

LAYERS OF COMPOSITE NANOMATERIALS AS PROTOTYPE OF A TENSORESISTOR SENSOR

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Abstract

The layers of various materials are discussed. They including nanomaterials containing carbon nanotubes with tensoresistive properties. The investigated layers are divided into two groups: without (group I) and with carbon nanotubes (group II). From materials of group I is most suitable for the manufacture of strain sensors for medical purposes, is an elastomer with microchannels filled with a conductive liquid. Such a strain sensor can detect small bends of parts of the human body with an error of 8%. In group II, carbon nanotubes located between layers of natural rubber or between flexible layers of polydimethylsiloxane showed acceptable values of strain sensitivity and maximum deformation of ~ 40 and ~ 500 %, respectively. Based on layers (thickness ~ 0.5÷1.5 µm) of biocompatible composite nanomaterials in bovine serum albumin or microcrystalline cellulose and carbon nanotubes (concentration ≤ 2 wt. %), prototypes of deformation sensors (tensoresistors) showed high positive characteristics. In particular, bipolar behavior, strain sensitivity ~ 160, small hysteresis (≤ 3 %) after training cycles (deformation/deformation) more than 25 times, the possibility of applying an aqueous dispersion of nanomaterials to the human skin by the 3-D printer.

Further improvement (in particular, an increase in the linear deformation region and a decrease in deformation, a decrease in hysteresis) of the parameters of composite nanomaterials in a matrix of biological materials and a filler made of carbon nanotubes will allow the use of deformation sensors, both non-invasive and invasive medical applications.

Keyword: tensoresistor, layers, composite nanomaterial, carbon nanotube, bovine serum albumin, microcrystalline cellulose

Introduction

Deformation sensors (strain gauges) are among the ones claimed in practical applications. To research, development and creation with advanced characteristics, as well as new types of sensors, close attention is paid. For example, in the database of the Scopus system, about a thousand documents of information on new developments of load cells are reflected every year, in which tens of percent are occupied by sensors for medical purposes.

Indeed, recently in medical practice there has been an interest in strain gauges that could easily be attached to clothing or directly to the body of a person. Monitoring of human body movements can be classified into two categories: detection of large-scale (for example, movement of hands, feet) and small-scale movements (for example, blinking, swallowing). In the first category it is important to monitor the condition: limbs, joints, chest, as well as tumors, deformation of muscle tissue in the postoperative therapy, etc. In the second category, for diagnostic purposes, it is necessary to detect signs of: damaged vocal cords, respiratory diseases, angina pectoris, changes in the spatial gap between the bones, Parkinson's disease, etc.: For such purposes, numerous and varied strain sensors are required that must meet the requirements: high elongation ($> 10\%$), flexibility ($> 10\%$), strain sensitivity ($S \gg 10$), durability, rapid reaction/recovery rate and biocompatibility.

The simplest and most wide-spread strain gauges are based on the phenomenon of resistance variation under strain and called tensoresistors. The strain sensitivity of these devices is determined as $S = \delta R/\varepsilon$, where $\delta R = \Delta R/R_0$, R_0 is the initial resistance, ΔR is the absolute resistance variation under strain, $\varepsilon = \Delta l/l$, l is the initial length of a sensitive element, and Δl is the absolute variation in its length.

Conventional tensoresistors are fabricated from metal or semiconductor materials. Meander-shaped tensoresistors formed from a metallic foil have the low temperature resistance coefficient ($\alpha \leq 10^{-5} \text{ K}^{-1}$) and relatively wide strain measurement range ($\varepsilon = \pm 5\%$), but the low strain sensitivity ($S \leq 10$). Semiconductor tensoresistors are characterized by the high sensitivity ($S \sim 100 \div 200$), very low strain ($\varepsilon \leq 0.2\%$), and high temperature resistance coefficient ($\alpha \geq 10^{-3} \text{ K}^{-1}$) [1]. Note that both the metal and semiconductor tensoresistors have insufficient elasticity and strongly restrict movements of a biological object, because their moduli of elasticity E exceed the value characteristic of a human skin by several orders of magnitude ($E \sim (25 \div 220 \text{ kPa}, \varepsilon \gg 1\%)$) [2].

In this work, we briefly describe different layers with the tensoresistive properties (hereinafter, tensoresistors) that were designed using original methods and/or materials and their potential applications in medicine. The investigated devices are divided into two groups. Group I is formed from the tensoresistors that do not contain carbon nanotubes (CNTs) and group II, from the tensoresistors containing CNTs or based on nanocomposites with CNTs.

2. Layers – Group I

A great number of tensoresistors have been developed and fabricated using nanoparticles and nanotechnologies. However, the high strain sensitivity ($S \geq 100$) is often attained in a very narrow strain range ($\varepsilon \leq 1\%$), which is not suitable for medical applications. Indeed, to control movements of human body parts, a strain of $\varepsilon \geq 10\%$ is usually required. In [3], the materials based on ZnO nanowires characterized by $S \approx 1250$ and $\varepsilon \leq 1\%$ were reported. In a hybrid material consisting of ZnO nanowires fixed on polystyrene nano- and microfibers, the high ε values ($\leq 50\%$) and relatively low S values (~ 100) were established [4]. A tensoresistor is encapsulated in a polydimethylsiloxane (PDMS) film and has the high moisture resistance. However, the excessively high resistance ($\geq 10^9 \Omega$) and, consequently, high intrinsic noise level of the material significantly restrict the strain measurement accuracy.

The parameters $S \sim 10$ and $\varepsilon \sim (20\div 80)$ % were obtained in a tensoresistor based on the thermoplastic elastomer containing ~ 50 wt.% of soot [5]. The proposed sensor, however, rapidly loses its strain sensitivity ($S \leq 0.1$) at $\varepsilon \leq 10$ % and can probably be used to detect fabric strain.

The graphite layers deposited onto natural rubber substrates exhibit the tensoresistive effect with the high parameters: $S \sim 12\div 346$ and $\varepsilon \leq 246$ % [6]. Nevertheless, their $\delta R(\varepsilon)$ dependences are strongly nonlinear, especially in the range of $\varepsilon \geq 100$ %. The strong nonlinearity of the $\delta R(\varepsilon)$ dependence is caused mainly by the behavior of pure rubber, i.e., by the strong nonlinearity of the stress induced during straining the rubber. Hence, the use of such layers as tensoresistors is complicated by the difficulty of bringing the $\delta R(\varepsilon)$ curves to the linear shape with good accuracy.

In [7], an original tensoresistor consisting of a silicone elastomer with microchannels filled with a conductive liquid was developed to control movements of different human body parts. The strain (tension) increases the length and decreases the width of a microchannel and, thus, leads to the corresponding increase in its resistance. Testing of the tensoresistor showed that it has a strain of $\varepsilon \leq 300$ % and a sensitivity of $S \leq 3$ at bending angles of $\theta < 120^\circ$; the strain measurement error was ~ 8 %. Obviously, this sensor is inapplicable to detecting movements of human body parts, where the angles can be in the range of $\theta \geq 120^\circ$, e.g., in total finger, knee, or elbow flexions.

3. Layers – Group II

3.1 Carbon nanotubes

Carbon nanotubes (CNTs) have the unique properties, including high strength, heat and electric conductivity, and optical transparency. Nanocomposites with even minor (< 10 %) CNT additions acquire special characteristics. Depending on a fabrication technique used and nanomaterial composition, the tensoresistive effect in the CNT-based layers is either enhanced or suppressed. Indeed, the layers consisting of multiwalled CNTs (MWCNTs) added with AgNO_3 in a concentration of $2\div 10$ g/l deposited onto PDMS substrates exhibit a stable resistance upon multiple bendings in the angle range from -180° to $+180^\circ$ and have almost no tensoresistive properties [8].

Study of the MWCNT films used as tensoresistors showed the almost linear $\delta R(\varepsilon)$ dependence and absence of the hysteresis under loading and unloading in combination with the high stability of a signal detected for 2-hour testing at $\varepsilon \leq 10$ [9]. Such a tensoresistor, however, appeared highly sensitive to various gases, moisture, and working temperature; i.e., it should be protected against environmental factors.

The tensoresistors in the form of thin films containing aligned single-walled CNTs (SWCNTs) on flexible substrates exhibit the excellent elasticity ($\varepsilon \sim 280$ %), but the very low sensitivity ($S \leq 0.8$), high hysteresis, and insufficient strain measurement accuracy [10]. A MWCNT film placed between natural rubber layers showed the higher strain sensitivity ($S \sim 43$) at $\varepsilon \sim 620$ % [6]. However, the $\delta R(\varepsilon)$ dependence for this film is approximately linear only at $\varepsilon \leq 100$ %.

A new type of the tensoresistor based on SWCNTs encapsulated in the PDMS layers was proposed in [11]. The parameters of $S \leq 6.3$ and $\varepsilon \leq 10$ % and the moisture

resistance higher than that of the tensoresistor without a protective layer were reported. For the MWCNT film-based tensoresistor, the linear $\delta R(\varepsilon)$ portions were observed at $\varepsilon \leq 0.1\%$ and $S \leq 0.35$ [12]. A similar tensoresistor based on graphene encapsulated between the PDMS films showed the high sensitivity ($S \sim 30$), but the low ($\leq 1\%$) ε value [13]. Such a tensoresistor can apparently be used for fragile (rigid) objects, but not in medicine, where the high strain ($\varepsilon \geq 10\%$) is needed.

The parameters suitable for monitoring the strain of human organs were obtained in different CNT/PDMS tensoresistor structures [14,15]. However, these devices demonstrate the high nonlinear responses and hysteresis in combination with the insufficient elasticity. For these structures, we have $E \sim 0.4\div 3.5$ MPa [16–18], whereas epidermal applications require the materials with $E \sim 25\div 220$ kPa [2]). The modulus of elasticity of PDMS increases after adding CNTs; therefore, the discrepancy between elasticity values for human skin and the tensoresistor grows. In addition, absorption of water (moisture) by PDMS leads to the enhancing rigidity and aging. The material becomes fragile and its E value significantly increases over the modulus of elasticity of human skin. Indeed, to exactly detect human skin movements, it is necessary to use high-efficiency strain gauges containing more elastic (soft) materials than PDMS. Many drawbacks of the tensoresistor based on the CNT-containing film encapsulated in the PDMS layers were eliminated using the modified PDMS (the so-called Ecoflex silicone rubber). The CNT/Ecoflex PDMS tensoresistor is characterized by $\varepsilon \sim 500\%$, broad $\delta R(\varepsilon)$ linearity portions, and negligible hysteresis ($\varepsilon < 150\%$), as well as high stability and repeatability of a detected signal during multiple (~ 2000) loading/unloading cycles [19].

Both in the CNT/PDMS and CNT/Ecoflex PDMS structures, PDMS is polymerized by heat treatment at a temperature of 70°C for 2 h. Certainly, this procedure complicates fabrication of the devices.

3.2 Composite materials with carbon nanotubes

The thin (< 100 nm) SWCNT-containing films on flexible polyethylene naphthalate substrates exhibited the optical transparency and resistance variation with the bending angle θ [20]. The bending sensitivity $S_\theta = \delta R/\delta\theta$ was found to be $\sim 0.08\%$ /deg at $\theta = \pm 180^\circ$. Here, θ is the bending angle and $\delta\theta$ is the θ increment; at $\theta = 0$, there was no film bending.

The composite nanomaterials containing CNTs deserve high attention. For example, the films consisting of polymethyl methacrylate (PMMA) matrix filled with MWCNTs exhibited a linear strain of $\varepsilon \leq 1\%$ at 0.75 wt.% of MWCNTs [21]. In [22], a 80- μm -thick buckypaper was fabricated from thermoplastic polyurethane (TPU) and MWCNTs and the value of $\varepsilon \approx 180\%$ at a ratio of 80:20 between TPU and CNTs was attained. The tensoresistor, however, had a very narrow region of the linear strain dependence of the output signal ($\varepsilon \leq 1\%$) and the low strain sensitivity ($S \leq 2$).

Study of many nanocomposites included in epoxy polymers and CNTs showed that with an increase in the MWCNT concentration between 1–10 wt.% the conductivity σ increases from 10^{-2} to 10^2 S/m and the S value decreases from ~ 22 to ~ 3 [23–25].

The layers consisting of the carboxymethyl cellulose (CMC) matrix filled with ~ 5 wt. % of MWCNTs demonstrate the high conductivity ($\sigma \sim 10^4$ S/m), $\alpha \leq 10^{-5} \text{ K}^{-1}$,

and $S \sim 10$ [26,27]. Laser techniques and nanotechnologies make it possible to control the characteristics of a tensoresistor in wide ranges; in particular, the main parameter, i.e., conductivity, can be changed within $\sigma \sim 10^{-1} \div 10^4$ S/m. The degradation testing of the CMC/MWCNT layers showed no significant σ variations upon multiple bendings of flexible substrates. In particular, upon layer bending by $\theta = \pm 180^\circ$ with a bending radius of 1 mm for up to 10 cycles, the conductivity hysteresis was no larger than 20% relative to its initial value. The hysteresis decreased with increasing number of measurement cycles and was no larger than 8% after 300 cycles. The high strain sensitivity ($S_\theta \sim 0.80$ %/grad) was demonstrated on the CMC/MWCNT nanocomposite layers with thicknesses of $0.2 \div 10$ μm . This is higher than the parameter of $S_\theta \sim 0.08$ %/grad reported in [20]. The layers did not exfoliate from substrates upon multiple bendings, did not crack, and kept their initial exterior.

Various strain gauges containing CNTs were reviewed in [28–31]. Their operation is based on the measurements of resistance or capacitance of strained layers. In the first case, these are tensoresistors and the presented examples can be added with our group-II sensors. In the second case, the gauges are capacitive and usually consist of three layers; the flexible layer is placed between two MWCNT layers. Despite the acceptable parameters ($S_\theta \sim 0.2$ %/grad and $\varepsilon \leq 100$ %), the repeatability of the characteristics is complicated.

Above we described some tensoresistors that are promising for medical applications. Of special importance is their use as miniature epidermic strain or pressure gauges for controlling the recovery after complex surgery and tactile sense recovery. The authors of [32] carried out investigations in this direction: they formed miniature skin pressure gauge prototypes using a 3D printer [32]. However, the direct contact of the strain gauge with the human skin surface is allowed only at the high biocompatibility. Certainly, this approach is valid for the above-mentioned tensoresistors, including those based on CNTs.

Since CNTs and CNT-based nanocomposites are relatively new materials, the health and ecology risks have been thoroughly investigated. Numerous experiments with CNTs revealed both positive and negative effects. The positive effects of CNTs are the possibility of vector drug delivery to different (including brain) organism parts [33–36] and neuron and neurite growth assistance [37, 38]. The negative effects are acceleration of the destruction of duplex DNA fragments [39] and blood thrombocyte aggregation [40].

By now, the following aspects concerning CNTs have been established [41–45]: pure CNTs are more dangerous than functionalized ones; the CNT toxicity significantly weakens in a composite nanomaterial; the CNT toxicity is lower than the toxicity of asbestos particles; in a biological medium, oxidative fermentation and biodegradation of CNTs occur; and citrullination in cells can be indicative of cytotoxicity of CNTs at the early diagnostic stages [46]. The bovine serum albumin molecules are adsorbed and uniformly cover the SWCNT surface layer by layer; bovine fibrinogen molecules behave similarly. Thus, the modified SWCNTs appear almost nontoxic [47–49].

3.3 Biocompatible composite material with carbon nanotubes

In [50] we proposed a strain gage based on layers of biocompatible composite nanomaterials. An aqueous dispersion of composite nanomaterials consisting of a

matrix of bovine serum albumin (BSA) or microcrystalline cellulose (MCC) and a filler – MWCNT is prepared. The components in aqueous dispersions have the following ratios: 20 % by weight BSA/0.5 % by weight MWCNT; 3% by weight MCC/0.2% by weight MWCNT.

The procedure for preparation of aqueous dispersion is typical for all materials considered in previous works [50]. In particular, in order to obtain an aqueous dispersion of 20 % by weight BSA/0.5% by weight MWCNT, the following steps are taken:

1. MWNT is added to the distilled water and the dispersion is stirred in a magnetic stirrer for 30 minutes and then dispersed in an ultrasonic disperser at a temperature of ≤ 30 °C for 30 minutes until a homogeneous black dispersion is obtained. The concentration of MWCNTs is selected in the range 0.5÷1% by weight.

2. BSA powder is introduced into the aqueous dispersion of MWNT in a concentration of 20÷25 % by weight, so that the ratio of 20% by weight of BSA/2 % by weight of MWCNT and water is the rest. The dispersion is then placed in an ultrasonic bath and dispersed at a temperature of ≤ 40 °C for 60 minutes until a homogeneous BSA/MWCNT dispersion of black color is obtained.

3. BSA/MWCNT dispersion is decanted within 24 hours, filtered and poured into another vessel. Further, the film of the BSA/MWNT aqueous dispersion is silk-screened onto a substrate. In this case, layers of paper, or textiles, or polyethylene terephthalate (PET) with thicknesses up to 50 μm serve as a flexible substrate. After drying at room temperature, the 0.05÷0.5 μm thick layers on a flexible substrate appear as a prototype of a strain gauge with a strain-sensitive layer of the BSA/MWCNT composite nanomaterial. On the free surface of the film, i.e. Electrical measurements are carried out on the surface bordering the air. In the same way, aqueous dispersions of 3% by weight MCC/0.2% by weight MWCNTs are made, and prototypes of the strain gauge are also generated on their basis.

The composite materials used in the preparation of aqueous dispersions of composite nanomaterials are biocompatible. Some of their characteristics are described below.

Biomaterial BSA from AMRESCO with code 0332-100G and CAS # 9048-46-8 was used as the matrix of the composite BSA/MWCNT nanomaterial. As a filler in the composite nanomaterial, MWCNT of the "Taunit-MD" type is used. The main parameters of these carbon nanotubes are: outer diameter – 30÷80 nm; internal diameter – 10÷20 nm; length – ≥ 20 μm ; total amount of impurities after purification – $\leq 1\%$; bulk density – 0.03÷0.5 g/cm^3 ; Specific surface area – 180-200 m^2/g ; thermal stability in air – ≤ 600 °C.

After the drying of the moisture, the composite concentration of the constituent parts of the composite nanomaterial changes. In fact, if the aqueous dispersion was 20 % by weight of BSA/0.5 % by weight of MWCNT, then after deposition on the substrates and drying, a composite nanomaterial layer composed of BSA/~ 2 wt. % MWCNT is formed.

In Fig. 1 shows the appearance of a typical layer with a thickness $d \sim 0.5$ μm , made of a composite BSA/MWNT nanomaterial deposited on a calico. Usually, the layers were strips 5÷7 mm wide and 25÷30 mm long. Fig. 2 shows a photo of the mechanical part of the installation, allowing measurements of the sensor parameters

for bending deformations (concavity, curvature). The following parameters are recorded: number of cycles, number of steps, resistance, operating temperature, measurement time of each step. The bending radius r is adjustable in the range of $0.5 \div 10$ mm. In all cases, we used $r = 2$ mm.

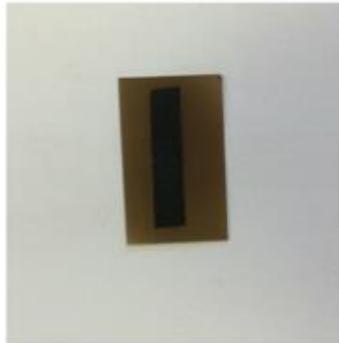


Fig. 1 Typical layers of BSA/MWCNT composite nanomaterial on a chintz substrate



Fig. 2 Photo of the mechanical part of the installation, in the middle (between the "paws") of which the sample is fixed

In Fig. 2, electrodes are seen from aluminum and getinax rods with cuts in which the ends of the sensor are fixed. One step corresponds to a 2° angle θ of the electrode rotation, i.e. bending the sensor. The step speed (bending) is adjustable in the range $0.2 \div 2$ step/s. The bending range can be $\Delta\theta = \pm 180^\circ$. At $\theta = 0$ the sensor is not deformed; at $\theta > 0$ the sensor is concave (the free surface is concave); at $\theta < 0$ the sensor is bent (the free surface is bent). In our experiment, one complete cycle contained about 280 steps, i.e. the sensor received bends in the range $\Delta\theta = \pm 140^\circ$. The bending speed is ~ 0.5 step/s, i.e. $1^\circ/\text{s}$, one measurement cycle lasted ~ 560 s. For some sensors, the total number n of measurement cycles reached $n \sim 50$, and the number of steps $\sim 200,000$.

In Fig. 3 shows a typical dependence of the resistance R on the angle θ for a sensor based on a film of the BSA/MWNT composite nanomaterial for a number of measurement cycles $n = 30$. It can be seen that the curve $R(\theta)$ is continuous and practically linear for small ranges $\Delta\theta$, for example, $\Delta\theta = 20^\circ$. At initial cycles ($n = 1-10$), hysteresis is observed on $R(\theta)$, which gradually decrease with increasing n , and at $n \geq 25$ practical disappear. For example, for $n = 1$ and fixed $\theta = 0$, the hysteresis range for R reaches $10 \div 15\%$, and for a fixed R the hysteresis range for θ is 30% . However, as the cycles increase and at $n \geq 25$, the hysteresis values decrease significantly and they do not exceed $1-2\%$ in one measurement cycle. With an increase in n , the absolute value of R is insignificantly increased. In particular, for the case shown in Fig. 3, with $\theta = 0$, the sensor resistance varies from $56.5 \text{ k}\Omega$ to $57.1 \text{ k}\Omega$, with registration cycles $n = 1$ and $n = 30$, respectively.

According to Fig. 3, the strain gage considered is a bipolar strain gauge. The physical mechanism of the bipolar behavior of the strain sensor is related to the following: compression (concavity) increases, and stretching (curvature) reduces the density of contacts between CNTs at bending points of the film. Accordingly, during compression, the electrical conductivity increases, and decreases with stretching.

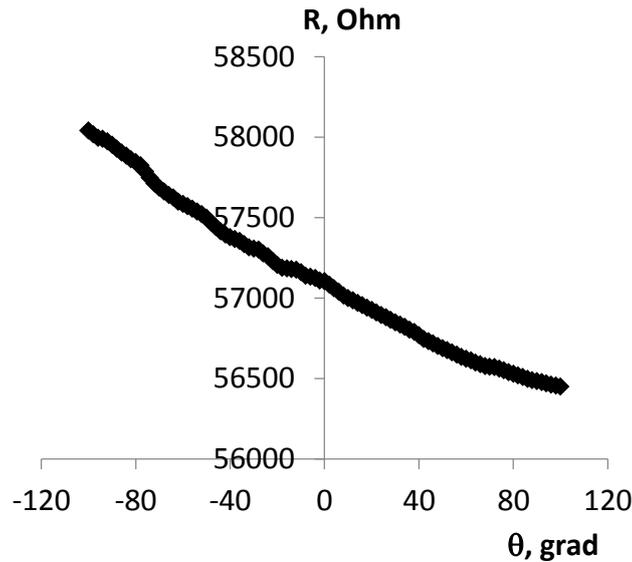


Fig. 3 Typical dependence $R(\theta)$ for layers of composite nanomaterial BSA/MWCNT

From $R(\theta)$ the sensitivity was calculated: $S_\theta \sim 2 \cdot 10^{-3} \text{ deg}^{-1}$ and $S \sim 40$. They have acceptable a order and exceed the values achieved in the prototype. The value of S was determined taking into account the bending radius $r = 2 \text{ mm}$ and the thickness $d \approx 0.5 \mu\text{m}$, as $S = (\Delta R/R_0)/(d/r)$ according to the geometry of the film.

Similar $R(\theta)$ curves were recorded for films of the composite nanomaterial MCC/MWCNT. Some parameters of the sensors obtained by processing $R(\theta)$ are given in Tab.1. The specific resistivity $R(\theta)$ of the layers is determined in the absence of deformation, i.e. at $\theta = 0$

Tab. 1 Some parameters of strain sensors

Composite nanomaterial	$d, \mu\text{m}$	$\rho, \text{mOhm}\cdot\text{m}$	$S_\theta, \text{deg}^{-1}$	S
BSA/MWCNT	$\sim 0,5$	~ 60	$\sim 2 \cdot 10^{-3}$	~ 40
	$\sim 0,2$	~ 80	$\sim 5 \cdot 10^{-3}$	~ 100
MCC/MWCNT	$\sim 0,4$	~ 20	$\sim 13 \cdot 10^{-3}$	~ 150
	$\sim 0,1$	~ 40	$\sim 17 \cdot 10^{-3}$	~ 160

In Tab. 1 shows the measured sensor data (accuracy in order of magnitude), from which the correlation follows: high bend strain sensitivity is realized on thinner films having relatively low resistivities. We note that the obtained values of $S_\theta \sim (13 \div 17) \cdot 10^{-3} \text{ deg}^{-1}$ and $S \sim 100 \div 160$ exceed by more than an order of magnitude those in the strain gauges based on metal films and have the same order for strain gages on the basis of semiconductors.

We note some important properties of the proposed sensor:

- bipolar strain gauge has a high tensile sensitivity with respect to bending - 10^{-2} deg^{-1} ; low resistivity – $\leq 1 \text{ Ohm}$;
- The sensor is a film with a thickness of $\leq 0.5 \mu\text{m}$ from a composite nanomaterial consisting of a matrix of biological material (bovine serum albumin or

microcrystalline cellulose) and multilayered carbon nanotubes in small amounts (≤ 3 % by weight);

- the ability to form on the human skin with a 3-D printer;
- a simple technology for preparing films on the surface of a flexible substrate that does not require heat treatment;
- the sensor can be applied directly to the human skin;
- due to the high sensitivity and small mass-dimensions, the proposed sensor is promising as a pressure sensor and as a sensor of tactile sensation;
- for a large number (more than 25) of the bending cycles, the hysteresis for the resistive characteristics is negligible – $\leq 1\%$.

The advantage of the deformation sensors described on the basis of the layers of composite BSA / MWNT and CMC/MWCNT nanomaterials is the possibility of varying the consistency, hardness, modulus of elasticity, strain sensitivity and specific electrical conductivity, depending on the preparation conditions and the concentration composition of the material. Also these composite nanomaterials are biocompatible materials and on their basis it is possible to realize strain gages, both non-invasive and invasive medical applications. Therefore, for each specific task, you can select the necessary parameters of the sensor, in particular, the modulus of elasticity for its formation not only on the skin of a person, but also on the skin of various biological objects. Considered composite nanomaterials because of their biocompatibility, electrical conductivity and the possibility of application to the skin surface, are promising for the rapidly developing direction of "Skin Electronics".

Thus, the task has been accomplished. A bipolar strain sensor based on biocompatible nanomaterials with increased sensitivity and the possibility of its formation on the surface of human skin is proposed.

4. Conclusions

The overwhelming majority of diagnostic and therapeutic devices and systems require various sensors, including strain gauges. In particular, they are used to control the recovery after surgical operations or test thigmesthesia. In this work, we discussed some types of the layers with the tensoresistive properties and possibility of designing original medical tensoresistors on their basis. The analyzed materials were divided in two groups: without CNTs (group I) and with them (group II).

(i) The group-I device most promising for medical applications is an original tensoresistor, which represents a silicone elastomer containing microchannels filled with a conductive liquid [7]. Such a tensoresistor detects small bendings ($\theta < 120^\circ$) of human body parts with an error of 8%.

(ii) The group-II tensoresistors, which are based on thin films containing aligned SWCNTs on flexible substrates, exhibit the excellent elasticity ($\varepsilon \sim 280$ %), but very low strain sensitivity ($S \leq 0.8$), high hysteresis, and low strain measurement accuracy [10]. The MWCNT film placed between the natural rubber layers demonstrated the highest strain sensitivity ($S \sim 43$) at $\varepsilon \sim 620$ % [6]. However, their $\delta R(\varepsilon)$ dependences are approximately linear only at $\varepsilon \leq 100$ %.

(iii) In many cases, the CNT films were encapsulated between flexible PDMS layers. The tensoresistors of this type exhibit the highest parameters, including the maximum strain of $\varepsilon \sim 500\%$ and the approximately linear dependence of the relative resistance variation on ε in the range of $\varepsilon < 150\%$, as well as the stability and repeatability of the detected signal upon multiple loading/unloading cycles (~ 2000) [19].

(iv) Nevertheless, the above-mentioned gauges cannot be directly laminated onto a complex curvilinear human skin surface to control the skin surface dynamics with high accuracy. This limitation is related to the fact that the PDMS polymerization requires heat treatment at a temperature of 70°C for 2 h.

(v) In epoxy nanocomposites, the high strain sensitivity (~ 22) is implemented at the low MWCNT concentration ($\sim 1\text{ wt.}\%$) [23–25].

(vi) The layers based of a nanocomposite consisting of CMC and MWCNTs showed the quite acceptable parameters, i.e., the high electrical conductivity ($10^{-1} \div 10^{-4}\text{ S/m}$) and a bending sensitivity of $\sim 0.80\%/\text{grad}$.

Based on the layers of composite BSA/MWCNT and MCC/MWCNT nanomaterials, prototype tensoresistors of bipolar behavior and tensor sensitivity values of $\sim 100 \div 160$ [50] are realized. The bipolar strain sensor has a high tensile sensitivity with respect to bending -10^{-2} deg^{-1} , low specific resistance $- \leq 1\text{ Ohm}\cdot\text{m}$ and small hysteresis ($\leq 3\%$) after training cycles (deformation increases/deformation decreases) more than 25 times. The aqueous dispersion of the proposed nanomaterials contains biocompatible materials (matrix) and a small amount of carbon nanotubes (filler, $\leq 3\text{ wt.}\%$). Water dispersions can be applied by a 3-D printer on human skin, which is very promising in the development of the direction of "Skin Electronics".

In most cases, the region of tensoresistor linearity should be broadened, which is a complex problem. To do this, it is necessary to take into account not only the substrate elasticity, but also transparency of tunnel contacts at the points of nanotube adjustment in the CNT-containing layers [50,51]. In some cases, the above-described tensoresistors have the characteristics suitable for applications in medicine. However, their safety at the lamination onto the human skin has still been investigated and the results of these investigations are of crucial importance [32]. In addition, it should be taken into account that the tensoresistors need to be protected from moisture, temperature, gases, and other effects during their operation.

Thus, the results obtained yield a promising outlook of fabrication of the tensoresistors containing carbon nanotubes or nanocomposites based on them.

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