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Validation of carbon fibers recycling by pyro-gasification: The influence of oxidation conditions to obtain clean fibers and promote fiber/matrix adhesion in epoxy composites

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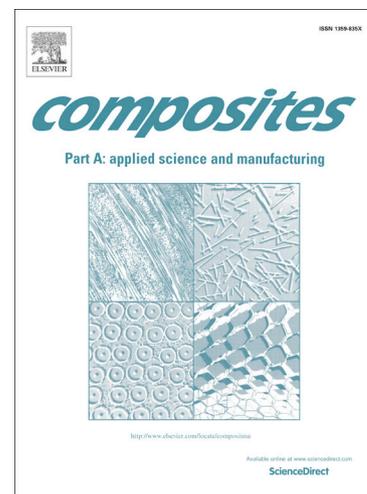
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Validation of carbon fibers recycling by pyro-gasification: the influence of oxidation conditions to obtain clean fibers and promote fiber/matrix adhesion in epoxy composites

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Abstract

This work aims at demonstrating, at a pilot plant scale, the potential of the pyro-gasification process to produce carbon fibers (CF) as secondary raw materials. The solid residue obtained upon pyrolysis was characterized and oxidized, applying different process conditions to provide clean fibers. The same process was applied to virgin fibers, thus highlighting the protective action that char provides to CF during the oxidation step. The recovered fibers were used to produce new short fiber composites which, upon optimization of the mixing and curing conditions, were competitive with the performance of pristine fibers composites. Indeed, the oxidation leaves an oxygen rich surface which positively interacts with the epoxy resin, thus promoting adhesion without the requirement of an additional sizing process after the CFs recycling. These results provided sufficient validation of the recovered CF quality, thus leading to the scale up of the process to produce an integrated pyro-gasification semi—industrial plant.

Keywords: carbon fibers; recycling; Process monitoring; fiber/matrix bond

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1. Introduction

In recent decades, carbon fibres (CFs) have found widespread application in a growing number of fields, such as automotive, aerospace and defence, wind turbines, sport, and leisure [1].

Though their discovery dates back to T.A. Edison in 1879 [2], their application as high-performance light-weight reinforcement has just recently had a boost mainly in luxury-related high added value fields, such as aerospace, defence, wind turbines, sport and leisure.

Consequently, the carbon fibre industry has been experiencing a steady growth which is lately expanding towards more mass-oriented market segments such as the mainstream automotive and motorcycles, where they are applied in the form of CF Reinforced Polymers (CFRPs) to replace metal parts in vehicles in order to provide them with lighter weight. Accordingly, the demand for carbon fibers, that grew from 27000 tons in 2009 to 53000 tons in 2014, is foreseen to more than double by 2021 with an expected request of 116000 tons [3]. Such a boost in the CFRP exploitation is now raising the awareness about their fate: a strong increase in CF waste is indeed expected, coming both from the production processes (prepreg offcuts; offcuts and scraps of cured composites) and the End of Life products (EoL).

The current EU legislation does not provide specific regulation for composites' waste. Their disposal is indirectly involved in the 2000/53/EC EU Directive, which requires a 95% recovery and 85% recycling extent of total End-of-Life Vehicle weight by 2015 and limits the use of non-metal components if not complying with the Directive requirements. However, while attempts are made at obtaining green composites [4] and green nanocomposites [5], thermoset CFRPs still dominate the market, and presently they cannot be easily recycled or recovered, neither by disassembling of their components nor by re-melting and re-moulding. Hence research efforts are focusing on adequate recovery techniques for these components to match the EU Directives. Though several disposal techniques are presently available for treating CFRPs [6], they are still far from optimized and they are characterized by some serious drawbacks. For example, mechanical treatment leads to powdery materials with low added value, which can be mainly

applied as fillers [7]. When, however, valuable material recovery is pursued, either thermally or chemically, it necessarily involves some preliminary shredding and crushing treatment of the waste, with a significant energy consumption. Moreover, thermal treatments have to be carefully controlled in order to avoid loss of valuable products or undesired modifications in the chemistry of the recovered products [8-10], while solvolysis brings in additional chemicals which then require their own disposal [11]. On the other hand, energy recovery, which mainly consists of incineration treatments of mixed waste streams, leads to the loss of valuable materials and the production of polluting emissions, imposing the use of expensive gas cleaning devices. Moreover, the latter approach does not take into account the notion of secondary raw material, first introduced by the EU Directive 2008/98/EC, which has the purpose of moving the EU closer to a 'recycling society', seeking to avoid waste generation and using it instead as a resource.

Considering the still relatively high cost of the virgin fibers, both in terms of economic (approx. 30 €/kg [12]) and energetic cost (183-286 MJ/kg [13]), a process able to give back CFs with a lower energy consumption than the production of virgin fibers appears environmentally attractive and offers economic benefits to manufacturers. In this frame, the acquisition of technological skills allowing an added value recovery of wastes, instead of their simple disposal, is a key enabling process in the implementation of the EU requirements.

Several companies offer CFRPs recovery services and their recycling into marketable products [14] with the aim of addressing the issue of EoL CFRP parts. The most appealing approach is represented by pyrolysis, a process in which organic materials are thermally decomposed into simpler components when subjected to strong heat under an oxygen deprived atmosphere. When pyrolysis is applied to CFRPs, treated as a single flow of waste, it involves the thermal cracking of the matrix fraction, no matter if thermoplastic or thermosetting, producing a volatile stream made of a condensable component (pyrolysis oil) and a non-condensable fraction (gas). These fractions can both be used as a source of valuable products for further manufacturing [15] or as a

fuel. In the latter case, the high carbon and hydrogen contents of both volatile and non-volatile components result in a high calorific value which can be profitably used to practically fully sustain the pyrolysis process [16]. At the end of the process a solid residue can be recovered, that in the case of CFRPs is mainly composed of carbon fibers. Reports from industry suggest that the production of recovered CFs (Re-CFs) through pyrolysis of CFRPs waste will consume only 5-10% of the energy required for the production of virgin fibers [8;17]. During the process, a layer of pyrolytic carbon can form onto the fibers [8;18] hampering a good adhesion when infused with new resin. However, these Re-CFs can be considered highly valuable products after an upgrading process based on oxidative treatment [15;19] which gives back fibers in a suitable condition to be used as feedstocks in a secondary raw material generation approach.

In order to optimize the whole pyrolytic process, Curti S.p.A. has recently proposed an innovative static-bed batch pilot reactor [20;21] able to combine, in one single process, the main advantages of the different disposal techniques. In fact, pyrolysis can be carried out on the whole parts, up to 2 m in diameter, in order to save the energy costs of shredding the feed wastes, and simultaneously recovering energy and materials. Moreover, though the pyrolysis tests were carried out in a demonstrative pilot plant, which was not optimized in terms of energy balance, the gaseous and liquid by-products display an overall Gross Calorific Value (GCV) able to sustain about 75% of the process energy requirement. It is hence possible to foresee that, upon a convenient optimization of the plant energy issues during scale up, the process might reach a complete energetic self-sustainability [16].

The present work aims thus at demonstrating the potential of the recovered carbon fibers as secondary raw materials, validating a process able to recycle the composite's carbon-fibers fraction and close their Life Cycle in a Cradle-to-Cradle approach. While it is well known that pyrolysis is an established method to recover discarded composites parts or production wastes, the literature reporting real plants data are still a few since most of the reported works are performed on a muffle furnace [22]. Hence this work might help to promote the bridging of the

gap between academic basic research and the competitive industrial production which is presently the weakest link in an innovative process development. The possibility of proving the value of the recycled carbon fibers for further use would, indeed, validate the overall recycling process. Hence, in this study the solid residue (carbon fibers covered by a carbonaceous layer) obtained upon pyrolysis in Curti's pyrolysis pilot plant was characterized and subjected to a further oxidation step in different working conditions to provide clean fibers. For the sake of comparison, the same process was applied to the corresponding virgin fibers, in order to assess the impact of the oxidation step onto their properties, without the bias of the pyrolysis treatment, with the aim of helping to identify the most convenient oxidation conditions. The effects of the process on the recovered fibers, as well as on virgin fibers, were evaluated by SEM and Raman. Finally, the reinforcement behaviour of virgin and recovered fibers, with or without the oxidation treatment, was tested in the production of Chopped-CFRPs.

2. Experimental

2.1 Materials

Virgin chopped fibers (20 mm) were obtained cutting down Unidirectional Fabric UC 301 based on Toray T700S 12K dry fabrics. These fibers will be labelled as "VF". The solid residue derived from pyrolysis of CFRPs was supplied by Curti S.p.A. The epoxy composite cured samples based on the same Toray T700S 12K dry fabrics were supplied by Ri-Ba Composites srl and include cured scraps coming from different stages of the manufacturing process. The two components epoxy resin used for chopped fiber composites production is the ElanTech EC157/W61 Polymer/Hardener system obtained from Elantas.

2.2 Pyrolysis experiments

The CFRCs pyrolysis experiments were carried out in a batch pilot plant provided by Curti S.p.A. at their site which is 2.0m wide in diameter and able to treat up to 70 kilograms of Composites materials per pyrolysis cycle. The feedstock dimension has to fit within the pyrolysis chamber, and thus the maximum allowed size is slightly less than 2m in length for rigid

materials. The pilot plant is equipped with a hydraulic guard to prevent air infiltration during the process and provide intrinsic safety to the overall process. The pyrolysis batches were performed isothermally at 500°C [16]. In a typical run, CFRCs scraps are placed into the reactor. After closing the lid, the reaction chamber is flushed with nitrogen in order to remove air, then the system is heated at 8 °C/min rate up to the set point, and then maintained at 500°C for 150 mins overall residence time. The solid residue recovered at the end of the process, is composed of a fibrous material covered in carbonaceous layer and such fibers will be further identified as “Pys”.

2.3 Post-Pyrolysis oxidation treatments

The oxidation treatment was carried out both on the solid residue derived from the pyrolysis at 500°C of CFRPs cured scraps (Pys) and on the virgin fibers (VF). After a preliminary TGA assessment, a small sample (tenths of mg) of the virgin and pyrolyzed carbon fiber fabric was isothermally treated at 500°C or 600°C for 10, 20, 30, 40, 50 and 60 mins in air. Then, according to the obtained results, two specific treatment conditions were selected, namely 500°C for 20 and 60 minutes and at 600°C for 20 minutes, and a higher amount of downsized (2cm) and disentangled fibers, sufficient for further characterization and composite production, was treated accordingly. Since the proposed treatments are intended for a lab scale production (max 20g CFs per composite panel), fibers' downsizing and disentanglement were carried out manually. All the oxidized samples, upon cooling to Room Temperature (RT), were weighed and characterized by Scanning Electron Microscopy (SEM) and Raman spectroscopy. The obtained carbon fibers and their labelling samples are reported in Table 1.

2.4 Chopped Carbon Fiber Reinforced Polymers (Re-CCFRPs) Production

Carbon Fibers of the average 2cm length (20g), either pristine (out of the pyrolysis reactor, Comp-VF) and only pyrolyzed (Comp-Py) or after muffle treatments in different thermal condition (Comp-VF and Comp-Py 500 or 600, oxidized at 500 or 600°C, respectively) and time (eg. Comp-VF and Comp-Py 500.20 or 500.60, oxidized at 500°C for 20 or 60 min, respectively), were mixed with a pre-mixed two-components epoxy resin mixture in a

fiber/matrix=60/40 weight ratio for the production of Re-CCFRPs. The resin formulation was prepared according to the supplier Technical Data Sheet (hardener: prepolymer = 17:100 weight ratio) prior to the manual mixing with the 2cm CFs. The mixture was stirred until complete uptake of the resin by the CFs, then the resin/Re-CF mixture (33.3g) was poured into a 100 x 100 x 5 mm mould and hot-press cured at 50bar pressure according to the following procedure: the mould was inserted in the press with the plates already heated at 70°C, where it was kept in isotherm for 30 minutes, then the temperature was raised at 110°C at which temperature the sample was kept isothermally for further 45 minutes. After cooling down to RT, each composite panel was cut into 100x15 mm strips in order to perform thermal and mechanical characterization. The prepared composite materials are reported in Table 2.

2.5 Methods

Thermogravimetric analysis (TGA) was carried out using a TA Instruments SDT-Q600 apparatus. Preliminary oxidative treatment experiments were carried out on approximately 15-30 mg of material in oxidizing atmosphere (air: flow rate 100ml/min) from RT to either 500°C or 600°C where samples were kept isothermally for 60 minutes. TGA runs intended for fiber fraction determination were carried out in triplicate for each sample, on approximately 20-30mg of composite, heating them from RT to 500°C at 20°C/min heating rate in inert atmosphere (nitrogen: flow rate 100ml/min) leaving it in isotherm for 15 minutes, then cooling the sample down to 300°C before switching to oxidizing atmosphere (air: flow rate 100ml/min) before heating again at 20°C/min heating rate up to 500°C, where the sample is once again kept isothermally for 15 minutes. Here the sample undergoes complete oxidation of the char layer, before starting a continuous constant degradation of the fiber itself. This point is easily recognizable in the first derivative of the sample weight loss curve, being the point where the curve goes back to a flat trend, and it is thus taken as the composite fiber content. In order to investigate the morphological aspect of the fibers and the fracture surface of the composites, micrographs were taken with a Scanning Electron Microscope (SEM) ZEISS EVO 50 EP in

Environmental mode with ≈ 100 Pa pressure in the chamber, equipped with INCAEnergy 350

EDX microanalysis system. The distribution of fiber diameters was determined with the help of an image analysis software, measuring about 100 fibers in two different images (50 fibers per image) per fiber type. Raman spectra on fibers were recorded with an Ar⁺ laser light source (514.5 nm). The Raman spectrometer is a Leica DMLM Renishaw 1000 RAMAN Micro-Spectrometer equipped with microscope (objectives 5x, 20x, and 50x), a rejection filter (notch or edge), a monochromator (1200 lines/mm) and a charge-coupled device thermoelectrically cooled (203 K) detector. Apparent Density (AD) was determined for each coupon produced for mechanical tests (roughly 100x10x2.5mm) as the ratio between measured weight and volume. The Average Apparent Density (AAD) has been determined averaging all the calculated AD for each composite batch. Dynamic mechanical analysis (DMA) was performed with a NETZSCH 242 E Artemis analyzer in three-point bending configuration with a 40mm span, with 1 Hz oscillation frequency and 20mm oscillation amplitude, heating from RT up to 150°C a 3°C/min heating rate; samples for DMA are about 50x10x2.5mm (the exact dimensions were measured for each coupon). Tensile tests were carried out at room temperature with an Instron-type tensile testing machine (REMET TC10) equipped with a 10kN load cell, using a crosshead speed of 5 mm/min and initial gauge length of 50 mm. Five specimen were tested for each formulation, chosen among those with the AD values closest to the AAD and the results were averaged.

3. Results and discussion

Since the pyrolysis process is intended to be applied for recycling purposes, no regular shape and thickness of the feed is expected, hence the solid residue output of the process might be variable in size and shape. Depending on the size of the feed objects, it was observed that when thickness exceeds few prepreg layers, i.e. in the case of thick composites [23;24], the outer layers display an almost complete lack of residues and low resistance to separation. The inner layers, instead, are characterized by the presence of some resin residue that prevents the fiber layers from an easy separation and makes the woven carbon fiber mats stiffer and harder to separate [16]. In all

cases, however, a thin layer of pyrolytic carbon was observed to coat CFs recovered after pyrolysis. In order to selectively remove the amorphous pyrolytic carbon, as well as some residual resin, without damaging the fibers, it is possible to perform an oxidative treatment (which, in this context, is well known also as gasification [22]) that, in order to facilitate the scale up of the whole process, should be preferentially carried out at a temperature compatible with the condition applied for the pyrolytic batch, i.e. 500 and 600°C [16]. However, it was reported in the literature [6], that the oxidation conditions might play a crucial role on the resulting fibers properties. Hence, with the aim of assessing the intrinsic effects that such treatment might have on carbon fibers, besides what might have happened during pyrolysis, virgin dry fibers (VFs) were subjected to the same oxidative conditions applied to remove char from the pyrolytically recovered ones (Pys).

3.1 Preliminary investigation for the determination of the oxidation treatment condition

First, both virgin and pyrolytically treated fibers were analysed by TGA in oxidizing atmosphere applying a fast heating segment to the target temperature, then 60 minutes' isotherm at 500°C and 600°C respectively, in order to provide a preliminary assessment of the treatment impact on the samples' weight loss as depicted in Figure 1. Both VFs thermograms, Figure 1a and 1b, show a double weight loss event regardless of the temperature at which the isotherm has been carried out, namely 500 or 600°C. The first event, which begins around 310°C (T_{onset}), takes place during the heating of the sample while the second one occurs during the isotherm step, i.e. above 500°C. The first weight loss is comparable for the two samples (1.2% in the two runs).

Moreover, while in both cases the first degradation event is characterized by a common weight loss rate around 0.5 %wt/min, the second one, located during the isotherm, is strongly affected by the temperature set point. At 500°C (Figure 1a) the weight loss rate is about fifty times slower than the first event (0.01%wt/min) and stays constant along the whole isotherm step. Treating the sample at 600°C (Figure 1b) generally speeds up the process and the weight loss rate increases; after 20 minutes isotherm, however, the degradation process reaches almost the same rate as the

first weight loss (0.4%wt/min). Preliminary thermogravimetric analyses were analogously performed on pyrolyzed solid residues (Figure 1c and 1d). In this case, both thermograms show a single weight loss event starting around 400°C, thus lacking the 1.2% low temperature loss. The absence of the latter feature in the pyrolyzed fibers suggests that such event might be due to the thermal decomposition of the fiber sizing, that is expected to be present only in the virgin fibers: according to the literature [25], for the same kind of dry fibers this surface treatment is reported to represent about 1.1-1.3% of the fibers weight, and it is indeed expected to degrade at lower temperatures than the fibers themselves. Pyrolyzed fibers, hence, display just a steady degradation whose rate depends once again on the applied isotherm temperature. In the case of the pyrolyzed fibers the rate is higher: in particular, the loss rate in the isotherm at 500°C gets steady after 20' isotherm and is 5 times higher than the one registered for the virgin fibers (0.05%wt/min for Pys vs 0.01%wt/min for VFs), while for the 600°C isotherm the rate doubles (0.8%wt/min for Pys vs 0.4%wt/min for VFs). The observed trends account for the fact that during the isotherm at 600°C the fibers themselves are degrading, while the increase in the overall weight loss rate for the pyrolyzed specimens can be associated with the burning off of the char residue covering the fibers' surface. With the aim of assessing the possibility to scale up the process, after downsizing and disentangling the fabric, fibers (both VFs and Pys) were thus oxidized, in aliquots ranging around the tens of grams, at 500°C and 600°C for 10, 20, 30, 40, 50, and 60 minutes. In Figure 2 small samples of Py fibers after oxidation at 500°C and 600°C are reported, together with VFs and Pys for the sake of comparison. In this case fabrics were purposefully non-disentangled prior to the treatment, with the aim of highlighting the difference in their aspect as a function of the oxidation conditions. As a matter of fact, it can be noticed that the aspect of the fibers changes when treated at 600°C for more than 30 minutes, with the fabric that shrinks, loses its glossy look and each tow that starts coming easily apart. This observation well compares with the TGA trend observed in Figure 1, where smaller sized pyrolyzed fibers begin to display a severe weight loss after about 30 minutes at 600°C.

The weight losses registered for each of the above discussed treatment are displayed in Figure 3, showing that the trend is quite similar to the TGA curves, and thus validating the simulated oxidation profiles reported in Figure 1. In particular, Py fibers show that, when treated at 500°C, they first degrade faster, then reach a stable weight loss trend after 20 minutes, both in TGA and in muffle oven; at 600°C too, after 20 minutes the degradation reaches a stable trend. Hence the up-scaling of the oxidative process to hundreds of grams of disentangled shortened fibers (required for further production of the composite panels) is carried out for both virgin and pyrolyzed fibers only for selected conditions, chosen according to such observations, i.e. at 500°C for 20 (samples labelled VF_500.20 and Py_500.20) and 60 minutes (VF_500.60 and Py_500.60) and at 600°C for 20 minutes (VF_600.20 and Py_600.20). Data obtained for these batches are reported in Table 1 and a deeper investigation of such fibers is detailed hereafter.

3.2 Characterization of oxidized fibers

Data reported in Table 1 demonstrates that the up-scaling of the oxidative treatment well compares with the previously reported weight loss data. The average diameter of untreated VFs, as measured from SEM pictures, agrees with literature data for T700 standard fibers [26], and it is slightly affected by the mildest treatment (-2.8% for VF_500.20). This observation supports the previous finding that the preliminary weight loss in VFs, already beginning around 300°C, could be correlated to the loss of the sizing. Both the harsher treatments (500°C for 60 minutes and 600°C for 20 minutes) produce a comparable decrease, around 10% of the original value, in the average diameter which is higher than VF_500.20, while the weight loss for VS_600.20 is almost twice than VF_500.60. The Py fibers, as obtained from the pyrolytic treatment, show an average diameter of about 7.67 μm which is about 10% greater than the starting pristine VF, as expected for a fiber covered in a layer of char deriving from resin pyrolysis. The fibers are strongly affected already by the oxidation carried out at 500°C for 20 minutes, which is able to reduce the diameter to the original T700 fiber value (VF) prior any oxidative treatment, i.e. fibers still coated in sizing. Increasing the residence time up to 60 minutes leads to a 3.5%

decrease in the average diameter with respect to pristine virgin fibers, similarly to the diameter reduction obtained with the oxidizing process carried out at 600°C for 20 minutes. Both processes reached a diameter value comparable to VF 500-20. The performances registered for VF and Py fibers in the different oxidation conditions highlight the fact that virgin fibers appear more prone to degrade in oxidizing atmosphere than pyrolyzed ones (about -10% in diameter for VFs vs. -3.5% for Pys): this behaviour might find an explanation in the protective action that the char layer might impart onto the fibers' surface. The overall VFs diameter decrease can be only partly justified with the loss of sizing (just 1.2% weight loss from TGA results can be attributed to the loss of the surface sizing), which would however apply just to the milder 500.20 oxidation condition. The same treatment when applied to Pys, whose outer layer is made of char, appears to be not even sufficient for char removal. Stronger oxidation conditions (500.60 or 600.20), when applied to Py fibers, lead indeed to a further decrease in diameter reaching the same value as VF 500-20, which is taken as the size of the carbon fibers, once the sizing has been removed, thus accounting for the complete burning out of the char layer. When the same harsher treatments are applied onto VFs, their degradation is definitely higher, with an average diameter 10% smaller than pristine fibers, confirming the tendency of virgin fibers to undergo a higher degradation. It is well known in the literature [27] that thermo-oxidative degradation of carbon fibers is a complex process where two important factors play an important role: while the tendency of C atoms to reach their oxidized state (CO or CO₂) is the thermodynamic driving force of the chemical process, factors hampering the oxygen diffusion towards the graphitic carbon can act as a limiting factor for the degradation process. While it was already demonstrated that fibers protected by a resin layer, when treated in air, degrade less promptly than naked ones [7], in this context, the amorphous carbon deposit might represent the sacrificial layer subtracting the oxygen from reaching the fibers' graphitic surface. Moreover, though the diameter decrease is similar, the weight loss associated with the 600.20 treatment is definitely higher both for VFs and for Pys, possibly owing to the oxidation of the carbon fibers starting

from the unprotected fibers ends, in conditions where the graphitic C oxidation is favoured (graphitic C is reported to be stable below 600°C) [27]. It is indeed worth to note the fibers are downsized prior to the thermal treatment, thus emphasizing this issue.

The hypothesis of char removal from the pyrolyzed fibers is verified via SEM imaging (Figure 4): the micrograph reported in Figure 4a clearly shows that the pyrolyzed solid residue, analysed as received from the pyrolysis reactor, is made of fibers with a rough surface and spotted resin residues. These residues link together the fibers and make them stiff. Previous work proved that such rigid fibers are not conveniently wetted by resin precursor when used for a new composites production [16]. Py_500.20 SEM micrograph (Figure 4b) does not display the spotted resin residues anymore, while the rough surface remains, as a symptom of an incomplete coating residue removal; both Py_500.60 and Py_600.20 instead (Figure 4c and 4d respectively), show a smooth surface, as expected upon char removal. Worth noting is that in none of the applied oxidative conditions pitting or local damaging of the fibers surface is observed, suggesting that the applied conditions from Figure 4c and 4d should be convenient for char removal without affecting the fibers. Even when the most aggressive oxidation treatment is applied (600°C for 20 minutes), the fibers appear intact and no sign of damaged surface or local degradation are visible, as instead observed by Pimenta [28]. The EDX analysis carried out on the differently treated fibers shows that, as expected, an increase in the Oxygen atomic fraction at the fibers surface is observed (Table 1), and the extent of such increase depends on the applied oxidation conditions. Worth noting is that while the actual Oxygen content recorded after an analogous oxidation step stays quite similar for both the virgin and pyrolyzed fibers, the overall air treatments seems to affect more significantly the surface of virgin fibers, where the oxygen fraction before treatment is significantly lower than in the pyrolyzed ones (2.6% for VF vs 4.6% for Py, as reported in Table 1).

Further confirmation of the previously discussed effects of the oxidative treatments is sought via Raman spectroscopy: this technique, when coupled with a microscope to guide the probe, allows

to precisely record spectra in the areas of interest. Raman spectra of both virgin and pyrolyzed fibers, pristine and after different oxidation treatments, are thus reported in Figure 5. The Raman spectra of the virgin and pyrolyzed fibers, without any additional treatment (Figure 5A and 5B, curves (a)), focused in the 1100-1800 cm^{-1} spectral range where the most interesting events can be observed (Figure 5), display two significant peaks at 1560 and 1360 cm^{-1} respectively. These signals are well known in the literature [29] for carbonaceous materials and they belong to absorptions typical of both graphitic and amorphous carbon, the so-called G and D peaks respectively. The G-peak is attributed to the bond stretching of all pairs of sp^2 carbon atoms in both rings and chains, while the D-peak is due to the defect induced on the sp^2 structure [29]. Though the two absorptions are both present in pristine VF and Py fibers, the intensity of the signals in the pyrolyzed fibers is definitely lower than in the virgin ones. While evaluation of the relative intensities of these two signals can be directly correlated to the fraction of graphitic and amorphous carbon it is, however, quite difficult to provide significant evidence of D/G peak ratio modification when low graphitization fibers (low modulus) are analysed, as in this case. Nevertheless, the sharpness of the signals in VFs can be related to the lack of organic residues and the broadness and poor definition of peaks in Pys is an evidence of resin and char residue deposited on the fibers surface [30]. The oxidative process has almost no influence on the Raman spectra of virgin fibers (Figure 4A, spectra b to d), as expected owing to the lack of surface char. Raman spectrum of pyrolyzed/oxidized solid residues instead (Figure 5B, spectra b to d) changes as a function of the applied treatment. Indeed, Py_500.20 shows a similarly poorly defined spectrum (Figure 5B spectrum b) as the one recorded for the plain untreated Py fibers: this observation is thus a further proof that these oxidation conditions are not adequate to completely remove the char from fibers' surface. D and G peaks become narrower and sharper when the oxidation process is carried out in more aggressively conditions (Figure 5B, spectra c and d), thus accounting for char-free fibers. Since no significant differences in the D and G peak definition can be observed, we can assume that an oxidizing process at 500 for 60 minutes and at

600°C for, at least, 20 minutes, are both sufficient to clear the fibers surface from char and resin after the pyrolysis of CFRPs, and this is in good agreement with the observation of the weight loss during the oxidative process and with SEM micrographs discussion.

3.2 Composites production and characterization

Recycled carbon fibres from high-technology applications cannot presently be reused for the same original applications, not only because of the possible lack in performance outlined in previous studies, but mainly owing to a form factor which cannot be controlled when dealing with a waste stream as a process feeding [6]. Therefore, new appropriate applications have to be developed in order to reuse the fibres and chopped fibers composites might thus be the most convenient approach. Though in general short-fibers reinforced materials cannot perform as good as the long fiber ones, nevertheless they can be used for a wide number of applications such as internal panels for automotive, lightweight sports equipment and, more generally, where lightness is a premium property, while performance not as much. Thus, the possibility of using some recycled fibers, whose mechanical properties can be around 80/90% of the initial values, depending on the applied recycling process [31-33], might be economically promising. This approach might also help widening the fields of use of such chopped carbon fiber composites, since the secondary raw material approach might provide a wider and possibly cheaper source for the reinforcement, without weighing on the pristine fibers market. A preliminary attempt at re-using the fibers after pyrolysis and oxidation carried out on the fiber produced in the Curti pilot plant suggested that the obtained composites could reach good performances [16].

However, such a preliminary work was not carried out in optimized conditions, thus no actual reliable conclusion could be drawn. Hence, in the present work, the previously discussed fibers, both virgin and pyrolyzed, which were chopped down to a suitable length (about 20mm), were mixed with a two-components epoxy resin formulation (feed: CCF/resin=60/40 ratio) in order to produce Short Carbon Fibers Reinforced Composites (SCFRC) based on both the pristine and oxidized virgin fibers (Comp-VF) and the pyrolyzed (Comp-Py) ones. In this case, fibers length

was shortened with respect to previous work (20 vs 25mm) [16] to provide a better mixing with the resin, thus also allowing to increase their content in the final composite from 50 to 60%wt. Moreover, the curing cycle was optimized with respect to the preliminary work, with the addition of a low T isothermal step promoting an efficient resin and fiber mixing to improve the compactness of the obtained panels. While all the previously discussed fibers were used to produce composites, as reported in Table 2, Py fibers without any additional treatment lead to strongly heterogeneous samples, with voids and separation between resin rich regions and dry fibers areas, detectable even by a naked eye. Composites were obtained as flat panels that were then cut in coupons suitable for further characterization. Each of the obtained coupons was measured and weighed in order to obtain an index of the compactness of the sample, defined as Apparent Density (AD): the AD of each coupon has then been averaged in order to provide information about the overall homogeneity of the samples. Comp-Py shows the lowest Average Apparent Density (AAD) out of all the produced panels confirming that no good compaction can be reached when rigid char coated fibers are used, since the amorphous carbon coating layers prevents the fibers bundles from correctly being impregnated by the resin, thus making the composites unsuitable for further characterization, as previously reported [16]. SEM micrographs (Figure 6) of samples purposefully fractured, clearly highlight the difference between Comp-Py with scarcely impregnated fibers, which keeps also a prevailing unidirectional orientation as in the starting bundle, and a poor resin infiltration among them (Figure 6A and 6C), and Comp-Py_500.60 which shows a homogenous mix of fibers and resin (Figure 6B and 6C). The latter is also representative of all the other Comp-X panels. For all the other samples, the overall AAD was significantly improved with respect to the preliminary work [16] upon the application of the modified procedure. It is also worth to point out that none of the fibers has been subjected to a further sizing treatment after the oxidation process: hence, besides the untreated VFs, none of the fibers brings a surface coupling agent helping to promote adhesion toward the polymer matrix in the composite production.

With the aim of assessing the actual carbon fibers fraction in each composite, all the samples were analyzed by TGA. Measurements were carried out first in an inert atmosphere up to 500°C to pyrolyze the resin component; then, after lowering the temperature down to 300°C, the atmosphere was switched to air to remove the carbonaceous residue derived from the incomplete resin degradation (the same phenomenon that occurs during the pyrolysis process) by oxidation at a temperature which is raised again up to 500°C where the sample is kept isothermally for 30'. The cooling step before switching to the oxidizing atmosphere is applied to slow down the oxidation of the char residue, thus avoiding an uncontrolled heat release that might negatively affect the fiber stability. It was, indeed, proved earlier in the present paper that, in those circumstances, the resin can be completely removed, as displayed in Figure 7A for the process applied to the pure epoxy resin, while the fibers are safely maintained (Figure 7B), thus providing a quick and reliable method for the determination of the fiber fraction in the composite, as reported in Table 2. TGA thermograms display indeed a first degradation process attributed to thermal degradation of the resin component [19] that, irrespective of the fiber used, begins around 300°C, and a second stepwise weight loss attributed to the oxidative degradation of the char residue, occurring upon the second heating process in oxidizing atmosphere. As displayed in Figure 7 for Comp-VF 500-60, when the carbon fibers themselves begin to undergo thermal degradation after switching to the oxidizing atmosphere, the 1st derivative of the weight loss curve perfectly highlights the change in the process rate, thus proving the threshold limit taken in order to define the resin content in the samples reported in Table 2. The adopted TGA process displays that the fiber content is well representative of the resin/fiber original feed, with no substantial modification.

Mechanical stress/strain measurements in tensile mode were carried out with the aim of providing comparative properties of the composites obtained with recycled fibers with respect to those obtained from virgin pristine fibers as well with those obtained from oxidized virgin fibers. Owing to the previously discussed lack of good compaction, mechanical tests were not carried

out on Comp-Py specimen. As a guideline, five samples for each formulation were analyzed, selecting those whose specific AD was the highest, in order to avoid voids and imperfections as much as possible. Test results, recorded in Table 2, show that higher mechanical performances were obtained with respect to the preliminary data [16]. Besides an expected increase in the mechanical properties due to the augmented fiber fraction in the composites, the obtained data stem also from the better compaction achieved in the present case (see AAD in Table 2). When comparing the properties of Comp-VF with the ones registered for composites obtained from oxidized virgin fibers, the latter display a significant drop in their ultimate performance at break. On the other hand, the properties of Comp-VF well compare with those observed for the composites produced with all the pyrolyzed/oxidized fibers, both in terms of Young modulus and of ultimate strength and elongation, with a slight decrease for the sample treated up to 600°C, Comp-Py_600.20. Such a result represents a significant improvement with respect to the preliminary data [16], since it demonstrates that the pyro-gasified fibers can reach properties comparable to the analogue virgin ones. It is worth to point out that Comp-VF performance would benefit, among other parameters, of the surface sizing treatment that might help promote fiber matrix adhesion and which was reasonably removed upon oxidation. The latter statement stems from the observation that all the oxidized VF fibers display a decrease in their diameter, thus supporting the hypothesis of outer layers removal, and with them the sizing too. In this case the lack of performance might be due to some decrease in the single fiber properties upon oxidation treatment, and some lack of adhesion, which is not sufficiently replaced by the oxidized groups that forms on the carbon fibers during oxidation. The presence of such oxidized groups which, upon curing of the epoxy matrix, might promote covalent bonds with the resin via the oxygen rich moieties on the fiber surface, thus acting as a multifunctional cross-linker as sketched in Figure 8, could be one of the reasons of their ability to provide a reinforcing action comparable, or even better, than the sizing coated VF. Such a possibility looks attractive also for the use of the pyro-gasified fibers in the presence of different matrices, such as phenolic resins or

polyurethanes, etc. The surface oxygen content measured by EDX (Table 1) indeed, well compares with the Comp-VF fiber series as well as Comp_Py performance, besides the one of Comp-Py_600.20. In the latter case, indeed, the slight decrease of the mechanical performance is associated to the highest surface oxygen fraction. It is worth to note that both Comp-VF_600.20 and Comp-Py_600.20, the composites obtained out of the fibers treated at the highest temperature, do not display the best results in terms of mechanical behavior, suggesting that such a high temperature, besides being able to completely remove char residues, could be detrimental for the fiber properties as previously reported by Meredith [31]. Moreover, it should also be kept in mind that the pyrolytic fibers studied in this work are obtained working at 500°C, hence the possibility of oxidizing the fibers at the same temperature used for pyrolysis can foresee the application of an *in line* thermal treatment carried out directly on the hot solid residue at the end of the pyrolysis process. Finally, the obtained positive result was proof of the reliability of the obtained recovered carbon fibers when used as secondary raw material, thus encouraging a significant investment by Curti S.p.A. to promote the scale up of the overall process to provide an integrated pyro-gasification semi-industrial plant, that is presently being finalized.

4. Conclusions

In the present work, the application of an oxidative treatment was assessed both on virgin and on pyrolyzed carbon fibers, showing that no additional damage comes to the fibers that were already subjected to high temperature treatment in the pyrolysis batch. On the contrary, the char layer, whose removal requires the oxidation treatment, acts as a protective coating hampering an excessive damage of the fibers. Moreover, when such oxidized fibers are used to produce short fiber reinforced composites upon reduction of their length to 2 cm, their final performances are comparable to those of a pristine fibers composite, where fibers still bear a sizing treatment. This behavior can be ascribed to the formation of oxidized groups on the fiber surface which can promote chemical adhesion between the graphitic layer and the crosslinking matrix. Hence, while for the pyrolytic fibers to be positively re-used an additional oxidation treatment is

necessary, here it was demonstrated that such a treatment can be carried out in the same condition as the pyrolysis process and is able to boost the fiber/matrix adhesion, given that oxidation conditions are finely controlled and tuned for application. These results provided sufficient validation of the recycled CF quality, which lead to the scale up of the process to produce an integrated pyro-gasification semi—industrial plant.

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Captions to Figures

Figure 1. Thermogravimetric analysis (TGA) in oxidizing atmosphere of VFs, a) and b), and Pys, c) and d). Set point temperature at 500°C, a) and c), and 600°C, b) and d).

Figure 2. Picture of a sequence of small fabric samples made of VFs and Pys at the top of the picture, and different Py samples, after oxidation at 500°C (left column) and 600°C (right column) as a function of time, as specified in the figure.

Figure 3. Mass loss of Pys and VFs after oxidation at 500°C and 600°C as a function of time.

Figure 4. SEM micrographs of (a) Pyrolyzed solid residue, Py; (b) Py_500.20; (c) Py_500.60; (d) Py_600.20. Scale bar: 10µm.

Figure 5. Raman Spectra of (A) VFs and (B) Pys after different oxidation treatments: (a) no treatment; (b) 500°C for 20 minutes; (c) 500°C for 60 minutes; (d) 600°C for 20 minutes.

Figure 6. SEM micrographs at different magnification, 1000x (A and B) and 5000x (C and D), of fracture surfaces of Comp-Py (A and C) and of Comp-Py_500.60 (B and D).

Figure 7. TGA thermograms of pure epoxy resin and of Comp-VF 500-60 showing the approach used to determine the fiber fraction in the composites. First the weight losses of the pure resin are identified, then in the composite the residual weight is taken where no more degradation ascribed to the resin is present: this value is considered as the fiber fraction.

Figure 8. Sketch of the reactivity of oxidized groups on surface of the pyro-oxidized fibers in the presence of epoxy resin promoting fiber/matrix interphase adhesion.

Table 1. Data concerning the oxidative treatments carried out on fiber batches suitable for further composite panel production.

| | T_{ox} | t_{ox} | Weight loss | Average diameter | Variation in diameter ^{a)} | Atom fraction ^{b)} | |
|-----------|----------|----------|-------------|-------------------|-------------------------------------|-----------------------------|---------------|
| | | | | | | C | O |
| | (°C) | (min) | (wt%) | (μm) | (%) | (%) | (%) |
| VF | -- | -- | -- | $7,00 \pm 0,51$ | -- | $97,4 \pm 0,5$ | $2,6 \pm 0,5$ |
| VF_500.20 | 500 | 20 | 4 | $6,80 \pm 0,62$ | -2.8 | $95,0 \pm 0,5$ | $5,0 \pm 0,5$ |
| VF_500.60 | 500 | 60 | 9 | $6,32 \pm 0,69$ | -9.7 | $93,0 \pm 0,6$ | $7,0 \pm 0,6$ |
| VF_600.20 | 600 | 20 | 17 | $6,26 \pm 0,63$ | -10.6 | $93,4 \pm 0,9$ | $6,6 \pm 0,9$ |
| Py | -- | -- | -- | $7,67 \pm 0,52$ | +9.5 | $95,4 \pm 0,6$ | $4,6 \pm 0,6$ |
| Py_500.20 | 500 | 20 | 8 | $6,99 \pm 0,52$ | 0 | $95,1 \pm 0,5$ | $4,9 \pm 0,5$ |
| Py_500.60 | 500 | 60 | 12 | $6,75 \pm 0,45$ | -3.5 | $92,3 \pm 0,3$ | $7,7 \pm 0,3$ |
| Py_600.20 | 600 | 20 | 18 | $6,76 \pm 0,41$ | -3.5 | $92,1 \pm 1,1$ | $7,9 \pm 1,1$ |

a) The diameter variation is referred to the untreated VF.

b) Based on EDX surface analysis.

Table 2. Thermo-mechanical properties of chopped carbon fiber reinforced composites.

| | AAD^a | Fiber fraction^b | T_g^c | E | σ_b | ε_b |
|----------------|------------------------|---------------------------------------|----------------------------------|----------|----------------------|----------------------|
| | (g/cm ³) | (%) | (°C) | (GPa) | (MPa) | (%) |
| Comp-VF | 1.38±0.04 | 62 | 102 | 3.9±0.4 | 140±18 | 7±1 |
| Comp-VF_500.20 | 1.37±0.04 | 61 | 99 | 3.9±0.3 | 102±22 | 5±2 |
| Comp-VF_500.60 | 1.37±0.03 | 65 | 100 | 4.3±0.5 | 106±10 | 4±1 |
| Comp-VF_600.20 | 1.37±0.05 | 60 | 99 | 3.8±1.8 | 97±31 | 3±1 |
| Comp-Py | 0.9±0.21 | / | / | n.d. | n.d. | n.d. |
| Comp-Py_500.20 | 1.32±0.05 | 61 | 103 | 4.1±0.3 | 149±27 | 6±1 |
| Comp-Py_500.60 | 1.34±0.02 | 62 | 99 | 3.7±0.4 | 132±17 | 6±1 |
| Comp-Py_600.20 | 1.33±0.02 | 58 | 100 | 3.2±0.4 | 133±22 | 7±2 |

^a Average Apparent Density (AAD) determined as the average of the ratio between measured weight and volume of the single bars as cut in the convenient dimension for mechanical tests.

^b Calculated by thermogravimetric analysis as described in the experimental section.

^c Determined by DMA analysis.

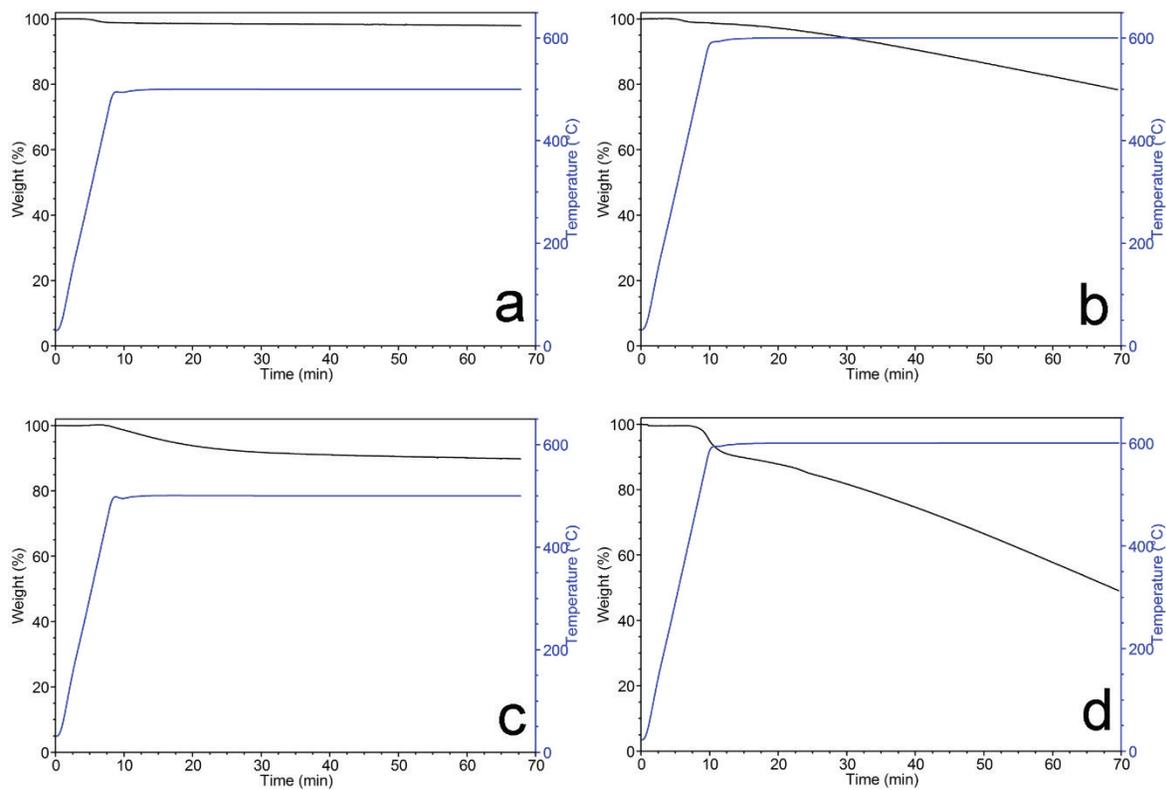


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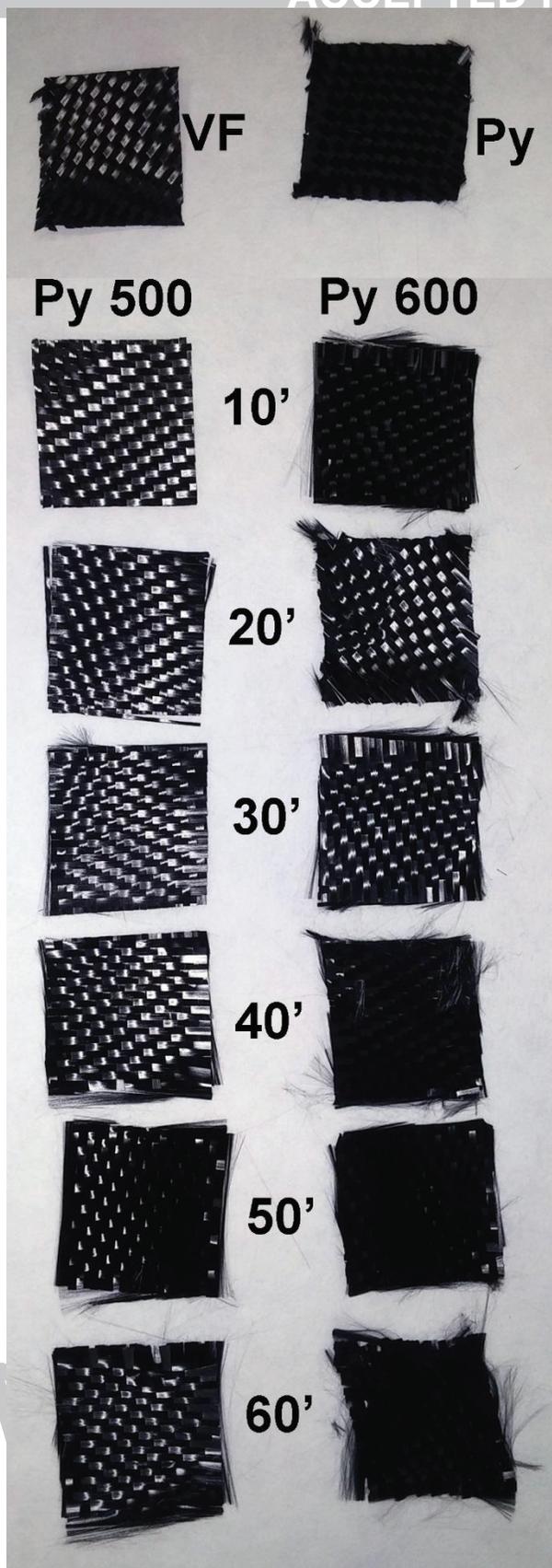


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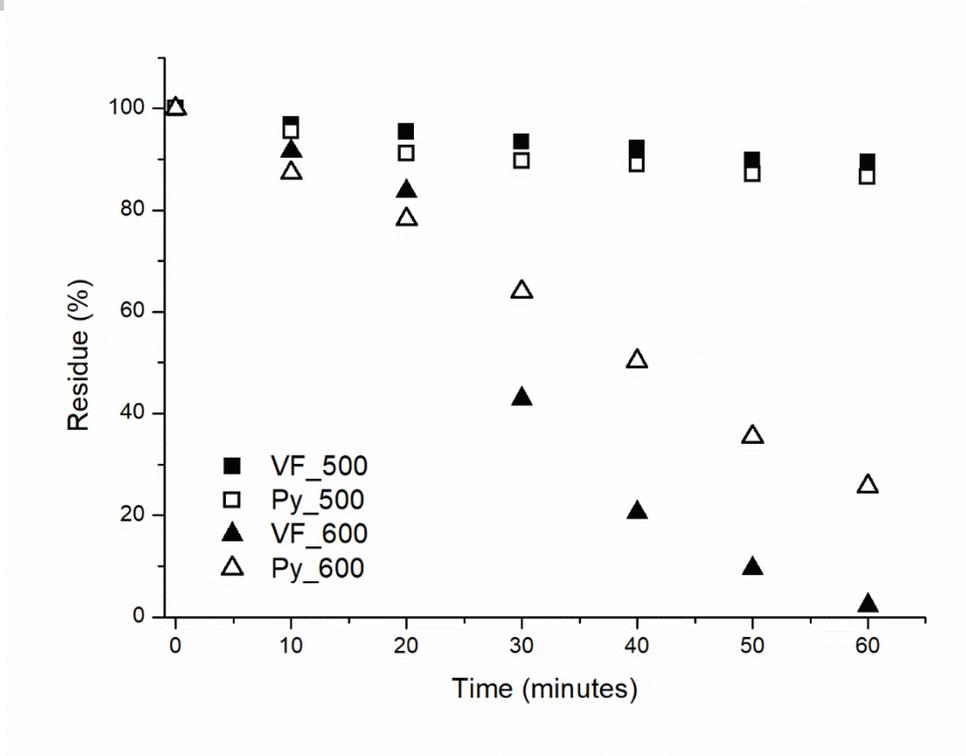


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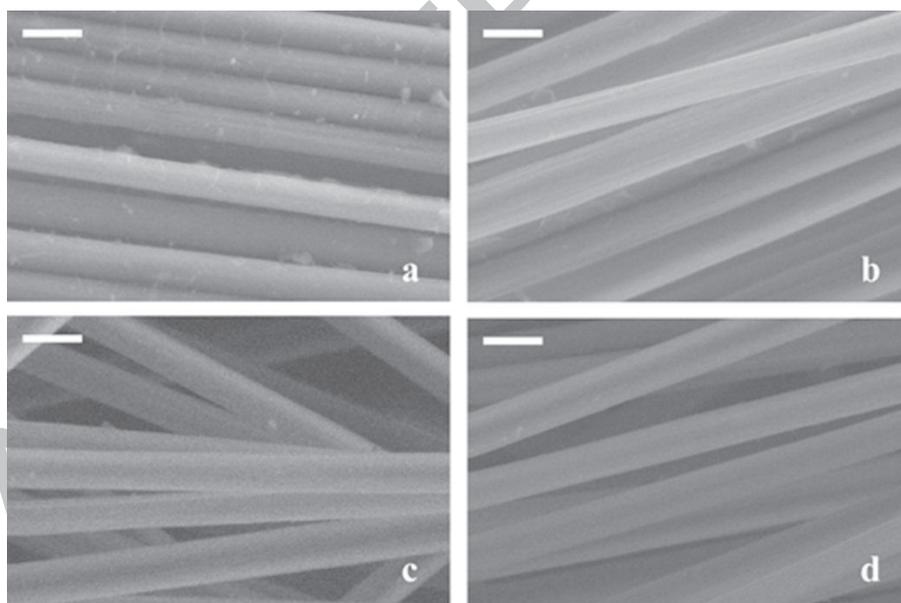


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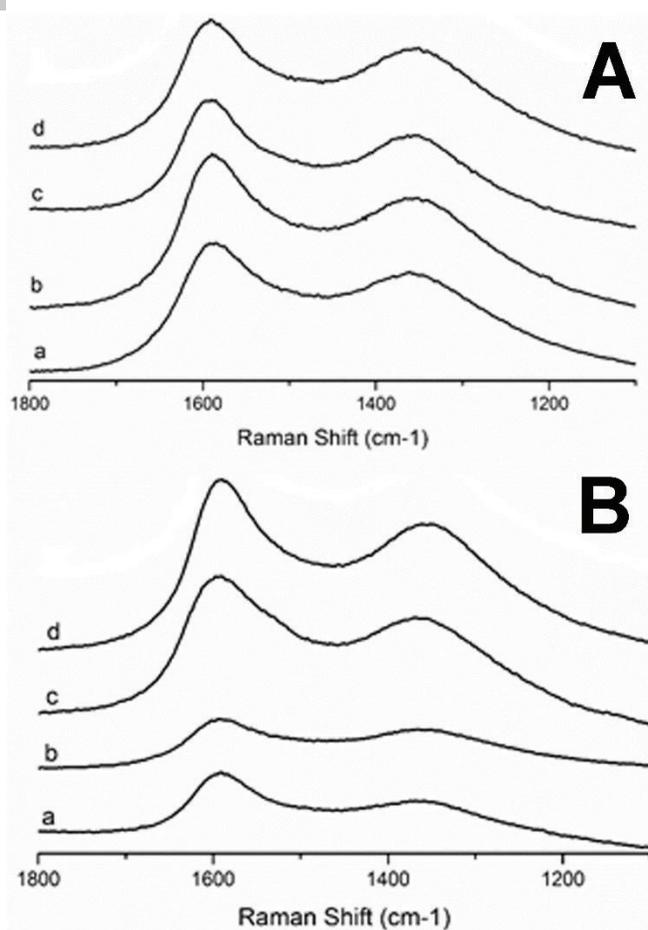


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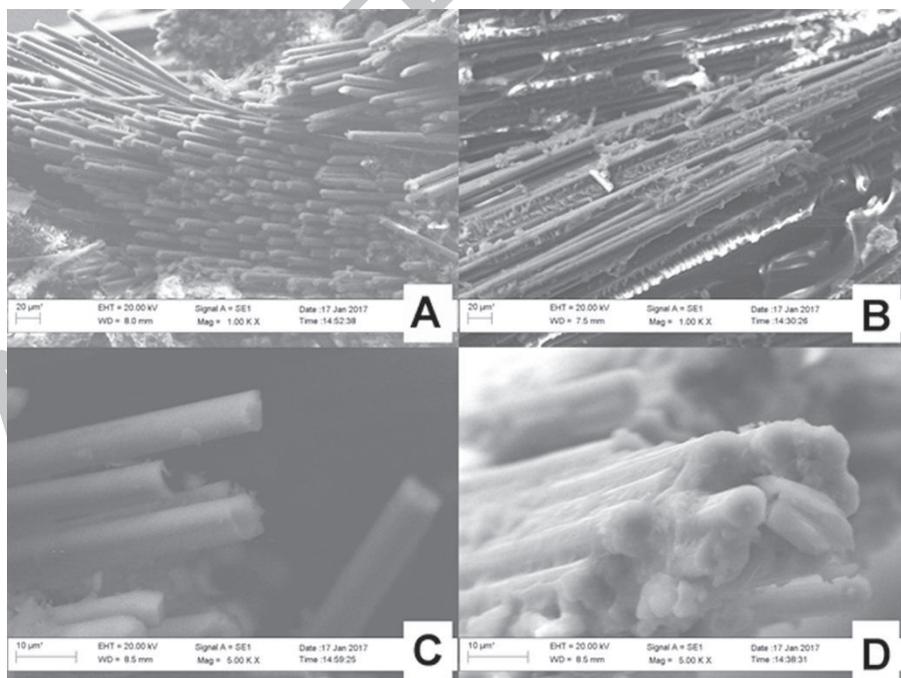


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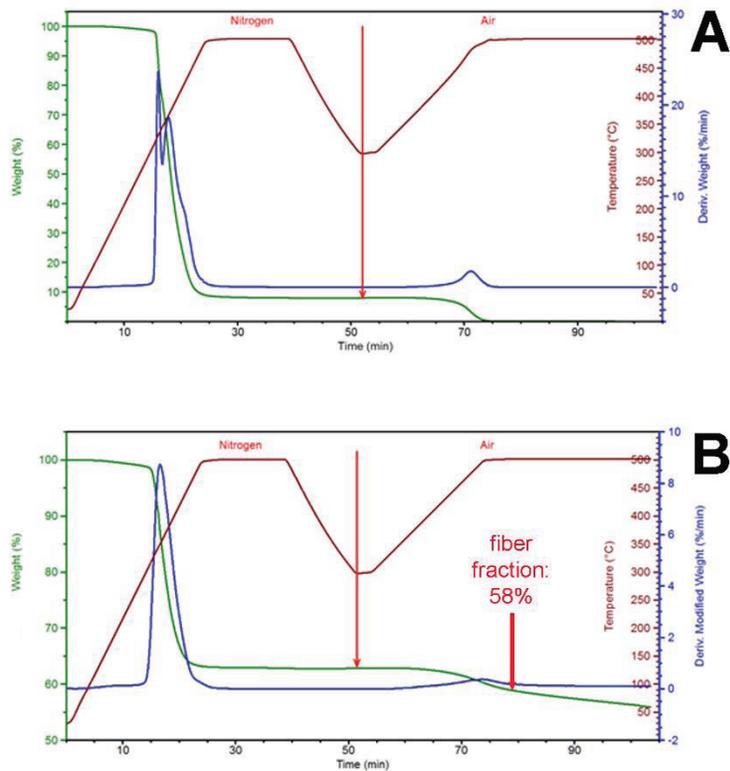


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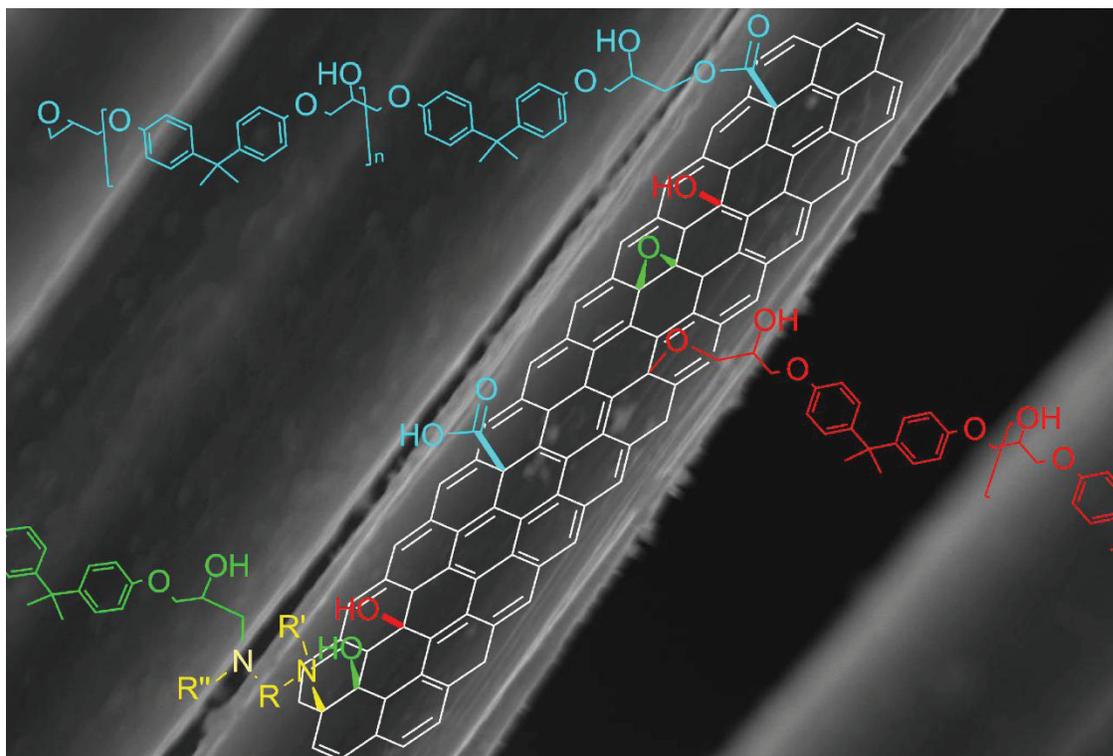


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