RECUPERAREA FIBRELOR DIN DEȘEURI DE MATERIALE COMPOZITE CU AJUTORUL PIROLIZEI
FIBER RECOVERY THROUGH PYROLYSIS OF FIBER REINFORCED COMPOSITE WASTE

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In this moment plastics provide a fundamental contribution in all activity fields: cars, aircraft, electronics, building, domestic daily activities, packing, etc. so the consumption of plastics has increased drastically. The disposal of plastic composite wastes is a serious environmental problem as they are not biodegradable. As a consequence, our work is focused in recycling of carbon fibers and glass fibers from waste composites through pyrolysis and partial oxidation.

In momentul actual materialele plastice oferă o contribuție fundamentală în toate domeniile de activitate: mașini, aeronave, electronică, clădiri, activități zilnice, ambalare etc., astfel încât consumul de materiale plastice a crescut drastic. Eliminarea deșeurilor compozite reprezintă o problemă serioasă de mediu, deoarece acestea nu sunt biodegradabile. Ca o consecință, activitățile de cercetare prezentate în acest articol sunt axate pe reciclarea fibrelor de carbon și a fibrelor de sticlă din deșeurile compozite prin piroliză și oxidare parțială.

Keywords: *recycling, carbon fiber, glass fiber*

1. Introduction

For a sustainable future, the environmental requirements of the European and Romanian legislation impose the valorization of industrial and municipal wastes [1]. Fibers such as carbon fiber, glass fiber, polypropylene fibers have been widely preferred for the latest relevant studies to improve mechanical properties like flexural strength [2,3]. Also, fibers are used in sandwich structures, structures that present low weight, good corrosion resistance [4-6], thermal resistance, fatigue and good buckling resistance [7,8] Therefore the demand for carbon material composites is growing due to the applications for renewable energy systems [9,10], aerospace [11] and automotive [12]. A variety of methods have been investigated for reusing high value carbon fiber from carbon fiber reinforced composites through recycling. The main recycling points is to decompose the polymeric matrix with each different methods leaving clean carbon fibers. So far, several methods to recycle carbon fiber reinforced composite (CFRP) and glass fiber reinforced plastic (GFRP) wastes have been investigated. The typical recycling methods could be classification into three systems: mechanical recycling, chemical process and thermal processing

The plastic polymer components commonly used include thermoset polyester, phenolic resin, epoxy resin, polypropylene and vinyl ester resin. It is the mixture of components embedded in the matrix that make composites difficult to recycle and the reason why such a high percentage is sent to landfill.

In the case of CFRP and GFRP, they are neither fusible nor soluble and certainly they cannot be remoulded into another shape [13,14]. But, in the pyrolysis process the inorganic part or reinforced materials that have good thermal stability (glass or carbon fibers) remain unmodified and they can be recycled into other composites [14,15].

With all information and experimental data achieved we are trying to use the knowledge as a proposal for resolving the problem concerning

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plastic and composites wastes. There are many reference data in polymer handbooks or various monographs and reviews [16,17].

Many authors agree that the water obtaining in thermal decomposition of plastics comes from the original moisture of samples or can be formed during pyrolysis, when the polymers contain functional groups with oxygen (-OH, -COOH etc.) [14, 18, 19].

Carbon fibers reinforced plastics have an almost infinite service lifetime. But when it is time to recycle them, they cannot simply be melted down like metals. The best that can be done is to mill or shred them to reclaim the carbon fibers, which shortens the fibers dramatically. There are many industrial applications that don't need the full strength of full-length fibers reinforcement. For example, chopped reclaimed carbon fibers are used in consumer electronics, such as laptops, where it provides excellent reinforcement of the plastics used, even if it lacks the strength-to-weight ratio of an aerospace component [20].

Usually, 10% of a vehicle's weight is made up of plastics and GFRP, and for some lightweight vehicles this may be up to 20%. Composites are increasingly used since they have the advantages of strength, durability and corrosion resistance together with low weight.

Part of difficulties encountered in dealing with wastes from plastic composite was related to their diversity, being developed specifically for each individual application. On the other hand, plastic composites have a large amount of reinforced materials that often are expensive and the interest is to be recuperated. Since these reinforced materials will stay in the solid product during the thermal processes, our work is focus on pyrolysis applied for recycling of fibers from composites waste.

2. Materials and Methods

2.1. Tested materials

The experiments were performed on used carbon fiber reinforced polymer used in aircraft manufacturing and glass reinforced plastic, from research chemical laboratory wastes. The materials were selected by their large applications and the energy consumption required for their production.

CFRP is mainly use in aerospace industry, automotive industry, bikes, etc., and GFRP in automotive industry, swimming pools, tanks. The tested materials are shown in Figure 1 (a, b) while the results from their elemental analysis are presented in Table 1.

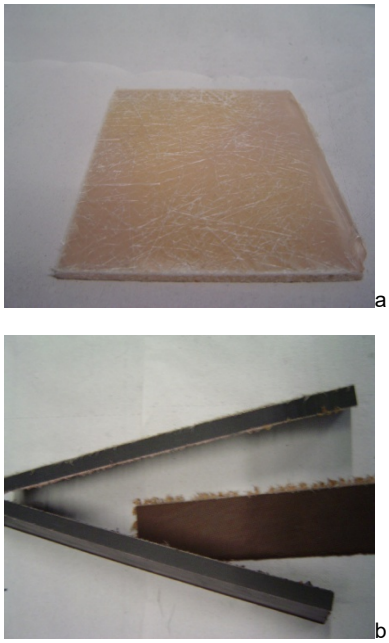

Fig 1 - Waste material used in experimental tests a) GFRP, b) CFRP / *Deşeuri utilizate în testele experimentale a) GFRP, b) CFRP.*

2.2. Investigation methods

The materials behaviours during pyrolysis and partial oxidation was investigated through thermogravimetric analysis (TGA) by using a thermogravimetric analyser SETSYS Evolution TGA, from SETARAM Instruments.

The quality of fibers recovered after thermochemical treatments was made by Scanning Electron Microscopy (SEM) coupled at energy dispersive X-Ray spectrometry (EDX) using a JEOL Scanning Electron Microscope.

3. Results

3.1. Thermogravimetric analysis

The two types of materials were tested first to understand their decomposition capability and secondly to assess the possibility of recovering the fibers with the aim of recycling them for new application.

With these purposes, the samples were washed, dried and cut into pieces of 3x10mm, the

Table 1

Elemental analysis results for tested materials (%wt.) /
Rezultatele analizei elementale pentru materialele testate (% masice)

Material	Elemental Analysis				
	N	C	H	S	O
CFRP	5.29	78.29	2.32	4.10	5.67
GFRP	nd(*)	58.25	5.80	nd	45.90

(*) nd – non-detected

mass of samples varying between 85-160mg. First step in this work was to identify the temperature range of major mass loss for each sample through controlled thermochemical decomposition, in oxygen-free atmosphere (pyrolysis) and under partial oxidation conditions.

These thermogravimetric studies were performed in non-isothermal mode with heating rate of 10K·min^{-1} until the established final temperature of 700°C was reached, with a fixed flow rate of 20mL·min^{-1} of nitrogen, used as carrier gas.

For the case of cleaning the fibers, a pyrolysis combined with a partial oxidation we used. For pyrolysis step the same nitrogen flow rate was kept, and for the oxidation zone a mix of helium and oxygen (72+28%vol) was used as oxidation agent, at a flow rate of 16mL·min^{-1}.

3.1.1. Glass Fiber Reinforced Polymer

The TGA analysis shows that tested materials have a high content of organic matter, up to 72% of the initial mass being lost during applied pyrolysis, as it can be seen in Figure 2. The polymer matrix starts to decompose 322±5°C and is quickly destroyed, the thermal range of decomposition when the maximum mass loss is registered being very short, 322 - 435 °C.

Thus, the yield of solid fraction, representing the glass fibers, recovered after pyrolysis is 28% and 25% after oxidation. These close values of solid fraction remained after oxygen-free treatment show the pyrolysis at 700°C is a valuable technique to treat waste GFRP for relatively clean glass fibers recovery.

Searching for a manner to obtain an improved quality of these fibers, it can be assumed that applying an oxidation step will allow to remove the residual carbon materials remained on the glass fibers.

Figures 3 contains the representative mass loss diagrams registered oxidation processes applied further to the solid residues remained after waste GFRP pyrolysis. As it can be seen, the partial oxidation induced an additional mass loss, which took place in a large thermal range (450 - 800°C).

With the aim of substantiate the assumption that ATG results offered, an investigation of recovered fibers surface have been carried out. Indeed, SEM and EDX analysis show that after pyrolysis small amount of carbon deposits are attached on the surface of fibers recovered after pyrolysis. These deposits appear to be removed after applied partial oxidation process, the recovered fibers being much cleaner and well separated, while the peak of carbon disappear in the EDX spectrum registered for fibers from combined pyrolysis and partial oxidation processes.

These aspects are highlighted in Figures 4 (a-SEM, b-EDX) and 5 (a-SEM, b-EDX) where SEM images and EDX spectrums obtained for fibers recovered after GFRP pyrolysis and oxidation are presented.

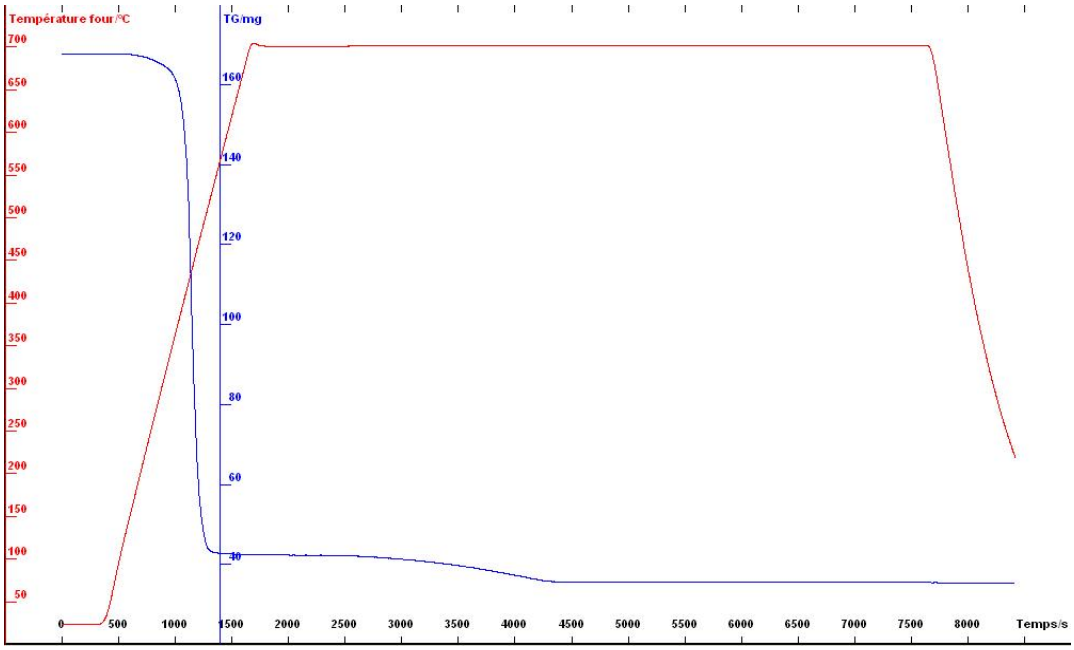

Fig. 2 - Mass loss during GFRP pyrolysis / *Pierderea de masă în timpul pirolizei GFRP.*

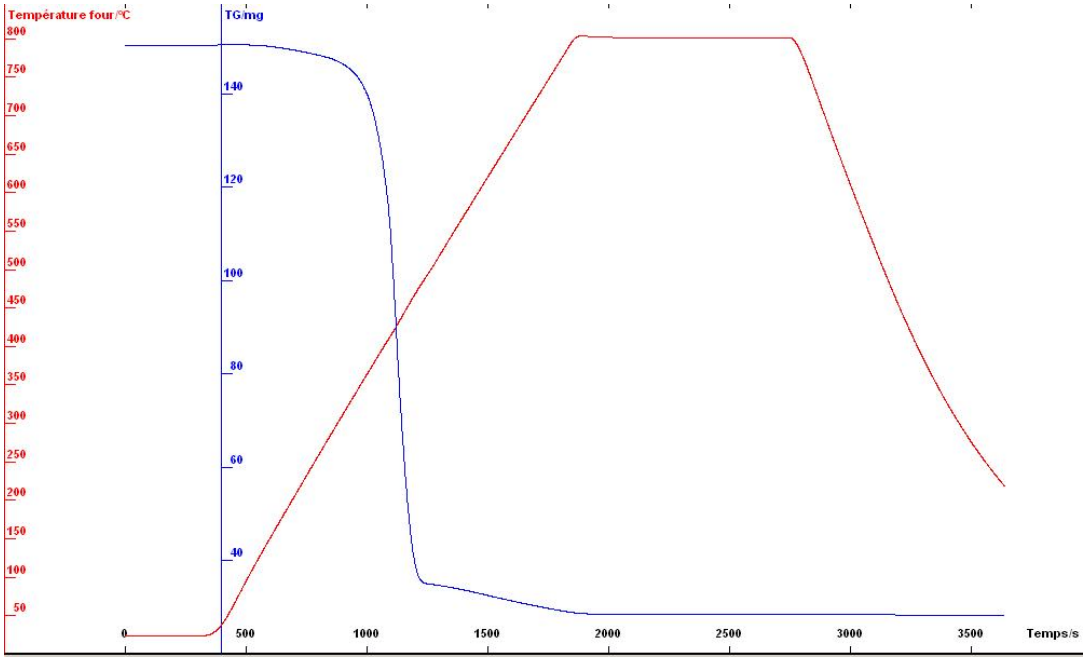

Fig. 3 - Mass loss during GFRP pyrolysis followed by partial oxidation / *Pierderea de masă în timpul pirolizei urmată de oxidarea parțială a GFRP.*

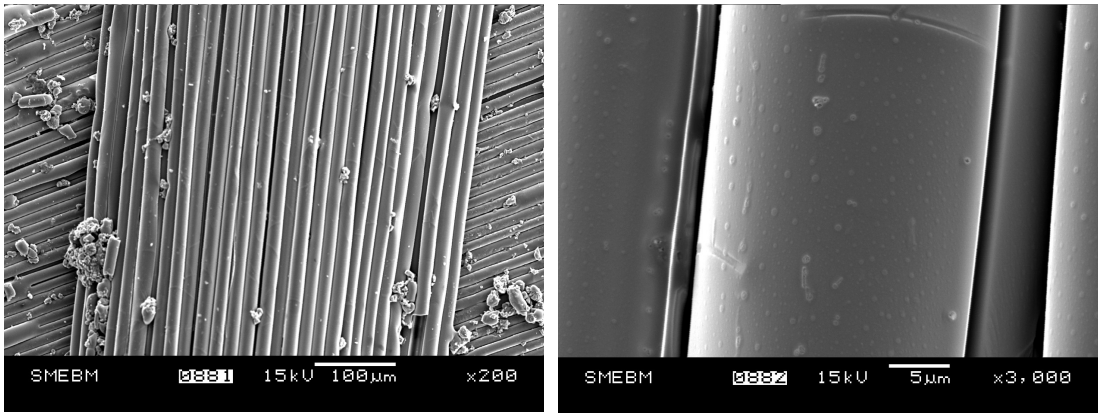

Fig. 4 - a) SEM analysis after GFRP pyrolysis / *Analiza SEM după piroliza GFRP*

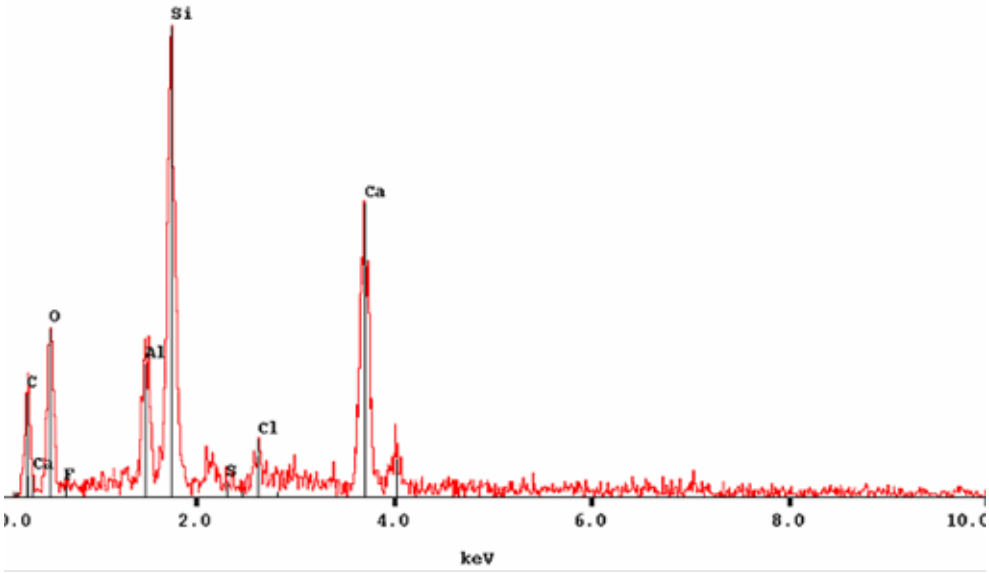

Fig. 4 - b) EDX analysis after GFRP pyrolysis / *Analiza EDX după piroliza GFRP.*

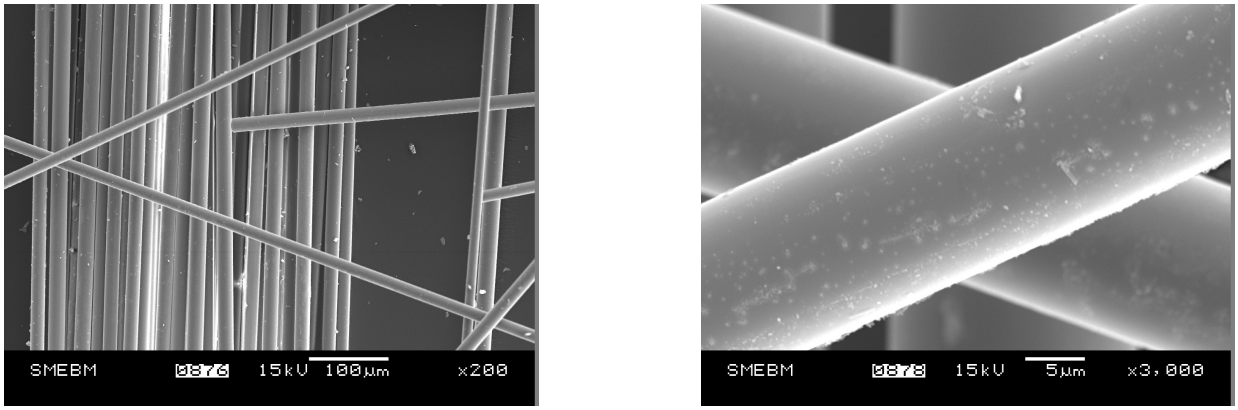

Fig. 5. - a) SEM analysis after GFRP pyrolysis followed by partial oxidation */ Analiza SEM după piroliză urmată de oxidarea GFRP.*

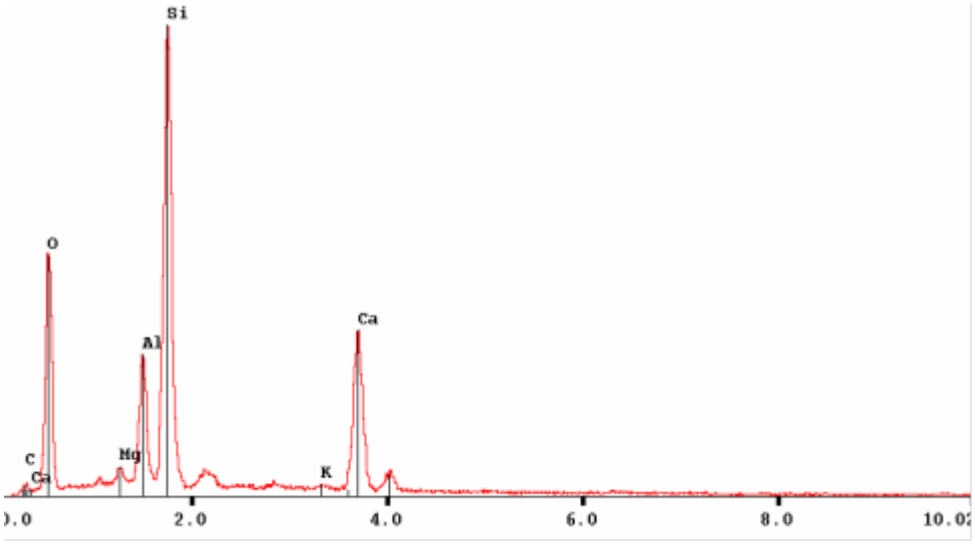

Fig. 5 - b) EDX analysis after GFRP pyrolysis followed by partial oxidation */ Analiza EDX după piroliză urmată de oxidarea GFRP.*

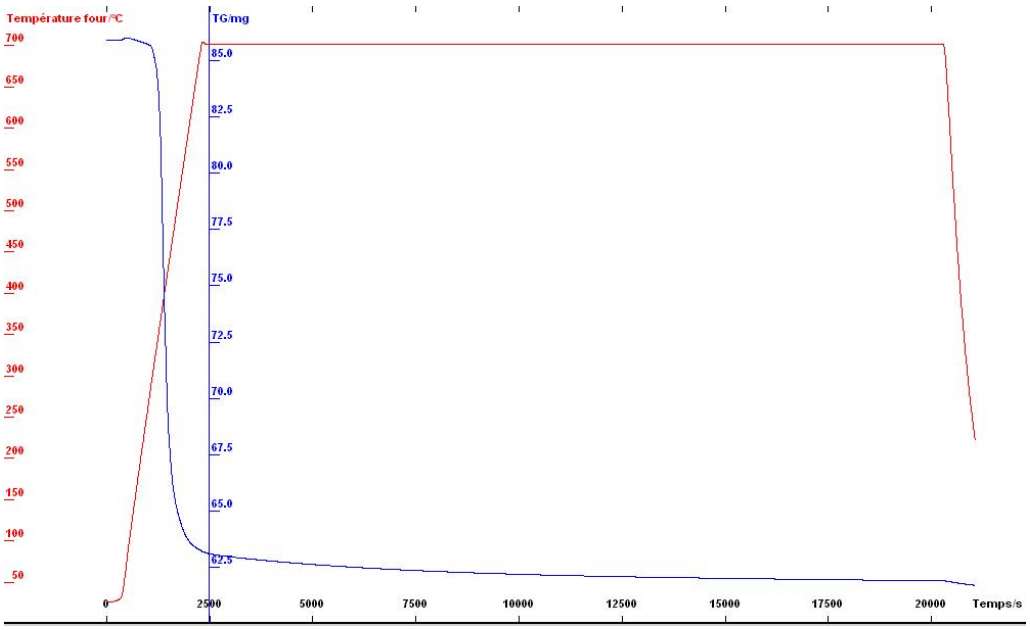

Fig. 6 - Mass loss during CFRP pyrolysis / *Pierderea de masă în timpul pirolizei CFRP.*

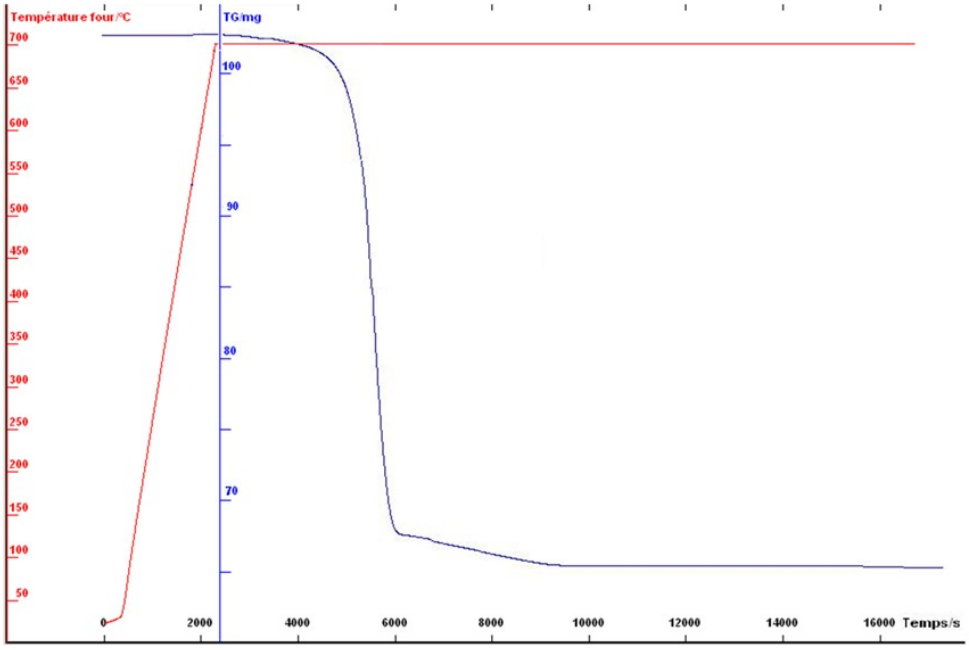

Fig. 7- Mass loss during CFRP pyrolysis followed by partial oxidation */ Pierderea de masă în timpul pirolizei urmată de oxidarea parțială a CFRP.*

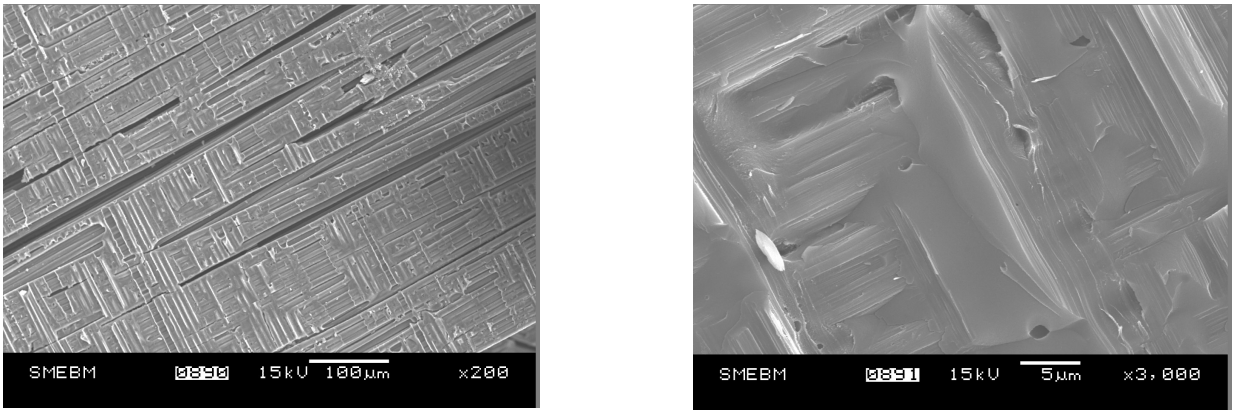

Fig. 8. - a) SEM analysis after CFRP pyrolysis/ *Analiza SEM după piroliza CFRP*

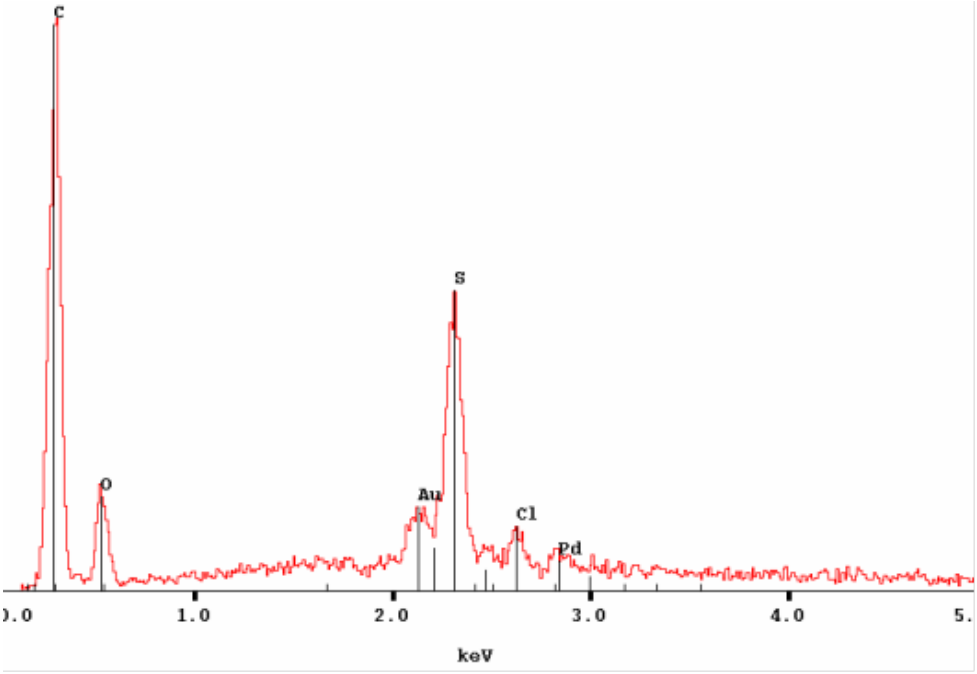

Fig. 8 - b) EDX analysis after CFRP pyrolysis */ Analiza EDX după piroliza CFRP.*

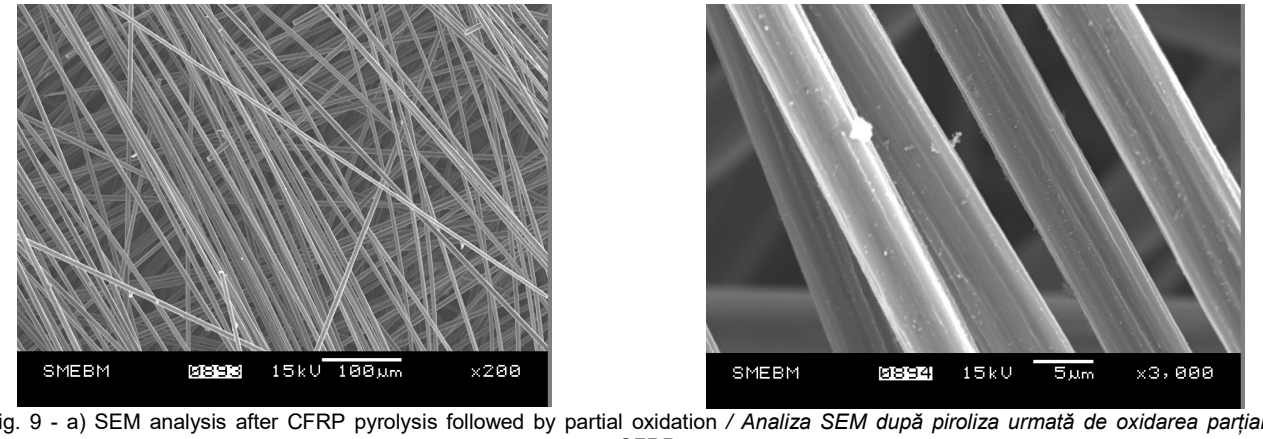

Fig. 9 - a) SEM analysis after CFRP pyrolysis followed by partial oxidation / *Analiza SEM după piroliza urmată de oxidarea parțială a CFRP.*

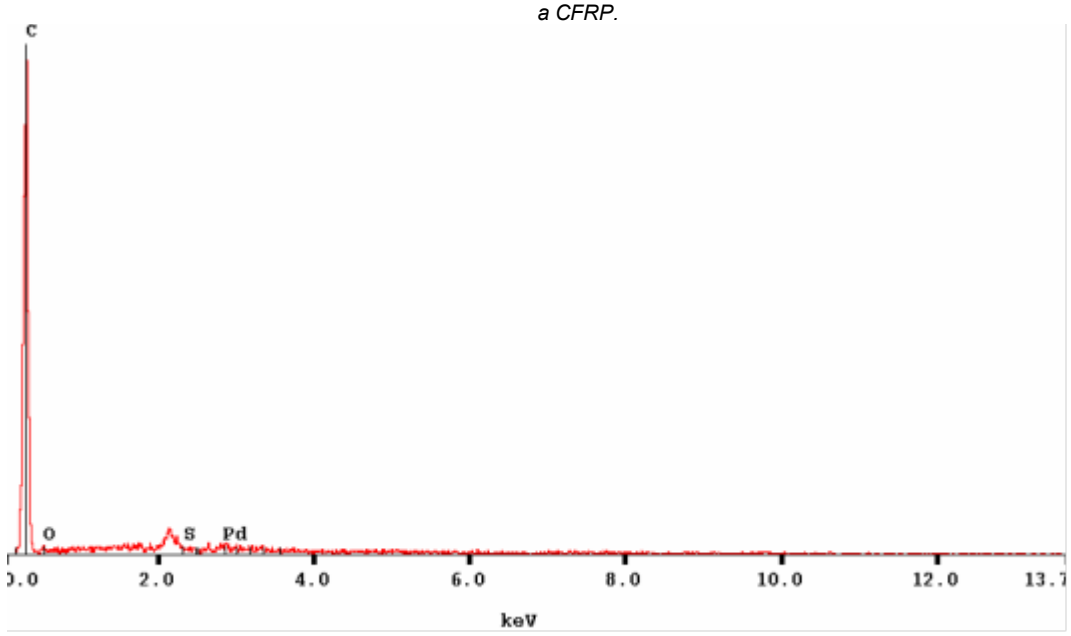

Fig. 9 - b) EDX analysis after CFRP pyrolysis followed by oxidation/ *Analiza EDX după piroliza urmată de oxidarea parțială a CFRP.*

3.1.2 Carbon Fiber Reinforced Plastic

Following the same approach, during the tests applied to waste CFRP it was found that during pyrolysis the mass loss reached only a 28% reported to the initial mass. It appears that the tested CFRP samples contain at least 70% of carbon fibers as reinforcing materials, which are stable in oxygen-free atmosphere at 700°C. During oxidation tests, the recorded mass loss ranged up to 100%, being coherent considering the CFRP contains only carbon-based compounds.

The mass loss and thermal ranges for CFRP during pyrolysis and pyrolysis followed by partial oxidation conditions are displayed in Figures 6 and 7. As the curves show, the polymer matrix became instable at 350°C and pursue a decomposition profile that end at 570°C. The characteristic SEM images captured for recovered fibers are presented in Figure 8.a), where unfinished decomposition of polymer matrix is revealed. Fibers are completely covered with polymer, proving that pyrolysis at 700°C is not a proper treatment for this type of polymer removal. As consequence, in the EDX spectrum (Figure 8.b)) large amounts of oxygen and sulphur are present.

Coupling the pyrolysis process with partial oxidation, induced an additional mass loss of 7 to 10% that led to individual fiber recovery, as it is visible in SEM images from Figure 9.a). Indeed, the EDX spectrum (Figure 9.b)) is showing the disappearance of oxygen and sulphur element. Nevertheless, rare and fine carbon deposits are still present on the recycled carbon fibers, which might limit their further uses.

3.2. Bench scale

In order to verify the thermal range of wastes decomposition and the yields of solid residues at a larger scale, a bench-scale installation was used that consists in a cylindrical steel reactor electrically heated, with a maximum installed power of 5kW. The vapours produced during pyrolysis process were condensed by metal condenser cooled with water. The liquid fraction was collected into a 1L glass flask immersed in ice bath, while the gaseous fraction was collected in Tedlar bags [21].

This is a fixed bed reactor, featured with multiple thermocouples system placed at different level inside the reactor. Being connected to a data

Table 2

Pyrolysis product yields at 800°C, for different power range
Randamentul produsilor de piroliza la 800°C, la diferite puteri ale cuptorului electric

Material	Oven power range	Pyrolysis products (%wt)		
		Solid Residue	Condensable	Gas
CFRP	25%	74.50	18.60 (liquid)	6.90
	50%	74.30	18.70 (liquid)	7.00
	100%	74.10	18.80 (liquid)	7.10
GFRP	25%	18.40	54.00 (liquid)	27.60
	50%	18.20	54.50 (liquid)	27.30
	100%	18.00	55.00 (liquid)	27.00

acquisition system, thermocouples allowed the development of thermal transfer study in the decomposing bed, as well as the temperature profile assessment inside the reactor during the thermochemical process.

In order to establish the yield of pyrolysis products, the liquid collected in the glass flask and the residual fibers remaining in the reactor after the experiment were weighting, while the gas yield was calculated by difference.

Experimental set-up limits: The mass sample was limited by waste density. Thus, the reactor couldn't be filled with more than 600(±5%)g of sample. Another limit is related to the condensation system, especially during the maximum range of degassing. As seen in the ATG curves, when the specific decomposition temperature is reached, the mass loss become intensive and so the corresponding amount of pyrolysis vapours need to be quickly condensed in the cooling system for an appropriate quantification of the yield of condensable and gaseous pyrolysis products.

The pyrolysis tests were carried out at 800°C (as reference temperature, which ensure 700°C inside the reactor), the residence time at this temperature was 10min and the variable parameter was the heating rate induced by the power range of the electrical heater. With this purpose, the experiments run at 3 different power range: 25% (corresponding to a measured heating rate of 7(±2)°C/min), 50% (measured heating rate of 15(±2)°C/min), and 100% (measured heating rate of 30(±3)°C/min) of maximum power. In Table 2 are presented the obtained yields of pyrolysis products.

It appears that the heating rate do not influence the decomposition behaviour in used experimental set-up. Compared to those obtained in TGA tests, the values of solid residues are slightly higher for CFRP, but significantly different for GFRP (28% of solid residue recovered after pyrolysis in TGA). This difference might come from the material nonuniformity which has increasing influence when cutting small pieces that can contain more or less polymer fraction, as it was the case for TGA.

4. Conclusions

This work adresed the topic of using thermochemical processing applied to waste carbon fiber reinforced plastics (CFRP) and glass fiber reinforced plastic (GFRP) with the aim of recovering the fibers. Working with simple pyrolysis and coupled pyrolysis / partial oxidation revealed a number of features that can influence the process managemnet in the pathway of obtining valuable recycled glass and carbon fibers. It was found that pyrolysis alone can be applied with limeted quality results only for GFRP, for CFRP being inefficient in removing the polymer from the material. Once the pyrolysis is coupled with partial oxidation process, SEM images showed that the carbon-based deposits produced during pyrolysis were completely removed through partial oxydation, and a smooth and clean fiber surface was obtained. Based on these results, it can be assumed that the oxidation step has favorable effect on the quality of the recovered fibers.

Tests on samples incorporating the recovered glass/carbon fibers need be done and compared to a controlled sample containing only virgin fibers.

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