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Resistive pressure sensors fabricated from polymer thick film composites containing carbon nanotubes*

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Polymer composites with carbon nanotubes (CNT) are new group of materials with a broad possibilities of application perspectives in many branches of the industry. In presented papers authors are investigating properties of sensor structures used in pressure sensor systems with CNT layers fabricated using thick film technology. One of the main difficulties to overcome was preparation of polymer-nanotube composition sample. Composition of carbon nanotubes in PMMA-PBMA polymer resin was prepared by modified mixing process used in thick film material preparation. Sensor structure was fabricated by printing polymer-nanotube areas with polymer-silver paths as connection electrodes on polyester substrate foil. Four type of compositions with different content of CNT were prepared: 0.1%; 0.25%; 0.5%. For different CNT content in printed thick film layers, samples exhibited resistance was around 100 kΩ, 2 MΩ, 200 MΩ respectively. Dependence between sensor resistance and force tension is nearly linear and similar for all samples. Significant decrease of resistance under tension was observed, and changes in resistance were more symptomatic for samples with higher CNT content. Distinct time hysteresis was observed during resistance measurements.

Keywords: resistive polymer nanocomposite, contact resistance, pressure sensors, carbon nanotubes, thick film technology
***Słowa kluczowe*:** polimerowy nanokompozyt rezystywny, rezystancja stykowa, czujnik ciśnienia, nanorurki węglowe, technologia grubowarstwowa

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1. INTRODUCTION

One of the method used for pressure measurement is survey of resistance fluctuations in two layer structure affected by mechanical tension [1]. It is widely used method in application such as electronic foil keypads, potentiometers or pressure sensors [2-3]. Resistance changes are also observed during pressing of fine grained graphite or carbon black [4], or polymer resin filled with carbonic material [5]. Those methods are well known for decades and it is defined that with rise of applied pressure contact resistance is decreasing. All this changes have linear characteristic in logarithmic coordinates.

Since their discovery at the end of last century [6], carbon nanotubes (CNT) and fulerens structures have attracted extensive attention in many branches of industry. One of the key application is fabrication of nanotube-polymer composites for construction, electronic and mechatronic systems [7-9]. Tanks to the one dimensional structure of nanotubes it is possible to obtain composite material with completely new electrical and mechanical properties, in comparison to graphite or carbon black polymer composites.

2. MATERIALS AND PREPARATION

One of the key elements used in preparation of samples was polymer-nanotube composition. Nanostructured materials investigated in conducted research were multiwalled carbon nanotubes (MWCNT) obtained by a gas phase nucleation process. Characteristic dimensions of nanotubes estimated by SEM observations were 30 x 2000 nm (see Fig. 1). Polymer base used was poly(methyl metacrylate) and poly(butyl metacrylate) copolymer (PMMA-PBMA) resin as 34% butyl carbide acetate solution. Usually used in thick film technology mechanical grinding in mortar resulted with unsatisfying mixtures, with high ratio of nanotube agglomerates and low level of homogenization in polymer resin. Therefore solvent suspension of CNT was ultrasonically stirred for two hours to obtain required degree of dispersion, stirred for one hour more with added resin, and finally three-roll-milled and grind in mortar for more homogenization. Such compositions were formally used for fabrication of transparent thick film electrodes [10].

Three types of composite materials were fabricated with different amount of nanotube content: 0,1% , 0,25%, and 0,5% CNT described later as 0,1CNT, 0,25CNT, 0,5CNT respectively.

Carbon nanotube compositions and silver composition DP 5000E were screen printed on 80 μm polyester substrate. To avoid thermal contraction of substrate during composition hardening processes, polyester foil was first thermally threated

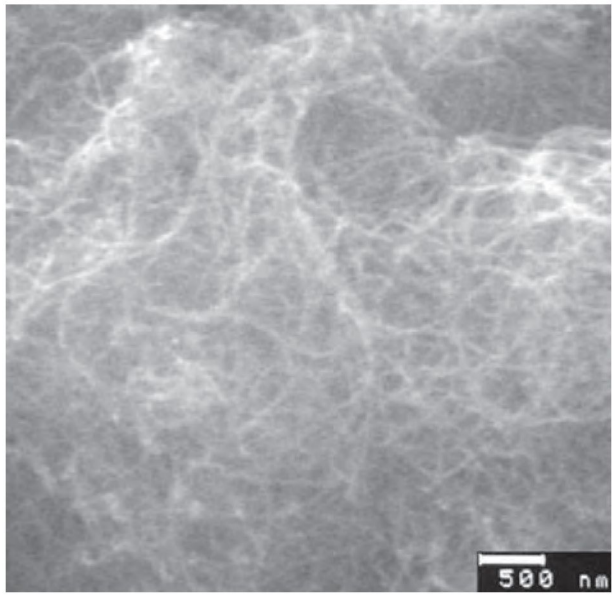

Fig. 1. SEM image of used CNT material.
Rys. 1. Zdjęcie SEM zastosowanego materiału nanorurek.

in 150°C for 30 minutes. After cooling the substrate to room temperature, silver pattern was screen printed on foil and thermally threated in 130°C for 30 minutes to evaporate solvents. During next step selected CNT composition was screen printed as second layer and thermally threated for 30 minutes. SEM image of obtained polymer-nanotube layers is presented in Fig. 2.

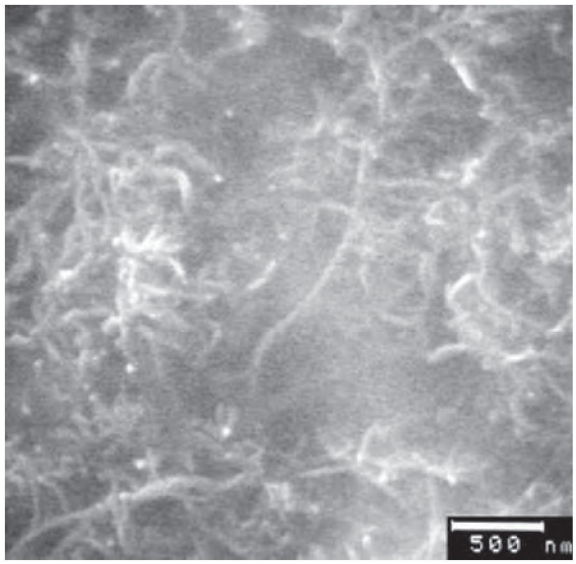

Fig. 2. SEM image of obtained CNT-polymer layer.
Rys. 2. Zdjęcie SEM otrzymanej warstwy polimerowo-nanorurkowej.

To evaluate curing temperature influence on CNT layer resistance, separate samples were threated in four different temperatures: 120°C, 130°C, 140°C and 150°C.

Measurement pattern consist of silver paths and CNT areas is presented in Fig. 3. Contact resistance was measured between electrodes numbered 1 and 2. between electrodes 2 and 3 sheet resistance of printed CNT layer was measured.

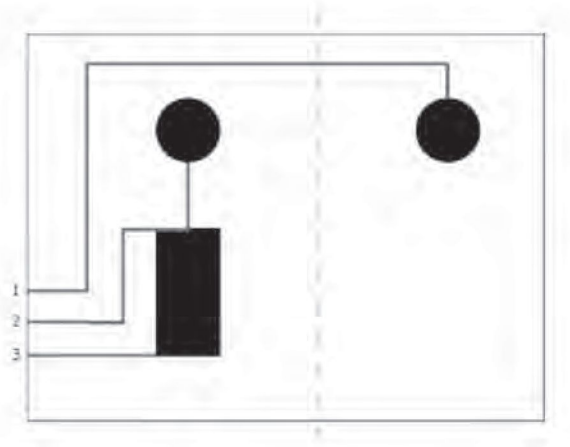

Fig. 3. Measurement pattern with silver paths (grey) and carbon nanotube areas (black).
Rys. 3. Wzór pomiarowy ze ścieżkami srebrowymi (szare) i obszarami zawierającymi nanorurki (czarne).

3. EXPERIMENTAL

Fabricated samples were first investigated for electric impedance and phase angle differences in relation to carbon nanotube content in printed layers. Impedance spectroscopy was measured with RLC bridge in frequency range from 100 Hz to 2 MHz. Phase angle shifts were measured in the same range of frequencies as for impedance spectroscopy. Contact resistance measurement laboratory stand consists of ohmmeter and specially build balance beam stand generating pressure. Symbolic schema of the laboratory stand used in contact resistance measurement is presented in Fig. 4.

Investigated sample (2) is bended along axis selected in Fig. 3 and placed on rigid base (1). With specially matched weight, defined vertical force is generated and directed to sample by rubber cylinder (3) with basis area of 0,1 cm^2. Resistance measurement is realized through electrodes 1 and 2. Sheet resistance measured on electrodes 2 and 3 is used as reference point to eliminate resistance of layer and to measure only contact resistance.

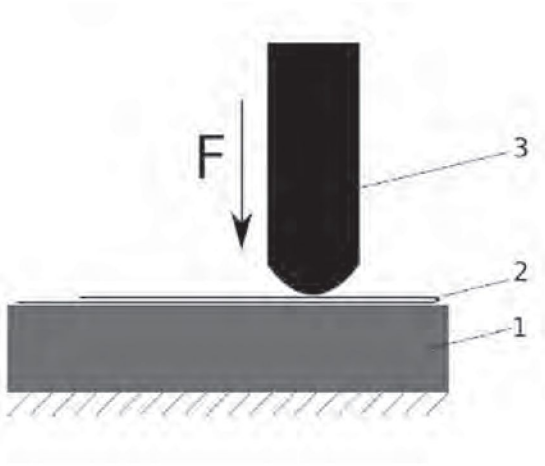

Fig. 4. Schematic of the laboratory stand used in contact resistance measurements.
Rys. 4. Schemat stanowiska laboratoryjnego do pomiaru rezystancji stykowej.

4. RESULTS AND DISCUSSION

In Figure 5 relation between curing temperature and resistance of measured samples is presented. For all three compositions (0,1CNT, 0,25CNT, 0,5CNT) significant drop of resistance was observed in 120°C – 140°C temperature spectrum. Resistance changes were similar for all compositions and were observed in range of 68 to 78% for samples 0,1CNT to 0,5CNT respectively. No major differences were observed between 140°C and 150°C temperatures. In correlation to obtained results, optimal hardening process parameters were selected to be 150°C temperature in 30 minutes time. All successive samples were prepared with this parameters set.

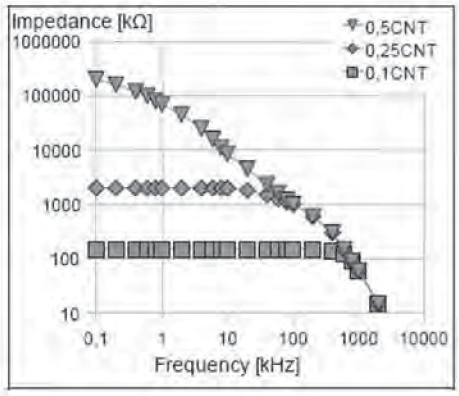

Fig. 5. Relation between hardening and temperature resistance of measured samples.
Rys. 5. Zależność pomiędzy temperaturą utwardzania a rezystancją próbek pomiarowych.

In Fig. 6 relation between frequency changes and sample impedance is presented for all three polymer-nanotube samples.

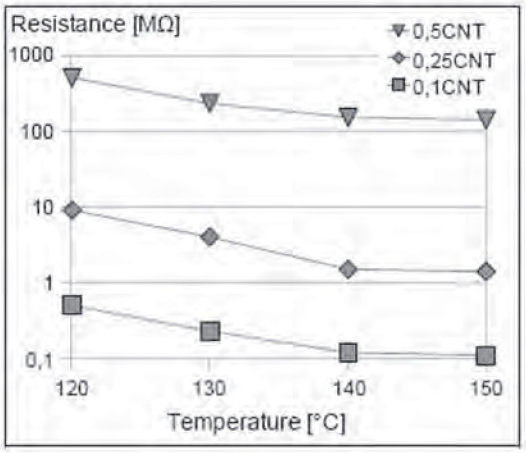

Fig. 6. Relation between frequency changes and sample impedance.
Rys. 6. Zależność pomiędzy zmianami częstotliwości a impedancją próbek.

It was observed that for higher CNT content characteristic frequency is higher, above witch drop of the impedance is significant. For 0,1CNT sample no characteristic frequency was observed and impedance was changing through whole frequency spectrum.

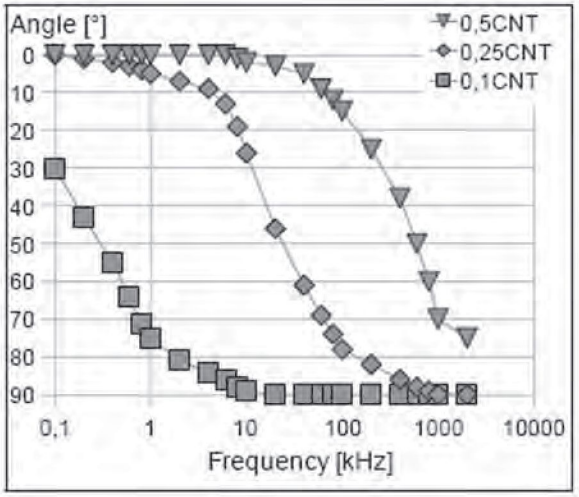

Fig. 7. Relation between frequency changes and phase angle changes.
Rys. 7. Zależność pomiędzy zmianami częstotliwości a zmianami kąta fazowego.

In Fig. 7 results from measurements of phase angle changes are presented. Measurements of the angle were conducted in the same frequency spectrum as for impedance measurements. For sample 0,5CNT capacity component is noticed around 10kHz frequency, with maximum measured phase angle value of -80° around 2 MHz. For sample 0,1CNT phase angle is asymptotic in whole measured frequency spectrum from 30° to 90°. Again angle values are negative what indicates capacitive nature of investigated samples. This nature is noted for samples with content of conductive material near percolation threshold. Beside resistive component it is also observed ascending capacitive component which is caused by gaps between conductive parts in paths formed in dielectric polymer resin.

Samples made of 0,1CNT compositions behave as being near percolation threshold. Similar characteristics were obtained for 3,5% of Sakap-6 carbon black in polyesterimide resin [11].

Resistance changes measured under different tension for investigated sensors are included in Figure 7. Resistance measurements were conducted for force tension changes in range from 400N to 4kN. Observed dependence between sensor resistance and force tension was nearly linear and similar for all samples.

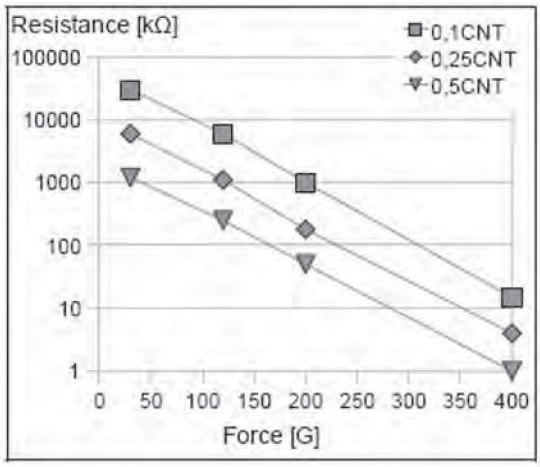

Fig. 8. Relation between tension changes and sample resistance
Rys. 8. Zależność pomiędzy zmianami nacisku a zmianami rezystancji

During first measurements resistance values demonstrated high spread which might be caused by low CNT content. Under pressure tension measure resistance of polymer-nanotube composite was changing dramatically as if there was constant change in contact surface of printed areas. This might be related to continuous increase of contacts along with increasing tension force. This effect was stabilized

after couple full cycles of pressure change. Significant decrease of resistance under tension was observed. It was greater than for corresponding samples with other carbon filling [12].

4. CONCLUSION

Polymer composites containing carbon nanotubes were investigated. Samples with 0,1% to 0,5% CNT content in composition were prepared. Specially developed pattern of screen printed silver paths and carbon nanotube areas was fabricated for pressure measurement through contact resistance changes. In range of tension force changes from 400N to 4kN investigated samples demonstrated over thousandfold (exactly 1500) change in measured contact resistance. This is way above resistance changes measured for other carbonic filling material such as fine grained graphite or carbon black.

Based on impedance and phase angle changes in selected frequency spectrum it is possible to define conductance mechanism in investigated composites. Results obtained from this experiments implicate that compositions with 0,1% nanotube content are nearby percolation threshold for this type of mixture.

Fabricated this way pressure sensors demonstrate desirable effects such as few orders higher sensitivity than with the use of conventional graphite layers. It seams that this is good direction in development of more sensitive pressure sensors for microsystems. More experiments are planed to be conducted to evaluate usage of other resins and other types of carbon nanotubes for production of this structures.

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REZYSTYWNE CZUJNIKI NACISKU WYTWORZONE Z GRUBOWARSTWOWYCH KOMPOZYTÓW POLIMEROWYCH ZAWIERAJĄCYCH NANORURKI WĘGLOWE

Kompozyty polimerowe zawierające nanorurki węglowe (CNT) stanowią nową grupę materiałów o szerokim zakresie zastosowań w wielu gałęziach przemysłu. Poniższa publikacja zawiera wyniki badań nad właściwościami grubowarstwowych struktur polimerowych zawierających nanorurki węglowe zastosowanymi jako czujniki nacisku. Jednym z głównych trudności napotkanych przy wytwarzaniu struktur pomiarowych było wytworzenia polimerowo-nanorurkowej kompozycji grubowarstwowej. Przy zastosowaniu specjalnie dostosowanej techniki mieszania udało się wytworzyć kompozycję opartą o żywice PMMA-PBMA. Układ pomiarowy został naniesiony na podłoże polimerowe techniką sitodruku zarówno w przypadku polimerowo-nanorurkowych obszarów czujnika jak i polimerowo-srebrowych kontaktów pomiarowych. Do badań wykorzystano cztery rodzaje kompozycji zawierające odpowiednio 0.1%, 0.25% i 0.5% wagowo nanorurek które po nadrukowaniu wykazywały rezystancję ścieżek na poziomie 100 kΩ, 2 MΩ i 200 MΩ. Zależność pomiędzy zmianami siły nacisku a zmianami rezystancji okazała się niemal liniowa dla wszystkich próbek. Zaobserwowano znaczące zmiany w rezystancji pod wpływem siły nacisku które były bardziej znamienne dla próbek o dużej zawartości nanorurek. Zaobserwowano również histerezę zmian rezystancji dla wszystkich próbek.