

Recovering of Carbon Fiber from PPS and PEKK Composites and their Valorization by Ceramization Process of their Surface

Carmela Borriello^{a*}, Pierpaolo Iovane^a, Sabrina Portofino^a, Gabriella Rametta^b, Loredana Tammaro^a, Sergio Galvagno^{a,c}

^aSSPT Department, PROMAS Division. NANO Laboratory, ENEA

^bTERIN Department, FSD Division. DIN Laboratory, ENEA

^{a,b}Portici Research Centre, Piazzale E. Fermi, 1, 80055 Portici (NA), Italy

^cIMAST S.c.ar.l., Technological District on Eng. of polymeric and composite, Materials and Structures, 80133 Napoli, Italy
 carmela.borriello@enea.it

Carbon fiber composites result very attractive as lightweight materials able to substitute iron-based materials in terms of mechanical properties and performances. Indeed, the Carbon Fiber Reinforced Plastics (CFRP) world demand has arisen from 72 kton in 2013 to 83 kton in 2014, with a growth rate of 15%, so estimating in 2022 a possible demand of 191 kton [Witten and Mathes, 2018].

In the coming years, the introduction of such wide amount of CFRP on the market that will generate waste (30% in weight of CFRP scraps are already present as processing industrial waste) makes necessary to develop technically and economically sustainable recycling processes. Furthermore, the exploitation on the market of recovered fibers represents a fundamental node to ensure the closure of the cycle and the economic sustainability of the process [Pimienta and Pino, 2011]. CF are mainly employed as reinforcement in thermosetting matrix, even if in recent years new composite materials based on thermoplastic technopolymers such as PPS and PEKK are starting to play an important role especially in the aeronautical field [Tadini et al., 2017]. This work reports preliminary results relating to the application of a carbon fiber recovery patented process developed by ENEA [Galvagno et al. 2002; Cornacchia et al. 2009] to this new type of composite materials. Besides the recovered fibers have been employed in ceramization processes with silicon metal. Indeed the presence of ceramic layer (e.g. SiC or Si₃N₄) improves their properties covering surface defects and making fiber more stable to oxidation [Sugimoto et al. 2019], so allowing to expand their application sectors [Guidatti et al. 2019, Turchetti et al., 2011].

1. Introduction

Carbon fiber (CF) market is constantly growing over the last years. Since 2010, the annual growth rate is found to be 11,45% and for 2022 a global CF-demand of about 120,5k tons can be estimated. [Witten and Mathes, 2018]. Almost the entire carbon fiber production is processed into composite materials (Carbon Composites; CC). The majority of composite materials however is equipped with a polymer matrix (127,8 kt, 83% carbon-fiber-reinforced polymer; CFRP). The global CC-Demand for 2018 can be estimated to be 154,7 kt, causing consequently a wide production of waste. For this reason the development of recycling processes is fundamental and, in accordance with the principles of the circular economy and protection of natural resources, these processes would allow the availability of secondary raw materials (e.g. recycled fibers) at a reduced cost compared to virgin ones. In addition this would contribute to the reduction of the energy and environmental impacts due to initial production processes, that often involve high consumption of energy and raw materials. So far different recycling methods based on thermal, mechanical and chemical treatments have been developed over the years [Pimienta and Pino, 2011]. Nevertheless the composites recycling industry is relatively young and is still in the early stages of developing a market for the recycled materials, despite the technology to recycle carbon fiber composites has existed for several years and is capable of yielding a

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product with mechanical properties similar to the virgin material. The quality of recovered carbon fiber (rCF), is sometimes comparable with virgin fiber: carbon fibers recovered by pyrolysis, retains at least 90% of its tensile strength with no change in modulus (ELG Carbon Fibre). Other players using chemical recycling process (Vartega, R&M International, Shocker Composites) claim that their fibers exhibit the same mechanical properties of virgin carbon fiber. Furthermore for many applications there is a need for discontinuous fiber formats, which suggests an opportunity where rCF might offer a more sustainable and economical alternative to virgin material. Actually, the aerospace market generates the most carbon fiber waste, and commercial rCF suppliers often look to this industry as a source for recycle. Based on market opportunity, they have begun to shift their focus from the downcycling of rCF into lower-performance products finding appropriate applications that benefit from the material's properties.

Recently, the industry moves toward increased use of thermoplastic composites, particularly PPS and PEKK-based ones [Tadini et al., 2017]. These materials represent a new set of recycling opportunities because thermoplastics can be remelted and reshaped several times, and the aerospace industry has more opportunity to reabsorb some of its own scrap into secondary applications, potentially reusing both fiber and matrix. The objective is to retain the high mechanical properties of thermoplastic composites and to reduce the overall environmental impact at an affordable cost. Although a reduction in size of the fibers and a progressive degradation of the matrix properties could be detected after melting and reuse cycles even in thermoplastics. For this reason it's advisable to explore alternative recovery way also for these materials.

In this work carbon fiber recovery process, developed by ENEA for thermosetting composites [Galvagno et al. 2002; Cornacchia et al. 2009], was successfully applied to PPS/CF and PEKK/CF composites scraps. Besides rCF were coated with ceramic layer by reaction with Silicon at high temperature in nitrogen and argon atmosphere. Morphology, size and length distribution of the products were analyzed by Scanning Electron Microscopy (SEM). Thermogravimetric analysis (TGA) was performed on CF composites. SEM-EDS and Raman spectroscopy were also used to characterize rCF and ceramic coated rCF.

2. Materials and method

2.1 CF recovery process

PPS/CF (Cetex TC1100, www.toraytac.com) and PEKK/CF (cytek, www.cytek.com) composites scraps materials derived from sheet lamination based additive manufacturing post processing were kindly supplied by Aerosoft. The data sheets indicate a resin content of nearly 34% wt. in both materials.

Recovery tests have been performed on 5 g of sample in a tubular furnace Lenton (LTF 12/100/610 model) using the carbon fiber recovery process developed by ENEA [Galvagno et al. 2002].

2.2 Ceramization process

Recovered fibers were mixed with silicon powder sized <40 µm (Alfa Aesar) for Si₃N₄ or SiC fiber surface functionalization. Tests have been performed by a HT tubular furnace (Nabertherm RHTH 120/300/18), able to operate up to 1800°C in controlled atmosphere. Two different atmosphere were used: reactive nitrogen and inert argon at the flow rate of 1 L/min. Process conditions are summarized in the Table 1.

Table 1: Conditions of rCF ceramization processes

Test	Temperature (°C)	Time (min)	Atmosphere	Reagent
1	1650	90	nitrogen	Silicon
2	1550	90	argon	Silicon

After ceramization, SiC microtubes were obtained by heating the sample obtained by test 2 in a tubular furnace Lenton up to 700°C in flowing air (3 L/min) and keeping them for 1 h at 700°C. Finally the furnace was left to cool down to room temperature.

2.3 Characterization

Thermal analysis was carried out on a simultaneous TGA/DSC Netzsch instrument (Jupiter STA449 F3) in nitrogen or air atmosphere at the heating rate of 10 °C/min from 30 to 900 °C.

SEM analysis was performed by Thermo Fisher Scientific "Phenom Pure" scanning electron microscope with upgrade to Phenom ProX. Energy Dispersive Spectroscopy (EDS) was used for the elemental identification with the Phenom (15kV).

Raman spectra were obtained at room temperature with a microRaman spectrometer (Renishaw inVia, UK, 514 nm excitation wavelength, laser power 30 mW). A Leica DMLM optical microscope connected online with the Raman instrument permits to focus on the sample.

3. Results and discussion

Thermal degradation of PPS/CF and PEKK/CF composites was investigated in nitrogen and air atmosphere to study the thermal behaviour of the composites and to identify the temperature range for the recovery process.

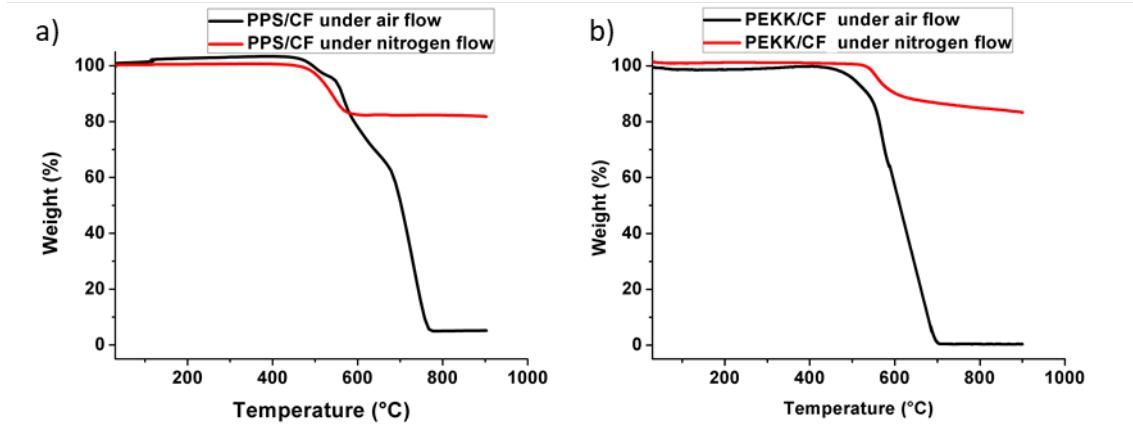


Figure 1. Thermogravimetric analysis of PPS/CF composites (a) and PEKK/CF composites (b) in air and in nitrogen flow.

The TGA curves of PPS/CF composites are reported in Figure 1a. In nitrogen atmosphere PPS is thermally stable up to 450°C; above this temperature the thermogram exhibits only one fast degradation step with a weight loss of about 18% corresponding to the complete loss of sulfur and hydrogen on the benzene rings of PPS structure and the breaking of benzene rings. The high residual content observed (about 82 wt%) is due to the formation of carbonaceous residue, derived by the carbonization of polymeric matrix, and to the CF content in the composite. PPS can be decomposed in nitrogen atmosphere but much solid remains as residue (Perng, 2000).

In air atmosphere, PPS/CF is thermally decomposed at several stages: the initial weight loss of hydrogen and sulphur is followed by the formation of aromatic thiols that later decompose [LI et al., 2002]. The last step (above 680°C) is attributed to the decomposition of CF. At 900°C the combustion is almost complete leaving a residual mass of about 5 %.

Figure 1b reports the PEKK/CF thermograms recorded in nitrogen and air atmosphere. According to literature [Tadini et al., 2017] the PEKK polymer decomposition starts at 520 °C and in nitrogen leaves, also in this case, a high percentage of residue (about 83%) derived from char and CF content. Indeed char content of PEKK is usually about 60% of starting weight It is worth recalling that the investigated composite contain 34 % wt of polymer (technical data sheet), that means that in nitrogen atmosphere it decomposes to about 20 % of char and 66 % wt of CF. The two contributions give rise to the high residue (86 %), value in good accordance with that obtained from the TGA curve.

The temperature range to be applied for the carbon fiber recovery process developed by ENEA was also identified. The optimized process conditions allows to obtain 65-69 % wt of rCF respect the starting composites. This result is perfectly in accordance with CF percentage reported in data sheet and observed in the TGA analysis.

SEM characterization confirms the fibers structure. In Figure 2 SEM micrographs of rCF recovered from PPS/CF (a) and PEKK/CF (b) composites are showed. After the recovering process, the carbon polymeric matrix is absent, the fibers present regular and uniform shape, smooth surface, a constant diameter (about 7 μm) as well as a wide length distribution comparable to that of the starting material (from 5 to 400 μm). However, commonly recycle techniques cannot completely avoid the introduction of defects that could decrease the chemical stability of CFs and their mechanical properties. Besides scrap fibers coming from finishing process often undergo a length reduction that further get worse their properties. One of the possible solutions is the coating of the CF surfaces with ceramic materials such as silicon nitride or silicon carbide [Sugimoto et al. 2019].

For this reason in this work two different operative conditions of rCF ceramization were applied and are listed in the table 1. In both cases an excess of silicon was used respect to rCF and in order to compare the reaction products, the processes were conducted in two different atmospheres: reactive nitrogen and inert argon.

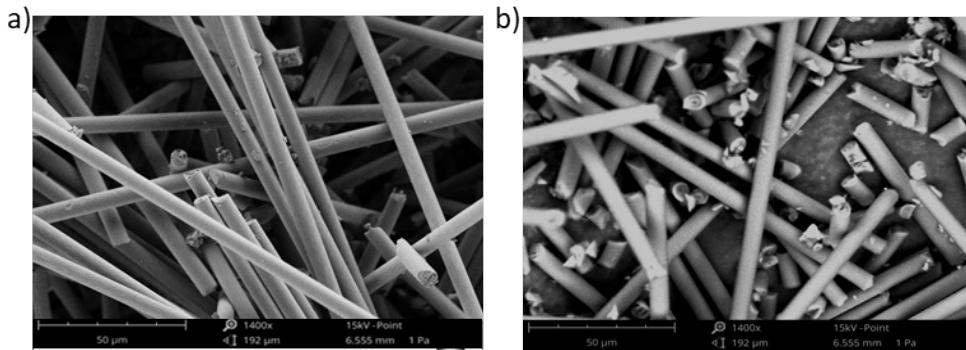


Figure 2. SEM images of rCF from PPS/CF (a) and PEKK/CF (b).

Figure 3a shows SEM images of rCF after ceramization process in nitrogen atmosphere. It's evident the presence of an homogeneous ceramic coating on the rCF surface. Reaction by-products are also present due to the silicon excess used in the process. In future it could be interesting to study the optimization Si/rCF ratio and/or to find a valid products purification process.

SEM-EDS analysis (Figure 3b) on the surface of coated rCF reveals the presence of Si, N and C elements leaving to suppose the presence of silicon nitride and silicon carbide on rCF surface after test 1.

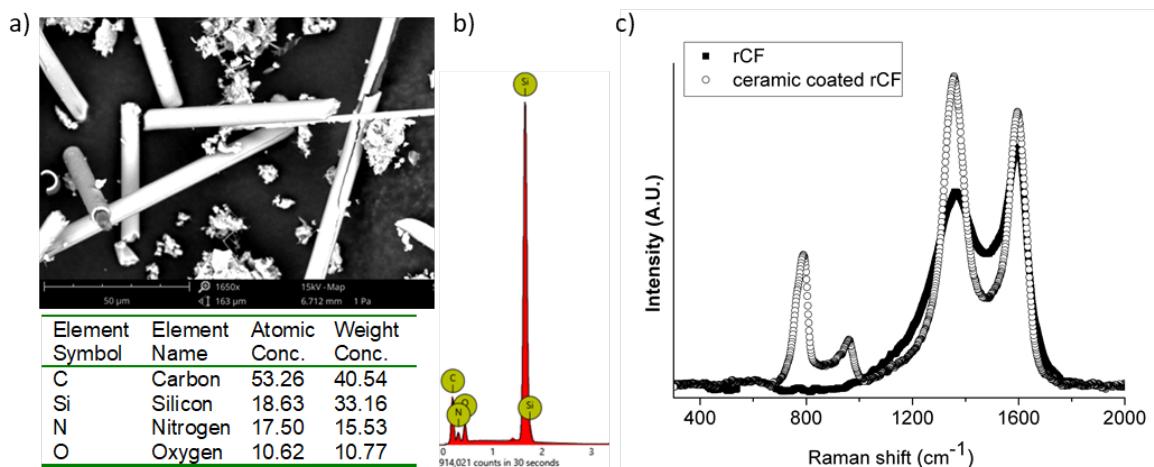


Figure 3. SEM image of ceramic coated rCF (a), EDS analysis (b) and Raman spectra (c) after test 1

Raman spectra recorded on as-produced and ceramic coated rCF are compared in figure 3c. In rCF spectrum two Raman peaks are detected at ~ 1360 cm⁻¹ and ~ 1600 cm⁻¹, typical of graphite corresponding to the D and the G peak, respectively. The G-band indicates a high degree of symmetry and an ordered structure; the bands from 1250 to 1450 cm⁻¹ correspond to a disorder-induced phonon mode with a high intensity for disordered carbon materials [Borriello et al., 2018]

Coated rCF spectrum shows the bands of the starting rCF, although shape and intensity of these bands are affected by high temperature synthesis process. Also the presence of the transverse optical (TO) at ~795 cm⁻¹ and longitudinal optical (LO) at ~ 960 cm⁻¹ bands are detected and confirm the presence of 3C-SiC (β -SiC) [Bechelany et al., 2007].

No evidence of silicon nitride Raman signals [Jiang et al., 2000] is clearly visible, only shoulders of TO and LO bands could be due to the nitride contribution but also to other SiC polytypes [Zielinski, 2012]. However the presence of nitrogen in SEM-EDS analysis doesn't completely exclude that nitride could be present in small quantity or as dopant of SiC and the Raman signal are too small to be detected in the analysed zone. SiC formation respect to Si_3N_4 is probably favoured because of the process temperature [Liu et al., 2020].

To verify the resistance to oxidation of ceramic coated rCF (derived from test 1), thermogravimetric analysis was performed heating the fibers up to 900°C in air flow and compared to uncoated rCF (Figure 4). The results show that coating can effectively improve the anti-oxidation ability of rCF in the air environment. Uncoated rCF are stable up to around 500 °C. The TG curve of uncoated rCF started to decrease rapidly and

decomposed completely around 750 °C. The coated rCF are stable up to 800 °C and than started to lose weight from 800 to 930°C due to the burnout of the carbon residue. Around 1000 °C, the residual weight of coated rCF is more than 92%.

The mass loss of coated rCF was very small, which means the oxidation rate of coated CF is slower than uncoated rCF. When compared with the temperature of other silicon based coatings that were fabricated with the traditional sol-gel method, the decomposition temperature of SiC coated CF seems to be improved. [Yang G. et al., 2018].

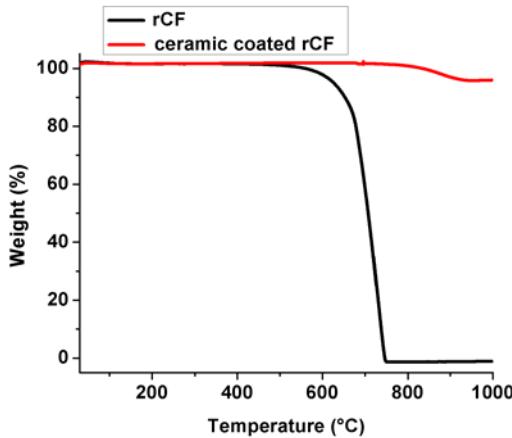


Figure 4. Thermogravimetric analysis of neat rCF and ceramic coated rCF.

After test 2 rCF were coated with silicon carbide only (characterization is not reported) and organic carbon was burnt at 700°C for an hour under air flow so removing rCF core of ceramic microtubes. SEM micrographs and SEM EDS analysis confirm the formation of SiC microtubes (Figure 5). In this way rCF acts as a template for the formation of ceramic microtubes of about 7 μm.

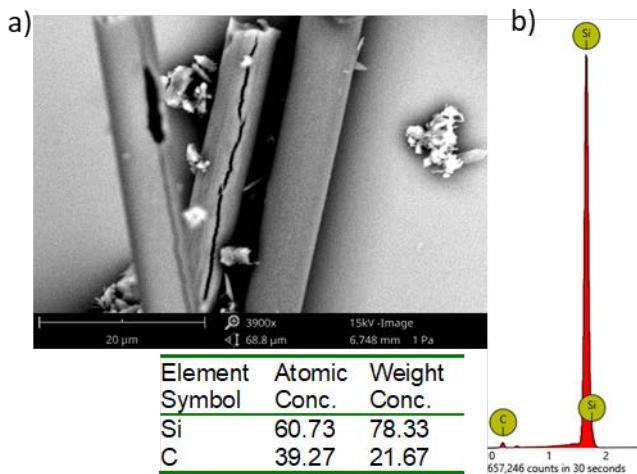


Figure 5. SEM image of ceramic microtubes (a) and SEM- EDS analysis on their surface (b).

At the temperature here used (below 1000°C) carbon fibers usually maintain their shape and no pores due to formation and accumulation of gases are observed on the coating. Planar cracks are present and could be ascribed to the thermal shock during the cooling process (Yang, Materials 2018).

4. Conclusions

Recovered carbon fibers (rCF) have been successfully obtained starting from PPS/CF and PEKK/CF composite scraps materials derived from sheet lamination based additive manufacturing processes. Due to the finishing treatment carbon fibers are a mixture of a wide range length (from 5 to 400 μm).

Experiments demonstrated the effectiveness of the thermal-based patented method developed for thermosetting polymers for the investigated materials. RCF show clean surface and diameters and length comparable to the starting fibers.

The recovered fibers were used as template for high temperature ceramic synthesis. In particular, ceramic coated carbon fibers were prepared from silicon in flowing nitrogen and argon atmospheres and ceramic microtubes were synthetized by memory shape method. Under selected process conditions silicon carbide coated carbon fibers and silicon carbide microtubes were obtained as main products.

The results of the present work may suggest a valuable exploitation way to reuse low cost fibers with variable length in specific applications where resistance towards oxidation or aggressive environment are required as well as catalytic applications of materials based on ceramic microtubes.

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