KINETIC OF THE HYDROLYSIS OF THREE DIFFERENT CARBON FIBRE REINFORCED EPOXY (CFRE) IN HIGH TEMPERATURE AND HIGH PRESSURE WATER

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Abstract

High temperature and high pressure hydrolysis experiment of three different Carbon fiber reinforced epoxy (CFRE) composites were carried out. Isothermal experiments at different reaction times were performed using six tubular batch reactors of 20 ml, with the aim to gain a better understanding of the effect of temperature and time and to determine the kinetic parameters. The temperature was set between 320°C and 360°C and the reaction time was set between 0 and 185 min. The kinetic parameters were determined using a heterogeneous kinetic model, often used in the solid state kinetic. The model used proved to be effective in fitting our data. It also proved to be effective for the determination of the kinetic parameters. Calculated parameters are in the range those found in literature.

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1. Introduction

Epoxy resins have been widely used for the manufacturing of Carbon Fiber Reinforced Epoxy (CFRE). Companies involved in the composite are now looking for recycling solutions. Therefore, many recycling processes have been developed since 2000's. In the hydrolysis process, high temperature and high pressure water is used to remove the resin material from the fibers.

The first step of a comprehensive study of a process is the identification parameters that affect the process efficiency. The second step is the understanding the way that those parameters affect the process. Five parameters were identified in the literature as the most influencial : temperature (T), reaction time (t) [1]–[3], granulometry [4], amount of water in the reactor vessel ($V_{water}/V_{reactor}$) and amount of composite material (m_{CFRP}/m_{water}) [1].

The aim of this work is to gain a better understanding of the effect of the temperature and the reaction time. This is achieved by studying the kinetics of the process. Many studies were found in the literature on the solid-state kinetic. But, only a few of these works were devoted to the study of the kinetics of the hydrolysis of the epoxy resin. Pinero-Hernanz et al [3] studied the kinetics of the hydrolysis of a pre-preg CFRE between 260°C and 300°C. The pre-exponential factor and the activation energy were respectively 24.4x10^3 g^{-1} min^{-1} and 35.5 kJ mol^{-1}. Yuyan Liu et al [5] studied the hydrolysis of an epoxy resin between 260°C and 300°C and found an activation energy of 123.5 kJ mol^{-1}. El Ghazzaoui [1] studied the hydrolysis of two CFRE. One was treated at temperatures between 310°C and 340°C. The analysis of the results shows a pre-exponential factor of 14.4 x 10^{75} g^{-1} s^{-1} and an activation energy of 868.5 kJ mol^{-1}. The second one was treated at temperatures between 340°C and 360°C. The pre-exponential factor and the activation energy were respectively 26.6 x 10^{39} g^{-1} s^{-1} and 507.5 kJ mol^{-1}. A more recent study by Gong et al [6] investigated the kinetics of DDS-cured DGEBA epoxy resin in hot water at temperatures between 300°C to 330°C. The results show an activation energy of 170.7 kJ mol^{-1}. These kinetic parameters are global parameters that result from several chemical reactions leading to the resin degradation.

In this work, the kinetics of the resin degradation during the hydrolysis of three different CFRE were investigated. Experiments were performed in six tubular batch reactors of 20 ml. A kinetic model found in the literature was used to determine the global kinetics parameters.

2. Experimental

Three different CFRE were used in this study. Two of them (CPP3 and CPP2) were epoxy-amine cured and reinforced with carbon fibres. The third one (CPNP) was an epoxy-amine uncured sheet reinforced with carbon fibre. Waste off-cuts of carbon fiber reinforced epoxy resin were used. They were collected from the production waste in aeronautics industry. Some characteristics of the different CFRE used in this study are reported in Table 1.

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

Table 1. Characteristics of the CFRE.

CFRE	Fibres alignment	Samples Dimension (mm)	Number of samples	Samples weight (g)	Resin
CPP3	multidirectional	19.5 x 8.4 x 9	1	2.2	Resin1
CPP2	unidirectional	19.3 x 12.5 x 8	1	2.8	Resin2
CPNP	unidirectional	20 x 12.5 x 0.33	10	1,4	Resin2

Experiments were performed in small batch reactors of about 20 mL, build with a Swagelok® connector SS-16-VCR-6-DM and two Swagelok® caps SS-16-VCR-CP. One of the two caps was instrumented with one K-Type thermocouples. This enabled the measurement of the temperature in the liquid phase. 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 the temperature inside the reactor to be set at ±1°C. The different temperatures were acquired using an Agilent unit 34970A with an acquisition card 34902A. At the end of the hydrolysis treatment, the reactor caps are first cooled by spraying cold water on the upper lid of

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the reactor, and then the reactor was cooled in a bath of cold water. The cooling water jet allows the cover contracts on the body of the reactor, thus avoiding the infiltration of water, which would be due to a larger contraction of the connector from the cover, when the reactor is immersed in the cold water bath.

Table 2 shows the value of the different parameters used in this study.

Table 2. Experimental conditions.

CFRE	T (°C)	t (min)	m_{CFRE}/m_{water}	$V_{water}/V_{reactor}$
CPP3	320; 330; 340; 350; 360	5 - 120	0.22	0.5
CPP2	340; 350; 360	5 - 120	0.28	0.5
CPNP	340; 350; 360	5 - 185	0.14	0.5

3. Results and discussions

Figure 1 shows the plots of the experimental resin degradation ratio for the three different CFRE versus the reaction time at different temperatures. It can be seen that, the shape of the evolution of the resin degradation ratio (α) is highly dependent on both temperature and time.

$$\alpha = (m_i - m_f) / m_i \tag{1}$$

Where m_i and m_f are respectively the initial and final weight of the resin in the CFRE.

3.1. Effect of reaction time

Figure 1 (a) shows the evolution of the resin degradation ratio in CPP3 plotted versus the reaction time, for 5 temperatures (320, 330, 340, 350, and 360°C). For lower temperatures, the curve has presented an s-shape profile (see the insert included in Figure 1 (a)). This shape disappears gradually as the temperature increase. The degradation curve can be divided into three phases: an acceleration phase (Phase 1), in the second phase (Phase 2), the acceleration is far more important, the third phase (Phase 3) is a deceleration phase where the resin degradation ratio reached a maximum value. The same behavior was observed for CPP2 and CPNP.

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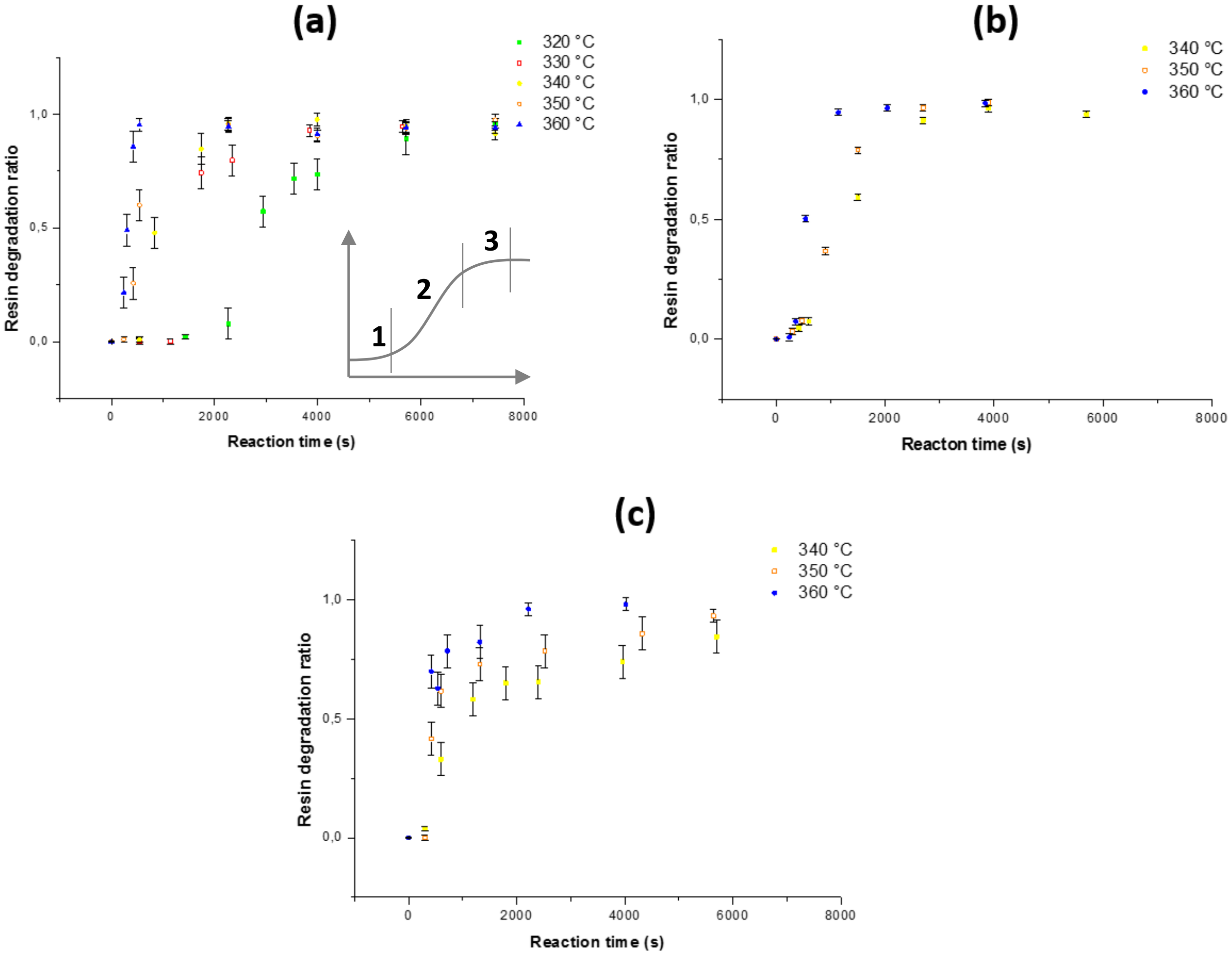

Figure 1. Evolution of the resin degradation ratio for composite CPP3 (a), CPP2 (b) and CPNP (c).

3.2. Effect of temperature

Comparing the curves obtained for CPP3, significant differences can be observed. First, when the temperature increases, the duration of phase 1 decreases dramatically. At 320°C, this phase lasts longer than 30 min. This phase almost disappears at 360°C. As a consequence, by the increasing the temperature, the resin degradation in phase 1 is accelerated. In phase 2, the increase of the temperature also leads to a reduction of the duration of the phase. At 320°C this phase lasts about 10 min, whereas at 340°C it lasts only about 5 min. As a consequence, increasing the temperature also leads to the acceleration of the resin degradation. Furthermore, the slope of the curve is significantly higher than in phase 1. As a consequence, the phase 2 is the phase with the fastest degradation rate. As expected, the reaction time required to reach the maximum degradation is strongly affected by temperature. At 320°C, this time is approximately 120 min. Whereas, at 360°C this time is only 9 min. Similar results regarding the influence of time and temperature were obtained in the case of CPP2 composites (Figure 1 (b)) and CPNP (Figure 1 (c)).

In order to assess a quantitative evaluation of the kinetic behavior of the 3 different composite materials, two characteristic times were defined:

- t_{50}, the required reaction time to achieve 0.5 resin degradation ratio
- t_{90}, the required reaction time to achieve 0.9 resin degradation ratio

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The characteristic time t_{50} allows the evaluation of the degradation rate in the phase 1 and in the beginning of the phase 2. The characteristic time t_{90} allows the evaluation of the degradation rate in the phase 3 and in the end of phase 2. The comparison of the characteristic times of the different composite materials allows the evaluation the discrepancies of the degradation rate.

For any of the composites CPP3, CPP2 and CPNP, as expected, t_{50} and t_{90} decreases when the temperature increases. It is also observed that the gap between t_{50} and t_{90} decreases when the temperature increase.

In the case of the composite CPP3, at 330°C, $t_{50} > t_{90}$. This means that the degradation is slower at the beginning than at the end of the process. The same observation is made for 340°C and 360°C. A similar behavior is observed in the case of the composite CPP2. However, in the case of the composite CPNP, the reverse behavior is observed. For all the studied temperatures, $t_{50} < t_{90}$. This means that the degradation is slower at the end of the process than at the beginning.

The different behaviors between CPP3 and CPP2 on the one side and CPNP on the other side can be explained by differences existing in the materials composition, such as: the resin composition, the polymerization state of the resin and the sample size.

3.3. Evaluation of the kinetics model

In this study, the third order Avrami-Erofeev kinetic model (AE3) was used to fit our experimental data. The fit has been performed with the Origin ® software. The AE3 model is given by equation 1.

$$\alpha = 1 - exp(-k.t)^3 \qquad (2)$$

Where k is the reaction rate constant.

The reaction rate constant is often expressed using the Arrhenius law:

$$k = A.exp(-E_a / RT) \qquad (3)$$

Where $A\ (s^{-1})$ is the pre-exponential factor and $E_a\ (J\ mol^{-1})$ is the activation energy, $R\ (J\ mol^{-1}\ K^{-1})$ is the ideal gas constant and $T(K)$ is the temperature.

Another expression of the AE3 model is obtained by replacing k in equation 2 by the expression in equation 3:

$$\alpha = 1 - exp(-A.t.e^{-Ea / RT})^3 \qquad (4)$$

Figure 2 shows the predictions of the AE3 model plotted against the experimental data, for composite CPP3 (Figure 2 (a)), CPP2 (Figure 2 (b)) and CPNP (Figure 2 (c)). The accuracy of the AE3 model was evaluated by performing a linear regression using the y=x function. A perfect correlation between the model and the experimental data is achieved when all the points are on the y=x line.

Figures (a) and (b) show the predictions of the AE3 model for composites CPP3 and CPP2. In both cases, the values are close enough to the y = x line. However, the fit seems to be slightly better in the case of composite CPP2. This observation is confirmed by the correlation coefficients which are respectively 0.97 and 0.99. Therefore, it can be concluded that the AE3 model is effective for the

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fitting of our experimental data. Figures (c) shows the predictions of the AE3 model for composite CPNP. The values are quite far from the line y = x. Therefore, the AE3 model is not suitable for the composite CPNP.

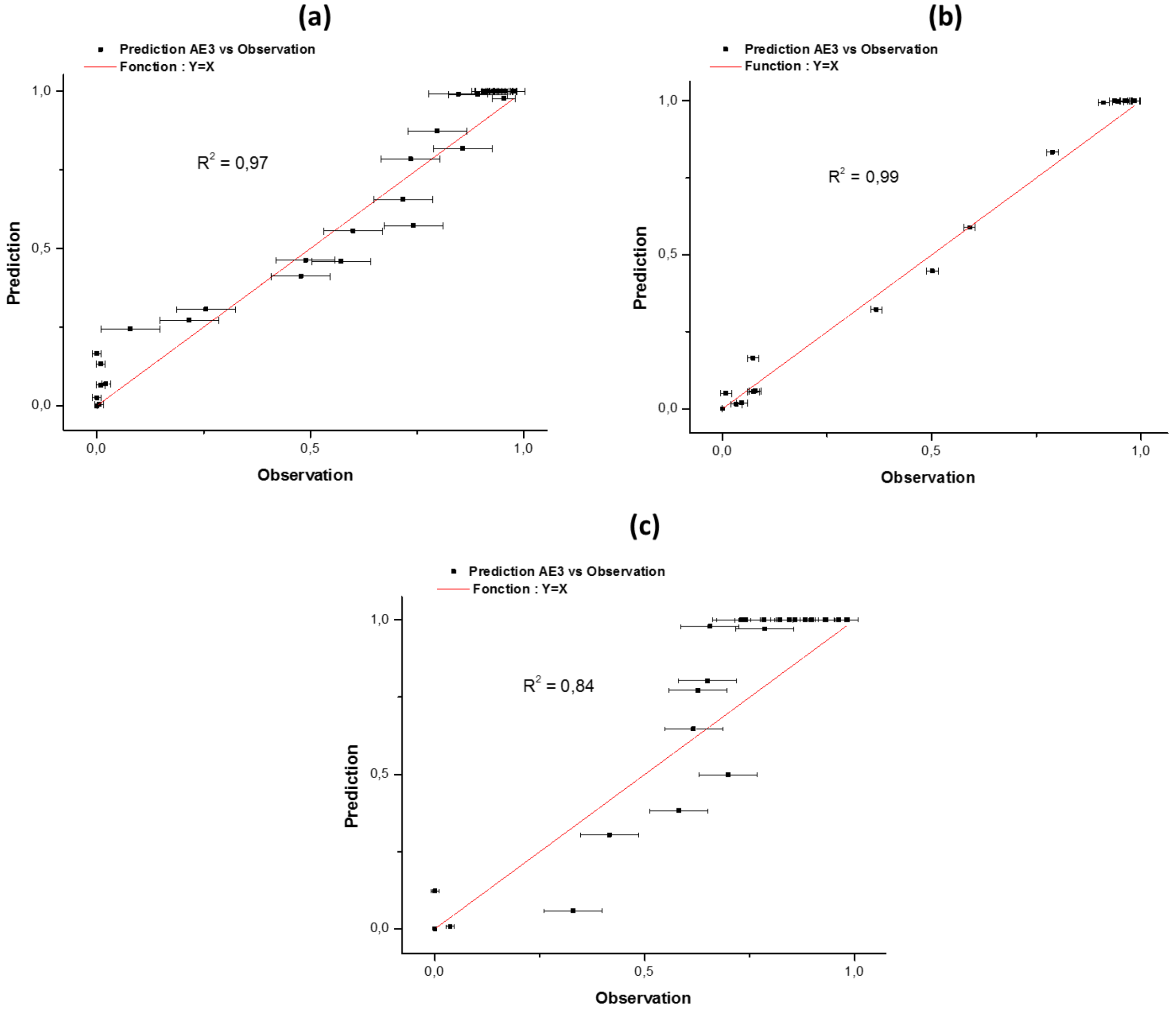

Figure 2. Evaluation of the predictions of the AE3 model.

Composites CPP2 and CPNP, which nevertheless contain the same resin material, show a very different kinetic behavior. Whereas composites CPP3 and CPP2, which contain different resin materials, show a very similar kinetic behavior. The main similarities between these two composites are their polymerization state and their sample size. Therefore, these two parameters appear to have an important effect on the resin degradation kinetics.

3.4. Determination of the kinetics constants

As the AE3 model is not suitable for the composite CPNP, only the kinetics constants for composites CPP3 and CPP2 was determined.

Table 3 shows the values of the reaction rate constant for composite CPP3 and CPP2 for the studied temperatures.

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Table 3. Reaction rate constant and reaction order for composite CPP3 and CPP2.

***T* (°C)**	***k* (s^{-1})**	
	CPP3	CPP2
320	2.89×10^{-3}	--
330	5.45×10^{-4}	--
340	9.62×10^{-4}	6.41×10^{-4}
350	17.2×10^{-4}	5.1×10^{-4}
360	26.6×10^{-4}	15.6×10^{-4}

The activation energy E_a and the pre-exponential factor A are determined by plotting the natural logarithm of k versus the inverse of the temperature, according to equation 4.

$$Ln(k) = ln(A) - E_a / RT \tag{5}$$

The slope of the line resulting from the linear regression of ln$k$ (1/T) gives us the activation energy and the ordinate at the origin gives us the pre-exponential factor. Table 4 shows the values determined for composites CPP3 and CPP2.

Table 4. Activation energy and pre-exponential factor for composites CPP3 and CPP2.

	CPP3	**CPP2**
***Ea* (J mol^{-1} K^{-1})**	188×10^3	143×10^3
***A* (s^{-1})**	1.15×10^{13}	9.47×10^{13}

The activation energy determined for composite CPP3 and CPP2 are of the same order of magnitude, respectively 188 kJ and 143 kJ. The pre-exponential factors are also of the same order of magnitude, respectively 1.15×10^{13} s^{-1} and 9.47×10^{13} s^{-1}. These observations are in agreement with previous observations on the similar behavior of the two materials. Comparing our results in term of activation energy with those of previous works in the literature, we found that our activation energies are close to those of Yuyan Liu et al [2], El Ghazzaoui [3] and Gong et al [4]. However, there is an order of magnitude of difference between our results and those of Pinero-Hernanz et al [1]. This difference can be due to the fact that Pinero-Hernanz et al used a pre-preg CFRE.

3. Conclusions

Three different Carbon Fibres Reinforced Epoxy was proved to be successfully decomposed in high pressure and high temperature water. The kinetics of the decomposition is highly dependent on temperature and time. In the lower temperature range, the evolution of the yield of decomposition shows an s-curve that disappears in higher temperature. The third order Avrami-Erofeev model proved to be suitable for the fitting of our experimental results in the case of composite CPP3 and CPP2. Applying this model to our results in term of activation energy, the numerical values found are close those found in the literature. In most studies, the kinetics of the hydrolysis process is investigated using a mass kinetic method. Another approached mentioned, but not developed by El Ghazzaoui [1] is to consider the hydrolysis process as a combination of three different processes: chemical reaction, mass transfer and heat transfer. Then three kinetic studies must be performed in different ways in this case. A detailed understanding of the overall kinetics results from the combination of these three studies.

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