3rd International Conference
"Advanced Composite Materials Engineering"
COMAT 2010
27- 29 October 2010, Brasov, Romania

# GLASS FIBRES RECOVERY FROM ORGANIC MATRIX COMPOSITES

**Violeta Popescu[1], George L. Popescu[1], Marioara Moldovan[2], Nicolaie Jumate[1]**
[1] Technical University of Cluj-Napoca, Cluj-Napoca, ROMANIA, violeta.popescu@chem.utcluj.ro
[2] Babeş-Bolyai University, "Raluca Ripan" Institute for Research in Chemistry, Cluj-Napoca, ROMANIA,

***Abstract:*** *This study presents the results obtained by our team regarding the recycling of glass fibber reinforced composites wastes. The materials were recycled by two step pyrolysis, in order to recover the glass fibers and to obtain a liquid fuel. Clean glass fibers were recovered after pyrolysis. The morphology of the fibber was studied by electron microscopy. The yield on liquid products depends on the composite type.*
***Keyword:*** *fibers, organic matrix composites, recycling, pyrolysis*

## 1. INTRODUCTION

Organic matrix composites (OMC) reinforced with fibers gains an important place in the market due to their improved mechanical properties comparing to plastic materials.
Related to composite materials recycling, investigations approached the following directions [1-3]:

- **Materials recycling –** aims the recycling of composite materials as filler or reinforcing materials for the obtaining of other composites.
- **Pyrolysis recycling** – aims both organic matrix and reinforcing materials recycling.
- **Energy recovery –** aims to use the energy content of polymeric composite matrix.

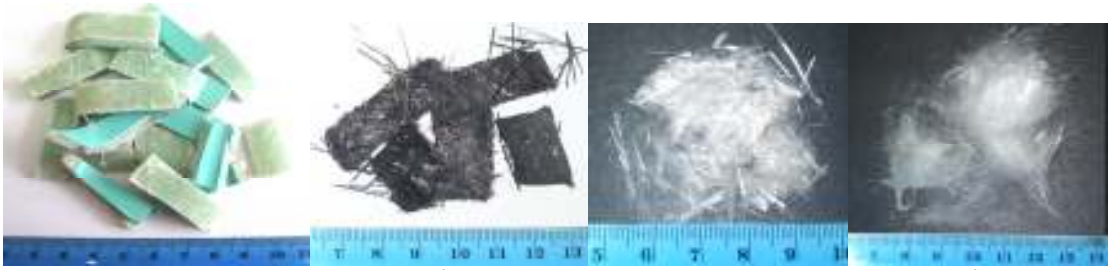
***Materials recycling***
A powder of composite material reinforced with glass fibers (GF) can be incorporated in a polystyrene matrix for the obtaining of composite materials sheets, processed subsequently by thermoforming methods [4]. Industrial waste of composites reinforced with Kevlar and graphite fibers can be milled and used as reinforcing materials for epoxy resin matrix of for polyurethane foams. Small fibers (under 0.5 mm) added in epoxy resin or polyurethane foam matrix (1%), determine an important improvement in mechanical properties of obtained materials in comparison with the properties of un-reinforced material.
Other methods involved selective dissolution [5,6] of matrix or hydrolysis processes applied in order to recover fibers, fillers and valuable materials from organic matrix.
The recycling assessing the recycling potential of glass fibres reinforced plastic (GRP) waste in concrete and cement composites was studied by Asokan et al [7]. The experimental results revealed that the mean compressive strength of concrete composites using 5%–50% GRP waste powder under water curing varied from 37 N/mm$^2$ to 19 N/mm$^2$. Increase in the concentration of GRP waste decreased the compressive strength. However, increase in curing duration (14–180 days) resulted in improving the compressive strength of concrete with 5% GRP application to 45.75 N/mm$^2$. Moreover, the density of concrete with 50% GRP waste was reduced by about 12% as compared to the control sample. The bending strength in terms of modules of rupture (MOR) of 12 mm thickness cement composites developed using 5% GRP waste fibre attained 16.5 N/mm$^2$ [7].
***Pyrolysis*** can be applied before or after composite materials milling. The recovered reinforcing materials can be used for the obtaining of fine powders used as fillers. The method can be applied especially in the case of automotive and aerospace industry waste that contains large quantities of fillers. For composites containing fibers, tissues, or valuable matrix resins the problem is to recover and recycle them in the most efficient way. Fuels or chemical reagents can be obtained and valuable reinforcing materials are released.
Pyrolysis was studied in order to recover fibers and to convert the organic matrix in row materials or fuels.
Adrian M. Cunliffe, Williams P.T. et. al. [8] has studied organic matrix composite pyrolysis in fixed bed reactor, at temperatures of 350-800°C. The organic matrix was made of polyesters, epoxy resins, polypropylene

reinforced with glass or carbon fibers. They sowed that the polymer matrix and pyrolysis temperature markedly influenced both the product mass balance and pyrolysis gas composition. At higher pyrolysis temperatures, the decomposition of calcium carbonate filler had a noticeable effect on the product yields and gas composition. The average molecular mass and mass range of the pyrolysis oils and waxes were dependent on the composite matrix. Decomposition of the various polymer matrices was generally a single stage process. However, composites with phenolic and epoxy resin matrices continued to lose mass steadily after polymer decomposition had ended. This may be related to carbonisation of the remaining solids.
The oil derived from pyrolysis had fuel properties similar to a petroleum-derived gas oil, in terms of viscosity, sulphur content and distillation range [9,10]. The authors mentioned above [8-10] recovered clean fibers and made a series of experiments related to possible uses of recovered fibers.
Amelia Torres et al [11] made a study related the composition liquid products obtained in the pyrolysis of fibre-glass polyester sheet moulding compound, using GC-MS chromatography. They concluded that concerning the effect of temperature on the pyrolysis process, no significant influence was observed over 400°C, neither in the pyrolysis yields nor in the characteristics of the liquid and gaseous products obtained. The most appropriate temperature range for recycling SMC by pyrolysis is 400–500°C, since no decomposition of the inorganic matter ($CaCO_3$) is produced, the decomposition of the organic matter is complete, and the same yields and types of products are obtained than at the higher temperatures, while less energy is required [11].
The same team [12] sowed that the yield of the liquid products obtained by pyrolysis of sheet moulding compound (SMC) of fibre-glass and ortho-phthalic polyester depend also on the particularities of the composites. In this case, the quantity of the solid residue was 72–82 wt%, gas yields of 6–12 wt% and liquid yields of 9–13 wt%. The pyrolysis liquids are a complex mixture of C5–C20 organic compounds, mainly aromatic and with numerous oxygenated compounds. They have high gross calorific values (34–37 MJ/kg) and are non-polluting liquid fuels. About 40% weight of such liquids could be used as petrol and the remaining 60% could be mixed with fuel oils. The gas fraction produced is very rich in CO and $CO_2$. Consequently, its gross calorific values are rather low (13.9–16.4 MJ $m^3$ N); however, it can have energy source to self-sustain the process [12].
Didier Perrin et al [13] elaborated a laboratory scale process of management of waste of composite materials from SMC, as reinforcing fillers for thermoplastic materials, including both mechanical and chemical processes. The fibrous part was increased by partial dissolution of calcium carbonate present in the crushed products SMC. Then, a process of partial solvolysis was developed aiming at strong increasing the interfacial mechanical properties by functionalising of SMC load incorporated into polypropylene/grafted maleic anhydride polypropylene. At this effect, they investigated a treatment with hot diethylenetriamine in order to create a functionalisation, after scission of the bond ester of unsaturated polyester, as bridging amino-succinimide. The effect of this recycling way by partial solvolysis was checked from the mechanical properties of the resulting reinforced PP/PPgma material: although a lower of Young modulus, better yield stress and especially resilience were observed [13].
Weirong Dang [14] made a study related to the use of nitric acid in the process of composite materials recycling. The matrix was decomposed in nitric acid solution, and then the decomposed product was repolymerized with original resin. Flexural strength of the recycled resin was higher than that of virgin resin until the content of the neutralized extract, which was available from degradation of epoxy resin, was not more than 30 wt% of the original resin. The reinforcement of glass fiber could be separated and recovered. The existence of the reinforcement did not affect decomposition the matrix [14].
Fluidized bed technology for recycling high-value glass fibers from nonmetal materials of waste Printed Circuit Boarsd (PCB) was investigated [15]. The thermoset resins in the nonmetal materials are decomposed in the temperature range from 400 to 600 °C. The GF are collected at high purity and recovery rate by the cyclone separators. Recycled glass fibres are analyzed by determination of their purity, morphology and surface chemical composition. They concluded that this novel technology for recycling GF from PCBs represents a promising way for recycling resources and resolving the environmental pollutions during recycling of waste PCBs.
**Energy recovery** involves composite materials incineration. For example, composite materials can be used in cement kilns. Organic matrix serves as fuel, while glass fibers enter into cement composition, without significantly influencing it's quality. A technological method that involves the incineration of composites in fluidized bed installations has been studied at Nottingham University [1].

## 2. EXPERIMENTAL DETAILS

Sheet moulding compounds (SMC) wastes from a local manufacturer were used for the experiments. The wastes consist on unsaturated polyester and glass fibres and 30 % calcium carbonate as filler.
A bench glass reactor was used for the pyrolysis experiment under air at atmospheric pressure. The pyrolysis products were collected in a weighted vessel in order to determine the yield of the pyrolysis. The temperature was increased in the reactor, until it reached 350 $^oC$.

Glass fibers reinforced composite materials were cut into pieces of about 1 $cm^2$. The fragments of composites were introduced into the reaction chamber. The decomposition took places with the formation of vapours that condensed and formed the liquid decomposition products. After the first step of pyrolysis, the organic matrix decomposed and the fibers remained covered with a carbonized organic material layer (fig. 1. b).
In order to remove the solid pyrolysis products from the surface of the glass fibres we applied two kinds of treatments. The both treatments involved the oxidation of the carbonaceous materials. The first one involved the oxidation of the products in air at elevated temperatures (700$^o$C) for 1/2 hours. After oxidation the glass fibber was washed in an ultrasonic bath using water and detergent in order to remove the oxidation products and the char from the surface of the fibers. Finally we obtained shiny clean fibers.



a b c d

**Figure 1:** Fragments of: a. organic matrix composites; b. OMC reinforced with glass fibber after first step of pyrolysis; c. recovered fibers from OMC by thermal treatment in two stages - before washing; d. recovered fibers from composite materials by thermal treatment in two stages - after washing;

The second treatment method involved the oxidation of the pyrolysis products at 550 $^o$C, for 2 hours. Lowering the temperature treatment the necessary time for the pyrolysis is longer (2 hours), but the fibers remains much cleaner after pyrolysis. It results a mixture of fibers (fig. 1.c) and powder of $CaCO_3$. After the fibers were washed into a ultrasonic bath, they look alike a glass wool (fig. 1.d).
SEM micrographs were recorded for the recovered fibers using a Philips XL 30 ESEM microscope.
The EDS spectra for the fibers after recovering were also recorded. An elemental quantitative analysis of the determined elements was made with a X-ray spectrometer, coupled to the electron microscope - Energy Dispersive Spectrometer (EDS), with a Si(Li) detector.

## 2. RESULTS AND DISCUSSIONS

### 2.1. The yield of the process

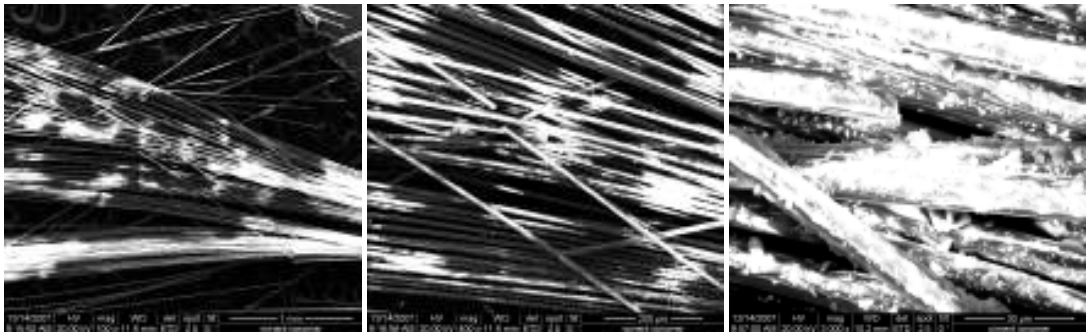
We calculated the yield of the process of pyrolysis in gaseous, liquid and solid residue. The yield in liquid products depends very much on the quantity of organic matrix in the composites. When subjected to pyrolysis industrial OMC composites cut from the edge of the panels, where the materials consists mainly on glass fibers and fillers, the yield in liquid products was very small (2,7 %), and he quantity of filler ($CaCO_3$ was important). Recycling SMC's containing higher content of organic matrix, the yield on liquid products vary between 27-36 %, gaseous products between 7-10 %, and glass fibers between 30 and 60 %. The results were not very reproducible because the concentration of organic matrix and of the glass was not homogenous in the waste.

### 2.2. Glass fibers recovery

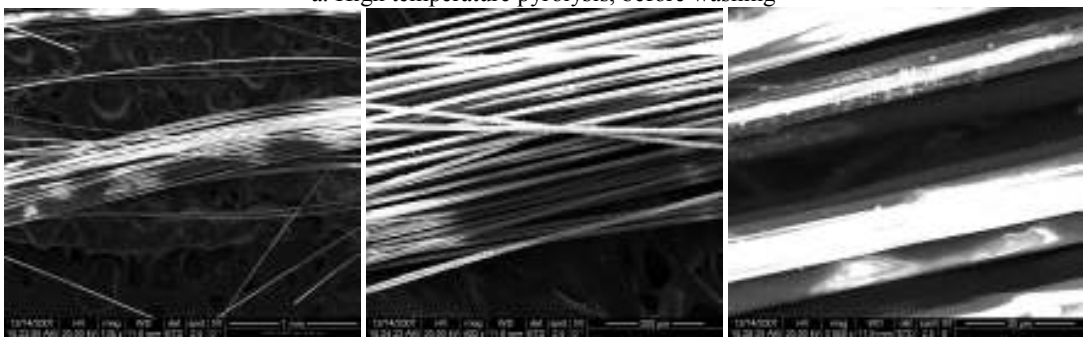
The fragments of SMC's before pyrolysis are presented in fig. 1 a. After the first step of pyrolysis we obtained fibers covered with a carbonized organic material layer (fig.1.b). We limited the increasing of the temperature of the decomposition in the first step because we wanted to avoid the formation of gaseous products. After the oxidative second step of pyrolysis we obtained the fibers presented in fig. 1.c. Washing glass fibers in an ultrasonic bath for removing a part of the remaining impurities we obtained shiny clean fibers (fig. 1.d).

### 2.3. Glass fibers characterization

At macroscopic level there are no differences between the fibers recovered at different temperatures. In order to underline the differences between the fibers obtained following the two methods, SEM micrographs were recorded. The obtained micrographs are presented in figure 2 and 3.



a. High temperature pyrolysis, before washing



b. Medium temperature pyrolysis before washing

**Figure 2.** SEM micrographs of the recycled fibers

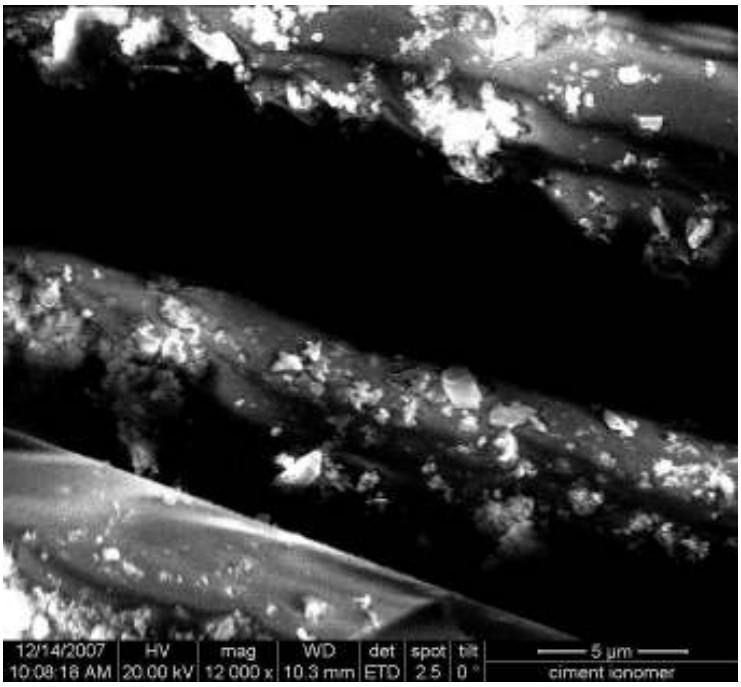



**Figure 3:** SEM micrographs of the recycled fibbers (high temperature pyrolysis)

SEM microscopy analysis revealed that at the surface of the fibers remained an important quantity of residual maters. The decreasing of the temperature and the increasing of the treatment time leads to a better removal of

the products resulted from the pyrolysis from the surface of the fibers. The remained materials from the surface of the fibers could be calcium carbonate or small peaces of glass fibers.
The surface of the fibers is rough, and the fibers suffered deformations when the temperature of pyrolysis was high. Fibers with rough surfaces were also obtained by Yanhong Zheng and co-authors [15]. They used a fluidized bad installation and their recovered fibers were damaged by the increasing of the temperature. They observed that the lower the fluidized bed temperature, the higher the uniformity surface of the RGF. In other words, the higher the fluidized bed temperature, the severer destroy to the surface of the RGF.
Static pyrolysis made by our team conducted to the same results. The surface of the fibers recycled in the second step at temperatures smaller than 600 $^{o}$C, is smoother than the surfaces of the fibers treated at higher temperatures (fig. 2).
In order to try to establish the nature of the particles from the surface of the fibers a EDS analysis was made, observing a washed sample of glass fibre. The results are presented in figure 4.
The surface of de examined fiber is very smooth, sowing that almost all organic phase has been decomposed. No deformations of the fibers have been observed. After washing in an ultrasonic bath, almost all the impurities from the fibers were removed.
The fibers have a very uniform distribution of the elements showing a very homogenous composition. More than that, the composition of the small impurity attached to the surface of the fibber is the same as the composition of the fibers, which mean that at least some of the impurities are formed from glass chips. Glass fibers contains beside silicon and oxygen, aluminium, magnesium, potassium and sodium. EDS spectra sown that the samples are covered with calcium and carbon. Calcium can come from the fillers based on $CaCO_3$ and the carbon traces remained from the decomposition of the organic matrix.

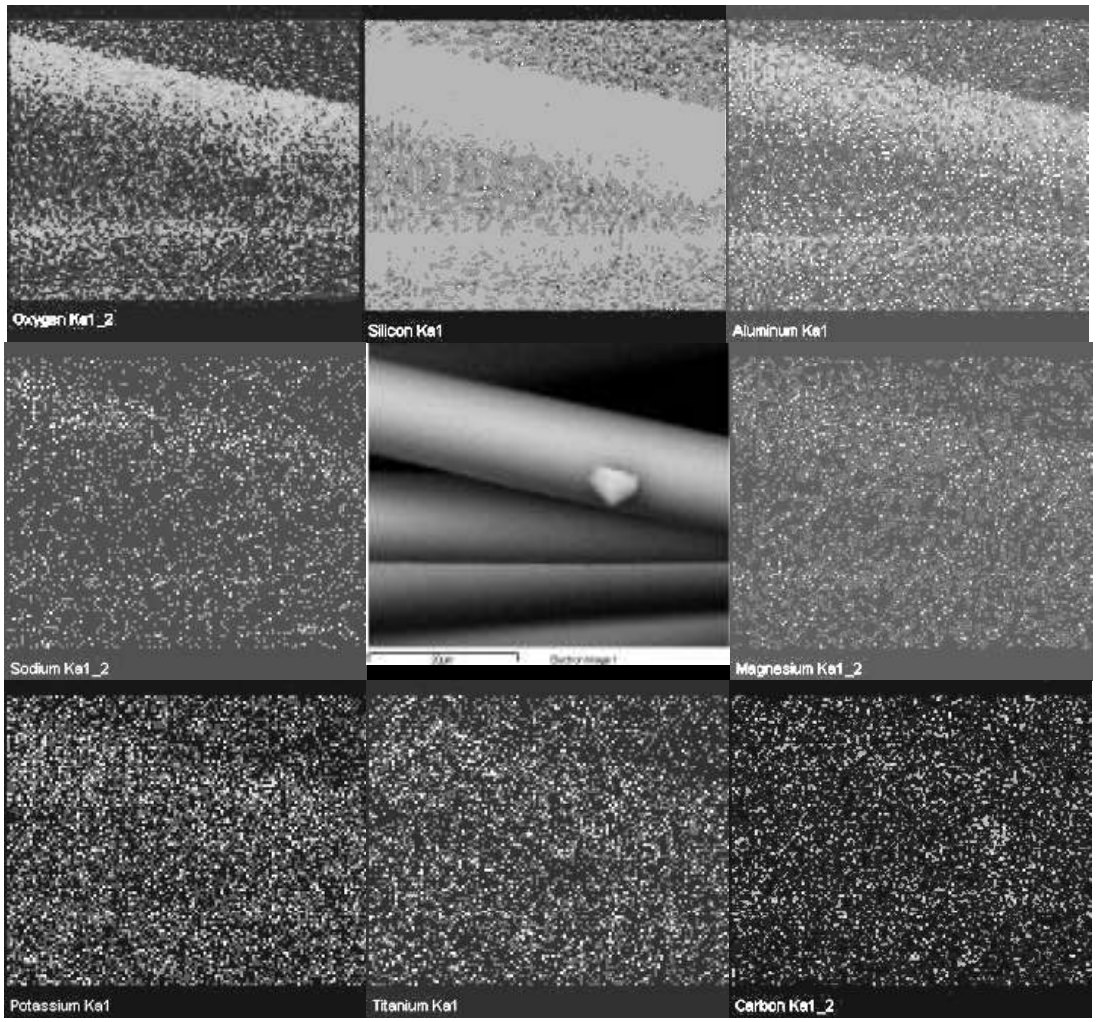



**Figure 4:** SEM micrograph and corresponding EDS elemental maps for oxygen, silicon, aluminum, sodium, magnesium, potassium, calcium, titanium, and carbon of washed glass fibers

## 3. CONCLUSIONS

Glass fibres reinforced plastic wastes can be successfully recycled leading to the recovery of oils with a complex content. The yield of liquid products depend on the type of composite waste varying from 2,7 to 37 %. In all studied cases clean glass fibers have been recovered following a two steep thermal decomposition process. In the first step the process took placed in the conditions of lack of oxygen, in order to limit the oxidation of the liquid products. The second step involved the decomposition of remained carbonous matters from the surface of the fibers in the presence of oxygen. When the second step was conducted at high temperatures, the obtained fibers suffered surface modifications and the obtained fibers were covered with small peaces of impurities. Reducing the temperature of the second step, the obtained fibers kept their smooth surfaces and the resulted materials contains smaller quantities of impurities. Further investigations are necessary in order to determine the properties of recycled glass fibers and to establish the composition of liquid degradation products.

## ACKNOWLEDGEMENT

The SMC wastes were assured by "S.C. Fibrex Co S.R.L", Crasna, Sălaj, Romania.

## REFERENCES

[1] Pickering S.J.: Recycling technologies for thermoset composite materials-current status, Composites Part A: Applied Science and Manufacturing, 37(8), 2006, p. 1206-1215, The 2nd International Conference: Advanced Polymer Composites for Structural Applications in Construction
[2] Skrifvars M.:, Nyström B.:, Material and Energy Recovery of Composite Waste by Incineration, SICOMP Technical Report TR 01-008, 2001.
[3] Boeing Environmental Technologies, 8, (4), 2003, http://www.boeingsuppliers.com/environmental /TechNotes/TechNotes2003-11.pdf
[4] Wilson Dru M.:, The Implementation of Recycled Thermoset Composites in Thermoforming Molds, Journal of Industrial Technology, 19 (2), 2003, p. 1-5.
[5] Papaspyrides C.D., Poulakis J.G., Arvanitopoulos C.D.: Recycling of glass fiber reinforced thermo-plastic composites. I. Ionomer and low density polyethylene based composites, Resources, Conservation and Recycling, 14 (2) 1995, p. 91-101,
[6] Zafeiropoulos N. E., Varelidis P. C., Papaspyrides C. D., Stern T., Marom G.: Characterisation of LDPE residual matrix deposited on glass fibres by a dissolution/reprecipitation recycling process, Composites Part A: Applied Science and Manufacturing, 30 (7), 1999, p. 831-838.
[7] Asokan P., Osmani M., Price A.D.F.:, Assessing the recycling potential of glass fibre reinforced plastic waste in concrete and cement composites, Journal of Cleaner Production, 17(9), 2009, p. 821-829.
[8] Cunliffe A.M., Jones N., Williams P.T.: Recycling of fibre-reinforced polymeric waste by pyrolysis: thermo-gravimetric and bench-scale investigations, J. Anal. Appl. Pyrolysis, 70, 2003, p. 315-338.
[9] Williams P. T., Cunliffe P. T., Jones N.: Recovery of value-added products from the pyrolytic recycling of glass-fibre-reinforced composite plastic waste, Journal of the Energy Institute, 78 (2), 2005 p. 51-61.
[10] Domínguez A., Blanco C. G., Barriocanal C., Alvarez R., Díez M. A.: Gas chromatographic study of the volatile products from co-pyrolysis of coal and polyethylene wastes, Journal of Cromatography A, 918 (1), 2001, p. 135-144
[11] Torres A., de Marco I., Caballero B.M., Laresgoiti M.F., Cabrero M.A., Chomona M.J.: GC-MS analysis of the liquid products obtained in the pyrolysis of fibre-glass polyester sheet moulding compound, Journal of Analytical and Applied Pyrolysis, 58–59, 2000, p. 189–203.
[12] Torresa A., de Marco I., Caballero B.M., Laresgoiti M.F., Legarretaa J.A., Cabreroa M.A., Gonzalez A., Chomon M.J., Gondra K.: Recycling by pyrolysis of thermoset composites: characteristics of the liquid and gaseous fuels obtained, Fuel, 79, 2000, p. 897–902.
[13] Perrin D, Guillermain C., Bergeret A., Lopez-Cuesta J.-M., Tersac G.: SMC composites waste management as reinforcing fillers in polypropylene by combination of mechanical and chemical recycling processes, J Mater. Sci., 41, 2006, p. 3593–3602,
[14] Dang W., Kubouchi M., Sembokuya H., Tsuda K.:, Chemical recycling of glass fiber reinforced epoxy resin cured with amine using nitric acid, Polymer, 46 (6), 2005, p. 1905-1912.
[15] Zheng Y., Shen Z, Ma S., Cai C., Zhao X., Xing Y., A novel approach to recycling of glass fibers from nonmetal materials of waste printed circuit boards, Journal of Hazardous Materials, 170 (2-3), 2009, p. 978-982.