JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 12, No. 3, March 2010, p. 715 - 717

Laser-synthesized carbon black for polymer-based composites reinforced by carbon fibres

L. GAVRILA FLORESCU, I. DINCA[a], E. POPOVICI, L. DUMITRACHE[b], R. IANCHIS[b], A. STAN[a], I. SANDU, A. STEFAN[a], Z. VULUGA[b], D. DONESCU[b], I. VOICU[*]
National Institute for Lasers, Plasma and Radiation Physics, P.O. Box MG-36, Bucharest, Romania
[a]*National Institute for Aerospatial Research, 220 Iuliu Maniu Bd., Bucharest, Romania*
[b]*Institute of Chemical Research, 202 Splaiul Independentei, CP 15-159, 76250 Bucharest, Romania*

Composites with epoxy matrix reinforced by carbon fibres and laser synthesized carbon nanostructures as additives were prepared and characterized. All the composites with a matrix of epoxy resin/carbon fibres revealed superior mechanical characteristics and the positive effect of carbon nanoadditives on the epoxy/carbon fibre matrix were observed both in mechanical characteristics and water resistance.

(Received June 23, 2009; accepted October 13, 2009)

Keywords: Laser, pyrolysis, Composite, Carbon nanostructures

1. Introduction

By combining properties from the parent constituents into a single material, low amounts of nanoscale fillers in polymer-based composites could have a dramatic increasing effect upon their resultant characteristics, particularly quantum size effects, where the normal bulk electronic structure is replaced by a series of discrete, electronic levels and surface/interface induced effects, as the result of the enormously increased specific surface. This provides an opportunity for multifunctionality and tailoring properties [1]. Carbon nanopowders are now some of the most used additives and their applicability is depending on the possibility to modulate their properties. In the frame of the effort to make the material interface to naturally interact with the surrounding matter, the final goal is to understand the role of filler modifications as a vehicle for controlling interfacial polymer structure.

2. Experimental

The laser-induced synthesis of carbon nanoparticles uses as precursors hydrocarbons with a high content of C/mole both in resonant processes (e.g. ethylene, butadiene) or in no resonant ones (acetylene, benzene). In the latter case, the negligible absorption of laser radiation requires the addition of a gaseous energy transfer agent, which can either react or interfere in the process [2]. Through the variation of the reactive gas composition and experimental parameters, the method allows to obtain carbon nanoparticles with different morphologies. In this respect, gas composition and flows were varied as well as laser power density and working pressure. Total flow up to 500 sccm were chosen for the reactive gas mixture, the working pressure was maintained in a range from 450 to 950 mbar while laser power density (for a laser beam diameter of 4 mm) was varied from ~ 4000 to 7000 W/cm^2. Sulphur hexafluoride (ν_3 = 947 cm^{-1}) and ethylene (ν_7 = 971 cm^{-1}) were used as energy transfer agent in no resonant laser-induced pyrolysis processes and nitrous oxide as oxidizer because of its low dissociation energy (D [N_2 – O] = 1.667 eV) and oxidizing character.

For composites, a relatively low viscosity (1500-2000 cP) standard epoxy resin type diglycidil ether of bisphenol A (Ropoxid P 401) modified with 10% hardener TETA 1 (triethanoltetramine), and 1-5% carbon nanopowder with different morphology were used. The microscale reinforcement was performed with carbon fibres type CARP193 (100%C; 193g/m^2, 25µm).

The experimental set up for the synthesis of carbon nanopowder was presented elsewhere [3] and the powder characteristics were investigated by transmission electron microscopy (TEM) using a TECNAI F30 G^2 microscope (linear resolution: 1Å) coupled with an energy dispersive X-ray (EDX) detector having a resolution of 133 eV). The Dynamic Light Scattering technique, with a Zetasizer Nano ZS instrument was used to estimate the aggregation of carbon nanoparticles on diluted samples (~0.1 g/l in toluene), after 2 minutes of dispersion by ultrasonication (P=20 W, amplitude 30%); three consecutive measurements of 3 minutes each were performed for each sample. The mechanic tests were performed by INSTRON 4301 installation.

3. Results and discussion

As the result of SF_6 decomposition used as energy transfer agent in no-resonant processes, fluorine alters the turbostratic structure by insertion between the graphene layers [4], whereas the controlled presence of oxygen changes drastically the structure (Fig. 1 (a)) to that of the fullerene-like one [5]. The ratio hydrocarbon/SF_6 flow rate is expected to be directly responsible for the temperature of the reaction flame and therefore it influences the material's structural, chemical and morphological properties. As the sensitizer's concentration decreases, the structure is changing and begins to form randomly distributed assemblies of graphene ribbons over longer range of orders (Fig. 1 (b)).

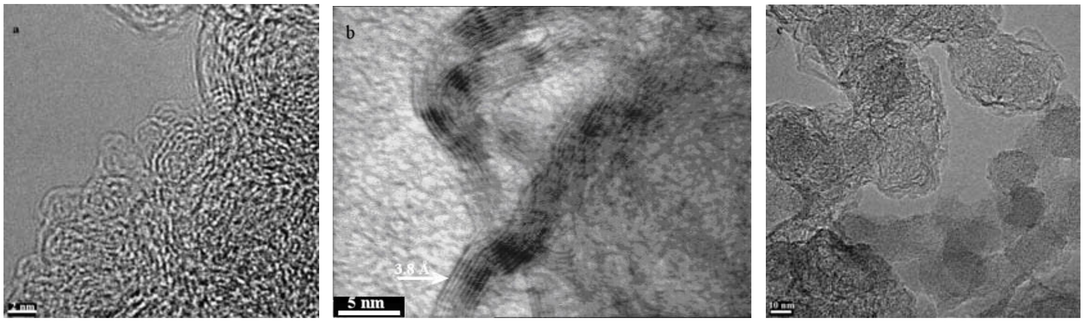
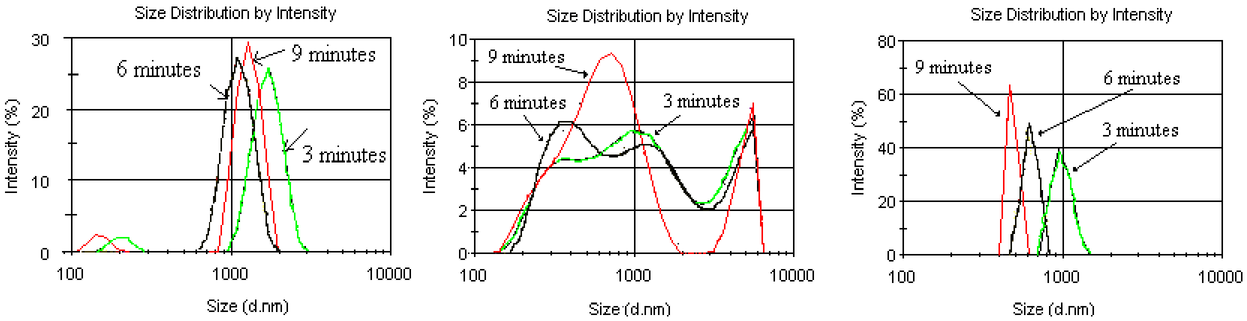


Fig. 1. (a) Fullerene-like structure; (b) Well developed graphene ribbons; (c) Chains of nanoparticles bonded by carbon nano-ribbons.

These assemblies of carbon nano-ribbons composing the porous carbon nanoparticles could present interesting applications due to their enhanced mechanical strength and chemical activity and, could be a source of graphenes [6]. To establish how the variation of hydrocarbon/SF_6 flow ratio could provoke casual changes in the graphene-ribbons' development, C_2H_2/SF_6 samples with C/F atomic ratio between 0.5 and 6 were prepared and investigated. At the same time, a fullerene-like sample from a $C_6H_6/C_2H_4/N_2O$ mixture was also synthesized.



a b c

Fig. 2. Dynamic light scattering investigations on samples obtained from: (a) C_2H_2/SF_6 gas mixtures - $(C/F)_{at}=0.5$; (b) C_2H_2/SF_6 gas mixture - $(C/F)_{at}=3$; (c) $C_6H_6/C_2H_4/N_2O$ gas mixture.

It is worth noting that all carbon nanoparticles form relatively large and fluffy aggregates (Fig. 1 (c)) and that for C_2H_2/SF_6 samples the process of fluffiness is slightly increasing with C/F atomic ratio.

Dynamic Light Scattering (DLS) investigations revealed the existence of an important number of large aggregates having mean dimensions which range generally between 400 and 1100 nm and make the physical dispersion in a matrix very difficult. As a result of significant presence of fluorine and sulphur, samples with a small (0.5 or 0.8) C/F atomic ratio present a more emphasized tendency of agglomeration (e.g. 1000-1100 nm for sample with C/F=0.5, Fig. 2 (a)) in spite of the existent end-capping process due to the presence of these SF_6 decomposition products, which can neutralize from the existent chemically active sites on the carbon particle's surface and so diminish the aggregation process.

With the decreasing of SF_6 concentration, these aggregates seem to stabilize dimensionally and, in the case of sample with C/F=3, to separate into well distinct size categories (Fig. 2 (b)). Investigations by transmission electron microscopy and its related technique (SAED and EELS) revealed at this SF_6 concentration an optimum for the formation of graphene-ribbons [4]. The aggregates' size increasing suggests the involvement of these carbon nanostructures in the particles' agglomeration process, all the more that for samples having $(C/F)_{at}$ >3, for which a diminishing of carbon-ribbons was observed, the dimension of the aggregates presents a slight tendency to decrease.

Carbon nanopowders with a fullerene-like structure ($C_6H_6/C_2H_4/N_2O$ gas mixture) present in time a tendency to decrease the dimensions of their aggregates (Fig. 2 (c)). Due to released fluorine and sulphur as the result of SF_6 decomposition, the reactive groups with a strong acid character (pH value of the aqueous dispersion of nanopowders is 2÷3) are able to react both with epoxy groups of the polymer and amine groups of the hardener; even in the absence of the last one, a rapid reticulation of the polymer matrix was observed at the mixing with this type of nanocarbon [7]. Although in the case of carbon nanopowders synthesized by laser pyrolysis of a gas mixture containing sulphur hexafluoride a very high viscosity increase of the nanocomposite mixture was observed, the addition of different other carbon-based fillers synthesized in the absence of SF_6 showed that stability at storage of the obtained nanocomposite was good and a less meaningful increase of the viscosity could be maintained up to ~2.5% carbon nanofiller. Nevertheless, the controlled chemical activity and morphology of the carbon nanopowder by appropriate gas composition and experimental parameters could lead to a significantly enhanced interfacial adhesion to polymer matrix and to a large improvement of strength and stiffness of the final composite. Studies regarding the use of samples obtained from a gas mixture with $(C/F)_{at} > 3$, which present the interesting structure with the well-developed graphene-ribbons and a much lower concentration of both fluorine and sulphur as well as of samples obtained from $C_6H_6/C_2H_4/N_2O$ gas mixture are in progress.

Some salient treasures of the obtained epoxy-based nanocomposites reinforced by carbon nanopowders and/or carbon fibres are presented in Table 1. The obtained nanocomposites revealed mechanothermal and tribological characteristics superior to those of pure polymer matrix. For the used epoxy matrix (Ropoxid P401), the beneficial effect of the nanocarbon additives could be expressed in the terms of 15÷20% increase of the mechanical resistance (from 90÷95 MPa to 108.8 or 120 MPa), 20÷25% increase of flexural modulus (from 2.8×10^4 to 3.12×10^4 and 3.6×10^4), almost 20% increase of thermal stability and 25÷38% diminishing of the friction coefficient (from 0.255 to 0.184). Regarding to water resistance, an improvement for the epoxy/nanocarbon composite around 400% was observed.

Table 1. Characteristics of epoxy-based nanocomposites reinforced by nanocarbon and/or carbon fibres.

Sample[*]	Flexural strength [MPa]	Flexural modulus x 10^4	Water absorption [%]	Friction coefficient	Thermal stability
Epoxy resin	95	2.8	0.69	0.255	50
Epoxy/NC(C_2H_2/C_2H_4)	108.8	3.12	0.16	0.184	59
Epoxy/NC($C_6H_6/C_2H_4/N_2O$)	120	3.6	< 0.16	-	57
Epoxy/FC	638	110	-	0.132	130
Epoxy/NC(C_2H_2/C_2H_4)/FC	650.6	136	-	0.13	138

[*] *NC –nanocarbon, 2% wt. in polymer; FC – carbon fibres*

Reinforcing polymeric matrices with carbon fibre resulted in spectacular growth of the mechanical characteristics. So, the flexural modulus increased from 2.8×10^4 (epoxy resin) to 1.38×10^6 for epoxy/FC composite, whose flexural strength increased considerably to 6380 daN/cm^2. A 2% nanocarbon adding to the composite increased this mechanical resistance over 6500 daN/cm^2. To note also that for this composite epoxy/carbon fibre/nanocarbon, thermal resistance has increased considerably.

4. Conclusions

Carbon nanopowders with different morphologies and chemical activity could be easily obtained and in-situ functionalised by laser induced pyrolysis of a hydrocarbon-based mixture. This morphology is strongly dependent of both gas composition and experimental parameters. Chemical functionalisation is an efficient mean to improve the interaction between filler and surrounding matter and the presence of heterogeneous atoms could change drastically the structural properties of the synthesized carbon nanopowder. The additional reinforcement with carbon fibres led to an important enhancement of mechanic characteristic. It is worth noting the important role of nanocarbon in the important decrease of water absorption and the necessity to optimize the matching carbon fibres/carbon nanopowder.

Acknowledgements

The authors gratefully acknowledge financial support from the Romanian Ministry of Education and Research, under Project PNCDI-II-71-125/2007 (MAVIAT).

References

[1] L. S. Schadler, S. K. Kumar, B. C. Benicevich, S. L. Lewis, S. E. Harton, MRS bulletin **32**, april 2007, www.mrs.org/bulletin.
[2] R. Alexandrescu, X. Armand, M. Cauchetier, N. Herlin, P. Petcu, I. Voicu, Carbon **36,** 1285 (1998).
[3] I. Morjan, I. Voicu, F. Dumitrache, I. Sandu, I. Soare, R. Alexandrescu, E. Vasile, I. Pasuk, R. Brydson, H. Daniels, B. Rand, Carbon **41,** 2913 (2003).
[4] I. Voicu, I. Morjan, L. Gavrila-Florescu, I. Sandu, E. Popovici, C. Logofatu, G. Stoian, C. T. Fleaca, R. Alexandrescu, I. Soare, F. Dumitrache, R. Bridson, B. Rand, Proceedings of the International Carbon Conference, The Robert Gordon University, Aberdeen, Scotland, 16-21 July 2006.
[5] I. Morjan, I. Voicu, R. Alexandrescu, I. Pasuk,I. Sandu, F. Dumitrache, I. Soare, T. C. Fleaca, M. Ploscaru, V. Ciupina, H. Daniels, A. Westwood, B. Rand, Carbon **42,** 1269 (2004).
[6] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, Science **306,** 666 (2004).
[7] L. Gavrila-Florescu, I. Morjan, E. Popovici, I. Sandu, I. Voicu, I. Dinca, A. Stefan, C. Serghe, L. Dumitrache, C. Nistor, V. Stefan, S. Serban, D. Donescu, G. Prodan, V. Ciupina, Materials Science and Engineering **27**(5-8), 1010 (2007).

---

[*] Corresponding author: ionvoicu2001@yahoo.com