INFLUENȚA MATERIALELOR SILICIOASE ASUPRA MODULULUI DE ELASTICITATE ŞI CONDUCTIVITĂȚII TERMICE ALE MATERIALELOR COMPOZITE POLIMERICE

INFLUENCE OF SILICEOUS MATERIALS ON THE ELASTICITY MODULUS AND THERMAL CONDUCTIVITY OF POLYMERIC COMPOSITE MATERIALS

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In the present work, polypropylene (PP) based composites filled with natural aluminosilicate materials were prepared. The volcanic tuff and kaolinite clay are used as filler in different proportions up to 15% by mass. PP composites filled with aluminosilicate materials were prepared using extrusion compounding and injection molding by dynamical melt processing.

The effects of filler content on the elasticity modulus and thermal conductivity of the composites were studied. Also, the morphology of the composites was evaluated by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).

The results showed that the elasticity modulus of composites improved with increasing the filler content. A better behavior is noticed in case of volcanic tuff using.

In lucrarea de față s-au preparat compozite pe bază de polipropilenă (PP) şi materiale alumino-silicatice naturale. Tuful vulcanic şi argila caolinitică au fost utilizate în diferite proporții, până la 15% din masă, ca material de umplutură. Compozitele pe bază de PP şi materiale aluminosilicatice au fost preparate utilizând procedeul de extrudare şi injecție prin prelucrare dinamică in topitură.

S-au studiat efectele conținutului de filler asupra modulului de elasticitate şi conductivității termice ale compozitelor. De asemenea, morfologia compozitelor a fost evaluată prin microscopie electronică de baleiaj (SEM) şi spectroscopie de raze X cu dispersia energiei (EDS).

Rezultatele au arătat că modulul de elasticitate al compozitelor s-a îmbunătățit cu creşterea conținutului de filer. O comportare mai bună s-a observat în cazul utilizării tufului vulcanic.

Keywords: *polypropylene, volcanic tuff, clay, elasticity modulus, thermal conductivity*

1. Introduction

In the last twenty years the interest for producing of polymeric composites with enhanced properties and reduced footprint on environment in comparison with those with neat polymer or with conventional micro- and macro-composites are increasing. Polymeric materials are reinforced with inorganic or organic fillers in order to improve the mechanical properties of the composite materials, extending their application areas and reducing the composite materials cost [1-8]. A few application examples of polymeric composites with filler are in packaging, automotive industry, aerospace and electronics industries or construction materials.

Clay and clay minerals such as montmorillonite, hectorite, saponite, kaolinite etc, were widely used as filler in rubber for many years mainly for reducing of polymer consumption and lowering the cost [2]. It is well known that mineral fillers increase the rigidity of the polymers, but they also decrease ductility and toughness. Some problems may arise concerning the morphology of composite, in fact the interaction at the polymer-filler interface, the homogeneity of filler distribution, the filler orientation in the case of filler anisometric particles, and the polymer-filler adhesion.

The most commonly used fillers for polypropylene (PP) composites are calcium carbonate, talc, glass fibers, mica, silica, wood flour and carbon nanotubes [4,5,9-15].Though there are studies regarding to the polymer - clay composites from micro- up to nano-size, very few of them are reported to the use of tuff in thermoplastic composites [16,17]. Therefore, our research study was carried out in order to determine the performance of volcanic tuff compared with clay – a very abundant phyllosilicate resource, in thermoplastics, in particular polypropylene composites. In this paper we give the preliminary

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results regarding to the elasticity modulus and thermal conductivity of PP- volcanic tuff and PP-clay composites and their morphology. Further, the properties of composites will be optimized in order to obtain thermal insulating biodegradable composite materials with mechanical characteristics similar to usual insulating materials (such as expanded or extruded polystyrene) and superior in terms of thermal (and sound) insulating and biochemical attack protection characteristics.

2. Experimental

2.1. Materials

In order to prepare the polymeric composites filled with silico-aluminate materials, the polypropylene (PP) and two natural rocks - volcanic tuff and clay respectively, are used.

PP homopolymer Moplen HP500N produced by LyondellBasell Polymers with a melt flow index of 12 g/10 min (230 °C/2.16 kg) and a density of 0.90 g/cm^3 was used as matrix for composite preparation. MA-PP Polybond 3200 from Crompton (USA) containing 1.0 wt% grafted maleic anhydride and with a density of 0.91 g/cm^3 and a melting point of 157 °C was used as a compatibilizing agent.

The volcanic tuff and clay were ground in a laboratory tubular ball mill. Their main characteristics evaluated by chemical, X-ray diffraction and particle size analyses are presented in Table 1.

Table 1

Characteristics of tuff and clay used
Caracteristicile tufului şi argilei utilizate

Characteristics *Caracteristici*	Volcanic tuff *Tuf vulcanic*	Clay *Argilă*
L.O.I. /P.C.,%	9.26	7.31
SiO_2, %	66.65	66.33
Al_2O_3, %	11.37	20.46
Fe_2O_3,%	1.60	1.91
CaO, %	3.23	1.11
MgO, %	0.92	0.30
Na_2O, %	3.73	0.12
K_2O, %	2.58	1.55
SO_3, %	0.24	0.03
Cl^-, %	0.006	nd.
Main minerals identified / *Principalele minerale identificate*	Clinoptilolite - heulandite / *Clinoptilolit-heulandit*; +++ Kaolinite/*caolinit* + Quartz/*cuarț* +	Kaolinite/ *Caolinit* ++ Quartz/*cuarț* ++
Particle size distribution D_{50}/ *Distribuția granulometrică a particolelor* $D_{50,\ \mu m}$	21.8	5.6

nd - not determined

Volcanic tuff contains as main mineral clinoptilolite, $(Na,K,Ca)_{2\text{-}3}Al_3(Al,Si)_2Si_{13}O_{36}\cdot 12H_2O$ / heulandite, $(Ca,Na)_{2\text{-}3}Al_3(Al,Si)_2Si_{13}O_{36}\cdot 12H_2O$, from zeolites group while clay contains kaolinite, $Al_4[(OH)_8|Si_4O_{10}]$ from phyllosilicates group, both groups belonging of layered silicate minerals. Clay contains particle smaller than tuff, even if both materials have had the same 90 micron sieve residue after grinding (R_{oo9} = 6.0-6.1%).

2.2. Obtaining of composite materials

PP based composites with different content of filler (0, 5, 10 and 15%) were prepared in laboratory conditions. All compositions contain 5% compatibilizing agent MA-PP.

The composites were obtained on DSE 20 Brabender co-rotating twin screw extruder, at 220 rpm and 160±5°C. The components were prior mixed in a rotating mixer for 15 minutes and the obtained mixture was introduced in the hopper feed of extruder. Extruder temperature profile from hopper to die was 180, 185, 190, 200, 210, and 220°C, respectively. The extruded filaments passed through the water cooling bath and were granulated with a Brabender Pelletizer. Pelletized composites were conditioned in an oven for 4 h at 80 °C and injection molded (Engel 23/40) to obtain standard specimens for mechanical characterization. The injection temperature was set to 220 °C, the temperature of the mold being maintained at 50 °C.

2.3 Methods used

The mineralogical compounds from tuff and clay were identified by XRD method using a Siemens D5000 diffractometer (CuKα, λ=1.5405Å), while the particle size distribution was carried out with a Malvern Mastersizer 2000E laser granulometer.

The effects of filler content on the elasticity modulus, thermal conductivity and morphology of the composites were studied.

Young's modulus was determined according to ISO 527 at a crosshead speed of 2 mm/min, using an Instron 3382 Universal Testing Machine and five dog-bone shaped specimens from each sample.

Measurements of thermal conductivity were done on samples with dimensions of 150x150x5 mm prepared by compression molding at the working temperature of 180 ± 5 ° C, pressure of 300 kgf / cm^2 and preheating and pressing time of 4-8 min. / 2 min. The thermal conductivity was determined using a hot plate apparatus type EP500 manufactured by Lambda – Messtechnik,

The morphology of the composites was evaluated by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) using Quanta Inspect F scanning electron microscope with FEG (field emission gun) and X-Ray Energy Dispersive Spectroscopy with 133 eV resolution at MnK. The fractured surfaces of the test samples were coated with a gold thin layer.

3. Results and discussions

3.1 Influence of the filler on elasticity modulus

The relationship between the elasticity modulus of neat PP and the amount of the filler added into PP matrix is shown in Figure 1.

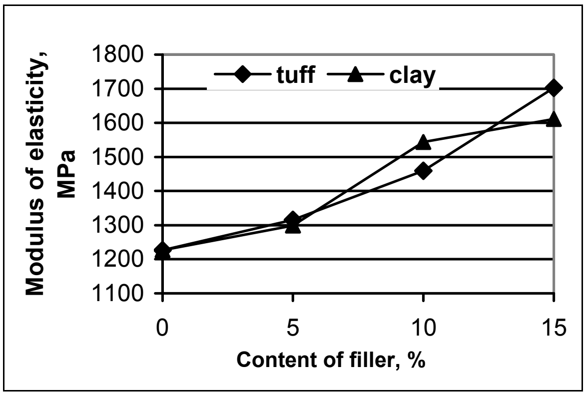


Fig. 1- Elasticity modulus of PP based composites depending on type and amount of filler/ *Modulul de elasticitate al compozitelor pe bază de PP în funcție de tipul şi proporția fillerului.*

The elasticity modulus of composites increases as the filler content increases from 0 to 15 wt%. The maximum value is observed at the 15% tuff. In comparison with the reference sample (only PP) the elasticity modulus increased by 38.7% for the composite filled with 15% tuff and by 31.3% for 15% clay respectively. A positive influence on elasticity modulus was reported in the work [5] in case of PP composites filled with talc, $Mg_3Si_4O_{10}$ $(OH)_2$ - a mineral which belongs to silicate group also. A possible explanation for the favorable effect exerted by both fillers on the Young's modulus of composites based on PP could be their homogenous distribution in PP matrix and a good adhesion between the two phases.

3.2. Influence of the filler on thermal conductivity

Thermal conductivity of samples was measured for the compositions including 5% and 15% filler, at two temperatures: 10°C and 25°C respectively. The variation of the thermal conductivity of PP filled with tuff and clay in comparison with neat PP is shown in Figure 2. It is evidenced that the thermal conductivity of PP based composites depends on the type and content of the filler.

It is noticed that the clay has a very little influence on the thermal conductivity; compared to the sample containing only PP (considered as reference; λ=100%), the limits of variation of PP samples filled with clay ranging between 99.75-101.61% at 10 °C and 99.63 -100.22% at 25 °C respectively.

The influence of tuff on thermal conductivity is more pronounced Thus, adding of low amount of tuff in PP matrix have as result an increasing of the thermal conductivity with approximately 4% compared with neat PP, for the both temperatures. Increase of tuff's amount to 15% determines an improvement of the insulating capacity of the PP-tuff composites, the relative thermal conductivity being in the range of 94.7 – 97.8% depending on the temperature. So, the using of large amount of tuff has beneficial effect on the insulating properties of the composites in comparison with clay.

3.3. Influence of the filler on composite's morphology

The filler dispersion and the morphology of the compositions based on PP filled with 5 and 15 wt.% filler were studied in comparison with the pure PP by SEM analyses (Figs. 3 and 4 a,c,e and g) and by energy dispersive X-ray spectroscopy (EDS). The EDS spectra of the polymer composites and their elemental composition are presented in Figures 4 b,d,f and h.

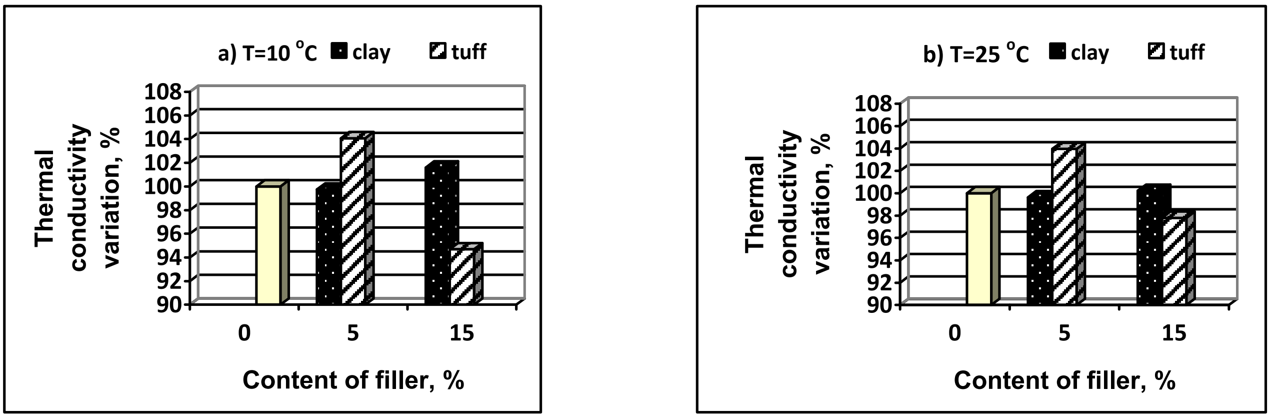
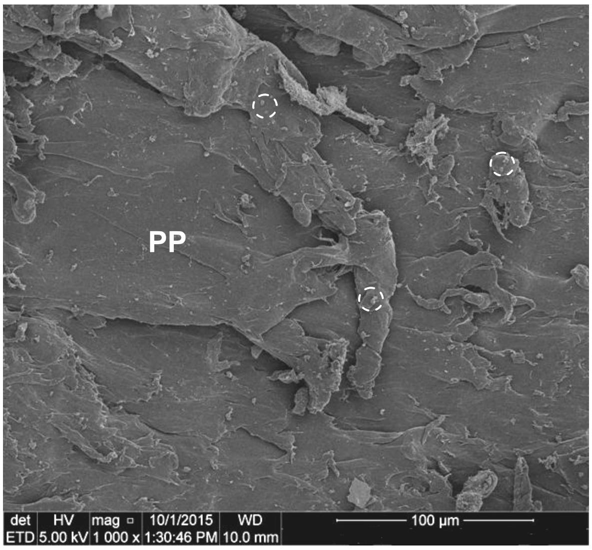
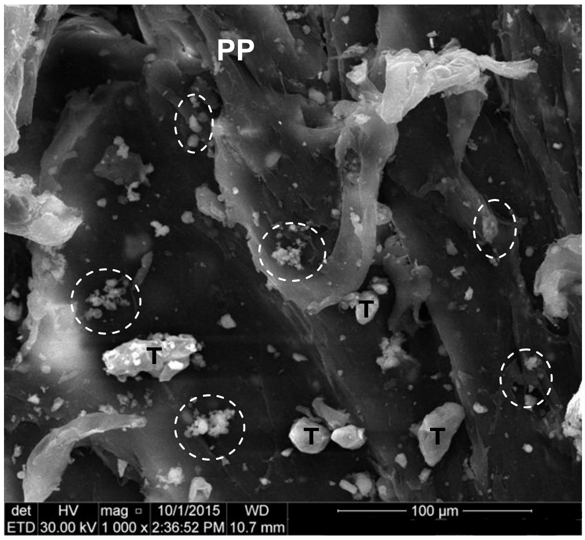


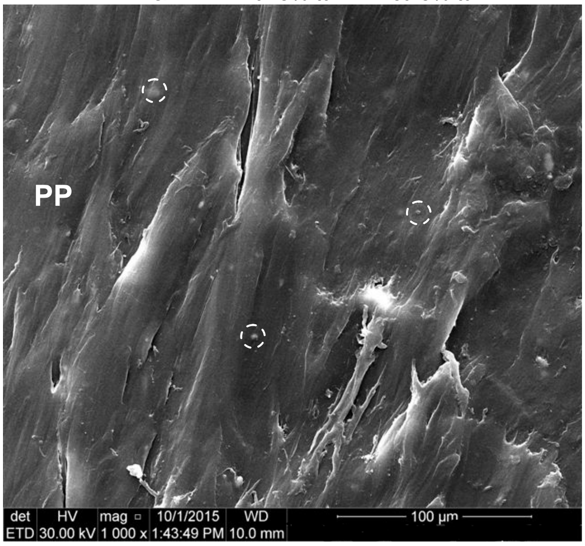
Fig. 2 - Thermal conductivity variation of PP based composites depending on type and amount of filler at: a) 10 °C; b) 25°C/ *Variația conductivității termice a compozitelor pe bază de PP în funcție de tipul şi proporția filerului, la: a) 10 °C; b) 25°C.*



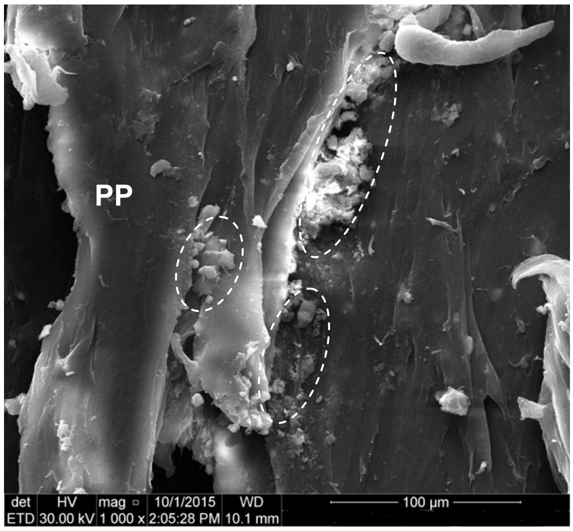
a. PP with 5% tuff/ PP cu 5% tuf



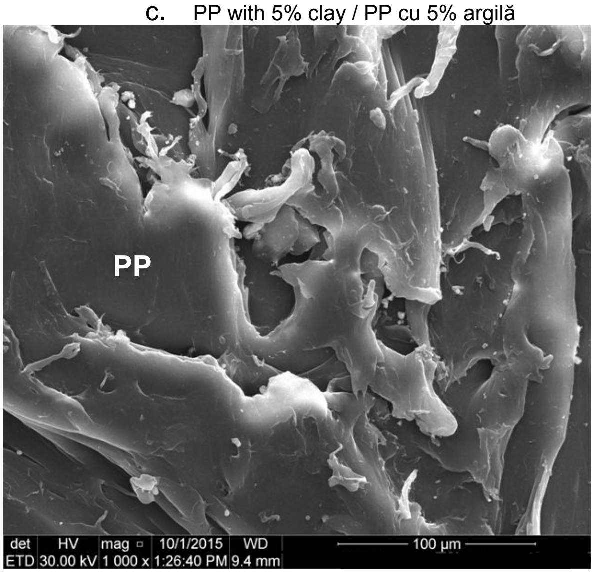
b. PP with 15% tuff / PP cu 15% tuf



c. PP with 5% clay / PP cu 5% argilă



d. PP with 15%clay / PP cu 15% argilă



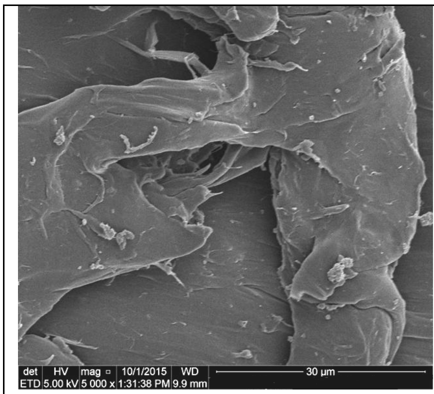
e. Neat PP / PP

Fig. 3 – SEM micrographs (x 1000) of the PP based composites (a-d) and of neat PP (e);with dashed line are shown the areas that contain filler / *Micrografii SEM (x 1000) ale compozitelor pe bază de PP (a-d) şi ale matricei PP (e); cu linie punctată sunt indicate zonele care conțin filer.*

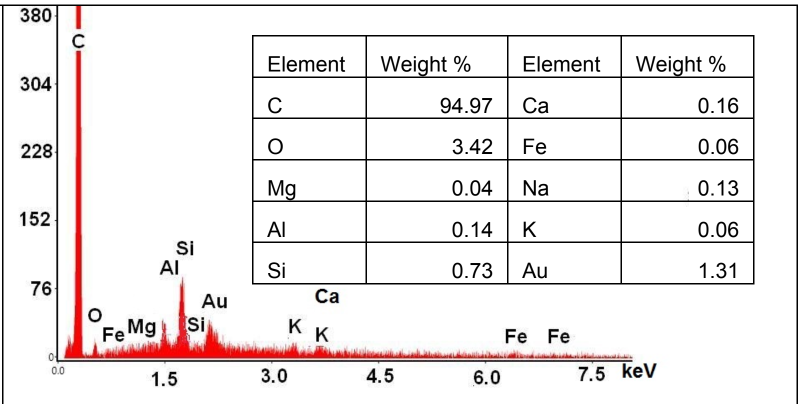
The fractured surfaces of a PP composite with 5% tuff (Fig. 3a) and 5% clay (Fig. 3c) show that filler is finely dispersed and embedded into the polymer matrix, which indicates a homogeneous distribution of tuff and clay in the PP matrix and a good adhesion between the two phases. Increasing of filler content to 15% led to agglomerations of tuff (Fig. 3b), but uniformly distributed into PP matrix. In the case of PP - kaolinite clay composite (Fig. 3d) agglomerates seems to be distributed preferentially after one direction into PP matrix. The agglomerations of clay are smaller than those of tuff, in according with its particle size distributions. The information obtained by SEM /EDS analyses could explain the improvement in properties of PP-tuff composite.

EDS' spectra of the PP-filler composites confirm the presence of carbon as main component. Elemental analyses revealed amounts of 94.97 - 94.08 wt. % for PP composites filled with 5% tuff or clay, and of 83.36% - 86.48% for PP composites filled with 15% tuff and clay respectively.

These values are enough closely of the imposed /prescribed components' dosages which demonstrates that the method used for preparation of PP-tuff / PP-clay composites was appropriate. The other identified elements (Si, Al, Mg, alkali) proceed from tuff and clay composition respectively. In the PP-15% tuff composite were detected small quantities of Cu and Zn, additional to chemical analyses.

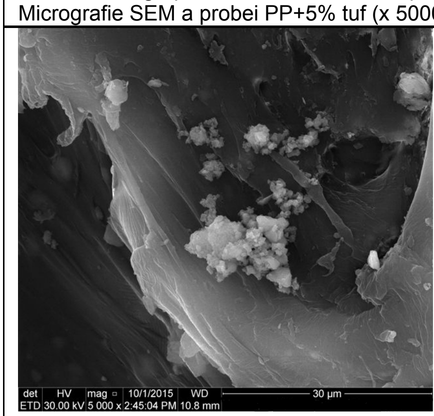


a.SEM micrograph of PP+ 5% tuff sample / Micrografie SEM a probei PP+5% tuf (x 5000)

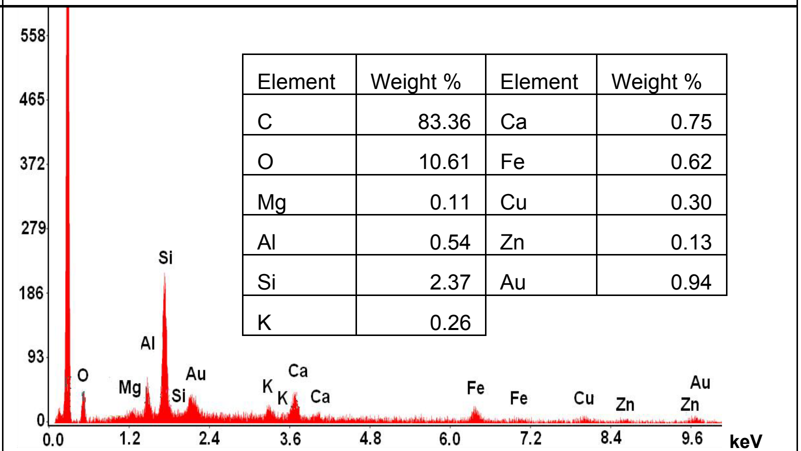


Element	Weight %	Element	Weight %
C	94.97	Ca	0.16
O	3.42	Fe	0.06
Mg	0.04	Na	0.13
Al	0.14	K	0.06
Si	0.73	Au	1.31

b.EDS spectrum of PP+5% tuff sample / Spectul EDS al probei PP+5% tuf

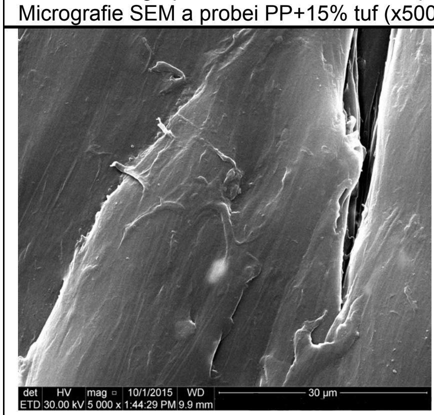


c.SEM micrograph of PP+15% tuff sample / Micrografie SEM a probei PP+15% tuf (x5000)

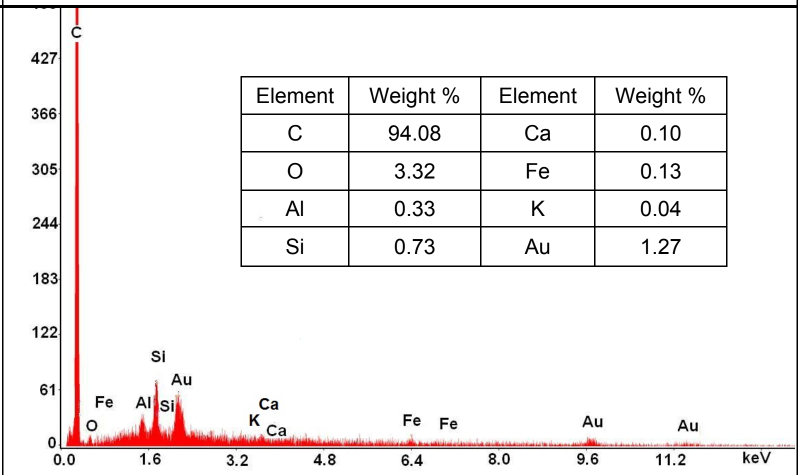


Element	Weight %	Element	Weight %
C	83.36	Ca	0.75
O	10.61	Fe	0.62
Mg	0.11	Cu	0.30
Al	0.54	Zn	0.13
Si	2.37	Au	0.94
K	0.26		

d.EDS spectrum of PP+5% tuff sample / Spectul EDS al probei PP+15% tuf



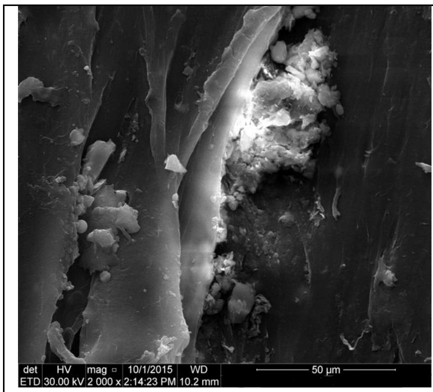
e.SEM micrograph of PP+5% clay sample / Micrografie SEM a probei PP+5% argilă(x 5000)



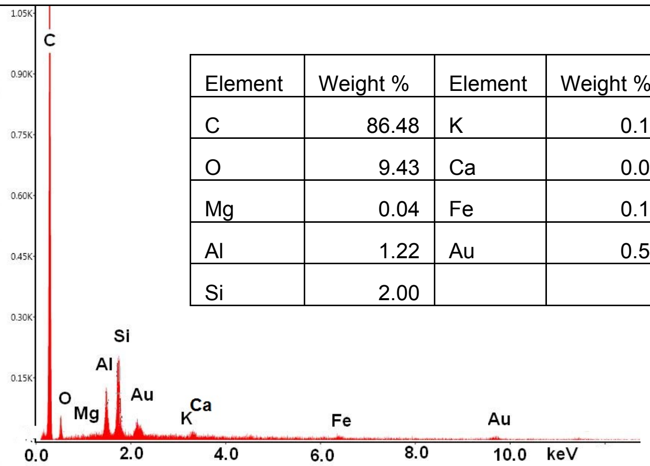
Element	Weight %	Element	Weight %
C	94.08	Ca	0.10
O	3.32	Fe	0.13
Al	0.33	K	0.04
Si	0.73	Au	1.27

f.EDS spectrum of PP+5% clay sample / Spectrul EDS al probei PP+5% argilă

Fig. 4 continues on next page



g.SEM micrograph of PP+ 15% clay sample / Micrografie SEM a probei PP+15% argilă(x 2000)



Element	Weight %	Element	Weight %
C	86.48	K	0.10
O	9.43	Ca	0.08
Mg	0.04	Fe	0.11
Al	1.22	Au	0.54
Si	2.00		

h.EDS spectrum of PP+15% clay sample/ Spectrul EDS al probei PP+15% argilă

Fig. 4 - SEM micrographs and EDS spectra of PP-tuff (a – d) and PP-clay (e – h) composites / *Micrografiile SEM şi spectrele EDS ale compozitelor PP-tuf (a – d) şi PP-argila (e – h).*

4. Conclusions

Based on the experimental data obtained in this research it can draw the following conclusions:

- Elasticity modulus of PP composites increases with increasing of the filler amount; the volcanic tuff exerts a stronger effect than clay, growth being situated in range of 7.2 – 38.7% compared with 5.9-31.3%.
- The influence of filler on the thermal conductivity is quite different. Adding of the small amount of tuff in PP matrix has as result a slight increasing of the thermal conductivity with approximately 4% while the higher amount determines a diminish of thermal conductivity, therefore an improvement in insulating capacity of composites. The clay practically exerts no influence on thermal conductivity, for the proportion up to 15%.
- The SEM analyses showed a homogeneous distribution of tuff and clay into the PP matrix and a good adhesion between the two phases. EDS spectra combined with elemental analyses of the composites showed a good correlation between the prescribed and real composition of composites and that the method of obtaining is properly.
- By choosing of amount and type of filler it can be modeled the properties of composite materials towards increasing of the elasticity modulus and insulation capacity of the composite materials based on PP matrix. The use of volcanic tuff in amount of 15% leads to the best thermal and mechanical properties of the PP based composite.
- Cheap fillers like volcanic tuff and kaolinite clay can be effectively used as good reinforcements for PP matrix.

Further research will be conducted for optimization of the PP-filler properties and obtaining of thermal insulating biodegradable composite materials.

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MANIFESTĂRI ŞTIINȚIFICE / SCIENTIFIC EVENTS

SOCIETY OF GLASS
Diary 2016

29 Feb - 4th March

CelSian – NCNG International Glass Technology Course for the Glass Industry in the UK

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Sheffield, Society of Glass Technology/British Glass Building
http://www.glasstrend.nl/web/events-CelSian-NCNG-glass-technology-course-29feb-4march-2016.php
Contact 'Neil Simpson' <neilsimpsonfsgt@btinternet.com>; 'Elize Harmelink' <elize.harmelink@celsian.nl>

16–19 March
Fensterbau/Frontale 2016, Nürnberg, Germany.
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The Chinese Ceramics Society, No.11, Sanlihe Road, Beijing, China.
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25–29 May
Recent Advances in Glass and Ceramics Conservation, ICOM-CC Glass and Ceramics Working Group Interim Meeting,
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Professor Kazimierz Pawlak, The Eugeniusz Geppert Academy of Art and Design,
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ul. Traugutta 19/21, 50-416 Wrocław, Poland. Email icom@asp.wroc.pl Web www.asp.wroc.pl/ICOM_ASP

17–22 May
Tenth World Biomaterials Congress, Montreal, Canada.
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