

FABRICATION AND INVESTIGATION OF CONDUCTIVE POLYMERIC NANOCARBON COMPOSITES BASED ON IODINE - FUNCTIONALIZED MULTI - WALLED CARBON NANOTUBES

S.H. ABDULLAYEVA^{1,2}, A.B. HUSEYNOV¹, I.G. NAZAROV³,
A.O. ISRAFILOV¹, N.M. MADATLY³

¹*Research & Development Center for Hi-Technologies (RDCHT), MCHT,
İnşaatçılar ave. 2, Az - 1073, Baku, Azerbaijan*

²*G.M. Abdullayev Institute of Physics, Azerbaijan NAS,
H.Javid ave. 33, AZ-1143 Baku, Azerbaijan*

³*Baku branch of the Moscow State University named after M.V. Lomonosov (MSU),
F.Agayev str 9., AZ - 1141, Baku, Azerbaijan
e-mail: asker.huseynov@rambler.ru*

The present article is dedicated to the synthesis of multiwalled carbon nanotubes (MWNTs) by aerosol - assisted chemical vapour deposition method, the functionalization of their surface by crystalline iodine, and the preparation on the basis of the latest new electrically conductive polymeric nanocomposites. For this purpose, 3 polymers were chosen as polymer matrices: silicone, polyurethane and epoxy resin. For the final nanocomposites, the current-voltage characteristics were measured and on the basis of the obtained data the electrical conductivity of polymer composites were determined. Moreover, in this paper, the influence of the functionalization process as well as the type of used polymers on the electrical properties of composites is also discussed.

Keywords: MWCNTs, Aerosol-assisted chemical vapour deposition (AACVD), ferrocene, cyclohexane, xylene, polymers, silicone, epoxy, polyurethane, conductive polymer nanocomposites, functionalization, iodine, volt-ampere characteristics, Raman spectroscopy, SEM; IR spectroscopy.

PACS: 61.48.De

INTRODUCTION

One of the actual and progressive trends of nanoindustry, in particular, modern materials science is the creation of new functional and structural materials with specified properties [1]. Among them, the most promising and in great demand nanomaterials over the past two decades that has attracted tremendous attention of the researches from both an academic and industrial point of view are novel conductive polymer composite materials with fundamentally and specified new properties by means of the nanometer-scale components addition [2, 3]. The electrical conductivity of polymers - dielectrics can be imparted by incorporating conductive fillers, provided retaining their polymeric characteristics. Outstanding characteristics of innovative high-tech material - carbon nanotubes such as excellent electrical and thermal conductivity, high stiffness and tensile strength, an extremely large surface area, miniscule size, unique atomic structure etc. make them perfect candidates as nanofillers i.e., as a reinforcement instead of other conventional materials in resulting polymer composites to improve their chemical and physical properties [4-6].

However there are two significant limitations in developing high performance polymer /CNTs composites: homogeneous dispersion of carbon nanotubes in the matrices and low interfacial interaction between nanotubes and polymers [7]. In this connection the chemical modification of the graphitic sidewalls and tips of CNT have key roles to prevent nanotubes aggregation owing to strong intermolecular Van der Waals forces between them, which helps to better disperse and stabilize the CNTs and enhance their chemical affinity to engineering polymer matrices [8,9].

Conductive polymer nanocomposites open wide prospects for their potential practical application in many different areas such as transistors [10], sensing materials [11], energy storage and energy conversion devices [12], biomedical applications (biosensors, drug delivery systems, biomedical implants and tissue engineering) [13] and so on. In the literature [14-19] there are scanty data on the research in the field of iodination of MWCNTs, and there is practically no information [20] on nanocomposites based on them. In this connection the aim of our present work is to produce new conducting polymers - nanocarbon composites based on iodine - functionalized multi-walled carbon nanotubes and epoxy, silicone and polyurethane polymers and to study the effect of the functionalization of CNTs on the electrochemical characteristics of the final materials.

2. EXPERIMENTAL PROCEDURES DETAILS

2.1. Aerosol - assisted chemical vapour deposition (AACVD) synthesis process of MWCNTs and its purification

The AACVD synthesis setup and the standard procedure are described in detail in the work [21]. Briefly, experiments on the synthesis of multiwalled carbon nanotubes were carried out in the laboratory setup using ferrocene (Fc) as the precursor of the catalyst, and cyclohexane (CyH) as the raw carbon material.

A chemical quartz beaker (200 ml volume) containing a solution of ferrocene in cyclohexane with a quantitative ratio of 20 mg / ml was placed in an aerosol generator (nebulizer) where it was ultrasonically exposed. As a carrier (diluting) gas and a reducing agent were used high purity argon and hydrogen with a space velocity of

1.1 l / min and 0.1 l / min, respectively. The generated aerosol by the flow of argon gas is transported to the reactor, where in the hot zone of the tubular furnace occurs thermolysis of the organometallic precursor and the growth of multi-walled carbon nanotubes. The

synthesis temperature was 900 °C. For uniform deposition of carbon nanotubes during the AACVD process, the electric furnace was automatically moved along the length of the reactor at a rate 10 mm / min. The principal scheme of the experimental setup is illustrated in Fig. 1.

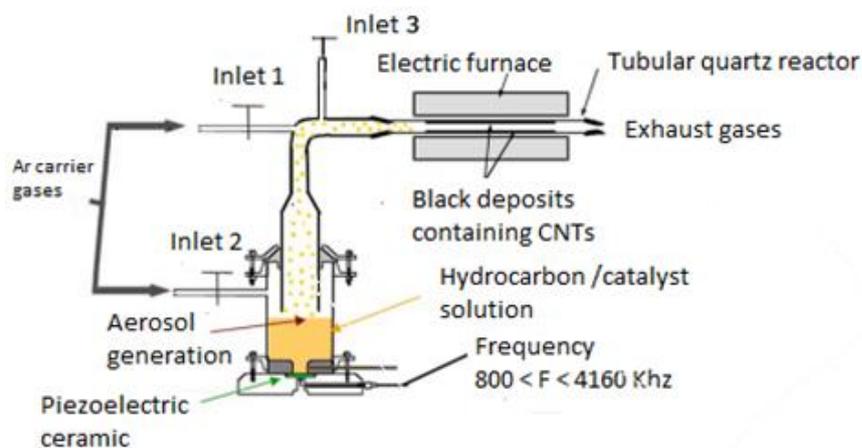


Fig. 1. Schematic illustration of the experimental device used for the aerosol-assisted CCVD process.



Fig. 2. The stage of purification of MWCNTs from tarry substances by extraction method: a) MWCNTs suspension with solvent during extraction; b) MWCNTs suspension with solvent after extraction.

The purification process of multiwalled carbon nanotubes from by-products was carried out by two well-known methods.

The purification process of MWCNTs from tarry impurities was carried out as a result of extraction using xylene and cyclohexane as solvents in volume - weight ratio (ml / g) of 30: 1 heated to 80 °C. Herewith the transparent xylene painted in yellowish color. Purification was carried out until the color disappears completely (Fig. 2). Then, to remove the catalytic iron (Fe) particles, the carbon nanotubes released from the tarrys were treated with dilute nitric acid (28% HNO_3) at a moderate temperature ($T = 80$ °C) for 2 hours and constant stirring.

2.2. Obtaining of functionalized MWCNTs by direct iodination the surface of carbon nanotubes (I - MWCNTs)

2.2.1. The method of direct iodination of MWCNTs

The required amount of a sample of synthesized MWCNTs and commercial crystalline iodine was weighed to the accuracy 0.1 mg and placed in a thick-walled quartz reactor, the open end of which was sealed.

The reactor was placed in a tubular muffle furnace in which it was at 350 °C for 3 hours. As the temperature was raised, the crystalline iodine passed to the vapor state and reacted with multiwalled carbon nanotubes to form the C-I bond. At the end of the reaction time, the reactor was cooled, after which the end of the quartz tube was cut and the obtained target product was recovered from the reactor. As a test experiment, a small amount of the formed modified nanotubes was washed with ethanol, as a result of which ethanol acquired a red color. This indicated that during the reaction, not all of the iodine reacted with the MWCNTs, and some of it was absorbed into the pores of the carbon nanotubes.

Two samples were prepared from the final product. The first sample was a functionalized MWCNTs, in which both chemically (covalently) bound iodine and adsorbed iodine were present (Ch + ads. I - MWCNTs). In the second sample, iodine was bound to MWNTs only by covalent bonds (Ch I - MWCNTs). It was obtained as a result of repeated washing of the first sample with alcohol until the color of iodine completely disappears. The final samples were placed in a drying cabinet and kept until the alcohol was completely evaporated at a temperature of 1200 °C.

In particular, when preparing first sample for 1 gram of initial nanotubes, 3 grams of crystalline iodine was consumed, and thus the concentration of the latter in the sample was 75 wt % or 23.6 mmol / g. By weighing the sample after washing it with alcohol and drying, it was determined that in the second sample the iodine concentration was 57.6 % by weight or 10.7 mmol / g.

The iodinated MWCNTs were characterized by Scanning electron microscopy (SEM), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR).

2.3. Preparation of polymers (epoxy, silicone and polyurethane) / I - MWCNTs nanocomposites

As a starting materials for the preparation of polymer nanocomposites – multi-walled carbon nanotubes were used several polymeric resins – polyurethane, silicone and epoxy and various types of MWCNTs samples such as impurity-free (resin, iron catalyst particles) MWNCNTs, MWNCNTs sample with a chemically bound iodine (Ch I – MWCNTs) and a sample containing simultaneously chemically bound and adsorbed iodine (Ch + ads. I – MWCNTs).

Dispersing of carbon nanotubes was carried out in liquid resins and as a result of their subsequent polymerization a solid nanocomposites (MWCNTs / polymer) was obtained.

A required amount of polymer resin (in the case of an epoxy resin, also a hardener) and dispersible samples of carbon nanotubes were weighed in a beaker. The contents of the chemical glass with a spatula were carefully transferred to the lower plate of the mixer. Further, above the lower plate, an upper plate with a clearance of 200 micrometers was mounted, connected to an electric motor with a rotation speed of 450 rpm. The dispersion time was 10 minutes and the temperature was 20 °C. The resulting mixture of components was transferred to metal rectangular shapes with dimensions (length = 15 mm, width = 10 mm, thickness = 4 mm) and placed in a thermostat at a temperature of 100 °C where a polymerization process was carried out for 8 hours. Then, the electrical characteristics and surface morphology of the solid samples of the composites were examined. Figure 3 displays a laboratory made dispersing device for the preparation of polymer - carbon nanotubes composite [22].



Fig. 3. Dispersing device for the preparation of polymer-carbon nanotubes composite.

3. RESULTS AND DISCUSSION

3.1. The results of purification of synthesized MWCNTs from tarry impurities

Weighing of sample of obtained MWCNTs before and after washing with solvents (xylene, cyclohexane) showed that the amount of tarries in the pristine sample was 8.5 wt %.

3.2. The results of purification of MWCNs from the iron content

The processing of the MWCNTs sample with dilute nitric acid in accordance with the procedure described in the experimental section 2.1 reduced the initial iron content from 7.2 mass% to 3.5 mass%.

3.3. Scanning electron microscopy (SEM)

SEM photographs of synthesized MWCNTs and its elemental analysis are presented in Figure 4.

From the photograph of the synthesized carbon nanotubes a) it is observed that the average diameter of the obtained nanotubes is 37 nm, and the result of its elemental analysis b) showed that the weight percentage of carbon is 99.5 % and the residual amounts of the iron catalyst are 0.5 %.

As can be seen from the above photographs, carbon nanotubes were not severely degraded in the process of functionalization, but, as expected, their elemental composition changed.

According to elemental analysis, iodine was fixed on the surface of iodinated samples. In the sample (Ch I – MWCNTs) in which both the chemically bound and adsorbed forms are present, the amount of iodine is 4.9 weight.%, and in the sample (Ch + ads. I – MWCNTs) from which loosely bound iodine was washed – only 0.2 weight.%, which obviously corresponded to the chemically bound iodine on the MWCNTs surface.

3.4. Fourier transform infrared (FTIR) spectroscopy

The initial synthesized (pristine) MWCNTs and the iodine modified samples prepared on their basis were studied by IR spectroscopy (Figures 8 -10).

The IR spectrum of the initial (non-functionalized) MWCNTs sample demonstrate the presence of absorption bands in the 3430 and 1652 cm^{-1} regions related to the stretching vibrations OH and C = O, respectively.

The presence of these groups can be explained by the treatment of carbon nanotubes sample with nitric acid (28% HNO_3) in the process of purification from iron impurities.

In the IR spectrum of the sample (Ch I – MWCNTs) with chemically modified iodine, in contrast to the pristine sample, an intense peak of C-I appears in the range of absorption regions of 550-570 cm^{-1} , corresponding to chemically bound iodine. A similar band is also observed in the IR spectrum of the sample (Ch + ads. I – MWCNTs) which indicates the presence of chemically bound iodine in both samples.

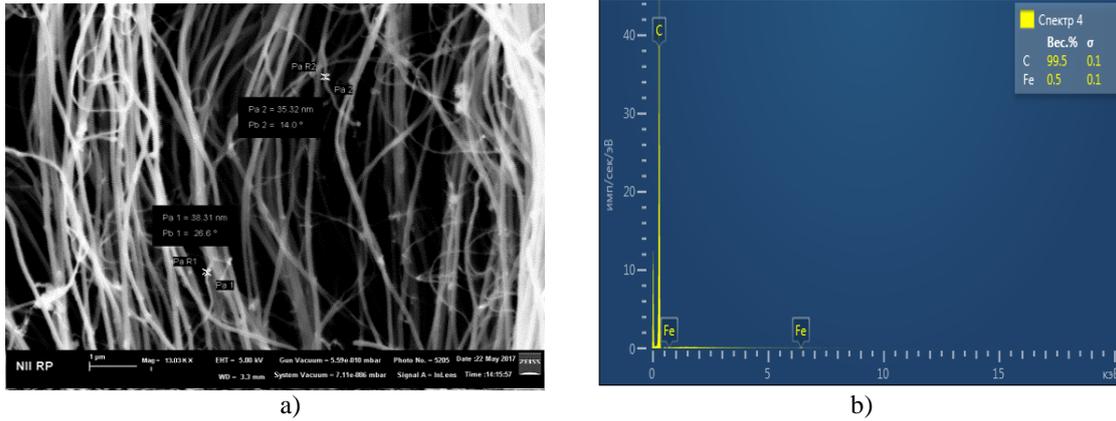


Fig. 4. a) SEM micrographs of synthesized MWNTs ($T = 900^{\circ}\text{C}$, $\text{Fc}:\text{CyH} = 20 \text{ mg / ml}$).

SEM photographs of functionalized MWCNTs and their elemental analysis are presented in Figures 5-6.

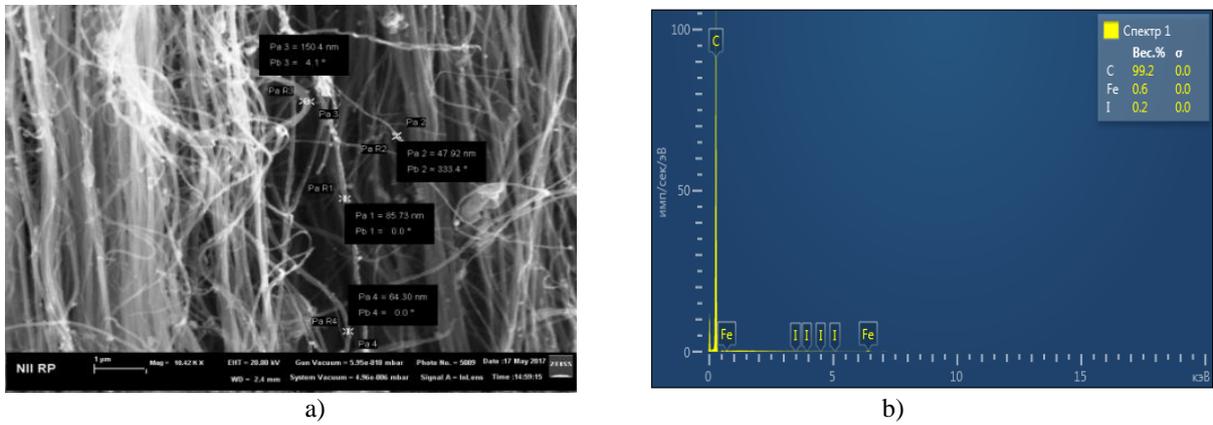


Fig. 5. a) SEM photograph and b) elemental analysis of Ch I – MWCNTs sample.

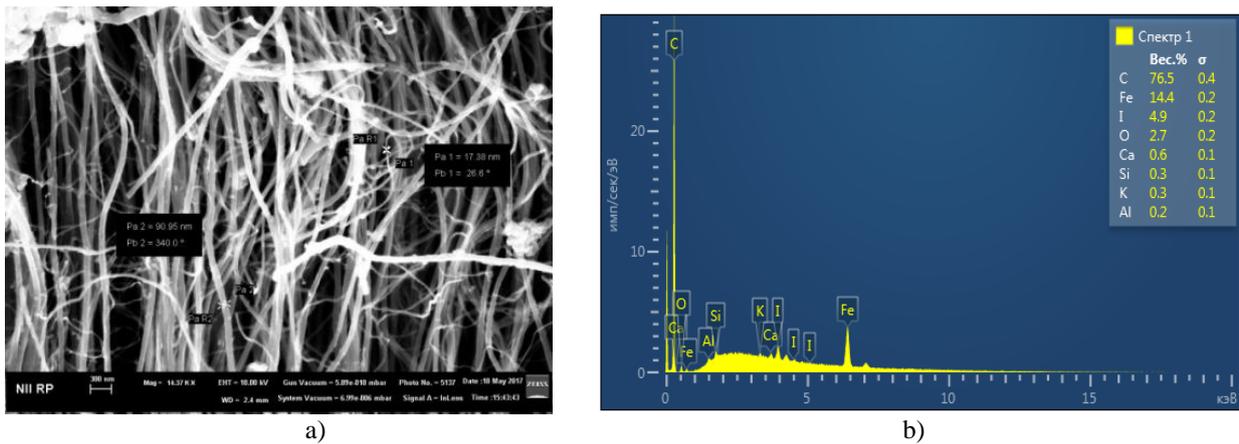


Fig 6. a) SEM photograph and b) elemental analysis of Ch + ads. I – MWCNTs sample.

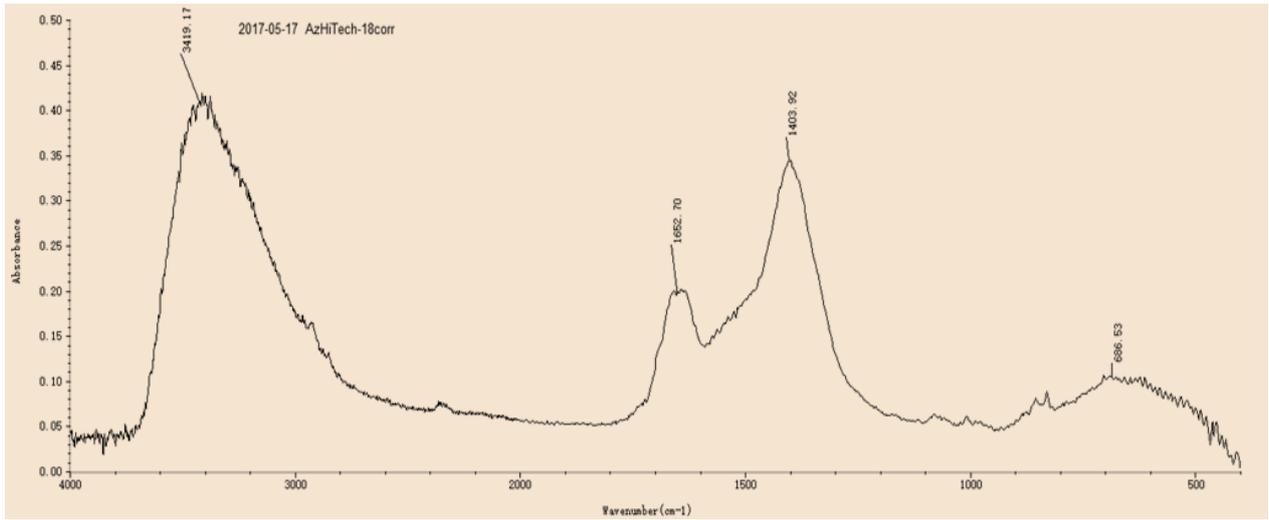


Fig. 7. The IR spectrum of the pristine sample of MWCNTs.

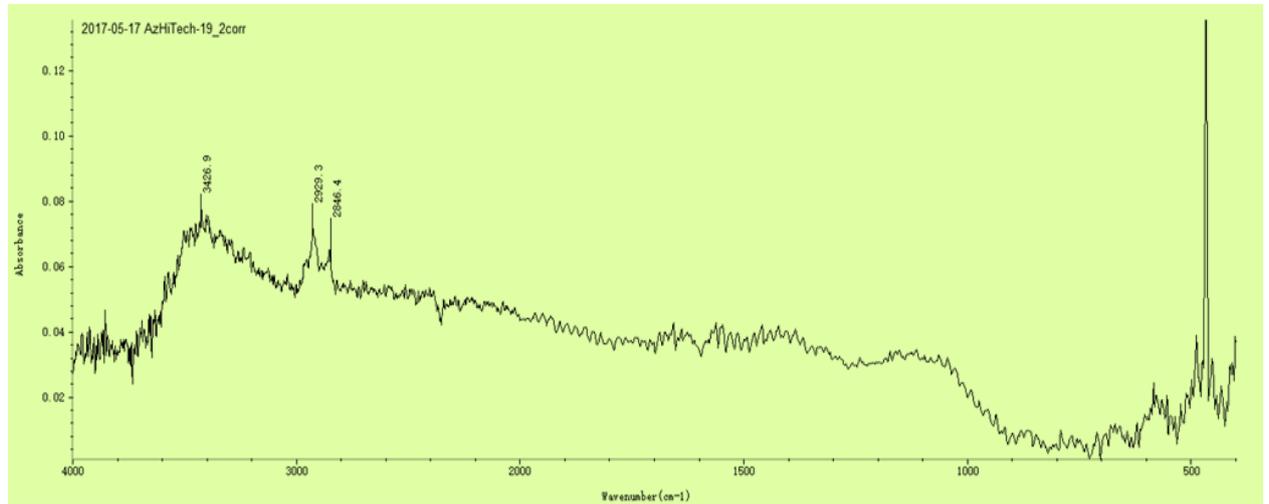


Fig. 8. The IR spectrum of the Ch I – MWCNTs sample.

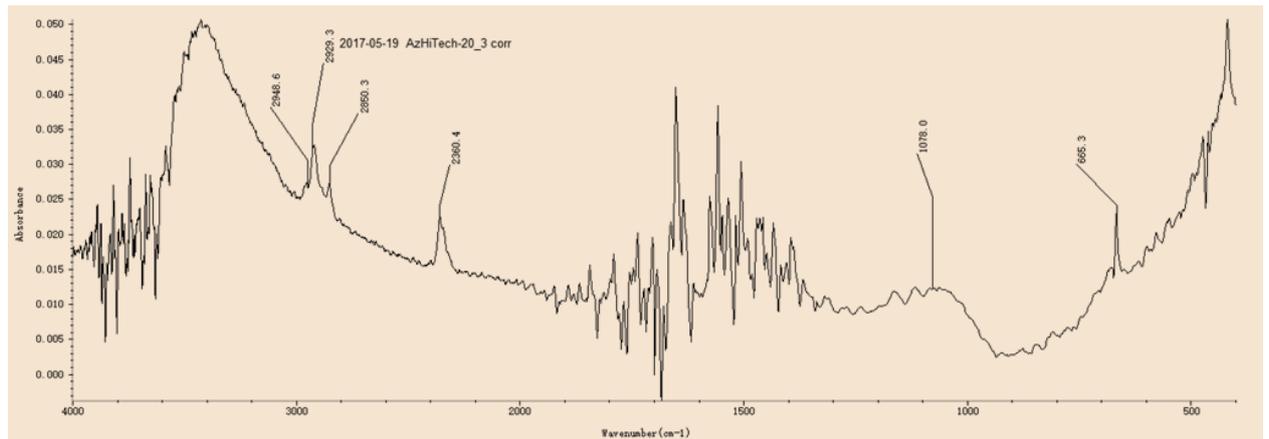


Fig. 9. The IR spectrum of the Ch + ads. I – MWCNTs sample.

3.5. Investigation of manufactured nanocarbon – polymer composites

On the basis of 3 samples of carbon nanotubes (pristine and 2 types of iodine -modified MWCNTs) and also based on 3 polymers: polyurethane, silicone and epoxy, 9 samples of nanocarbon – polymer composites were prepared for which their current-voltage characteristics were measured (Figures 10-14).

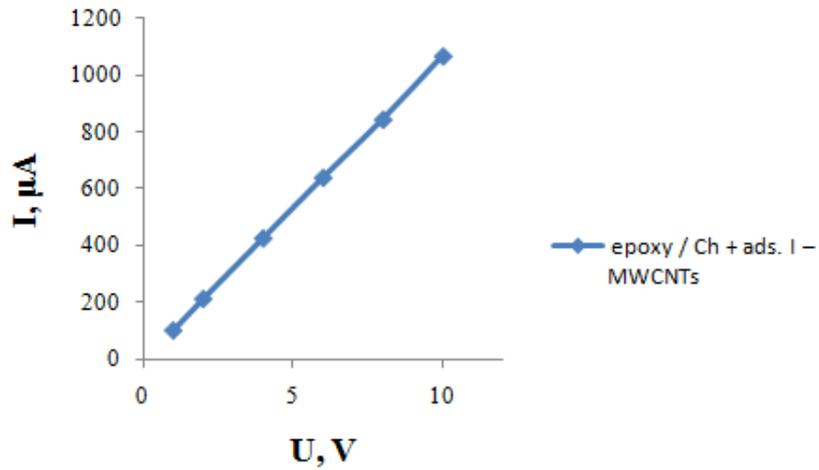


Fig. 10. Volt – ampere characteristics of polymeric nanocomposites based on epoxy / (Ch + ads.I – MWCNTs).

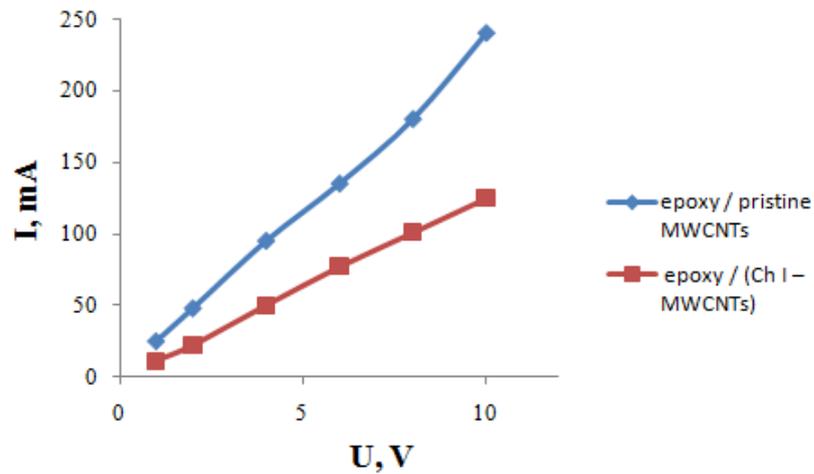


Fig. 11. Volt – ampere characteristics of polymeric nanocomposites based on epoxy / pristine MWCNTs and epoxy / (Ch I – MWCNTs).

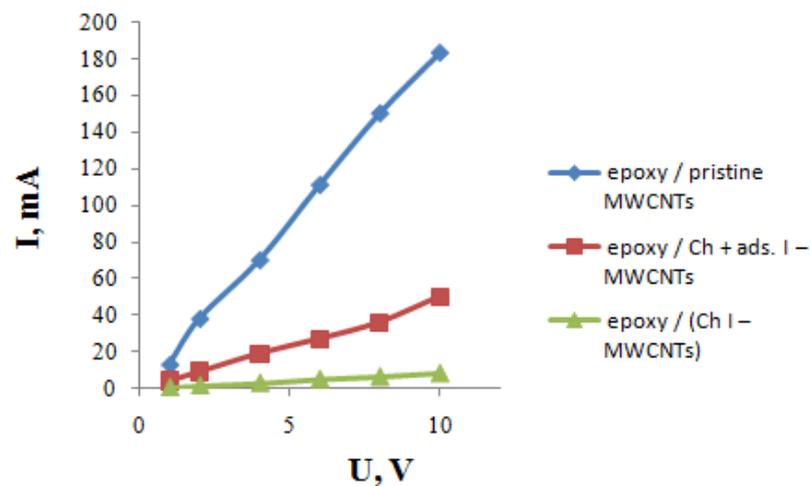


Fig. 12. Volt – ampere characteristics of polymeric nanocomposites based on epoxy / pristine MWCNTs, epoxy / Ch + ads. I – MWCNTs and epoxy / (Ch I – MWCNTs).

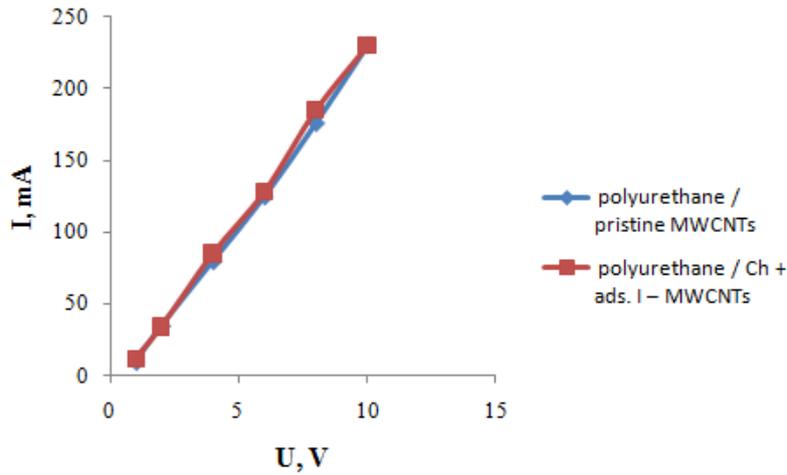


Fig. 13. Volt – ampere characteristics of polymeric nanocomposites based on polyurethane / pristine MWCNTs and polyurethane / (Ch + ads.I – MWCNTs).

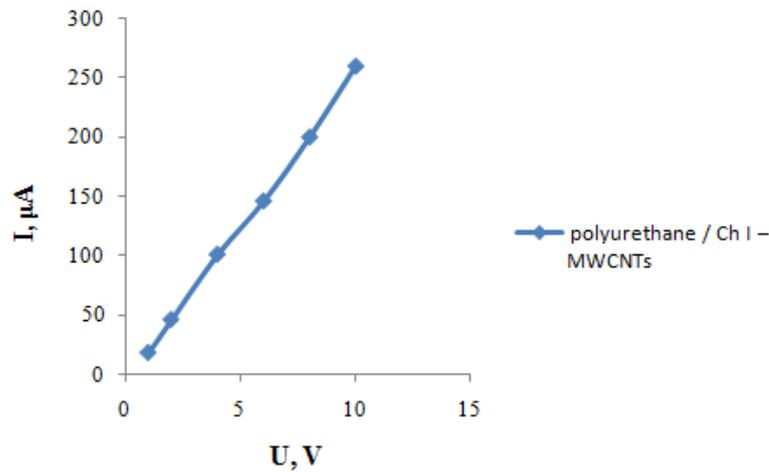


Fig. 14. Volt – ampere characteristics of polymeric nanocomposites based on polyurethane / Ch I – MWCNTs.

Based on these volt – ampere characteristics by the formulas:

$R = U / I$, where R is the resistance {Om}, U is the potential difference {V}, I is the current {A};

$\rho = R * L / S$, where ρ is the resistivity {Om * m}, L is the distance between the measured faces, {m}, S is the cross-sectional area of the sample; {m²};

$\sigma = 1 / \rho$, {S / m}, where σ is the conductivity;

The electrical resistance, specific resistance and conductivity were calculated (Table 1).

Table 1.

Electrical properties of polymer-nanocomposite materials based on volt – ampere measurements.

Nº of samples	Sample composition	R, Om	ρ , Om·m	σ' , cm·m ⁻¹
1	PY + 5weight. % pristine MWCNTs	49	0,1225	8,2
2	PY + 5 weight. %Ch I – MWCNTs	36625	109,9	$9,1 \cdot 10^{-3}$
3	PY + 5 weight. %Ch + ads. I – MWCNTs	49	0,1225	8,2
4	Silicone+ 5 weight. % pristine MWCNTs	58	0,179	5,57
5	Silicone +5 weight. %Ch I – MWCNTs	221	0,51	1,95
6	Silicone +5 weight. %Ch + ads. I – MWCNTs	1300	3,91	0,26
7	Epoxy + 5 weight. % pristine MWCNTs	42	0,065	15,3
8	Epoxy + 5 weight. %Ch I – MWCNTs	83	0,1	10,0
9	Epoxy + 5 weight. %Ch + ads. I – MWCNTs	9400	30,14	$33,1 \cdot 10^{-3}$

As can be seen from the table, the composite with the highest specific electrical conductivity consists of epoxy resin and pristine multiwalled carbon nanotubes.

From the table also shows the influence of the nature of the polymer matrix on the electrical conductivity of composites. Thus, in 3 samples with the same nanocarbon additive (5 weight.% pristine MWCNTs), during the transition from an epoxy resin matrix to a polyurethane specific conductivity decreased from 15.3 to 8.2 Sm / m, and in the case of a silicone polymer, even lower – 5.57 Sm / m. At the same time, when changing to iodine - containing carbon nanoadditives (№ 2, 5, 8), the nature of the matrix effect is changing. In this case, the composite with an epoxy matrix also has the highest electrical conductivity, but the least is a silicone one.

It also follows from the data of the table 1 that the type of bonding of iodine (chemical, adsorption) with carbon nanotubes also affects the electrical conductivity of the composites. Thus, for composites based on epoxide and silicone in the case of MWCTs functionalized with covalently bound iodine (samples № 8, 5), the electrical conductivity is much higher than when iodine is present in the composite simultaneously in two forms, both chemically bound and adsorbed iodine (samples № 9, 6). For polyurethane composites (samples № 8, 5), the

electrical conductivity also differed greatly, but in the case of covalently bound iodine it was lower.

CONCLUSIONS

1. Multi-walled carbon nanotubes were synthesized by using of Aerosol-assisted chemical vapour deposition method (AACVD), their purification and functionalization with iodine-containing groups was carried out. The composition and structure of synthesized and modified CNTs are determined by elemental analysis, IR, SEM and AFM microscopy.

2. Based on the obtained MWCNTs and polymeric materials including polyurethane, silicone and polyepoxide, new CNT / polymer composites have been developed. For the fabricated nanostructured composites, volt-ampere characteristics are recorded and the resistivity and conductivity values are determined. It is shown that the electrophysical properties of nanocomposites based on iodine-modified MWCNTs are influenced both by the type of bonding of iodine with a carbon nanotubes (chemical bonding or physical adsorption) and by the nature of the polymer matrix in the composite.

-
- [1] S. Nikam *et al.* Advanced Nanomaterials and Nanotechnology. Proceedings of the 2nd International Conference on Advanced Nanomaterials and Nanotechnology. 2013. Vol. 143. pp. 2-21.
- [2] G. Lota *et al.* Carbon nanotubes and their composites in electrochemical applications. Energy Environ. Sci. 2011. Vol. 4, n. 5, pp. 1592-1605.
- [3] J. Dimitrios *et al.* Carbon Nanotubes Enhanced Aerospace Composite Materials. 2013. pp. 155-183.
- [4] D. Untereker, S. Lyu, J. Schley, G. Martinez, L. Lohstreter. Maximum Conductivity of Packed Nanoparticles and Their Polymer Composites. ACS Appl. Mater. Interfaces. 2009, Vol. 1, n.1, pp. 97-101.
- [5] S. Yengejeh *et al.* A Primer on the Geometry of Carbon Nanotubes and Their Modifications. Applied Sciences and Technology. 2015. pp. 17-29.
- [6] K. Grabowski, P. Zbyrad, T. Uhl, W. Staszewski, P. Packo. Multiscale electro-mechanical modeling of carbon nanotube composites. Computational Materials Science. 2017. 135. pp. 169-180.
- [7] S. Bose, R. Khare, P. Moldenaers. Assessing the strengths and weaknesses of various types of pre-treatments of carbon nanotubes on the properties of polymer / carbon nanotubes composites: A critical review. Polymer. 2010. pp. 975 -993.
- [8] S. Rana, R. Prasanth, L. Tan. Handbook of Polymer Nanocomposites. Processing, Performance and Application. 2015. Vol. B. pp. 104-117.
- [9] Swain *et al.* Polymer Carbon Nanotube Nanocomposites: A Novel Material Asian J. Chem. 2010. Vol. 22, n.1, pp. 1-15.
- [10] S. Bal, S Samal. Carbon nanotube reinforced polymer composites – A state of the art. Indian Academy of Sciences. 2007. Vol 30, n. 4, pp. 379-386. Insight into the Broad Field of Polymer Nanocomposites: From Carbon Nanotubes. to Clay Nanoplatelets, via Metal Nanoparticles. E. Stefanescu. Materials. 2009. Vol. 2. pp. 2095-2153.
- [11] K. Shehzad *et al.* Effect of the carbon nanotube size dispersity on the electrical properties and pressure sensing of the polymer composites. J Mater Sci. 2016. 51. pp 11014-11020.
- [12] S. Swain *et al.* Polymer Carbon Nanotube Nanocomposites: A Novel Material. Asian Journal of Chemistry. 2010. Vol. 22, № 1, pp 1-15.
- [13] G. Kaur *et al.* Electrically conductive polymers and composites for biomedical applications. The Royal Society of Chemistry. 2013. pp. 2-17
- [14] T. Michel *et al.* EXAFS investigations of iodine-doped carbon nanotubes. The American Physical Society. 2006. Vol. B, n.73. p. 195419-1-195419-4.
- [15] Z. Qian *et al.* Facile synthesis of halogenated multi-walled carbon nanotubes and their unusual photoluminescence. J. Mater. Chem. 2012. Vol. 22, pp. 22113 -22119.
- [16] D. Janas *et al.* Iodine monochloride as a powerful enhancer of electrical conductivity of carbon nanotube wires. Carbon. 2014. Vol 73, pp. 225-233.
- [17] N. Zainal. Preparation and Characterization of Iodine-doped Multi-wall Carbon Nanotubes. AIP Conference Proceedings 1017. 2008. Vol. 159, pp. 159 -163. doi: 10.1063/1.2940618.
- [18] W. Zhou *et al.* Raman scattering and thermogravimetric analysis of iodine-doped multiwall carbon nanotubes. Applied Physics Letters. 2002. Vol. 80, n.4, pp. 2553-2555.
- [19] T. Michel *et al.* Structural selective charge transfer in iodine-doped carbon nanotubes. Journal of

Physics and Chemistry of Solids.Vol. 67. 2006, pp. 1190-1192.

- [20] *Fan L-n, Xu X-c.* A stable iodine-doped multi-walled carbon nanotube-polypyrrole composite with improved electrical property. *Composites Science and Technology.* 2015. doi: 10.1016/j.compscitech.2015.09.014.
- [21] *S. Abdullayeva et al.* Characterization of high quality carbon nanotubes synthesized via Aerosol - CVD.

Journal of Advances in Physics. 2015. Vol .11, n.4, pp 3229-3237.

- [22] *S. Abdullayeva.* Carbon Nanotubes Dispersion in Polymers by Two-Factor Mechanical Method. *Advances in Materials Physics and Chemistry.* 2016. Vol. 6. pp 29 -304. DOI: 10.4236/ampc.2016.611028.

Receviied: 05.09.2017