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Laser Stimulation the Electroconductivity of Composite Layers with Multiwalled Carbon Nanotubes

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Electroconductivity laser stimulation (irradiation) of composite layers based on carboxymethyl cellulose (CMC) and multiwalled carbon nanotubes (MWCNT) has been researched. The layers were deposited on the following substrates: flexible such as polyimide, polyester, aluminum foil paper, cotton fabric and shop paper (~80 g/m²); hard substrates such as Si/SiO_2 and cover glass. The conductivity of layers with thickness 0.5 ÷10 µm was improved more on 500 % /(W/cm²) after laser stimulation (wavelength 970 nm, emission specific power P_S~0.05÷1 W/cm², concentration C~0.05 wt.% MWCNT).

Keywords: Carboxymethyl cellulose, Multiwalled carbon nanotubes, Composite layers, Electroconductivity, Laser stimulation.

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1. INTRODUCTION

According Layers based on randomly interlaced carbon nanotubes (so-called buckypaper) were observed and had high specific conductivity σ ~ 10÷50 kS/m [1, 2]. Buckypaper layers based on MWCNT had specific conductivity about ~10 kS/m and their electrical properties depended on many factors including type of MWCNT and methods of their purification [3]. Buckypaper layers are promising for creating of different sensors (such as mechanical stress sensors) and elastomers for biomedical application (such as artificial muscle). They are also in demand as in the conventional electronics, and a flexible electronics. For example, the connecting layer between integrated circuit elements or conductive elements to a flexible solar panel.

Layers such as buckypaper containing a small amount of carbon nanotubes are of interest. These layers can be much safer than the layers buckypaper consisting only of carbon nanotubes.

In this paper we present results of investigation related to electroconductivity laser stimulation of layers based on biocompatible material carboxymethyl cellulose as matrix and MWCNT as a filler deposited on different substrates.

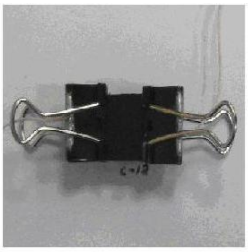
2. SAMPLES PREPARATION AND MEASURMENT TECHNIQUES

Bimetallic catalyst FeMo/MgO was used during MWCNT preparation. MWCNT synthesis ran at temperature ~900 °C in Ar and CH_4 gas flow during 40 minutes. Obtained material to receive stable results was oxidized in 8.8 M solution of hydrogen peroxide during 60 min. MWCNT concentration C in material was 95±1 wt. %. Moreover the following procedures were fulfilled: purification, drying etc. [4].

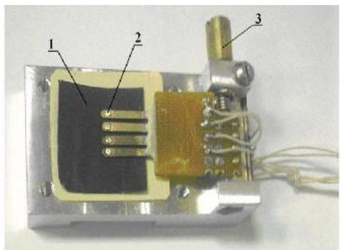
We used CMC in the form of aqueous solution (~4 wt. % CMC), which was σ ~ 0.4 S/m at t= 25°C. It was thoroughly mixed mechanically in a magnetic stirrer and ultrasonic (US) bath for about 60 min and about 30 min, respectively. MWCNT filler was added in finished matrix, after that the aqueous dispersion consisting of CMC and MWCNT was subjected to mix in a magnetic stirrer and US bath for ~90 min and ~90 min, respectively.

Water dispersion based on 4 wt. % CMC and C ≈0.05-5 wt. % MWCNT was deposited on the substrates cover. Method of application described in [5]. The layers were deposited on the following substrates: flexible – such as polyimide, polyester, aluminum foil paper, cotton fabric and shop paper (80 g/m²); hard – such as Si/SiO_2 and cover glass.

Two layers (samples) with the size of 20 × 10 mm² deposited on the substrate and they were separated by a gap having a width of ~0.2 mm. After deposition when layers were wet (transition state "wet") one layer was covered by lightproof film and the second one was irradiated with continuous laser radiation during 5 minutes with power density P_s ≈0.1÷1 W/cm² and wavelength 970 nm. Width and electrical properties of layers were measured after drying. Weight in the dry state of the layers decreased 6÷7 times relative weight in the liquid state. Sample conductivity was measured by two-probe or four-probe methods. All electrical measurements were performed in "current source" mode. The current was in the range 0.1÷10 mA. Measuring probes and appearance of the samples are shown in fig. 1.



a



b

Fig. 1 – Measuring probes for: a – two-probe method (resistance per square of the surface), sample on CS substrate; b – four-

probe method (1 – sample on OP substrate, 2 - side-wall probe with silver tips, 3 – the screw for probe pressing force control).

The main result is that specific conductivity of layers obtained after laser stimulation (irradiation) has been improved as coefficient of laser stimulation: $\sigma_s=(\sigma_L-\sigma)/\sigma$, where σ is a specific conductivity unirradiated samples, σ_L is a value of specific conductivity after laser irradiation.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The laser stimulation improves specific conductivity of layer in "liquid" or transition state. These changes were observed for all samples deposited on different substrates, while change of specific conductivity of samples deposited on hard substrates (cover glass and Si/SiO_2) was σ_s~15÷280 %. Typical values of σ_s increase in layers on the substrates of the cover glass are shown in Table 1. The relative error of the values C and σ_s do not exceed 10%. The average value of for each number of samples are measured 4 layers. The average value of σ_s for each number of samples obtained after the measurement of 4 layers.

Table 1 – Average values σ_s of the laser stimulation the conductivity of layers (transition state "wet", P_s ~ 0.5 W/cm^2) on the substrate of the cover glass.

Samples, #	*C*, wt. % MWCNT	σ_s, % (average)
1	0.05	275
2	0.11	205
3	0.25	146
4	0.5	85
5	1.1	48
6	2.0	25
7	5.0	17

Apparently, a significant positive effect of layers conductivity increasing after laser stimulation is partially connected with structure of MWCNT. Carbon nanotubes are oriented along electric field of light similarly to conductive filaments in a dielectric matrix [2]. In the "wet" state when the MWCNT still have an ability to turn or move in the layer, they liable to laser irradiation. Therefore, a certain amount of MWCNT will be oriented along the direction of the electric field and the average conductivity of the layer will be increased relative to the initial state when MWCNT are randomly distributed in layer.

Specific conductivity of composite dry layers after stimulation with thickness 0.5 ÷ 10 μm based on C ~10 wt.% MWCNT was roughly ~250 ÷ 500 S/m. Laser irradiation increased the specific conductivity of dried samples obtained by laser stimulation or without it. In both cases, their relative increase the σ_s to approximately linearly dependent on the P_s, and it was in the range σ_s/P_s~6÷12%/(W/cm^2). To the dried layer under a slight increase in conductivity effect (stimulation) of the laser radiation, apparently due to thermal overheating of the samples 50 ° C. This is evidenced by the results of measurements of the temperature dependence of the conductivity of the layers.

In the case of laser stimulation of the layers in the "liquid" state for some samples the value of σ_s/P_s exceeds 500 %/(W/cm2). It can be assumed that most improve the conductivity is due to the influence of the laser beam on the carbon nanotube. Apparently, due to the orientation of randomly distributed along the MWCNT of the electric field of the light wave laser light stimulates a significant increase in the conductivity of the samples.

Investigated layers lost moisture after drying; their weight decreased approximately in 3-4 times in comparison with weight of initial samples. Therefore MWCNT concentration in these samples increased to C ~15÷280 wt. %, but it was lower in comparison with MWCNT concentration (C ≈100 wt. %) in buckypaper layers [3]. Specific conductivity of composite layers could be improved at the expense of optimal selection of preparation technology and laser stimulation without MWCNT concentration increasing.

Thus specific conductivity of examined composite material based on biocompatible matrix CMC and MWCNT can be significantly improved by laser irradiation. Moreover these layers have good adhesion on soft substrates and cannot be changed by mechanical influence. They are promising for different applications, such as: membrane production for nanosized particles and materials for flexible electronics; security of electronic circuits and biological objects from electromagnetic radiation; elastomers and voltage-sensing device production; biological tissues growing (nerve cells and muscles etc.).

4. CONCLUCION

Laser stimulation increased the conductivity of the composite layers based on carboxymethyl cellulose as matrix and multiwalled carbon nanotubes as a filler. Considerable quantitative increase (over 500%/(W/cm^2)) reached in the layers containing the least amount of neck nanotubes (~ 0.05 wt.% MWCNT, transition state "wet").

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