

# DEVELOPMENTS IN LASER SYNTHESIS OF NANOSCALE CARBONS FOR POLYMER-BASED COMPOSITES.

*Lavinia Gavrilă-Florescu<sup>1\*</sup>, Eugeniu Vasile<sup>2</sup>, Liviu Dumitrache<sup>4</sup>, Ana Stan<sup>3</sup>, Raluca Ianchis<sup>4</sup>, Ion Sandu<sup>1</sup>, Ruxandra Birjega<sup>1</sup>*

<sup>1</sup> National Institute for Lasers, Plasma and Radiation Physics, P.O.Box MG-36, 077125 Bucharest, Romania

<sup>2</sup> METAV, 16-18 Zapada Meilor St., 71529 Bucharest, Romania

<sup>3</sup> National Institute for Aerospace Research, 220 Iuliu Maniu Bd., Bucharest, Romania

<sup>4</sup> National Institute of Research and Development for Chemistry and Petrochemistry - ICECHIM, 202 Spl. Independentei, 060021 Bucharest

## Introduction

The perfection of structure of composite materials increases with decreasing dimensions of component particles and their applicability depends on how well the components' properties can be manipulated. Due to its particular characteristics, carbon nanostructures are nowadays one of the additives most widely used for numerous composite combinations. Synthesis of nanostructured materials using laser as energy source is an unconventional modern and versatile method which, capitalizing very particular characteristics of laser radiation, presents tempting technological features [1]. The method proved its ability for producing carbon nanopowders with controlled size and morphology [2].

Enabling carbon materials improves their functional properties and the efforts are concentrated on the direction of bringing these materials into a system that can interfere in naturally with the surrounding matrix. It became a usual practice to adapt the filler's surface in the view of a special application [3]

## Experimental

The synthesis method of laser-induced pyrolysis [4] uses as precursors hydrocarbons with a high content of C/mole, either in resonant processes (ethylene, butadiene) or non-resonant ones (acetylene, benzene), when the negligible radiation's absorption by the precursors requires the addition of an energy transfer gas, which can either react or interfere. The method allows obtaining carbon nanoparticles with different morphologies and a successful functionalization with reactive functional groups could be achieved in-situ by controlling the gas mixture composition and appropriate experimental parameters.

The flow and composition of the reactive gases were changed as well as the laser power density and working pressure. Total flows up to 400 sccm were chosen for the reactive gas mixture; pressure was varied in the range 450–

950 mbar and the laser power from 500 to 900 W (power densities from ~ 4000 to 7000 W/cm<sup>2</sup> - for a laser beam of 4 mm diameter).

The powder characteristics were investigated by electron microscopy (TEM coupled with EDX and/or SAED, HREM), electron energy loss spectroscopy (EELS), X-ray diffraction (XRD) spectroscopy and Raman spectrometry. The complementary data regarding the particles' size and aggregation were obtained by Dynamic Light Scattering (DLS) investigations. The exhaust gases collected downstream the reaction chamber in an IR cell and/or liquid nitrogen trap were analyzed by Raman and FTIR spectrometry.

The development of composite materials was fulfilled by incorporating different laser-synthesized carbon nanopowder into domestic epoxy resin type Ropoxid P401. Additionally, this nano-scale reinforcement was also used in conjunction with micro-scale structures like carbon fibers.

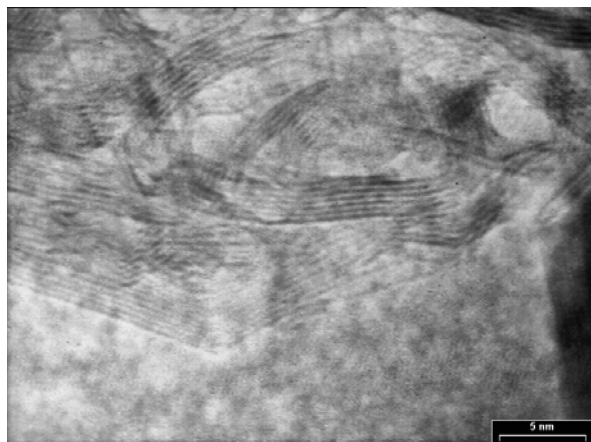
## Results and discussions

The morphology of carbon nanopowders and the chemical properties of their surfaces depend on gas mixture composition and experimental parameters; consequently, different behaviour of carbon nanopowders used for epoxy-based composites was observed. Uniform dispersion is difficult because carbon nanoparticles agglomerate. In this respect, their chemical functionalization constitutes an efficient means of improving dispersion in the polymer matrix.

Laser synthesized carbon nanopowders are formed by very fine and almost round particles, with a size having a narrow range log-normal distribution. Depending on experimental parameters and particularly on gas composition, carbon nanoparticles have different morphologies and their size lies in the field of 10 and 50 nm. High resolution electron transmission microscopy and dynamic light scattering investigations revealed their tendency to form aggregates of several hundreds of nanometers.

The addition of an oxidizer in the reactive gas mixture leads to the fullerene-like structure. The increased chemical activity of such a nanocarbon, due to the presence of active localized conjugated double bonds in fullerene molecules as well as to dangling bonds or other active sites like >C=O, -OH, -COOH revealed by XPS or FTIR investigations, evidenced, for example, a beneficial effect on the polymer matrix alone regarding the modulus of elasticity: from 2500 MPa for the pure epoxy polymer matrix to 3250 MPa for epoxy /2.5% nanocarbon (fullerene-like).

Laser-induced pyrolysis of pure hydrocarbons leads to carbon nanopowders with a turbostratic structure. The negligible absorption of laser radiation by some of precursors (e.g. acetylene) requires an energy transfer agent like sulphur hexafluoride that could decompose and release fluorine and sulphur, which could interfere in system and modify the powder morphology [2].



**Fig.1.** HREM image of a sample synthesized from  $C_2H_2/SF_6$  with a  $(C/F)_{at}$  ratio = 3

These nanocarbons proved to be more reactive due to acid groups able to react both with epoxy groups of the polymer and amine groups of the hardener; as the  $SF_6$  concentration decreases, chemical reactivity diminishes and structures are characterized by randomly distributed graphene ribbons (Figure 1). The effect proved to be in close connection with  $SF_6$  concentration. In this case it is supposed that curing effect of the composite material could be controlled experimentally and the more frequent graphene bands could enhance its mechanical properties.

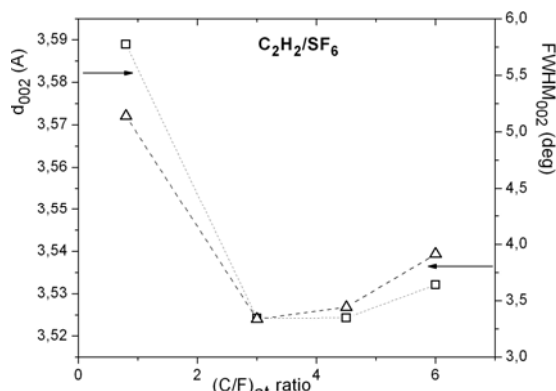
The salient features of the exploratory samples synthesized from  $C_2H_2/SF_6$  with various  $(C/F)_{at}$  ratio and  $C_2H_4/SF_6$  gas mixtures are presented in Table 1. The relatively larger values for particles' dimension,  $d$ , and the high of stacked graphene layers,  $L_c$ , forming a BSU (Basic Structural Unit) as well as the dimensions of the formed graphene layers,  $L_a$ , are observed in the case of  $C_2H_2/SF_6$  samples with  $(C/F)_{at} = 3$  ( $C_2H_2/SF_6:9/1$ )<sub>vol</sub> and 4.5 ( $C_2H_2/SF_6:13.3/1$ )<sub>vol</sub>.

**Table 1. Experimental Data of Samples from Hydrocarbon/ $SF_6$  with Different  $(C/F)_{at}$  Ratio**

Sample	$C_2H_2/SF_6$				$C_2H_4/SF_6$
	0.8	3	4.5	6	
$(C/F)_{at}$	0.8	3	4.5	6	3
$d$ [nm]	24	27	29	31	31
$D$ [nm]	390	650	680	560	-
$L_a$ [Å]	33.5	36	37	36	20
$d_{002}$ [Å]	3.59	3.524	3.525	3.536	3.648
$L_c$ [Å]	16	24	23	21	22
$V_{BSU}$	14,09	24,42	24,72	21,36	6,91

This is confirmed by XRD investigations which show for these samples higher intensities for (002) peaks (XRD pattern not shown), lower distance between graphene layers,  $d_{002}$ , and full width at half maximum, FWHM (Figure 2). The BSU volume, deriving from  $L_a$  and  $L_c$  values, is larger

in both of these two cases, and the process of agglomeration, evaluated through the aggregates' dimension  $D$ , is more accentuated, suggesting that carbon nanoparticles could be linked through the formed graphene ribbons.



**Fig. 2.** The variation of  $d_{002}$  and  $FWHM_{002}$  values for samples obtained from  $C_2H_2/SF_6$  gas mixtures with different  $C/F$  at. ratio

Compared to a composite epoxy (R401)/2% nanocarbon ( $C_6H_6/C_2H_4/N_2O$ ) with a bending strength of 118 MPa and tensile modulus of 13.7 GPa, a composite obtained from R401 epoxy resin with 2% nanocarbon ( $C_2H_2/SF_6$ ;  $C/F = 3$ ) showed a bending strength of 121 MPa and a tensile modulus of 15.2 GPa.

## Conclusions

The morphology of laser synthesized carbon nanoparticles is related to gas composition and experimental parameters. The properties of composites are affected by those of the addition material. Preliminary results showed that carbon nanopowders characterized by a higher content of graphene ribbons lead to composites with similar results of those obtained with fullerene-like nanocarbons.

## Acknowledgement

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