Research of strength and conducting properties of composite material modified by carbon nanotubes

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Abstract. The article studies the fabrication mechanism of semiconducting composite polymer material based on methyl methacrylate, butyl methacrylate and methacrylic acid co-polymer doped with carbon nanotubes (CNT). A mechanism for fabrication of composite polymer material modified with carbon nanotubes has been developed, and experimental studies of the strength, electrical and physical characteristics of the materials obtained have been carried out.

1. Introduction
To date, research into new polymeric materials that consist of high-molecular compounds with different chemical properties, the so-called co-polymers, is being intensively carried out. There are a great number of articles [1-3] on the study of polymers based on methacrylic acid esters. Due to their unique properties, these polymer compounds are in demand not only in industry but also in medicine. There are studies [4], that confirm the possibility of joint polymerization of the three structural monomers: butyl methacrylate (BMA), methyl methacrylate (MMA) and methacrylic acid (MAA). Homo- and copolymers possess a number of properties that are very important for materials used in electronics.

To date, the most promising method for fabrication of semiconductive and conductive polymeric materials is the use of nanofillers, which results in the production of polymer nanocomposites. The most common nanomaterials with unique properties are carbon nanotubes (CNTs). The exceptional mechanical and electrical properties of CNTs [5, 6] make it possible to use them as nanofillers in order to obtain new materials with predictable properties and characteristics. Modification of CNTs in the polymer matrix can lead to a significant improvement in the mechanical characteristics of the initial polymers (co-polymers) as well as to an increase in their conductivity. This will result in much wider application of polymeric materials in electronics, medicine, energy, etc. That is why fabrication of composite materials based on CNTs and the study of physical, chemical and mechanical properties of polymer nanocomposites is relevant.

In the present work, the following monomers are investigated: methyl methacrylate (monomers of methacrylic ester), butyl methacrylate (monomers of butyric ester), and methacrylic acid (MMA-BMA-MC). According to the type of conductivity, polymers based on selected monomers (polymethyl methacrylate, polybutyl methacrylate, polymethacrylic acid) are dielectrics [7–8]. Incorporated into a polymer matrix based on the three selected components, nanotubes will provide a material that can be used in many engineering designs. The use of CNTs as fillers in polymeric materials will improve
their performance characteristics. Conductive properties acquired by these materials will significantly expand the scope of their application.

2. Experiment
Polymer material that is a filled acrylic composition of the “powder - liquid” type which sets hard at a room temperature was chosen. As polymer powder, suspension of ternary copolymer of MMA, BMA and methacrylic acid is used. The suspension liquid of the polymer used is methyl methacrylate that contained an adduct of epoxy resin and methacrylic acid, dimethyl para-toluidine and a stabilizer. To obtain a composite polymer material with improved performance characteristics, CNTs were introduced into the polymer matrix. A series of samples were prepared (the size 15x10x5mm) with different proportions of CNT (from 0.01 to 0.05 wt.%) of the total mass of the polymer powder and a reference sample without CNTs (0 wt.%). These samples were subjected to tests to define the most significant strength characteristics of the material under study. First, the prepared samples were subjected to the Rockwell hardness test using the TKSM-14 hardness tester [9-11]. Hardness measurements were carried out by indenting the diamond indenter at a load of HRC 45 kgf/mm². The obtained values of hardness were averaged (Table 1). Further, the maximum permissible load, i.e. the destructive load for the prepared samples with different proportions of CNTs and the pure sample were measured. The measurements were carried out using the universal testing machine REM-50-1. The test lasted until the specimen had been destroyed with an initial load value applied to the specimen, 0.05 kN. The obtained values are given in Table 1.

Table 1. The values of hardness, maximum permissible load and destructive stress in samples of composite material based on a ternary copolymer with different proportions of CNT, σ is standard deviation.

| CNT proportion, % | 0  | 0.01 | 0.03 | 0.05 |
|-------------------|----|------|------|------|
| HRC 45 kge/mm²    | 39±4 | 44±2 | 52±4 | 68±2 |
| Maximum permissible stress F, % | 62.15 | 64.83 | 69.20 | 73.48 |
| Distructive stress when under pressure σsd, MPa | 0.041 | 0.043 | 0.046 | 0.049 |

Figure 1. Conductivity of the material at different values of potential difference for frequencies of 200 kHz is a 1, 300 kHz is a 2, and 400 kHz is a 3.
Analysis of the results allowed us to conclude that the introduction of carbon nanotubes into the polymer matrix in an amount of 0.05% of its weight provides a significant improvement in the strength characteristics of the polymer material.

Conductivity of nanocomposite material based on a ternary copolymer with different proportions of carbon nanotubes was studied. Tests were carried out using a precision digital LCR parameter meter. To measure conductivity, a potential difference in the range from –1 V to 20 V with frequencies of 200 kHz, 300 kHz, and 400 kHz was applied to the obtained samples (Fig. 1).

The experimental dependences obtained can be explained if one considers that the concentration of CNTs in a polymer material is fairly beyond percolation threshold. If this is the case, nanotubes introduced into the polymer matrix act as additional resistance that are parallel to the existing resistance network in the polymer medium. Then, the value of conductivity can be represented as follows:

\[ G = G_{pol} + G_{CNT}, \]  

where \( G_{pol} \) is a polymer conductivity, \( G_{CNT} \) is a CNT conductivity.

Accordingly, an increase in conductivity at low frequencies is due to the fall in CNT resistance in the low-frequency zone, which is well known from theoretical studies described in [12]. The experimental data obtained are in complete agreement with the theoretical calculations [13–14], where it was concluded that the amplitude of the first harmonic of the current with increasing amplitude of the alternating field undergoes complex decreasing oscillations. This allows, in a wide range of values, using an alternating electric field to control the amplitude of this harmonic and, in turn, to use the obtained regularities to control the quality of the samples and define proportions of CNTs according to the current-voltage characteristics made in different frequency ranges.

3. Results and discussion

Using the values of conductivity (Fig. 1) and the sizes of the samples of the composite material, in terms of conductivity, we obtain \( \sigma = 2.3 \times 10^{-1} \) Cm * cm\(^{-1}\). According to [15], specific conductivity of materials classified as semiconductors lies within a range \( \sigma = 10^{-4} – 10^7 \) Cm * cm\(^{-1}\).

Thus, our conductivity values are within the range of conductivity values that are characteristic to semiconductors. This proves that the obtained composite material based on a dielectric polymer becomes a semiconductor after it has been modified with CNT.

The study of temperature dependence of electrical conductivity or resistance of semiconductors underlies one of the most common methods for defining the width of the band gap. It is known that distribution of electrons over energy bands is characterized by the Fermi-Dirac function. [16-17]:

\[ f(E) = \frac{1}{1 + e^{\frac{E - E_F}{kT}}} \]  

\( E \) is an electron energy, \( E_F \) is a Fermi energy, \( k \) is a Boltzmann’s constant, \( T \) is a temperature.

In pure semiconductor, the Fermi level with respect to the edge of the valence band is approximately equal to half of the width of the band gap, thus: \( E - E_F = 1/2\Delta E \).

Since conductivity in a semiconductor is proportional to charge carriers concentration, then it is proportional to the Fermi-Dirac function, respectively, the following is true:

\[ \sigma = \sigma_0 \frac{1}{1 + e^{\frac{\Delta E}{kT}}} \]  

(3)
$\sigma_0$ is a constant that depends on the given semiconductor, $R = \frac{1}{\sigma}$ is a resistance, then:
$$R = A \cdot e^{\frac{\Delta E}{kT}} \quad (A \text{ – coefficient that is dependent on the physical properties of semiconductor}).$$

In order to define the width of the band gap, it is necessary to calculate the resistance value and plot the dependence $\ln R(1/T)$ (Fig. 2).

$$\ln R_1 = \ln A + \frac{\Delta E}{2kT_1}, \quad \ln R_2 = \ln A + \frac{\Delta E}{2kT_2}$$

(4)

$$\ln R_1 - \ln R_2 = \frac{\Delta E}{2k} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

(5)

$$\Delta E = 2k \left( \frac{\ln R_1 - \ln R_2}{\left( \frac{1}{T_1} - \frac{1}{T_2} \right)} \right)$$

(6)

where $\frac{\ln R_1 - \ln R_2}{\left( \frac{1}{T_1} - \frac{1}{T_2} \right)}$ is a slope tangent according to the dependency graph $\ln R(1/T)$.

Let $\tan \alpha = \frac{\ln R_1 - \ln R_2}{\left( \frac{1}{T_1} - \frac{1}{T_2} \right)}$, then we obtain: $\Delta E = 2k * \tan \alpha$. Using the dependencies obtained (Fig. 2), we find that $\Delta E = 0.4 eV$.

The obtained values for the forbidden zone prove that the composite material TREPOLIMER MMA-BMA-MK+CNT possesses semiconducting properties.

4. Conclusion
We created experimental samples of nanocomposite based on the ternary copolymer MMA + BMA + MC, which is a dielectric, and modified it by carbon nanotubes in different proportions (from 0.01 to 0.05 wt.%). Studies were performed to measure conductivity in samples of polymer nanocomposites with CNTs proportion of 0.05 wt.% at a potential difference in the range from -1 V to 20 V with 

\[4\]
current frequencies of 200 kHz, 300 kHz and 400 kHz. The presence of conductivity in the composite materials doped with carbon nanotubes has been established. A nonlinear dependence of conductivity on the applied voltage at different frequencies was found, which can be explained by the existence of additional resistances, which are carbon nanotubes introduced into the polymer matrix, which allows the amplitude of the first harmonic of the current to be controlled using an alternating electric field. This allowed us to use the obtained patterns to control the quality of the samples and establish the amounts of CNTs in them according to the current-voltage characteristics in different frequency ranges.

The obtained experimental results and calculations of the band gap in polymer nanocomposites make it possible to predict the creation of new polymer materials with varying conductive properties, which can be used in various fields, including micro and nanoelectronics.

5. References

[1] Semaan Ch 2013 Influence of wrapping on some properties of MWCNT-PMMA and MWCNT-PE composites Polymer Bulletin. 70 pp 1919-1936.
[2] Kim J S 2011 Improved electrical. conductivity of very long multi-walled carbon nanotube bundle/poly(methyl methacrylate) composites Carbon 49 pp 2127-2133.
[3] Zaporotskova I V 2013 About adsorption of the polyethylene monomer unit on the single-walled carbon nanotubes surface, European Polymer Congress Book of Abstracts Pisa pp 3-6.
[4] Elbakyan L S 2013 The polymers filled eith carbon nanotubes as new materials in stomatology European Polymer Congress pp 30-31
[5] Belonenko M B 2010 Vlijanie peremennogo.jelektricheskogo polja na. provodimost'. odnoslojnych uglerodnyh nanotrubok poluprovodnikovogo tipa Fizika i tehnika poluprovodnikov 44 pp 1248-1253.
[6] Boroznin S V, Zaporockova I V, Boroznina E V 2013 Kapilljarnye jeffekty v borouglerodnyh nanotrubkah Vestnik Volgogradskogo gosudarstvennogo universiteta. Seriya 10, Innovatsionnaya deyatelnost [Science Journal of Volgograd State University. Innovation Activity] 8 pp 38-43.
[7] Saito R, Dresselhaus M S , Dresselhaus G 1999 Physical properties of carbon nanotubes Imperial College Press 251 p.
[8] Kharris P 2003Uglerodnye nanotruby i rodstvennye struktry Novye materialy XXI veka . Tekhmosfera, Moscow 336 p.
[9] Bakhracheva Ju S 2013 Fracture toughness prediction by means of indentation test International Journal for Computational Civil and Structural Engineering 9 pp 21–24.
[10] Liu S F, Lin S, Swager T M 2016 An organocobalt-carbon nanotube chemiresistive carbon monoxide detector ACS Sens. 1(4) pp 354-357.
[11] Im J, Sterner E S , Swager T M 2016 Integrated gas sensing system of swcnt and cellulose polymer concentrator for benzene, toluene, and xylene Sensors 16(2) pp 183-185.
[12] Bakhracheva Y S, Vasilyev A V, Petikova T N 2016 Solution to the diffusion problem in the thermocyclic nitrocemementation of steel J. Materials science forum 870 pp 545-549 DOI: 10.4028/www.scientific.net/MSF.870.545
[13] Zaporototskova I V 2013 About adsorption of the polyethylene monomer unit on the single-walled carbon nanotubes surface European Polymer Congress Book of Abstracts Pisa 16 – 21 June pp 3-6.
[14] Condurache D 1997 On the dielectric behaviour of the polymethylmethacrylate Bul. Inst. politehn. Iasi. Sec. 43 pp 115-12
[15] Polikarpova N P, Zaporototskova I V, Boroznin S V, Zaporotok P A 2015 About using carbon nanotubes with amino group modification as sensors J. Nano-Electron. Phys. 7(4) pp 04089-04095.