PRELIMINARY INVESTIGATIONS ON SILICONE RESIN COMPOSITES WITH CARBON FILLER FOR DRY ELECTRODES APPLICATION

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Abstract

The paper presents results of investigations of basic material properties of novel composites based on silicone resin and carbon nanotubes as a filler. The motivation for the research is a need for materials which provide better mechanical properties than standard wet Ag/AgCl electrodes. However, a critical issue is also obtaining defined electrical characteristics in order to preserve an ability to effectively record biomedical signals such as electrocardiography (ECG). Within the introduction chapter, related researches and the current state-of-the-art in the context of dry electrodes technology were described. In the next step technological aspects of components processing and forming as well as the morphology of substrates used in the research were presented. Thermally-cured silicone resin was utilized to obtain elastic properties of the resulting material. The carbon nanotubes (CNT) were chosen as a conductive medium which provides defined electrical impedance. A developed technological process allowed to deliver samples of reproducible structure and properties. In the next chapter, methods and results of conducted experiments involving electrical, mechanical and thermal examination were presented. Finally, achieved outcomes are promising in the context of improvements of the designed composite. Especially the conductivity below 100 Ohms constitutes a significant motivation for further research in the field of dry electrodes for biosignals acquisition.

Keywords: *dry electrodes, ECG pads, silicone resin, carbon filler*

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Introduction

Nowadays, aging society struggling with rapid and stressful lifestyle suffers from civilization diseases paradoxically, especially in well-developed western countries. On the other hand, heart diseases constitute a major part of deaths worldwide. It has been calculated that almost two thousand people die each day because of cardiac disorders [1]. This gives the motivation to utilize top-notch technologies to provide sophisticated yet convenient medical services supporting the elderly and chronically ill patients. One example of emerging technology which seems to meet requirements of modern healthcare needs is telemedicine which combines achievements of multiple scientific branches such as electronics, computer science, and material engineering. This approach aims to provide remote medical services even in domestic conditions by utilizing wearable sensors which send physiological signals directly from households to medical facilities. Physicians may then analyze provided diagnostic data and decide if there is a need for any medical intervention. One of the major challenges is, however, a design of electrodes capable of capturing biosignals generated on the body surface as a result of heart activity or muscle movement. The issue of biopotential monitoring is definitely a complex challenge mainly due to the skin-electrode interface. From the theoretical point of view, the phenomenon which contributes significantly to the electrical properties of a conductor is a Helmholtz double layer. This effect is caused by ion separation and occurs on the contact between electrolyte and conductive medium. In practical application, it results in capacitance in the electrical circuit [2]. This problem can be effectively compensated by the use of wet chloride silver electrodes, however, some applications, e.g. textile-integrated solutions are still an area of development and improvements in the context of advanced materials. Apart from adjusting the interface resistance, the next vital aspect of electrode design is undoubtedly a need to ensure biocompatibility and application properties like formability or adhesion to other media. This gives a motivation to utilize recent advances in material science to find a solution which would be more efficient than traditional Ag-AgCl electrolyte electrodes for electrocardiography (ECG) measurement. It turns out that when used over an extended time period, wet electrodes tend to cause skin irritation and change electrical properties which may lead to reducing of a signal-to-noise ratio. Such side effects may be limited by dry composite electrodes. This was proved by investigating the performance of self-adhesive carbon nanotubes/adhesive polydimethylsiloxane (CNT/aPDMS) electrodes in a real long-term ECG measurement by Jaehyo Jung et al. [3]. Julia W.Y. Kam et al. also delivered a comparison of standard gel pads and novel metallic dry electrodes. Apart from superior mechanical properties and increased patient's comfort the latter also allowed to obtain reliable ECG signal. This was proved by significant positive correlation ratios (r = 0.54-0.89) of electrophysiological metrics calculated for these two independent systems [4]. Carbon nanotubes are willingly used as a nanofiller in various polymer compositions in particular - in conductive plastics applications. This approach is suitable in biomedical electrodes design. Adaptation of material properties can be achieved by surface modification of a filler [5]. Il-Seok Park et al. examined the impact of multiwall carbon nanotubes (MWCNT) addition on magnetic and mechanical properties of silicone elastomer-based composite. In this research, the carbon filler with an average thickness of 10 nm and over 95% purity was used. Authors applied only three concentrations of CNTs (0.2 wt%, 0.5 wt%, 0.7 wt%) as larger amounts of MWCNT caused difficulties in homogenization.

This research proved that proposed composites manifest interesting changes in mechanical and dielectric properties (particularly for the highest CNTs concentration) which makes them useful as dampers and actuator elements [6]. It was also confirmed that the use of MWCNT as an additive gives better results in comparison with carbon black (CB). M. Norkhairunnisa et al. tested 0.5 to 2% vol. concentration of carbon fillers in PDMS elastomer. One of the biggest difficulties in material preparation was an uneven distribution of CNT due to the formation of agglomerates. In this case conductivity plateau of -2.62 log σ[S/cm] was reached at 2% concentration of MWCNT. To achieve a similar result for CB a volume of 2.5% was needed. Another useful property of the CNT based composite is an increased thermal conductivity. However, as the authors concluded, preparation and surface treatment of MWCNT is very important to improve the properties of a final composite [7]. Jeong Hun Kim et al. proposed a universal flexible and conductive material for wearable applications. They developed new polydimethylsiloxane (PDMS) based composite with a CNT filler. Homogenic character of CNT dispersion in the matrix is crucial for electrical properties of final samples. They used isopropylic alcohol as a carbon filler solvent which was next evaporated from the mixture. This type of composite can be used in different applications including a flexible conductor which can replace wires in wearable electronics. Furthermore, a variable and strain-dependent resistance makes this material useful for mechanical sensors elements design. Research also proved that biopotential electrodes made of proposed composite have properties desired in such applications. To investigate this further, ECG signals were recorded for 7 days with PDMS+CNTs conductive pads. No deterioration in terms of a signal quality was found in comparison with standard Ag/C electrodes [8].

This study aims to provide a preliminary investigation of a new kind of composite dry electrodes. The best effect for the chosen application is provided by carbon nanotubes because in addition to excellent electrical properties CNTs provide better mechanical properties, which is not obtained in the case of amorphous carbon with a spherical structure. To verify the usability and durability of the proposed solution we conducted a set of material tests including electrical impedance and mechanical tensile strength measurements as well as verification of antibacterial properties.

Materials and Methods

As the carbon additive that was aimed to provide a conductivity of polymer matrix the commercially available multiwall carbon nanotubes (MWCNTs) (CNT Co., Ltd., Korea) were used. This powder component is obtained by catalytic chemical vapour deposition method using Fe catalyst. Carbon purity in raw multiwall carbon nanotubes was at least 95%. Before using, carbon nanotubes were chemically purified by heating under reflux in a mixture of boiling, concentrated sulfuric acids (VI) (98%) (Stanlab, Poland) and nitric acid (V) (65%) (Stanlab, Poland) in a ratio of 1:3 for about 16 h to completely remove amorphous carbon and traces of catalysts and to oxidize nanotubes' surface and obtain polar functional groups with a predominance of carboxyl groups. In turn, carboxylic groups were attached to the ends and walls of CNTs. The oxidized carbon nanotubes were eluted with demineralized water and ethanol until filtrate pH was stabilized. Used nanotubes had a diameter ranging from 10-40 nm and length in the range of 1-25 μm. For MWCNTs observation and their morphology the Field Emission Scanning Electron Microscope JEOL JSM- 7800F was used. The instrument has a field emission gun and is also equipped with an EDX (energy dispersive X-ray) detector for chemical analysis and a STEM (Scanning Transmission Electron Microscopy). The analysis was carried out with an accelerating voltage of 30 kV. Results in the form of pictures were taken in a bright field. Nanopowder of MWCNTs, used as a carbon nanofiller, was added to ethanol and exposed to ultrasonic waves. For TEM method, one drop of the suspension was placed on a copper 300 mesh grid coated with holey carbon film. Then the sample was dehydrated at 40°C.

The polymer matrix was obtained by mixing hydroxy functional polydimethyl siloxane polymer (Elastomer 80N, Wacker, Germany) and high-temperature vulcanizing silicon rubber (Polsil Gum 100/30, Silikony Polskie, Poland). Both components were mixed together at a ratio of 5:4. The preliminary part of this research included also the design of the technological process of obtaining samples of defined geometry in laboratory conditions. The viscosity of used polymeric components implied a necessity to find a method to achieve a homogeneous structure of the final composition. After many trials, a laboratory triple roller was used to mix components together. This device contains three independent shafts moving axially in opposite phase driven by an electric motor. The gap between rollers can be easily adjusted to obtain optimal friction generated between moving parts and material being processed. Each polymer substrate was dispensed one after another onto the first shaft and proceeded through all moving parts until obtaining homogeneous and consistent composition (FIG. 1).

FIG. 1. Silicone matrix with carbon additive during preprocessing on a triple roller.

After thorough mixing, purified multi-wall carbon nanotubes in various concentrations were added into the polymer premix. After homogenization, a crosslinking system dedicated to polysiloxanes based on hydrogen siloxane-co-dimethylsiloxane was added to the mixing matrix. This substrate consisted of an inhibitor based on 3,5-dimethyl-3-hexanol and a platinum addition polymer catalyst (all Evonik, Germany). Finally, samples with three concentrations of the nanofiller were obtained: "1" – 10 wt%, "2" – 7.5 wt%, "3" – 5 wt%. The next step involved forming samples between Teflon plates in the hydraulic press under a load of approximately 1.5 tons at room temperature. In the following part rectangles of the size of 20 x 40 mm were cut from flat samples and immediately placed between Teflon separators in a steel die with an electric heater connected. One part of the samples was then formed and crosslinked in a hydraulic press under a load of 5 tons at 150°C for 30 min. The second part was placed in an incubator under a pressure generated by steel blocks at 150°C (45 min).

TABLE 1. Characteristics of materials resistance measured in DC.

Sample	R [Ω] 1. pad	R [Ω] 2. pad	R [Ω] 3. pad	R [Ω] mean	σ [S/m]
10% hot pressing	4.36	3.64	1.56	3.19	2.63
7.5% hot pressing	1.38	5.43	3.92	3.58	2.98
5% hot pressing	80.54	72.78	68.61	73.98	0.12
10% crosslinking in oven	14.80	1.34	2.91	6.35	0.74
7.5% crosslinking in oven	4.42	1.21	4.85	3.49	1.57
5% crosslinking in oven	83.26	61.65	72.43	72.45	0.05

In the next step, a basic electrical study was carried out to verify the usefulness of obtained samples as electrode materials. Keysight 34461A multimeter as 4-wire ohmmeter was used to directly measure direct current (DC) resistance (TABLE 1). The same device was applied as an ammeter in the alternating current (AC) setup. For impedance measurements, a functional generator SIGLENT SDG1025 was utilized as a sinusoidal signal source and Boonton 1130 analyzer for voltage measurement. Both devices were connected in a standard voltmeter-ammeter method configuration.

In this examination, three different carbon filler concentrations and two manufacturing methods (hot pressing and cold forming with crosslinking in an oven) were investigated. Then three pads from each forming/composition variant were cut out to increase accuracy and verify the bulk homogeneity. First, DC resistance was measured which was a base for calculation of conductivity of the material. AC parameters were also recorded. Two flat, square-shaped copper electrodes were prepared for measurements by soldering the connecting wires (FIG. 2). Samples were then placed between electrodes and the measurements were taken under a static load of 1 kg (perpendicular to the surface of the sample).

Mechanical testing of the composites was performed using Zwick-1435 machine with strips samples (5 x 80 mm). All materials were compared for tensile strength (Rm) and Young's modulus (E). The behavior of materials under *in vitro* conditions was checked, keeping them for 7 days in 0.9% NaCl and the effect of the environment on the mechanical properties of the materials was determined. The durability conditions for testing of the materials for dry electrodes were chosen for the duration of the device during the long-term ECG test.

The composite material was also microbiologically tested by contacting it with bacteria *E.coli* using Kriba-Miller test (agar/24 h). The aim of this experiment was to check possible antibacterial properties that may be an effect of the introduction of CNTs into the polymer matrix.

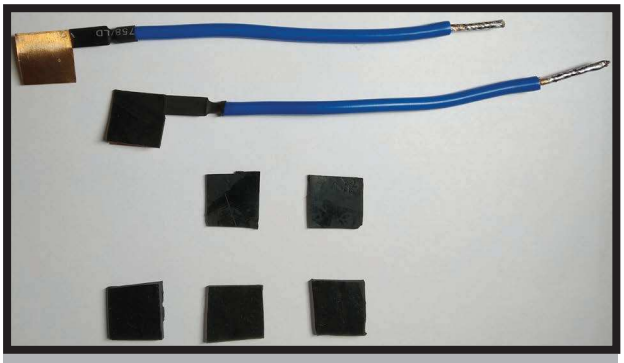

FIG. 2. Copper electrodes and cut pads of the composite samples.

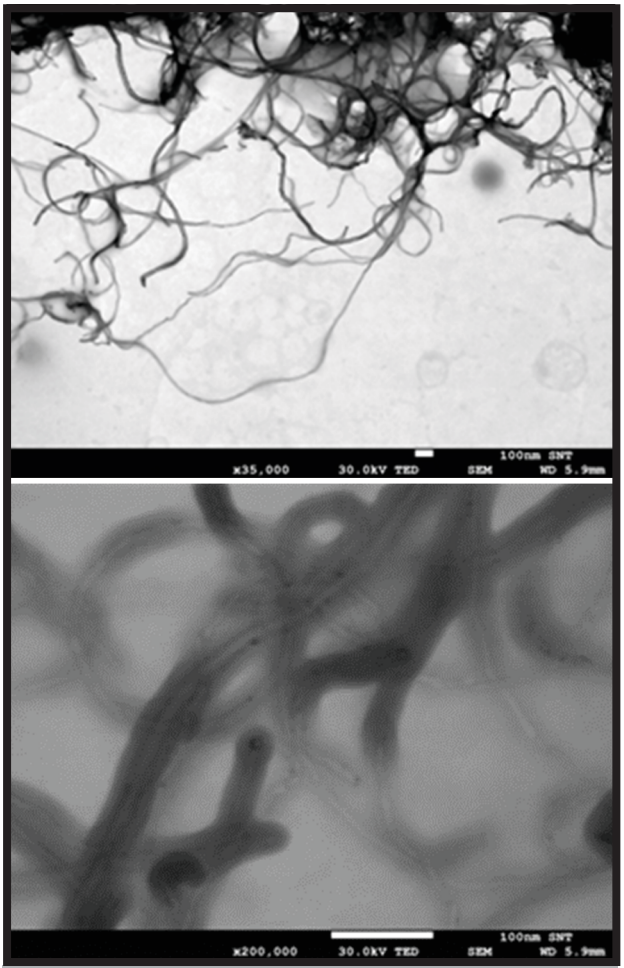

FIG. 3. STEM micrographs of multiwall carbon nanotubes (MWCNTs).

Result and Discussion

The carbon nanofiller's morphology from the STEM is presented in FIG. 3. The analysis shows that the used nanotubes have a diameter smaller than 40 nm, which is consistent with the producer declaration. The declared length was not confirmed due to method limitations.

Mechanical properties

A set of the hot-pressed samples was tested for mechanical properties such as Young's modulus (E) and tensile strength (Rm). Low values of the standard deviation indicated homogeneous filler distribution in the resin. The filler concentrations (10 wt%, 7.5 wt%, 5 wt%) were selected based on the previous experiments with mixing process and optimized.

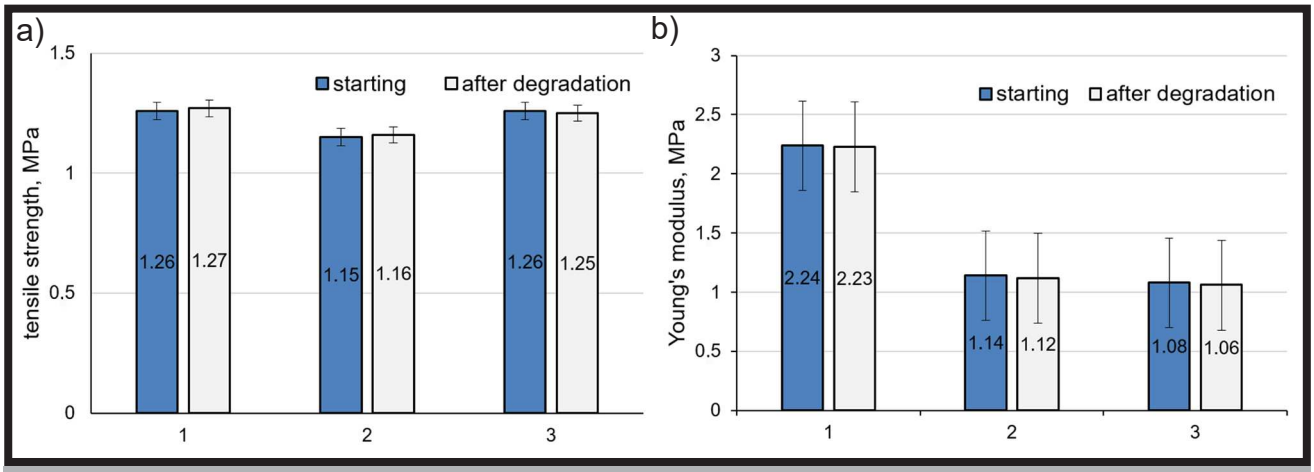

FIG. 4. Comparison of mechanical properties of the starting materials and materials after the degradation (7 days/37°C/0.9% NaCl): a) tensile strength, b) Young's modulus. ("1" – 10 wt% MWCNT, "2" – 7.5 wt% MWCNT, "3" – 5 wt% MWCNT)

TABLE 2. Characteristics of materials impedance measured in AC.

Sample	|Z| Ω 10Hz	|Z| Ω 100Hz	|Z| Ω 1000Hz	|Z| Ω 10000Hz
10% hot pressing	0.85	0.58	0.63	0.54
7.5% hot pressing	1.58	1.00	1.18	1.37
5% hot pressing	95.78	49.36	37.20	37.08
10% crosslinking in oven	3.28	2.71	3.23	3.47
7.5% crosslinking in oven	1.22	1.15	0.94	1.12
5% crosslinking in oven	26.07	24.44	29.33	46.21

Addition of 10 wt% of MWCNT resulted in a significant increase in Young's modulus and material stiffness, which can cause its breaking and crushing during exploitation. Both materials (5 wt% and 7.5 wt% MWCNT) had similar strength and significantly lower Young's modulus values. Despite the above observation, all tested materials had properties that allow their application as dry electrodes. Tensile strength was measured before and after the incubation in solution simulating degradation environment (contact skin – electrode, 0.9% NaCl) to determine durability of the proposed material. This *in vitro* experiment was carried out using a saline solution, which is similar to human sweat. Results show that no degradation was observed (FIG. 4). All materials which work as a dry electrode were stable under *in vitro* conditions.

Electrical parameters

Obtained results indicated a variation of parameters between samples that were formed in a cold press and crosslinked in a laboratory oven. The electrical conductivity of all samples was in a range from 0.05 to 2.98 S/m (TABLE 1) which is sufficient result for electrode applications [9]. The number of frequency data points in AC investigation might not be enough to fully represent the conductivity mechanism but this test was performed only to verify a bandwidth from the viewpoint of biosignals acquisition. The measured spectrum range was between 10 Hz and 10 kHz which corresponds to biopotential nature. Resulting linear characteristics indicate the lack of reactance part in the impedance (TABLE 2), which is desired in the context of reliable electrical biosignal acquisition.

Microbiological properties

Bacteria seeded on an agar medium and then cultured in vitro for 24 h/42°C were contacted with the tested materials. Due to the thickness of plastics (above 400 μm), the non-standard sizes of the samples submitted for testing were used. The test materials were kept in contact with the bacteria for 24 h and then the form of the bacterial biofilm was assessed (FIG. 5). In the literature, there are reports on the bactericidal properties of MWCNT [10-11]. Considering the long working time of the electrode applied directly to the human skin, the antibacterial properties of the electrodes would be desirable. Unfortunately, the results of the study indicated that the materials do not have antibacterial properties. After the set time of the experiment, a uniform bacterial layer appeared on all materials (FIG 5). In order to obtain antibacterial properties for the polymer matrix, it would be necessary to introduce proven additives with a bactericidal effect, e.g. nanometric silver [12].

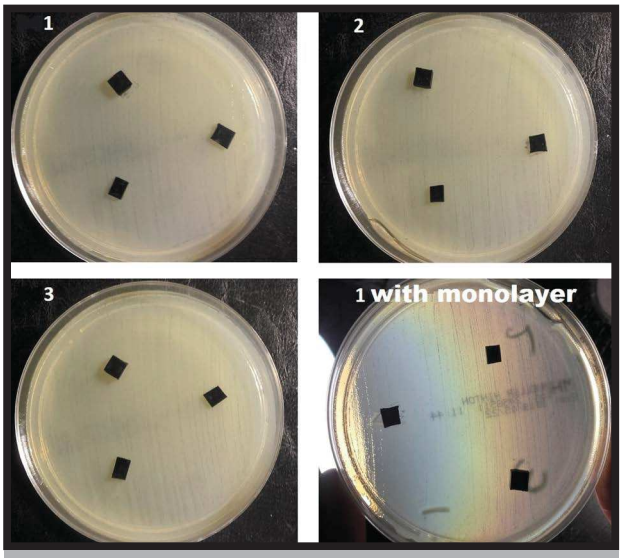

FIG. 5. Microbiological testing; no inhibition zone for bacteria *E.coli.*

Conclusions

Application of a carbon nanofiller such as graphite oxide, graphite, carbon nanotubes, graphene enabled to obtain a conductive polymer material with satisfactory mechanical properties. Results of breaking strength, deformation resistance and Young's modulus tests of the samples after degradation suggest that this material can be integrated with textiles.

A designed technology of processing of the proposed substrates allows to prepare in laboratory conditions a composite material with high CNTs homogenization in the silicone resin. A fact that the nanofiller was very evenly dispersed in the polymer matrix was proven by repetitive results of the mechanical tests. It turns out that, besides the addition of the carbon nanotubes also curing methodology has a significant impact on the resulting electrical properties. None of the prepared samples have antibacterial properties. However, the proposed material is certainly durable in the *in vivo* conditions. In the future, it is planned to conduct further research on the designed composite in the context of electrophysiological applications. Measured resistance of the tested samples was several ohms and featured linear bandwidth in a biopotential range. These results meet requirements for dry electrodes. On the other hand, the obtained material composition and its properties make it a promising alternative to the current standard solutions based on wet electrodes.

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