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IMPACT OF SUBCRITICAL AND SUPERCRITICAL WATER ON BOTH DEPOLYMERIZATION KINETICS OF NYLON 6 AND RECYCLING CARBON FIBERS FROM WASTE COMPOSITE

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Abstract

Carbon fibers reinforced Polymers (CFRP) are extensively used. Their residues are being discarded every year, which creates serious ecological and social problems. Many efforts have been launched in their further utilization after use. Chemical recycling using sub and supercritical fluids shows good prospects for recycling carbon fibers. Thus, solvolysis of waste CFRP was investigated. The experiments were carried out at temperatures in subcritical (280-350°C) and in supercritical (400-600°C) regions under the estimated pressure of 25 MPa for reaction times of 1-120 min. Carbon rate recovered in liquid phase was measured by Total Organic Carbon (TOC). The microstructure of the recovered carbon fibers was observed using scanning electron microscopy (SEM). In subcritical region, the rate of decomposition efficiency reached 98.95 wt.% at 280°C in 30 min while , in supercritical region, the resin removal has already reached 97.18 wt.% at 400°C in only 15 min. Carbon rate recovered in liquid phase was in agreement with decomposition rate for both regions. The results revealed clean carbon fibers without physical damages and present tensile strength close to one of virgin fibers. In subcritical region, the identification of the recovered organic products indicated that monomer of the resin and other molecules were obtained. Assuming a pseudo-first order reaction, the degradation kinetics was studied and the activation energy was evaluated to be 77.79 kJ/mol and 45.81 kJ/mol in the subcritical and supercritical regions respectively. This difference in overall kinetics parameters clearly highlights that the reaction mechanism pathways are different in both regions.

1- INTRODUCTION

Regardless their good resistance and high rigidity, composite materials present the advantage of being lightweight, compared to steel and aluminium. Thus, they are employed in many industrial fields such as automotive and aeronautics. The worldwide demand for composites reached approximately 47,000 tons in 2008 and expected to be 208,000 tons by 2020 [1]. This amount of production is accompanied by a significant amount of waste which is currently landfilled or incinerated. However, these options contradict sustainable development. Thus, the European directives (1999/31/EC) and (2000/76/EC) have been initiated in order to minimize as much as possible the amount of waste destined to landfill and incineration. This motivates new researches to opt for recycling.

The criterion of carbon fibers recycling is related to the preservation of the mechanical properties of the recovered fibers in order to be reused in a composite [2]. A special interest in carbon fibers based composites is considered in this paper. Mechanical and pyrolysis process have been the first ones identified to treat composite wastes. However, they have limited potential to recover carbon fibers with good mechanical properties as those of virgin carbon fibers. Indeed, mechanical treatment does not separate resin from fibers and pyrolysis should cope with charring issues. Therefore steam thermolysis and solvolysis were recently deeper investigated. On the one hand, steam thermolysis has shown two main advantages compared to pyrolysis process [3]: the resin elimination is improved using the same temperature conditions and the steam partially inhibits char deposit on the carbon fibers surface. On the other hand, solvolysis in supercritical fluids has shown good results to recover carbon fibers that can be reused [4]. Recently, Morin *et al.* [4] reviewed these methods for the recycling of carbon fibers reinforced polymers and concluded that chemical recycling is a favourable process to recover carbon fibers with good surface and mechanical properties. For this purpose, solvolysis of carbon fibers reinforced composites has been extensively investigated. Numerous teams carried out experiments using batch or semi-continuous reactors in near- or supercritical conditions of water [5-7], in supercritical alcohols [8, 9] or in mixtures [9]. In our previous work [10], the efficiency of different solvent (water, ethanol and acetone) was studied. Results showed that in a viewpoint of reactivity, water and ethanol were more efficient compared to acetone. However, water takes advantages in the ecological point of view and is the solvent selected for deeper investigations.

Experiments using solvolysis processes were done in the sub and the supercritical regions of water. For this purpose, a composite based on a thermoplastic resin (polyamide 6) was used. In this paper, we are interested in understanding the process of decomposition of resin using the two “states” of water. The depolymerisation mechanism of aliphatic resins such as poly lactams (nylon 6) is not well known using these operating conditions since it depends on the chemical composition of resin and the experimental conditions. This study is focused on the solvolysis efficiency regarding the properties of recovered fibers on the one hand. On the other hand, a preliminary reaction scheme of the resin elimination is drawn together with a kinetics study at sub and supercritical conditions.

2- MATERIALS AND METHODS

2. 1- Materials

Cut-off Carbostamp UD Tape composites (Torayca T700S MOE carbon fibers and PA6 resin) were used as a raw material. The PA6 resin was used as a target of the decomposition

experiments. It represents 39-40 % in the cut-off strips. Strips of composite are provided by a composite manufacturer with a thickness of 0.28 mm.

The amount of the resin in the composite was experimentally determined (TGA and normalized oxidation procedure) and compared to the company data. The amount of resin is equal to 39.0 wt. %. In addition, the amount of carbon was also evaluated (Total organic carbon using a solid module) in the resin and was about 78.1 wt. %. Both values are then used to provide efficiency parameters.

2.2- Hydrothermal process

Figure 1 shows the principle of the experimental setup to determine the optimum conditions to decompose the PA6 resin in near-and supercritical water.

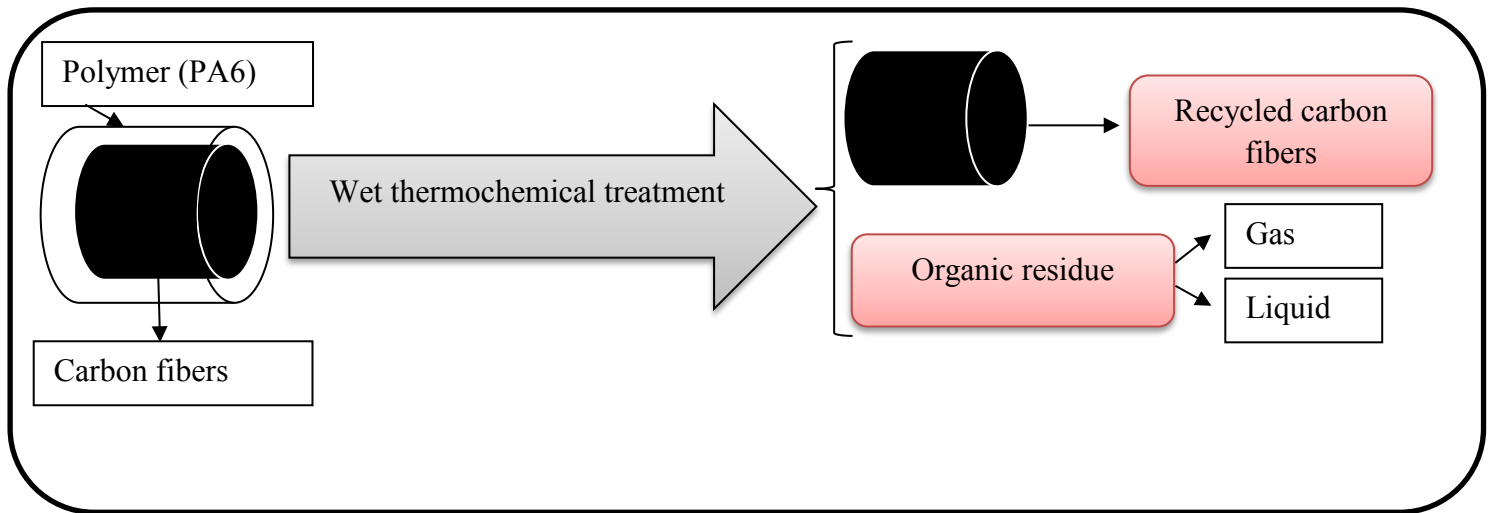


Figure 1: Solvolysis process.

The 5 mL batch reactor was composed of 316 stainless steel. A given weight of the composite (about 0.1 g) was put in the reactor and then filled with ultrapure water. The volume of liquid calculated at room temperature depends on its density at the desired temperature and pressure. Thermodynamics properties were determined by Water&Steam software (Springer). An oven (chromatographic or muffle oven Nabertherm) was preheated at the desired temperature (280-350°C) or (400-600°C) before introducing reactors. The reaction time started as the reactor reached the desired temperature. At the end of the experiments, the reactor was cooled down to room temperature and the three phases (solid, liquid, and gas) were separated. The volume of gas and the mass of the solid were measured. The results are provided in terms of resin removal rather than total mass loss and of carbon rate, calculated as follows:

$$\text{Resin removal (\%)} = \frac{\text{Weight of composite} - \text{weight of solid residue}}{\text{Weight of resin in composite}} \times 100 \quad (1)$$

$$\text{Carbon rate (\%)} = \frac{\text{Carbon rate measured in liquid phase}}{\text{Carbon rate in resin}} \times 100 \quad (2)$$

2.3- Analyses

After reaction, the hydrothermal vessels recovered from subcritical treatment were cooled down in ice water to room temperature, and then opened. Reactors from supercritical treatment were cooled down in air during 40 min, and then gas phase was collected (if applicable) and liquid phase was separated for analysis.

The Total Organic Carbon in the aqueous phase was measured with a TOC analyzer (Shimadzu TOC-VCSH). The molecules present in the liquid phase were analyzed by GC-MS (GC-MS-TQ8030, Shimadzu) using a nonpolar capillary column (Column flow =1.56 mL/min).

The fibers recovered were analyzed by Environmental Scanning Electron Microscopy (ESEM Philips XL30 FEG) with a Back-Scattering Electron detector in order to observe their physical appearance. Figure 2 presents ESEM pictures of the composite (a) which is a monolithic structure versus the virgin carbon fibers (b).

The tensile strength (INSTRON 5942) of the composite, virgin and recovered fibers was measured using at least 30 isolated fibers. The tensile strength of virgin fibers is equal to 4931.29 ± 530 MPa.

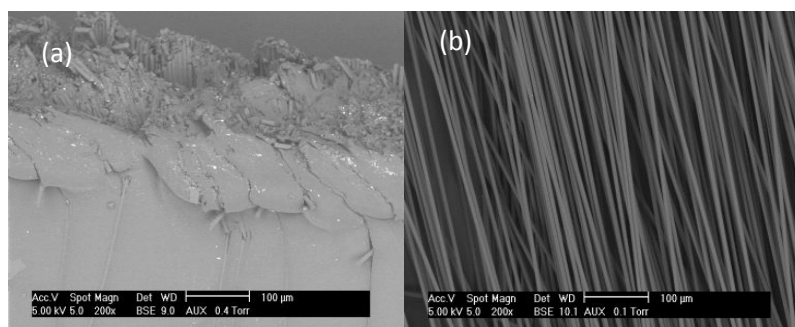


Figure 2: ESEM micrographs of composite (a) and virgin carbon fibers (b).

3- RESULTS AND DISCUSSION

Hydrothermal conversion was performed to degrade the PA6 resin from the composite and to recover carbon fibers. Using this process, resin could be dissolved in the liquid phase, remained in the solid phase or converted in volatile molecules in gaseous phase. Several experiments in subcritical [280-350°C] and supercritical water [400-600°C] were carried out in order to evaluate the resin decomposition as well as the properties of recovered carbon fibers over reaction time (1 to 120 min).

As mentioned previously, this study is focused on two key points. On the one hand, a preliminary study is made in subcritical and supercritical water in order to understand the pathway of the reaction of resin decomposition. On the other hand, a kinetic study was realized in order to compare the kinetic parameters in sub and supercritical regions.

3.1- Efficiency of hydrothermal treatment

This section is dedicated to the evaluation of hydrothermal treatment efficiency. Efficiency is first evaluated using the rate of eliminated resin over the hydrothermal treatment. The main issue regarding the reuse of recovered carbon fibers is their mechanical properties. Thus, the properties of recovered carbon fibers are measured and compared to the virgin ones.

3.1.1- Conversion using subcritical water

Figure 3 shows the results of the decomposition efficiency (rate of eliminated resin) as a function of reaction time at each reaction temperature: 280, 310 and 350°C. The amount of resin eliminated from the solid residue increased rapidly with reaction time using the three reaction temperatures considered. The maximal rate reached almost 100% after 15 to 30 min of reaction time, and then is quite stabilized to the maximal value. Figure 3 shows that the process efficiency (rate of eliminated resin) increased linearly during the first moments of reaction. This linear domain was [5-30min], [5-30min] and decreased to [5-15min] at 280, 310 and 350°C respectively. Thus, the kinetics of the reaction is faster as the temperature increased.

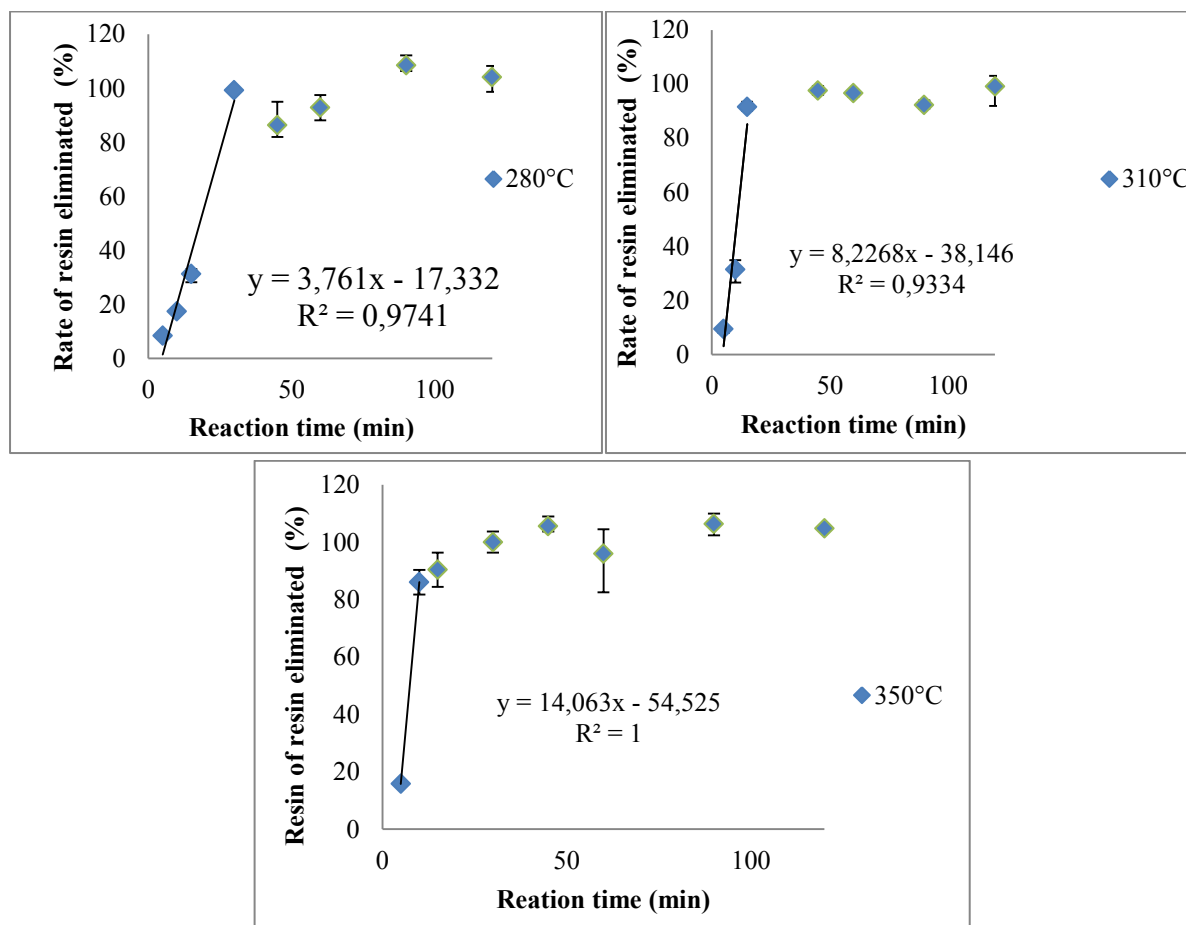


Figure 3: Rate of resin eliminated vs reaction time at 280°C, 310°C, and 350°C.

3.1.2- Conversion using supercritical water

Figure 4 presents the rate of eliminated resin using supercritical conditions. Reaction temperature was set at 400, 425, 450 and 500°C. The rates of eliminated resin increased rapidly with reaction times. The maximal value was reached for less than 15 min of reaction time. As for the reaction in subcritical conditions, the evolving is quite linear during the first reaction times and then reached a plateau. The time required to achieve the resin elimination is lower than using subcritical conditions meaning that the kinetics has been improved with the temperature and the state of water.

Regarding literature, the reactions involved at sub and supercritical conditions should be different [11]. Ionic reactions are expected to be improved at subcritical conditions while radical reactions are enhanced in supercritical water. Radical reactions would also improve

oxidation therefore the quality of recovered carbon fibers in terms of mechanical properties is the most important data for recycling.

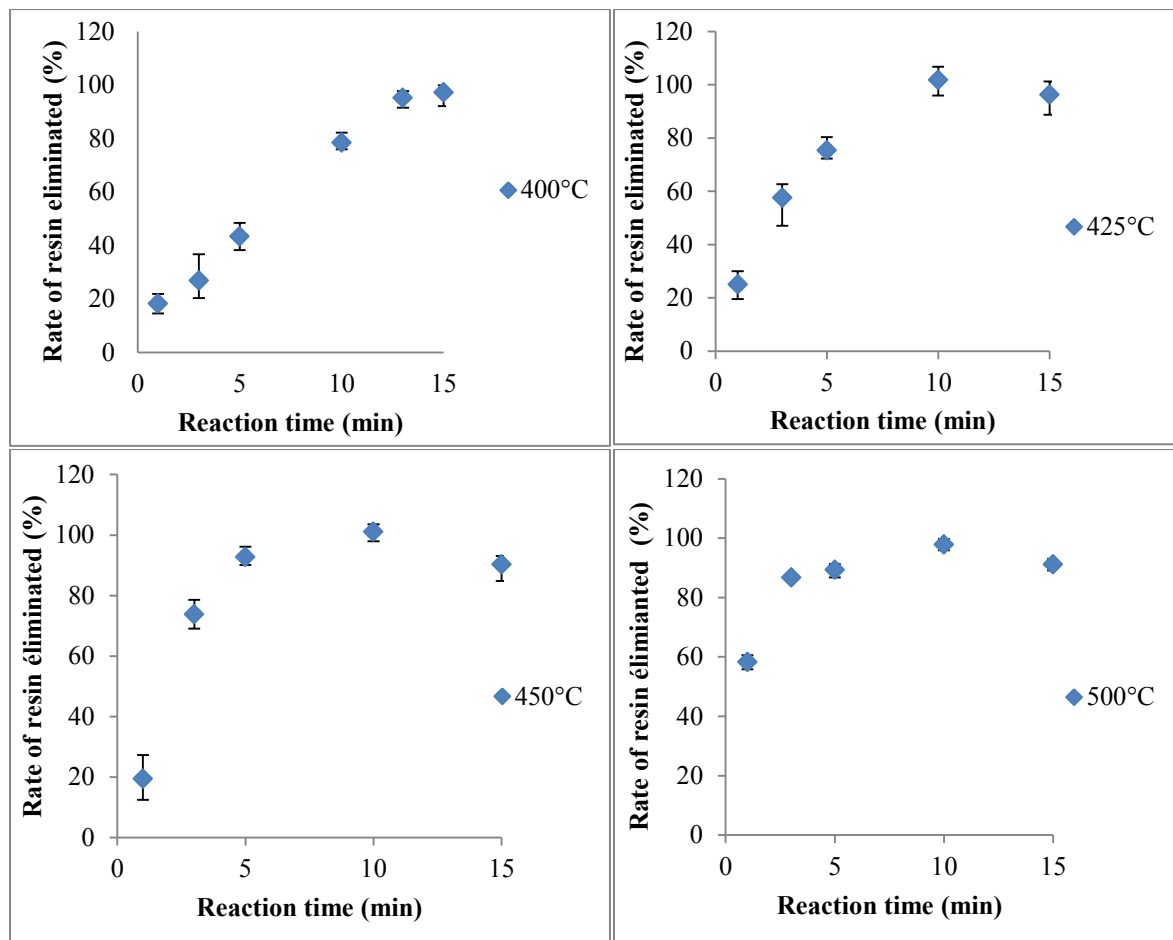


Figure 4: Rate of eliminated vs reaction time at 400, 425, 450 and 500°C.

3.1.3- Properties of recovered carbon fibers

Recovered carbon fibers are especially characterized regarding their mechanical properties for further use. However, in order to understand the solvolysis process, surface properties are also characterized.

Surface properties

Remaining solid phase from hydrothermal treatment was observed using Environmental Scanning Electron Microscopy (ESEM). Figure 5 presents ESEM pictures of some remaining solids. The diameter of fibers is equal to 7 μm . Figure 5 shows that the surface of fibers recovered are quite close to that of the virgin carbon fibers. The fibers are well-separated from balls of resin deposited. Locally some resin deposits are still observed. We noted that there are no visible damages on carbon fibers surface using ESEM resolution. Otherwise, small white particles are observed on the fibers surface. EDS micro-analysis confirmed that these particles are attributed to titanium. These particles may be due to the impurities present on the precursor of PAN. A small amount of minerals and metals has been measured after dissolving composite in acidic oxidizing solution. The main metals observed were titanium, nickel and iron.

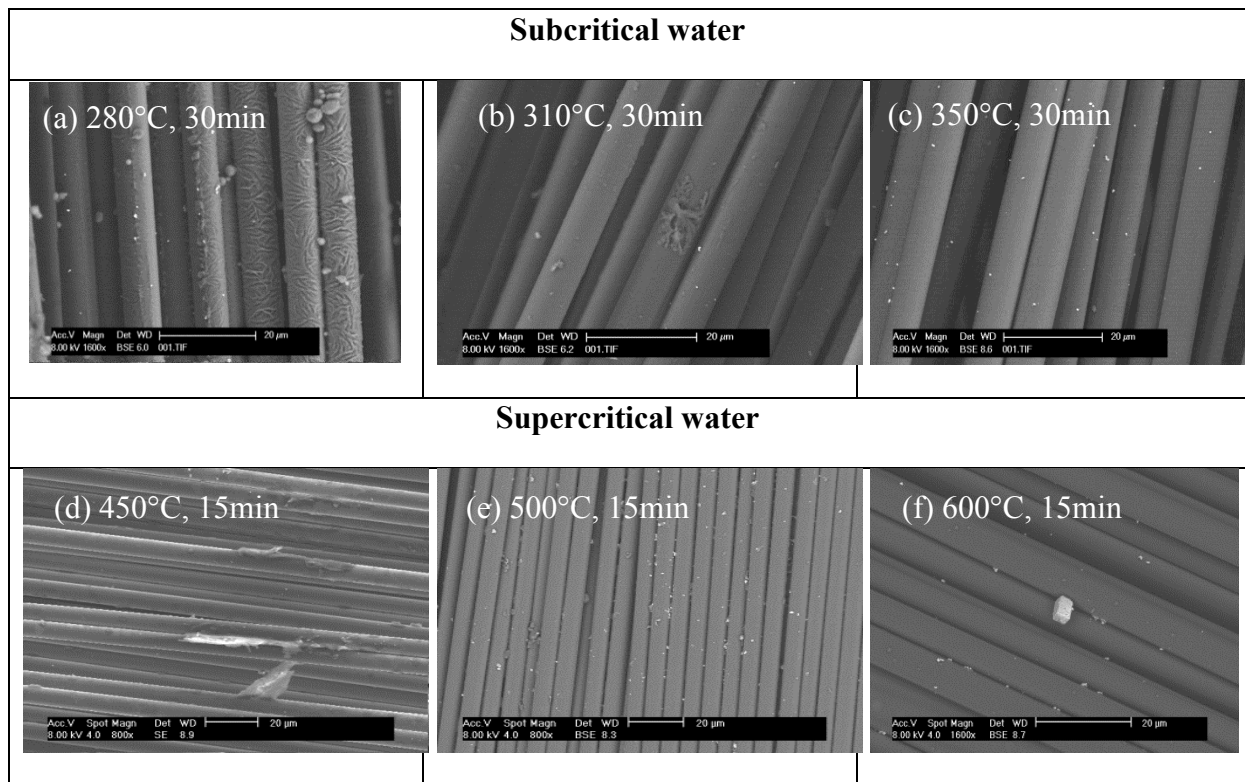


Figure 5: ESEM micrographs of remaining composite after hydrothermal treatment using ultrapure water at 15min: (a) 280°C, (b) 310°C, (c) 350°C and at 15min: (d) 450°C- (e) 500°C-(f) 600°C.

To complete the characterization of recovered carbon fibers and especially to determine the best conditions able to provide recycled carbon fibers, the mechanical properties were also determined.

Mechanical properties

The fibers obtained in sub- and supercritical conditions were subjected to tensile strength tests. All of the recovered fibers were analyzed. As mentioned in Figure 3 and 4, reaction times of 15 and 30 min are sufficient to provide maximal resin elimination. Therefore, Table 1 only lists the mechanical properties measured for the “optimal” reaction time at each temperature. Tensile properties should be compared to that of the virgin carbon fibers (4931.29 ± 530 MPa). As shown in Table 1, the tensile strength of recovered carbon fibers is not affected by hydrothermal treatment in both regions. The values of tensile strength of recovered carbon fibers are situated in the 10% of the margin of error of the tensile strength of virgin carbon fibers. It means that the process is suitable for obtaining fibers with good mechanical properties. Besides, the values of standard deviation of recovered carbon fibers are higher than that of virgin carbon fibers, meaning that the tensile strength values are more dispersed over the selected fibers. This observation would be a key item since this deviation indicates that the sizes of defects originating the rupture are more heterogeneous. These defects could be due to physical or chemical treatment. The physical treatment improves surface roughness which could serve as mechanical anchorings [5]. The chemical treatment adds some oxygenated functions at the surface. Bai *et al.* [7] studied the chemical recycling of carbon fibers reinforced epoxy resin using supercritical water oxidation. They concluded that oxygenated groups on carbon fibers microstructure impacted their mechanical properties, since they observed a loss of 38% in tensile strength for a decomposition efficiency of 100.2

wt.%. Supercritical water, which produces hydroxyl radicals, would rather affect the microstructure of carbon fibers than subcritical water media.

Water state	Reaction time (min)	Temperature (°C)	Tensile strength (MPa)	Standard deviation
Subcritical	30	280	4579.79	998
	30	310	4407.53	984
	30	350	4631.24	974
Supercritical	15	450	4432.51	545
	15	500	4378.10	717
	15	600	4675.28	972

Table 1: Mechanical properties of recovered carbon fibers in subcritical and supercritical water.

3.2- Suggested reaction schemes

As seen previously, the subcritical and supercritical water are convenient media to remove resin from carbon based composites. Temperature and reaction time have been highlighted as influencing parameters. In order to provide a reaction scheme, the first question is to determine whether the resin removal is a depolymerization or degradation pathway.

Figure 6 shows the rate of eliminated resin versus the rate of carbon recovered in the liquid phase. At the beginning (less than 30 min) the curves follow a linear trend. In addition, the slope is very close to 1. This would mean that the resin decomposed exists totally in the liquid phase which means that the polyamide 6 is totally depolymerized in other molecules in the liquid phase. Thus, the reaction involved is a depolymerization rather than a degradation since no gaseous phase was recovered in these conditions.

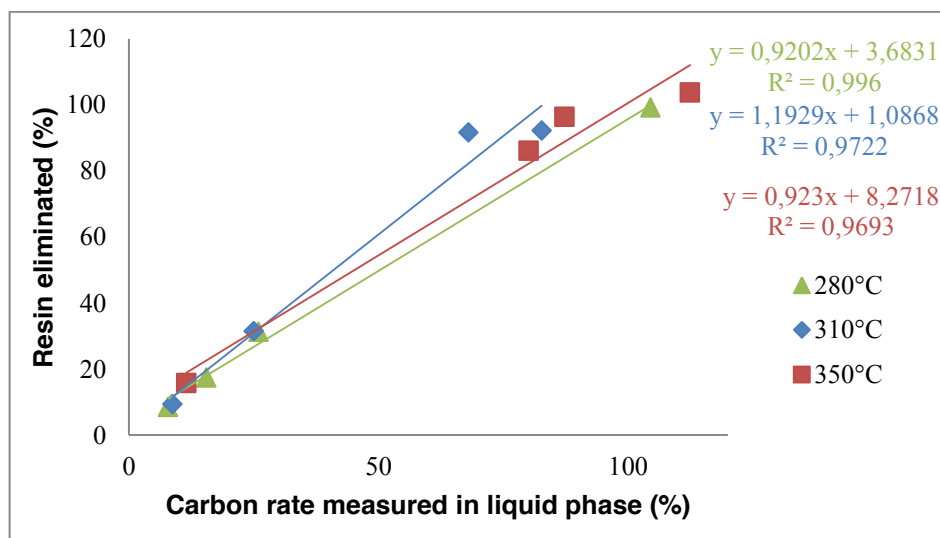
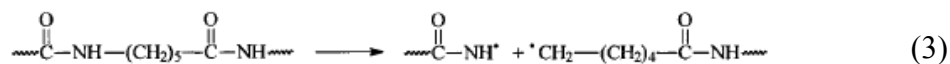


Figure 6: Rate of resin eliminated vs rate of carbon present in liquid phase at 280°C, 310°C and 350°C.

At the atomic scale in the domain of linearity, the reaction of decomposition should begin with the shrinking of oligomers and monomers from the resin. GC-MS analysis revealed the presence of caprolactam (monomer of PA6) and other molecules. At short times (5 and 10 min), only the molecules of caprolactam were identified. Heavier and lower molecules than caprolactam were also identified at longer reaction times: 1-8-Diazacyclotetradecane-2,9,-dione, 1-Methylcaprolactam, 2-oxepanone, 7-hexyl, trans-2-hexene, 6-Hydroxyhexanoic acid, 1-cyclopentène-1-carboxylic acid and cyclopentanone.

Products coming from the decomposition of PA6 could be classified into three categories:

- products formed in the absence of a nucleophile at temperatures less than 300°C by intramolecular reaction at terminal groups and the polymer chain
- products mainly composed by cyclic oligomer and small gaseous molecules formed by the scission of the bond CH₂-NH in the absence of a nucleophile at temperatures more than 300°C
- products formed in the presence of nucleophile. For this case, the weakness is situated on the peptide bond which is hydrolyzed from 280°C and also on the alkyl-amid bonds which undergo homolytic scission at temperature greater than 500°C as seen in the equation below [11].



We are interested in the third category of products since we use water as nucleophile. As reported in the literature [12] the depolymerization of PA6 into caprolactam could produce an intermediate which is the aminocaproic acid as presented in the Figure 7. However, this intermediate was not detected by GC-MS. The reaction is likely very fast and does not let us identify it.

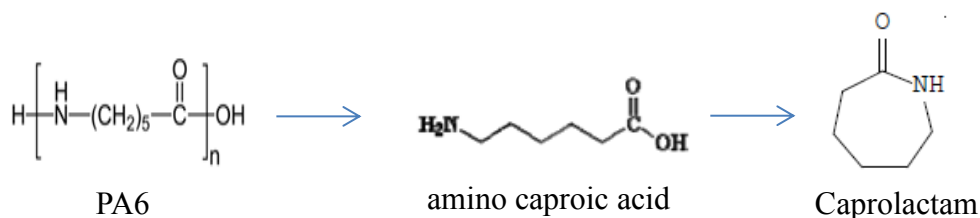


Figure 7: Depolymerization of PA6 to caprolactam.

In the range of temperature 200 - 300°C, ionic product of water increases up to around 10⁻¹¹ [13]. To form 6-aminocaproic acid, the decomposition reaction should be initiated on the carbon nitrogen bond (C-N). In the subcritical water medium, H⁺ ions could react with the amide functional group to form ammonium functional group. This center of positive charges induces the hydroxylation of the carbon in the amide functional group. The carbonyl group is thus transformed into a carboxylic acid group. The amine and the carboxylic acid are functional groups existing in both sides of the molecule. The resulting molecule is 6-aminocaproic acid. Finally, 6-aminocaproic acid quickly dehydrates and cyclizes to produce ε-caprolactam.

To summarize, the reaction scheme of PA6 depolymerization would be the hydrolysis of amides to form aminocaproic acid followed by the cyclodehydration of aminocaproic acid to

caprolactam [12, 14]. This type of chemical scission is supported by Chen et al. [14] and Iwaya et al [15].

A scheme reaction is proposed in Figure 8: the detection of heavier molecules than caprolactam suggests a repolymerization phenomenon. Caprolactam could be transformed into 1-Methylcaprolactam or could react with another identical molecule to produce 1-8-Diazacyclotetradecane-2,9,-dione. This latter could be transformed into 2-oxepanione, 7-hexyl. The trans-2-hexene should come from the degradation of 2-oxepanione, 7-hexyl. However, 6-hydroxy, hexanoic acid could come either from the degradation of 2-oxepanione, 7-hexyl or from the ring cleavage of caprolactone [16]. 6-hydroxy, hexanoic acid could react with Ammonia in order to form 6-hydroxyhexanamide which could undergo an intramolecular dehydration to form caprolactam. 6-hydroxy, hexanoic acid could react with Ammonia in order to form 6-hydroxyhexanamide which could undergo an intramolecular dehydration to form caprolactam.

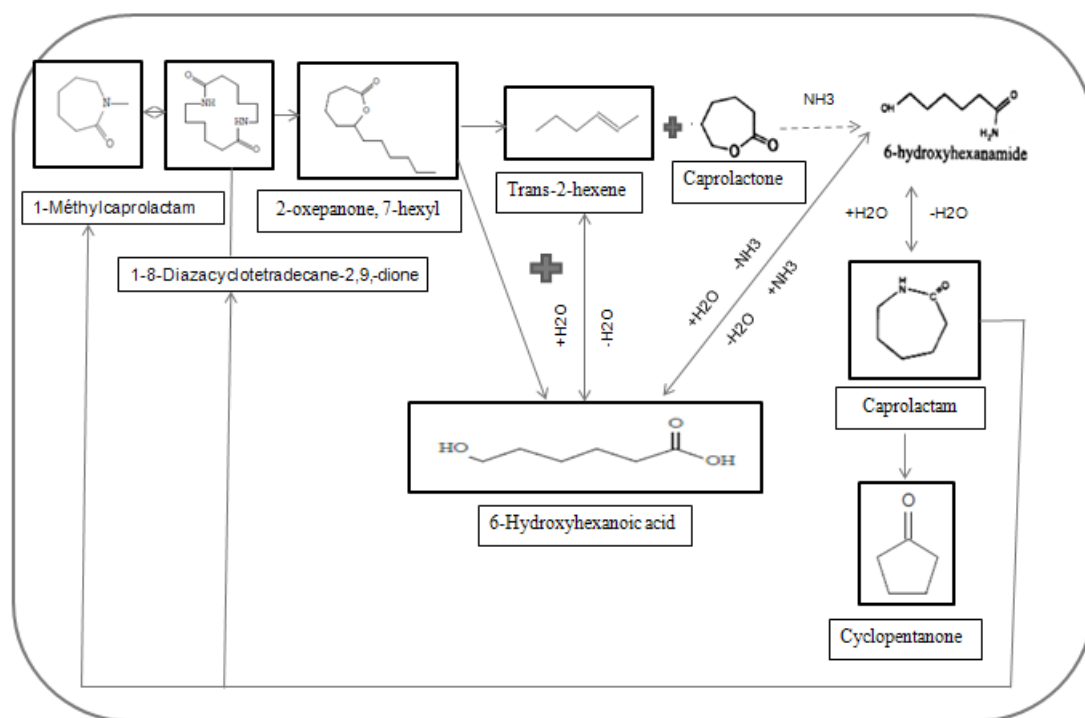


Figure 8: reaction scheme (framed molecules are detected by GC-MS).

3.3- Kinetics study

In this section, kinetics in sub and supercritical regions is discussed. Kinetics of PA6 can be treated as a pseudo-first-order reaction. Decomposition kinetics of resin is described using the following equations:

$$\frac{-d[\text{PA6}]}{dt} = k [\text{PA6}]^\alpha [\text{H}_2\text{O}]^\beta \quad (4)$$

$$\frac{-d[\text{PA6}]}{dt} = k_{\text{app}} [\text{PA6}]^\alpha \quad (\text{excess of H}_2\text{O}) \quad (5)$$

$$\frac{-dm_{\text{PA6}}}{dt} = k_{\text{app}} m_{\text{PA6}} \quad (6)$$

$$\ln \left(\frac{m_0}{M_{PA6}} \right) = k_{app} t \quad (7)$$

[PA6] : Concentration of PA6

α : Partial order of PA6, β : partial order of H₂O

m_0 : Initial mass of PA6 and m_{PA6} : Residual mass of PA6 at t

k: Rate constant

t: Reaction time

The activation energy is calculated by the Arrhenius equation:

$$k = A e^{(-E_a/R T)} \quad (8)$$

k: Rate constant

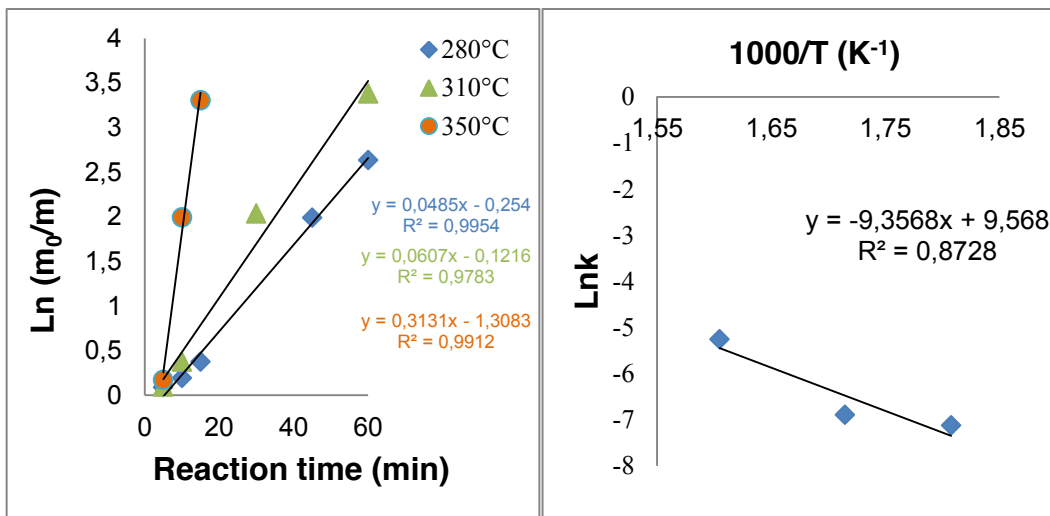
A: Pre-exponential factor

E_a : Activation energy

R : Gas constant

T: Temperature

Figure 9 shows $\ln(m_0/m)$ versus reaction time at 280, 310 and 350°C, and at 400, 425, 450 and 500°C. In addition $\ln k$ versus $1/T$ is also plotted in order to determine the activation energies.



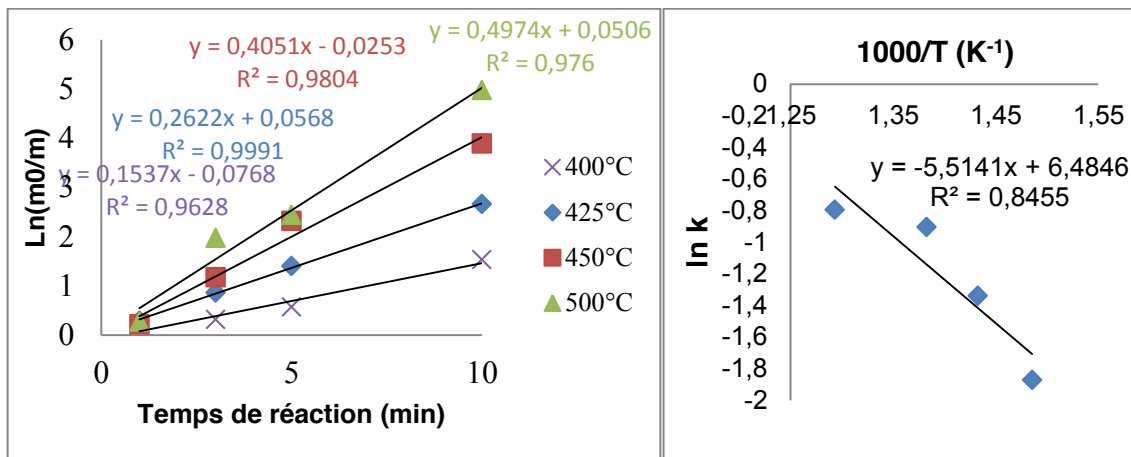


Figure 9: $\ln\left(\frac{m_0}{m}\right)$ vs reaction time in sub and supercritical conditions.

Figure 9 shows $\ln(m_0/m)$ versus reaction time at 280, 310 and 350°C. Up to 15 min (at 350°C) and 60 min (at 310 and 250°C), the pseudo-first order describes properly the experimental results. Activation energy was then calculated from these three temperatures and was equal to 77.79 kJ/mol. This activation energy corresponds to the depolymerization of the resin into different lighter molecules (oligomers and monomers). Iwaya *et al.* [15] experimentally determined activation energy of 97.1 kJ/mol in the range of temperature 300-360°C. However, the authors studied precisely the reaction from pure PA6 sheet to 6-aminocaproic acid, while the present study only follows the disappearance of PA6 mass. Therefore the experimental value is in agreement with the literature.

In supercritical conditions, the activation energy for the overall reaction of degradation of the resin is evaluated to 45.81 kJ/mol. This current value is lower than that determined in subcritical water (77.79 kJ/mol). Thus, in supercritical water, the depolymerization of the resin is more accelerated than in subcritical water. As said previously, reaction mechanisms of PA6 degradation should be different in both regions. In subcritical water, ionic reactions are expected to be enhanced. Whereas, in supercritical water, radical reactions take over. In addition, the hydrodynamic in the two regions is different which implies that transfer limitations are different (liquid, gas and supercritical phases should be compared).

4- CONCLUSIONS

The aim of this work is to understand the decomposition of the resin in sub and supercritical regions. The ability of water as solvent-reagent for chemical recycling of carbon fibers reinforced PA6 has been also investigated. On the one hand, experiments were performed at 280, 310, and 350 ° C and 17-20 MPa for reaction times ranging from 5 to 120 min. On the other hand, experiments were performed at 400, 425, 450, and 500 ° C and 25 MPa for reaction times ranging from 1 to 15 min. In subcritical water, a reaction scheme based on identified molecules was proposed. In fact, resin was completely depolymerized into other molecules. Only caprolactam was detected in liquid phase recovered in short reaction times (10-30min). Above 15-30min (depending on the temperature), heavier molecules were detected. Thus, a repolymerization phenomenon was supposed to occur. This latter disappears at longer reaction times since lighter molecules were detected. SEM analyses and tensile strength tests on the recovered fibers showed clean fibers without damages retaining almost 100% of the strength of virgin fibers. Kinetics was studied as a pseudo-first-order reaction. The E_a was evaluated at 77.79 kJ / mol and 45.81 kJ / mol in sub and supercritical regions

respectively. It confirms that the reaction mechanisms are not similar in both regions and that the decomposition of the resin is favored in supercritical water.

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