Studying of a sensitive material based on Ecoflex and CNTs for flexible strain sensors

N A Demidenko¹, A V Kuksin¹, E S Davydova¹, V A Zaborova²,³, L P Ichkitidze¹,⁴, S P Bordovsky⁴ and A Yu Gerasimenko¹,⁴,⁵

¹ Institute of biomedical systems, National Research University of Electronic Technology, Zelenograd, Moscow, Shokin Square 1, Russia
² Department of Sports Medicine and Medical Rehabilitation, I.M. Sechenov First Moscow State Medical University, Moscow, Bolshaya Pirogovskaya street 2-4, Russia
³ Sports Adaptology Lab, Moscow Institute of Physics and Technology (National Research University), Moscow, Institutskiy per. 9, Russia
⁴ Institute for Bionic Technologies and Engineering, I.M. Sechenov First Moscow State Medical University, Moscow, Bolshaya Pirogovskaya street 2-4, Russia
⁵ Institute of Nanotechnology of Microelectronics of the Russian Academy of Sciences, Moscow, Leninsky Prospekt 32A, Russia

Abstract. Nowadays there is a great need for the development of flexible strain sensors that can register human body's movements. In the field of wearable and smart electronics such sensors are actively being developed. Resistive-type flexible sensors are the easiest to manufacture. Their mechanism of sensitivity to deformations is based on a change in electrical resistance during deformations. In this work, we have developed the functional material for strain sensor with high tensile properties, strength and electrical conductivity. This material based on a matrix of silicone elastomer and a multi-walled carbon nanotubes (MCNTs) filler. The material showed a high elongation of 950 % with a tensile strength of 1.437 MPa. The manufacturing process included laser structuring of MCNTs to form an electrically conductive network. The linear gauge factor was 3.4, and the angular gauge factor was 0.26.

1. Introduction

The sensors are widely used both in industry and in the biomedicine. Recently, wearable flexible devices aimed at non-invasive monitoring of human health and physical activities were especially interesting. Flexibility of traditional metal and semiconductor sensors is not flexible enough for this purposes. Traditional sensors usually have high values of the gauge factor only in a limited range of deformation (up to 1 %). For example, in semiconductor materials based on ZnO, the gauge factor of 1250 was obtained at a deformation of less than 1 % [1].

Resistive and capacitive sensors are most commonly used to register human motion [2,3]. Generally they are made by a combination of elastomeric substrates (polydimethylsiloxane (PDMS), polyurethane, polycrylonitrile, Ecoflex silicones) and conductive fillers (metal and carbon nanoparticles) [4]. Substrates make these nanocomposite materials stretchable. However, there are some limitations. Incompatibility between rigid conductive components and a sufficiently soft elastomeric matrix can lead to high hysteresis, low sensitivity and fragility [5]. The development of methods that make it possible to obtain materials with high elongation and low hysteresis, high values of sensitivity to deformation and strength is an important task. In addition, for biomedical devices that
come into contact with the human body, a high degree of biocompatibility, absence of toxicity, and softness of mechanical properties are extremely important [6-10].

In this work sensitive material using a simple technology for laser formation of electrically conductive networks of carbon nanotubes (CNTs) in an Ecoflex silicone matrix was developed. The sensitive material has a small hysteresis (<5%), high tensile strength and remarkable linear sensitivity to deformations.

2. Materials and methods

2.1. Components of a sensitive material

As a filler, we used MCNTs with an outer diameter of 8-30 nm, an inner diameter of 5-15 nm, a length of ≥20 μm, a specific surface of ≥270 m²/g, and a bulk density of 0.025-0.06 g/cm³. The matrix was a silicone elastomer Ecoflex 00-10 on platinum. The dynamic viscosity of silicone in a mixed state is 140 Pa·s, modulus of elasticity at 100 % elongation is 125 kPa, Shore hardness is 10 A, density is 1.04 g/cm³, operating temperature range is from -19 ºС to +232 ºС. Carbon fiber electrodes were included in the finished sensitive material.

2.2. Manufacturing of a sensitive material

The manufacturing process of the sensitive material is shown in figure 1. The first step was to add MCNTs to Ecoflex silicone in the liquid phase at 3 wt% MCNTs. Solution of components was thoroughly mixed for 5 minutes at least. The solution was placed in a vacuum chamber and degassed to remove air microbubbles. Thereafter, the Ecoflex/MCNTs nanocomposite was prepared by stencil printing. The Ecoflex/MCNTs solution was placed in a plastic U-shaped mold. Electrodes were added so that the solution completely covered them. The solution with the electrodes in the mold was left at room temperature (23±5 ºС) until complete polymerization (~4 hours). After complete polymerization, the nanocomposite was structured with laser radiation to reduce the resistivity values, form welded joints between nanotubes, and form a structured conductive CNTs network inside the nanocomposite. The effect of the formation electrically conductive network of nanotubes in polymers and the improvement of mechanical and electrical properties was obtained earlier [7]. The laser irradiation parameters were: wavelength 1064 nm, radiation power 12 W, irradiation time 2 minutes. Finally, the laser-structured Ecoflex/MWCNT nanocomposite with electrodes was sealed on both sides with a layer of pure silicone to create an insulating and fully biocompatible coating.

![Figure 1. Manufacturing process of the strain-sensitive nanomaterial.](image-url)
2.3. Gauge Factor Calculation
To determine the gauge factor (GF), resistance in comparison with strain (tensile/bending) studies were conducted using a test setup (figure 2).

According to the results of the study, the GF were calculated using formulas (1) for tension (linear sensitivity GF\textsubscript{e}) and (2) for bending (angular sensitivity GF\textsubscript{a})

\begin{equation}
GF_e = \frac{\Delta R/R}{\Delta l/l}
\end{equation}

where \( R \) is the initial resistance, \( \Delta R \) is the absolute change in resistance after deformation, \( l \) is the initial length of the sensitive element, \( \Delta l \) is the absolute change in its length

\begin{equation}
GF_a = \frac{\Delta R/R}{d/r}
\end{equation}

where \( r \) is the bending radius, \( d \) is the coating thickness.

![Test setup](image)

**Figure 2.** Test setup: 1 - displacement module, 2 - moving head in coordinates (x; y; z) of displacement module, 3 - sample of sensitive material, 4 - digital multimeter connected to the sample of material, 5 - measuring ruler, 6 - personal computer to control the movement module.

2.4. Calculating elastic modulus and Tensile Strength
The research technique was based on the construction of the loading curve and the determination of the elastic deformation limit from its linear region, and the calculation of the elastic modulus (\( E \)) was carried out according to the formula (3):

\begin{equation}
E = \frac{F l}{S \Delta l}
\end{equation}

where \( F \) is the applied force, \( l \) is the initial length of the sample, \( S \) is the surface area to which the force is applied, \( \Delta l \) is the elongation of the sample as a result of the application of the force.

Tensile strength \( \sigma \) was calculated by the formula (4):

\begin{equation}
\sigma = \frac{F_m}{A_0}
\end{equation}

where \( F_m \) is the maximum load applied to the sample; \( A_0 \) is the initial cross-sectional area of the sample.

3. Results

3.1. Structure of sensitive material
The appearance and microstructure of the developed material are shown in Figure 3. The dimensions of the material were 3.5\times1.5\times5 mm. Images of the microstructure were obtained using an FEI Helios NanoLab 650 scanning electron microscope. The accelerating voltage of the electron column was 2 kV, the current of the electron probe was 21 pA.
During the manufacturing process, the material was irradiated with a pulsed laser, which left the characteristic deepening (figure 3b). As you can see from figure 3c, a network of carbon nanotubes is formed within the material, which provides functional characteristics. Nanotubes form long connections >100 nm throughout the entire volume of the material.

3.2. Mechanism of sensitivity to deformations and Gauge Factor

The loading process (tension and bending) obtained with the test setup is shown in figure 4.

The graphs of the dependence of electrical resistance (figure 5) demonstrate the behavior of the material during deformations. In fact, the material serves as a resistor under an applied voltage (tension). When deformation is applied, the electrical resistance of the conducting network of CNTs in the material changes due to changes in geometric dimensions (length and cross-sectional area), piezoresistive properties of CNTs, tunneling effect or the mechanism of separation (formation and restoration of bonds).

Figure 3. External view of the developed sensitive material (a), SEM images with increase ×60000 (b), ×240000 (c).

Figure 4. Sensitive material before stretching (a), during stretching (b), in bending (c).

Figure 5. Graph of electrical resistance from elongation (a) according to bending (b).
From the graph in figure 5a, it can be seen that stretching the material by 30 mm (100% of the original length) results in a linear increase in electrical resistance up to 760 kΩ (black line). Gradually shrinking the material (red line) from 30 mm to 0 mm leads to a decrease in resistance with little hysteresis. The maximum resistance deviation was at the point of tension by 0.025 m and amounted to 20 kΩ. The tensile hysteresis was ~ 4%. From the graph in figure 5b, it can be seen that bending the sample from 0° to 180° (black line) resulted in a gradual increase in resistance to 195 kΩ. Bending the material from 180° to 0° (red line) resulted in a decrease in resistance. Reverse bending of the material from 0° to -180° (black line) resulted in a gradual increase in resistance to 195 kΩ. Reverse bending of the material from -180° to 0° (black line) resulted in a decrease in resistance. The largest resistance deviation was 5 kΩ. Thus, the bending hysteresis was ~3%. The following coefficients were obtained: linear $GF_e=3.4$, angular $GF_a=0.26$. Low values of the $GF_a$ indicate a low sensitivity of the material to bending.

3.3. Elastic modulus and Tensile Strength

It can be seen from the tension diagram (figure 6) that the linear section of elastic deformation occupies a significant part of the total graph (53%). The elastic deformation of the sensitive material is in the range of elongation from 0-0.1 m. The elastic deformation limit is in the elongation region of 0.1 m at a load force of 16.9 N. The average value of the elastic modulus was 166.85 kPa. The calculated tensile strength is 1.437 MPa. The maximum elongation of the material from the original length to irreversible damage was 950%.

![Figure 6. Tensile diagram of the sensor.](image)

4. Conclusion

A simple technology has been developed for manufacturing a strain-sensitive material for flexible sensors. The use of laser radiation made it possible to form a tridimensional network of nanotubes inside a silicone dielectric, which provided the necessary mechanical and electrical characteristics. Due to its high strength, elongation, flexibility and sensitivity, this material opens up broad prospects for the development of wearable, sensitive to deformations (tension, bending, pressure) resistive sensors in the field of flexible electronics.

Acknowledgments

This study was supported by the Ministry of Science and Higher Education of the Russian Federation No. 075-03-2020-216 from 27.12.2019.
References

[1] Kamišalic A, Fister I, Turkanovic M, and Karakatic S 2018 Sensors 18 6 1714
[2] Zhou J, Gu Y, Fei P, Mai W, Gao Y, Yang R, Bao G and Wang Z 2008 Nano Lett. 8 9 3035
[3] Zhang R, Ding J, Liu C and Yang E 2018 ACS Appl. Energy Mater. 1 5 2048
[4] Song J, Do K, Koo J, Son D and Kim D 2019 Mater. Research Soc. 44 643
[5] Sun Z, Yang S, Zhao P, Zhang J, Yang Y, Ye X, Zhao X, Cui N, Tong Y, Liu Y, Chen X and Tang Q 2020 Appl. Mater. & Interfaces 12 11 13287
[6] Markov A, Wördenweber R, Ichkitidze L P, Gerasimenko A Yu, Kurilova U E, Suetina I A, Mezentseva M V, Offenhäusser A and Telyshev D V 2020 Nanomaterials 10 12 2492
[7] Demidenko N A, Kuksin A V, Murashko D T, Cherepanova N G, Semak A E, Bychkov V N and Gerasimenko A Yu 2020 3D Print. Optics and Additive Photonic Manufacturing II 11349 113490U
[8] Gerasimenko A Yu, Kurilova U E, Savelyev M S, Murashko D T and Glukhova O E 2021 Compos. Struct. 260 113517
[9] Zhurbina N N, Kurilova U E, Ichkitidze L P, Podgaetsky V M, Selishchev S V, Suetina I A, Mezentseva M V, Eganova E M, Pavlov A A and Gerasimenko A Yu 2016 Proc. Of SPIE 9917 991718
[10] Gerasimenko A Y, Ten G N, Ryabkin D I, Shcherbakova N E, Morozova E A and Ichkitidze L P 2020 Spectrochim. Acta. Part A Mol. Biomol. Spectrosc. 227 117682