

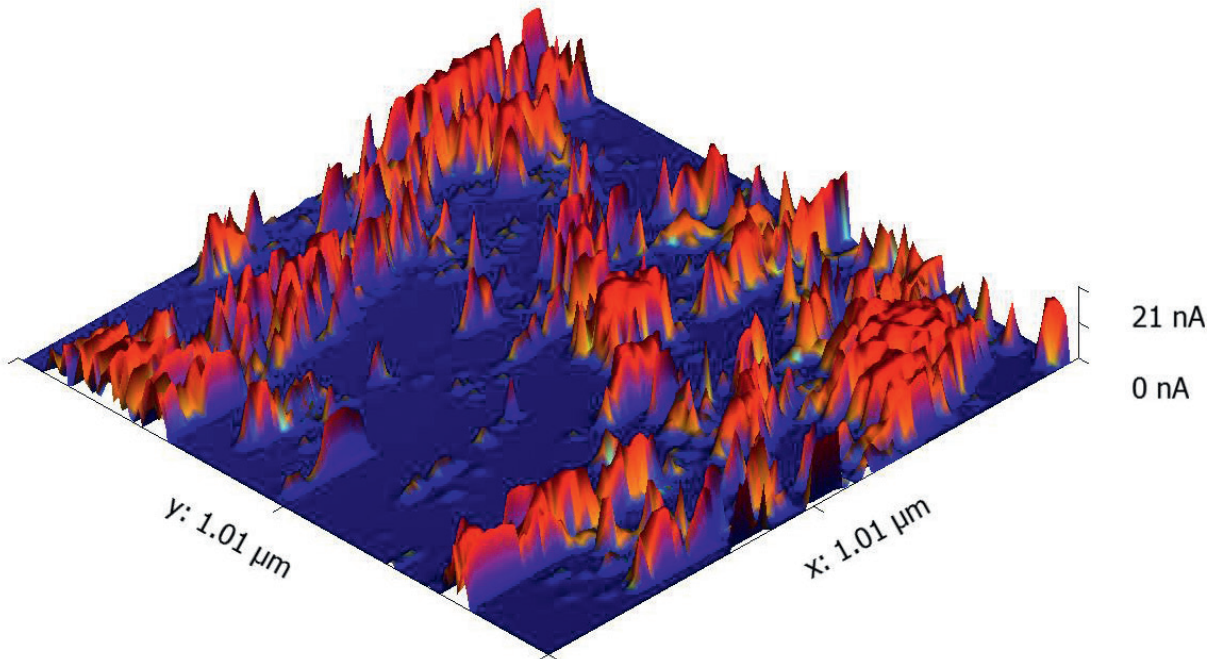


RIGA TECHNICAL  
UNIVERSITY

**Santa Stepina**

# CONDUCTIVE NANOSTRUCTURED POLYMER COMPOSITES FOR FUEL AND VOLATILE ORGANIC COMPOUND VAPOUR DETECTION

Summary of the Doctoral Thesis



**RIGA TECHNICAL UNIVERSITY**

Faculty of Materials Science and Applied Chemistry

Institute of Technical Physics

**Santa Stepina**

Doctoral Student of the Study Programme “Materials Science”

**CONDUCTIVE NANOSTRUCTURED POLYMER  
COMPOSITES FOR FUEL AND VOLATILE  
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Scientific supervisor

Professor Dr. habil. Phys.

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# **DOCTORAL THESIS PROPOSED TO RIGA TECHNICAL UNIVERSITY FOR THE PROMOTION TO THE SCIENTIFIC DEGREE OF DOCTOR OF ENGINEERING SCIENCES**

To be granted the scientific degree of Doctor of Engineering Sciences, the present Doctoral Thesis has been submitted for the defence at the open meeting of RTU Promotion Council on December 19, 2018 at the Faculty of Materials Science and Applied Chemistry of Riga Technical University, 3/7 Paula Valdena Street, Room 272.

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## **DECLARATION OF ACADEMIC INTEGRITY**

I hereby declare that the Doctoral Thesis submitted for the review to Riga Technical University for the promotion to the scientific degree of Doctor of Engineering Sciences is my own. I confirm that this Doctoral Thesis had not been submitted to any other university for the promotion to a scientific degree.

Santa Stepina ..... (signature)

Date: .....

The Doctoral Thesis has been written in Latvian. It consists of Introduction; 3 chapters; Conclusions; 65 figures; 8 tables; 3 appendices; the total number of pages is 100. The Bibliography contains 151 titles.

## ACKNOWLEDGEMENTS

Doctoral thesis is a teamwork the development of which I cannot imagine without participation of colleagues and family support. I would like to express my great thanks to the scientific supervisor of the Doctoral Thesis Maris Knite for giving me opportunity to work actively in science from the first year of bachelor studies and purposefully guided to me to doctoral studies. Thank you for the opportunity to present my work in various international conferences in France, Spain, Estonia, etc. Thank you for giving persistent motivation and lifting the “bar” ever higher, as well as thank you for helping explain and analyse the obtained results.

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## TABLE OF CONTENTS

TABLE OF CONTENTS .....	5
ABBREVIATIONS .....	6
GENERAL DESCRIPTION OF THE WORK .....	7
Introduction .....	7
Aim .....	7
Tasks .....	7
Scientific novelty .....	8
Practical significance .....	8
Composition and amount of work .....	8
Approbation of work and publications .....	8
Thesis .....	9
Thesis Content .....	10
Review of literature .....	10
Methodological part .....	11
Experimental part .....	12
Summary of doctoral thesis conclusions .....	28
References .....	29
Approbation .....	31

## ABREVIATIONS

$\frac{\Delta R}{R_{o(\infty)}}$  – change of relative electrical resistance at time t when t tends to  $\infty$

$\frac{\Delta R}{R_{o(t)}}$  – change of relative electrical resistance at time t

$t_0$  – moment of time, when a sample is in VOC vapours of given concentration

$\sigma_o$  – electro conductive phase conductivity

$\varphi_c$  – composite's critical concentration,

AC – alternating current

AFM – atomic force microscope

BTEX – benzene, toluene, ethylbenzene and xylene

CB – graphitized carbon black nanoparticles

CNT – short multi-walled carbon nanotubes

CPC – conductive polymer composites

DBP – dibutylphthalate

DC – direct current

EC – ethyl cellulose

EVA – ethylene vinyl acetate copolymer

EVA-CB – ethylene vinyl acetate and nanostructured carbon black composite

EVA-CNT - ethylene vinyl acetate and nanostructured carbon nanotubes composite

EVA-CNT-CB – ethylene vinyl acetate and carbon nanofillers hybrid composite

He – helium

PCA – principal component analysis

PCL – polycaprolactam

PEO – polyethylene oxide

P-NCC – polymer-nanostructured carbon composite

PVAc – polyvinyl acetate

PVP – Polyvinylpyrrolidone

RTU – Riga Technical University

t – critical index

VA – vinyl acetate

VOC – volatile organic compounds

$\tau$  – relaxation time constant

A – amplitude that describes the reaction

$\tau$  – reaction time constant

$\varphi$  – electro conductive phase volume fraction

# GENERAL DESCRIPTION OF THE WORK

## Introduction

The development of methods and materials for volatile organic compound (VOC) detection is a well known scientific field [1]–[5]. VOCs are all around us – in cleaning supplies, in various household items, and are used in manufacturing of foods and other products. Thus people are easily exposed to VOCs and it can harm their health. In order to control VOC concentration in air, air sampling checks are carried out. Mostly analytical methods like gas chromatography are used. It is time consuming and requires trained staff, however is very precise. It is a challenge to develop sensors or sensor materials that are mobile, quick, and precise. In most cases, sensor materials that are mobile are not that precise and the devices cannot measure the VOC concentration in air unless the type of VOC is not manually typed in. The most precise methods are immobile like gas chromatography. Gas chromatography can be used for VOC vapours as well as liquids. This method is very precise, but usually there cannot be real time detection since the air sample needs to be collected and transported to the gas chromatograph in order to perform the analysis.

Very promising materials for precise and selective VOC detection are conductive polymer composites (CPC) with nanoparticles. Materials of this type in comparison to metal oxide sensors do not require high temperatures, because they work in room temperature. With CPCs it is possible to achieve a wide detection range. It can be done by choosing an adequate polymer matrix and conductive nanofiller. It is also important to acquire VOC vapour selectivity and a comparatively quick way to evaluate this selectivity.

In this Doctoral Thesis polymer-nanostructured carbon composite (P-NCC) is developed for VOC and fuel vapour detection. Various sample preparation methods, temperature influence and selectivity have been evaluated, as well as its influence on P-NCC VOC vapour sensing effect.

## Aim

The aim of the Thesis is to develop P-NCC for VOC and fuel vapour detection as well as to evaluate the matrix material and conductive nanofiller influence on the VOC vapour sensing effect and to evaluate temperature influence on VOC and fuel sensing effect.

## Tasks

1. To develop P-NCC.
2. To determine electro conductive filler influence on VOC vapour sensing effect (including hybrid composites).
3. To evaluate composite layer thickness influence on VOC vapour sensing abilities.
4. To evaluate spin coating rotation speed influence on sensing abilities (if spin coating is used for sample preparation).
5. To determine substrate influence on VOC vapour sensing effect.



6. To evaluate the degree of orientation (anisotropy) using DC and AC voltage, as well as to determine anisotropy influence on VOC vapour sensing effect.
7. To determine temperature influence on VOC vapour sensing abilities.
8. To test P-NCC sensing abilities of fuel vapour and to analyse the results.
9. To use principal component analysis (PCA) in order to determine VOC vapour selectivity.

#### **Scientific novelty**

- Using PCA it is demonstrated that P-NCC can differentiate various VOC vapours irrespective of vapour concentration.
- With changes in the main content of diesel fuel P-NCC shows different sensing effect allowing the detection of differing sensing effects in diesel fuels with different chemical content.

#### **Practical significance**

New P-NCC has been developed that could be used in manufacturing. This P-NCC shows high VOC vapour sensing effect and selectivity. The developed composite can be used for further research with the goal of using it in fuel vapour quality control.

#### **Composition and scope of work**

The Doctoral Thesis is written in Latvian e, it contains Introduction, 3 main chapters, Conclusions, list of literature, 3 annexes, and 65 figures. The Thesis in total has 100 pages and there are references to 151 literature source.

#### **Approbation of work and publications**

The results of the Doctoral Thesis have been published in six journal articles and in full text conference proceedings. Four of the articles have been indexed in SCOPUS or Web of Science data bases. The results of the Doctoral Thesis have been presented in 24 local and international conferences.

## THESES

1. Of all ethylene-vinyl acetate and various carbon allotropic composites, EVA-CB (ethylene vinyl acetate and nanostructured carbon black composite) exhibits the greatest change in relative electrical resistance, due to greater mobility of carbon black and a more uniform dispersion in matrix compared to carbon nanotubes.
2. Carbon black degree of dispersion and arrangement in polymer matrix noticeably influence PNCC sensing effect, which is proved by using various manufacturing methods.
3. EVA-CB shows different sensing effect on various volatile organic compound vapours. Processing sensing effect data with principal component analysis it is possible to evaluate EVA-CB sensing effect selectivity.
4. Compared to the results of gas chromatography, it has been determined that the ethylene vinyl acetate and nanostructured carbon black composite sensor experimental setup is able to distinguish between different diesel vapours depending on their chemical composition.

## CONTENT OF THESIS

### Literature review

Literature review mainly analyses the possibilities of detecting VOC vapour and discusses the mechanisms of known sensors. At the beginning of the literature review, the hazards of VOCs and their vapours are assessed, including the current air quality monitoring measures and specified limits. Even a mundane substance such as gasoline or diesel fuel can prove to be harmful to health and can even endanger life. Further, VOC sensors are discussed both experimental and commercially available with emphasis on conductive polymer composites (CPC), which can be used as sensors for detecting fuels and other VOC fumes. CPC sensor material resistivity in VOC vapours changes based on the transient tunnel effect, which is a quantum physics phenomenon [6]–[11]. Various materials can be used as matrices and fillers in polymers such as PEO (polyethylene oxide), EVA (ethylene vinyl acetate copolymer), PCL (polycaprolactam), EC (ethyl cellulose), PVAc (polyvinyl acetate), and also complicated copolymers such as poly (vinyl butyral)-co-vinyl alcohol-co-vinyl acetate [12], [13]. It is also possible to use electrically conductive polymers such as PVP (polyvinylpyrrolidone) [14], [15]. Carbon particles in various allotropic forms are popular as fillers. The literature review describes different types and techniques of composite manufacturing and their impact on sensitivity of the VOC vapour. The theoretical description of CPC sensor effect and the theory of sensory effects developed on the basis of percolation theory and tunnelling are also given. I. Balberg made an important contribution to this explanation [5], [16], finding that there is a sufficiently thin layer (less than 1.2 nm) between the two adjacent particles (including aggregates and agglomerates) in which the tunnelling currents can exist. Maris Knite conducted similar experiments [1], [2], where the results indicate that the model of tunnelling currents can describe small deformations of the composite ( $\Delta l/l_0 < 0,1$ ). However, in case of a larger deformation the quantity of electrical channels reduces because of a turn off of tunnelling currents. Based on this theory, Knite et al. [2] researched and theoretically described the chemical sensory effect caused by the diffusion of VOC molecules in the test sample. The relative electrical resistance change with time is explained by G. Lee and his colleagues in their article on graphene chemical sensors [17]. It is suggested there that the diffusion of VOC molecules in the test sample can be described by two exponential equations. This agrees with G. Sakale's dissertation [18] on the description of the relaxation time with a sum of two exponents. Both authors point to the fact that vapour molecules desorb both from the top layers (which happens many times faster) and from deeper layers (which takes place over a longer period of time).

The last chapter in the literature review is dedicated to fuel characterization and a review of fuel detectors. As previously mentioned, commercial vapour sensors are unable to detect VOCs rapidly, accurately, inexpensively, and with mobility. The same applies to fuel vapours.

From the literature review, it can be concluded that the polymer and electro conductive filler composite development requires taking into account the effect of the filler on sensitivity and selectivity. One of the tasks is to investigate the effect of the composite film application method

and of substrate selection on the sensitivity to VOC vapour. The possibilities of applying the sensor sensitivity model offered by G. Lee will also be tested for the sensor samples made for the Doctoral Thesis. The experimental part describes the development and investigation of P-NCC arranged in an external electric field, the study of the sensitivity to fuel vapour, and the vapour selectivity of the VOC.

### Methodological part

In this work, EVA (Sigma Aldrich) is used as the matrix material for which the ethylene part is nonpolar and vinyl acetate is polar. For this reason, EVA-based CPCs are capable of detecting both polar and non-polar VOCs. On the basis of a preliminary study, an EVA of 40 % vinyl acetate (VA) was selected.

Using EVA copolymer, three different compositions were created, using graphitized carbon black nanoparticles and short multi walled carbon nanotubes as electro conductive fillers. Both of these nano-fillers were used for the third composition.

Graphitized carbon black nanoparticles (CB) PRINTEX XE-2 with an average particle size of 30 nm were used as an electro conductive filler for the first composite material (EVA-CB). Particle surface area is 950 m<sup>2</sup> / g and DBP (dibutylphthalate) absorption is 380 ml / 100 g. PRINTEX XE-2 is a high-conductivity carbon, which is widely used for electro-conductive elastomers.

Short multi-walled carbon nanotubes (CNTs) purchased from CheapTubes were used as a conductive filler for the creation of the second type of composite material (EVA-CNT); the outer diameter of nanotubes is 50–80 nm, but the internal diameter is 5–15 nm, the length is 0.5–2 μm. The CNT's specific surface area is 40 m<sup>2</sup>/g with an electrical conductivity of 100 S/m.

In the development of the third composite material both of the above-mentioned fillers (CB and CNT) dispersed in the ethylene-vinyl acetate copolymer matrix was used, thus forming a nanostructured hybrid composite.

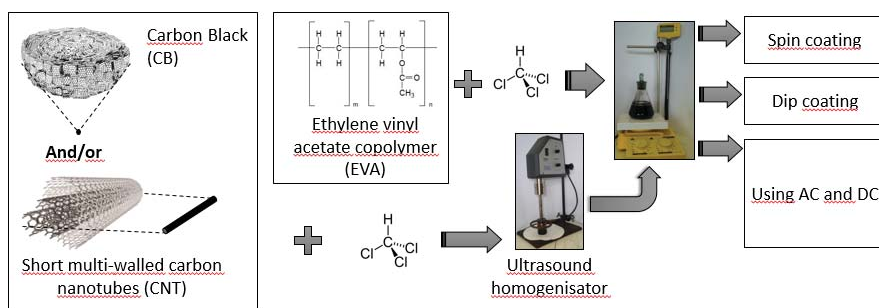


Fig. 1. EVA-CB, EVA-CNT and EVA-CB-CNT preparation scheme. Figures are taken from [19], [20].

All three composites were obtained following the scheme shown in Fig. 1. The mixing of the electro conductive filler with chloroform was carried out using an ultrasonic homogenizer after which the mixture was added to a polymeric solution in chloroform mixed with a magnetic stirrer for 2 hours. The final mixture was mixed on a magnetic stirrer for another two hours. Subsequently, the mixture was applied to the substrate and the chloroform evaporated.

The methodological part describes the details of the substrates used in the work and the equipment used in both the composite manufacturing process and the research process.

### Experimental part

In the first section of the experimental part – "Characterization of polymer – nanostructured carbon composite" – the location of nanoparticles in the polymer matrix has been described and studied, as well as the percolation threshold and critical concentration has been determined. According to the theory of statistical percolation, the electrical conductivity of a composite is described by the equation

$$\sigma = \sigma_o |\varphi - \varphi_c|^t \quad (1.1)$$

where

$\sigma_o$  – conductivity of electro conductive phase;

$\varphi_c$  – critical concentration of composite;

$\varphi$  – fraction of electro conductive phase volume;

t – critical index, which describes peculiarities of the electro conductive network [21].

The scaling law of statistical percolation calls for the logarithmation of Equation (1.1) and for the search for the  $\varphi_c$  value until the obtained data is best described by a linear function. The optimal fit of experimental data with linear function is considered to be the case when the highest value of  $R^2$  is achieved. Figure 2 shows the percolation curves that characterize the electrical conductivity of all composites. The critical concentration is 3 phr for EVA-CB composites and 13 phr for EVA-CNT. The critical concentrations of percolation were obtained and described already within the framework of the Master Thesis. With the used experimental equipment (upper resistivity limit 100 M $\Omega$ ) the closest measurable composition for EVA-CB is with 7.75 phr, while for EVA-CNT it is a composite of 30 phr, which are then used in future studies.

Second section of the experimental part – "Polymer-nanostructured carbon composite sensing effect" – is divided into several sub-chapters that describe the sensory effect, its dependence on the materials used, the sensitivity of different VOCs and their selectivity, and also a research on the detection of fuel vapour in air. The first subsection of this section describes the basic principles of the sensory effect and the fitting of experimental data with theoretical formulas. The sensory effect studied in this Thesis consists of three stages: the first – when the sample is in a neutral environment, the second – when it is exposed to the VOC's vapour effects (for a fixed period), and the last one – when the sample is again in a neutral environment to relax.

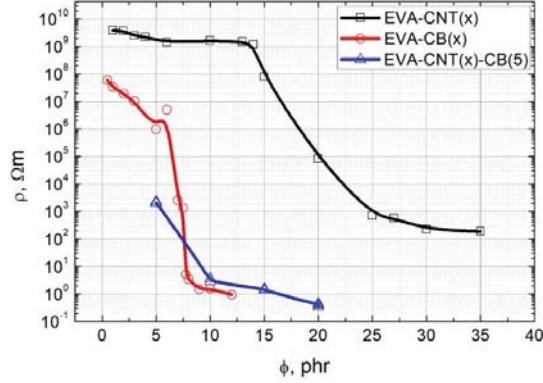


Fig. 2. EVA-CB, EVA-CNT and EVA-CB-CNT percolation thresholds.

G. Lee [17] with colleagues suggest to describe the stage at which the sample is exposed to the influence of VOC vapour by the following formula:

$$(\text{sensitivity}) = A_f \left( 1 - e^{-\frac{t-t_0}{\tau_f}} \right) + A_s \left( 1 - e^{-\frac{t-t_0}{\tau_s}} \right) \quad (1.2)$$

where  $A$  is amplitude that describes the reaction;  $t_0$  is moment of time, when the sample is in VOC vapours of given concentration;  $\tau$  is reaction time constant.

The stage in which VOC vapour is supplied can be divided into two sub-stages: the fast sub-stage (in Formula (1.2) with index  $f$ ) and the slow reaction sub-stage (with index  $s$ ). The time interval when the vapour molecules adsorb onto the surface and diffuse into the upper layers of the sample is considered the fast reaction sub-stage, but when the vapour molecules are diffusing in the deeper layers of the sample – the slow reaction sub-stage. G. Sakale came to a similar conclusion in her Doctoral Thesis [18] and in a 2010 article [22] studying the relationships in sensor relaxation. She proposed to describe the obtained electrical relaxation data with the equation

$$\frac{\Delta R}{R_{o(t)}} = \frac{\Delta R}{R_{o(\infty)}} + A \cdot e^{-\frac{t}{\tau}} \quad (1.3)$$

where  $\frac{\Delta R}{R_{o(t)}}$  is relative electrical resistance change at time  $t$  (in this work it is called sensing effect or sensory effect, but in G. Lee work it is called sensitivity);  $\frac{\Delta R}{R_{o(\infty)}}$  is relative electrical resistance change in time  $t$ , when  $t$  tends to  $\infty$ ;  $\tau$  is relaxation time constant; and  $A$  is amplitude of the reaction describing parameter.

It should be noted that the two authors incorrectly define the sensitivity of the sensors as there are no vapour masses or concentrations in the formulas that cause a change in relative resistance. The equation may also have two exponents depending on whether or not the vapour

molecules were diffusing in the top layers or deep in the test sample during the reception of the sensory effect. If the VOC molecules also travel to the deepest layers of the sample, then the relaxation process is a two-exponential process, as well as a vapour diffusion process. This explanation can be supplemented by mass changes.

Figures 3 and 4 show the fitting of experimentally obtained data with the above formulas using two exponentials.

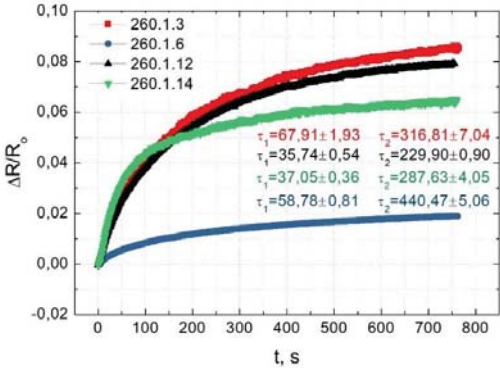


Fig. 3. The 2nd phase of the sensing effect described by formula (1.2).

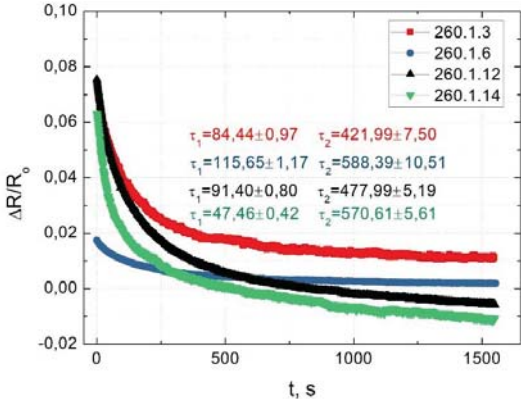


Fig. 4. The 3rd phase of the sensing effect described by formula (1.3).

The next section of the Doctoral Thesis describes the creation of composites of different compositions using as a filler either CB or CNT, or a mixture of both fillers CNT and CB, thus creating hybrid composites. In all composites, EVA was used as a matrix material. Composites composed of CNT and CB were already studied in the Bachelor and Master Theses therefore in this chapter hybrid composites and their operation in comparison with pre-made composites were discussed more widely.

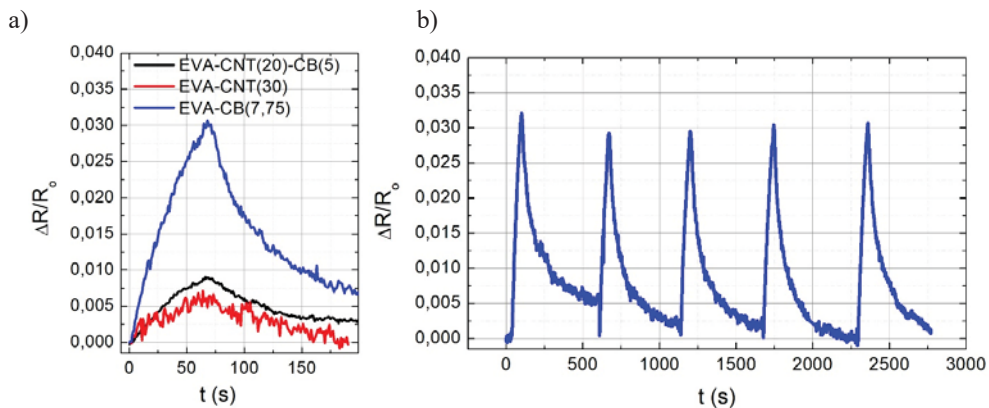


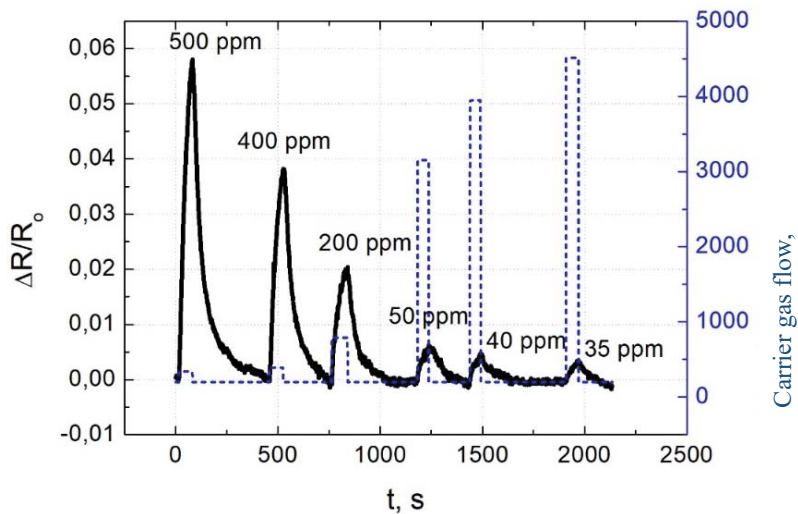
Fig. 5. EVA-CB, EVA-CNT and EVA-CB-CNT relative electrical resistance change in toluene (400 ppm) vapours (a) and EVA-CB relative electrical resistance change in toluene (400 ppm) vapours (b). Exposure time in vapours 60 seconds.

Figure 5 clearly shows that the creation of hybrid composites did not result in a greater change in the relative electrical resistance than in the composites containing CB nanoparticles. The study of hybrid composites is difficult due to their high initial resistance. For all hybrid composites, the starting resistance was from 0.20 M $\Omega$  to 55 M $\Omega$ . In a further study the EVA-CB composite with 7.75 phr CB was chosen, which also shows the largest change in the measurable relative electrical resistance.

Already in the Bachelor Thesis it was discovered that EVA-CB exhibits a greater change in the relative electrical resistance in non-polar VOC vapour and a lower sensing effect in polar VOC vapour. In this work, four of the most popular substances – benzene, toluene, ethylbenzene and m-xylene – abbreviated as BTEX, were further studied. BTEX is frequently occurring in fuels and their vapours. It should also be mentioned that benzene is harmful to health and is restricted to 1 % in fuel. The sensor effect in the vapour of these four substances is shown in Figs. 6 and 7 where the sensor effects of benzene and toluene vapour have been measured with the Kin-TEX FlexStream automated gas generation device, therefore the carrier gas flow measured in standard cubic centimetres (sccm) is also indicated. Accordingly, with increasing carrier gas flow the concentration of VOC vapour in the sample measurement chamber decreases, thus, it is possible to obtain different VOC vapour concentrations.



a) Toluene



b) Benzene

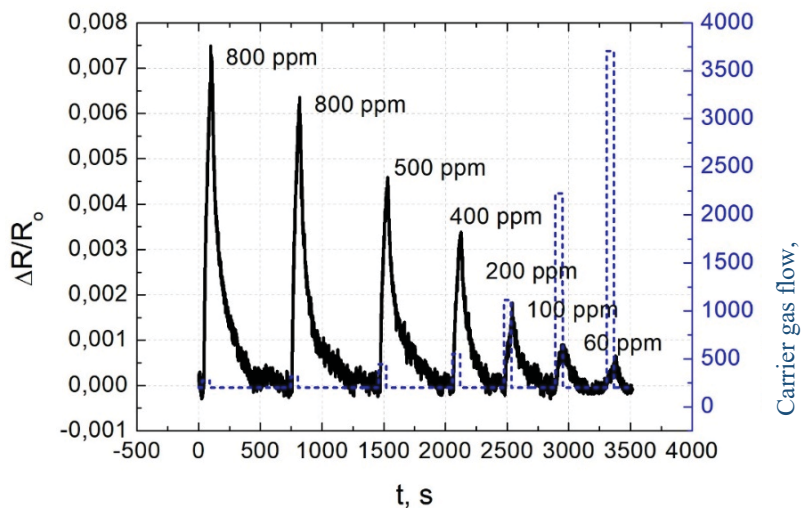
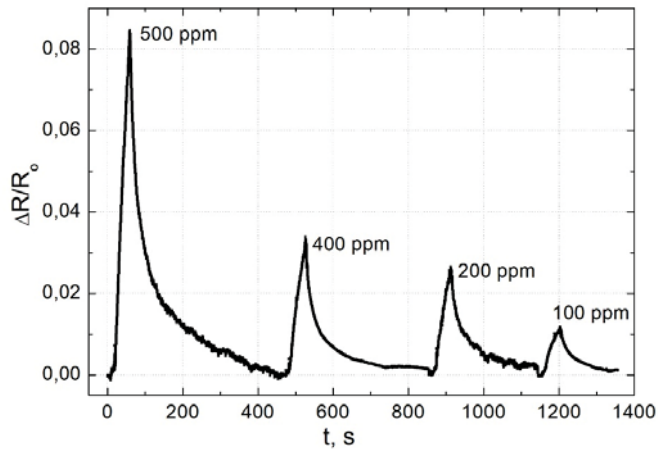


Fig 6. EVA-CB (7.75 phr) relative electrical resistance change (60 seconds) versus time (a) in toluene and (b) benzene vapours for various vapour concentrations.

a) Ethylbenzene



b) m-xylene

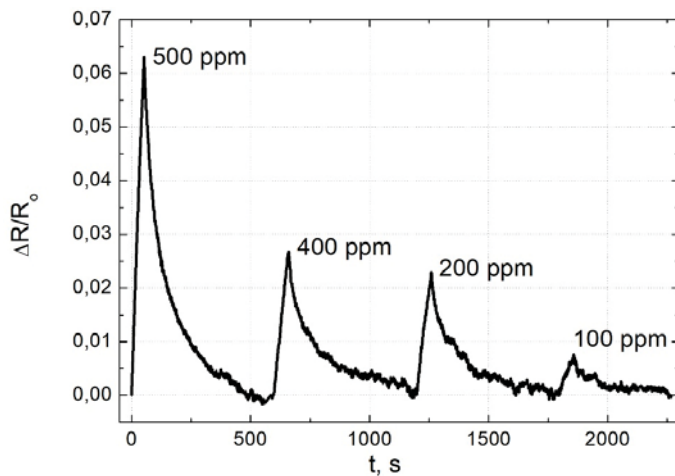


Fig. 7. EVA-CB (7.75 phr) relative electrical resistance change (60 seconds) versus time (a) ethylbenzene and (b) m-xylene vapours for various vapour concentrations.

The results shown in Fig. 7 were obtained without gas generation equipment. A certain VOC vapour concentration was obtained by evaporating a specific amount of substance in a sealed container (desiccator) to obtain a specific concentration. Figures 6 and 7 show that the change in the relative electrical resistance of BTEX vapours increases with increasing concentrations. When comparing the maximum electrical resistance value at each concentration

for all BTEX vapours, the relationship shown in Fig. 8 indicates that with increasing BTEX vapour concentration the EVA-CB sensory effect is linearly increasing. Similarly, for all tested VOC vapour sensors repeatability tests have been carried out where they have been found to be repeatable, that is to say, their relative electrical resistance changes are the same for even several measurements in a row.

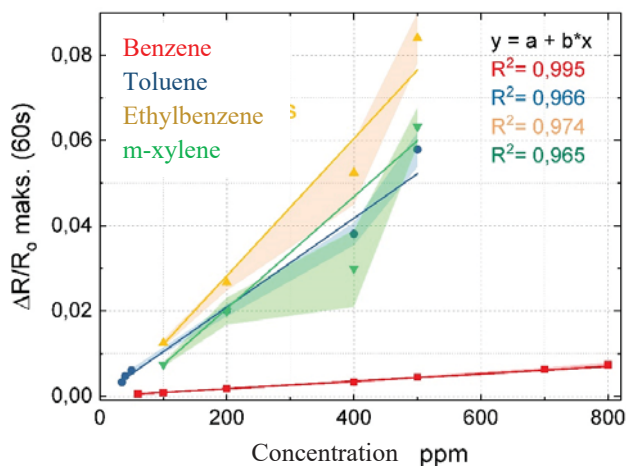


Fig. 8. EVA-CB (7.75 phr) maximum relative electrical resistance value after 60 seconds versus vapour concentration.

In the Doctoral Thesis the smallest distinguishable concentration is determined by performing sensory-effect measurements, where analysing the obtained sensing effects in toluene vapours it is concluded that it is easy to distinguish 15 ppm concentration difference, for example, 35 and 50 ppm. The data of all measured sensory effects were also compiled using the principal component analysis (PCA). The PCA is essentially a data-reduction technique where the obtained data can be reduced to up to two main components. The first principal component is the combination of linear variables that lists as many total discrepancies as possible. The second principal component is the combination of linear variables and has the maximum mismatch between all combinations of this type [23]. Figure 9 shows PCA BTEX vapour sensor effects at different concentrations. Data processing with this method allows us to distinguish the vapour of different substances from each other, thus allowing to identify the vapour of the investigated substance.

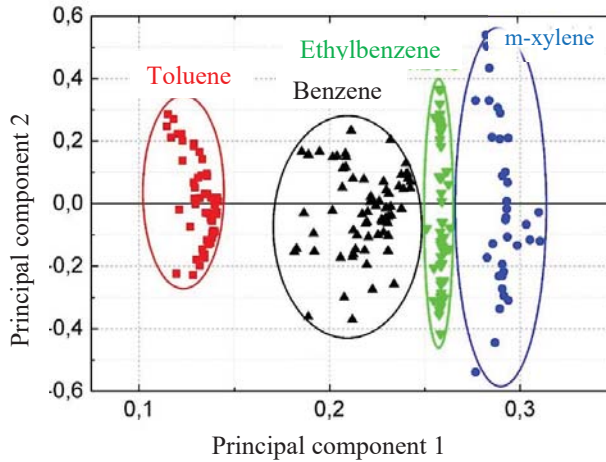


Fig. 9. EVA-CB (7.75 phr) sensing effect measurements in various VOC vapours at different concentrations processed with PCA.

The next section – "Detection of fuel vapour" – describes the application of the samples made in the detection of fuel vapour. Already in the Master Thesis, it was discovered that the EVA-CB composite can determine the changes in the petrol base content. To continue this study, additional benzene and toluene were added to petrol with the aim of ascertaining how it would affect the sensitivity to the VOC vapour. The experiments showed that petrol with the addition of toluene reduced the sensitivity to the VOC vapour, the same was observed in the case of the addition of benzene. These results indicate that adding of auxiliary toluene or benzene to the fuel cannot improve the sensitivity to the VOC vapour.

Seven diesel grades of the same brand from different gas stations were taken for further fuel research. As shown in Fig. 10, Sample No. 6 shows the greatest sensory effect, and the lowest sensory effect is shown in Sample No. 7, which is pure biodiesel. It should also be noted that Sample No. 9 is diesel fuel with 5 % biodiesel fuel. The remaining samples are of the same grade as diesel.

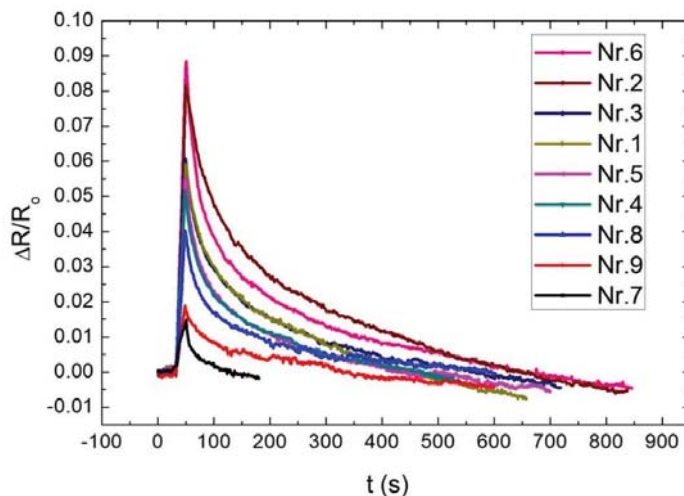


Fig. 10. EVA-CB (7.75 phr) relative electrical resistance change in diesel fuel vapours (15 sec.; 12.172 ml/l), using various diesel fuel samples.

To explain the results, gas chromatograms were acquired at the State Forensic Science Bureau using the Agilent GC / MS system, which includes Agilent Technologies 6890N Network GC System and Agilent Technologies 5975B inert XL EI / CI MSD. Helium was used as carrier gas, starting temperature was 40 °C and end temperature was 290 °C, heating rate was 10 °C/min. Figure 11 shows the gas chromatogram for diesel fuel containing 5 % biodiesel and the chromatograms of the remaining diesel fuel samples are shown in Annex 3 of the Doctoral Thesis.

After evaluating the results of the obtained chromatograms, it was found that the decrease of the amount of long hydrocarbon molecules and the increase of the amount of short molecules in diesel fuel results in an increase in the relative electrical resistance of the EVA-CB in diesel fuel vapours. From this, it can be concluded that the sensitivity to the VOC vapours is influenced by the change in the main content of diesel fuel, in this case, the length of hydrocarbon chains. However, it should be noted that in comparison to changes in the composition of gasoline that were discussed in the Master Thesis diesel contains a lot of small amounts of substances. In addition, these substances can vary widely between the samples of diesel fuel of the same grade and brand, which makes it difficult to explain the sensitivity of diesel fuel and to justify the sensory changes.

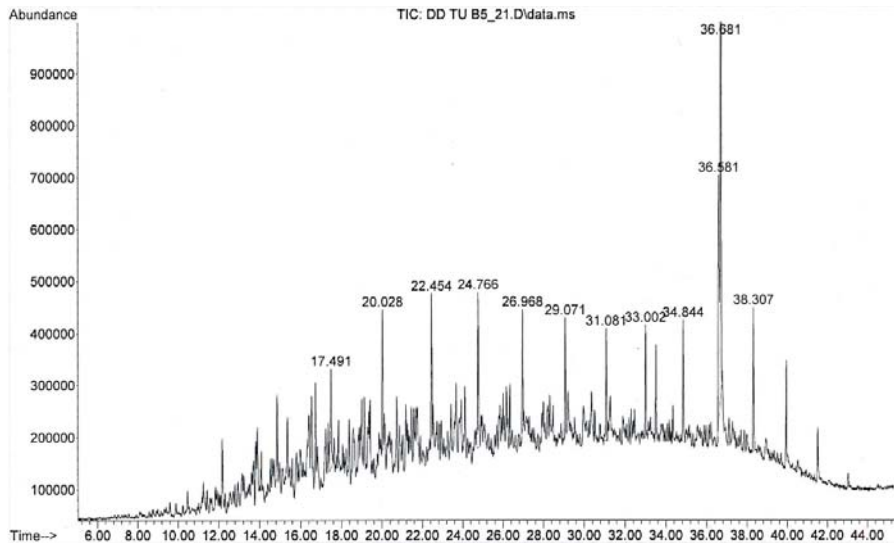


Fig. 11. Gas chromatogram for diesel fuel with 5 % biodiesel fuel additive.

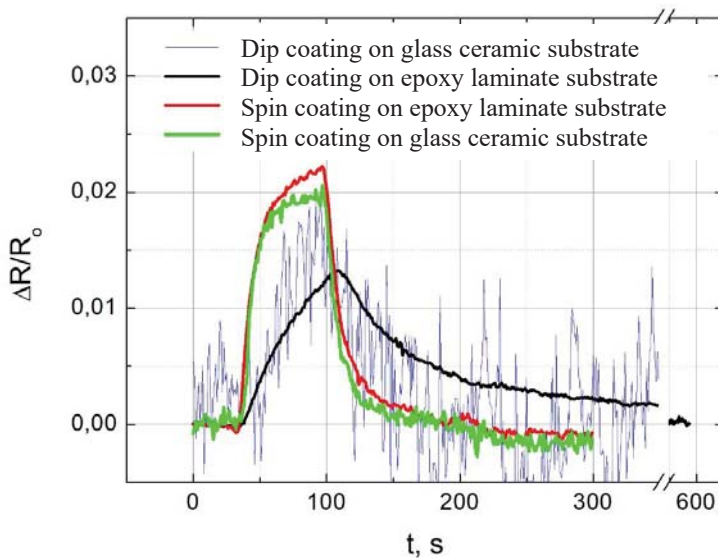


Fig. 12. EVA-CB (7.75 phr) relative electrical resistance change (60 seconds) versus time in 500 ppm toluene vapours.

The Section "Polymer – Nanostructured Carbon Composite Sensor Affecting Factors" is dedicated to explaining sensory effect changes that occur due to changing the production methods, or materials. Previous studies have already found that sensory effects are influenced by both the choice of composite components and choice of component concentrations. It was

also found that the thickness of the composite layer affects the sensory effect. Different methods of application of a composite on a substrate were studied and compared. Figure 12 shows the variation in the relative electrical resistance for the various EVA-CB (7.75 phr) samples. The greatest relative electrical resistance change is observed for the samples made by using spin coating. Significantly lower relative electrical resistance is observed for the specimens obtained by dip coating. It was also observed that various substrate and electrode materials influence relative electrical resistance change.

Sensory effect repeatability measurements were performed on all samples. For the samples produced by dip coating on an epoxy laminate base with copper electrodes the first one to three measurements are required to stabilize the sensor, but when spin coating is used then after fabrication and before further measurements can be performed, three to five measurements are required to stabilize the sensor effect. It has been found that the samples fabricated by spin coating are considerably thinner than those made with dip coating. If the dip coating is performed manually (without specialized equipment), the thickness of the layer may be even above 100  $\mu\text{m}$ . In both cases, the thickness of the composite layer is also affected by the amount of solvent used during preparation or, in other words, the viscosity of the composite solution.

For a more detailed investigation why the sensor effect differs for the samples made with different manufacturing methods, the surface relief mapping with AFM (atomic force microscope) was applied to pure substrate and the substrate coated composite, which is shown in Fig. 13. AFM images were taken in the Institute of Technical Physics of RTU Faculty of Materials Science and Applied Chemistry. The epoxy laminate substrate is much rougher than the substrate of the glass ceramic, which means that the composite solution applied to the base of the epoxy laminate is tighter with the curvature, increasing the area of the specific surface. Using a glass ceramic substrate (dip coating), a much thicker sample is obtained, whose adhesion to the glass ceramic substrate is worse. The glass ceramic substrate is made with silver electrodes, so the electrodes can have poor adhesion to the composite, which explains the unstable sensor effect shown in Fig. 12.

The produced composite materials were also mapped to the composite surface of the electrically conductive filler channels with the AFM conductive probe as shown in Fig. 14. In this figure four electro conductive channel nano-mapping pictures are shown, where black parts are nonconductive polymer and white parts are electro conductive channels made from conductive carbon black. Also, along with AFM images information was obtained on the distribution of electrically conducting channels using modified A. Berzina's method for characterizing the distribution of these channels [24].



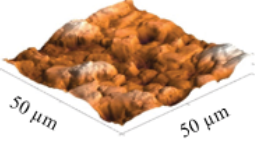
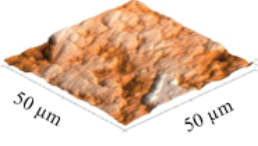
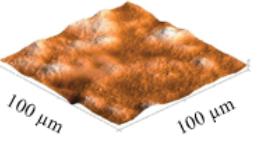
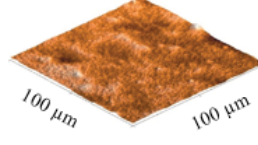
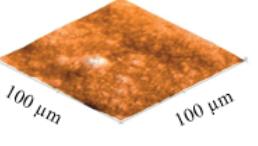
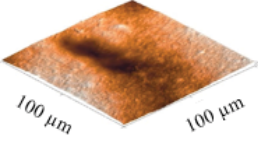
	Epoxy laminate substrate	Glass ceramic substrate
Surface of substrate	 6,6 $\mu\text{m}$	 3,6 $\mu\text{m}$
Spin coating	 6,7 $\mu\text{m}$	 3,3 $\mu\text{m}$
Dip coating	 2,4 $\mu\text{m}$	 3,0 $\mu\text{m}$

Fig. 13. EVA-CB (7.75 phr) the surface relief nano-mapping.

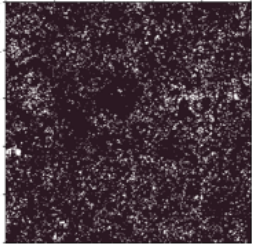
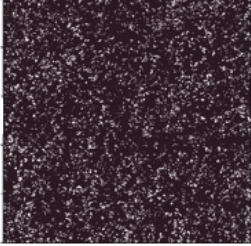
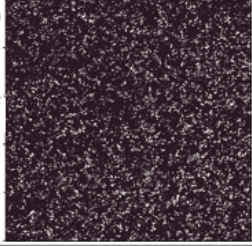
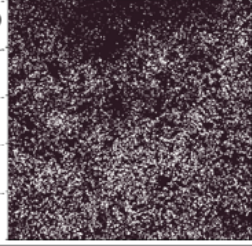
	Epoxy laminate substrate	Glass ceramic substrate
Spin coating	 0 $\mu\text{m}$ 20 40 60 80	 0 $\mu\text{m}$ 20 40 60 80
Dip coating	 0 $\mu\text{m}$ 20 40 60 80	 0 $\mu\text{m}$ 20 40 60 80

Fig. 14. EVA-CB (7.75 phr) electro conductive channel nano-mapping for various samples.



In the application of composite solution using the spin coating the rotation speed of the device should also be taken into account. As shown in Fig. 15, producing of different EVA-CB composites with different rotational speeds can produce a different sensory effect. Reducing the rotational speed from (in this case the maximum) 4500 rpm (revolutions per minute) to 1000 rpm, the sensing effect increased, however, further reduction of the rotational speed leads to decrease of sensor effect. This means that, with a speed of 250 to 1000 rpm, the effect increases with increasing rotational speed based on the change in thickness. However, increasing the speed even more, the thickness of the composite layer decreases so much that during the sensor test the composite reaches the saturation (electrical resistance cannot increase further). In order to obtain the maximum change in the relative electrical resistance, an optimal (compromise) 1000 rpm rotation speed is required in the sample manufacturing process. This applies to samples where composite mixture is made with previously mentioned concentrations (to defined viscosity).

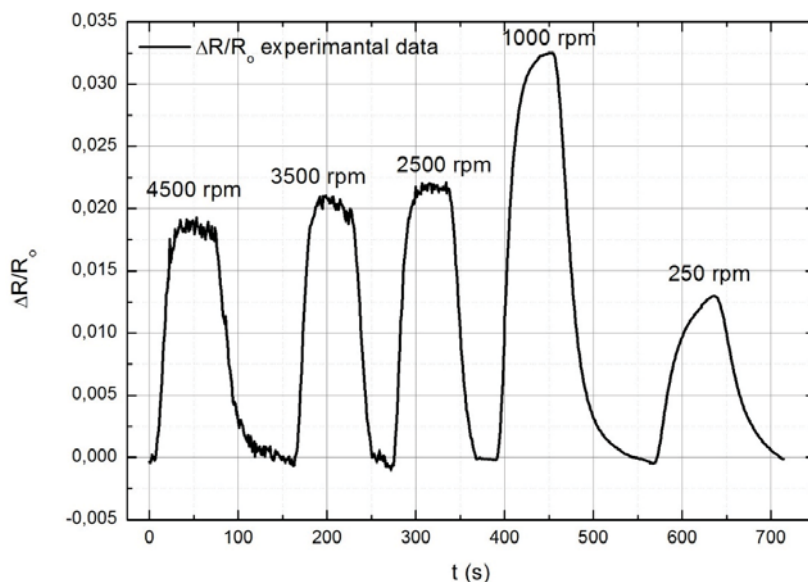


Fig. 15. EVA-CB (7.75 phr) relative electrical resistance change versus time in 500 ppm toluene vapours, using epoxy laminate substrate (60 seconds in vapours).

As already mentioned above, with increasing rotational speed the thickness of the composite layer decreases and the initial resistance of composite increases.

The produced samples were tested to determine how temperature affects EVA-CB sensory effect – the relative electrical resistance change. At first samples were tested from 35 to 45 °C in toluene vapour at 500 ppm vapour concentration (Fig. 16). Testing samples in this temperature range did not produce any sensory enhancements. The only thing that changed was the relaxation speed. This means that as the temperature rose the relative electrical resistance decreased faster. It should also be noted that these samples were made on special, heated base

plates (for more details see the methodological part of the Doctoral Thesis), which in this case affected the stability of the resistance. This could be explained by the use of pivoting electrodes, which were placed on substrates by the manufacturer and were different from the other electrodes used in the presented research.

Next, a sensory change in gasoline vapours (with octane number 95) was tested by increasing the temperature to 45 °C (Fig. 16). Here it is shown that the sensitivity is considerably higher at 35 °C, which could be explained by the peculiarities of gasoline composition. Namely, gasoline consists of different substances with different evaporation temperatures, if one (or more) of these substances evaporate at 35 °C, then the sensor effect will be considerably higher at the given temperature.

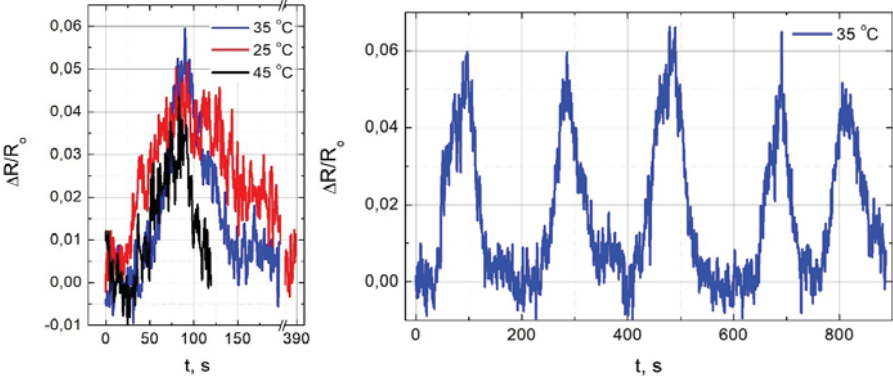


Fig. 16. EVA-CB (7.75 phr) relative electrical resistance change in toluene vapours (60 sec.; 500 ppm) at various temperatures (a) and repeatability (b).

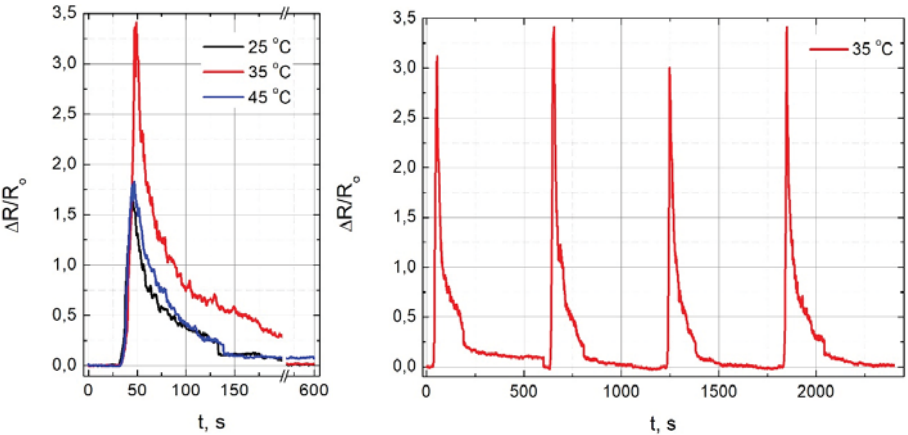


Fig. 17. EVA-CB (7.75 phr) relative electrical resistance change in saturated gasoline vapours (15 sec.) at various temperatures (a) and repeatability (b).

One of the tasks of the Thesis was to study how sensing effect changes if during sample production either a DC voltage or AC voltage is used (nanoparticle orientation and adjustment

along the electric field lines). As shown in Fig. 18, the composite, which was produced using DC, shows the sensing effect if the conductivity is measured parallel to the applied direction of the electric field. Using an AC, a much larger change in relative electrical resistance is obtained, measured parallel and perpendicular to the direction of the field. However, it should be emphasized that the use of AC also increases the relaxation time of the sample.

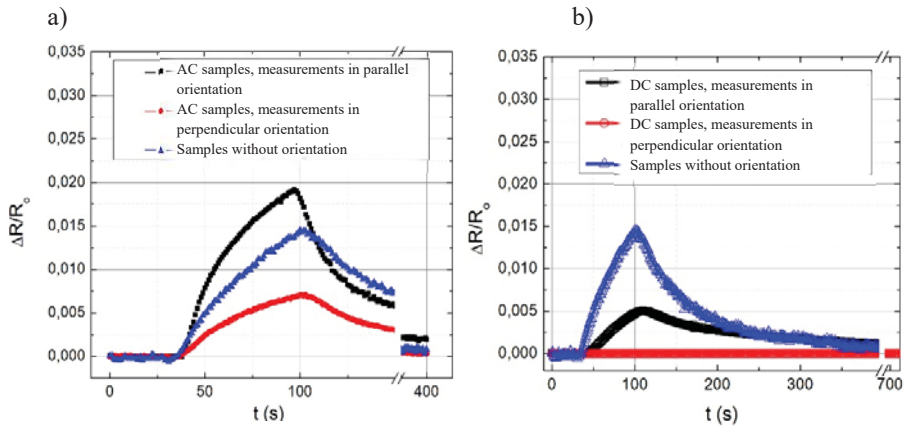


Fig. 18. EVA-CB relative electrical resistance change versus time for samples, which are produced using (a) AC voltage ( $E=60$  V/cm) and (b) DC voltage ( $E=200$  V/cm). 500 ppm toluene, 60 seconds in vapours.

Table 1 shows the electrical conductivity and the ratio (anisotropy<sup>1</sup>) of samples made using AC or DC voltage where L.1 to L.4 are the samples made using DC voltage and M.1 to M.4 are examples made with AC voltage. It can be seen here that the average anisotropy is very similar in the cases of both AC and DC, however, looking at the sensor effects there is a drastic change. An alternating current sample shows the greatest sensory effect if it was measured in parallel, which was also expected by analysing the data in the literature. However, in the case of DC this relationship was not fulfilled, the unoriented sample here showed the greatest sensory effect. This could be explained by the fact that, in the case of DC, higher voltage ( $E = 200$  V / cm) was needed to produce the arrangement of nanoparticles, which in turn caused the material to warm up and, accordingly, the thermal motion of the matrix molecules prevented the nanoparticles from being adjusted.

<sup>1</sup> Anisotropy is the ratio of electrical conductivity, where the conductance measured along the direction of orientation is divided by the conductivity measured perpendicular to the orientation direction.

Table 1

## Sample Conductivity and Anisotropy

Sample No.	Specific resistance		Conductivity $\sigma$ , S/m		<b>Anisotropy</b>	Average anisotropy
	Parallel	Perpendicular	Parallel	Perpendicular		
L.1	10.1717	33.2765	0.0983	0.0301	<b>3.2715</b>	3.0083
L.2	6.1657	25.6446	0.1622	0.0390	<b>4.1592</b>	
L.3	7.6086	22.6370	0.1314	0.0442	<b>2.9752</b>	
L.4	10.7289	17.4584	0.0932	0.0573	<b>1.6272</b>	
M.1	366.1670	1027.0197	0.0027	0.0010	<b>2.8048</b>	3.3896
M.2	204.5710	943.9656	0.0049	0.0011	<b>4.6144</b>	
M.3	677.8930	2190.6371	0.0015	0.0005	<b>3.2315</b>	
M.4	506.4890	1472.6952	0.0020	0.0007	<b>2.9077</b>	

## SUMMARY OF THE DOCTORAL THESIS CONCLUSIONS

1. As part of the Doctoral Thesis three composites of different compositions were made using two fillers: carbon black and carbon nanotubes. Of the three composites the greatest change in relative electrical resistance was shown by the ethylene vinyl acetate nanostructured carbon black composite which was then used in further studies.
2. The sensory effect of ethylene vinyl acetate nanostructured carbon black composite is linearly increasing as the BTEX vapour concentration is increased. The relaxation time of the composite increases as well when the BTEX vapour concentration is increased.
3. The EVA-CB (7.75 phr) sensory effect is repeatable and the relative electrical resistance change remains unchanged even if the previous measurement has not been completed (composite relaxation has not been achieved).
4. Using PCA it is possible to distinguish vapours within the range of 35 to 800 ppm of different substances regardless of their concentration in air.
5. EVA-CB (7.75 phr) has a reduced sensitivity to petrol (octane number 95) with additional benzene or toluene added.
6. Gas chromatography shows that EVA-CB (7.75 phr) is capable of detecting changes in the main content of diesel fuel.
7. At 35 °C temperature the EVA-CB (7.75 phr) sensory effect in gasoline vapour is rapidly increasing due to increased evaporation of individual gasoline components. In contrast, the sensitivity of EVA-CB (7.75 phr) in toluene stays unchanged from 25 to 45°C.
8. Using composite application with spin coating it is possible to obtain a higher relative electrical resistance change with a maximum that depends on the rotation speed. EVA-CB (7.75 phr) of the highest relative electrical resistance change can be achieved at a rotational speed of 1000 rpm.
9. Using DC or AC during composite preparation, it is possible to obtain a composite with electrical conductivity anisotropy. The anisotropy of the sensor effect (relative electrical resistance change) was also found. In the case of an alternating voltage a composite with a higher sensitivity was obtained compared to the samples obtained with dip coating.
10. Comparing all of the produced samples the highest relative electrical resistivity change is observed in samples that were produced using a spin coating method with a rotation speed of 1000 rpm.

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## APPROBATION

### Projects and programmes:

1. RTU Doctoral Research Grant (1 December 2015 to 30 November of 2016).
2. National Research Programme IMIS2 – Multifunctional Materials and Composites, Photonics and Nanotechnologies. Project Nr. 3: Nanocomposite materials.
3. ESF project C1756: Development of innovative functional materials and nanomaterials for use in environmental technologies.
4. National programme V7632.2 "Development of innovative multifunctional materials, signal processing and informatics technologies for competitive science-intensive products." Project No 3 "Polymer composites containing nanostructured modifiers for application in intelligent materials and devices": "Physically active nanostructured polymer composites and development of their technologies".

### Results published in journal articles:

1. G. Sakale, M. Knite, V. Teteris, V. Tupureina, S. Stepina, E. Liepa. The investigation of sensing mechanism of ethanol vapour in polymer-nanostructured carbon composite. *Central European Journal of Physics*, 2011, Vol. 9, No. 2, 307–312. (SCOPUS; Web of Science).
2. Stepina, S., Sakale, G., Knite, M.. Ethylene vinylacetate copolymer and nanographite composite as chemical vapour sensor, *IOP Conference Series: Materials Science and Engineering*, 2013, 49, doi:10.1088/1757-899X/49/1/012017 (SCOPUS; Web of Science).
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### **Conference thesis:**

1. S. Stepina, E. Liepa, G. Šakale, M. Knite, V. Tupureina. Etanola tvaiku sensormateriāla izstrāde uz polimēra nanostrukturēta oglekļa kompozīta bāzes. 51. RTU studentu zinātniskās un tehniskās konferences materiālos, Rīga, Latvija, Aprīlis, 2010, 189. lpp.
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