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Pyrolysis of Fiberglass/Polyester Composites: Recovery and Characterization of Obtained Products

Glass fiber-reinforced polyester composite (GFRPs) scraps from manufacturing of polyester laminates were pyrolyzed at 500, 550 and 600°C in an 70 Kg innovative batch pilot plant that processes whole parts. The presence of a hydraulic guard guarantees the safety of the process. The influence of the maximum process temperature on yields and chemical-physical properties of pyrolysis products was investigated: the oil fraction was analysed by GC-MS, Viscometer and XRF, while the gas fraction was monitored online during the entire pyrolysis process by μ-GC. Substantial fractions of methane (20.7 vol%) and hydrogen (11.5 vol%) were produced. The solid residue (glass fibers covered by a thin carbonaceous layer) underwent an oxidative process at 500 and 600°C at different residence times to provide clean glass fibers free of organic residues. The effects of both pyrolysis and oxidative step on the glass fibers, obtained in different process conditions, were evaluated by SEM and Raman spectroscopy.

Keywords: *Pyrolysis, fiberglass, glass fibers, material recovery, waste.*

1. INTRODUCTION

Glass fiber reinforced polymers (GFRPs) are composite materials widely used for construction, automotive, boating and aeronautic applications thanks to their good strength-to-weight ratio and corrosion resistance [1]. Furthermore, their composite nature and the type of cross-linked matrix results in materials that cover a wide range of mechanical, chemical and physical properties.

While their features make the GFRP widely adopted, the thermoset nature of the polymeric component makes them neither fusible nor soluble, thus preventing their direct remelting or remoulding. These materials, in addition to glass fibers and polymeric matrix, usually contain a large amount of inorganic filler, so that they are commonly regarded as difficult to recycle [2]. GFRPs therefore generally end up in landfills or incinerators with a negative environmental impact. Recently several alternatives for GFRP recovering were investigated including mechanical recycling [2, 3, 4] that involves mechanical size reduction of the composite scraps by shredding, crushing or milling. Although this process shows significant environmental advantages in terms of atmospheric and water pollution, the final product unfortunately has a low market value.

Although greener composites alternatives are being investigated [5, 6], the GFRP low cost and good properties are still unmatched.

In this context, pyrolysis can be regarded as an alternative and convenient method for recycling thermoset composites, as it involves thermal degradation of the organic components in complete absence of oxygen. This kind of atmosphere, indeed, prevents combustion, thus reducing the air pollution effects compared to incineration. Pyrolysis was applied, over the years, to different substrates, e.g. to carbonaceous materials, such as coal or wood [7, 8], biomasses [9, 10], municipal solid waste [11], packaging [12, 13] and tires [14, 15] for energy and valuable chemicals recovery. Thanks to its versatility the process was also applied to the pyrolysis of carbon fiber composites (CFRPs) where energy recovery to sustain the process is coupled to the recovery of re-usable carbon fibers [16, 17, 18].

During the pyrolytic process, the composite matrix is thermally degraded and converted into three main outcome streams: an oil and a gaseous fraction, which can be both used either as fuel or as chemical feedstock, and a solid residue made up of the composite reinforcement covered of a thin carbonaceous film and, at times, non-degradable inorganic fillers and additives from the polymer matrix. Pyrolysis looks very promising for composite recovery, since it allows the reuse of all the waste components and may also lead to the recovery of precious metals, as in the case of printed circuit boards [19, 20, 21]. In the case of GFRP [22, 23,

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24] pyrolysis leads to the recovery of the glass fibers as a secondary raw material, to be re-used both in new GRFP [25, 26] or for different applications [27]. In addition, the process does not require special pre-treatments, hence reducing, or even completely preventing, preliminary complex disassembling processes and shredding. This could be a crucial advantage in case of recovery of large parts such as boat hulls or vessel components. Indeed, the current vessel disposal aims at its final demolition, going through a first step of reclamation and securing (manual operation of dismantling, separation of parts of the boat and recovery of recyclable fractions), followed by tearing the hull down and finally burying in landfills all the non-recoverable fractions (including the GFRP components). Currently, only a limited number of countries, such as Germany and the Netherlands, has regulations restricting GFRP disposal in landfills. Moreover, though sinking of vessels erased from the register of boating is illegal worldwide, it is still a widespread practice, with an even higher negative environmental impact than GFRP landfill disposal. Hence, the availability of a secure and possibly self-sustained process for end-of-life GFRP treatment would be very welcome.

In this context, the authors developed a batch pyrolysis system that employs an innovative reaction chamber plunged in a water tank and loaded through a hydraulic guard, to ensure the sealing of the chamber and a highly safe process [14, 28, 29]. The purpose of that investigation was to develop a pyrolytic process, viable for composite materials which are otherwise hardly recoverable such as thick CFRP [30, 31, 32] and that could be both environmentally and financially sustainable. The pilot plant was first optimized for non-shredded tires [14], in order to test the influence of several parameters on the products (temperature, pressure, residence time and quality of tires). More recently, the pyrolysis process was also carried out on carbon fiber reinforced composites in epoxy resin [16, 18]. The work showed that pyrolysis-recovered carbon fibers can be a viable alternative to commercially-available pristine virgin fibers. These studies also revealed some additional added values features when compared to state-of-the-art recovery technologies: steel wires and carbon char (in the case of tyres), and carbon fibers (in the case of CFRPs) produced in the prototype plant as solid residues received positive evaluations by end-users that tested them as secondary raw materials in the production of new items or compounds for sale.

Owing to the high flexibility demonstrated by the previously discussed pyrolysis process, the present study was carried out to evaluate the disposability of non-shredded fiberglass scraps in this novel pyrolysis pilot plant to provide a simple method for recovering large and non-shredded fiberglass composites. The recovery of chemical feedstocks from the polymeric resin and the simultaneous fibers separation appear indeed rewarding features of the present process. In particular GFRP polyester resin laminates, which are extremely versatile and ideal for use in various fields of application (nautical, trains, civil and industrial insulation, furniture and furnishings, special vehicles, insulation for ventilation equipment, structures for amusement parks, swimming pools, containers, structures for packaging and transporting, wind power, etc.), were treated.

The products obtained upon the polyester resin pyrolytic thermo-decomposition were fully characterized and the need for additional post-pyrolysis treatments to allow for re-use of the fibrous glass solid residue, was assessed. The pyrolysis streams were independently analysed: the oil fraction was investigated by Gas Chromatography Mass Spectrometry (GC-MS), Viscometer and X-ray Fluorescence analysis (XRF) while the gaseous fraction was monitored online during the entire duration of the pyrolysis process by a micro-Gas Chromatography (μ-GC). Finally the effect of an oxidative thermal post-treatment at 500 or 600°C on the glass fibers, previously obtained in different working conditions, was studied via Scanning Electron Microscopy (SEM) and Raman spectroscopy. This investigation is promoted within the AdriaHub collaborative action [33] as part of the Adriatic IPA Cross-Border Cooperation Programme.

2. MATERIALS AND METHODS

2.1 Materials

The glass fiber-reinforced composites (GFRPs) studied in this work were cut-out scraps (sheet rolls with thickness 2.5 mm, width about 250 mm and length up to 3 m) coming from the manufacturing process of laminates, supplied by Vetroresina S.p.A. The samples were composed of a polyester matrix reinforced with an isotropic glass fiber mat and covered on one side with a protective low density polyethylene (LDPE) thin film that makes up 4.4 wt% of the overall material weight (Figure 1). All samples were pyrolyzed without any further treatment: no shredding nor crushing were applied.

Figure 1. Typical glass fibers reinforced polyester resin laminate scraps (a) and the LDPE protective film (b)

2.2 Methods

Thermogravimetric analysis (TGA) was carried out using a TA Instruments SDT-Q600 apparatus. Preliminary pyrolysis experiments were carried out on 25-40 mg of material in nitrogen atmosphere (100ml/min gas flow) starting with an heating segment from RT to 500, 550 and 600°C at 8°C/min heating rate, followed by an isothermal step long enough to reach an overall batch processing time of 150 minutes. The temperature of 500°C was then reached for all the measurements, the atmosphere was changed to oxidative (air: 100ml/min gas flow) and samples were kept isothermally for additional 60 minutes.

This peculiar engineering plant involves co-condensation of oil and process water. For this reason, after draining the demister, the two fractions were separated with a centrifuge operating at 4200 rpm for 6 minutes. The oil fraction was characterized by GC-MS analysis using a Thermo FOCUS GC, coupled to a DSQ mass spectrometer as detector and equipped with a Supelco SPB™ fused silica capillary column. The set-up identifies compounds that constitute the lighter oil's fraction. Benzene, toluene, ethylbenzene, p-xylene and styrene were quantified by calibration curves of the individual compounds at known concentrations [34].

The dynamic viscosity was determined at 25°C using a digital Brookfield viscometer – Model DV-II +, spindle "I" with a rotational speed of 50 rpm.

X-Ray Fluorescence spectra were recorded on a PANalytical AxiosMAX Advanced XRF Spectrometer, equipped with an X-ray tube target with rhodium, set to a power of 2.4 kW.

The gaseous phase was analyzed in situ with a Micro-Gas Chromatograph Agilent 490 Micro-GC placed on-line in the pilot plant so no active sampling is required. Two columns were used in this analysis: a Molsieve 5 Å (MS, 20 m) with molecular sieves made of zeolites as stationary phase and argon as carrier gas. The MS column was held at 80°C throughout the experiment. This column separates H_2, O_2, N_2, CO and CH_4. The second column was a PoraPLOT U (PPU, 10 m) with divinilbenzen-ethylene glycol/dimethylacrylate as stationary phase and helium as carrier gas. The PPU column was held at 90°C throughout the experiment. This second column aims at CO_2, C_2H_4, C_2H_6 and hydrocarbons up to C_3, with the possibility of detecting even the C4 fraction. The detector used by the device was a Thermal Conductivity Detector (TCD). Quantification was performed by comparison against a blend of gases of known composition. The quantity of gas released was estimated by the difference between the initial weight of GFRPs and the amount of obtained liquids and solids.

The calorific value of the gas (GCV) was calculated, according to UNI 7839, based on the actual obtained composition.

Infrared spectroscopy was performed in ATR mode using a Bruker Alpha spectrophotometer equipped with diamond crystal and a resolution of 4 cm^{-1}.

In order to investigate the morphological aspect of the glass fibers after pyrolysis and pyrolysis/oxidation treat–ments, micrographs were taken with a Scanning Electron Microscope (SEM) ZEISS EVO 50 EP in Environmental mode with ≈100 Pa pressure in the chamber.

Raman spectra on fibers were recorded with an Ar^+ laser light source (514.5 nm). The Raman spectrometer was also equipped with 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 thermo–electrically cooled (203 K) detector.

2.3 Pyrolysis experiments

The pyrolysis experiments were carried out in a batch pilot plant [28, 29] (Figure 2) with an internal volume of 5.5 m^3 provided by Curti S.p.A. that can treat up to 70 kilograms of fiberglass reinforced composites per pyrolysis cycle. It is composed of two parts, the lower being a tank containing water, which acts as hydraulic guard, the upper a mobile bell whose lifting allows the sample insertion and the removal of the solid residue at the end of the process. The latter element is double walled hosting electric resistances with a total power of 21000 W.

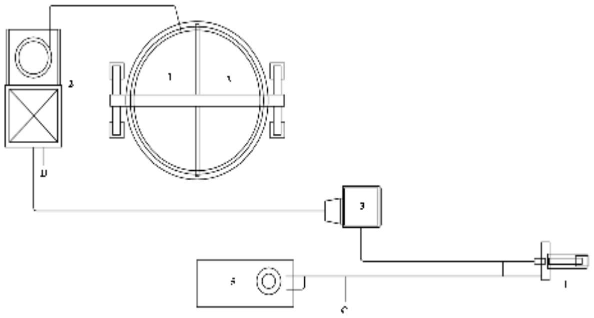

Figure 2. Schematic layout of the experimental pyrolysis pilot plant: pyrolysis chamber (1); demister (2); acid gas scrubber (3); fan (4); burners (5); collection point of solid residue (A); collection point of pyrolysis oil and water (B); bleed point of pyrolysis gas (C)

The pyrolysis batches were performed isothermally at different temperatures, namely 500, 550 and 600°C, as defined upon preliminary TGA investigation. Since the presence of polyethylene has been reported to lead to the formation of waxes which could condense at a low process temperature [35], pyrolytic tests at temperature below 500°C were not performed to avoid pipeline obstruction.

In a typical run, 20 kg of GFRPs scraps were placed in the reactor. After closing the lid, the reaction chamber was flushed with nitrogen to remove air, then the system was heated at 8°C/min rate up to the set point, and then kept at the desired temperature up to a total residence time of 150 minutes.

All the gases generated in the process were extracted from the reactor and partially condensed in a water cooled coil. The uncondensed gas proceeded to the gas bleed point for online characterization via Gas Chromatography (GC) whereas the obtained liquid fraction, from now on referred to as the oil fraction, was collected via a demister and subsequently characterized.

During heating, the water from the hydraulic guard facing the inner chamber evaporates, forming steam that adds up to the pyrolysis products flow, hence requiring a separation step of the vaporized water from the oily products in the demister.

After 150 mins the resistances were switched off and the reactor began to cool down; this was considered the end-point of the test. When the temperature decreased below 100°C, the upper bell of the reactor was opened to remove the solid residue that were named P500, P550 or P600 depending on the pyrolysis temperature.

2.4 Post pyrolysis oxidation treatments

The oxidation treatments were carried out on the solid residues derived from the pyrolysis. 200g of the glass fibers with a superficial carbonaceous residue, as obtained from pyrolysis, were inserted in a muffle furnace at 500 or 600°C and isothermally kept for different residence times (10, 20, 30, 40, 50 and 60 mins) in order to determine a suitable oxidation step duration. The recovered glass fibers were labelled PX-O500xY and PX-O600xY (where X is the pyrolysis temperature and Y the residence time) and they were characterized by Scanning Electron Microscopy (SEM) and Raman spectroscopy.

3. RESULTS AND DISCUSSIONS

3.1 Pyrolysis batch experiments

In order to assess conditions for pyrolysis experiments, a preliminary thermogravimetric investigation (TGA) of GFRP scraps without the LDPE protective film was carried out in dynamic mode and inert atmosphere (N_2). The thermogravimetric curve reported in Figure 3 shows a single weight loss event starting at around 300°C, whose onset (Tonset) is determined to be approximately at 310°C. The degradation process appears almost complete at 500°C already and it leads to a constant weight residue (38.6 wt%) after 92 minutes isotherm at 500°C. This preliminary TGA experiment does not take into account the presence of the LDPE coating. However, since literature [35] reports that the presence of polyethylene leads to the formation of waxes which could condense at low process temperature, pyrolytic tests at temperature below 500°C were not performed in order to avoid pipeline obstruction. TGA experiments also show that oxidative conditions applied to the solid pyrolytic residue cause a further weight loss (final residue after oxidative treatment about 33.5 wt%). It is worth to note that, since TGA experiments were carried out directly on scraps, the intrinsic uncertainty associated with those measures is quite high, owing to the fact that the real fiber glass content in the mg-sized sample is rather unknown and uncontrollable.

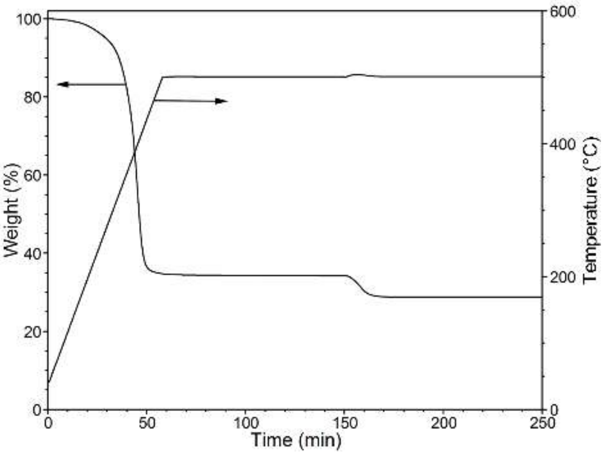

Figure 3. TGA curve of GFRPs polyester laminate without LDPE protective film, simulating a pyrolysis cycle batch carried out in inert atmosphere at 500°C, and a further 60 minutes oxidation treatment at 500°C

Hence, given TGA results, the range 500-600°C was selected for further pyrolysis experiments in the pilot plant, running batches every 50°C, namely at 500, 550 and 600°C.

Once suitable temperature ranges were identified, pyrolysis experiments were performed in an innovative and safe batch static kiln [28, 29] with a raw material load of about 20 kg. Worth noting is that this innovative pilot plant (with an internal volume of 5.5 m^3) allows the loading of non-shredded scraps up to 2 meters diameter size. The pyrolytic process on GFRPs led to three main products streams, i.e. a gas phase, an oil fraction and a solid residue whose relative ratios depend on the applied reaction conditions (such as temperature and residence time). After determining the optimal residence time for the materials to be 150 minutes, of which the effective pyrolysis step takes only about 20-30 minutes to complete (Figure 3), different temperatures were tested.

Figure 4 shows the yields of the obtained solid residue, oil and gas (the latter calculated by difference) upon pyrolysis as a function of the reaction temperature. Only limited differences appear in products distribution at 500 and 550°C: the total amount of the solid residue, composed of glass fibers covered of a black layer similar to coke in appearance, and the oil fraction tend to slightly decrease from 44.3 to 43.8 wt% and from 19.8 to 19.2 wt% respectively, whereas the gas portion marginally increases.

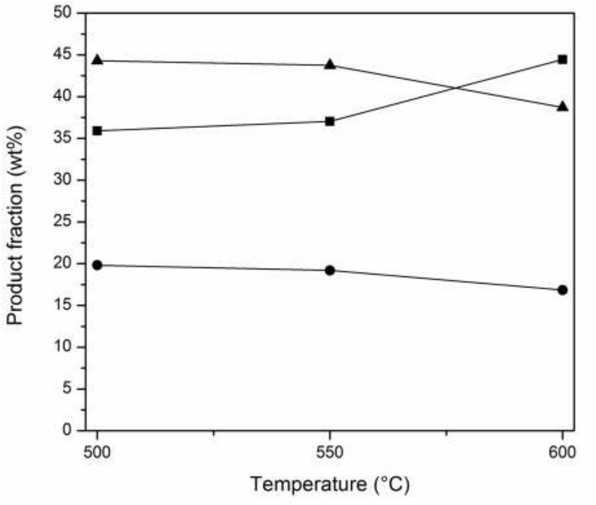

Figure 4. Products distribution at different pyrolysis temperature: (▲) solid residue, (■) pyrolysis gas and (●) oil fraction

When the process temperature increases to 600°C, the solid residue and the oil fraction further decrease to 38.7 wt% and 16.9 wt% respectively. As a consequence, the non-condensable fraction, increases from 37.0 to 44.4 wt%. Thus, in the highest temperature experiment (600°C), the oil/gas weight ratio decreases from 0.54 to 0.38. A similar trend was reported for the pyrolysis of other polymer matrix composite materials such as tires [36, 37] and explained taking into account further cracking of evolved volatile matter at elevated temperatures [37]. The increase in the gaseous fraction can also explain the lower solid residue observed at 600°C. Indeed, since the char consists mainly of glass fibers and a carbonaceous layer including a solid hydrocarbon fraction, such a result suggests that higher temperature (600°C) volatilizes some of the solid hydrocarbon content of the char [38] and decomposes some oil vapors to incondensable gases.

3.2 Pyrolysis gas

The volatile mixture evolving during the pyrolysis tests was continuously monitored online through a μ-GC in order to correlate the gas composition with the applied process conditions. The average composition of the pyrolysis gas produced at different pyrolysis temperatures and Gross Calorific Value (GCV) of each mixture are reported in Table 1. A number of gases are detected, such as: carbon oxides (CO and CO_2), hydrogen, methane, ethane, and ethylene; furthermore the sum of detected propane and propylene is named C_3, while the sum of 1-butene, n-butane, 1,3-butadiene, iso-butylene is named C_4. "Others" is the sum of the other indeterminate incondensable species, mainly composed of C_{4+}.

Table 1. Chemical composition and GCV of the gas produced by pyrolysis of GFRPs scraps at different process temperature

Pyrolysis gas components (vol%)	Process temperature (°C)		
	500	550	600
H_2	5.8	7.5	11.5
CH_4	10.6	15.4	20.7
CO	24.2	24.0	21.8
CO_2	32.6	26.0	20.4
C_2H_4	4.8	5.0	5.2
C_2H_6	2.8	3.3	3.7
C_3	1.4	1.4	1.3
C_4	2.6	2.7	2.5
Others	15.2	14.7	12.9
GCV (MJ/Nm^3)	31.1	33.3	34.1

At 500°C the main evolved compound is CO_2 (32.6 vol%) followed by CO (24.2 vol%) primarily generated upon the breakdown of oxygen-rich moieties which are abundant in the polyester resin formulation. In these experimental conditions there are also considerable fractions of methane (10.6 vol%) and hydrogen (5.8 vol%). With the increase of the process temperature the pyrolysis gas is enriched in the most volatile components such as H_2 and CH_4 while a significant reduction in oxides content is registered, mainly due to a decrease of the carbon dioxide component from 32.6 to 20.4 vol%. Torres et al. [22] did not detect the presence of hydrogen in the gaseous fraction obtained by pyrolysis of similar GFR polyester resins. In that work, the Authors obtained very high concentrations of carbon oxides and reported that the C_1-C_4 species reach a maximum of 9.4 vol% at 700°C. Lopez et al. [27] at 550°C found concentrations of CO (21.46 vol%) and CO2 (37.51 vol%), comparable with those determined in the current study, though in their work the hydrogen fraction was just 2.3 vol%.

Since it is renown that the calorific value of a gas is a function of the chemical composition and relative amounts of components, the data obtained by μ-GC analysis (Table 1) were used to evaluate the GCV of the gaseous fractions according to the standard method UNI 7839 (Table 1). The calculated GCV was observed to increase from 31.1 to 34.1 MJ/Nm^3 by increasing pyrolysis temperatures. This is mainly due to the above mentioned decrease of CO_2, which of course has no calorific potential at all, and to the high content of H_2 and C_1-C_4 compounds. Thus, the current values are higher than those reported by Torres et al. [39] (14.6 and 14.1 MJ/Nm^3 at 500 and 600°C respectively) and slightly better than data obtained from Lopez et al. [27] (26.0 MJ/Nm^3 at 550°C).

3.3 Pyrolysis oil

The GFRPs pyrolysis output stream that is recovered upon condensation within the cooling system is a complex mixture of organic compounds whose relative concentrations are primarily influenced by the process temperature and by the chemical nature of the polymeric resins [39]. GC-MS analysis revealed the presence of benzene and its alkyl derivatives (such as toluene, ethylbenzene, cymene, propylbenzene), styrene and α-methylstyrene, benzaldehyde and acetophenone, indene and its derivatives, naphthalene and methylnaphtha–lenes. Among the detected compounds, benzene, toluene, ethylbenzene and styrene have the highest market values as a source of light aromatics, hence their separate quantification was carried out in each batch and the results are reported in Table 2. The maximum concentration of the compounds of interest is registered in the pyrolysis oil produced at 550°C and corresponds to 84.3 g/l.

Table 2. Benzene, toluene, ethylbenzene and styrene content in oils obtained at different temperatures

Oil components (g/l)	Process temperature (°C)		
	500	550	600
Benzene	3.4	9.5	6.8
Toluene	15.0	31.1	27.3
Ethylbenzene	16.7	30.0	21.5
Styrene	7.9	13.7	13.6

In order to estimate their potential commercial value, oils produced via pyrolysis at different tempe–ratures were analyzed by XRF to highlight the presence of possible contamination. The results are reported in Table 3 together with their density and viscosity.

Table 3. XRF analysis, density and viscosity of the oils obtained by pyrolysis at different temperatures

Oil contaminants (wt%)	Process temperature (°C)		
	500	550	600
Cl	-	0.07	0.06
Na	0.16	-	0.33
Si	0.03	0.01	0.02
Al	-	-	0.02
S	0.05	0.01	0.02
Characteristics			
Density (g/cm3)	1.013	1.011	1.014
Viscosity (cSt)	27.1	16.2	20.1

All the oils are composed mainly of carbon, hydrogen, nitrogen, and oxygen and just small amounts of sodium (0.16-0.33 wt%) and sulphur (0.01-0.05 wt%)

were found in all the analysed samples. Silicon and chlorine are always well below 0.1 wt%. The low content of sulfur and halogens, together with the total absence of heavy metals, make the obtained pyrolysis oils suitable for use as fuel without requiring any further purification process. The density of the obtained oils is constant with the process temperature while the viscosity values vary, in agreement with the content of light aromatic oils (Table 2) in the range 16.2-27.1 cSt.

3.4 Pyrolysis solid residue and recovered glass fibers

The black solid residue recovered from the reactor at the end of the pyrolysis run (Figure 5A) maintains the shape of the fed fiberglass reinforced composite scraps. This residue, whose amount decreases from 44.3 to 38.7 wt% increasing the process temperature from 500 to 600°C (Figure 4), is composed of glass fibers mats where the fibers are randomly arranged and kept together by a thin cohesive carbonaceous layer that provides the overall black colour (Figure 5A).

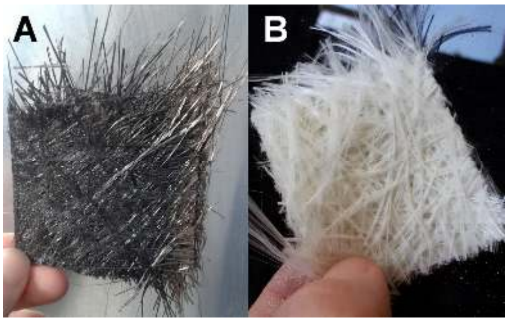

Figure 5. Solid residue recovered from pyrolysis batches at 500°C (A) and clean recovered glass fibers after oxidation at 500°C (B)

In Figure 6A, B and C, SEM micrographs of solid residues obtained at different pyrolysis conditions are reported. All the fibers show an uneven surface, due to char deposits, as previously stated [23, 27] and their average diameter decreases from 15.0 to 13.5 µm as the process temperature is increased from 500 to 600°C (Table 4).

In order to quantify the extent of char fraction and the thickness of the carbonaceous layer, the carbon residue was completely removed with the application of an oxidizing treatment at 500°C for 60 minutes, as demonstrated by the picture reported in Figure 5B where the fibers whiten.

During the oxidizing treatment of about 200 g of solid residue we registered a weight loss whose entity decreases from 21.3 to 12.2 wt% by increasing the pyrolysis process temperature. As previously reported by Torres et al. [26], this weight loss is due to the carbonaceous layer decomposition and its trend is in accordance with the decreasing quantity of solid residue collected after pyrolysis (Figure 4). The glass fiber content in the pyrolysis-oxidized residues, calculated according to the equations proposed by Torres et al. [26], corresponds to an average of about 34 wt%.

The char decomposition is demonstrated also by SEM analysis. As an example, in Figure 6A and D we report the micrographs of the solid residue obtained from the pyrolysis of GFRPs at 500°C, before and after the oxidation treatment at 500°C for 60 minutes. They clearly show that the glass fibers change from a bundle with a rough surface, to smooth, flawless and isolated entities.

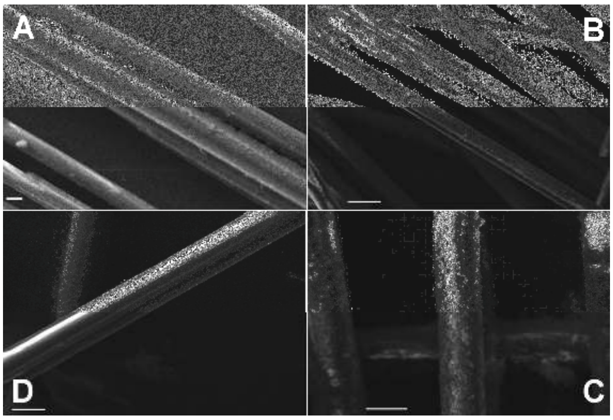

Figure 6. SEM micrographs of P500 (A) scale bar 10 µm, P550 (B) scale bar 20 µm, P600 (C) scale bar 10 µm, and P500-O500x60 (D) scale bar 10 µm

Moreover the fibers average diameter (Table 4), calculated from the SEM micrographs, after oxidation appears reduced to a common value of 12.5 µm. By considering this value as the diameter of the virgin uncoated fibers, it was possible to estimate the thickness of the carbonaceous layer after different pyrolysis conditions (Table 4). The data reported in Table 4 show again a decrease of the calculated thickness of the char from 1.25 to 0.50 µm when the pyrolysis process temperature increases from 500 to 600°C, in accordance with the registered weight losses during oxidation.

Table 4. Sizing of the carbon deposits on the glass fibers obtained at different pyrolytic process temperature

Pyrolysis process temperature (°C)	Average diameter of the glass fiber (µm)		Carbonaceous layer thickness (µm)
	After pyrolysis process	After oxidation process	
500	15.0	12.5	1.25
550	14.8	12.5	1.15
600	13.5	12.5	0.50

The disappearance of the carbon residue deposited on glass fibers, as a function of oxidation temperature and time residence, was also assessed by Raman spectroscopy coupled to an optical microscope to guide the Raman probe.

In particular, this investigation was performed on 200 g of the solid residue obtained by pyrolysis at 500°C (P500) and further subjected to an oxidation treatment at 500°C for 10, 20, 30, 40, 50 and 60 mins (called P500-O500xY, where Y is the residence time in minutes). The Raman spectrum of P500 is shown in Figure 7A and exhibits two evident broad peaks at 1560 and 1360 cm^{-1} that are well known absorptions for carbonaceous materials as the so-called G- and D-peaks respectively. In particular, the G-peak is ascribed to the bond stretching of all pairs of sp2 atoms in both carbon rings and chains, while the D-peak is due to the defect induced on the sp2 structure [40].

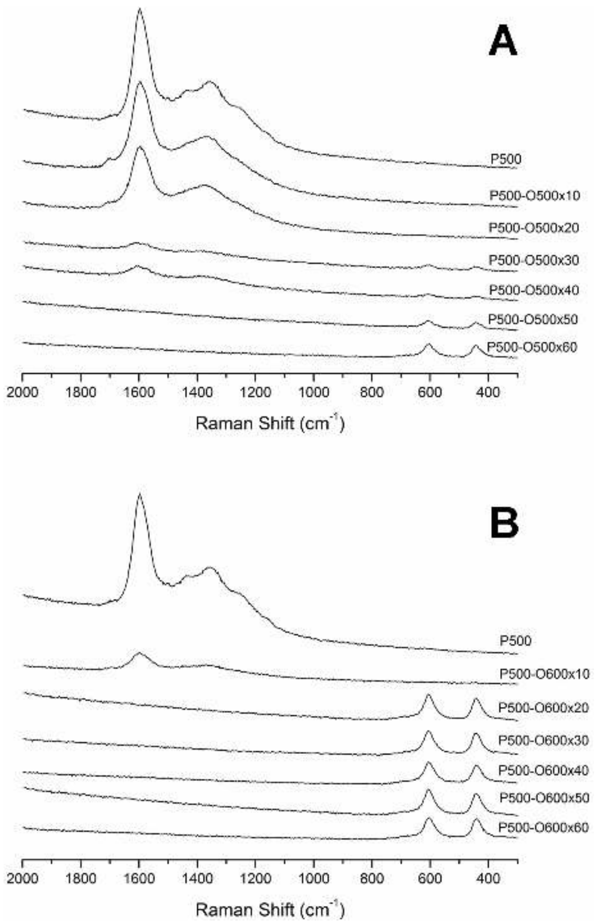

Figure 7. Raman spectra of solid residue obtained by pyrolysis at 500°C before and after oxidization in air at 500 (A) and 600°C (B) for different residence times, according to the labels in the Figure

The presence and intensity of these peaks can be correlated with the presence or lack of organic residues (amorphous carbonaceous layer) [41] and it is taken as a guarantee that the oxidation process provides a surface free from any residual resin, as observed qualitatively by naked eye and SEM micrographs (Figure 5B and Figure 6D, respectively).

The same broad Raman absorptions are observed in the fibers oxidized at 500°C for up to 40 minutes treatment (Figure 7A, curves P500-O500x10, x20, x30 and x40). Further increasing the oxidation time (Figure 7A, curves P500-O500x50 and x60), the carbonaceous peaks are absent, thus suggesting an almost complete removal of residual resin. The complete removal of the organic residue results in the appearance of two new peaks at lower Raman shift (around 605 and 440 cm^{-1}), that can be ascribed to the presence of Si-O-Si linkages of the glass fibers [42] (Figure 7A). The complete lack of these signals when char is present accounts for the carbonaceous layer covering homogeneously the surface fibers, thus fully hiding the glass.

To evaluate the effect of higher oxidation tempera– tures on glass fibers, the solid residue obtained by pyrolysis at 500°C (P500) was also subjected to oxidation at 600°C for 10, 20, 30, 40, 50 and 60 minutes (called P500-O600xY, where Y is the residence time in minutes) and the regression of the carbonaceous residue was followed again by Raman spectroscopy (Figure 7B).

At 600°C, only 20 minutes are needed to completely remove the carbonaceous residue from the surface of the fibers, as evidenced by the disappearance of the characteristic peaks around 1560 and 1360 cm^{-1}. By increasing the residence times, no structural changes of the glass fibers were shown by Raman analysis.

When applying the minimum oxidation time residence necessary for the complete removal of the carbonaceous layer (50 minutes at 500°C and 20 minutes at 600°C) to the solid residues from pyrolysis at 550 (P550) and 600°C (P600), Raman spectroscopy (Figure 8) confirms once again the complete removal of the carbonaceous coating without inducing detectable structural changes.

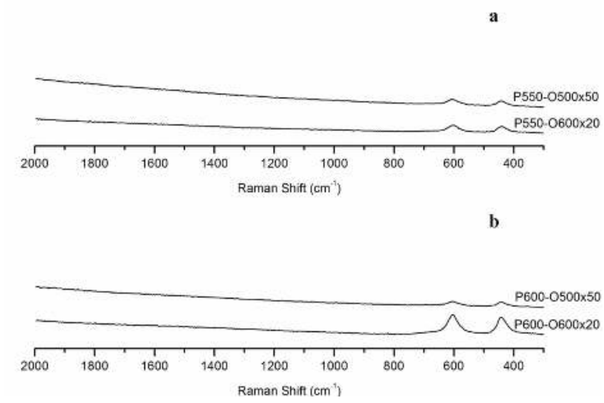

Figure 8. Raman spectra of P550-O500x20 and x50 (a) and P600-O600x20 and x50 (b)

Furthermore, longer oxidation times do not induce visible surface damages of the glass fibers whose average diameter stays constant at 12.5 μm when the oxidation time increases from 10 to 50 minutes also at higher temperatures.

These data confirm previous findings observed on pyrolyzed carbon fibers from carbon fiber reinforced composites pyrolysis, that show similar conditions for the complete removal of the outer carbon layers [14]. Moreover, by running the pyrolysis and the oxidation processes at the same temperature (e.g. isothermal between 500-600°C), it is possible to plan an in line thermal treatment carried out directly on the hot solid residue at the end of the pyrolysis process, when up-scaling to an industrial plant.

4. CONCLUSION

Pyrolysis proved itself a highly suitable method for recovering valuable products and energy from GFRPs scraps. The innovative proposed process, with a hydraulic guard that guarantees process safety, was applied on whole parts of GFR polyester resin laminates, thus saving the energy costs of shredding, and yielding an oil (≈20 wt%), a gas (≈40 wt%) and a solid residue (≈40 wt%). The pyrolysis gas appears significantly rich in H_2 and CH_4 while the high content of light aromatic compounds, the low content of sulfur and halogens, together with the total absence of heavy metals, make the obtained oil fraction suitable as fuel without the need for any further purification process or as raw material. Moreover, we have demonstrated that, by a further oxidation treatment at temperature between

500-600°C, it is possible to obtain clean glass fibers suitable to be re-used: at 500°C the time of air exposure should be 50 minutes or more; at 600°C the oxidative residence time should be about 20 minutes in order to limit the energy cost.

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NOMENCLATURE

GFRPs	Glass fiber reinforced polymers
CFRPs	Carbon fiber reinforced polymers
GC-MS	Gas Cromatography-Mass spectroscopy
XRF	X-ray Fluorescence analysis
μ-GC	micro-Gas Chromatography
SEM	Scanning Electron Microscopy
LDPE	Low Density Polyethylene
TGA	Thermogravimetric analysis
GCV	Gross calorific value
MS	Molsieve
PPU	PoraPLOT U
TCD	Thermal Conductivity Detector
ATR	Attenuated total reflectance

ПИРОЛИЗА КОМПОЗИТА ОД СТАКЛЕНИХ/ПОЛИЕСТЕР ВЛАКАНА: РЕКОНСТРУКЦИЈА И КАРАКТЕРИЗАЦИЈА ДОБИЈЕНИХ ПРОИЗВОДА

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Композити од полиестера ојачани стакленим влакнима (GFRPs) као отпаци из производње полиестерских ламината су разложени на 500, 550 и 600 °C у 70Kg иновативним пилот постројењима која обрађују читаве делове. Присуство хидрауличне заштите гарантује сигурност процеса. Утицај максималне температуре процеса на течење и физичко хемијске карактеристике пиролизе производа је испитиван: фракција уља је анализирана помоћу GC-MC, вискозиметром и XRF, док је фракција гаса праћена током читавог процеса пиролизе путем μ-GC. Значајна фракција метана (20,7 vol%) и водоника (11,5 vol%) је произведена. Чврсти остатак (стаклена влакна покривена танким угљеничним слојем) је прошао кроз процес оксидације на 500 и 600 °C у различитим временским распонима да би се обезбедила чиста стаклена влакна без органских остатака. Ефекти обе пиролизе и кораци оксидације стаклених влакана, добијених у различитим процесним условима, процењивани су СЕМ-ом и Raman спектроскопијом.