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To cite this article: E D Skutin *et al* 2018 *J. Phys.: Conf. Ser.* **944** 012110

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Gas sensitivity of polymeric composites with carbon nanotubes

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Abstract. The possibility of application for carbon nanotubes DEALTOM as a conductive filler for composite sensors based on polysiloxanes is shown. Sensors show predicted results on sensitivity and selectivity. Nanotubes according to chemical, physical and mechanical characteristics are suitable for modifying of specified composites and are applicable for work with rather aggressive reagents.

1. Introduction

Combination of nano- and biotechnologies, computer, information and cognitive technologies in a single chain enables the emergence of new scientific trends on creation of inanimate matter intellectual systems, which can be used in a wide number of areas from industrial production to ecology and medicine. One of a recent trends is a chemical analysis with the use of multi-touch gas-analysis systems called «electronic nose» [1, 2]. The basis of these systems is an array of sensors characterized by the sensitivity to a broad range or the whole class of analyzed substances (analytes).

Nowadays a wide range of various sensors can be used in sensor arrays, but chemoresistors based on composites with the application of nanotubes are of special interest. Carbon nanotubes have a number of unique properties making their usage in chemical sensors very prospective. A large surface area of nanotubes provides efficient adsorption of molecules in many substances, and modification of carbon nanotubes surface by polymers can increase both selectivity, and sensitivity of sensors [3].

Nanocomposite materials can also provide important advantages for sensors: the possibility of sensitivity control by alteration of a quantitative relationship and the nature of filler and polymer interaction, little response time owing to a fast diffusion of analyte molecules into the volume of a film and the expansion in a variety of sensitive layers [4].

The purpose of this work is to examine gas sensitivity in a hybrid sensor array comprising polymeric composite sensors based on three variously modified polysiloxanes with electroconductive filler in the form of carbon black and DEALTOM nanotubes.

2. Problem statement

DEALTOM multi-wall carbon nanotubes (MWCNT) are polycrystalline graphite carbon filamentary structures of a cylindrical shape with the internal channel. MWCNTs without cleaning (immediately after reactor) are the powder consisting of nanotubes in two sizes with an external diameter $D_{out1} = 49.3$ nm or $D_{out2} = 72.0$ nm, respectively according to Transmission Electron Microscope (TEM) data. The inner diameter of nanotubes according to TEM is $D_{in} = 13.3$ nm. The rough estimate of upper bound for nanotubes' length based on Scanning Electron Microscope (SEM) data gives the value of $L = 5$ μ m. Multi-wall carbon nanotubes DEALTOM are synthesized by the original method



that is a low-temperature thermocatalytic pyrolysis of hydrocarbons, which allows one to create low cost carbon nanotubes.

The low cost, portability, mobility and low power consumption are necessary requirements to multi-touch gas analyzers in which therefore the usage of simple sensors, like chemoresistors based on the polymeric composites is preferable. Chemoresistive composite-based sensors using stationary phases for a gas chromatography (GC) as a polymeric matrix are objects of special interest. Distinctive features of these polymeric phases are a higher polymer purity with eliminated traces of catalysts, monomers, solvents and other undesirable impurities, and a narrower molecular-weight distribution compared to general purpose industrial polymers. Liquid GC phases in the form of three variously modified polysiloxanes such as Polydimethyl-siloxane (PDMS), Polycyanopropyl methyl-siloxane (PCPMS) and Polyphenylmethyl-siloxane (PPhMS) have been used as an isolating polymeric matrix of composites in this paper.

The experience in using systems with uniform sensor arrays shows, however, that they are capable to detect rather limited range of analytes. This results in the need to create hybrid arrays with the sensors of different functioning principles, or to apply specific operating modes in systems [5]. In particular, the application of a pulse mode in analytes' supply makes possible to use sensory response kinetic features as an additional information factor about the analyzed object composition [6].

3. Theory

The text of your paper should be formatted as follows: The intensity of composite sensors' response is first of all determined by a thermodynamic activity of analyte in a polymer matrix and by its ability to bring the matrix to swelling. To estimate the swelling extent in polymeric matrix of composites in solvent vapors it is possible to use such characteristic as solubility parameter δ , introduced by Hildebrand to describe nonelectrolyte solutions [6]. We can propose the polymer solubility and its swelling ability if values of these parameters are close for a polymer and a solvent $\delta_p \approx \delta_s$.

The solubility parameter is calculated from the relationship

$$\delta = (\Delta E/V)^{1/2}, \quad (1)$$

where ΔE is a cohesive energy defined as $\Delta E = \Delta H - RT$; ΔH is a latent heat of a substance evaporation; R is a universal gas constant; T is an absolute temperature; V is a molar substance volume.

The square of solubility parameter represents a cohesive energy density, i.e. its value in a molar volume unit ($\delta^2 = \Delta E/V$). The cohesive energy value ΔE is additive and is presented as the contribution sum $\sum_i \Delta E_i^*$ from each atom and kind of intermolecular interaction. The calculation of cohesive energy density by the increment method can be accomplished by the equation:

$$\delta^2 = \frac{\sum_i \Delta E_i^*}{N_A \sum_i \Delta V_i}, \quad (2)$$

where $\sum_i \Delta E_i^*$ is the increments sum of cohesive energy for all atoms and bonds in a solvent molecule or in a repeating polymer macromolecule link; $N_A \sum_i \Delta V_i$ is the increments sum of van der Waals molecule volume or the repeating macromolecule link. The values of increments ΔE_i^* and ΔV_i are given in [6].

Table 1 provides the values of solubility parameters δ calculated by the method of increments for the solvents used in this paper as analytes, and for the polymers used in this work as the basis of polymeric composites.

Table 1. The values solubility parameters δ for analytes and polymers.

№	Name	$\sum_i \Delta E_i^*$ (J/mol)	$N_A \sum_i \Delta V_i$ (cm ³ /mol)	δ (MPa ^{1/2})
Solvents				
1	Petroleum ether	-	-	14.3
2	n-Hexane	16642	114.8	15.5
3	Chloroform	13310	71.4	17.5
4	Toluene	20740	96.0	18.3
5	Acetone	15515	59.2	20.9
6	Ethanol	29669	51.0	26.1
7	2-Propanol	32382	68.2	28.1
8	Butanol	28219	88.1	23.1
Polymers				
1	PDMS	23580.9	125.3	17.7
2	PCPMS	15483.6	59.6	20.7
3	PPhMS	21081.3	96.7	19.0

4. Experimental technique

The experimental multi-touch system represents a structure of three functional units: a sensor array, a sampling subsystem and a signal processing unit of sensor array.

4.1. Sensor array

The sensor array basis comprised 8 polymercomposite (PC) sensors. Composite chemoresistors can be considered as narrow selective among resistive sensors. The liquid phases for gas chromatography, presented in Table 2, were used as the isolating polymeric matrix of composites, and structural formulas of monomeric links of these polymers are given in fig. 1. The carbon black (CB) N472 with particle size of 20...25 nm, and DEALTOM MWCNTs were used as electroconductive fillers of composites.

PC sensors were made in the form of film chemoresistors with applying a toluene solution of a proper composite on a mica substrate, with a preliminary vacuum deposition of contact pads and Ag electrodes on the substrate. The production ended with drying of finished sensors in the open air until a complete solvent elimination that was controlled according to the stabilization of electric resistance R_0 .

Table 2. Materials of polymeric matrices for electroconductive composites.

№	Notation	Polymer	Brand of GC phase
1	PDMS	Poly(dimethyl-siloxane)	SE-30
2	PCPMS	Poly(cyanopropylmethyl-siloxane)	OV-105
3	PPhMS	Poly(phenylmethyl-siloxane)	OV-17

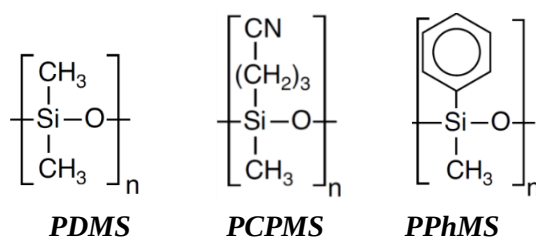


Figure 1. Structural formulas of polymers' monomeric links.

Wide sensitivity sensors, i.e. one thermo-catalytic (TC) sensor and two metal-oxide (MO) sensors with the various operation temperature were additionally implemented into the structure of system sensor array. The characteristics of both additional TC and MO sensors, and fabricated PC sensors with the filler in the form of CB and MWCNTs are given in Table 3.

TC sensors operation is based on a measurement of thermal effect in a reaction of catalytic oxidation of analytes by air oxygen with a heated thermoresistor covered by a catalytic layer of platinum or palladium deposited on aluminum oxide. The peculiarity of these sensors is a wide sensitivity to almost any combustible substances capable to oxidation on active centers of the catalyst [8].

Table 3. Characteristics of the used sensors.

№	Type	Basic material	Filler (% wt)	
			CB	MWCNT
1	TC	Al ₂ O ₃ +Pd	-	-
2	MO	SnO ₂	-	-
3	MO	SnO ₂	-	-
4	PC	PCPMS (OV – 105)	10	-
5	PC	PPhMS (OV – 17)	10	-
6	PC	PPhMS (OV – 17)	-	25
7	PC	PCPMS (OV – 105)	-	25
8	PC	PCPMS (OV – 105)	-	20
9	PC	PDMS (SE – 30)	10	-
10	PC	PDMS (SE – 30)	-	25
11	PC	PPhMS (OV – 17)	-	10

Two thin-film (~1 μm) metal-oxide SnO₂ sensors have been made on mica substrates by the method of thermal deposition of metal tin with its further oxidation at the temperature of 773 K in the air. MO sensors among resistive devices have an average selectivity [9].

4.2. Sampling subsystem

The sensor array was placed in a 21 ml measuring cell, which was blown by the air pump with 50 ml/min speed. Pulse samples' dosing was performed with 3...5 % accuracy, by air-vapor mixture injecting of analytes' saturated vapors in the air line by means of a syringe. The results of chromatographic calibration of these samples, which was carried out on the gas chromatograph «Chromos GH-1000», are presented in [10].

4.3. Signal processing unit of sensor array

Collection and processing of analog data from the sensor array were conducted by E14-140 measuring module produced by «L-Card» under control of *LGraph2* program. The sample identification problem was solved by processing of obtained signal sampling in the whole sensor array by means of artificial neuron network made in the form of a multilayer perceptron. The necessary network inputs n_i

corresponded to the product $n_i = n_s \times n_t$, where n_s is a number of sensors in array and n_t is a number of points in a discrete kinetic sampling of their signals. Every analyte in an output layer of neuron network was assigned with a proper neuron, its signal level showed the analyte content in the sample.

5. Results discussion

Characteristic property of polymeric nanocomposites is a percolation nature of their electroconductivity. The nanocomposite conductivity sharply increases achieving a threshold concentration of a conductive filler (a percolation threshold). In this paper, the percolation threshold of nanocomposites based on polysiloxanes was achieved by a stepwise 5 % increase in mass concentration of MWCNTs in a polymeric matrix up to the demonstration of sensitivity to analytes by the chemoresistors. Noticeable gas sensitivity appeared as a rule under decreasing of electric resistance to 1...2 MΩ in chemoresistors. At the same time, a further increase of MWCNT concentration led to a noticeable decrease in resistance and removal from the percolation threshold with the sensitivity loss.

The values of solubility parameters calculated by the method of increments for the solvents used in this paper as analytes, and for the polymers used in this paper as a polymeric composites basis are given in Table 1. The obtained values of indicators allow us to predict a good sensitivity to nonpolar analytes (petroleum ether, n-hexane and acetone) and a weak sensitivity to polar alcohols for PC sensors based on polysiloxanes (SE-30, OV-17 and OV-105).

The example of experimental data with responses of hybrid sensor array to n-hexane sample obtained by the measuring module E14-140 under *LGraph 2* program control is presented in fig. 2. Numbers of curves in the figures correspond to numbers of sensors in Table 3.

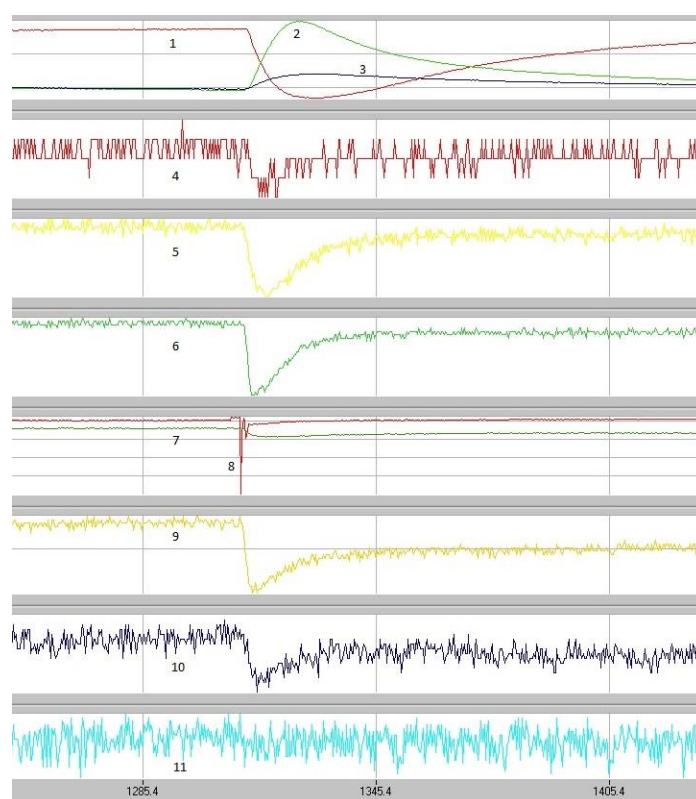


Figure 2. A sensor array response to a 5 ml air-vapor sample under 437 ppm n-Hexane concentration.

These data show that a satisfactory sensitivity of sensors can be achieved by the increase of mass

share of carbon nanotubes up to 20–25 %. However, the necessary concentration of nanotubes exceeds significantly the required amount of carbon black (10 %). Thus, sensor № 11 (10 % MWCNT), for example, does not show the sensitivity to any of the used analytes.

The comparison of sensors' responses with carbon black (for instance, № 5 CB 10 % wt) and sensors with carbon nanotubes (for example, № 6 MWCNT 25 % wt) shows that in case of n-hexane, petroleum ether and acetone, the modification of a polymer by carbon nanotubes does not lead to a noticeable change in sensors' characteristics. The responses of such sensors are almost identical taking into account the noise level in their signals. However, in case of ethanol, the sensor № 6 has shown a minor improvement of sensitivity compared to the sensor № 5.

6. Conclusions

Carbon nanotubes DEALTOM demonstrate a good possibility of their use as a conductive filler for composite sensors based on polysiloxanes, showing expected results in sensitivity and selectivity. It should be noted that DEALTOM MWCNTs in chemical, physical and mechanical characteristics are suitable for modifying of any composite materials since they are characterized by very high hardness and corrosion resistance (they are insoluble neither in «aqua regia», nor in strong alkaline solutions). It has allowed us to use them as a suitable material to work with rather aggressive reagents. Moreover, a big surface size of nanotubes provides their high adsorbability.

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