

## Multifunctional composites and nanocomposites with applications in the aerospace industry

Ion DINCA<sup>1</sup>, Adriana STEFAN<sup>1</sup>, Ana STAN<sup>1</sup>, Sorina GAMAN<sup>1</sup>,  
Lavinia GAVRILA-FLORESCU<sup>2</sup>, Dan DONESCU<sup>3</sup>, Zina VULUGA<sup>3</sup>, Liviu DUMITRACHE<sup>3</sup>,  
Gabriel PRODAN<sup>4</sup>

<sup>1</sup> National Institute for Aerospace Research “Elie Carafoli”, Iuliu Maniu 220 Bd., Bucharest, Romania, [dincaion@incas.ro](mailto:dincaion@incas.ro), [dincaion@yahoo.com](mailto:dincaion@yahoo.com)

<sup>2</sup> National Institute for Lasers, Plasma and Radiation Physics, P.O. Box MG-36, Bucharest, Romania,

<sup>3</sup> Institute of Chemical Research, 202 Splaiul Independentei, CP 15-159, 76250, Bucharest, Romania,

<sup>4</sup> Ovidius University of Constanta, 124 Mamaia Bd., P.O. Box 8600, Constanta, Romania

DOI: 10.13111/2066-8201.2009.1.1.8

### Abstract

*Polymer nanocomposites (PNCs) ,namely, nanoparticles dispersed in a polymer matrix, have garnered academic and industrial interest since 1990.*

*This is due to the very attractive properties of nanostructured fillers, as carbon nanotubes, laser synthesized nanocarbon and layered silicates; PNCs do not expand the performance space of traditional filled polymers, but introduce new properties, low volume additions (1÷5 %) of nanoparticles such as carbon nanotubes and montmorillonite providing properties and enhancements comparable to those achieved by conventional loadings (15-40%) of traditional fillers [1].*

*Most important, tough, are value –added such as reduced permeability, flame retardant, increased resistance to oxidation and ablation. Also, the effect of carbon nanotubes on grain boundary sliding in zirconia polycrystals as re- reentry shield, or thermal barrier [2]represents a matter of interest.*

*Multifunctional composites are materials with carbon fibre or glass fibre as reinforcing networking in nanoadditivated polymer matrix.*

*In aerospace technique these may be antistatic, antilightning, anti radar protectors, as paints, laminates and as sandwich structure. Though the most important application of nanocomposites is their usability in the engineered structural composites.*

*The work presents a partial synthesis of researches performed in this field by the consortium INCAS, INFLPR, ICECHIM, Ovidius University within the CEEX Programme 2005.*

### 1. Introduction

The attention payed to the nanocomposites and nanotechnologies is a direct consequence of the synthesis, in 1985 (Smalley and Kroto) of fullerene (as the third existential form of pure carbon after diamond and graphite), stable and structurally ordered.

The discovery of the carbon nanotubes (Sumio Iijima-1991) developed the interest for the nanocomposites.

The carbon nanotubes may be suggestively presented as cylinders made of graphene sheets (hexagonal graphitic crystals) convoluted in one or more layers, opened or closed at the edges.

The essential characteristics of carbon nanotubes are the following:

- The tensile strength is 100 times greater than steel
- The electrical conductivity is analogous to Copper

- The thermal conductivity is equal to diamante’s
- They may be used as semiconductors
- They may be used for hydrogen or methanol storage to be employed as fuel cell.
- They can be used as antistatic, anti lighting and antiradar additives for aerospace industry

The restrictions regarding the use of carbon nanotubes in performing the advanced structural composites are:

- Long rods and tissues made of carbon nanotubes haven’t been obtained until now
- The use of catalysts in the making process of carbon nanotubes generates impurities in the carbon nanotubes sample.

The second type of additives used for nanomaterials, the nanoclays, is of interest because of their tixotropic characteristics, as fillers to attenuate the air permeability of tyres and fuel tank,

as a replacement for talc powder and for dioxide of titanium. Their characteristics may be used in the vehicle and aerospace industry.

The tensile strength, the elasticity modulus and the flame retardance of composites are increased due to the nanoclays fillers.

Toyota was the first society which commercialized vehicles with nanocomposites parts. Toyota Nylon Clay Hybrid (NCH-6) was the first commercialized nanocomposite material provided by Okada and co-worker in 1980.

One of the restrictions related to the use of the layered silicates is represented by their compatibilization with the resin matrix [3].

Polymer nanocomposite materials are novel alternatives to traditional composites and bulk materials in many applications due to their multifunctional properties, unique structure, and large surface area of nanoscale fillers. Among these attributes, excess surface area differentiates the nanoscale fillers from their macroscale counterparts and provides an additional mechanical reinforcement mechanism through modifications to the matrix material surrounding the nanofiller.

The characteristics of traditional and nanoscale fillers are presented in table no. 1.

Table no. 1. Characteristics of traditional and nanoscale fillers: shape, size, properties, dimensions and uses [1]

	APPROXIMATE SHAPE	SMALLEST DIMENSION (NM)	ASPECT RATIO	ELASTIC MODULUS (GPA)	ELECTRICAL CONDUCTIVITY (S/CM)	THERMAL CONDUCTIVITY (W/M*K)
<b>Traditional fillers</b>						
Carbon black	Agglomerate of spheres	10-100	1-5	-	10-100	0.1-0.4
Carbon fibre	rods	5000-20000	10-50	300-800	0.1-10	100-1000
Carbon graphite	plate	250-500	15-50	500-600	1-10	100-500
E-glass	rod	10000-20000	20-30	75	-	-
Mineral: CaCO <sub>3</sub>	sphere	45-70	~ 1	35	-	3-5
Mineral:silica	Agglomerate of spheres	8000-30000	5-10	30-200	-	1-10
Mineral: talc, china clay	platelet	5000-20000	5-10	1-70	-	1-10
<b>Nanoscale fillers</b>						
Carbon nanofiber	rod	50-100	50-200	500	700-1000	10-20
Carbon MWNTs	rod	5-50	100-10000	1000	500-10000	100-1000
Carbon SWNTs	rod	0.6-1.8	100-10000	1500	1000-10000	1000
Aluminosilicate nanoclay	plate	1-10	50-1000	200-250	-	1-10
Nano-TiO <sub>2</sub>	sphere	10-40	~ 1	230000	10 <sup>-11</sup> -10 <sup>-12</sup>	12
Nano-Al <sub>2</sub> O <sub>3</sub>	sphere	300	~ 1	50	10 <sup>-14</sup>	20-30

The characteristics of nanocarbon and nanoclays fillers may provide new and improved materials with applications in the aerospace industry [5], [6].

The main objective of the work is the study of two categories of materials:

- a. Epoxy resin additives with nanoclays, carbon nanotubes or with laser synthesized carbon black;
- b. Composites with the nanoadditivated matrix reinforced with glass or carbon fibre

Preliminary results suggest that some of these addition agents lead to samples of

nanocomposites with significant improvement of their aimed properties.

## 2. Experiments

### 2.1. Materials

The matrix is represented by Ropoxid P 401 (R), a liquid epoxy resin type diglycidyl ether of bisphenol A modified with 10% hardener TETA1 (Triethylenetetramine), provided by SC Policolor SA Bucharest. The polymeric matrix is filled with 3 types of additives. One of the nanostructured filler is the carbon nanopowder obtained by laser-

induced pyrolysis of hydrocarbon-based mixture of  $C_2H_2/SF_6$ ,  $C_2H_2/C_2H_4$ ,  $C_6H_6/C_2H_4$ . The composites with carbon nanopowder are compared to the composites filled with carbon nanotubes (singlewall and multiwall carbon nanotubes obtained from Shenzhen Nano-Technologies Port Co -China) or to nanoclays. Two types of organically modified montmorillonite have been used: one with methyl tallow bis-2-hydroxyethyl ammonium chloride, Cloisite 30B and the other with methyl dihydrogenated tallow ammonium sulfate, Cloisite 93A, purchased from Southern Clay Products; the tallow composition is: fat acids with ~65%  $C_{18}$ ; ~30%  $C_{16}$ ; ~5%  $C_{14}$ . The silicate was dried for 4 hours at 80°C before utilization.

The filled epoxy matrix is reinforced with carbon fibre tissue 3K (three thousand filaments) having a thickness of 250  $\mu m$  and 193  $g/cm^2$  or with glass fibre of 240  $\mu m$ .

## 2.2. Methods and Instrumentation

To evaluate the effects of the nanoadditives, composites with the same matrix and different type of nanostructured fillers were prepared and characterized. The nanofillers were dispersed into the polymer matrix using the ultrasonication method. With Bandelin Sonopuls instrument (using a 2000 Watt power) different quantities of each nanofiller has been dispersed for 30 minutes. The nanoadditivated epoxy resin is cured with the TETA1 Hardner. The curing takes place at room temperature during 24 hours. 7 days after samples preparation they are mechanically tested with Instron 4301. Notice that the curing process of prepared samples is considerable accelerated in a microwave furnace (2.45 GHz, 130 W).

The shape and the size of the nanoparticles were observed by High Resolution Transmission Electron Microscopy (HRTEM) coupled with selected area electron diffraction (SAED), on Philips CM120ST instrument.

## 3. Results and discussions

The preliminary results suggest that there is a close relation between the improved characteristics of the obtained nanocomposites and filler's properties. The properties of a composite are greatly influenced by the size scale of its component phases and the degree of mixing between them. Depending on the nature of the components employed (layered silicate, carbon-based nanomaterials, and polymer matrix) and the

method of preparation, significant differences in composite properties may be obtained [4].

Usually the wear resistance of polymer increases when they are filled with nanoadditives which are bonded with the matrix. The tribological tests refer to the determination of the friction coefficient and nanomaterial gravimetric wear conjugated with the metallic or nonmetallic materials of samples from the friction process.

Given the exceptional mechanical properties and low densities associated with typical nanoreinforcements, nanocomposites may result in strength and stiffness weight ratios unachievable with traditional composite materials, offering substantial weight savings for weight –critical applications. The mechanical tests refer to the determination of the tensile strength, elasticity modulus and the Shore hardness.

The TEM images of the nanoadditivated resin relieve a good dispersion of MWCNTs , SWCNTs and nanoclays, but a dissatisfactory dispersion of nanocarbon.

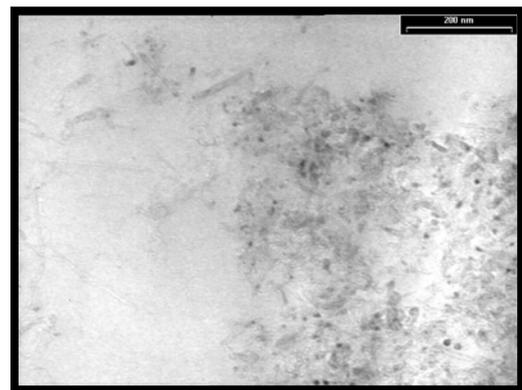
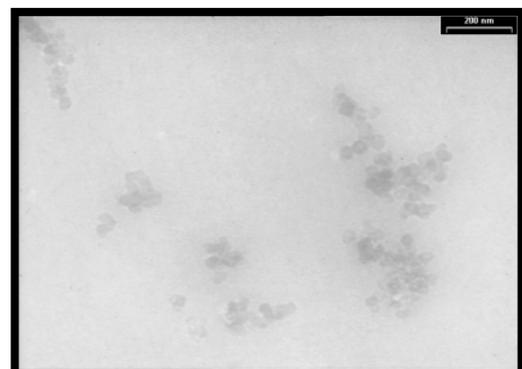


Fig.1. Single wall carbon nanotubes



b)

Fig.2. 15 nm carbon nanoparticle groups dispersed into the polymer matrix dispersed into the matrix

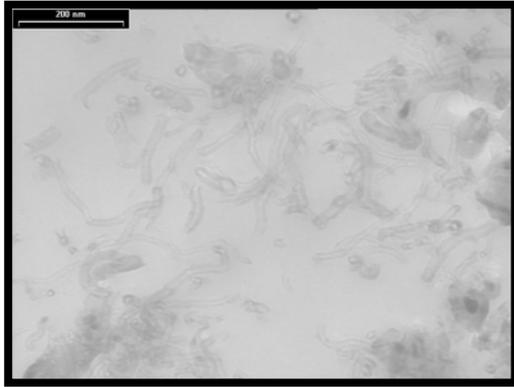


Fig. 3 TEM detail- the length

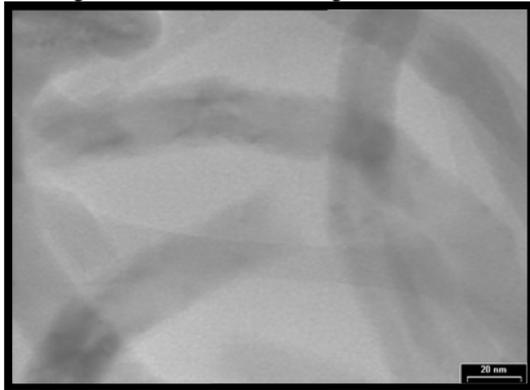


Fig.4. TEM detail- the tubular structure of carbon nanotubes and the crystalline areas-the dark spots on the walls

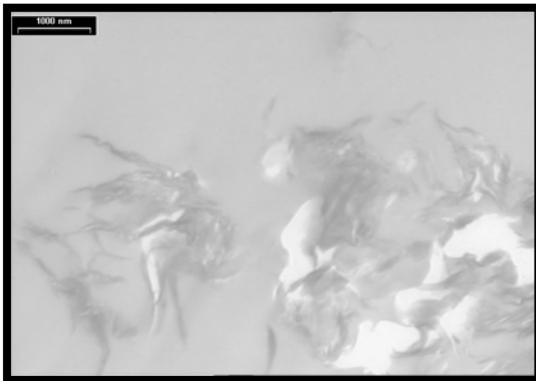


Fig. 5. TEM image: polymer – nanoclay Cloisite 93A

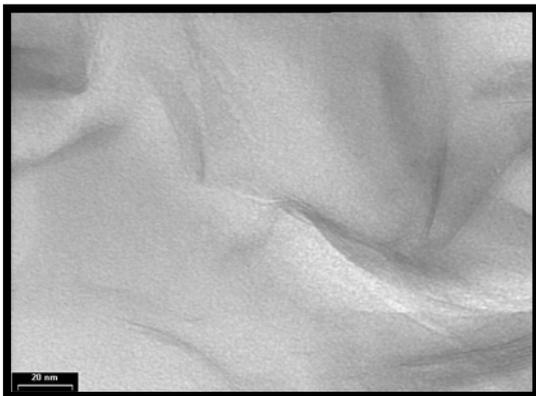


Fig.6. Exfoliated nanoclay Cloisite 30B

The tensile strength of the epoxy matrix increases with the addition of nanofillers. The composites containing nanocarbon presented low values of tensile strength compared to the epoxy matrix.

The strong adhesion between the polymer and filler with uniform dispersion of the organosilicate in the polymer matrix is reflected in the increase of the modulus of elasticity.

Table no.2 there presents the thermo-mechanical results of the prepared samples.

Table no. 2. Thermo-mechanical tests for the nanoadditivated matrix

No	The material	Tensile strength MPa	Shore Hardness	Thermal stability °C
1	P 401	95	75	50
2	P401 + 2% Montmorillonite 30B	102.5	83	56
3	P 401 + 2% Montmorillonite 93A	92.2	83	56
4	P 401 + 2% C2H2/C2H4	115	81	59
5	P 401 + 2% C2H2/SF6	85 – 90	79	56
6	P 401 + 2% C6H6/C2H2	86	79	56
7	P 401 + 2% MWCNTs –China	121.8	85	59
8	P 401 + 2% SWCNTs – China	96	77	55
9	P 401 + 2% MWCNTs -Greece	98	77	55
11	P401+2% C2H4/C6H6/N2O	120	83	57

Where:

- P 401 –is the epoxy resin
- C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>/SF<sub>6</sub>, C<sub>6</sub>H<sub>6</sub>/C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>/C<sub>6</sub>H<sub>6</sub>/N<sub>2</sub>O –are laser synthesized nanocarbon particles (INFLPR)
- MWCNTs- are multiwall carbon nanotubes
- SWCNTs – are single wall carbon nanotubes

Table no. 3. The elasticity modulus of the nanoadditivated matrix

No	The material	Modulus of elasticity x 10 <sup>4</sup>
1	P401	2.8
2	P 401 + 2% MWNTs	3.42
3	P 401 + 2% C2H2/C2H4	3.60
4	P401 + 2% Montmorillonite 30B	3.1
5	P 401 + 2% C2H4/C6H6/N2O	3.6

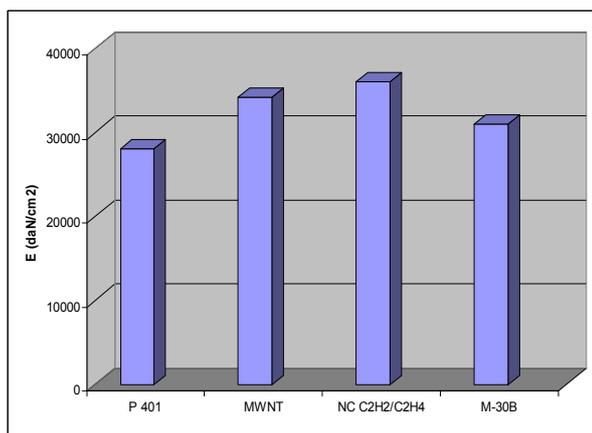


Fig. 7. Modulus of elasticity epoxy resin P401 + nanostructured additives

The systems epoxy resin – MWCNTs-China and epoxy resin- nanocarbon had better thermo-mechanical properties than the simple matrix.

The system P 401-MWCNTs had a 121.8 MPa tensile strength and the epoxy resin P401 had a 90÷100 MPa tensile strength.

Also the system epoxy – montmorillonite had better thermo-mechanical properties compared to the resin. As for the shore hardness and the thermal stability no relevant results were obtained .

The nanoadditivated matrix is used to prepare the carbon fibre or glass fibre reinforced composites. The samples are made of 11 tissue plies impregnated with the additivated matrix. The thermo-mechanical properties of the composite depend on the efficient dispersion of the nanoadditive into the polymeric matrix and on the efficient impregnation of the tissue plies.

The tensile strength of the nanoadditivated composites is lower than the strength of the non-additivated composite. The elasticity modulus increases with the addition of different types of nanofillers.

The thermo-mechanical results of the carbon from the glass fibre reinforced composites are presented in table no. 4.

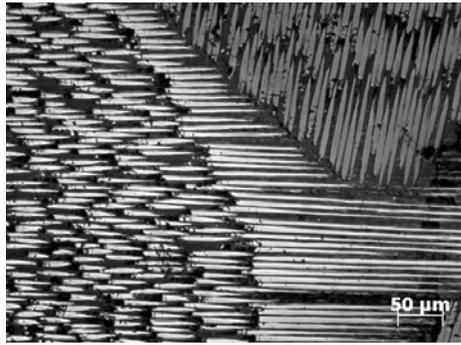
Table no. 4 The thermo-mechanical results of the carbon from glass fibre reinforced composites

No.	The material	Tensile strength MPa	Modulus of Elasticity MPa	Shore Hardness	Thermal Stability 0 C	Friction coefficient
1	Epoxy resin P401	95	2.8 x10 <sup>4</sup>	75	55	0.2
2	CF/P401	638	1.1 x10 <sup>4</sup>	86	130	0.132
3	GF/P401	416	2.3 x10 <sup>3</sup>	83	129	0.25
4	CF/P401+MWCNTs-functionalized(2%)	490.7	1.38 x10 <sup>4</sup>	87	131	0.134
5	CF/P401+MWCNTs	490	1.38 x10 <sup>4</sup>	87	136	0.134
6	CF/P401+SWCNTs	480	1.38 x10 <sup>4</sup>	86	128	0.130
7	CF/P401+carbon nanofibres	430	1.28 x10 <sup>4</sup>	85	135	0.130
8	CF/P401+nanocarbon (C2-H23-/C2H4)	650.6	1.36 x10 <sup>4</sup>	88	138	0.130
9	CF/P401+nanocarbon(C2-H23-/C6H6)	599	1.3 x10 <sup>4</sup>	88	137	0.130
10	CF/P401+Montmorilonit	440	-	87	130	0.143
11	GF/P401+Montmorilonit	366	-	86	120	0.22
12	GF/ P401+ MWNTs-functionalized	391.4	-	85	120	0.19

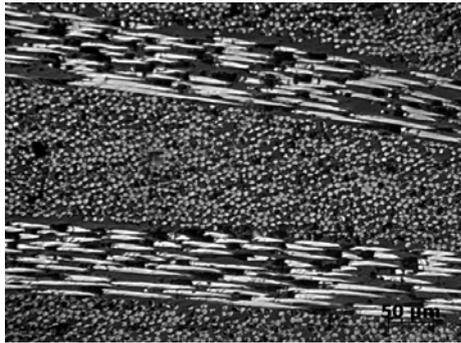
Where:

- CF –is carbon fabric
- GF- is glass fabric
- nanocarbon(C2-H23-/C2H4) – are laser synthesized nanocarbon particles (INFLPR)
- nanocarbon(C2-H23-/C6H6)- are laser synthesized nanocarbon particles (INFLPR)
- MWCNTs-functionalized – are multiwall carbon nanotubes functionalized with “-OH” and “-OOH” groups

The microstructural images of the carbon reinforced composites are presented in figures 8, 9.

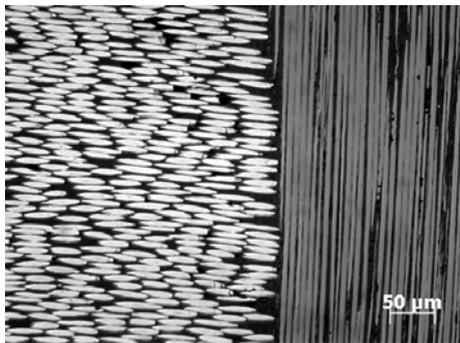


Front image\_200x

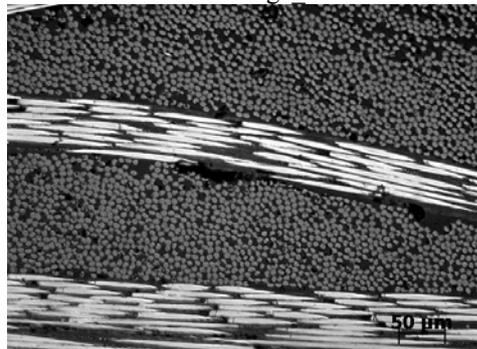


Cross section\_200x

Fig. 8. The sample carbon fibre/ non-additivated matrix (200x)



Front image 200x



Cross section\_200x

Fig.9. The sample carbon fibre/ nanoadditivated matrix (200x)

All the nanocomposites CF/epoxy resin present improved mechanical properties beside the systems epoxy resin-nanoadditives

The most notable effects can be observed at the Shore Hardness and at the modulus of elasticity (a boost of 25%÷30%)

The tensile strengths for the samples with nanoadditivated matrix were inferior to those with non-additivated matrix, excepting the nanocomposite CF/P401 + nanocarbon (C<sub>2</sub>H<sub>2</sub>-/C<sub>2</sub>H<sub>4</sub>).

#### 4. Conclusions

The nanoparticles are fillers that improve some functional properties of polymers, but they cannot be reinforcement structures like the carbon or glass fibre. The development of threads and tissues made of carbon nanotubes may represent a great evolution in the scientific area.

The thermo-mechanical (10-15%) and tribological properties of nanocomposites are improved due to proportions until 2% of nanoadditives. Adding more than 2% nanoparticles the rheological properties of the polymers are deteriorated: the viscosity increase from 1800 MPa\*s until 4000-5000 MPa\*s.

The nanocomposites researches will be developed following up the achievement of multifunctional composites and nanocomposites with improved antistatic, anti lightning and antiradar properties, applied in the aerospace and transportation industry.

#### REFERENCES

- [1] KAREN I. WINEY AND RICHARD A. VAIA - *Polymer nanocomposites* (MRS Bulletin, vol. 32 April 2007)
- [2] MAREN DARAKTCHIEV and all. - *Effects of carbon nanotubes on grain boundary sliding in zirconia polycrystals* (Advanced Materials, June 2004)
- [3] E. CHIFU - *Chimie coloidală* ( Ed Didactica si Pedagogica, 1969)
- [4] PARK C, PARK O, LIM J, KIM H - *"The Fabrication of Syndiotactic Polystyrene/ Organophilic Clay Nanocomposites and Their Properties"*, Polymer 42; 2001: 7465-7475
- [5] L GAVRILA-FLORESCU, I MORJAN, E POPOVICI, I SANDU, I VOICU, I. DINCA A STEFAN,, L DUMITRACHE, C NISTOR, V STEFAN, S SERBAN, D DONESCU - *"Laser synthesized carbon nanopowders for nanoscale reinforced hybride composites"* ,Materials Science & Engineering (Elsevier Science Publisher) C27 (2007) 1010-1014
- [6] I. DINCA, A. STEFAN, C. SERGHIE, L. DUMITRACHE, Z. VULUGA, D. DONESCU, A. DRAGOMIRESCU, G. PRODAN, V. CIUPINA, L. GAVRILA-FLORESCU, E. POPOVICI, I. SANDU - *"Hybrid polymer composites reinforced by layered silicate and laser synthesized nanocarbons"*, Applied surface science, (Elsevier Science Publisher), vol. 254, nr 4.