Hydrothermal Depolymerization of Carbon-Based Composites

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ABSTRACT

The global demand of carbon fiber is increasing, therefore an increasing amount of carbon fiber reinforced polymer waste is produced. Carbon fibers are high added value materials which would be recycled at the composite end of life to offer positive impacts on environment and economic development. Hydrothermal treatments in water or in solvents are also gaining more attention to recycle carbon fibers and valorize polymer matrix into useful materials at the same time. This study focuses on the impact of operating conditions on the depolymerization of the matrix and on the surface quality of the fibers.

Carbon fibers reinforced PA6 (thermoplastic polymer, 45 wt. %) are depolymerized in sub and supercritical water (T_c=374°C and P_c=22.1MPa). The experiments were carried out in batch reactors of 5mL at various operating conditions. The whole operating conditions are suitable to remove the polymer from the carbon fibers. A minimum of 39 wt. % of resin is removed in all cases after 30 min treatment while the surface quality of the fibers remains close to their virgin state. The increase of pressure and temperature favors the kinetics, however reaction time plays an important role on the carbon distribution. Indeed, repolymerization reaction (carbonization) is supposed to occur and discussed.

INTRODUCTION

Although composites materials appeared during World War II, Carbon Fibers Reinforced Polymers (CFRP) found firstly use in aeronautic industry around the eighties'. Currently CFRP are gaining more attention due to their key use in many various industrial sectors such as aerospace, automotive, electronics industries as well as wind energy sectors and sport materials. Thus the global demand of carbon fiber is worldwide increasing. The production was estimated to be 46 000 tons in 2011 and it is expected to reach 140 000 tons in 2020 [1]. At the same time, the amount of wastes generated increases. However, these hazardous wastes have to follow the EU Directives (1993/31/EC and 2000/53/EC) that regulates their end-of-life. These directives imply a management of the composite wastes, especially with a special effort to recycle the carbon fiber [2]. CFRP could be classified in two categories of polymers: thermoplastic and thermosetting. The latter is the most difficult to manage with thermochemical treatments due to its properties. Indeed, an increase of temperature results in a reinforcement of the tridimensional network of the polymer. On the contrary, thermoplastics are able to smelt that can favor the recycling of the carbon fibers.

Carbon fibers are high added value materials as their price is 50 to 150 times higher than glass fiber. Their recycling in circular processes offers highly positive impacts on environment and economic development [3]. Indeed, carbon fibers contained in the composite materials would be reused after recovery rather than destroyed, e.g. by incineration. Recycling of carbon fiber requires a “deconstruction” process consisting in removing of the polymer matrix with the return of the embedded fiber in a state close to its virgin. New processes are in development to respond to these requests: pyrolysis [4], steam-thermolysis [5] and solvolysis [6]. Among solvolysis processes, sub and supercritical fluids such as water, methanol, ethanol or propan-1-ol, have been studied either or not in mixtures [6-8] to remove the resin from the carbon fibers. However carbon fibers recycling could be achieved simultaneously with chemicals or energy recovery (energetic verctor). Hydrothermal treatments could open interesting solution for simultaneous recycling of carbon fibers and valorization of the polymer matrix into building blocks at the same time. To achieve depolymerization process, i.e. resin removal and organic molecules recovered in the liquid phase, water was particularly considered as a benign option compared to other solvents. Some recent studies were realized in water at sub or supercritical conditions (T_c = 374°C and P_c = 22.1 MPa) for thermosettings or thermoplastics removal [6, 9-13]. The main focuses of these studies were the resin removal and the properties of the carbon fibers recovered (surface and mechanical properties) at various operating conditions, including alkali catalysts. Oxidation reactions were also pointed out to explain the degradation of carbon fibers that results in a degradation of mechanical properties [12]. The literature demonstrates a lack of knowledge as the chemicals recovery was concerns. Ondwudili *et al.* discussed chemicals recovery in the liquid phase (phenol and aniline) by using alkali catalyst [13], while Morin *et al.* mentioned the decomposition of epoxy resin into lower molecular weight organic compounds [6]. Therefore our study concerns the depolymerization of CFRP as regards to carbon fiber and chemicals recovery.

Literature reports studies realized using thermosettings rather than thermoplastics resins [6]. However, the development of thermoplastics composites is nowadays twice as high as for thermosettings. The present work concerns the use of carbon fibers reinforced Polyamide 6 (PA6, $[\text{-NH-C}_5\text{H}_{10}\text{-CO-}]_n$) which is an aliphatic thermoplastic. This is a composite developed for high productivity for automotive, sport and leisure, aerospace and industry markets. Experiments were carried out to evaluate the effect of temperature, pressure and reaction time on the resin removal and on the distribution of organic carbon. The present paper discusses only the effect of some operating conditions on the hydrothermal depolymerization of the resin towards resin removal and the ability to recover chemicals.

MATERIALS AND METHODS

Raw material:

Cut-off of Carbostamp UD Tape composites (Torayca T700S MOE carbon fibers and PA6 resin equal to 45 wt. %) are used raw material. Strips of composite are provided by a composite manufacturer with a thickness of 0.28 mm. The resin in the cut-off strips represents 40-45 wt. % of the composite. As the resin is not only composed of PA6 but contains also mineral or other organic charges, the total mass of resin is not only due to PA6.

A complementary experiment has been carried out in our laboratory to evaluate the mass of polymer in the composite using chemical degradation in sulfuric acid. The average mass loss reached 42.45 wt. %. This value is lower than that indicated in the composite properties. Two reasons can explain this difference. On the one hand, the raw material issued from cut-off meaning that the resin impregnation did not reach its steady-state and thus its desired quantity in the composite. On the other hand, the resin (45 wt. %) contains PA6 and minerals, metals and other compounds which are not necessary degraded during the thermochemical or chemical reactions carried out. Thus the total mass loss of the composite is lower than the theoretical value.

Batch reactor and experimental protocol:

Experiments in sub and supercritical water were carried out in stainless steel 316 mini-autoclaves (MA) of 5 mL. A NABERTHERM oven was preheated at the desired temperature (350 or 400°C) before introducing reactors. The heating rate was around 40°C min^{-1} and the plateau duration varied from 0 to 120 min. The pressure reached 25 MPa, since the temperature stabilized in the reactors. The reactors were filled with ultrapure water and composite. Taking into account the size of the inner volume of the reactors, the mass of composite is of about 0.1 g. the volume of water was adjusted to reach the desired temperature/pressure couple. At the end of the experiments the three phases are separated and collected. The mass of the dry solid residue was then compared to its initial mass to evaluate the total mass loss.

Analyses:

The efficiency of the treatment was evaluated through the analyses of the liquid and the solid phases. The carbon fibers clean-up was observed using the Environmental Scanning Electron Microscope (ESEM, Philips XL30 FEG) with a back-scattering electron (BSE) detector. Micro analysis of some regions at the surface was also realized with EDS detector.

Total Organic Carbon in the liquid phase was measured with a TOC analyzer (Shimadzu TOC-5050). TOC values are “normalized” to the initial mass of composite to be compared to each other.

RESULTS

Prior to present and discuss the results, Figure 1 presents ESEM pictures of the composite (a) and of the virgin carbon fibers (b). Thus, clean-up of carbon fibers can be successfully observed from ESEM pictures.

The efficiency of hydrothermal conversion of organics is basically evaluated by studying the effect of operating conditions such as reaction temperature, pressure, reaction time and catalyst. In this present work, the three first parameters were studied and the focus in the present paper is on reaction time and temperature (sub and supercritical media).

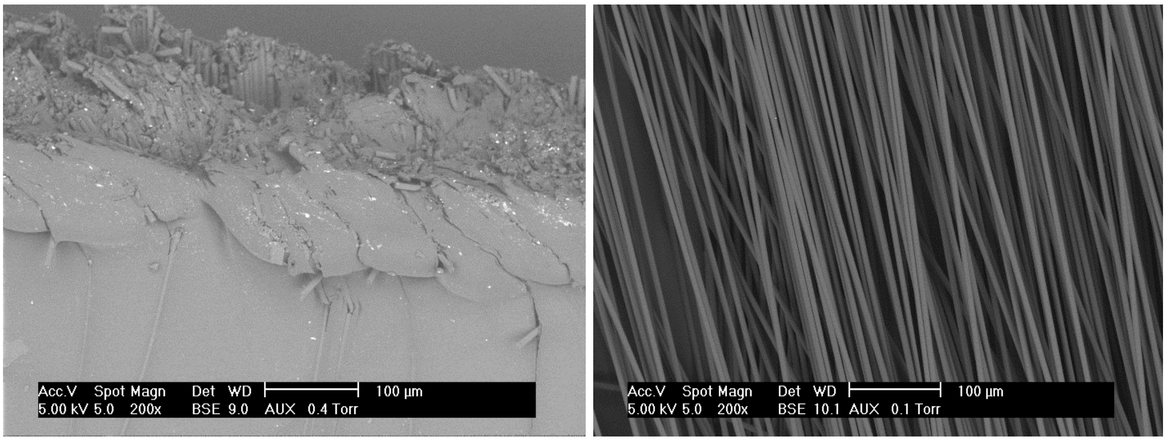

Figure 1: ESEM pictures of (a) composite and (b) virgin carbon fibers.

Conversion in supercritical water:

The experiments were carried out at 400°C and 25 MPa in the range of 15-120 min of reaction time. The mass loss of the composite increased rapidly with reaction time, as the mass loss reached 39 wt. % in 15 min (Table 1). In the range of reaction time studied the mass loss varied between 39 and 41 wt. %. Theses mass losses are closed to 42.5 wt. % obtained during the thermal or the chemical experiments, however this maximum mass loss was not reached with the current operating conditions. Although the maximum value was reached at 60 min of reaction time, the differences of mass loss at various reaction times did not exceed 2%. Thus the trend observed is an increase of the mass loss until 60 min followed by its slight decrease. Total Organic Carbon was also measured in the liquid phase. This value increased rapidly as the depolymerization starts during the first 15 min, then it slightly decreased until 60 min. Between 60 and 120 min, TOC values increased in the liquid phase. Using a TOC value of 24 g L^{-1}, the amount of organic carbon in the liquid phase represents 20 mg while an estimation of the organic carbon from the resin would represents less than 25 mg. Thus at 60 min the mass loss is maximum while the amount of carbon in the liquid phase is minimum. This experiment was reproduced 3 times and the result was confirmed. At the end of the experiments considered, volume of gas produced was too low to be measured. Especially in the case of 60 min reaction time, the high resin removal and the low TOC value would result in a transfer of carbon to gas phase. The concomitant variations of TOC and mass loss of the composite are not directly related and can be explained by using microscopy imaging of the composite surface.

Table 1: results of composite mass loss as function of reaction time.

Temperature (°C)	Pressure (MPa)	Reaction time (min)	Initial mass of water (g)	Total mass loss (%)	TOC (g L^{-1})
400	25	0	0.8327	0.00	0
400	25	15	0.8327	39.00	27.01
400	25	30	0.8327	40.60	27.14
400	25	60	0.8327	41.03	23.75
400	25	90	0.8327	39.35	27.72
400	25	120	0.8327	39.26	26.97

Remaining composites from the experiments have been observed using ESEM. The images presented in Figure 2 demonstrate that fibers are separated from each other from 15 min of reaction time. Back-scattering electrons (BSE) are analyzed by the detector meaning that the contrast results from different chemical natures. Thus the bright spots observed are related to chemical compounds that are different from carbon fibers, such as resin, minerals and so on. Degradations of the carbon fibers, such as micro fissures, are not highlighted with this procedure. A microanalysis with EDS detector indicates that some bright spots are due to minerals (platinium, titanium or alkali compounds) while the extended zones contains already carbon, oxygen and sometimes alkalis. These latter zones would be attributed to resin or other organic compounds. As the number and the size of bright zones increased with reaction time, one can suppose that resin, modified resin or a new polymer are deposed on the surface. In this last case, repolymerization reactions would be involved in, especially due to phenols. However the increase of TOC in the liquid phase is related to the liquefaction of the whole composite. At long reaction time, cleaned carbon fibers can be attacked by supercritical water. However, ESEM pictures realized with BSE detector are not able to highlight degradations on the carbon fibers surface. The increase of TOC value in the liquid could be explained by the conversion of the carbon fiber but this assumption is not confirmed by ESEM pictures.

The results presented were obtained in supercritical water that is supposed to improve reaction kinetics. The work is completed at subcritical conditions to study the impact on chemicals recovery.

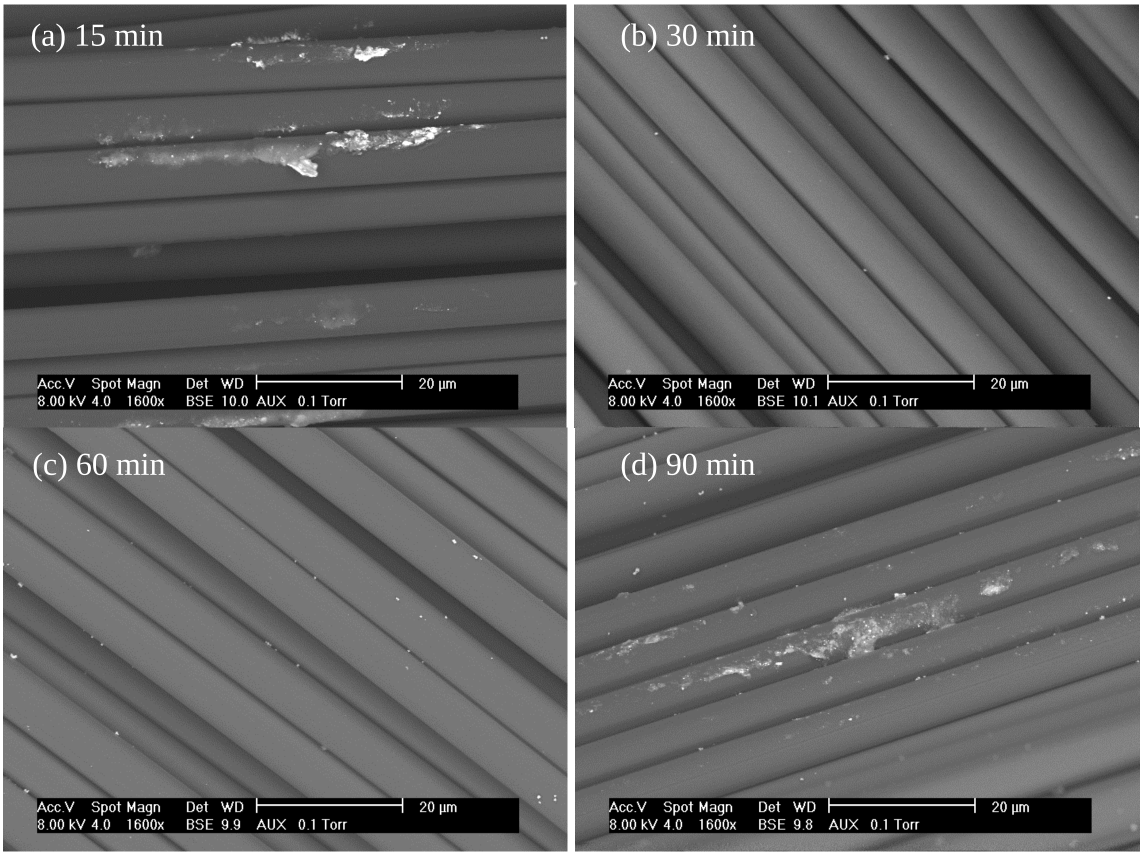

Figure 2: ESEM pictures of remaining composite after a treatment of: (a) 15 min, (b) 30 min, (c) 60 min and (d) 90min at 400°C and 25 MPa.

Conversion in subcritical water:

The experiments were carried out at 350°C and 25 MPa in the range of 15-120 min of reaction time. The mass loss of the composite increased with reaction time and reached about 40 wt. % at 30 min (Table 2). In the range of reaction time studied the mass loss varied between 40.6 and 41.7 wt. % that is closed to the theoretical maximal mass loss of 42.5 wt. %. After 15 min of reaction time, the degradation is of about 13 wt. % that corresponds to 1/3 of the polymer mass in the composite. Thus 30 min of reaction time is required to reach high depolymerization efficiency. Total Organic Carbon was also measured in the liquid phase. This value increased with the depolymerization reaction and remains constant from 60 to 90 min. In this case, the mass of carbon recovered in the liquid phase equals to 34 mg. One can also notice that the TOC value increased at 120 min together with the resin removal. In the literature, research works discussed that long reaction time and molecular oxygen could result in an attack of carbon fiber [12]. The near supercritical water used for these experiments could produce significant amount of radicals especially for a long reaction time [14]. No gaseous phase was obtained at this temperature, or was too small to be determined.

Table 2: results of composite mass loss as function of reaction time.

Temperature (°C)	Pressure (MPa)	Reaction time (min)	Initial mass of water (g)	Total mass loss (%)	TOC (g L^{-1})
350	25	0	3.13	0.00	0.00
350	25	15	3.13	13.31	1.11
350	25	30	3.13	40.62	12.90
350	25	45	3.13	41.27	10.80
350	25	60	3.13	41.21	10.87
350	25	90	3.13	41.04	10.87
350	25	120	3.13	41.74	11.28

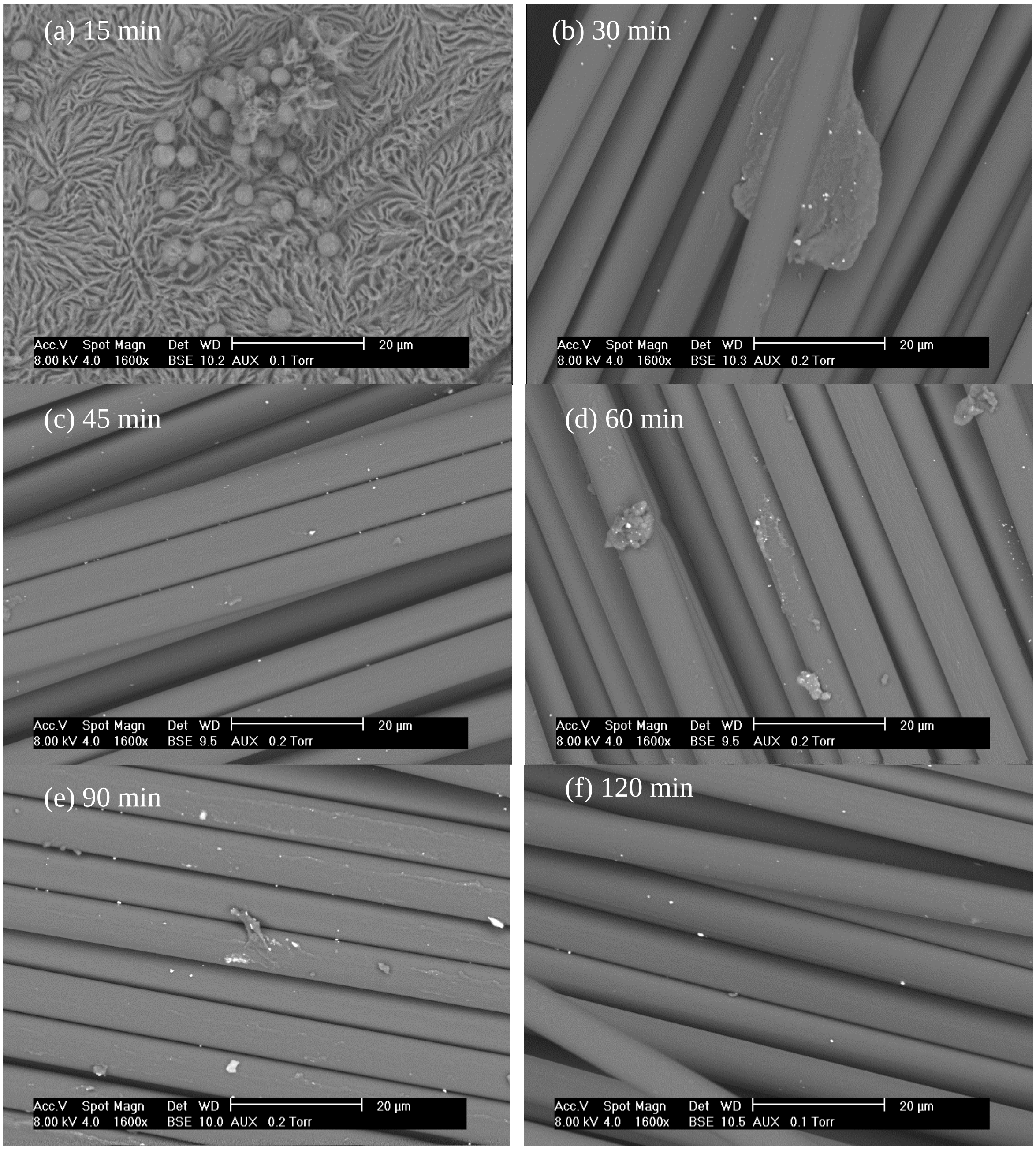

Figure 3: ESEM pictures of remaining composite after a treatment at 350°C and 25 MPa.

ESEM pictures from Figure 3 show that the clean-up is not visibly achieved at 15 min of reaction time; the resin is observed rather than carbon fibers. However the morphology of the surface has changed and the process seems to be heterogeneous due to the thickness variability of the remained resin. The spherical particles observed, which are mainly composed of carbon, let us consider that repolymerization reaction could occur before the cooling step. Although some pieces of resin are observed for other reaction time, the polymer seems to be efficiently removed from 30 min. Even using high magnification, the surface of fibers seems to be not affected by acid or basic attack, and the diameter of carbon fibers was not varying.

As for the supercritical conditions, any carbon fiber degradation was highlighted using ESEM. On the contrary, confocal microscopy highlights that a large amount of “defaults” appeared on the surface of remained carbon fiber at 120 min (Figure 4). A chemical analysis of these regions indicates that they are composed of organic compounds which are slightly different from the original resin. This chemical observation could explain that the modification of the surface was not highlighted with ESEM. Moreover the depth of this default is of about 1 µm while carbon fiber diameter is more or less 6 µm. These “defaults” are also observed on carbon fibers recovered after 30, 45 and 60 min with a chemical composition quite similar. However their number increased with reaction time. This complementary work is in progress to determine the nature of these chemical compounds and the statistical representation of these degradations.

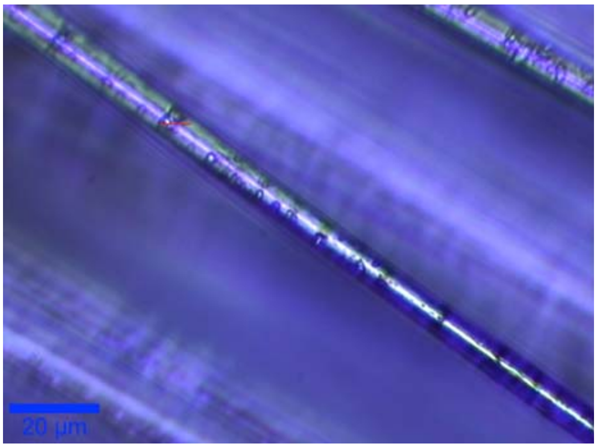

Figure 4: picture of remaining composite using confocal microscopy after a treatment of 120 min at 350°C and 25 MPa.

CONCLUSION

Depolymerisation of carbon fiber reinforced PA6 was realized in this study. Among the experiments carried out, the effect of temperature and reaction time was discussed. Based on the resin removal, hydrothermal conversion of resin is quite achieved under a pressure of 25 MPa after 15 and 30 min at 400 and 350°C respectively. These moderate temperatures result in a liquefaction process as a too small fraction of resin was converted to the gaseous phase. A long reaction time seems to be not required to achieve complete resin degradation as some polymerization reactions could occur and modify the carbon fibers surfaces. The main organic carbon from the resin is transferred to the liquid and Total Organic Carbon (TOC) values seem to indicate a higher content at 350°C meaning that carbon fiber was attacked. As the

ESEM pictures confirmed the resin removal, this technique did not highlight degradations on the carbon fibers. Confocal microscopy was then used for the sample obtained at 350°C, 25 MPA and 120 min and we observed lots of contrast regions on the carbon fibers. These regions are assumed to be composed of organic molecules (chemical analysis) that are closed to the original PA6 resins. This observation would then explain why carbon fibers seem to be recovered as their original state using ESEM. Mechanical essays were not performed due to the limited size of the fibers recovered. The next step of this study is to determine the characteristic organic functions of this “new” compound and its mechanism of formation (repolymerization reactions or resin transformation directly at the surface), and to study to what extend the mechanical properties are related to these surface modifications.

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