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Stability of carbon fiber surface functionality at elevated temperatures and its influence on interfacial adhesion

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ABSTRACT

The thermal stability of the surface chemistry of a surface treated carbon fiber, from room temperature to 1000 °C, was investigated by X-ray photoelectron spectroscopy. Within a range of temperatures from room temperature to 400 °C, the only surface functionalities that decomposed were carboxylic acids and dangling nitrogen containing functionalities like amines, amides or nitriles. Significant amounts of water were desorbed as well. This study enabled the testing of the coherence of the fitting of the C(1s), O(1s) and N(1s) peaks. Particularly, when considering the fitting of in the O(1s) peak, carboxylic acids were shown to be included in a single component peak centered at a binding energy of 532.1 eV. The reaction of the carbon fiber surface and an acrylate resin at high temperature, because of the decomposition of carboxylic acids, was highlighted by differential scanning calorimetry. The thermal history of the composite material during its manufacture appeared to be a major influence on the nature of the interactions generated at the fiber–matrix interface and the resulting mechanical properties.

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1. Introduction

It is now admitted that the physico-chemical and mechanical properties of a composite material are not only dependent on the characteristics of the reinforcement material and the matrix but also on the properties of the interface/interphase [1,2]. The properties of the interphase region depend on the conditions used during the manufacturing (thermal history, pressure, process of impregnation of the fibers by the matrix) [3,4]. Factors influencing adhesion strength are mechanical interlocking [5,6], physical (dispersive [7], polar [8], acid–base [9–11]) and chemical interactions [12,13], the presence of defects [14] (lack of cohesion [15], voids) and remaining stress due to the thermal history of the composite material [16] or the cure volume shrinkage of the matrix [17]. Thus, when considering carbon fibers (CFs), the two main surface parameters that will establish the properties of the interphase are surface topography and surface chemistry. The influence of the surface chemistry (generation of physical and chemical interactions) is directly linked to the thermal history of the composite material during the impregnation of the fibers by the matrix and the cure of the matrix. In some cases, the impregnation of the fibers and the polymerization of the matrix are done at room temperature, where the surface chemistry is stable and completely available for interacting with the monomers/oligomers/polymers of the matrix. In other cases, the thermal history during the cure can lead the composite material to undergo higher temperatures. For example, the initiation of the polymerization of vinyl ester resins without the use of a catalyst is typically done at around 150 °C. In the case of high performance thermoplastics (polycarbonate, polyethersulfone...), high temperatures are used for the impregnation of the fibers (values above the glass transition temperature of the polymer). It can be done at 300 °C or higher [18]. It is also known that the density of physical interactions at the interface has an influence on the mechanical properties of the thermoplastic composite [19,20]. Therefore, it is necessary to evaluate the stability of the surface chemistry of the CF regarding temperature in order to determine which particular surface functionalities are susceptible to be active and generate interactions with the matrix. Moreover, the thermal degradation of the surface chemistry potentially generates gas (CO, CO_2, H_2O) that can create some defects in the interphase and have a negative impact on adhesion strength. Some significant work regarding the stability of the surface chemistry of active carbon materials has been done, most of the time by thermal programmed desorption (TPD) coupled with mass spectroscopy [21]. This technique is very useful for a qualitative characterization of the surface chemistry of carbon materials. The analysis of the surface chemistry is non-direct, as it is based on the quantification of the gases that are generated when the surface functional groups decompose under temperature. The link between the production of those gases and specific groups is still the object of some controversy, because it can depend on the heating rate, the geometry of the experimental

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Table 1
Physical properties of Panex® 35 CFs (data provided by the manufacturer).

Tensile strength (MPa)	4137
Tensile modulus (GPa)	242
Density (g/cc)	1.81
Diameter (μm)	7.2

device used for the analysis and the porosity of the sample. Some extra interactions of the surface functional groups with the gases that are generated (especially water) or extra reactions between adjacent surface functional groups can also take place during the analysis (condensation of two adjacent carboxylic acids into an anhydride acid for instance). That is why the quantification of the different functional groups originally present at the surface of the sample is challenging. Some attempt was made to couple TPD analysis with diffuse reflectance FT-IR spectroscopy in the case of activated carbons, but a direct quantification of specific functional groups was still not straightforward [22]. In some cases, the surface treatment generates micro-porosity that can be located below the outer surface of the fiber (oxidation by electro-chemical process or by strong acids like nitric acid) and some functional groups located in those micro-pores would not be able to interact with the matrix. TPD analysis would take them into account and overestimate the density of surface functional groups that influences the adhesion strength. For these reasons, using another analytical technique that only probes the outer surface of the CF seems to be necessary. Therefore, X-ray photoelectron spectroscopy (XPS) analysis, which characterizes the surface chemistry of the outer layers of the CF surface only, is the appropriate technique. It is also a direct analysis that does not lead to a change of the surface chemistry. Moreover, Moreno-Castilla et al. [23] claimed that the thermal stability of oxygen surface complexes decreases when their surface concentration increases. Indeed, they showed that the higher the original amount of oxygen on the surface of carbon materials, the lower after a thermal treatment at high temperature. Considering that the porosity also has an influence on the thermal stability of the surface functional groups, activated carbon (including activated CFs) may not be representative of surface treated CFs.

In this study, the thermal stability of the surface chemistry of a surface treated CF is investigated over a wide range of temperature (from room temperature to 1000 °C) at regular intervals (50 °C from room temperature to 400 °C, then every 100 °C from 400 °C to 1000 °C). For each case, the surface chemistry is characterized by XPS and each of the C(1s), O(1s) and N(1s) peaks is fitted with reference component peaks in order to suggest a coherent analysis of the surface chemistry. Other work already characterized the surface of CFs obtained after a complete reduction of the surface at high temperature (at least 600 °C) [24–26], but barely any study focused on the evolution of the surface chemistry at intermediate temperatures.

2. Materials and methods

2.1. Materials

Polyacrylonitrile (PAN) based high strength CFs Panex® 35 (50 k), produced by Zoltek Co. were used in this study. The fibers were neither surface treated nor sized. The manufacturer provided properties of these fibers are presented in Table 1.

As received CFs were surface treated in a reactive gas phase containing ozone through a continuous process in order to achieve a high density of oxygen-containing surface functional groups. Ozone was produced by a PWB-150 g ozone generator from Plasma Techniques Inc. The residence time of the fibers in the reactive gas phase was 2 minutes. More information about the surface properties generated by this surface treatment (topography at a micro and nano-scale, surface energy) and the influence on the tensile strength of the fibers have already been described [27].

Table 2
Temperatures corresponding to each zone of the furnace.

Temperature-zone 1 (°C)	Temperature-zone 2 (°C)	Temperature-zone 3 (°C)
Room temperature	Room temperature	Room temperature
95	100	90
140	150	140
190	200	190
230	250	240
260	300	260
250	350	240
250	400	250
300	500	320
300	600	320
300	700	340
400	800	420
400	900	470
400	1000	530

Ebecryl 600® diacrylate resin was provided by Cytec Industries Inc. It was degassed before use under vacuum. A temperature of 90 °C had to be set during the degassing in order to reduce its high viscosity.

2.2. Heat treatment in inert atmosphere

The surface treated fibers were continuously heated in a three zone furnace equipped with a quartz tube, as displayed in Fig. 1. The highest temperature was reached in zone 2. Zone 1 and zone 3 were heated at intermediate temperatures, so that the fibers were progressively heated to the maximum temperature and cooled down to room temperature progressively, as well. Each zone could be independently heated up to 1200 °C. The temperature corresponding to each zone, for each maximum temperature of exposure, is reported in Table 2. An extra zone that was not heated enabled a progressive cooling of the sample to a temperature close to room temperature before it was in contact with atmosphere. The quartz tube (diameter of 90 mm, length of 4.6 m) was continuously purged with two sources of high purity nitrogen. Each end of the quartz tube had two openings (diameter of 8 mm) that were used for the fibers to go through the furnace and for the purge with nitrogen. The oxygen concentration in the heated quartz tube was continuously measured and kept below 500 ppm during experiments. Thanks to a feedback control, the furnace could compensate the flow of cool nitrogen by sending more power in zone 1, so that the temperature of zone 2 was well established. The CF tow was driven at low and constant tension (2.5 N) by several low friction yarn guides (pulleys made of hard anodized aluminum). The heat-treated fibers were quickly picked up at the exit of the tube and transferred in a bag purged with high purity nitrogen until the XPS analysis. The elapsed time between sample collection and XPS analysis was 24–48 h. The yarn guides were washed with distilled water and the quartz tube was cleaned by pyrolysis in air before the experiment.

2.3. XPS analysis

XPS analysis of the CF surface was carried out with a Thermo Scientific K-Alpha X-ray photoelectron spectrometer equipped with a conventional electron energy analyzer. The latter was operated in the fixed transmission mode at constant pass energy of 200 eV for the survey spectra and 50 eV for the core level spectra. A monochromatic Al Kα source (1486.6 eV) operated at 420 W (14 kV; 30 mA) was used as incident radiation. Photo-emitted electrons were collected at a take-off angle of 90° from the sample and the pressure

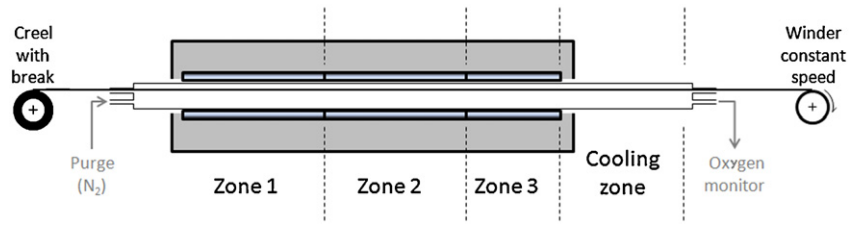

Fig. 1. Schematic of the process used in this study.

was about 10^{-7} Pa. The spectrometer energy scale was calibrated with respect to Ag $3d_{5/2}$, Au $4f_{7/2}$ and Cu $2p_{3/2}$ core level peaks, set with binding energies of 368.3, 84.0 and 932.7 eV respectively. All binding energies are referenced to the adventitious C(1s) peak located at 284.6 eV. Instrumental sensitivity factors were taken as C(1s):O(1s):N(1s) equals 1.000:2.930:1.800, respectively. For elemental quantification, the accuracy of the analysis was considered to be ±1%. C(1s), O(1s) and N(1s) core level spectra were fitted to GL functions (product of a Lorentzian by a Gaussian) using Avantage 4.44 software. The background was a Tougaard type for the C(1s) peak and "smart" for the O(1s) and N(1s) peaks. The parameters controlling the shape of the asymmetric component (graphitic component) were first estimated with the C(1s) core level spectra of the non-surface treated fiber because of its very low concentration of oxygen, knowing that this reference may contain a layer of turbostratic carbon coming from the carbonization step. The component peak positions used in C(1s), O(1s) and N(1s) curve fitting are presented in Table 3. Regarding the fitting of the C(1s) peak, there is evidence that two peak components are necessary in order to differentiate sp^2 and sp^3 hybridizations of carbon atoms in carbon materials, either in diamond-like structures [28] or amorphous carbon [29]. Not using a component peak for the sp^3 carbon atoms will lead to an overestimate of the quantity of C—O—R type functional groups. The O(1s) peak was fitted according to peak components proposed by Zielke et al. [30] and Biniak et al. [31]. A significant difference with the component proposed by Zielke et al. [30] is that we did not consider the component peak located at 534.2 eV to be related to carboxylic acids. Indeed, it would not have matched the binding energy of the component peak that decreased with temperatures ranging from room temperature to 200 °C, and corresponding to the degradation of carboxylic acids, as explained later. Our results suggested that both oxygen atoms contained in the carboxylic acid functionality were included in the component peak located at 532.1 eV. The N(1s) peak was fitted according to peak components suggested by Pels et al. [32] and Biniak et al. [31]. The full width at half maximum (FWHM) of all the component peaks was fixed to 2 eV, except for the Csp^2 and "shake up" component peaks, which were adjusted in order to obtain a fitting as close to the experimental spectrum as possible. The C(1s) peak fitting was done so that the total area of all the oxy-carbonated components could not be higher than the total area of the O(1s) peak and that the total area of all the nitro-carbonated components could not be higher than the total area of the N(1s) peak.

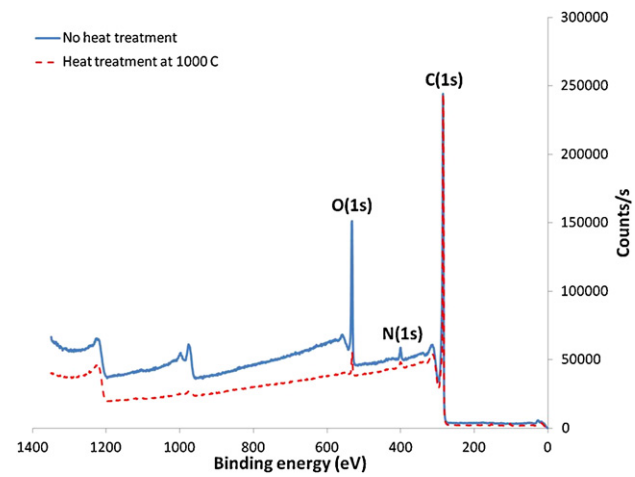

Fig. 2. Survey spectra of the surface treated fibers before and after exposure at 1000 °C (the intensity of the spectra have been normalized so that the intensities of the C(1s) peaks are identical).

2.4. Differential scanning calorimetry (DSC)

A Q2000 DSC apparatus from TA Instruments was used with liquid cells. A ramp from 25 °C to 250 °C with a rate of 5 °C min^{-1} in nitrogen atmosphere was used for the analysis.

3. Results and discussion

3.1. Elemental analysis

The typical survey spectra obtained with all the samples are displayed in Fig. 2. The only detected elements were carbon, oxygen and nitrogen. Their respective concentrations in surface treated fibers, before and after heat treatment, as well as in the case of non-surface treated fibers, is reported in Table 4. After surface treatment, the concentration of oxygen increased from 2% to 18%

Table 3
Binding energies of C(1s), O(1s) and N(1s) component peaks used for the fitting of XPS core level spectra.

C(1s)		O(1s)		N(1s)	
Binding energy (eV)	Component peak	Binding energy (eV)	Component peak	Binding energy (eV)	Component peak
284.4 ≪ 284.6	Csp^2	531.2 ≪ 531.4	Ph=O (quinone), Ph—C=O, amides	398.4 ≪ 399.0	Pyridine
284.9 ≪ 285.1	Csp^3	532.0 ≪ 532.2	C=O (ester, anhydride, amide), carboxylic acids	399.4 ≪ 399.8	Amines, amides, nitriles
284.8 ≪ 285.0	C—COOR	532.7 ≪ 532.9	R—OH, C—O—C	400.1 ≪ 400.7	Pyrrolidine, pyridone
285.4 ≪ 285.6	C—N	533.5 ≪ 533.7	Ph—OH, C—O (ester, anhydride)	401.1 ≪ 401.7	Pyridinium, protonated N
286.1 ≪ 286.4	C—O—R, C≡N	534.8 ≪ 535.2	Chemisorbed H_2O	403.7 ≪ 404.3	Shake up
287.4 ≪ 287.6	C=O	536.2 ≪ 536.6	Physisorbed H_2O	405.5 ≪ 405.7	NO_x
288.3 ≪ 288.9	COOR	538.2 ≪ 538.6	Shake up		
290.1 ≪ 290.5	Physisorbed H_20				
291.3 ≪ 291.7	Shake up				

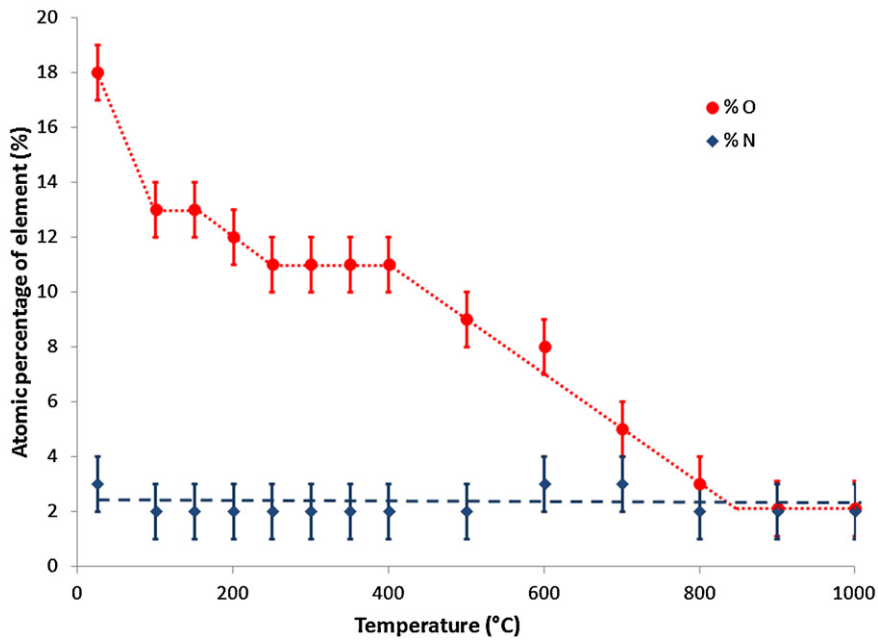

Fig. 3. Evolution of oxygen and nitrogen content at the surface of the CFs in function of the temperature.

and the concentration of nitrogen increased from traces (<1%) to 2%. The evolution of the concentration of oxygen and nitrogen in function of the temperature of exposure during the heat treatment is depicted in Fig. 3. The concentration of nitrogen stayed constant at around 2% whatever the temperature and remained higher than for the non-surface treated fibers. It showed that the nitrogen that was generated by the surface treatment or exposed after the removal of weakly boundary layers (remaining pyrolitic carbon generated during the carbonization step of the fiber) was very stable. When it comes to the concentration of oxygen, two major decreases occurred: the first one between room temperature and 100 °C (from 18% to 13%) and the second one between 400 °C and 900 °C (from 11% to 2%). A region of stability was found between 100 °C and 400 °C. After exposure to 1000 °C, the concentration was 2%, that is to say the same concentration as for non-surface treated fibers. Heating the fibers up to 1000 °C removed almost all the surface functionalities of the surface treated fibers. The fitting of each core level spectra is needed in order to characterize the evolution of the surface chemistry in function of the temperature and to suggest some mechanisms of degradation.

Table 4
Atomic concentration of carbon, oxygen and nitrogen measured by XPS.

Temperature (°C)	C (%)	O (%)	N (%)
25	79	18	3
100	85	13	2
150	85	13	2
200	86	12	2
250	87	11	2
300	87	11	2
350	87	11	2
400	87	11	2
500	89	9	2
600	89	8	3
700	92	5	3
800	95	3	2
900	96	2	2
1000	96	2	2
Untreated	98	2	<1

3.2. C(1s) peak

The relative area of each component peak of the C(1s), O(1s) and N (1s) peaks in function of the temperature is reported in Table 5. The values were obtained after removal of the contribution of the component peak corresponding to shake-up satellites. Regarding the evolution of the C(1s) peak in function of temperature, Fig. 4 presents the fitting of C(1s) peak corresponding to temperatures that induced a major change of the surface chemistry, that is to say 300 °C, 800 °C and 1 000 °C. The evolution of the area of each component peak in function of the temperature is presented in Fig. 5.

The relative area of the peak corresponding to C—N bond is constant within the whole range of temperature, which is in accordance with the fact that the concentration of nitrogen on the fiber surface was also constant.

Both peak components corresponding to COOR and C—COOR followed the same trend. A first significant drop was noticed between room temperature and 150 °C, which corresponds to the decomposition of isolated carboxylic acids. Then, a plateau was observed between 150 °C and 400 °C. This can be related to adjacent carboxylic acids condensing to form an anhydride acid group [25,33] which decomposes at higher temperature (typically between 300 °C and 600 °C). Anhydride acids are included in the same component peak. Therefore, the concentration of COOR bond type remained the same until the decomposition of the anhydride acid groups. A second drop of the relative surface area was observed between 400 °C and 800 °C, which corresponds to the decomposition of the anhydride acid groups but also to the decomposition of lactone groups [34,35]. Only pyrone functionalities, stable between 800 °C and 1000 °C, can explain the remaining signal corresponding to COOR bond type above 800 °C [34,35]. The area of the peak component corresponding to C—O—R type remained stable until 400 °C and then decreased sharply until 700 °C where it stabilized again. The decomposition of phenol groups typically takes place between 400 °C and 800 °C and ether functionalities decompose between 500 °C and 900 °C [35]. Above 450 °C, two phenols can condensate to give an ether group [36] but it cannot be seen with the fitting of the C(1s) peak since it corresponds to the same component peak. Some of those groups (probably phenols) were still stable between

Table 5
Relative area of each component peak of the C(1s), O (1s) and N (1s) peaks in function of the temperature.

Temperature (°C)	C(1s)								O(1s)						N(1s)		
	Csp^2	Csp^3	C—COOR	C—N	C—O—R	C=O	COOR	H_2O	Ph=O, Ph—C=O	C=O	R—OH, C—O—C	Ph—OH, C—O	H_2O chem	H_2O phys	Pyridine	Amines, amides, nitriles	Pyrrolidine, pyridone	Pyridinium
25	53	22	6	2	6	2	7	2	16	25	19	34	3	3	26	8	31	35
100	58	18	6	2	7	1	6	2	16	26	19	33	2	4	18	9	27	46
150	63	17	5	2	5	1	5	2	24	17	20	32	3	4	22	8	29	41
200	62	17	5	2	5	2	5	2	24	15	22	31	4	4	20	8	28	44
250	62	17	4	3	6	1	5	2	25	10	25	31	4	5	19	4	30	47
300	64	16	5	2	4	2	5	2	25	11	22	33	4	5	20	12	25	43
350	67	13	4	2	6	1	5	2	24	12	22	33	4	5	32	0	32	36
400	70	10	4	2	6	2	4	2	29	6	25	30	4	6	31	1	32	36
500	78	9	3	2	4	1	2	1	29	0	34	28	3	6	39	0	24	37
600	79	8	2	3	4	1	2	1	26	0	49	16	4	5	40	0	26	34
700	85	5	1	3	3	1	1	1	26	0	46	18	5	5	42	0	21	37
800	88	6	0	2	2	1	0	1	32	1	41	18	4	4	33	0	5	62
900	88	3	1	2	3	1	1	1	17	18	40	14	5	6	34	1	10	55
1000	87	4	1	2	3	1	1	1	11	18	49	14	4	4	34	0	11	55
Untreated	86	10	0	0	2	1	0	1	27	30	21	18	3	1	11	3	34	52

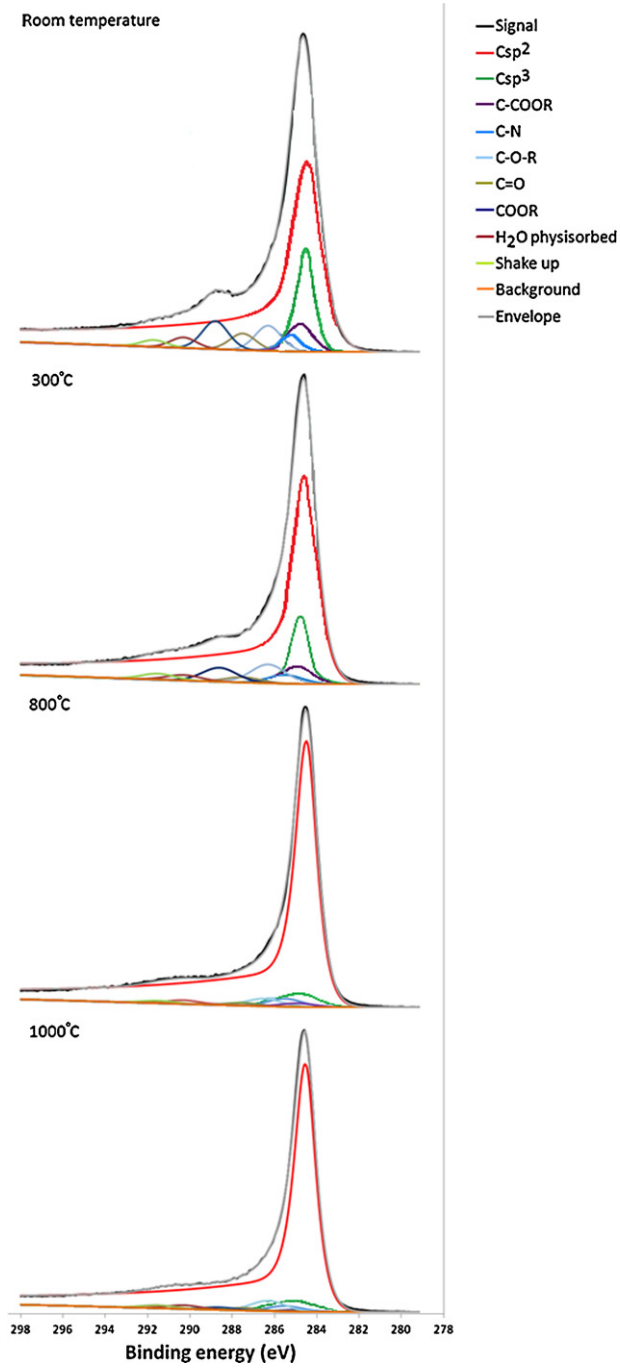

Fig. 4. Fitting of the C(1s) peak before and after exposure to heat treatment, respectively at 300 °C, 800 °C and 1000 °C.

800 °C and 1000 °C. The low concentration of carbonyl groups at the beginning of the experiment is a specificity of the surface treatment. A slight decrease of the relative area of the component peak related to carbonyl groups happened at 400 °C, which is consistent with work reported by Kohl et al. [22].

The evolution of the peak area corresponding to the two different hybridization states of carbon atoms, sp^2 and sp^3, is presented in Fig. 6. The relative area corresponding to the sp^2 hybridized carbon atoms increased between room temperature and 150 °C and between 300 °C and 700 °C, which corresponded well to the variation in oxygen concentration. The loss of oxygen-containing functional groups led to the formation of original graphite-like structures including C=C (double bonds). Indeed, it

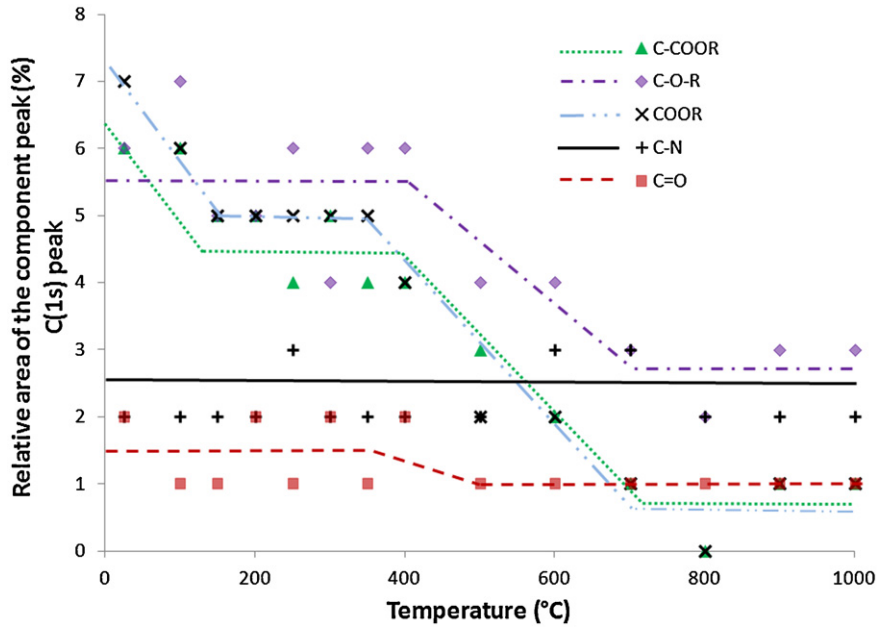

Fig. 5. Evolution of the relative area of the peak components of the C(1s) peak in function of the temperature.

was also directly linked to a decrease of the relative area of the sp^3 hybridized carbon atoms peak component.

The relative surface area of the component peak corresponding to physisorbed water was constant at 2%, from room temperature to 400 °C, and decreased slightly to reach a plateau at 1% from 400 °C to 1000 °C. Several mechanisms are at the origin of the adsorption of water at the surface of the fibers. Water originally at the surface of the fibers is desorbed but it is also produced by the decomposition of the different surface functional groups, potentially over the whole range of temperature [25]. That water was flushed away by the nitrogen flow but could be re-adsorbed in the cooler part of the furnace (zone 3 and cooling zone, Fig. 1) by the remaining oxygen-containing functional groups. Some water could also be adsorbed when the samples were transferred to the nitrogen-containing bags or when the sample was prepared for XPS analysis. Since the major part of the polar surface functionalities that can create physical interactions with water (hydrogen bonding, dipole-dipole interactions) was decomposed above 400 °C, the density of adsorption sites decreased and the final content of adsorbed water was divided by two.

3.3. O(1s) peak

The fitting of O(1s) peak is still the object of some debate, as it was fitted with only two component peaks corresponding to C—O and C=O bonds [20,25], or four component peaks [30] or even five component peaks [37]. Our study showed that a fitting with four component peaks corresponding to different oxygen-containing functional groups was working properly. Fig. 7 presents the fitting of O(1s) peak before and after a heating at 300 °C, 800 °C and

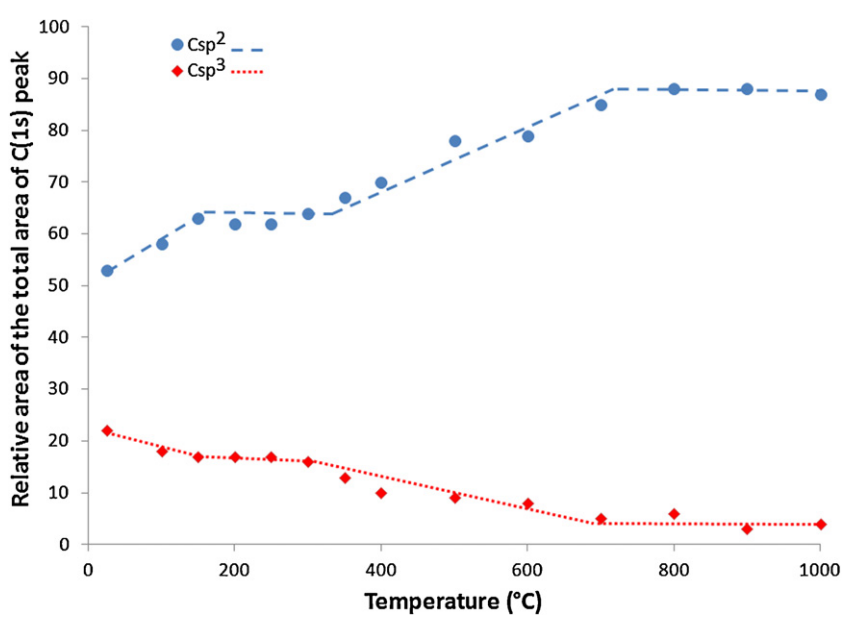

Fig. 6. Evolution of the relative area of the Csp^2 and Csp^3 component peaks in function of the temperature.

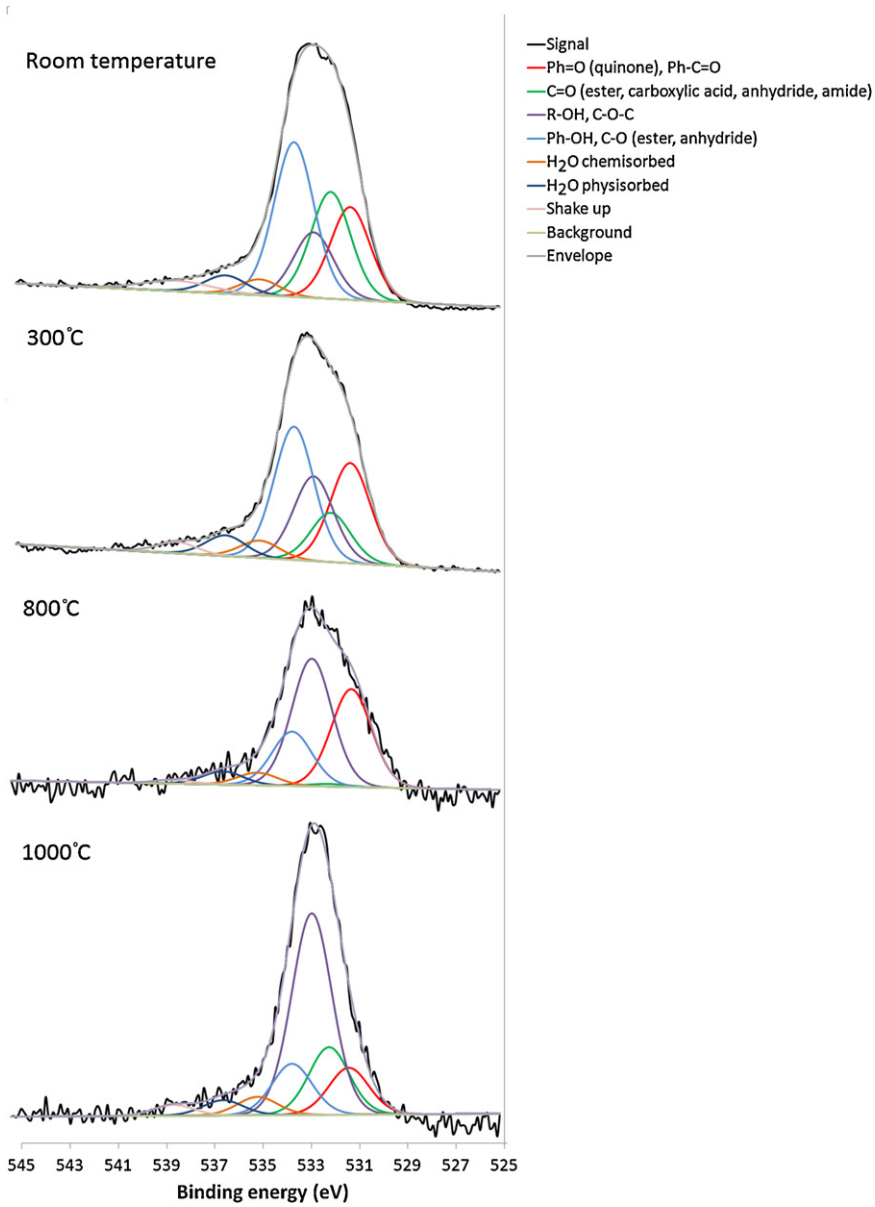

Fig. 7. Fitting of the O(1s) peak before and after exposure to heat treatment, respectively at 300 °C, 800 °C and 1000 °C.

1000 °C. The evolution of the relative area of each component peak in function of the temperature is presented in Fig. 8. The relative area of the component peak located at 532.1 eV decreased between room temperature and 200 °C. Only carboxylic acid groups could decompose within this range of temperature [34,35]. This decrease also took place simultaneously with the decrease of the peak component corresponding to carboxylic acids in the C(1s) peak. The three other component peaks did not decrease within that range of temperature, which proved that the carboxylic acids were included in only one component peak. Zielke et al. [30] considered that both oxygen atoms of the carboxylic acid functionality should be included in the same component peak, but at a higher binding energy (534.2 eV). Their fitting method was then used by others [37,38] and led Chiang et al. [24] to consider that some carboxylic acids were remaining at the surface of activated CFs after a heat treatment at temperatures above 600 °C in nitrogen and a cooling down in nitrogen too, which seems to be questionable. In fact their component peak located at 532.3 eV decreased sharply, which confirms our approach. Brender et al. [39] also noticed that the desorption of carboxylic acids was linked to a decrease of a component peak located at 531.8 eV, by coupling TPD and in situ XPS analysis. But they concluded that the two oxygen atoms of carboxylic acids should be considered separately in two component peaks, one at 531.8 eV (C═O bond) and one at 533.4 eV (C—O bond), despite of the fact that the component peak located at 533.4 eV did not seem to decrease between room temperature and 400 °C. Therefore, it seems that carboxylic acids should be included in a single peak located around 532.1 eV. It is confirmed by XPS characterization of model surfaces functionalized with carboxylic acids [40–42]. The fact that the two oxygen atoms are linked to the carbon atom with the same binding energy can be explained by the stabilization mechanism of the carboxylic acid group by resonance [43], as shown in Fig. 9. The decrease of the density of carboxylic acids between 100 °C and 250 °C is linked to a slight increase of the component peaks located at 531.3 eV and 532.8 eV. The condensation of carboxylic acids with carbonyls, leading to the creation of a lactone group [36] (increase of Ph—C═O and C—O—C functional groups) may explain those results. At higher temperature, between

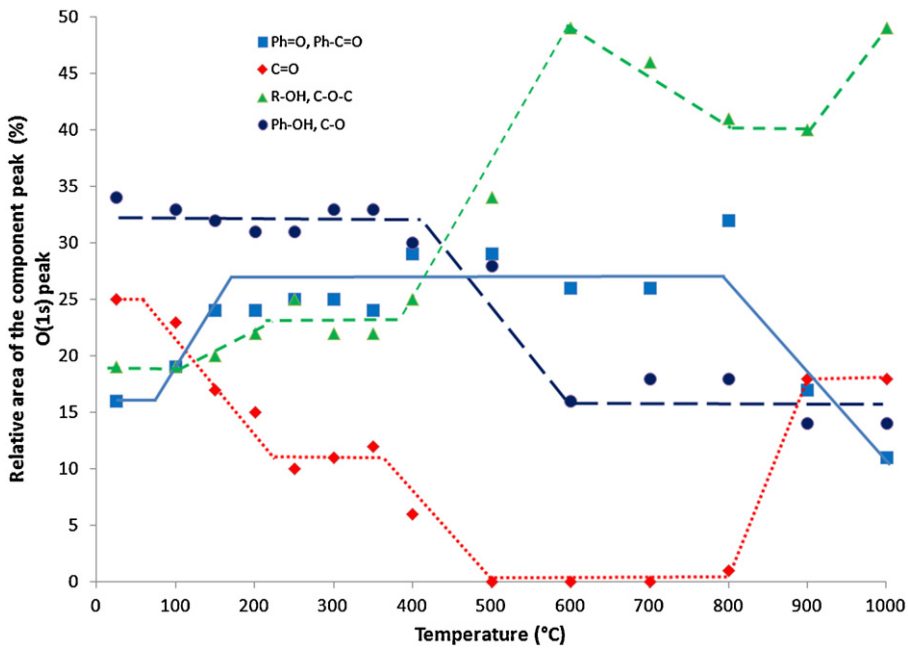

Fig. 8. Evolution of the relative area of the peak components of the O(1s) peak in function of the temperature.

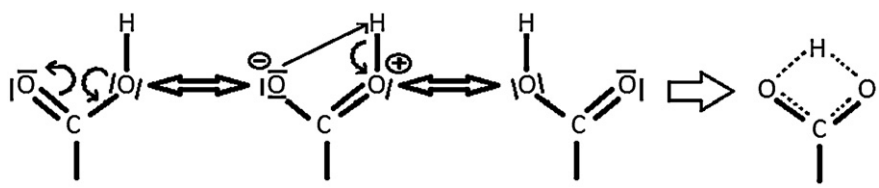

Fig. 9. Mechanism of stabilization of the carboxylic acid group by resonance.

350 °C and 600 °C, the relative area of the component peaks located at 532.1 eV and 533.6 eV decreased sharply while the relative area of the component peak located at 532.8 eV was sharply increasing. The decomposition of the anhydride acids originally present at the surface of the fiber or generated by the condensation of adjacent carboxylic acids was highlighted by the decrease of the density of C=O and C—O bonds, and the condensation of adjacent phenols to create ether functional groups was highlighted by the decrease of Ph—OH bonds and the increase of C—O—C bonds. Both mechanisms have been characterized in that range of temperature [36] and certainly can explain the variations of our spectra. This would exactly match with the decrease of the peak components corresponding to COOR and C—O—R bonds in the C(1s) peak. Between 600 °C and 800 °C, the surface chemistry was relatively stable. Only a slight decrease of the component peak located at 532.8 eV that can be related to the decomposition of ether functionalities was noticed. Between 800 °C and 1000 °C, a sharp increase of the relative area of the component peaks located at 532.1 eV and 532.8 eV occurred simultaneously with a sharp decrease of the relative area of the component peak located at 531.3 eV. This evolution was observed by Chiang et al. [24] as well. In this range of temperature, only the decomposition of quinones and pyrones is expected [34], as displayed in Fig. 10. The decrease of Ph-C=O and the creation of C=O bonds as well as C—O—C bonds support those observations. The surface chemistry of fibers that were surface treated and annealed appeared to be quite different from the surface chemistry of non-surface treated fibers. Indeed, the surface chemistry of non-surface treated fibers showed relatively more quinone and pyrone functional groups but less ether type groups than the surface chemistry of surface treated annealed fibers. Furthermore, the suggested fitting of the O(1s) peak suits perfectly the potential mechanisms that have been suggested by other analytical techniques like TPD.

3.4. N(1s) peak

Fig. 11 presents the fitting of N(1s) peak before and after a heating at 300 °C, 800 °C and 1000 °C. The evolution of the relative area of each component peak in function of the temperature is presented in Fig. 12. Basically, after the surface treatment, nitrogen existed in two main forms, either incorporated in the graphitic network within functional groups (like pyridine, pyrrolidine, pyridone. . .) or in dangling functionalities (like amine, amides and nitriles). These dangling functionalities later decomposed at 300 °C to completely disappear over 350 °C.

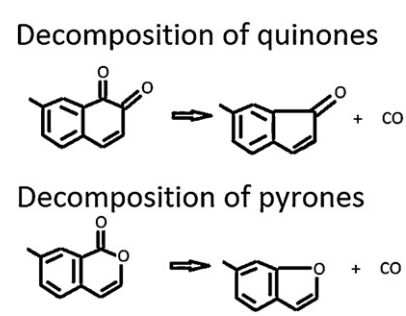

Fig. 10. Thermal decomposition mechanisms of quinones and pyrones.

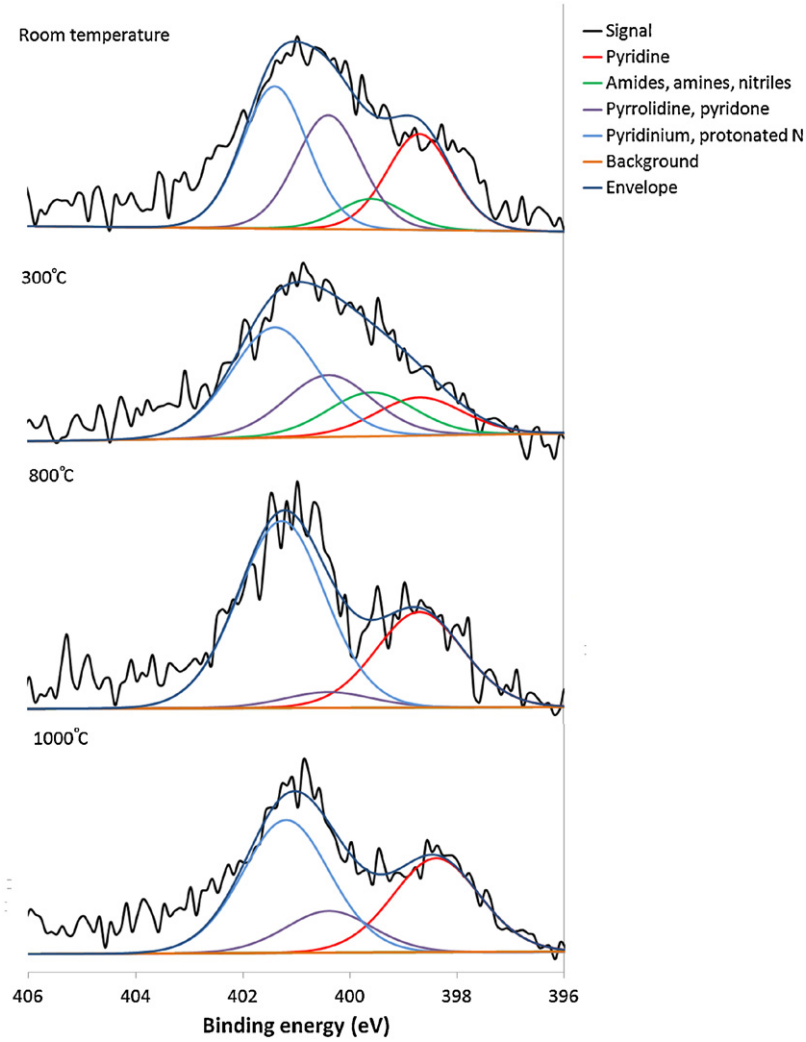

Fig. 11. Fitting of the N(1s) peak before and after exposure to heat treatment, respectively at 300 °C, 800 °C and 1000 °C.

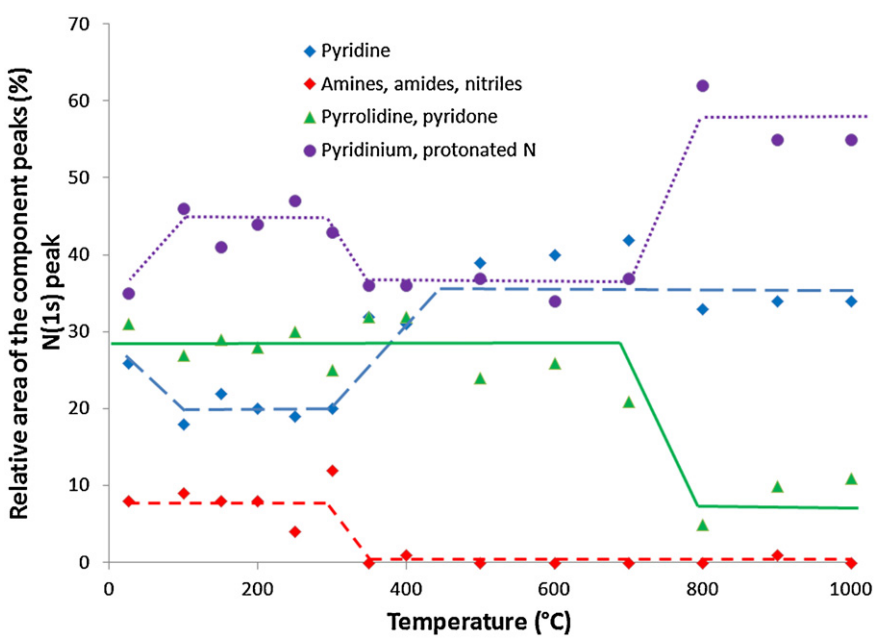

Fig. 12. Evolution of the relative area of the peak components of the N(1s) peak in function of the temperature.

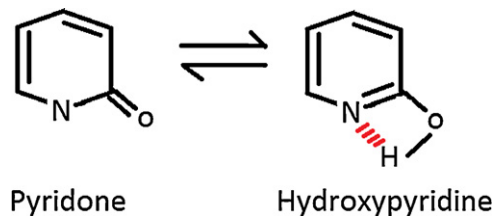

Fig. 13. Tautomerism between pyridone and hydroxypyridine.

Below 400 °C, the peak components of pyridine and pyridinium evolved in opposite ways. Between room temperature and 100 °C, the decrease of the relative area of the component peak related to pyridine was associated to an increase of the relative area of the component peak related to pyridinium. This range of temperature usually corresponds to the desorption of loosely bound water that is physically adsorbed at the surface of the fibers. This water may have reacted with pyridine and protonated it. The nitrogen-containing functional groups were stable between 100 °C and 350 °C. The hydrogen bond of pyridinium groups may have been broken to give pyridine. But at the same time, new amounts of water were released by the desorption of strongly adsorbed water (water bonded to oxygen-containing functionalities through hydrogen bonding). That water could have regenerated the pyridinium groups. Over 300 °C, after all water was desorbed, a significant decrease of the density of pyridinium groups was observed. The relative areas of the peaks corresponding to pyridine and pyridinium were back to their original values. Then, pyridine groups were stable up to 1000 °C, which is in accordance with work published by Mangun et al. [44]. Pyrrolidine and pyridone were stable until 700 °C. The increase of the density of protonated nitrogen above 700 °C corresponded to a disappearance of pyrrolidine and pyridone structures. This phenomenon was also reported by Pels et al. [32]. A tautomer structure of pyridone exists, as displayed in Fig. 13, but requires a significant amount of energy, as reminded by Moreno and Miller [45]. The generation of a hydrogen bond with the nitrogen atom may lead to a similar binding energy compared to protonated nitrogen. This mechanism might take place at high temperature and could be an explanation for the evolution of the relative areas of the component peaks corresponding to pyridone and protonated nitrogen above 700 °C. Finally, a very slight increase of the nitrogen content was measured between 600 °C and 800 °C (Fig. 3), suggesting that the surface may have reacted with the surrounding nitrogen, but it was very limited.

3.5. *Influence of the stability of the surface chemistry on interfacial adhesion in polymer composites*

Depending on the thermal history of the composite material during the manufacturing process, the thermal stability of the surface chemistry of the CFs may play a major role on its mechanical properties. Indeed, as mentioned in the introduction, the fibers can potentially be exposed to relatively high temperatures during the impregnation by the matrix (up to 350 °C with a polycarbonate matrix) or during the cure of the matrix (temperature of cure depending on the type of polymerization, the nature of the initiator and the exothermicity of the polymerization). Between room temperature and 400 °C, it was demonstrated that only carboxylic acids and dangling nitrogen containing functionalities were affected by the heat treatment. Adjacent carboxylic acids could condense into an anhydride acid group (which may or may not be more reactive depending on the type of matrix). The condensation could also be between adjacent carboxylic acids and phenols or carboxylic acids and carbonyls. Isolated carboxylic acids were decomposing into CO_2 and left radicals at the surface of the CFs, as shown in Fig. 14. Those radicals have the potential to generate covalent bonding with the matrix. That mechanism opens new perspectives about the improvement of interfacial adhesion in CF–polymer composites. Hüttinger et al. [46] suggested that the instability of carboxylic acids could create covalent bonding with polycarbonate or polyethersulfone. Their composites were processed at 330 °C and a clear improvement of the InterLaminar Shear Strength (ILSS) was observed. Zielke et al. [47] referred to a similar explanation for the creation of covalent bonding with polyetherimide in a study that involved a composite processing at 340 °C and short beam shear testing. Both studies claimed that the decomposition of isolated carboxylic acids enabled the creation of covalent bonding between the carbon fiber surface and the thermoplastics, consequently improving the adhesion strength at the interface.

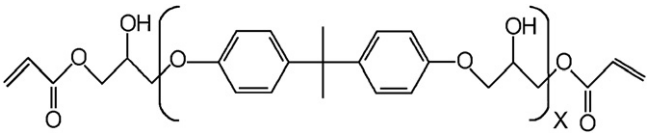

Fig. 15. Structure of the monomer of Ebecryl 600®.

The creation of radicals at the surface of CFs seemed to be suitable for the generation of covalent bonding with thermosets polymerizing through a radical process. That was investigated using Ebecryl 600®, a diacrylate resin with a polyether structure derived from di-glycidyl ether of bisphenol A (DGEBA) (Fig. 15). The DSC analysis of pure Ebecryl 600® highlighted a homopolymerization with a maximum reaction rate at 220 °C, showing that this resin is relatively stable at high temperature (Fig. 16). The same analysis, in the case of a composite (~40% of fibers by volume) with surface treated CFs showed an exothermic reaction starting at around 150 °C, with a maximum reaction rate at 173 °C. It is clear that the presence of the CF initiated a partial polymerization of the matrix, which was complete after an exposure above 250 °C, just as for pure resin. The reaction initiated by the fiber surface is located in a range of temperature corresponding to the decomposition of the carboxylic acids. Processing this composite at high temperature has the potential to create a higher density of covalent bonding

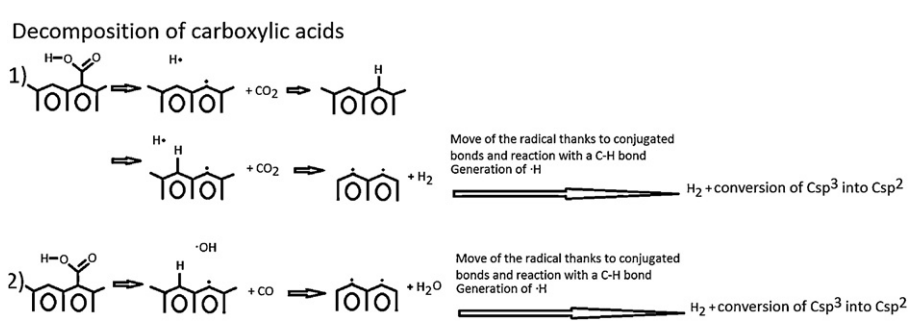

Fig. 14. Mechanisms of the decomposition of carboxylic acids under temperature.

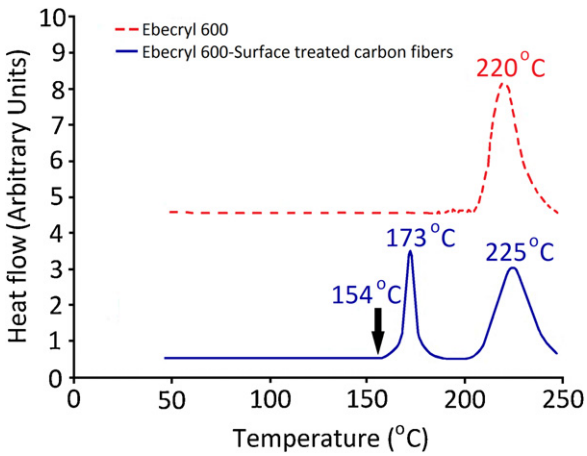

Fig. 16. DSC curves corresponding to the reaction of Ebecryl 600® with the CF surface under temperature and to the homopolymerization of Ebecryl 600®, reprinted from [48].
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at the interface in comparison to a processing at low temperature, which should have a clear impact on the interfacial adhesion and the mechanical properties of the associated composite. This phenomena was demonstrated [48] when comparing the adhesion strength between carbon fibers and Ebecryl 600® in composites cured by a thermal treatment (maximum temperature reached during the cure equal to 160 °C, for an hour) or by electron beam (maximum temperature reached during the cure equal to 100 °C, for one minute only).

The same mechanism should apply to all the resin systems polymerizing through a radical polymerization (vinylester, polyester). Our group [27] reported a significant increase of interfacial adhesion in CF–vinyl ester composites cured by thermal treatment at 150 °C when using the same surface treatment as the one described in Section 2.1 (both the 90° flexural strength and the ILSS greatly improved). The improvement of interfacial adhesion led to a change of the failure mode which switched from a pure interfacial rupture mode with non-surface treated fibers, to a mix-mode interfacial/cohesive rupture with surface treated fibers.

Meleshevich [49] reviewed the mechanisms that can affect an epoxide group when initiated by a radical. Among them is the cleavage of the epoxy ring initiating another radical entity that initiates further reactions. So, the mechanism presented here could potentially affect the interfacial adhesion with epoxy matrices too.

Overall, this study demonstrates once again that the mechanical properties of a composite material strongly depend on the parameters used during the manufacturing, especially during the curing process.

4. Conclusions

The thermal stability of the surface chemistry of surface treated CFs was investigated by XPS analysis. Within a range of temperature from room temperature to 400 °C, which corresponds to the typical temperatures that can be used in the polymer matrix composite manufacturing process, the only surface functionalities that decomposed were carboxylic acids and dangling nitrogen containing functionalities like amines, amides or nitriles. Significant amounts of water were desorbed too. A coherent fitting of the C(1s), O(1s) and N(1s) peaks was suggested. Particularly, carboxylic acids were shown to be included in a single component peak when considering the fitting of the O(1s) peak, at a binding energy of 532.1 eV. A graphitization of the fiber surface was directly connected to the desorption of surface functionalities. The decomposition of carboxylic acids, leading to the generation of radicals, is a strategic mechanism in the creation of covalent bonding between the CF surface and different types of polymer matrices (high temperature thermoplastics, thermosets polymerizing through a radical mechanism, etc.). The reaction of the CF surface and an acrylate resin at high temperature was highlighted by DSC. The thermal history of the composite materials during the manufacture (impregnation of the fibers by the matrix, cure) appeared to be a major influence on the nature of the interactions generated at the fiber–matrix interface, thus directly determining the level of interfacial adhesion and the mechanical properties of the corresponding composite. This study could also be valuable for research regarding the use of carbon materials as catalysts, as the surface chemistry plays a major role and can also undergo elevated temperatures during the manufacturing.

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