

BULETINUL INSTITUTULUI POLITEHNIC DIN IAȘI
Publicat de
Universitatea Tehnică „Gheorghe Asachi” din Iași
Volumul 62 (66), Numărul 2, 2016
Secția
CHIMIE și INGINERIE CHIMICĂ

GRAPHENE OBTAINED BY PYROLYTIC DECOMPOSITION IN N₂ ATMOSPHERE

BY

CĂTĂLINA NUȚESCU DUDUMAN^{1,*}, JOSÉ MARÍA GÓMEZ DE SALAZAR Y
CASO DE LOS COBOS², MARÍA ISABEL BARRENA PÉREZ²,
LAURA GARCIA SANCHEZ² and CONSUELO GÓMEZ DE CASTRO²

¹“Gheorghe Asachi” Technical University of Iași,
Department of Materials Science

²Complutense University of Madrid, Spain,
Department of Materials Science and Metallurgical Engineering

Received: May 5, 2016

Accepted for publication: June 2, 2016

Abstract. Graphene, an allotrope of carbon, is study in the last years because posed interesting chemical, optical and electrical properties. The paper describes the graphene obtaining method by the pyrolytic decomposition. As raw materials was used epoxy resin. The product of pyrolytic decomposition of the epoxy resin was characterized using several techniques: scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-Ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR). Experimental results indicate the nanostructure stacking of multiple layers of graphene; at 500 nm we can observe lamellas of graphene. On the base of the experimental data we can conclude that the pyrolytic decomposition product is graphene.

Keywords: Graphene, Epoxy resin, Pyrolysis, Characterization.

*Corresponding author; *e-mail*: catalinanutescu@yahoo.com

1. Introduction

Graphene is an allotrope of carbon, in which one atom of carbon forms each vertex, and can be two-dimensional, atomic-scale, honey-comb lattice. Graphene is the structural element of: graphite, charcoal, carbon nanotubes etc.

Study of graphene determined an enormous interest due to their properties that conduct to facile modification in order to produce other graphene-based materials (Stankovich *et al.*, 2006). Graphene was much studied because posed properties such as: about 100 times stronger than the strongest steel, conducts heat and electricity efficiently, is nearly transparent, nonlinear diamagnetism etc. Graphene are used as fillers to improve the thermal properties (Tang *et al.*, 2015). Graphene is a material which interesting chemical, optical and electrical properties, due to the graphene skeleton and the oxygen containing functional groups located on the base plane or at the sheet edges (Lerf *et al.*, 1998).

The first preparation method of graphene was realized by Hummers and Offeman (Hummers and Offeman, 1958), but the existence of graphite was predicted since 1940 (Wallace *et al.*, 1947).

Novoselov indicated a method to obtain the graphene sheets (Novoselov *et al.*, 2004a). The most currently used in the obtained of graphene are Hummers and Brodie methods (Novoselov *et al.*, 2004b; Botas *et al.*, 2013; Hummers and Offeman 1958; Park and Ruoff, 2009). The structural transformations in both methods included solvation/ hydration (You *et al.*, 2013). Using the Hummer method the degree of transformation is reported to be higher; these methods differs function of the acid type (nitric or sulfuric) and salt type (potassium chloride or potassium permanganate). The Engineering Group Antolin presented method for obtaining of graphene starting from carbon nano-fibers (Grupo Antolín Ingeniería *et al.*, 2012). Liu obtained graphene flakes using a process of electrochemical exfoliation of graphite bars, in different acid medium (Liu *et al.*, 2013). Stankovich obtained the graphene as nanosheets starting from a colloidal suspension exfoliated in water with hydrazine (Stankovich *et al.*, 2007). On the other hand graphene can be separated through the micromechanical cleavage of graphite (Novoselov *et al.*, 2004b; Novoselov *et al.*, 2005a, 2005b; Geim and Novoselov, 2007). In accordance with this approach, graphene sheets are separated from crystalline graphite either by rubbing small graphite crystals against each other or by means of an adhesive tape whose further dissolution in acid leads to separation of individual graphene sheets. This method permit separated single-layer graphene sheets, about 10 nm in width and roughly 100 nm in length, having an ordered structure. The simplest approach to the exfoliation of graphite into separate graphene sheets is based on the utilization of surface active organic liquids (Dresselhaus and Dresselhaus, 1981). Electric arc with graphite

electrodes burning in an inert gas atmosphere, is one of the most effective tools for the transformation of crystalline graphite into carbon surface structures (Krätschmer *et al.*, 1990; Iijima, 1991; Iijima and Ichihashi, 1993; Wu *et al.*, 2009; Pan *et al.*, 2016), and still of great interest today.

The present study is aimed to investigate the method for the synthesis of graphene by pyrolytic decomposition. This method is recommended because the use of corrosive acids is not necessary, that in other methods. The materials obtained by pyrolytic decomposition of epoxy resin in N₂ were characterized by techniques such as: SEM, TEM, XRD, FTIR.

2. Experimental

The raw material used in this research, was Epoxy Resin (Resoltech 1800) and as hardener was used Resoltech 1805. The ratio was 100:17. Gel time measurements were realized on Trombotech according to ISO 2535 at 23°C. The physical properties of materials are: density 1170 kg/m³, viscosity between 145-850 mPas function of temperature, gel time 120 min. The gas used was: Nitrogen (Premium) Air Products.

Morphological structure and chemical composition was examined by SEM and TEM before and after calcination. We used JEOL 6400 with an Oxford Link EDX microanalyser and Pentafet light sensor. The TEM used was a JEOL JEM-2100, that can work in accelerating voltage modes at 200 kV, obtaining a resolution of 0.14 nm, 0.25 nm between lines and points and may reach 1.200.000 increase times. For crystallinity material characterization XRD method was used. We used a Philips model X`Pert PDP3040 with a source K α 1 Cu α , 40 kV and 40 mA, and working with a curved single crystal monochromator copper in order to eliminate the contribution K α 2 and K α 1=1.547, K α 2=1.54439. The program which was used for the analysis of the diffraction patterns is X`Pert HihgScore Plus PANalytical (version 2.0).

For obtaining graphene from epoxy resin by pyrolytic decomposition in N₂ atmosphere was used experimental installation presented in Fig. 1. In the reactor (furnace – 1500°C), the thermal cycle was: heating to 900°C at 10°C/min, maintaining at 900°C until total decomposition, and cooling to room temperature. The N₂ gas flux was 5 L/min. The distilled fractions were collected using a refrigerated system.

3. Results and Discussions

After the pyrolysis process, the epoxy resin is transformed in a new material. Fig. 2 presents SEM images new material. We can see a pellicle formed by nanocrystals. The lamellas of multilayer graphene can be observed perfectly in the pictures. Structural characterization by TEM images, Fig. 3

show the intensity of electrons at different thicknesses and show a different morphology and transparent sheet as of the investigated area.

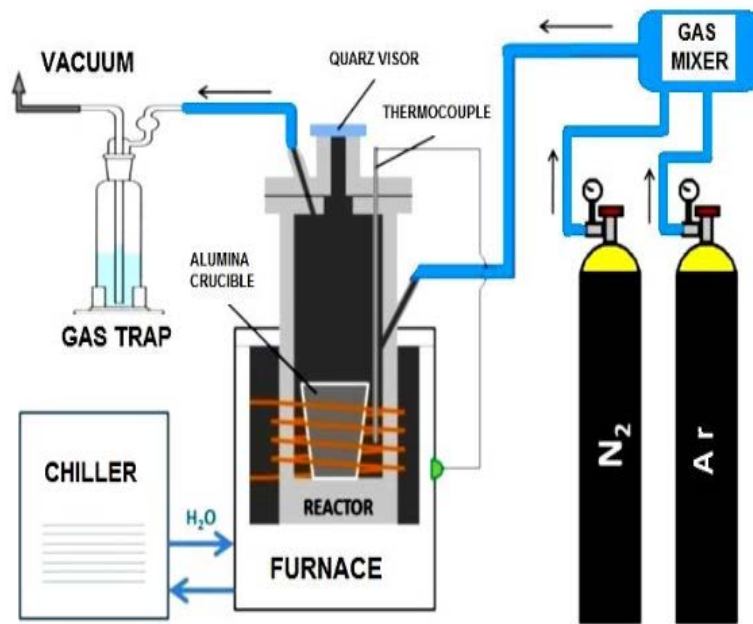


Fig. 1 – Equipment used in the experiment.

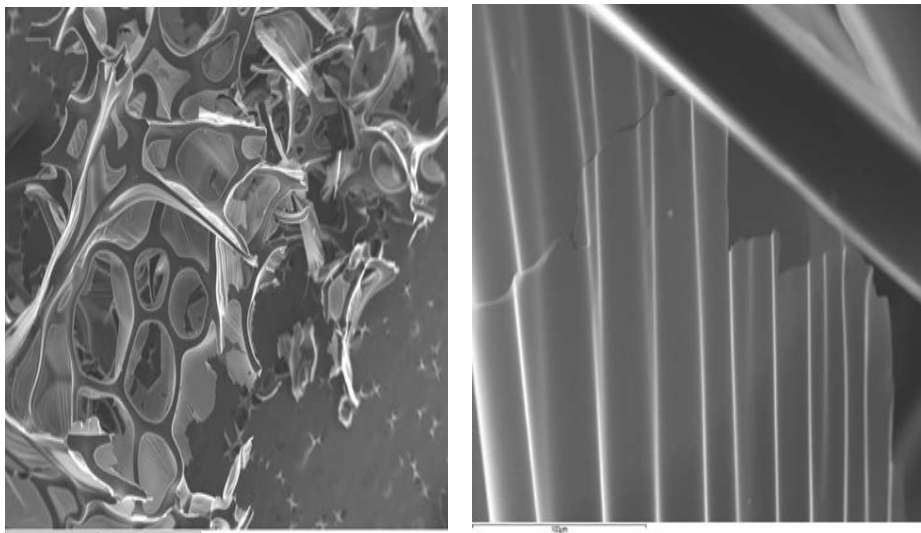


Fig. 2 – SEM micrographs of the lamellas.

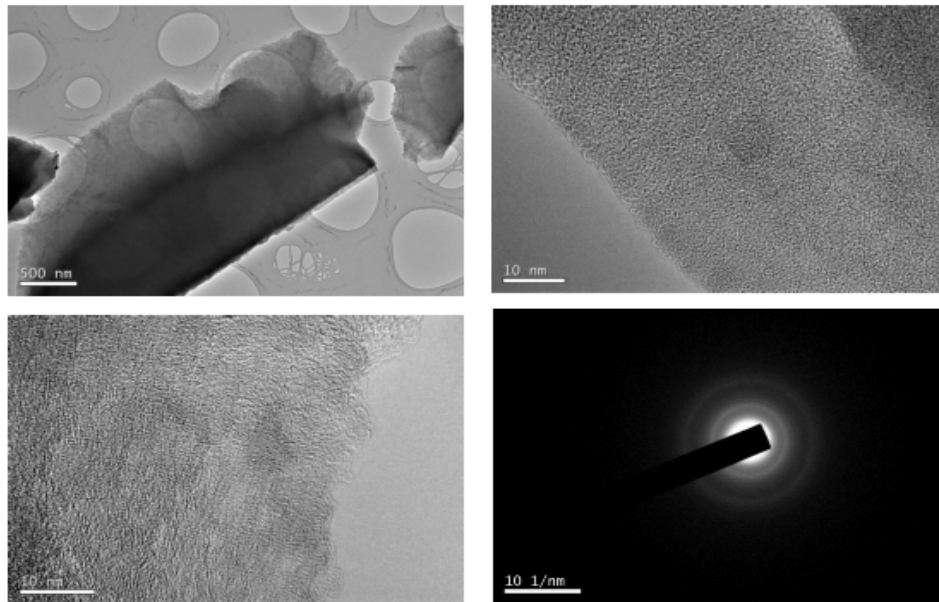


Fig. 3 – TEM and SEAD images.

Thick dark areas indicate on the nanostructure stacking of multiple layers of graphene. On a scale of 500 nm we can observe graphene lamellas.

The diffraction pattern of graphene is a hexagonal lattice. The XRD spectra measured in a range of 5° to 90° is shown in Fig. 4.

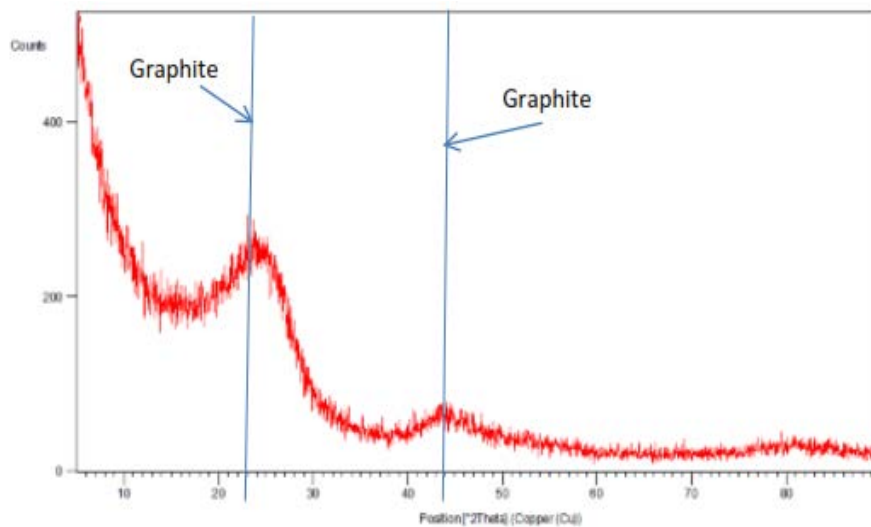


Fig. 4 – XRD diffractogram the pyrolytic graphene.

The 2θ values 23° and 44° correspond to graphite. Fourier transform infra-red spectra were carried out on a FTIR spectrometer, Nicolet Magna 750. By using FTIR we tried to understand the mechanism of graphene formation. Fig. 5 shows the peaks the formed compounds. FTIR spectral analysis was performed to confirm the chemical structure.

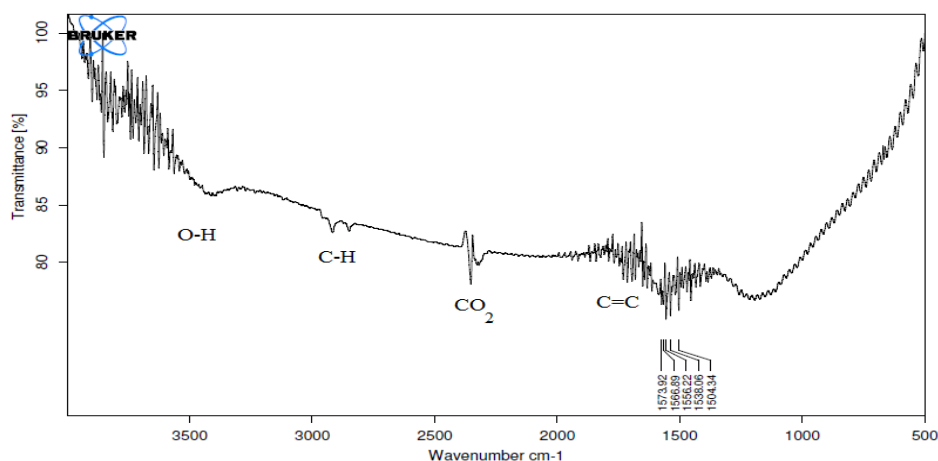


Fig. 5 – FTIR spectrum of the sample.

Fig. 5 summarizes the FTIR spectra and shows the typical characteristic bands for peaks at 2925, 2850, 1680 to 2000 and 1800-1600 cm^{-1} , which correspond to the O-H bond; the presence of alkyl groups is usually revealed by weak to medium absorptions in the 2850-2990 cm^{-1} region, owing to sp^3 C-H stretching vibrations of aromatic and aliphatic C-H, desorption CO_2 , aromatic C=C stretching groups, respectively. Interestingly, there is an increase of the C=C band peaks intensity.

4. Conclusions

From all results we concluded that the pyrolytic decomposition of an epoxy resin allows obtaining a very good reduced graphene. Microstructural characterization was made by SEM and TEM, showing the presence of graphene multilayer. At more magnification, the lamellas of multilayer graphene, can be observed perfectly. Also the characterization using XRD diffractograms and FTIR analysis demonstrate the obtaining of graphene through the described method.

Acknowledgements. This work was supported by Ministry of Economy and Competitiveness. Reference: MAT2013-46755-R

REFERENCES

- Botas C., Álvarez P., Blanco P., Granda M., Blanco C., Santamaría R., Romasanta L., Verdejo R., López-Manchado M., Menéndez R., *Graphene Materials with Different Structures Prepared from the Same Graphite by the Hummers and Brodie Methods Carbon*, **65**, 156-164 (2013).
- Dresselhaus M.S., Dresselhaus G., *Intercalation Compounds of Graphite*, Advances in Physics, **30** (1981).
- Geim A.K., Novoselov K.S., *The Rise of Graphene*, Nature Materilas, **6**, 183-891 (2007).
- Grupo Antolín Ingeniería EP 2 489 632 A1. 22.08.2012, pp. 1-16.
- Hummers W.S., Offeman R.E.J., *Preparation of Graphitic Oxide*, Journal of the American Chemical Society, **80**, 1339-1349 (1958).
- Iijima S., *Helical Microtubules of Graphitic Carbon*, Nature, **354**, 56-58 (1991).
- Iijima S., Ichihashi T., *Single-Shell Carbon Nanotubes of 1-nm Diameter*, Nature, **363**, 603-605 (1993).
- Krätschmer W., Lowell D., Fostiropoulos L., Huffman D., *Solid C60: A New Form of Carbon*, Nature, **347**, 354-358 (1990).
- Lerf A., He H., Forster M., Klinowski J., *Structure of Graphite Oxide Revisited*, Journal of Physical Chemistry B, **102**, 4477-4482 (1998).
- Liu J., Poh C.K., Zhan D., Lai L., Lim S.H., Wang L., Liu X., Sahoo N.G., Li C., Shen Z., Lin J., *Improved Synthesis of Graphene Flakes from the Multiple Electrochemical Exfoliation of Graphite Rod*, Nano Energy, **2**, 377-386 (2013).
- Novoselov K.S., Geim A.K., Morozov S.V., Jiang D., Zhang Y., *Dubonos Electric Field Effect in Atomically Thin*, Carbon Films Science, **306** (2004a).
- Novoselov K.S., Geim A.K., Morozov S.V., Jiang D., Zhang Y., Dubonos S.V., Grigorieva I.V., Firsov A.A., *Electric Field Effect in Atomically thin Carbon Films*, Science, **306** (2004b).
- Novoselov K.S., Jiang D., Schedin F., Booth T.J., Khotkevich V.V., Morozov S.V. *et al.*, *Two-Dimensional Atomic Crystals*, Proc. Natl. Acad. Sci. USA, **102** (2005a).
- Novoselov K.S., Geim A.K., Morozov S.V., Jiang D., Katsnelson M.I., Grigorieva I.V., Dubonos S.V., Firsov A.A., *Two-Dimensional Gas of Massless Dirac Fermions in Grapheme*, Nature, **438** (2005b).
- Pan Q., Chung C.C., He N., Jones J.L., Gao W., *Accelerated Thermal Decomposition of Graphene Oxide Films in Air via in Situ X-ray Diffraction Analysis*. Journal of Physical Chemistry C, **120**, 14984-14990 (2016).
- Park S., Ruoff R.S., *Chemical Methods for the Production of Graphenes*, Nature, Nanotechnology, **4**, 217-224 (2009).
- Stankovich S., Dikin D.A., Dommett G.H., Kohlhaas K.M., Zimney E.J., Stach E.A., Piner R.D., Nguyen S.T., Ruoff R.S., *Graphene-Based Composite Materials*, Nature, **442**, 282-286 (2006).
- Stankovich S., Dikin D.A. *et al.*, *Synthesis of Graphene-Based Nanosheets via Chemical Reduction of Exfoliated Graphite Oxide*, Carbon, **45**, 1558-1565 (2007).
- Tang B., Hu G., Gao H., Hai L., *Application of Graphene as filler to Improve Thermal Transport Property of Epoxy Resin for Thermal Interface Material*, International Journal of Heat and Mass Transfer, **85**, 420-429 (2015).

Wallace P.R., *The Band Theory of Graphite*, Physical Review, **71**, 622 (1947).

Wu Z.S., Ren W., Gao L., Zhao J., Chen Z., Liu B., Tang D., Yu B., Jiang C., Cheng H.M., *Synthesis of Graphene Sheets with High Electrical Conductivity and Good Thermal Stability by Hydrogen Arc Discharge Exfoliation*, ACS Nano, **3**, 411-417 (2009).

You S., Luzana S.M., Szabo T., Talyzin A.V., *Effect of Synthesis Method on Solvation and Exfoliation of Graphite Oxide*, Carbon, **52**, 171-180 (2013).

OBȚINEREA GRAFENULUI UTILIZÂND DESCOMPUNEREA PIROLITICĂ ÎN ATMOSFERĂ DE N₂

(Rezumat)

Lucrarea descrie obținerea grafenului prin metoda descompunerii pirolitice. Produsul de descompunere pirolitică a fost caracterizat folosind mai multe tehnici: difracție de raze X (XRD), microscopie electronică de baleiaj (SEM), microscopie electronică de transmisie (TEM), spectroscopie în infraroșu cu transformare Fourier (FTIR). Folosind datele rezultate din tehnicile menționate mai sus putem concluda că produsul descompunerii pirolitice este grafenul.