EFFECT OF THE SAMPLE GRANULOMETRY ON THE HYDROLYSIS OF CARBON FIBRE REINFORCED EPOXY (CFRE) IN HIGH TEMPERATURE AND HIGH PRESSURE WATER

Gidéon Simenou[1,2,3], Éric Le Gal La Salle[2], Jean-Luc Bailleul[1] and Jérôme Bellettre[1]

[1]Laboratoire de Thermocinétique de Nantes (LTN), UMR CNRS 6607, Ecole Polytechnique de l'Université de Nantes
Rue Christian Pauc, 44300 Nantes, France
Email: jean-luc.bailleul@univ-nantes.fr, web page: http://www.polytech.univ-nantes.fr/ltn/fr/
[2]Laboratoire Energétique, Mécanique et Matériaux (LE2M) de l'Institut Catholique des Arts et Métiers de Nantes (ICAM)
35 Avenue du champ de manœuvres, 44470 Carquefou, France
Email: eric.legallasalle@icam.fr, web page: http://www.icam.fr/
[3]Institut de Recherche Technologique Jules Verne (IRT Jules Verne)
Allée du Chaffault, 44340 Bouguenais, France
Email: sandy.moisan@itrt-jules-verne.fr, web page: http://www.irt-jules-verne.fr/

Keywords: hydrolysis, samples granulometry, epoxy resin

Abstract
Carbon Fibers Reinforced Epoxy hydrolysis experiments were performed in a 500 ml tubular batch reactor. The effect of sample granulometry on the resin degradation was investigated. The sample surface/volume ratio (*S/V*) varied in the range of 3 to 19 cm^{-1}. All sample weights were between 1 gram and 10 grams. The hydrolysis experiments were performed at a temperature (*T*) between 320°C and 360°C for a reaction time (*t*) between 360 and 2700 s. The hydrolysis was also performed on the neat resin at 320°C during 1800s. Results indicated that increasing the sample size seems to have a negative effect on the degradation rate of the resin. This result is more relevant in the case of the neat resin.

1. Introduction

Epoxy resins have been widely used for the manufacture of Carbon Fiber Reinforced Epoxy (CFRE). Companies involved in the composite are now looking for recycling solutions in order to set up a recycling industry. Therefore, many recycling processes have been developed since the 2000's. The hydrolysis process uses high temperature and high pressure water in order to remove resin material from the fibers. This process was developed allowing not only to allow the use of less hazardous solvents, but also to reduce the cycle time. When studying the degradation process of composite materials, it is usual to first identify parameters that will affect the effectiveness of the process. Four different parameters are frequently used to monitor the hydrolysis process: temperature (*T*), reaction time (*t*), amount of water in the reactor vessel ($V_{water}/V_{reactor}$) and amount of composite material (m_{CFRP}/m_{water}). Very few studies, as we know, were devoted to the study of the effect of other parameters, as the granulometry.

Excerpt from ISBN 978-3-00-053387-7

In the field of thermal degradation of resins, no works were found in the literature related to the effect of sample sizes. More studies were found on the effect of granulometry in the field of thermal degradation of biomass. Koufopanos et al [1] studied the pyrolysis of particles of biomass, the size of which lies between 1 and 25 mm. The study was performed using temperature between 350 to 700°C. They found that, reducing the particles size leads to the enhancement of the degradation ratio. In fact, when increasing the particle size, the time required to reach a given conversion rate increase. Most of the authors working on this subject have reached to the same conclusion [2], [3]. Demirbas et al [2] also found a similar result and tried to give an explanation to this finding. They explained that, in the case of a single particle, the heat flux diffuses gradually from the "shell" to the "core". This cause a thermal gradient inside the particles, which lead to a difference of temperature between the "shell" hotter than the "core". Following the same logic, the heat flux and the temperature level are higher in small particles than in bigger particles. In their work, Koufopanos et al [1] also suggests that for particles size below 1 mm, the kinetics of the process is controlled by the kinetics of the degradation. Whereas, for particles size upper 1 mm, the kinetics of the process is at least controlled by 3 phenomena's: degradation, heat transfer and mass transfer. The work of Beaumont et al [3] leads to a different conclusion. They studied the slow pyrolysis of wood of particles size from 0.05 to 0.5 mm. They found that particles size has no sensitive effect on the degradation yield.

This investigation was undertaken in order to collect information about the effect of the granulometry on the degradation of the resin, during the high temperature and high pressure hydrolysis of CFRE. This was achieved by studying the effect of the surface/volume ratio of CFRE and neat resin on the effectiveness of the resin degradation.

2. Experimental

The composite material used in this study was made of epoxy cured resin, reinforced with multidirectional carbon fibers. This was collected from the production waste and cut samples in two size (43 mm x 19 mm x 8 mm and 35 mm x 19 mm x 8 mm). Samples were further cut for our experiments. The neat resin was collected as uncured polymer. Both materials come from the aeronautics industry.

Three experiments were performed. In the first experiment, the precut samples 43 mm x 19 mm x 8 mm were further cut in planes transverse to the fibres. In the second experiment, the precut samples 35 mm x 19 mm x 8 mm were further cut in planes parallel to the fibres (Figure 1). In the third experiment, a silicon mold was used as the container for resin polymerization.

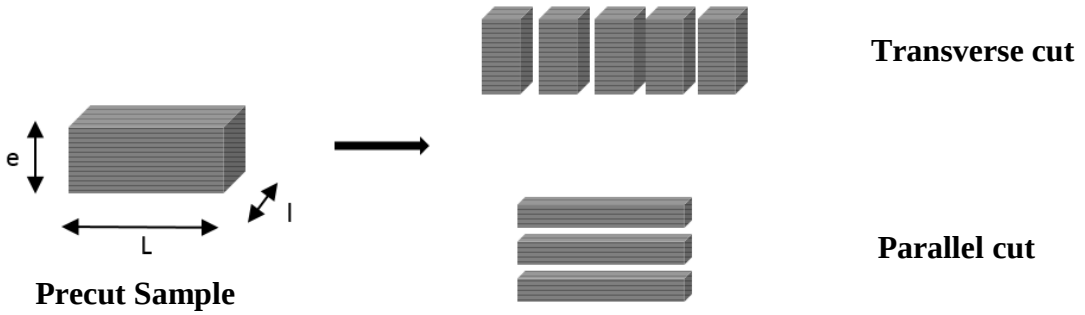

Figure 1. Samples cutting procedure.

Distilled water from Labogros-Grosseron® was used as solvent without further treatment.

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A tubular batch reactor was used to carry out the hydrolysis experiments. The detail description of the reactor system is presented in Figure 2. A tubular batch reactor of 587 ml capacity, with 316L stainless steel material was used (N°2). The heating was achieved by an inductive external equipment (N°2 and N°3). The temperature inside the reactor is measured with a type K thermocouple. The pressure is measured with a differential pressure gauge (N°1). Another thermocouple disposed on the external surface of the reactor is related to a control system (N°6, 7, 8). It took about 10 min to heat the reactor from room temperature to 320°C. The whole installation is scaled for a maximum condition of 270 bar and 510°C. Cooling is provided by circulating water in a shell closing over the reactor. It took about 30 min to cool the reactor from 320°C to under 100°C. For each experiment, samples are placed in a basket with three compartments, separated by perforated grids (Figure 3). Each compartment contains samples of different total surface/volume

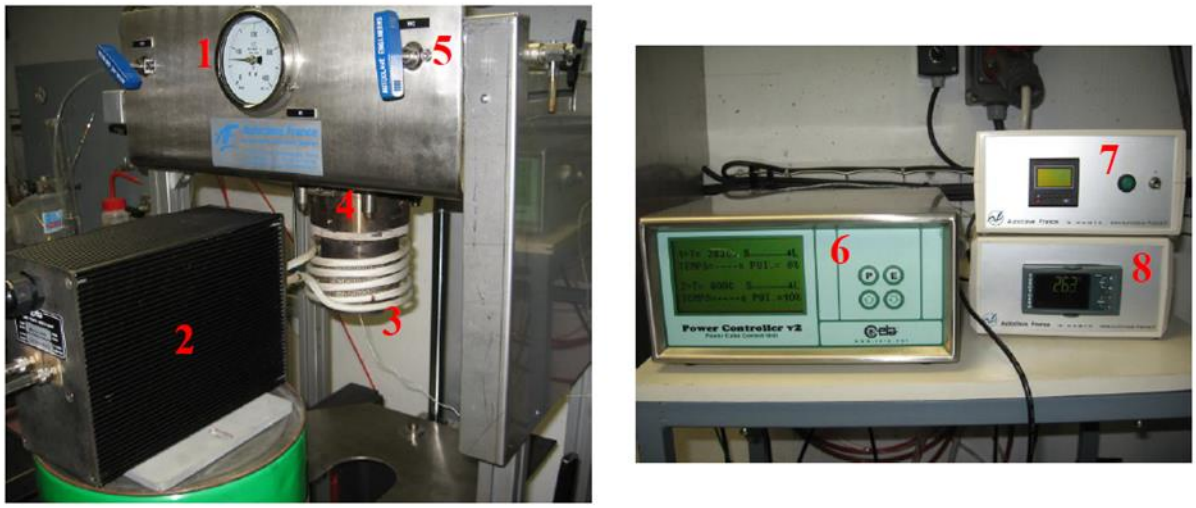

Figure 2. Experimental apparatus of the 587ml reactor- 1: pressure sensor (0-400bar à 5bars=div), 2: heating heads, 3: inductor, 4: reactor vessel, 5: outlet valves, 6: heating control unit, 7: timer, 8: temperature recorder.

Perforated grid basket

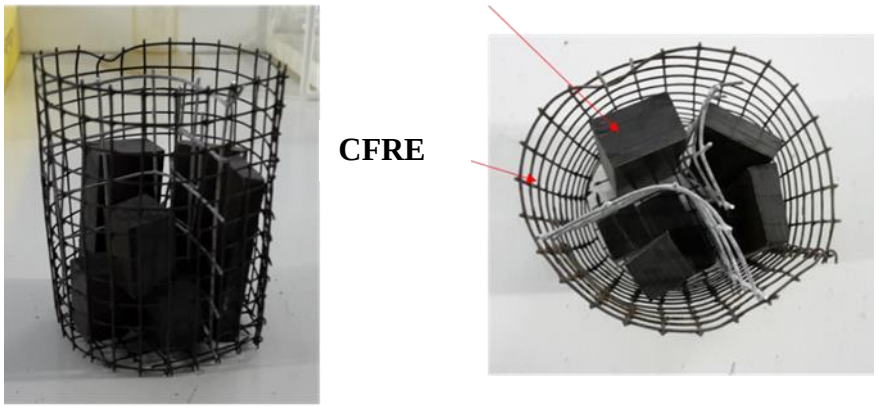

Figure 3. Samples layout in the perforated grid basket.

Parameters used in this study and the corresponding resin degradation ratio (α) are reported in Table 3.

$$\alpha = (m^{i}_{resin} - m^{f}_{resin}) / m^{i}_{resin}$$

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Where m^i and m^f are respectively the initial and final mass of resin.

Table 1. Experimental conditions and results.

Experiment	Material	T (°C)	t (s)	Cutting plane	Number of samples	Dimensions L x l x e (mm)	S/V(cm^{-1})	α
1	CFRE	320	2700	--	1	43 x 19 x 8	3.90	0.74
	CFRE	320	2700	⊥ fibres	11	4 x 19 x 8	8.60	0.60
	CFRE	320	2700	⊥ fibres	24	2 x 19 x 8	14.80	0.35
2	CFRE	320	2700	--	1	35 X 19 x 8	3.30	0.85
	CFRE	320	2700	// fibres	4	35 x 19 x 2	9.20	0.71
	CFRE	320	2700	// fibres	9	35 x 19 x 0,9	19.20	0.56
3	Neat Resin	320	1800	--	1	55 x 26 x 10	3.13	0.63
	Neat Resin	320	1800	⊥ fibres	2	55 x 26 x 5	5.13	0.31
	Neat Resin	320	1800	⊥ fibres	6	55 x 26 x 1,7	13.11	0

3. Results and discussions

Figure 3 shows the resin degradation ratio of experiments 1 and 2 for a hydrolysis temperature of 320°C and a reaction time of 45 min plotted versus the S/V ratio. It's clear that the degradation process is highly impacted by the sample size.

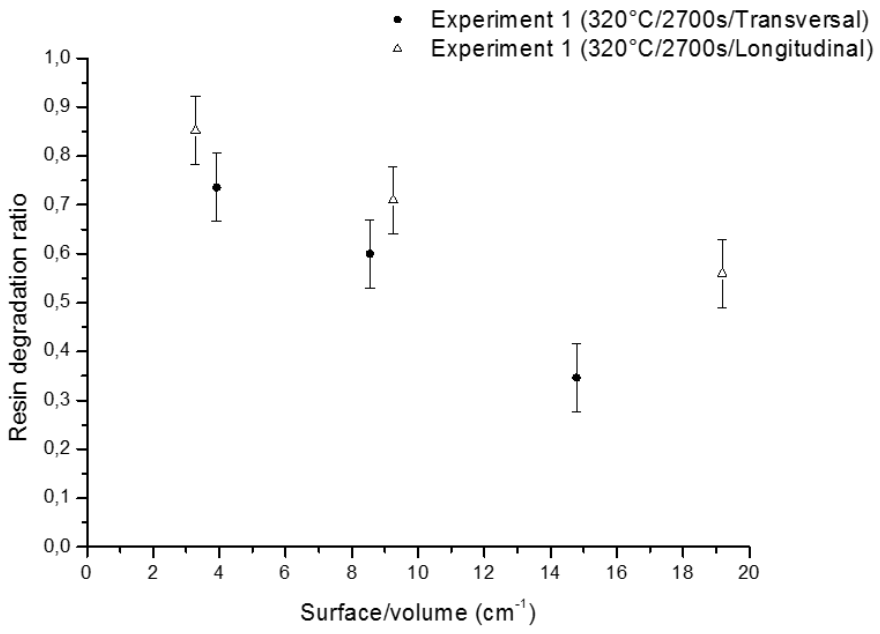

Figure 3. Evolution of the resin degradation ratio in CFRE platted against the S/V ratio.

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3.1. Effect of sample S/V ratio

In experiment 1, the resin degradation ratio is maximized (0.74 wt) for the sample size 43 mm x 19 mm x 8 mm, corresponding to S/V=3.9 cm^{-1}. The sample of size 4 mm x 19 mm x 8 mm, with the total S/V=8.6 cm^{-1} shows a lower resin degradation ratio of 0.6 wt. The lowest resin degradation ratio of 0.35 wt was achieved with the lowest sample size (2 mm x 19 mm x 8 mm). This result highlights an unexpected behavior. As the sample size decrease, the degradation rate of the resin decrease. This result is opposed to what expected, given the results obtained in the literature. In order to understand and explain this behavior, a thermal study of the hydrolysis process of the resin was carried out. We found that this unexpected effect of sample size, is due to thermal effects related to water. More details about this thermal study will be published in a future communication.

3.2. Effect of the cutting direction

In experiment 2, where samples were cut in the planes parallel to the fibres, the same effect has been observed. The resin degradation ratio is maximized (0.85 wt) for the highest sample size 35 mm x 19 mm x 8 mm, corresponding to S/V=3.3 cm^{-1}. The sample of size 35 mm x 19 mm x 2 mm, with S/V=9.2 cm^{-1} shows a lower resin degradation ratio of 0.71 wt. The lowest resin degradation ratio of 0.56 wt was achieved with the lowest sample size (35 mm x 19 mm x 0.2 mm).

The degradation ratio of the samples cut in the planes parallel to the fibres is globally higher than those cut in the transverse planes. However, the observed gaps are not high enough to conclude to a significant effect of the cutting direction.

3.2. Effect of sample S/V ratio on the neat resin degradation

Figure 4 represents the resin degradation ratio for different S/V ratio, in experiment 3 for the neat resin. In this case, the degradation process is also highly impacted by the sample granulometry. The resin degradation ratio is maximized (0.63 wt) for the highest sample size 55 mm x 26 mm x 10 mm, corresponding to S/V=3.13 cm^{-1}. The sample of size 55 mm x 26 mm x 5 mm, with the total S/V=5.13 cm^{-1} shows a lower resin degradation ratio of 0.31 wt. The lowest resin degradation ratio near 0 wt was achieved with the lowest sample size (55 mm x 26 mm x 1.7 mm). This result confirms the unexpected effect of the sample size observed in the case of the CFRE. The effect is even more significant in the case of the neat resin.

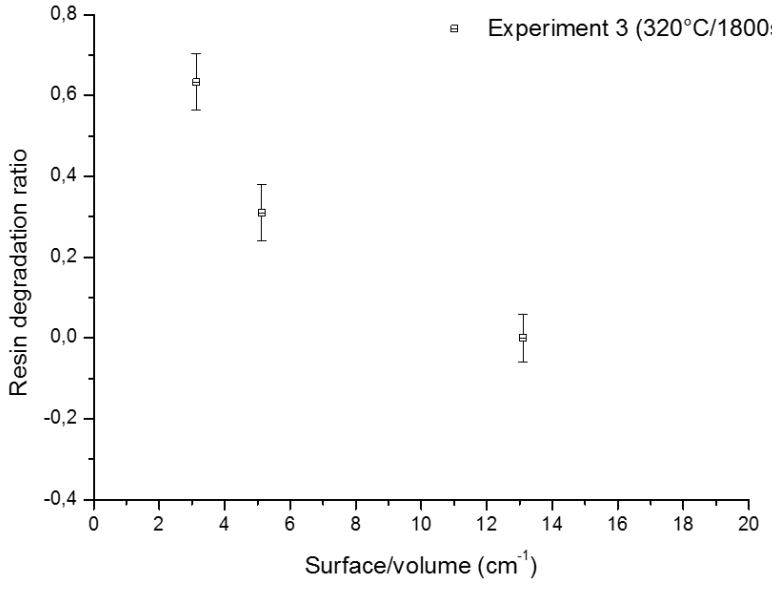

Figure 4. Evolution of the neat resin degradation ratio plotted against the S/V ratio.

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3. Conclusions

In this study, the hydrolysis of a Carbon Fiber Reinforced Epoxy in a tubular batch reactor at a hydrolysis temperature of 320°C were performed for different sample sizes. The results have shown that the effect of the sample size on the degradation of the resin is significant. As the sample size decreases, the degradation ratio decreases. This means that reducing the size of the sample lower than 43 mm x 19 mm x 8 mm has a negative effect on the degradation ratio. This is clearly a counter-intuitive and unexpected result and was also observed in the case of the neat resin. The effect of the cutting plane was investigated, but the observed differences were not enough to conclude to a significant effect of this parameter. We have shown that this unexpected effect of sample size, is due to a thermal effects related to the water.

Acknowledgments

This study is part of the PARCCA project supported by IRT Jules Verne (French Institute in Research and Technology in Advanced Manufacturing Technologies for Composite, Metallic and Hybrid Structures). The authors wish to associate the industrial and academic partners of this project; respectively AIRBUS Operations, VEOLIA, OMEGA SYSTEMES, SACMO and Laboratoire de Thermocinétique de Nantes (LTN), Institut Catholique d'Arts et Métiers (ICAM).

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