styrene-acid succinic (by deduction) which represents around 50% by weight of the total mass of the cross-linked resin. A longer time allows only the secondary reactions to occur and a degradation and/or dissolution of the remaining copolymer. However it also allows a better separation of the fibres and their recovery. A semi-continuous process could also improve this last point. Furthermore the more neutral pH induced by the renewal of the aqueous medium could limit the acid corrosion of the fibres [11].

The study of the influence of the chemical structure of polyester resins on the hydrolysis kinetics showed that hydrolysis of isophthalic polyester is slower than the one of orthophthalic polyester. However the influence of the chemical structure is not so noticeable on the apparent activation energies. The nature of ester bonds is thus not so influent. The recovery rates of PG in particular for those both resins showed that the structure of the polystyrene network in the resin could have an influence on the hydrolysis rate. The chemical structure influences the kinetics of the main secondary reactions. The kinetics for those both resins though indicates that they could be hydrolysed together. As composites made of glass fibres and iso- or ortho-phthalic polyesters represent more than 95% of the total volume of GFRC, this is an important point considering an industrial application of the hydrolysis process to recycle those materials.

Another polyester resin, based on DCPD at chain ends, was studied but the complexity of the structure of macromolecules makes impossible the determination of a global rate constant of hydrolysis. Furthermore this type of resin produces many different monomers and secondary products. It will then require a specific hydrolysis treatment. However the three resins can be hydrolysed in the same conditions (275 °C–60 bars). A higher temperature only leads to faster secondary reactions to the detriment of hydrolysis.

The diffusion processes, considered here to be included in the rate constant of hydrolysis, might play a role on the differences observed between the three types of studied resin. It will be necessary to characterise the involved types of diffusion process in order to describe more accurately the mechanisms of degradation during hydrolysis.

The proposed model thus gives only a global view and a first approach to the understanding of the mechanism of hydrolysis used to recycle composite materials made of unsaturated polyester resin and reinforced with glass fibres. Many points still have to be resolved but some quite smooth subcritical conditions (275°C–60 bars in water) were identified to recover valuable products.

Acknowledgements

This study was carried out as part of the EURECOMP project with funding received from the European Community's Seventh Framework Programme (FP7/2007–2013) under grant agreement n 218609. The authors wish to thank Thierry Foussard, R&D director at *CCP Composites* (Drocourt site) for his valuable help. The authors are extremely grateful to Fabrice Monteau and Karine Pouponneau from the *Laboratoire d'Etude des Résidus et des Contaminants dans les Aliments* (LABERCA) for their precious help during GC–MS analysis.

Appendix A

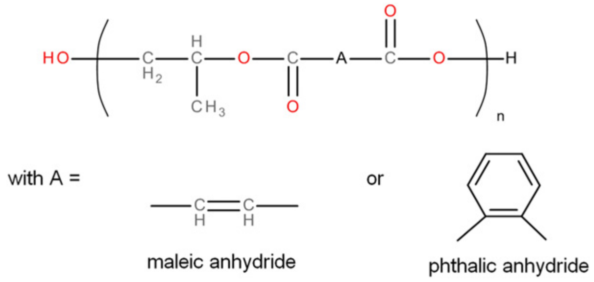


Fig. A.1. Theoretical structure of the polyester prepolymer of the resin A.

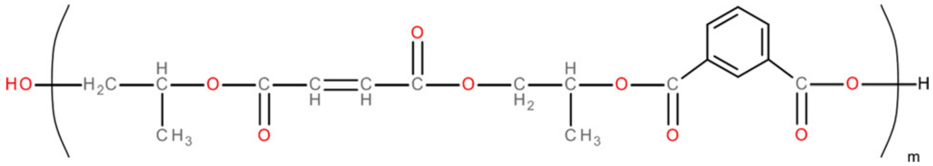


Fig. A.2. Theoretical structure of the polyester prepolymer of the resin B.

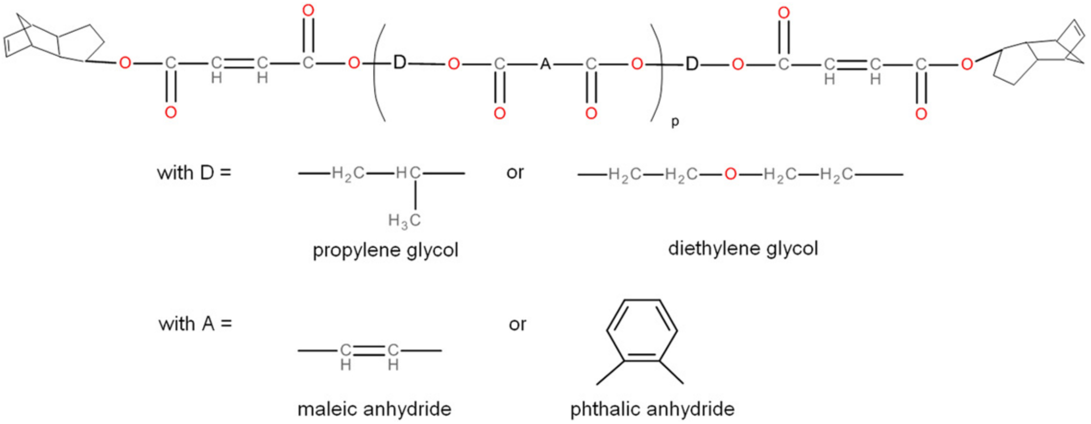


Fig. A.3. Theoretical structure of the polyester prepolymer of the resin C.

References

[1] Witten E. The composites market in Europe: market developments, challenges, and opportunities. AVK report. 2008. http://www.eucia.org/uploads/cf91cb671a72c3a9c26b2e91c6edab57.pdf.

[2] Yongxiang Y, Boom R, Irion B, van Heerden DJ, Kuiper P, de Wit H. Recycling of composite materials. Chemical Engineering and Processing: Process Intensification 2012;51:53–68.

[3] Pickering SJ, Kelly RM, Kennerley JR, Rudd CD, Fenwick NJ. A fluidised-bed process for the recovery of glass fibres from scrap thermoset composites. Composites Science and Technology 2000;60:509–23.

[4] Cunliffe AM, Williams PT. Characterisation of products from the recycling of glass fibre reinforced polyester waste by pyrolysis. Fuel 2003;82:2223–30.

[5] Palmer J, Ghita OR, Savage L, Evans KE. Successful closed-loop recycling of thermoset composites. Composites: Part A. 2009;40:490–8.

[6] Kamimura A, Yamada K, Kuratoni T, Taguchi Y, Tomonaga F. Effective depolymerization waste FRPs by treatment with DMAP and supercritical alcohol. Chemistry Letters 2006;35:586.

[7] Pinero-Hernanz R, Garcia-Cerna J, Dodds C, Hyde J, Poliakoff M, Cocero MJ, et al. Chemical recycling of carbon fibre composites using alcohols under subcritical and supercritical conditions. The Journal of Supercritical Fluids 2008;46:83–92.

[8] Pinero-Hernanz R, Dodds C, Hyde J, Garcia-Cerna J, Poliakoff M, Lester E, et al. Chemical recycling of carbon fibre reinforced composites in nearcritical and supercritical water. Composites: Part A 2008;39:454–61.

[9] Iwaya T, Tokuno S, Sasaki M, Goto M, Shibata K. Recycling of fiber reinforced plastics using depolymerization by solvothermal reaction with catalyst. Journal of Materials Science 2008;43:2452–6.

[10] Nakagawa T. FRP recycling technology using sub-critical water hydrolysis. JEC Composites Magazine March-April, 2008:40–3.

[11] Oliveux G, Le Gal La Salle E, Bailleul J-L. Chemical recyling of glass fibre reinforced composites using subcritical water. Composites: Part A 2012;43(11):1809–18.

[12] Brunner G. Near critical and supercritical water. Part I. Hydrolytic and hydrothermal processes. The Journal of Supercritical Fluids 2009;47:373–81.

[13] Akiya N, Savage PE. Roles of water for chemical reactions in high-temperature water. Chemical Reviews 2002;102:2725–50.

[14] Suyama K, Kubota M, Shirai M, Yoshida H. Effect of alcohols on the degradation of crosslinked unsaturated polyester in sub-critical water. Polymer Degradation and Stability 2006;91:983–6.

[15] Suyama K, Kubota M, Shirai M, Yoshida H. Degradation of crosslinked unsaturated polyesters in sub-critical water. Polymer Degradation and Stability 2007;92:317–22.

[16] Yates K, McClelland RA. Mechanisms of ester hydrolysis in aqueous sulfuric acids. Journal of the American Chemical Society 1967;89(11):2686–92.

[17] Lesutis HP, Gläser R, Liotta CL, Eckert CA. Acid/base-catalyzed ester hydrolysis in near-critical water. Chemical Communications 1999;20:2063–4.

[18] Patrick HR, Griffith K, Liotta CL, Eckert CA, Gläser R. Near-critical water: a benign medium for catalytic reactions. Industrial and Engineering Chemistry Research 2001;40(26):6063–7.

[19] Krammer P, Vogel H. Hydrolysis of esters in subcritical and supercritical water. The Journal of Supercritical Fluids 2000;16:189–206.

[20] Oliveux G, Le Gal La Salle E, Bailleul J-L, Heard PJ, Ball RJ, Hallam KR, Ghita O. Recyclage par solvolyse des matériaux composites thermodurcissables du transport de surface. Matériaux et Techniques 2012;100(5):493–503.

[21] Lowry TH, Richardson KS. Mechanism and theory in organic chemistry. 2nd ed. New York: Harper and Row; 1981. p. 242–3.

[22] Goldberg RN, Kishore N, Lennen RM. Thermodynamic quantities for the ionization reactions of buffers. Journal of Physical and Chemical Reference Data 2002;31(2):231–370.

[23] Apelblat A, Manzurola E, Balal NA. The solubilities of benzene polycarboxylic acids in water. Journal of Chemical Thermodynamics 2006;38:565–71.

[24] Read AJ. Ionization constants of benzoic acid from 25 to 250 °C and to 2000 bar. Journal of Solution Chemistry 1981;10(7):437–50.

[25] Marshall WL, Franck EU. Ion product of water substance, 0–1000 °C, 1–10,000 bars – new international formulation and its background. Journal of Physical and Chemical Reference Data 1981;10(2):295–304.

[26] Lemmon EW, McLinden MO, Friend DG. Thermophysical properties of fluid systems. In: The WebBook of chemistry NIST, standard reference data base NIST. Number 69. [ed.] P.J. Linstrom and W.G. Mallard. Gaithersburg: National Institute of Standards and Technology; http://webbook.nist.gov.

[27] Mundle SOC, Lacrampe-Couloume G, Lollar Sherwood B, Kluger R. Hydrolytic decarboxylation of carboxylic acids and the formation of protonated carbonic acid. Journal of the American Chemical Society 2010;132:2430–6.

[28] Dunn JB, Burns ML, Hunter SE, Savage PE. Hydrothermal stability of aromatic carboxylic acids. The Journal of Supercritical Fluids 2003;27(3):263–74.

[29] Disselkamp RS, Harris BD, Patel JN, Hart TR, Peden CHF. Propanal synthesis from aqueous propylene glycol/hydrogen peroxide on a Ru/alumina catalyst. Inorganic Chemistry Communications 2008;11:561–3.

[30] Dai Z, Hatano B, Tagaya H. Catalytic dehydration of propylene glycol with salts in near-critical water. Applied Catalysis A: General 2004;258:189–93.

[31] Debellefontaine H, Striolo P, Chakchouk M, Foussard J-N, Besombes-Vailhe J. Nouveaux procédés d'oxydation chimique pour l'élimination des rejets aqueux phénolés. Revue des sciences de l'eau 1992;5(4):555–72.

[32] Clayden J, Greeves N, Warren S, Wothers P. Chimie Organique. [trans.] André Pousse. De Boeck Université; 2003. p. 1102–4.

[33] Pritchard JG, Long FA. Hydrolysis of ethylene oxide derivatives in deuterium oxide-water mixtures. Journal of American Chemical Society 1956;78(23):6009–13.

[34] Bélan F, Bellenger V, Mortaigne B, Verdu J. Relationship between the structure and hydrolysis rate of unsaturated polyester prepolymers. Polymer Degradation and Stability 1997;56:301–9.

[35] Bélan F, Bellenger V, Mortaigne B, Verdu J, Yang YS. Hydrolytic stability of unsaturated polyester prepolymers. Composites Science and Technology 1996;56:733–7.

[36] Oliveux G, Le Gal La Salle E, Bailleul J-L. Recycling by hydrolysis thermosetting composite materials of sustainable transport. In: AIP Conf. Proc. International Conference on Advances in Materials and Processing (AMPT 2010). 1315: 209–14.