Functional features of the nanocomposites, based on CNT

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Abstract – This article includes working out and trial of technological process of manufacturing functional nanocomposite on the basis of the epoxy resin and multiwall carbon nanotubes (CNT) of the Taunit-MD type. We discuss two advanced variants of implementing this nanocomposite: first of them - increasing strength of fiber composite material; second - using acquired material electric conductivity for determining temperature and pressure (deformation) changes. Material was prepared by means of a planetary mixer and ceramic grinding bodies. We performed dispersion quality analysis by means of an atomic-force microscope. This analysis demonstrated uniform distribution of the nanoparticles over the solidified material surface. Strength analysis result allowed obtaining data on material and matrix modulus of elasticity and strength changing. Material electric conductivity study allowed obtaining coefficients of thermo- and pressure sensitivity for sensors with different orientation of carbon nanotubes with weight content of 1%, 2%, and 3%. Performed study data demonstrate potential of using CNT as conductive particles in composite unit, allowing, for example, perform monitoring of the structure condition.

Keywords - carbon nanotubes, epoxy resin, dispersion, agglomerates, composite material, strength, and sensor

I. INTRODUCTION

Carbon nanotubes (CNT) are one of the most promising nanoparticles. This form of carbon, being a graphene sheet, forming a pipe, has high mechanical and electric conductive features [1] - [3]. Their potential as reinforcing filling material for polymers was not implemented to full scale, mechanical and electrical features of produced composites have not reached predicted values. This is due to low carbon nanomaterials adhesion to polymer matrix and their higher inclination to agglomeration [4]–[6]. Following methods are used for destruction of the CNT agglomerates: ultrasonic exposure [7], [8], agitating with high shearing force [9], [10], etc. These methods don't always allow obtaining necessary material quantities, so carbon nanotubes dispersion quality verification is hindered. Solving these problems will allow wide utilization of produced carbon nanomaterial in composite structures.

High mechanical features assure reasonability of introducing nanotubes into polymers or metals. It is expected, that high strength nanophase, spread in the material volume, will assure high composition strength. Solving this task faces some difficulties, related to nanoparticles features [11]. At present many researchers deal with problems, related to producing composite materials, reinforced by carbon nanotubes.

Nanocomposite material on the basis of carbon nanotubes has high electric conductivity under low volumetric content (1-3 %) [12]. Electric conductivity under indicated low content of conductive material is defined by tunnel effect [13], [14], appearing between separate nanotubes. Electric conductivity can change under external factors (such as temperature, deformation or pressure) because of matrix geometrical dimensions changing and because of changing distance between nanotubes. Micro defects appearing will have major effect also influencing the conductivity. Sensors on the basis of CNT can have wide range of overall dimensions (from several microns to several centimeters), high sensitivity and universality. As of now, several CNT sensors types were designed [15] - [19].

These features of the carbon composite material allow using it as sensors for monitoring structures condition. Using resin as matrix of the carbon nanocomposite allows placing the sensor inside composite structures without disturbing its integrity. When correctly organizing monitoring system, it is possible to determine defects sizes and location. Complexes of devices on the basis of the CNT can be used for monitoring fatigue in aviation, for diagnostics of bridges, ships, and other structures, where fatigue is the main factor, determining service life and reliability. Variation of volumetric content and control over nanotubes orientation in polymer matrix allow

producing sensors with set features, improving sensitivity and simplifying structure service life and reliability evaluation.

This work deals with methods of preparing nanocomposite materials with carbon nanotubes and most promising variants of implementing this material.

II. RESEARCHED MATERIAL

TAUNIT-MT was used in this work. This material is presented by filamentary structures of the polycrystalline graphite in the form of bulk powder from black agglomerates. Agglomerates of micrometric size have structure of crossed bundles of multiwall tubes. Taunit-MD is a modified material with improved morphological and physical-mechanical parameters (TABLE I).

Taunit-MD parameters control was performed by transmission electron microscope JEOLJEM 2100 (Fig. 1). Images analysis shows than individual CNT size in collapsed form is 2 - 5 times smaller, than spread CNT length.

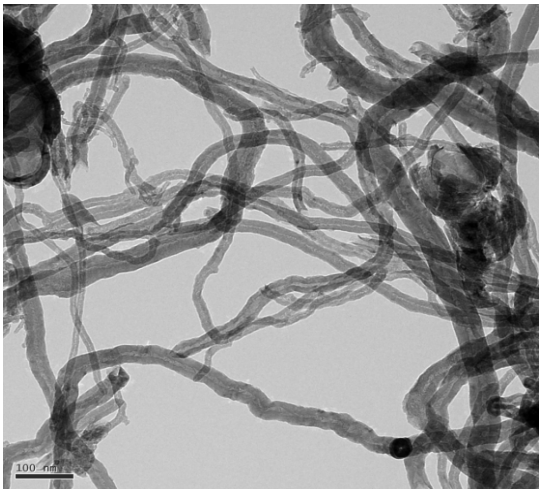

Fig. 1. CNT Taunit-MD in transmission electron microscope JEOL (25,000x)

TABLE I. CNT Taunit-MD general characteristics [20]

Parameters	**Taunit-MD**
Outside diameter, nm	8-15
Inside diameter, nm	4-8
Length, μm	2 and more
Total admixtures volume, % (after treating)	up to 5 (up to 1)
Balk density, g/cm3	0.03-0.05
Specific geometrical surface, m^2/g	300-320 and more
Thermal stability, °C	up to 600

Upon our research data CNT outside diameter is from 10 to 50 nm, inside diameter from 3 to 8 nm, length is more than 2 mkm.

III. MATERIAL PREPARATION

In order to achieve best electrical and mechanical features of the nanocomposite material it is better to use separate single wall carbon nanotubes, as they are more putty and have better electrical properties, which leads to increasing sensitivity of composite, base on such tubes. In order to make used product parameters closer to required, it is necessary do disperse CNT by strong shear in epoxy resin. Such exposure allows splitting big agglomerates and uniformly spreading the tubes in resin volume, facilitating producing homogenous suspension.

CNT dispersion was performed in mixer KURABO Mazerustar kk250 (Fig. 2), under mode 9-8, corresponding to platform rotating under speed of 1,700 rpm, and container rotation speed of 1,580 rpm. Dispersing was performed in epoxy resin ED-20 [21] by means of zirconium oxide (ZnO_2) balls with diameter of 1.2 - 1.5 mm with total weight, equal to mixture weight. When rotating in a vessel, balls generate shear forces, facilitating mechanical splitting and fragmentation of associated particles (agglomerates).

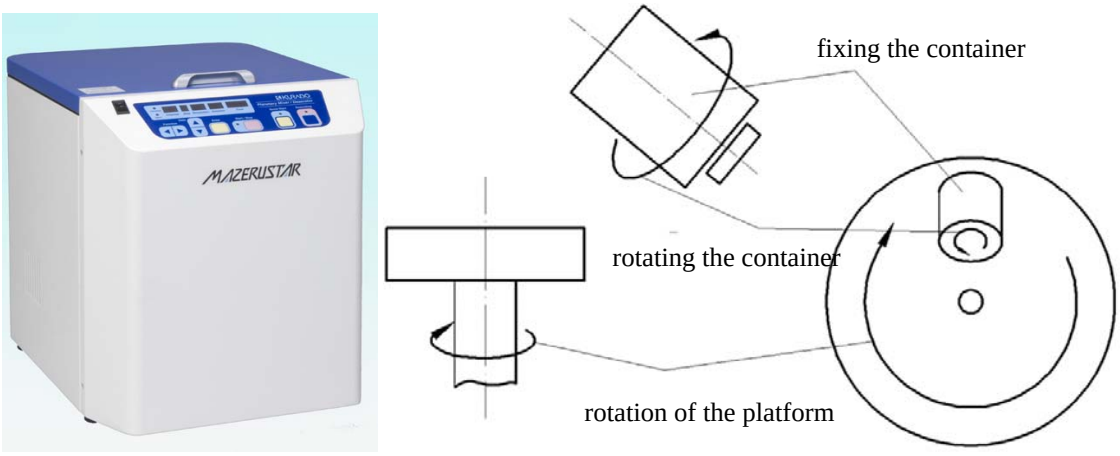

Fig. 2. Mixer KURABO Mazerustar kk250 and operating principle

Timeframes for obtaining better dispersion quality were determined experimentally with verifying by atomic-force microscope (Fig. 3-4), at the area of 20x20 mkm. Dispersion was performed during four time periods: 10 s, 50 s, 100 s, and 150 s.

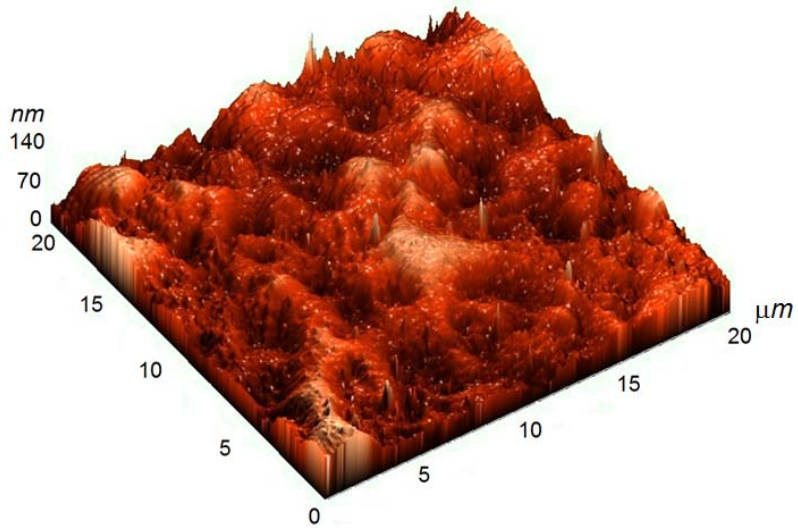

Fig. 3. Solidified material surface after 10 seconds treatment in planetary mixer

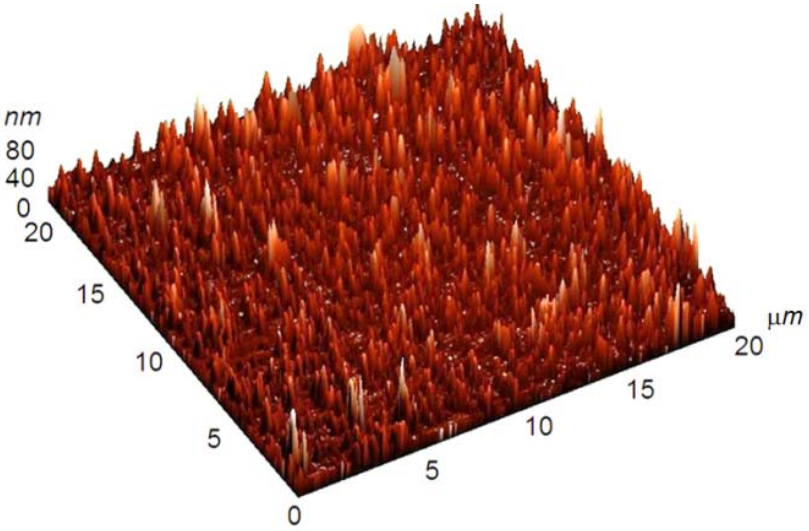

Fig. 4. Solidified material surface after 150 seconds treatment in planetary mixer

Based on obtained date we can conclude that enlarging dispersion period leads to decreasing surface granulation (from 150 nm to 80 nm). Solid particles (CNT) spreading (sharp peaks) becomes more homogenous.

IV. MATERIAL STRENGTH STUDY

Tvaron 709 fabric with plain structure was used as composite material for strength study. Fabric was saturated with treated suspension with CNT nanoparticles of mass share of 1 % and 2 %. Second fabric sample was reinforced by SiO_2 particles.

Strength of saturated fiber composite σ_1 is determined according to formula [22]

$$\sigma_1 = \left(E_f \cdot v + E_m \cdot (1 - v)\right) \cdot \varepsilon, \quad (1)$$

where:

E_f, E_m - fibers and matrix elasticity modulus, accordingly,

v - fibers volumetric share,

ε - total deformation.

After reorganizing formula (1) we can determine stress in matrix σ_m under fibers destructing deformation

$$\sigma_m = \frac{\sigma_1 - \sigma_f \cdot v}{1 - v}. \quad (2)$$

From formula (2) we can see, that for determining stresses in polymer matrix it is necessary to determine fibers strength σ_f. In order to do so we took 5 fibers from fabric Tvaron 709. Tests were performed on machine Instron 5942. We have determined maximum strength of 1,375 MPa and module of elasticity of 96.7 MPa. Module of elasticity was determined by means of Advanced Video Extensometer Instron.

5 types of samples were produced for investigating fiber composite strength: without nanoparticles; 1% SiO_2; 2% SiO_2; 1% CNT, and 2% CNT, from which we have cut samples with fibers orientation [0/90] and [±45].

Test results for samples with [0/90] fibers orientation are presented at Fig. 5 and in Table II.

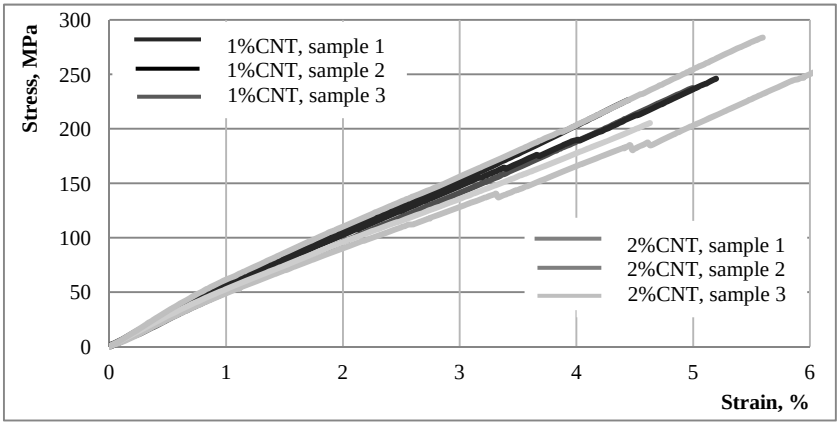

Fig. 5. Testing samples with CNT

TABLE II. Test results for samples with [0/90] fibers

Filler weight share	av. σ_{ts}, MPa	Filler reinforcement, %	av.E, GPa	σ_m, MPa
0	238	-	5.58	36.1
1% SiO_2	242	1.68	5.84	40.8
2% SiO_2	269	13.3	5.17	73.7
1% CNT	237	-0.521	4.84	34.6
2% CNT	248	4.14	4.59	47.8

Test results for samples with [±45] fibers orientation are presented at Fig. . 6 and in Table III.

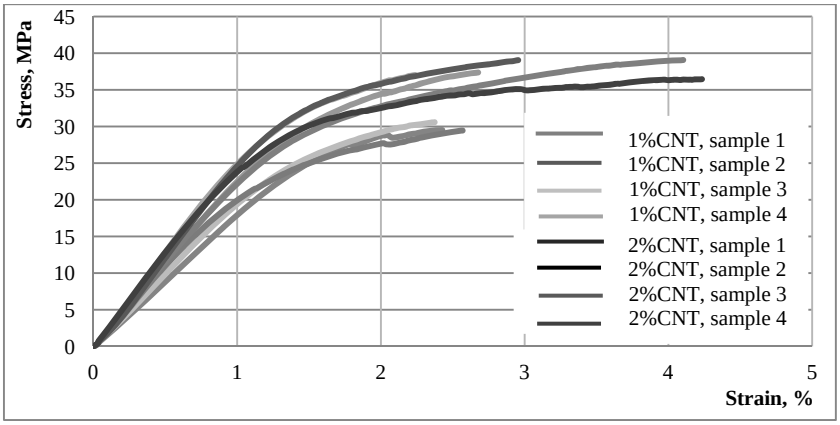

Fig. 6. Testing samples with CNT

TABLE III. Test results for samples with [±45] fibers

Weight share of the filler	av. $Б_{ts}$, MPa	Reinforcement with filler, %	av. E, GPa
0	32.8	-	2.51
1% SiO_2	36.1	10.1	2.69
2% SiO_2	39.5	20.4	2.60
1% CNT	31.7	-3.19	2.05
2% CNT	37.9	15.6	2.53

After analyzing obtained data we can conclude that adding nanoparticles to fiber composite with weight share up to 1% does not lead to noticeable strength improving. Adding 2 % of nanoparticles increase strength up to 10-20%, elasticity module decreases in majority of cases. That can be caused by non-quality dispersion or by not enough strong adhesive connection between nanoparticles and binding compound. Using silica oxide as filler turned to be more advantageous due to higher strength improving and lower price.

[0/90] fibers samples destruct in lateral direction with lamination and destruction of edge fabric fibers. We can see it at tests curves (small steps with decreasing sample stress).

In [±45] fibers samples polymer matrix destructs when fibers slide against each other.

V. ELECTRIC PROPERTIES EXAMINATION

CNT weight share in suspension for preparing samples is equal to 1%, 2% and 3%. CNT percolation threshold is at level of 1% [23], so, in order to simplify sensors electric features research, we are not considering lower nanoparticles content.

Glass is used as base for sensor in this work. Other materials (fabric, paper, etc.) can be also used, or sensor can be used without base.

Generated suspension was spread over glass with edges, covered with paper for assuring gap of 0.1 mm. Oriented location on nanotubes was assured by shear forces, applied by a spatula. After polymerization we cut films with traverse and longitude tubes orientation and produced sensor for research from these films. Final sensor is presented at Fig. 7, where: 1- glass plate, 2 - polymer carbon composite film, 3 - current conducting glue Kontaktol, 4 - silver conductors, and 5 - copper conductors.

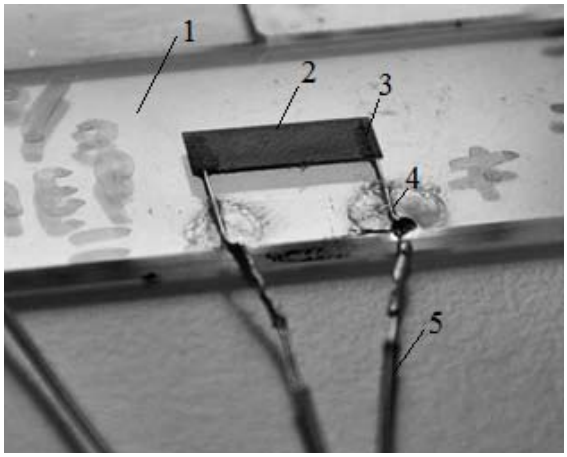

Fig. 7. Final sensor

Measurements were performed by implementing double-contacts method, by means of digital parameters measuring device LCR (LCR-78101G), manufactured by Good Will Instrument Co. Ltd. (GW Instek). Sensors readings were monitored under constant current and voltage of 2 V.

Samples resistance measuring results are presented in Table IV.

TABLE IV. Sensors resistance measuring results

CNT weight share, %	Orientation direction	Sample No.	Resistance, kOhm	Specific resistance, Ohm·m
1	longitude	1	102	3.64
		2	117	3.23
	traverse	1	281	9.32
		2	373	17.7
2	longitude	1	130	3.03
		2	147	2.69
	traverse	1	590	15.7
		2	513	12.8
3	longitude	1	1.72	0.126
		2	2.23	0.135
	traverse	1	6.77	0.371
		2	7.20	0.435

As we can see from Table IV, samples with traverse CNT orientation are characterized with higher (3 and more times) resistance than samples with longitude CNT orientation, indicating difference in nanotubes orientation.

A. Testing sensors under changing pressure

Tests were performed on machine Instron 5942. In order to assure uniform distribution, load was transferred through rubber gasket. Load was changing from 0 to 500 N that is equivalent to changing pressure from 0 to 30 bars. Typical sensor resistance dependence from pressure changing is indicated on Fig. 8 (CNT weight share is 2 %, tubes are oriented longitudinally).

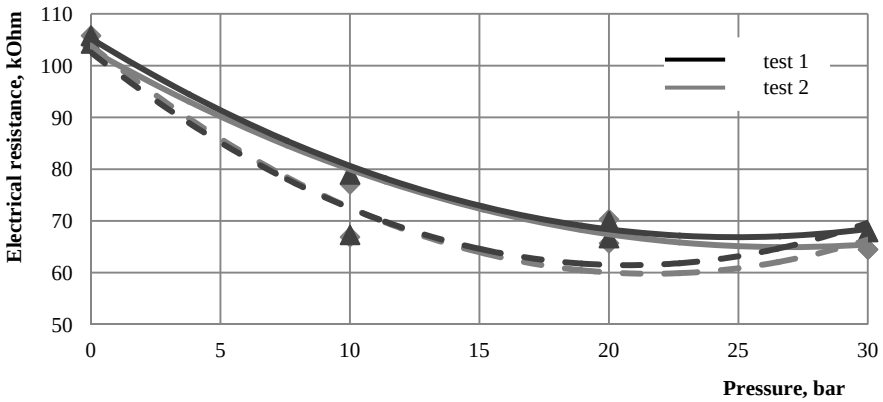

Fig. 8. Sensors resistance dependency from pressure changing (unloading is indicated by dotted line)

As it was supposed, resistance decrease under pressure increasing, because of nanotubes approximation and because of increasing quantity of contacts between them. Revealed dependences are not linear, may be because at first loading stage new contacts appearing process prevails, while later resistance decreases only because of nanotubes approximation. Pressure sensitivity coefficients for the most sensitive area (up to 10 bars) are presented in TABLE IV.

TABLE V. Investigated sensors pressure sensitivity coefficients

CNT content, %	Pressure sensitivity coefficient, Ohm/bar			
	Sample 1, longitude	Sample 2, longitude	Sample 1, traverse	Sample 2, traverse
1	303	402	-	-
2	397	255	51.5	66.9
3	21.0	7.82	3.84	4.69

Sensors with lower CNT content have higher sensitivity.

B. Testing sensors under changing temperature

Testing was performed by using water-bath Brookfield TC-502. Sensor sample was protected by water-proof pack and placed into water-bath; water temperature was changing from 27 °C to 90 °C.

Typical sensor resistance dependence from temperature changing is indicated on Fig. 9 (CNT weight share is 2 %, tubes are oriented longitudinally).

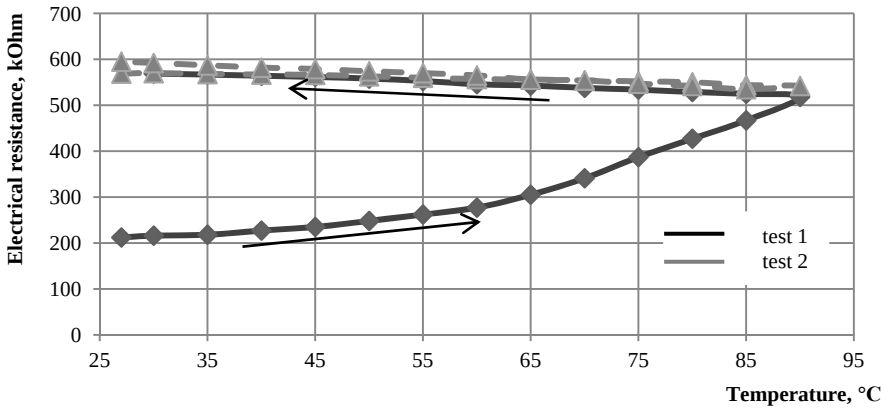

Fig. 9. Sensors resistance dependency from temperature changing (unloading is indicated by dotted line)

During first test all samples demonstrated resistance increasing under heating. Nanotubes prevent sample elongation under heating, leading to stress increasing around nanotubes. Under temperatures higher than 60 °C resin softens, leading to shifting resin against nanotubes and to contact deterioration. Moisture also evaporates from resin under heating. Under near 100 °C evaporation is more intensive. After heating up to 90 °C and at the beginning of cooling most moisture has already evaporated, so samples are stable.

Contrary to resin, nanotubes practically don't change their size under heating. So, nanotubes, oriented along shear, prevent sample elongation, but don't prevent traverse dimensions increasing. As tubes are located not strictly parallel, but are entangled between each other, cross section dimension increasing leads to contacts increasing and to decreasing resistance.

The nanotubes also change resistance under temperature change, but such change is not large (under temperature changing for 100 °C, resistance changes on less than 1% (according to research [24]).

TABLE VI presents thermal sensitivity coefficients for tested sensors.

TABLE VI. Thermal sensitivity coefficients

CNT content, %	Thermal sensitivity coefficient, Ohm/°C			
	Sample 1, longitude	Sample 2, longitude	Sample 1, traverse	Sample 2, traverse
1	2.42	4	7.59	9.27
2	1.03	1.09	4.8	3.35
3	0.0014	-	0.0134	0.02

As we can see from the table, samples with lower CNT content and traverse nanotubes orientation are characterized with higher thermal sensitivity coefficient.

VI. CONCLUSIONS

We have generated functioning composite nanomaterial on the basis of suspension from epoxy resin and CNT. Following results were obtained:

1) We've generated and tried technological process of generating functional nanocomposite on the basis of epoxy resin ED-20 and CNT of TAUNIT-MD type. We've examined problems of dispersing high-viscous epoxy resins suspensions with nanotubes. We've demonstrated method of dispersing CNT in viscous media by means of planetary mixer. Verification on atomic-force microscope demonstrated uniform spreading of solid particles and decreasing their height on the surface of the solidified material after treating during 150 seconds.

2) Research on strength of the composite material with added CNT demonstrated that: weight share of the CNT up to 1% does not result in noticeable strength increasing. Adding 2 % of nanoparticles increase strength up to 10-20%, elasticity module decreases in majority of cases. That can be caused by non-quality dispersion or by not enough strong adhesive connection between nanoparticles and binding compound.

3) We've generated method of producing sensors on the base of the ordered structure of functional nanocomposites with different CNT weight share; sensors electric resistance can be regulated in the range from several Ohm to hundreds Ohm. Sensors with lower CNT content are characterized with higher sensibility, but they are unstable and have high features dispersion, as CNT content is on the edge of percolation threshold.

This work demonstrates high perspective of using nanocomposite material on the basis of epoxy resin and CNT. Using CNT in composite structure allows performing monitoring structure condition. Used sensors will not decrease strength and will not increase structure weight.

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