

**Patrycja Zygoń<sup>1\*</sup>, Monika Gwoździk<sup>1</sup>, Jerzy Peszke<sup>2</sup>, Zygmunt Nitkiewicz<sup>1</sup>**

<sup>1</sup> Czestochowa University of Technology, Faculty of Materials Processing Technology and Applied Physics, Institute of Materials Engineering, al. Armii Krajowej 19, 42-200 Czestochowa, Poland

<sup>2</sup> Jan Długosz University in Czestochowa, al. Armii Krajowej 13/15, 42-200 Czestochowa, Poland

\*Corresponding author. E-mail: zygon@wip.pcz.pl

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## SURFACE TOPOGRAPHY OF CARBON NANOTUBES FORMING REINFORCING PHASE IN COMPOSITE MATERIALS

Carbon nanotubes are one of the strongest materials of unique mechanical, optical, electrical and electronic properties. Because of that they are mainly used as semiconductor materials constituting the reinforcing phase in composite materials. Most frequently nanotubes are obtained using the following methods: catalytic pyrolysis (CVD), electric arc method or by catalytic laser synthesis. The paper presents the results of studies on the topography of multiwall carbon nanotubes (MWCNTs) obtained by the CVD method, using an atomic forces microscope (AFM). Prior to the studies the nanotubes were cleaned using two methods - one part was cleaned in a mixture of concentrated sulphur and nitric acids, and the other in a mixture of perhydrol and acetic acid. Measurements of the surface topography using the Tapping Mode method were performed on the material prepared in this way, acquiring the data on the height and on the phase imaging.

**Keywords:** carbon nanotubes, composite material, method CVD

## TOPOGRAFIA POWIERZCHNI NANORUREK WĘGLOWYCH STANOWIĄCYCH FAZĘ ZBROJĄCĄ MATERIAŁÓW KOMPOZYTOWYCH

Nanorurki węglowe są jednymi z najsilniejszych i najmocniejszych znanych włókien o niezwykłych właściwościach mechanicznych, optycznych, elektrycznych i elektronowych. Dlatego głównie znalazły zastosowanie jako materiały półprzewodnikowe stanowiące fazę zbrojącą w materiałach kompozytowych. Nanorurki otrzymuje się głównie metodami: pirolizy katalitycznej (CVD), metodą elektrołukową lub poprzez katalityczną syntezę laserową. W pracy przedstawiono wyniki badań topografii wielościennych nanorurek węglowych (MWCNTs) otrzymanych metodą CVD przy pomocy mikroskopu sił atomowych (AFM). Przed badaniem nanorurki były oczyszczane dwoma metodami - jedną część oczyszczano w mieszaninie stężonych kwasów siarkowego i azotowego, drugą w mieszaninie perhydrolu i kwasu octowego. Na tak przygotowanym materiale przeprowadzono pomiary topografii powierzchni metodą Tapping Mode, zbierając dane z wysokości, amplitudy drgań i obrazowania fazowego.

**Słowa kluczowe:** nanorurki węglowe, kompozyty, metoda CVD

### INTRODUCTION

Carbon nanotubes (CNTs) belong to the group of so-called nanomaterials which feature unique physical properties, resulting directly from their structure of nanometric dimensions [1]. They were discovered in 1991 by S. Iijima as a new allotropic form of carbon [2]. Nanotubes are a material of huge potential, showing excellent electrical and mechanical properties and also significant chemical resistance. They have extremely high mechanical properties: tensile strength up to 500 GPa and the elasticity modulus of reaches 7÷8 TPa. At a small diameter (1÷80 nm) and a high aspect ratio (L/D even above 10,000) they are an attractive reinforcing material for polymers, ceramic materials and metals [3]. Certain types of nanotubes display

metallic properties, while the majority - semiconductor ones.

They are constructed of a single ring (single wall carbon nanotubes, SWCNT) or of a few (multiwall carbon nanotubes, MWCNT) concentric and coaxial cylinders, which are rolled single graphite planes, called graphene planes. Two types of nanotubes - chiral and non-chiral [4] are distinguished depending on the way of graphite plane rolling.

A few different methods have been developed to obtain nanotubes. They are produced using such techniques as: the electric arc method, catalytic laser synthesis and various types of chemical vapour depositions (CVD). A common feature of those methods is

carbon production in a gaseous phase (in electric arc, as result of evaporation by laser beam or through decomposition of carbon compounds) and then its condensation at a high temperature using appropriately chosen catalysts. Nanotubes obtained using different methods feature different degrees of structure perfection (damage), varying average dimensions as well as a scatter of dimensions. The material obtained after synthesis is always polluted with catalysts and also - to a different degree - with other products of carbon condensation (soot, fullerenes) [5].

Composites prepared using carbon nanotubes have not only good mechanical strength and electrical conductivity but also lend themselves easily to mechanical treatment without causing cracks that occur with carbon fibers [6].

## MATERIALS AND EXPERIMENTAL PROCEDURE

CNT CO. LTD carbon nanotubes, under the commercial name  $C_{TUBE}$  100, obtained using the thermal CVD method, were used as the studied material. The raw nanotubes were 1 to 25  $\mu\text{m}$  long, 10 to 80 nm in diameter, with the density of  $0.03 \pm 0.06 \text{ g/cm}^3$  and specific surface area of  $150 \div 250 \text{ m}^2/\text{g}$ .

Prior to the surface studies, the carbon nanotubes were subjected to cleaning to remove the amorphous carbon and the metallic pollutants originating from the catalysts used in their production. The cleaning was performed using a liquid phase. The nanotubes, prior to the studies, were cleaned using two methods - one part was cleaned in a mixture of concentrated sulphur and nitric acids, and the other in a mixture of perhydrol and acetic acid. The prepared beakers, containing carbon nanotubes and appropriate acids, were subjected to the action of ultrasound during 1 hour to break the agglomerates. Mixing by ultrasound consists in applying an alternating pressure caused by an acoustic wave in the area above the threshold of the cavities (holes) formation in the solution. Then the beakers were heated and maintained at the boiling point for approx. 10 hours. The heating of nanotubes with concentrated acids removes the metallic particles and amorphous carbon from their surface. Clean carbon nanotubes were obtained after draining and drying, which after the acid action contained carboxylated functional groups. Additionally, the cleaning modifies the CNTs' graphene structure, creating CNTs-X compounds (X - attached chemical group). In the case of cleaning using a mixture of sulphuric and nitric acids we obtain CNTs - COOH type compounds (Fig. 1).

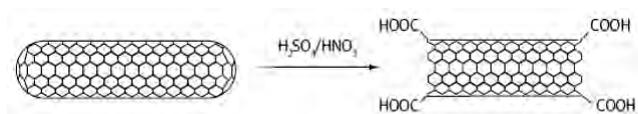


Fig. 1. Functionalisation of carbon nanotubes

Rys. 1. Funkcjonalizacja nanorurek węglowych

Measurements of the surface topography were performed on the material prepared in such a way; they were made on a VEECO MULTIMODE atomic forces microscope (AFM) with a NANOSCOPE controller by means of the Tapping Mode method, acquiring the data on the height and on the phase imaging. The surface studies were carried out on an area of  $1 \mu\text{m} \times 1 \mu\text{m}$ .

## COURSE OF TESTS

The microscopic analysis (Fig. 2) has shown that the carbon nanotubes cleaned in a mixture of concentrated sulphuric and nitric acids feature an angular shape, have a smooth surface and a metallic lustre. Their colour changes from silver to golden and they form large compact particles. In contrast, the nanotubes cleaned in perhydrol and acetic acid show a more developed surface and are jagged and black.

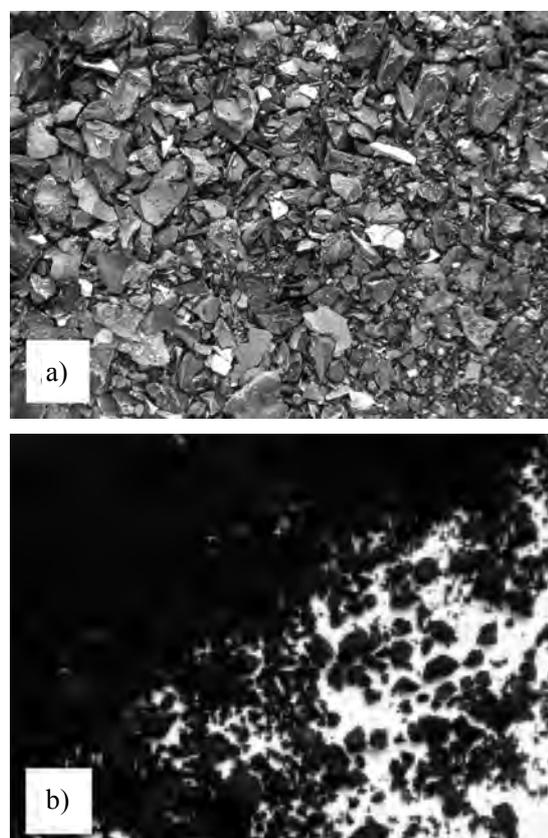


Fig. 2. Nanotubes cleaned in sulphuric and nitric acids (a) and cleaned in perhydrol and acetic acid (b)

Rys. 2. Nanorurki oczyszczone kwasami siarkowym i azotowym (a) oraz oczyszczone perhydrolem i kwasem octowym (b)

Figure 3a presents the image of nanotubes (cleaned in mixture of concentrated sulphuric and nitric acids) obtained during the studies on an atomic forces microscope (AFM). The nanotubes diameter is diversified and ranges from a few to  $\sim 70 \text{ nm}$ . The nanotubes differ in length and are bent in various directions. However, it is possible to notice places of low degree of entanglement (agglomerations).

A large cluster of nanotubes is visible on the 3D surface (Fig. 3b). It is noticeable that some of them are linearly arranged.

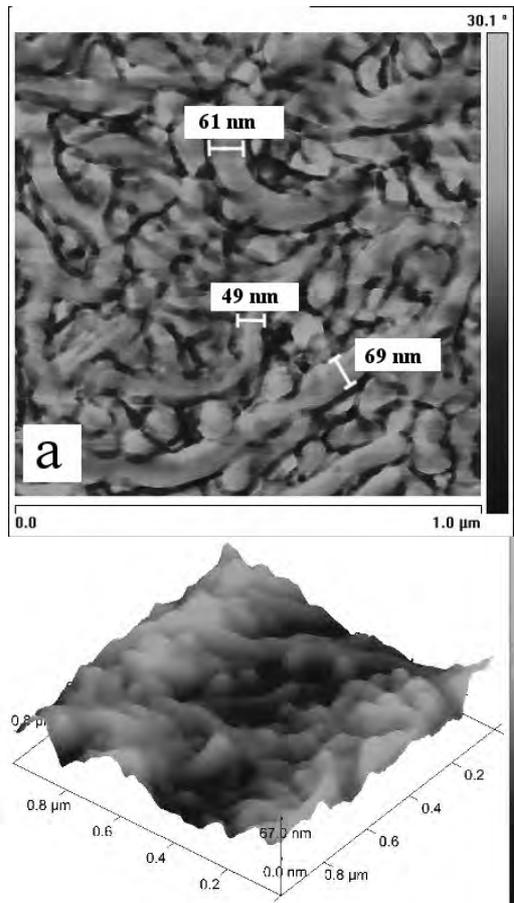


Fig. 3. Surface of nanotubes cleaned in sulphuric and nitric acids: a) 2D image (AFM); b) 3D image (AFM)

Rys. 3. Powierzchnia nanorurek oczyszczanych kwasami siarkowym i azotowym: a) obraz 2D (AFM); b) obraz 3D (AFM)

The surface image of the nanotubes cleaned in the mixture of perhydrol and acetic acid (Fig. 4a) is very close to the surface image of the nanotubes cleaned in the mixture of sulphuric and nitric acids. The nanotubes differ also in diameter, which is slightly smaller for the nanotubes cleaned in the mixture of concentrated acids. The diameter ranges from a few to ~50 nm. The length of the nanotubes is not the same and it is noticeable that the nanotubes are shorter and form larger agglomerations than those discussed earlier.

The 3D surface shows a linear arrangement of carbon nanotubes. The carbon nanotubes cleaned in the mixture of perhydrol and acetic acid are shorter and have smaller diameters than those cleaned in the mixture of sulphuric and nitric acids.

The obtained roughness results show (Fig. 5) higher Ra values for the nanotubes cleaned in perhydrol and acetic acid as compared to those cleaned in sulphuric and nitric acids. The lower roughness of the nanotubes cleaned in sulphuric and nitric acids is caused by the fact that after cleaning these nanotubes, they form smooth shapes with a metallic lustre.

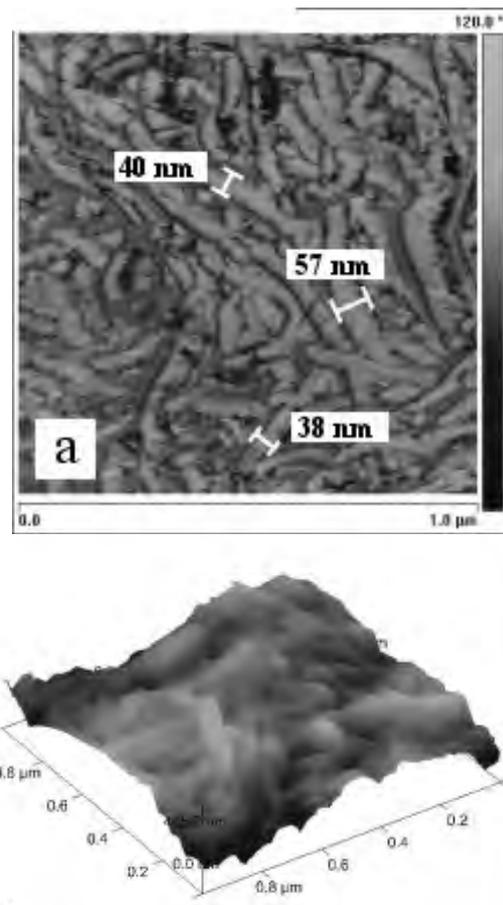


Fig. 4. Surface of nanotubes cleaned in perhydrol and acetic acid: a) 2D image (AFM); b) 3D image (AFM)

Rys. 4. Powierzchnia nanorurek oczyszczanych perhydrolem i kwasem octowym: a) obraz 2D (AFM); b) obraz 3D (AFM)

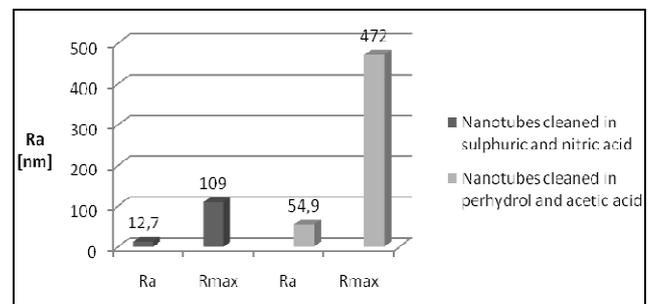


Fig. 5. Average arithmetical roughness for individual nanotubes: grey - nanotubes cleaned in perhydrol and acetic acid; black - nanotubes cleaned in sulphuric and nitric acid

Rys. 5. Parametry chropowatości dla poszczególnych nanorurek: szare - nanorurki oczyszczane perhydrolem i kwasem octowym; czarne - nanorurki oczyszczane kwasem azotowym i siarkowym

### SUMMARY

The studies on the nanotubes topography have shown that carbon nanotubes after the process of cleaning are smaller in length (Fig. 2a and Fig. 3a). Carbon nanotubes cleaned in perhydrol and acetic acid are shorter and smaller in diameter than the those cleaned in the mixture of sulphuric and nitric acids.

The cleaning of nanotubes allows one to break large, clusters of nanotubes (agglomerates) due to

which the nanotubes can be used for further modifications, because they do not lose their unique properties. Moreover, the nanotubes nature changes from hydrophobic to hydrophilic due to the creation of hydrogen bonds between CNTs-COOH and the solvent molecules.

Carbon nanotubes prepared in that way are the reinforcing phase in composites, increasing the strength and have a greater electric conductivity, which will be studied further.

Carbon nanotubes placed in a polymer matrix make composites that are good electrical conductors.

Nanotubes added in an amount of less than 10% wt. to various resins (including polycarbonate, nylon, polyester, polyamide) make the electrical conductivity higher than with conventional fillers such as soot, carbon fibers or glass fibers, at a lower weight concentration [7].

Composites obtained using carbon nanotubes not only have good mechanical strength and electrical conductivity, but are also easily subjected to mechanical treatment, without the formation of cracks that occur with carbon fibers. These materials promoted by metals (transition metals, silver) may be conductors or semiconductors of electricity, so they can carry an electrical current in any or in only one direction. It depends on e.g. the shape of the nanotubes. High temperature superconductors and those which work at room tem-

perature are used in the production of generators, electric motors, transformers, transmission lines, as well as in the production of frictionless bearings, and during the operation of levitating trains. It is supposed that carbon nanotubes may play the same role as silicon in semiconductors. They can be used as new mini diodes or a transistor in sizes much smaller than 200 nm.

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