

RIGA TECHNICAL UNIVERSITY

Faculty of Material Science and Applied Chemistry

Institute of Technical Physics

Gita SAKALE

Doctoral student of the study program “Material science”

**ELABORATION AND INVESTIGATION OF POLYMER-
NANOSTRUCTURED CARBON COMPOSITES FOR
APPLICATION AS CHEMICAL SENSORS**

Summary of doctoral thesis

Scientific supervisor
Dr. habil. phys., professor
Maris Knite

Riga 2012

UDK 678.5.067(043.2)

Ša 250 p

G. Sakale. Elaboration and investigation of polymer-nanostructured carbon composites for application as chemical sensors. Summary of doctoral thesis - Riga: Institute of Technical physics, 2012. - 35 pages.

Issued according to decision of RTU Institute of Technical Physics at 9 February 2012 protocol No.2

ISBN



This work has been supported by the European Social Fund within the project “Support for the implementation of doctoral studies at Riga Technical University”.

**THE DOCTORAL DISSERTATION IS PROMOTED TO BE
DEFENDED FOR THE DOCTORAL DEGREE IN SCIENCE
ENGINEERING IN RIGA TECHNICAL UNIVERSITY**

The doctoral dissertation for the doctoral degree in science engineering will be defended at 15⁰⁰ o'clock on 6th September 2012 at Riga Technical University, Faculty of Materials Science and Applied Chemistry, Riga, Azenes14/24, Room No. 272.

OFFICIAL OPONENTS

Dr.habil.sc.ing., professor, Mārtiņš Kalniņš
Riga Technical University, Institute of Polymer materials

Dr.phys., leading researcher, Jānis Kleperis
University of Latvia, Institute of Solid State Physics

Dr. of Phys. and Math. Sciences, professor, Ludmila Yu. Matzui
Kyiv National Taras Shevchenko University, Department of Physics

APPROVAL

I approve that I have elaborated the doctoral dissertation, which is submitted to be reviewed in Riga Technical University to qualify for doctoral degree in science engineering. The doctoral dissertation is not submitted anywhere else to qualify for scientific degree.

Gita Šakale(Signature)

Date:

ACKNOWLEDGEMENTS

The doctoral dissertation is a team work. I cannot imagine creation of the thesis without active involvement of colleagues and family support. Here I would like to express my gratitude to team mates.

At first I would like to express my gratitude to scientific supervisor Maris Knite for seeing in me a potential to become a scientist, who starting from bachelor studies purposely guided me to doctoral studies, brought into scientific world and gave opportunity to visit international scientific conferences in Slovakia, Switzerland, Portugal and etc. I would like to thank professor Knite for continuously raising the “lath” of tasks, which for me sometimes, starting to work on the task, seemed out of reach. However it developed my imagination and favored my development as experimentator.

I express my gratitude to the adviser of the doctoral dissertation Velta Tupureina for cheering up and wealthy humor in our scientific discussions, generous sharing of knowledge and experience, giving advices, careful reviewing of publications and the doctoral dissertation.

I express my gratitude to the adviser of the doctoral dissertation Valdis Teteris for teaching me not to be afraid of works, which are not common for ladies, like soldering. I thank him for given useful advices at the time of elaboration of experimental equipment and other technical solutions to successfully proceed with experiments as well. I express much gratitude to Valdis for reviewing the thesis.

I would like to thank my students Santa Stepina and Elina Liepa for productive and enthusiastic working in lab, doing experiments, processing and summarizing data, presenting result at international scientific conferences and Latvian Inventor Exhibition 2012.

I say thank my colleagues from the Institute of Technical Physics (Juris Z., Vija B., Kaspars O., Raimonds O., Artis L., Juris B.), who helped with advice and suggestions at the time of realizing experiments, helped to interpret results, made specific measurements, reviewed publications, expressed healthy critic to the thesis and helped to solve organizing queries.

I express my gratitude to colleagues from the Institute of Polymer materials for possibility to use the equipment and operative differential scanning calorimetry analysis making of elaborated composites.

I would like to thank to Dmitrijs Jakovļevs for obtained SEM images of composites and Einars Deksnis for the device prototype elaboration.

Finally I would like thank to my lovely family, Janis and friends, who believed in me, supported me and were with me at the time of doctoral dissertation elaboration!

Gita Š.

CONTENT

Abbreviations	6
General discription of the work.....	7
Introduction	7
Aim	7
Tasks.....	7
Scientific novelty.....	8
Practical novelty	8
Composition and volume of the thesis	8
Approbation and publications	8
THESIS	9
Content of the work	10
Review of literaty	10
Methodological part	11
Experimental part	13
Conclusions	30
References	32
List of publications	33

ABBREVIATIONS

- CB – „carbon black” carbon nanoparticles
D – diffusion coefficient
d – molecule diameter
 f_c – critical percolation concentration (percolation threshold)
HSP – Hansen solubility parameters
LMWCNT – long multi-wall carbon nanotubes
MWCNT – multi-wall carbon nanotubes
n – coefficient, which corresponds to diffusion mechanism
PEGCB – polyethylene glycol-carbon nanoparticle composite
phr – part per hundred rubber
PiCB – polyisoprene-carbon nanoparticle composite
PiCB24h – polyisoprene-carbon nanoparticle composite, CB dispersed in mixture of low viscosity, total stirring time 24h
PiCB48h – polyisoprene-carbon nanoparticle composite, CB dispersed in mixture of high viscosity, total stirring time 48h
PiCBRoll – polyisoprene-carbon nanoparticle composite, CB dispersed in polyisoprene using cold rolls.
PiGMWCNT – polyisoprene-long multi-wall carbon nanotubes composite
PiIMWCNT – polyisoprene-short multi-wall carbon nanotubes composite
PiMWCNT – polyisoprene-multi-wall carbon nanotubes composite
PiNCC – polyisoprene nanostructured carbon composite
PNCC – polymer nanostructured carbon composite
ppm – parts per million
PVAcCB – polyvinylacetate-carbon nanoparticle composite
R,m,l – 3 parameter measurement method: electrical resistance (R), mass (m) and length (l)
RED – relative energy difference
SMWCNT – short multi-wall carbon nanotubes
t – critical index of percolation, which shows how many direct electrical contacts particle has with other particles
VOC – volatile organic compounds
 V_R – electrical resistance change velocity (Ω/s)
 ε – dielectric permittivity

Example of composite abbreviation - PiCB4.424h means PiCB24h composite, which contains 4.4 parts per hundred rubber of CB.

GENERAL DISCRIPTION OF THE WORK

Introduction

Development of new sensor materials for volatile organic compound (VOC) detection is conducted because potential application of sensors is not limited only by air quality control purposes (indoors and outdoors) to avoid safety risk and prevent ecological disaster, in case of organic solvent or their mix leakage. Research results indicate that fermentation processes and bacteria growth in food and beverages is accompanied by VOC generation. Therefore, in food-processing industry production process progress and ready-made product quality can be controlled by VOC analysis (non-destructive method!). Similarly VOC control can be applied in agriculture because VOC (alcohols, aldehydes, ketones, aromatic compounds etc.) are generated while microorganisms metabolize nutrients. One of major and for today most researched sensor materials are those, which can be applied in medicine for people exhalation analysis (noninvasive method!). It is known that breath of people contain specific VOC as well. In case of certain disease VOC composition in exhalation of people changes.

Nowadays VOC analyses in these fields are done by analytical methods, for example, by gas chromatography, which is time consuming and trained people demanding method. Commercially indicative and selective sensor materials, which could detect VOC in real time of specific process, are purely available and VOC analyses are not applied.

The doctoral dissertation is devoted to investigation of conductive network of polymer-nanostructured carbon composite (PNCC) depending on used polymer matrix, electroconductive filler and composite production technology. PNCC capability to be used as electro resistive sensor material for VOC detection is evaluated and spectrum of detectable VOC is determined. PNCC sensing principle of VOC is explained and VOC diffusion process in PNCC analyzed.

Aim

Elaborate polymer-nanostructured carbon composite for VOC detection at concentrations, which are equal or below regulated VOC exposure limits in the air. Evaluate polymer matrix and electroconductive filler impact on VOC sensor effect of PNCC. Experimentally prove that VOC induced PNCC electrical resistance change mechanism is based on tunneling current decrease in thin layers of matrix between electroconductive filler aggregates.

Tasks

1. To elaborate polymer-nanostructured carbon composites and determine:
 - 1.1. percolation parameters of polyvinylacetate-nanostructured carbon composite (PVAcCB), polyethylene glycol-nanostructured carbon composite (PEGCB);

- 1.2. polyisoprene-nanostructured carbon composites (PiCB24h, PiCB48h, PiCBRoll, PiGMWCNT, PiSMWCNT) percolation parameters depending on used filler and production method;
- 1.3. VOC sensoreffect of PiCB24h, PiCB48h, PiCBRoll, PiGMWCNT, PiSMWCNT, PVAcCB and PEGCB composites.
2. To engineer the equipment for *in-situ* electrical resistance (R), mass (m) and length (l) change measurements in VOC atmosphere.
3. To perform *in-situ* R,m,l measurements:
 - 3.1. for polyisoprene-nanostructured carbon composites (PiNCC), with a purpose to find out fundamental principle of VOC sensor effect and electrical resistance change mechanism in the presence of VOC.

Scientific novelty

1. Applying originally developed research method, it is proved that PNCC VOC sensing mechanism is mainly based on filler aggregates inter distance increase caused by swelling of matrix thin layers between them. Therefore, tunneling currents decrease in thin layer of matrix and composite electrical resistance increases.
2. It is proved that several VOC induced electrical resistance change mechanisms in composite exist, which are based on: tunneling current decrease, destruction of conductive network and VOC electrical conductivity. Composite conductive network structure determines which electrical resistance change mechanism will appear in the composite.

Practical novelty

Produced new polymer-nanostructured carbon composites that have high sensitivity to VOC, are selective and capable to register VOC concentrations below regulated VOC exposure limits. Portative device prototype for VOC detection with integrated polymer-nanostructured carbon composite sensor element is elaborated as well.

Composition and volume of the thesis

The doctoral dissertation is written in Latvian, contains introduction, 3 basic chapters, conclusions, list of literature with 94 references, 2 annexes, 107 figures and full amount is 160 pages.

Approbation and publications

Results of the doctoral dissertation are published in 3 SCI journal papers, 3 SCI publications in conference proceedings and presented at 14 international scientific conferences.

THESIS

1. There are identified three VOC induced electrical resistance change mechanisms in polyisoprene-nanostructured carbon composite (PiNCC):

I. If PiNCC relative deformation is smaller than 0.01, then the VOC sensitivity of PiNCC is determined by tunneling current exponential decay with relative deformation increase. It is the basic reason why PiNCC exhibit comparatively high sensitivity to the presence of VOC.

II. When the PiNCC swelling in VOC progresses in time and reaches relative deformation values greater than 0.01, then destruction of conductive channel occurs in PiNCC. Polyisoprene thin layers between aggregates swell and aggregate inter distance increases to the degree that tunneling currents in PiNCC stop flowing and PiNCC electrical resistance increases exponentially with polynomial dependence on relative deformation:

$$\left(\frac{R}{R_0} = \left[1 + \frac{\Delta l}{l_0} \right] \cdot e^{A\left(\frac{\Delta l}{l_0}\right) + B\left(\frac{\Delta l}{l_0}\right)^2 + C\left(\frac{\Delta l}{l_0}\right)^3 + D\left(\frac{\Delta l}{l_0}\right)^4} \right).$$

III. If PiNCC relative deformation change is the same, when PiNCC exposed to VOC with diverse polarity, then PiNCC electrical resistance change is affected by VOC electrical conductivity with a circumstance that VOC conductance is far higher than matrix conductivity. VOC electrical resistance shunts PiNCC electrical resistance, as a result PiNCC total resistance increase is lower than predicted by tunneling current theory in PiNCC.

2. I and III are dominant electrical resistance change mechanisms in polyisoprene-multiwall carbon nanotube (PiMWCNT) composites. II electrical resistance change mechanism in PiMWCNT composites is not observed because, when composite swells, MWCNT have greater probability to retain and form indirect electrical contacts with other neighboring MWCNT. Both I and II electrical resistance change mechanisms coexist in polyisoprene-carbon nanoparticles composites (PiCB). Dominante mechanism in the composite is determined by conductive network structure and polyisoprene swelling extent in VOC, which depends on VOC compatibility with polyisoprene. The II electrical resistance change mechanism realizes faster in those PiCB composites, which have simpler shape of aggregates and less filler.

3. New method and original equipment for elastomer composite testing is developed by in-situ measuring of electrical resistance, mass and length change in the presence of VOC.

CONTENT OF THE WORK

Review of literature

Review of literature is made in a manner to cover broad application possibilities of VOC detection. VOCs are widespread in surrounding environment and VOC analyses can provide us with useful information in such fields as air quality control, chemical and petrochemical industry, food production, agriculture and medicine. Prospective sensor material types, detection limits, structure and working principles are described. In order of reaction type to the presence of VOC following chemical sensor groups are identified: physico-chemical, chemical and biosensors. Thereby slowly positioning a readers attention to polymer-nanostructured carbon composites (PNCC) as VOC sensor materials. Firstly, PNCC conductive network structure is discussed from the point of view of percolation theory. Analyzing results obtained by *Balberg*, we conclude that carbon nanoparticle structure and aggregate shape has an impact on the composites critical percolation parameters and electrical conductance [1], [2]. Statistical percolation can be applied to describe electrical percolation and conductance increase of the composite, if content of electroconductive filler is raised in a matrix. The fact that aggregates and agglomerates do not have direct contacts as it is predicted by statistical percolation should be taken in account. Aggregates, agglomerates are separated from each other by thin polymer layers. If the distance between aggregates and agglomerates does not exceed ~5-15nm, then they are connected electrically and between them in thin layer of matrix tunneling currents function [3]. Geometrical contacts between particles can be formed within aggregates and agglomerates. *Bauhofers* and *Kovacs* introduce the meaning of kinetic percolation – free particle movement, which promotes their agglomeration. Therefore a composite percolation threshold is achieved at much lower filler concentration [4]. The reason for kinetic percolation can be a number of external factors like low viscosity of the mixture, slow stirring intensity etc. Looking through scientific literature about PNCCs used for VOC detection, we realized that there is no experimental evidence and comprehensive explanation of observed VOC sensor effect in these materials. But it is clarified that PNCC VOC sensitivity is determined by VOC sorption into polymer matrix, but not into filler. Therefore VOC/polymer compatibility is important in a composite electrical resistance change. One of ruling factors for PNCC application as VOC sensor materials is effective diffusion process. In the current work diffusion process is viewed from material structure perspective in which the diffusion process takes place, but not in depending on external factors like temperature and pressure. We conclude, that polymer used as a composite matrix has to be with high macromolecule mobility and low cohesion energy not to impede VOC diffusion into the composite. Scientific literature evidences that VOC/polymer compatibility can successfully be assessed by Hansen solubility parameters, wettability coefficients or comparing dielectric permittivity values. Scientists have concluded that PNCC electrical

resistance change in the presence of VOC is determined by VOC molecule diameter as well [5]. Specific design the composite structure can provide that VOC separation is set by VOC molecule diameter but not by VOC/polymer compatibility. Summarizing above mentioned, we conclude, that we should experimentally prove tunneling currents existence in PNCC (in thin layer of matrix between aggregates). In other words VOC absorption induces polymer swelling and as a result filler particles inter-distance increase and tunneling currents between them exponentially decrease. As we conclude that VOC sensitivity of PNCC cannot be analyzed without diffusion, we decided that there is a need to do measurements, where sample increase in size, electrical resistance (tunneling currents) and sorption are measured simultaneously. Assessment of VOC diffusion in PNCC stimulated lack of information in literature about VOC diffusion mechanism in PNCC. In the current work polymer matrix selection influence on VOC sensitivity of PNCC, structure of PNCC and compatibility is analyzed as well.

Methodological part

Methodological part of the work contains description of used polymer matrixes materials: polyvinylacetate (PVAc), polyethylene glycol (PEG) and polyisoprene (Pi) and conductive fillers: carbon nanoparticles „carbon black” (CB), long and short multi wall carbon nanotubes (LMWCNT and SMWCNT). CB is purchased from Evonik Degussa GmbH. Average diameter of CB primary particle is 30nm, dibutylphthalate absorption 380ml/100g, specific surface area – 950m²/g. Long multi-wall carbon nanotube (LMWCNT), purchased from Aldrich; outer diameter is 40-60 nm and inner diameter is 5-10 nm, length 0,5-500µm, maximal aspect ratio 12500. Short multi wall carbon nanotubes (SMWCNT) were obtained from Italian Institute of Technology Smart Materials Platform. SMWCNT outer diameter is 50-80 nm, inner diameter is 5-15 nm, length 0,5-2µm, maximal aspect ratio 40. Specific surface area 40m²/g, electrical conductance 100S/cm and density 2.1 g/cm³. In methodological part production technology of PNCC is described. Schemes of production of PNCCs are shown in Fig. 1 and Fig. 2. Polyisoprene-carbon nanoparticle composites (PiCB) were prepared in three different ways. PiCB composites produced according to 1st method further will be labeled as PiCBRoll. According to 2nd method two types of PiCB composites were produced and further will be labeled as PiCB48h and PiCB24h. PiCB48h was produced directly as shown in Fig. 2 with over all stirring time 48 hours. But PiCB24h was produced modifying the 2nd method. CB dispersion in chloroform was added to polyisoprene/chloroform mixture, while polyisoprene did not start to dissolve in chloroform. The absolute stirring time of PiCB24h mixture was 24 hours. Other composites: PVAcCB, PEGCB, PiLMWCNT and PiSMWCNT were produced according to scheme shown on Fig. 2.

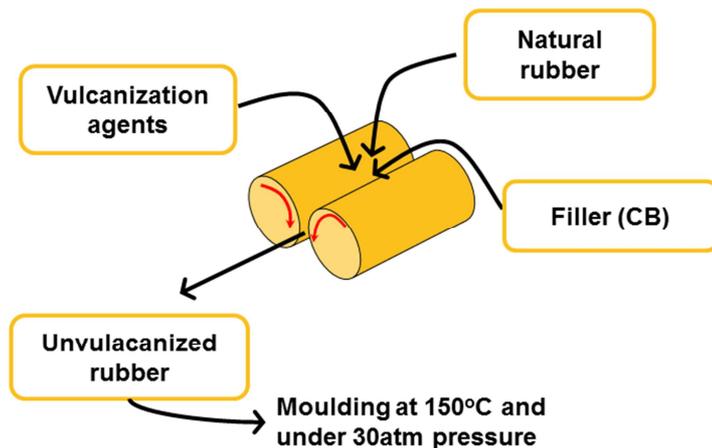


Fig. 1. PNCC production scheme according to the 1st method.

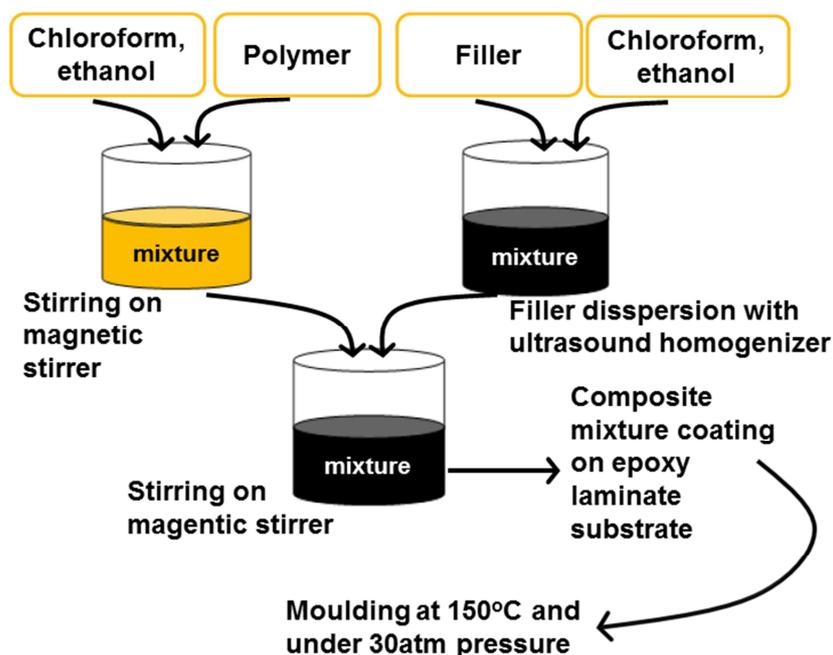


Fig. 2. PNCC production scheme according to the 2nd method.

A sample, which is subjected to VOC sensitivity tests, structure is shown in Fig.3 and described in methodological part of the work.

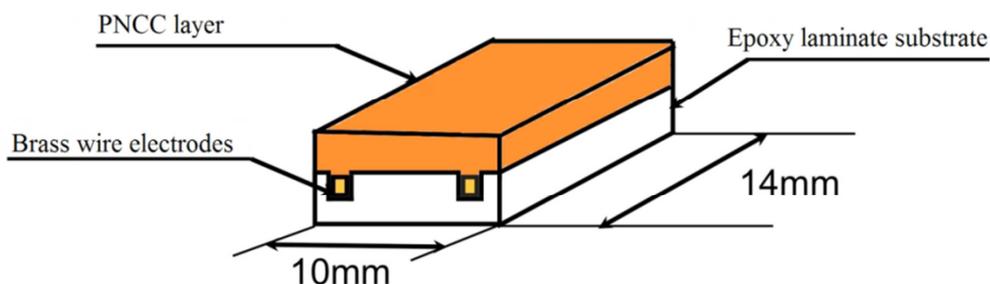


Fig.3. Schematic structure of PNCC sample.

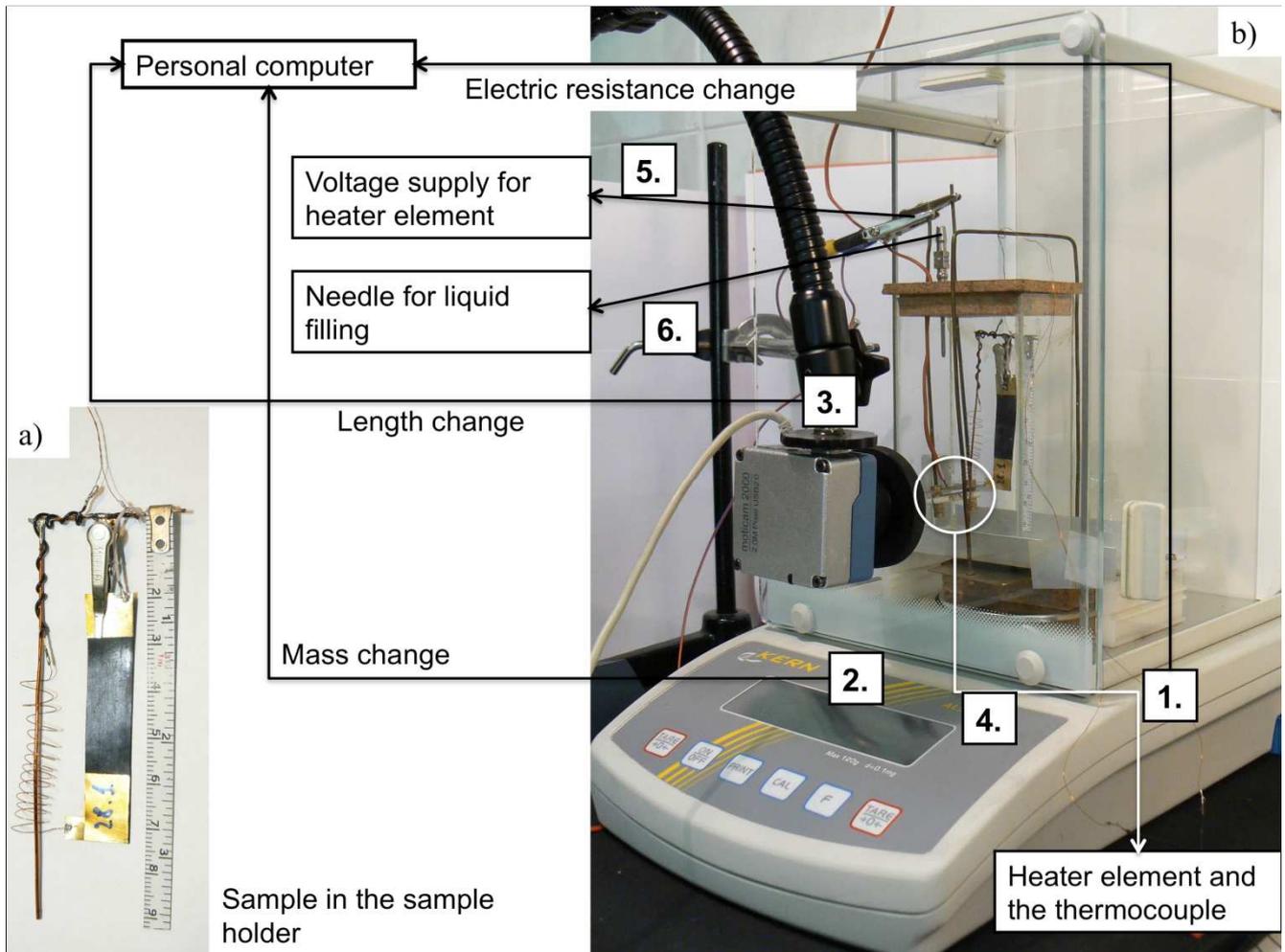


Fig.4 a) PNCC sample in the sample holder of special design. b) Experimental setup for simultaneous electrical resistance, mass and length measurements.

Methodological part contains description of used equipment for measurements and originally produced equipment for in-situ electrical resistance, mass and length change measurements in the presence of VOC (Fig.4). We assessed the equipment capability to maintain desirable VOC atmosphere for a certain time and determined measurement limiting factors of the equipment. Method of R,m,l measurements is discussed.

Experimental part

Experimental part subsection „VOC sensitivity of PNCC” basically can be divided in two subparts. In the first subpart we evaluate conductive network structure of PNCC depending on used elaboration method and composition of composite. A composite electrical conductivity, according to statistical percolation theory, is calculated by:

$$\sigma = \sigma_0 \cdot (f - f_c)^t, \quad (1)$$

where σ_0 - initial conductivity of the material (S/m), f – filler concentration, f_c – critical filler concentration (percolation threshold), t – critical index of percolation. In the equation $f > f_c$. Statistical percolation scaling law predicts to logarithm equation (1)

and to look for value of f_c till experimental data has the best fit with linear function. The best linear fit is reached, when the highest value of R^2 is achieved [6], [7]. We estimated obtained electrical percolation curves of produced composites (Fig.5) and determined percolation critical parameters (f_c and t) according to above made description. *Zavickis et.al* had determined PiCBRoll composite percolation critical parameters previously [7]. Table 1 contains all obtained percolation critical parameters of composites. The data is a base for composites conductive network structure interpretation.

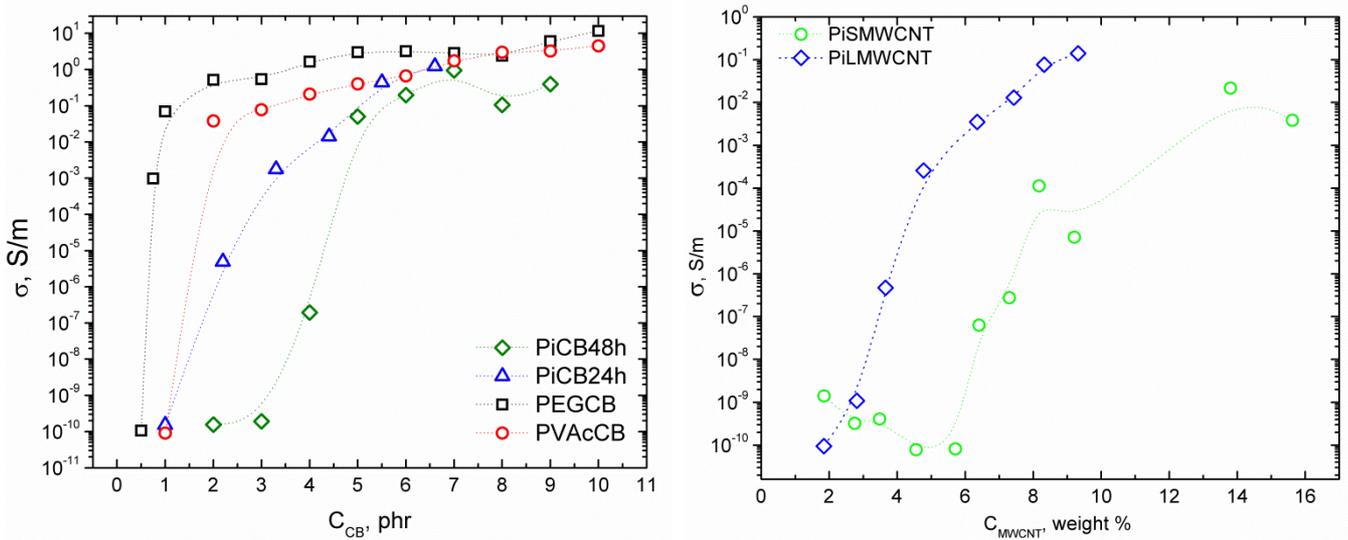


Fig.5. (on the left) PNCC conductivity versus CB concentration in the composite composition. (on the right) PiMWCNT conductivity versus MWCNT concentration in the composite composition.

Table 1. Percolation critical parameters of PNCC (phr – parts per hundred rubber).

Material	f_c , phr	t	Notes
PiCB24h	1,2	7,4	Influence of production technology
PiCB48h	2,6	1,078	
PiCBRoll	8,1	6,6	
PiCB48h	2,6	1,078	Influence of matrix
PVAcCB	2	2,05	
PEGCB	0,75	1,28	Influence of filler
PiCB48h	2,6	1,078	
PiGMWCNT	3,15 w.% = 3,4 phr	4,95	
PiSMWCNT	5,8 w.% = 6,13 phr	4,54	

CB dispersion quality in PiCB composites, obtained with different techniques, was evaluated by examining nitrogen fractured composite surface with scanning electron microscopy (SEM). Obtained images of PiCB composites are shown in Fig. 6.

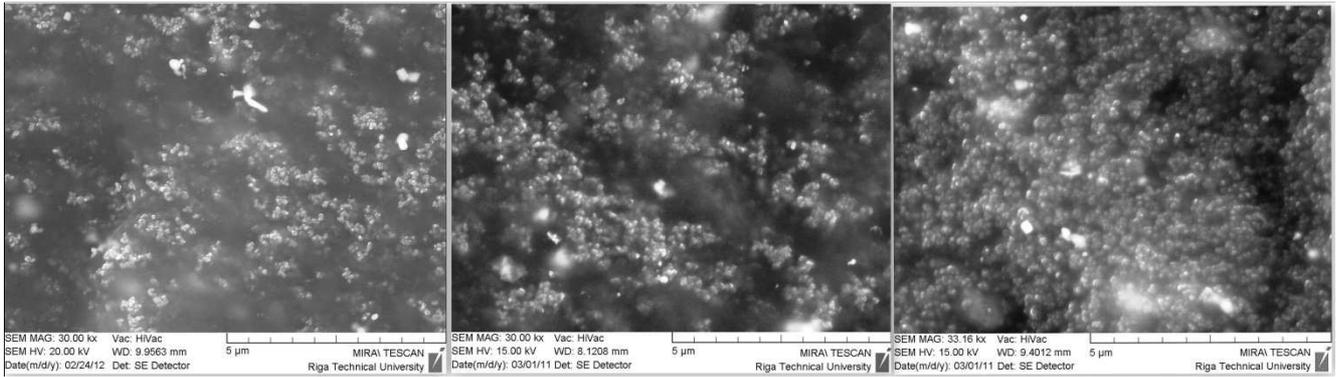


Fig. 6. SEM images of PiCB composites: (*on the left*) PiCB4.448h, (*in the middle*) PiCB4.424h and (*on the right*) PiCB10Roll.

Summarizing obtained results we conclude, that filler dispersion method has determinant effect on composite conductive network structure. Shear forces are exerted on carbon nanoparticle agglomerates, when filler in matrix is mixed utilizing „dry method” (1st method). In this case agglomerates are destroyed less than in case of carbon nanoparticle dispersion using ultrasound homogenizer. The statement proves obtained results: PiCBRoll critical index (t) value is 6,6 (see Table 1.). It means that one particle has at least 6,6 electroconductive contacts with other carbon nanoparticles and shape of the aggregate is more complex than for PiCB48h composites. Possible aggregates shapes of PiCB composites are visualized in Fig.7. Aggregate pictures are drawn taking in to account determined percolation critical parameters. PiCBRoll percolation threshold is high and the composite gain conductivity at higher filler concentrations due to extremely high matrix viscosity, when filler is added. Therefore, CB aggregates are more isolated from each other and higher filler concentration is needed to obtain percolation threshold. Composites produced with „wet method” (2nd method), where CB dispersed using ultrasound, have smaller CB aggregates and more spherical like shape than PiCBRoll composites, because CB nanoparticles have fewer contacts with other particles. However in this case determinant role plays viscosity of the mixture at the time of filler dispersion addition. CB aggregation and complex shape aggregate formation is promoted when filler is added to low viscosity mixture (Fig.7. b)). It is a reason why PiCB24h becomes conductive at lower filler concentrations than other PiCB composites (see Table 1.). On contrary, CB tendency to aggregate is suppressed if filler is added to high viscosity mixture (see PiCB48h in Table 1.). The composite obtains conductivity at higher filler concentrations and the shape of aggregates is simpler and more spherical like (Fig.7 a)).

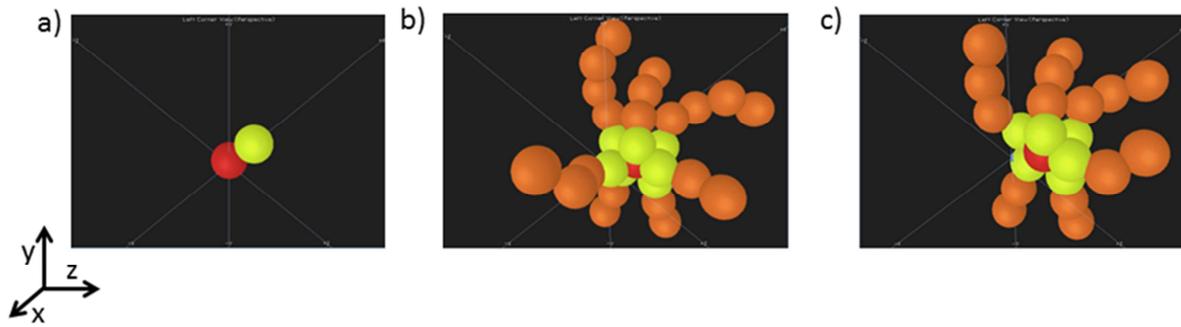


Fig.7. Shape of CB aggregates in PiCB composites a) PiCB48h, b) PiCB24h and c) PiCBRoll. Red sphere – CB nanoparticle that forms contacts with other CB particles. Green sphere – CB particle that forms electrically conductive contact with red sphere.

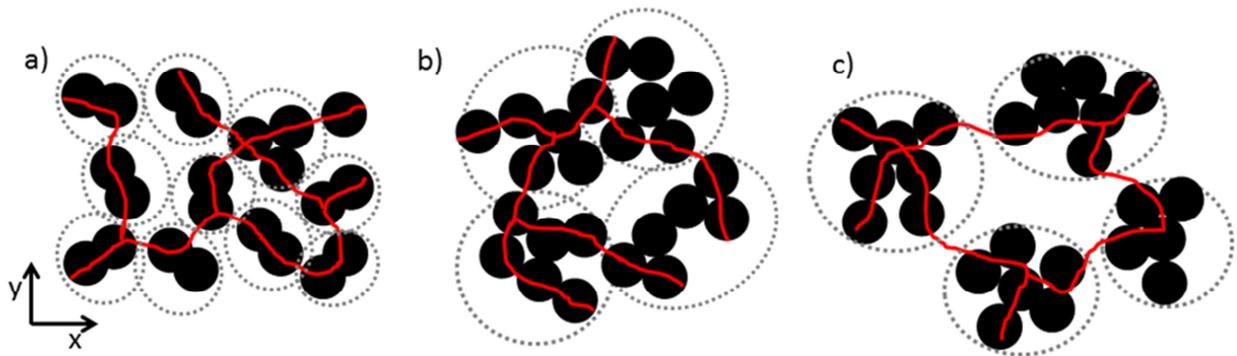


Fig.8. Electroconductive structure of PiCB composites: a) PiCB48h, b) PiCB24h and c) PiCBRoll. ● – carbon nanoparticle. CB aggregates in this composite circumscribed with grey dotted line. Red lines – tunneling currents formed within CB aggregates and agglomerates.

CB aggregate conductive network structure within the composite matrix is drawn to understand VOC induced PiNCC electrical resistance change. PiCB48h composite conductive network structure consists of simple shape CB aggregates, which are separated by thin polyisoprene layer (Fig.8 a)). Conductive network structure of PiCB24h is made of complex shape aggregates which in addition are mutually agglomerated (Fig.8 b)). PiCBRoll composite conductive network has equally complex shape aggregates as PiCB24h composite, but aggregates are not mutually agglomerated (Fig.8 c)).

PNCC conductivity according to determined percolation critical parameters is dependent on used polymer matrix structure (crystalline, amorphous, amorphous-cross linked) (see Table 1.). Percolation threshold is achieved at lower filler concentrations if crystalline polymer matrix with linear macromolecules is used for the composite production.

Percolation critical parameters were compared for produced PiNCC with different fillers. If MWCNT are used as filler, then lower percolation threshold is obtained in case of MWCNT with higher aspect ratio. Despite that fact, PiLMWCNT percolation threshold is far higher than for PiCB composites. Raised percolation threshold we relate

with LMWCNT spaghetti like structure (diminish aspect ratio). MWCNT/polymer interaction cannot be excluded as well. CB nanoparticle tendency to agglomerate greatly increases nanoparticle aspect ratio.

In the second subsection of the section „**VOC sensitivity of PNCC**” results concerning VOC sensitivity of PNCC, electrical resistance relaxation, repeatability and evaluation of matrix/VOC compatibility, comparing dielectric permittivity values and Hansen solubility parameters, are presented. Correlation between compatibility and the composite electrical resistance change in the presence of VOC is found.

For example, in Fig. 9 PiCB24h composite relative resistance change versus time is shown, when sample is exposed to toluene 2000ppm and relaxed in the air. PiCB24h composite samples differ from each other by CB content: 3.3; 4.4; 5.5 and 6.6 parts per hundred rubber (phr), respectively. The highest response is observed for PiCB24h composite with 4.4 phr of CB. This composite conforms to the region in percolation curve slightly above percolation threshold. Also for PVAcCB and PEGCB composites the highest electrical resistance change was observed for compositions slightly above percolation thresholds. However, for PiCB48h, PiLMWCNT and PiSMWCNT composites the highest response was observed for compositions far from percolation transition, where the best sensitivity is expected.

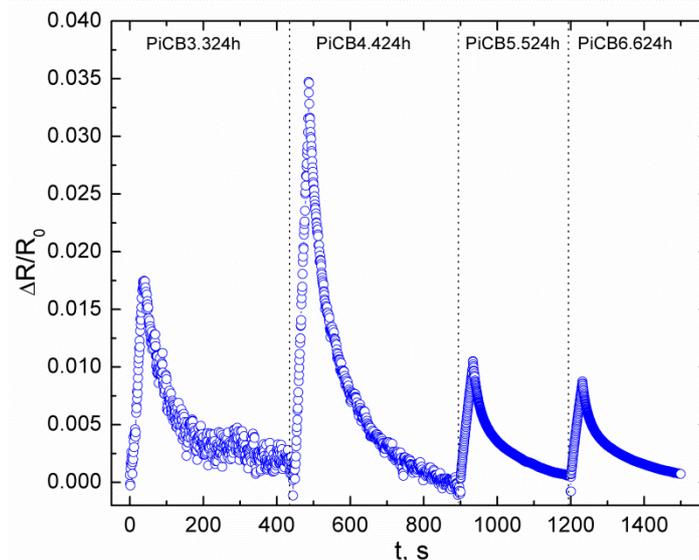


Fig. 9. Toluene (2000ppm) induced relative electrical resistance change ($\Delta R/R_0$) of PiCB24h composites depending on filler content in PiCB24h.

For gas sensor materials not only high sensitivity and fast response is expected, but also remarkably fast relaxation process – initial electrical resistance acquisition. Material capability to recover initial electrical resistance after interaction with VOC would be considered as advantage because it would give a possibility of frequent usage of a sensor. Electrical resistance relaxation data are described by equation and relaxation constants (τ) are determined:

$$\Delta R / R_{0(t)} = \Delta R / R_{0(\infty)} + A_1 \cdot \exp\left(-\frac{t}{\tau_1}\right), \quad (2)$$

where $\Delta R / R_{0(t)}$ – relative electrical resistance change in time t , $\Delta R / R_{0(\infty)}$ – relative electrical resistance change, when t tends to ∞ , t – time, s, τ_1 – relaxation time constant (s). At the beginning PiCB848h relative electrical resistance change in time was determined, when the composite exposed to increasing concentration of toluene (100 till 500ppm) and relaxation in the air was recorded as well. Electrical resistance relaxation curves for samples previously exposed to different toluene concentrations are shown in Fig.10.

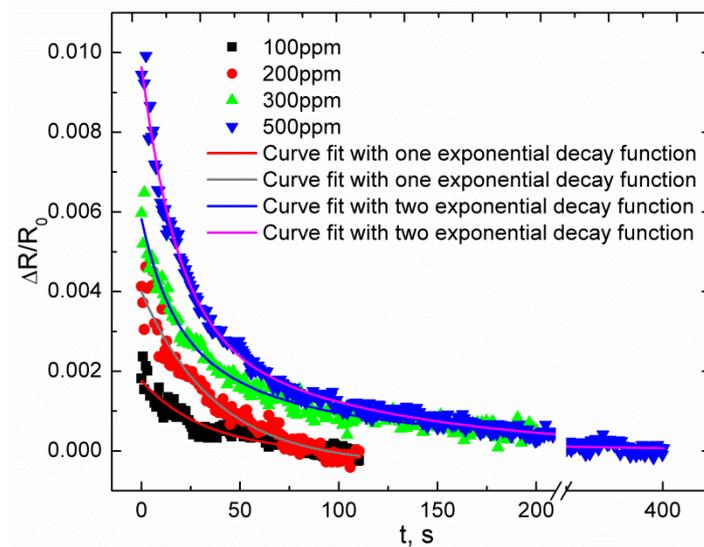


Fig.10. PiCB848h electrical resistance change in time after the sample was exposed to toluene. Experimental data are fitted with theoretical curves (Eq.(2)).

Produced composites were exposed to different VOCs and electrical resistance change was registered with a purpose to determine PNCC selectivity to particular VOC. PNCC selectivity is determined by VOC and matrix compatibility, which we evaluated, firstly, by comparing dielectric permittivity values (ϵ). The ϵ value for polyisoprene is 2,68 [9]. In Fig.11 PiCB4.424h and PiSMWCNT17 relative electrical resistance change in the presence of VOCs with diverse polarity are shown. From obtained results in Fig.11 can conclude that PNCC electrical resistance response greatly differ if VOCs are changed. In addition to that, as VOC ϵ value is closer to polyisoprene ϵ as electrical resistance change of PNCC is higher. VOC molecule dimensions impact on PNCC electrical resistance change velocity also has been examined (Fig.12 (on the left)). These measurements were performed by picking up VOC pairs that have equal diameter (d), but different values of ϵ and on contrary: different d and equal or close ϵ values. Obtained results indicate that PNCC electrical resistance change in the presence of VOC is mainly determined by VOC and composite matrix compatibility and molecule diameter has minor effect on electrical resistance change. Polyisoprene and VOC compatibility was examined also by comparing Hansen solubility parameters. Relative

energy difference (RED) between polyisoprene and VOC was determined. In Fig.12 (*on the right*) PiCB10Roll electrical resistance change velocity (V_R) with respect to value of RED is presented.

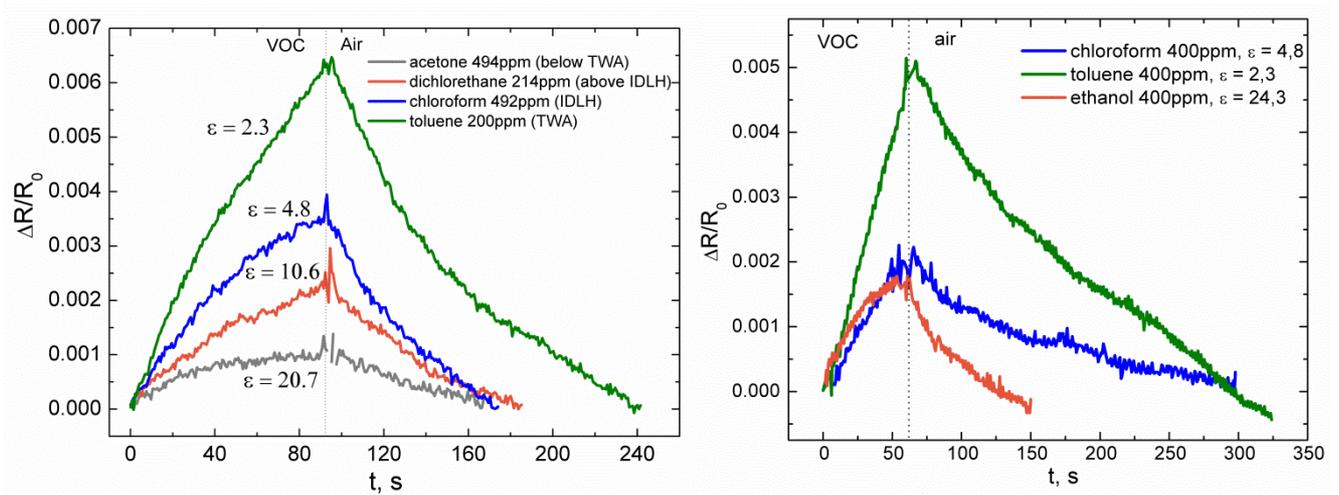


Fig.11 (*on the left*) Relative electrical resistance change of PiCB4.424h in VOC and relaxation in the air. TWA¹ and IDLH² are VOC concentration levels. (*on the right*) Relative electrical resistance change of PiSMWCNT17 in VOC and in the air.

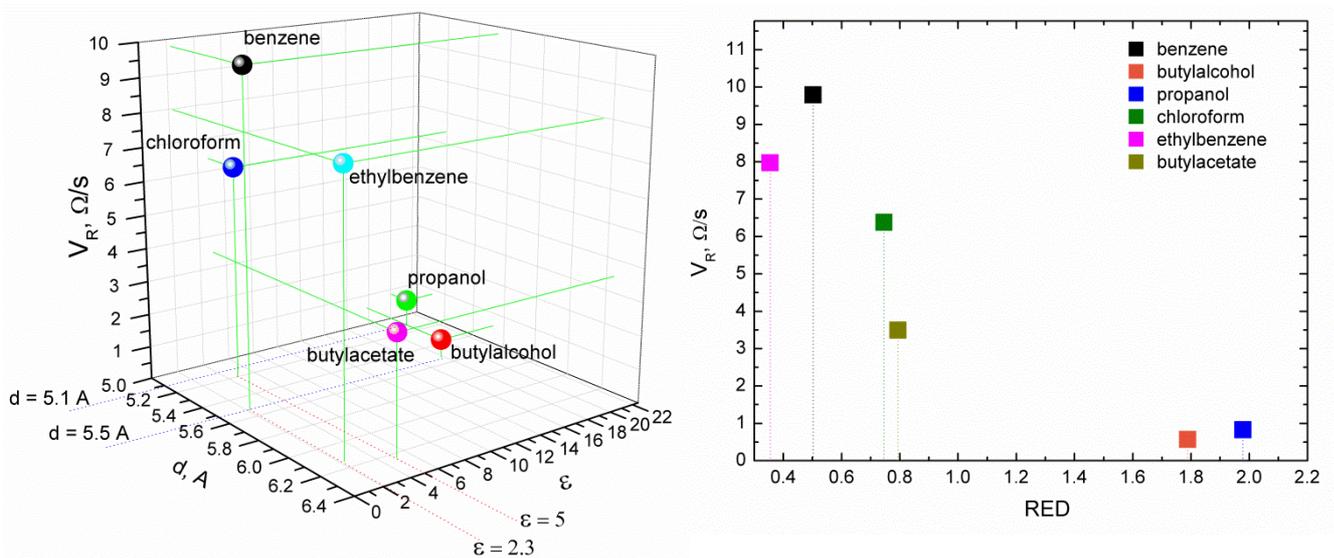


Fig.12. (*on the left*) Electrical resistance change velocity (V_R) of PiCB10Roll versus VOC molecule diameter (d) and values of ϵ . (*on the right*) Electrical resistance change velocity PiCB10Roll in different VOC versus relative energy difference (for polyisoprene and respective VOC).

¹ TWA - average, permissible VOC concentration in 8 hour working day and 40 hour working week.

² IDLH – VOC concentration which is immediatly dangerous to life and health of humans.

We conclude that correlation between V_R and RED exists: as VOC and Pi relative energy difference decreases, PiNCC electrical resistance change velocity increases, that is, sensitivity to VOC.

Experimental part subsection „**Simultaneous electrical resistance, mass and length change measurements**” contains description about originally developed method for simultaneous R,m,l measurements. PiNCC three parameter changes in time, when sample exposed to VOC, are discussed. Correlation between absorbed mass of VOC, relative deformation and the composite electrical resistance change is estimated. PiNCC 3 parameter change in time is assessed for samples with different production method and fillers used. Firstly, obtained data gave a possibility to explain in detail observed VOC sensor effect of PiNCC (electrical resistance change mechanism) and relaxation process in the air. Secondly, rather unique data were achieved about VOC diffusion in PiNCC. Only few research reports concerning VOC diffusion in PNCC are found in scientific literature. Obtained results of VOC diffusion in PiNCC are compared with diffusion theory in polymers.

One of R,m,l measurements for PiCB4.448h and PiSMWCNT17 composites in toluene vapour are given in Fig.13. Character for all R,m,l curves is similar and three characteristic areas are identified: a) first 1000s electrical resistance, mass and deformation of the sample increases; b) saturation, PiNCC has reached thermodynamic equilibrium in existing conditions; c) relaxation process after VOC is removed from the test chamber.

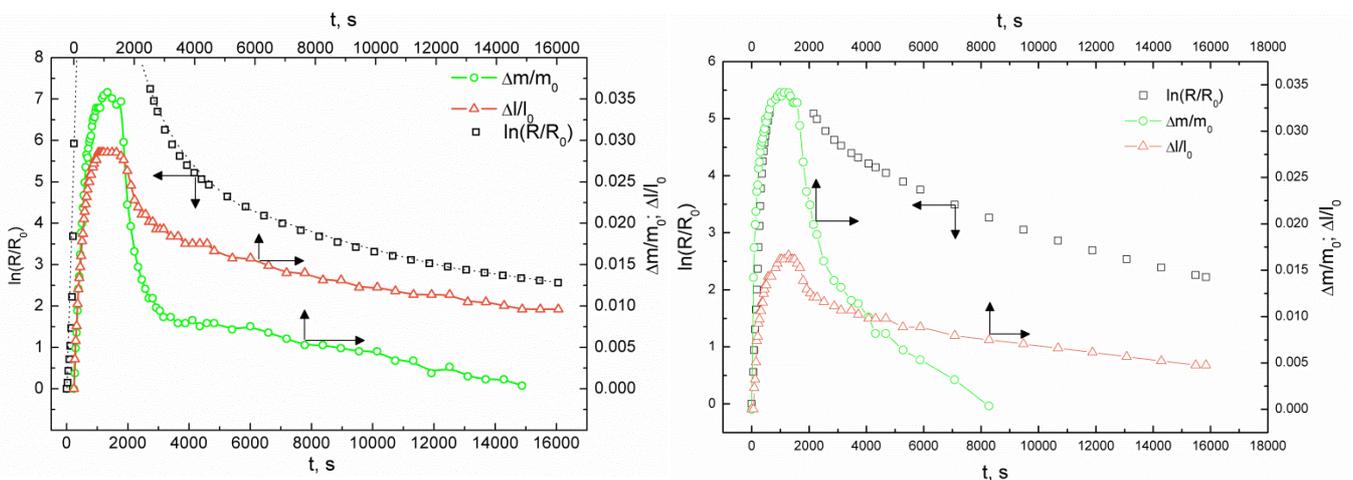


Fig.13. (on the left) PiCB4.448h and (on the right) PiSMWCNT17 electrical resistance, mass and length change in time, when sample exposed to toluene vapour and in the air after vapour removal.

R,m,l measurement made in VOC indicated that as better is VOC compatibility with polyisoprene as more VOC is absorbed, as higher is relative deformation and electrical resistance change. Therefore relaxation process is prolonged as well.

PiNCC capability to swell is directly affected by used filler. MWCNT act as reinforcement of polyisoprene and therefore polyisoprene swelling in PSMWCNT

composites is greatly limited. Due to entangled structure LMWCNT has more evident reinforcing action than SMWCNT. In Fig.13 R,m,l measurement results are shown for PiCB4.448h and PiSMWCNT17 composites. Comparing these results we noticed that at the same maximal relative mass change both composites have sharply different relative deformation values. We conclude the following: macromolecules are able to move simple shape CB aggregates/particles therefore CB restricts macromolecule mobility, but not swelling of the composite.

R,m,l measurement results indicate that electrical resistance relaxation process is related to ability of macromolecules to rearrange and to achieve equilibrium state which conforms with desorbed state. At a mean time macromolecules move particles closer to each other till their approximate initial distance is renewed and composites initial resistance is reached.

The section named „VOC diffusion into PNCC” is included in „**Simultaneous electrical resistance, mass and length change measurements**”, where VOC sorption results are presented. Equilibrium sorption for relatively short times from the point of view of diffusion theory can be described by [10], [11]:

$$\frac{m_t}{m_\infty} = \frac{4}{l} \left[\frac{Dt}{\pi} \right]^{\frac{1}{2}}, \quad (3)$$

where m_t is increase of weight in time t , m_∞ - increase of weight, when t tends to infinity, D – diffusion coefficient, l – thickness of a sample and t - time.

Depending on structure of polymer (crystalline, amorphous, amorphous-cross linked) VOC diffusion in polymer can vary from Fickian to non-Fickian. VOC diffusion mechanism in polymer is determined according to equation [10]:

$$\frac{m_t}{m_\infty} = k \cdot t^n, \quad (4)$$

where k is a constant, but n – constant which evidences about existing VOC diffusion mechanism in a polymer. If $n = 0.5$, then the rate of diffusion is much slower than molecular chain relaxation (Fick diffusion) [12],[13]. The amount of diffusant absorbed by a polymer in which this diffusion mechanism is valid can be registered by immediate rearrangement of macromolecules and a respective increase of electrical resistance. When diffusion is very fast compared with molecular chain relaxation, it is called Supercase II $n > 1$ or Case II and $n = 1$ [12],[13]. It means that macromolecules do not conform immediately and it take sufficiently longer time to rearrange positions toward equilibrium conformation consistent with sorbed state. If such a polymer matrix is used for sensor material, then it would cause delayed sensor response to the presence of vapour. The third type is anomalous diffusion ($0.5 < n < 1$) occurring, when rates of diffusion and molecular chain relaxation are comparable [12],[13] meaning that

polymer macromolecules conform almost immediately after absorption of the analyte. From the facts mentioned above follows that for real-time vapour concentration monitoring in the air and rapid response sensor materials value of n within $0.5 \leq n < 1$ (Fick or anomalous diffusion, respectively) is preferable.

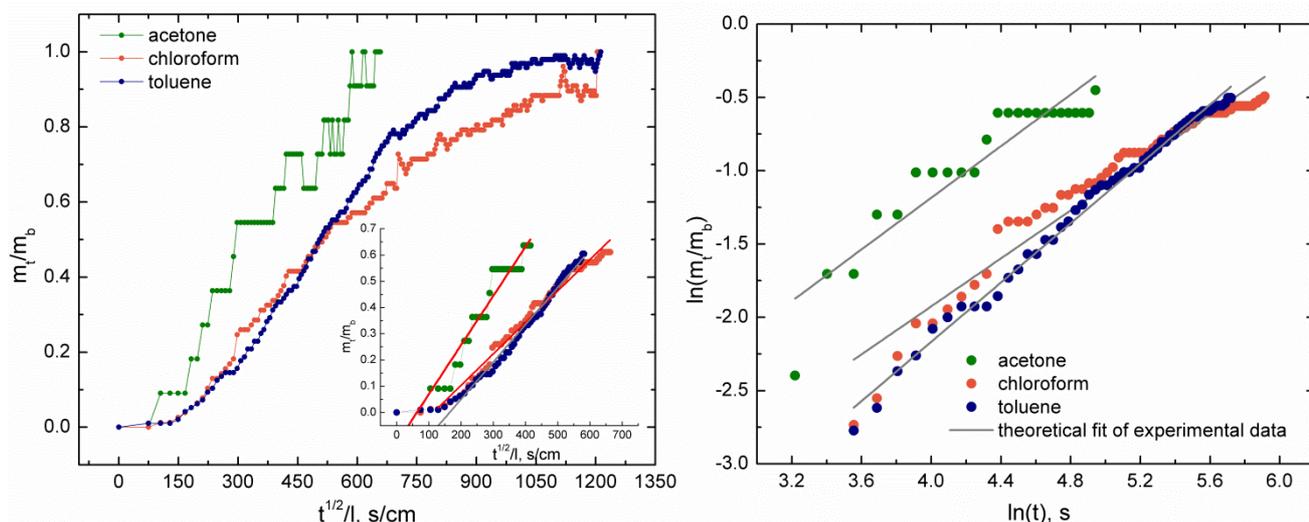


Fig.14. (*on the left*) Mass change in time of PiCB4.448h composite, when samples exposed to different VOC. Inset graph shows mass change in time till m_t/m_b reaches 0,6, for diffusion coefficient calculation purposes. (*on the right*) Logarithm of mass change in time of PiCB4.448h composite, when samples exposed to different VOCs.

In Fig.14 mass sorption results of PiCB4.448h composite in different VOC are presented. From experimental data, according to Eq.(3), VOC diffusion coefficient (Fig.14. (*on the left*)) and according to Eq.(4) diffusion mechanism (Fig.14. (*on the right*)) in PiCB4.448h composite is calculated. Determined diffusion coefficients and diffusion mechanism constants for PiNCC are summarized in Table 2. As all obtained values of n are within the limits from $\sim 0,5$ to ~ 1 , VOC diffusion in PiNCC is dominated by anomalous diffusion mechanism. It means that VOC diffusion speed is comparable with macromolecule mobility. R,m,l results evidence that macromolecules are linked with physical and chemical bonds to filler particles. Therefore, polyisoprene macromolecule ability to follow speed of VOC diffusion decreases with increasing diffusion speed.

Table 2. VOC diffusion coefficient (D) and diffusion mechanism (n) in PiNCC

Material	VOC	D, cm ² /s	n
PiCB4.448h	acetone	2,78·10 ⁻⁶	0,880
PiCB4.448h	toluene	3,27·10 ⁻⁷	1,011
PiCB4.448h	chloroform	2,64·10 ⁻⁷	0,756
PiCB848h	toluene	4,19·10 ⁻⁷	0,853
PiCB848h	chloroform	3,27·10 ⁻⁷	0,650
PiCB4.424h	ethylacetate	6,32·10 ⁻⁷	0,854
PiCB4.424h	toluene	4,13·10 ⁻⁷	0,702
PiCB10Roll	ethylacetate	2,86·10 ⁻⁷	0,598
PiCB10Roll	toluene	2,38·10 ⁻⁷	0,567
PiSMWCNT17	toluene	7,09·10 ⁻⁷	0,601
PiSMWCNT17	ethylacetate	2,73·10 ⁻⁷	0,473
PiLMWCNT7	ethylacetate	6,22·10 ⁻⁷	0,422

Anomalous diffusion

In experimental part subsection called „**Electrical resistance change mechanism of PiNCC**” electrical resistance change versus relative deformation of PiNCC is determined and VOC induced electrical resistance change mechanisms identified. Theoretically electrical resistance of electroconductive polymer composite is calculated taking into account number of particles, which take part in electroconductive channel formation and number of conducting paths [3],[14],[15]:

$$R = \frac{L}{N} \left(\frac{8\pi h s}{3a^2 e^2} \right) \exp(\gamma s_0), \quad (5)$$

where L – number of particles in a single conducting path, N – number of conducting paths, s_0 – least distance between conducting particles; a – effective cross area of tunneling, e – electron charge, γ – constant calculated by:

$$\gamma = \frac{4\pi}{h} \sqrt{2m\phi}, \quad (6)$$

where m – mass of the electron, h – Plank’s constant, ϕ – potential barrier height between particles. A composite electrical resistance versus particle inter-distance change, when a specimen is mechanically compressed, is calculated according to [3]:

$$\frac{R}{R_0} = \frac{s}{s_0} \exp[\gamma(s - s_0)], \quad (7)$$

where R_0 – initial electrical resistance of the composite, s_0 – initial distance between particles. When electroconductive composite is stretched, then particle inter-distance change is expressed as [14]:

$$s = s_0(1 + \varepsilon) = s_0 \left(1 + \frac{\Delta l}{l_0} \right), \quad (8)$$

where $\Delta l = l - l_0$, l_0 – initial length of a sample.
 Substitution of Eq.(8) into Eq. (7) yields [13]:

$$\ln R = \ln R_0 + \ln \left[1 + \frac{\Delta l}{l_0} \right] + A_0 \left(\frac{\Delta l}{l_0} \right), \quad (9)$$

where $A_0 = \gamma s_0$.

Firstly, VOC contribution in PiNCC electrical resistance change was examined. As utilized matrix in PiNCC composites is the same – polyisoprene, VOC impact assessment was done only for one PiNCC composition – PiCB4.448h. In Fig.15 PiCB4.448h electrical resistance versus relative deformation ($\Delta l/l_0$ till 0.01) is shown, when the sample is held in acetone, chloroform and toluene. Results indicate that the composites electrical resistance exponentially increases with respect to relative deformation and the data can be well fitted with Eq.(9) (see Fig.15 (*on the left*)), where equation member $\ln(1+\Delta l/l_0) \approx 0$. Measurement results prove that the composite VOC sensor effect is based on matrix swelling, distance increase of CB aggregates, tunneling current decrease and composites electrical resistance increase accordingly.

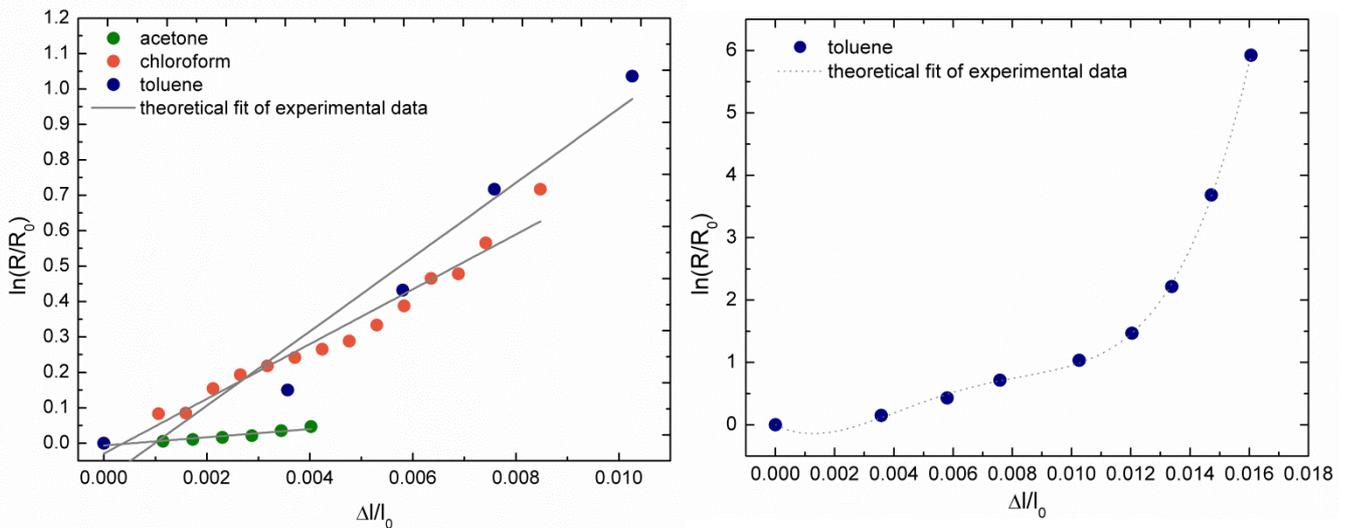


Fig.15. (*one the left*) PiCB4.448h electrical resistance change versus relative deformation in acetone, chloroform and toluene vapour. Solid line denotes theoretical fitting by Eq. (9) of experimental data (points). (*on the right*) PiCB4.448h electrical resistance change versus relative deformation in toluene vapour. Solid line denotes theoretical fitting by Eq. (10) of experimental data (points).

After measurements in different VOCs with the same composite, we realized that the composites electrical resistance change is affected by VOC electrical resistance³, when relative deformation is the same. If VOC conductivity is significantly higher than matrix conductivity, VOC electrical resistance shunts the composites electrical resistance. Accordingly, final electrical resistance change of the composite is less than it should be

³ Specific electrical resistance of tested VOC is: $1,2 \cdot 10^{10} \Omega m$ (toluene), $1,6 \cdot 10^6 \Omega m$ (chloroform) and $4,08 \cdot 10^4 \Omega m$ (acetone).

with respect to relative deformation. For example, toluene itself has the highest electrical resistance with value close to isolator ($\sim 10^{14}\Omega$). In toluene vapour PiCB4.448h has the largest electrical resistance change because toluene vapour does not shunt electrical resistance of the composite. In case of chloroform PiCB4.448h electrical resistance change is less, because chloroform vapour shunts electrical resistance of the composite. The highest degree of shunting is observed in case of acetone and therefore the composite electrical resistance change in this vapour is the smallest.

When PiCB4.448h was exposed to toluene, relative deformation larger than 0.01 was achieved and very rapid electrical resistance increase observed (Fig.15 (*on the right*)). This is explained with such inter-distance increase of CB aggregates, that tunneling currents cannot flow anymore. Electroconductive channel destruction occurs and total number of conducting paths (N) decrease in the composite. Therefore we conclude that electroconductive channel destruction in the composite realizes when the composite swelling in VOC proceeds and relative deformation exceeds 0.01 and the composite's electrical resistance increase exponentially with polynomial dependence on relative deformation. Mathematically this is described by equation:

$$\ln\left(\frac{R}{R_0}\right) = \ln\left(1 + \frac{\Delta l}{l_0}\right) + A\left(\frac{\Delta l}{l_0}\right) + B\left(\frac{\Delta l}{l_0}\right)^2 + C\left(\frac{\Delta l}{l_0}\right)^3 + D\left(\frac{\Delta l}{l_0}\right)^4 \quad (10)$$

Secondly, existing electrical resistance change mechanism in PiCB composites elaborated with different methods was examined. Obtained electrical resistance change versus relative deformation of PiCB composites is demonstrated in Fig.16. It is evident that in PiCB4.424h noticeably different electrical resistance change mechanism comparing to PiCB48h and PiCB10Roll exists. PiCB4.424h sharp electrical resistance increase we relate to conductive network structure of the composite. Even one element (aggregate/agglomerate) withdrawn from conductive network, which is made of only few elements, leads to extremely high electrical resistance increase of the composite. PiCB4.424h composite unlike others was exposed to twice reduced toluene vapour concentration. In this case electrical resistance change mechanism related to tunneling current decrease in thin layer of matrix, was not identified because the smallest length change measurable by used camera is $12\mu\text{m}$.

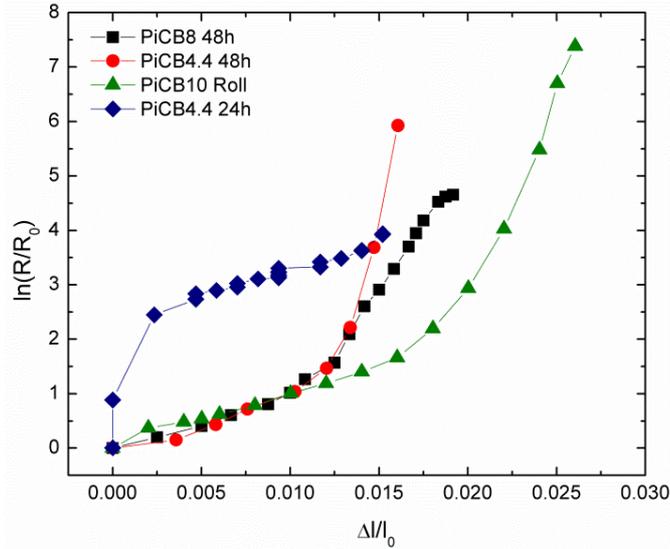


Fig.16. att. PiCB electrical resistance versus relative deformation, when samples exposed to toluene vapour.

Similar electrical resistance change mechanisms according to Eq.(9) and Eq.(10) were observed for PiCB4.448h, PiCB848h and PiCB10Roll composites. Two samples of PiCB48h composite containing 4.4 and 8 phr of CB were tested. PiCB4.448h corresponds to the composition in percolation transition region, but PiCB848h showed the highest sensitivity to VOC in previous experiments. PiCB4.448h, PiCB848h and PiCB10Roll composites electrical resistance change at relative deformation smaller than 0.01 is given in Fig.17 (*on the left*). We conclude that for all composites tested electrical resistance increases exponentially with respect to relative deformation. It proves that in these composites tunneling currents exist.

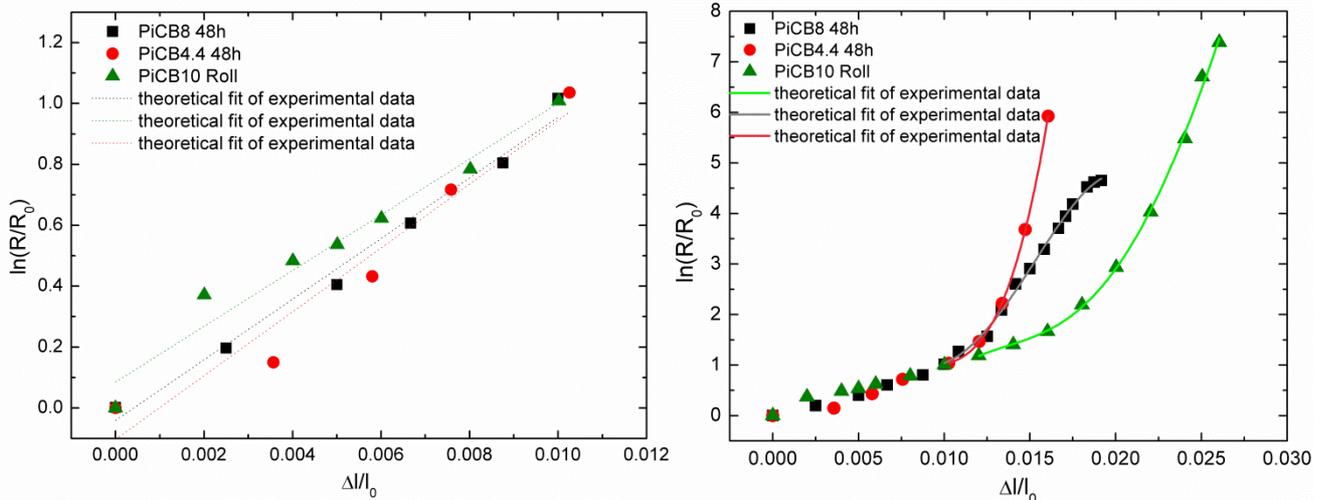


Fig.17. PiCB electrical resistance change versus relative deformation < 0.01 (*on the left*) and > 0.01 (*on the right*), when samples exposed to toluene vapour. Experimental data points theoretically fitted with Eq.(9) and Eq.(10).

If relative deformation of PiCB4.448h, PiCB848h and PiCB10Roll composites is larger than 0.01, then electrical resistance of tested composites increases sharply and it is

related to conductive channel destruction (Fig.17 (on the right)). We conclude that destruction of conductive channels is dependent on initial number of conducting paths. As the number of conduction paths is smaller as faster destruction of conducting channels occurs. For example, more rapidly this electrical resistance change mechanism realizes in PiCB4.448h, and then follows PiCB848h and PiCB10Roll. Obtained results also indicate that faster destruction of conductive channels occurs if conductive network is made of simple shape CB aggregates. Shape complexity of CB aggregates increases in the following order PiCB4.448h, PiCB848h and PiCB10Roll.

Thirdly, VOC induced electrical resistance change mechanism was examined for PiMWCNT composites. In Fig.18 PiSMWCNT17 and PiLMWCNT7 electrical resistance versus relative deformation in ethyl acetate vapour is shown. Results evidence that composites electrical resistance increases exponentially with respect to relative deformation. In case of PiMWCNT composites electrical resistance change mechanism related to destruction of conductive channels was not observed in experiments with ethyl acetate and toluene vapour as well. However, maximal relative deformation of PiSMWCNT17 composite in toluene vapour is 0.016. In our opinion, destruction of conductive channels in this case is not observed due to MWCNT larger surface area. When PiMWCNT composite swells, MWCNT has larger probability to form indirect conductive contacts with other nearby MWCNT, where tunneling current can exist.

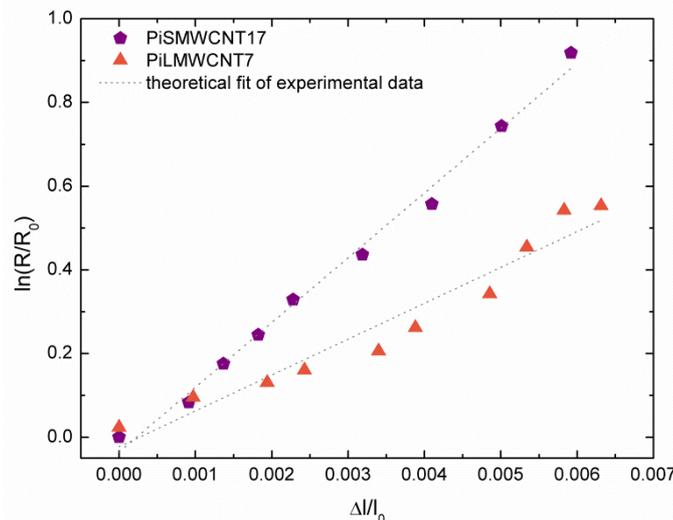


Fig.18. PSMWCNT electrical resistance change versus relative deformation, when samples exposed to ethyl acetate vapour. Experimental data points theoretically fitted with Eq.(9).

Summarizing results presented in the section „**Simultaneous electrical resistance, mass and length measurements**” following conclusions are made:

1. VOC induced 3 parameter change of PNCC is dependent on VOC and matrix compatibility. As better compatibility, as more VOC is absorbed, as lager is PNCC swelling and electrical resistance change.

2. Simultaneous electrical resistance and relative deformation change of the composite at the time of VOC detection and relaxation in the air indirectly indicate that CB filler is covalently bond with polyisoprene macromolecules.
3. PNCC ability to swell in the presence of VOC is dependent of used filler. CB restricts macromolecule mobility, but not swelling, because macromolecules can move CB aggregates/particles. MWCNT act as reinforcement of the polymer. LMWCNT has more evident reinforcing action than SMWCNT and it limits the composite expansion.
4. R,m,l measurement results evidence that electrical resistance relaxation process is related to macromolecule ability to rearrange and recover equilibrium state which corresponds to desorbed state. At a mean time macromolecules move particles closer to each other till their approximate initial distance is renewed and composite initial resistance is reached.
5. In PiNCC anomalous VOC diffusion mechanism exists and it conforms to comparable VOC diffusion velocity and polymer macromolecule mobility.
6. VOC diffusion analysis in PiNCC evidences that polyisoprene macromolecule ability to follow diffusion velocity decreases with increase of diffusion velocity, because macromolecules are bond to filler particles with chemical bonds.
7. Experimentally proved that PiNCC VOC sensor effect is based on VOC induced composite swelling, particle inter-distance increase, tunneling current decrease and composite electrical resistance exponentially increase with respect to relative deformation. In addition to that, in PiNCC two more electrical resistance change mechanisms have been observed, which are related to destruction of conductive channels and VOC electrical conductivity.
8. Electrical resistance change mechanism in the presence of diverse VOC for the same composite is dependent on PiNCC swelling and it is determined by VOC/polymer compatibility.
9. At the same relative deformation of PiNCC in different VOC electrical conductivity of the VOC must be taken into account. If it is remarkably higher than polymer (dielectric) conductivity, then VOC shunts composite electrical resistance.
10. VOC induced electrical resistance change mechanism is determined by the composite conductive network structure, its building elements (particles or nanotubes), aggregation extent of the filler, shape and size of aggregates and dispersion quality within the matrix as well.

In the last subsection of experimental part device prototype for VOC detection elaborated by student of Riga Technical University Einārs Deksnis (Fig.19) is described. In the prototype PiCB848h composite as VOC sensor element is integrated. In this section measurements representing the VOC detection threshold for PiCB848h and PiSMWCNT17 composites are also demonstrated. Measurements were made in the following order. Both composites and probe of photoionization detector were placed

into the test chamber. Toluene was injected into the test chamber. At the same time electrical resistance change of composites and toluene concentration increase by photoionization detector was monitored.

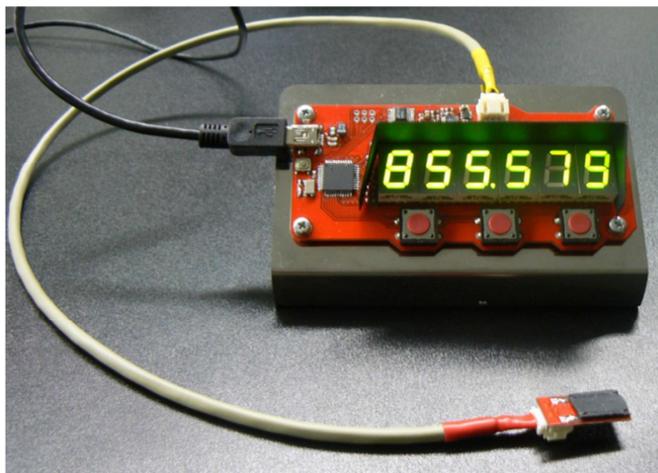


Fig.19. Device prototype with integrated PiCB848h sensor element.

CONCLUSIONS

1. New sensor material intended for volatile organic compound (VOC) detection is elaborated based on conductive filler (CB or MWCNT) and polyisoprene. VOC detection threshold of the sensor material is 75ppm (toluene), which is lower than regulated exposure limits. The working principle of sensor material is systematically researched using original setup and method.
2. Conducting network structure and electrical resistance of PiCB composite is dependent on filler dispersion technology in the matrix. If mixing using cold rolls is applied for filler dispersion, then the composite conductive network is made of isolated complex shape CB aggregates. In this case larger amount of CB filler is necessary to obtain conductive composite. If filler is dispersed in matrix by solution mixing method, then conductive network of the composite consists of simple shape CB aggregates, less filler is necessary to gain conductive composite. In this case shape complexity of CB aggregate is determined by viscosity of the mixture at the time of composite production.
3. Conductivity of PiMWCNT composites can be obtained at smaller filler concentrations if MWCNT with higher aspect ratio is used. Experimentally determined PiLMWCNT percolation threshold is remarkably higher than theoretically calculated due to LMWCNT spaghetti like structure, which significantly decreases aspect ratio of nanotubes. However, MWCNT/polymer interaction cannot be excluded as well.
4. PNCC conductivity, according to determined percolation parameters, is dependent on utilized matrix structure (crystalline, amorphous, amorphous-cross linked) used for a composite production. Percolation threshold is achieved at lower filler concentrations if crystalline polymer with linear and compactly arranged macromolecules is used.
5. PNCC with selective VOC sensor effect are elaborated; the sensor effect is reversible – PNCC after exposure to VOC recovers initial electrical resistance. Electrical resistance relaxation process is related to matrix macromolecule ability to rearrange and recover equilibrium state which corresponds to desorbed state of matrix. At a mean time macromolecules move particles closer to each other till their approximate initial distance is renewed and composite initial resistance is reached.
6. PNCC electrical resistance change in the presence of VOC is generally influenced by VOC compatibility with the composite matrix. VOC and polyisoprene compatibility is evaluated by comparing Hansen solubility parameters and relative energy difference. PiNCC sensitivity to VOC increases with relative energy difference decrease.
7. Three parameter change in time is registered using original setup and method, when PNCC samples are exposed to VOC and during relaxation in the air. PNCC three

parameter change is dependent on VOC and matrix compatibility. As better it is as larger amount of VOC is absorbed, higher swelling of the composite and larger electrical resistance change achieved.

8. Experimentally determined that in PiNCC anomalous VOC diffusion mechanism exists and it conforms to comparable VOC diffusion velocity and polymer macromolecule mobility. However, polyisoprene macromolecule ability to follow diffusion velocity decreases with increase of diffusion velocity, because macromolecules are bond to filler particles with chemical bonds.
9. Experimentally proved that PiNCC VOC sensor effect is based on VOC induced composite swelling, particle inter-distance increase, tunneling current decrease and composite electrical resistance exponentially increase with respect to relative deformation. In addition to that, two more electrical resistance change mechanisms have been observed in PiNCC, which are related to destruction of conductive channels and VOC electrical conductivity.

REFERENCES

- [1] Balberg I., *A comprehensive picture of the electrical phenomena in carbon black a “ polymer composites//Physical Review B – 2002 – Nr. 40 – 139.-143.lpp.*
- [2] Balberg I., Azulay D., Toker D., Millo O., *Percolation and tunneling in composite materials//International Journal Of Modern Physics B – 2004 – Nr.18 – 2091.-2121.lpp.*
- [3] Zhang X.W., Pan Y., Zheng Q., Yi X.S., *Time dependence of piezoresistance for the conductor-filled polymer composites//Journal of polymer science: B – 2000 – Nr.38 – 2739.-2749.lpp.*
- [4] Bauhofer W., Kovacs J.Z., *A review and analysis of electrical percolation in carbon nanotube polymer composites//Composites Science and Technology – 2009 – Nr.69 – 1486.-1498.lpp.*
- [5] Zeng W., Zhang M., Rong M., Zheng Q., *Conductive polymer composites as gas sensors with size-related molecular discrimination capability//Sensors and Actuators B: Chemical – 2007 – Nr.124 – 118.-126.lpp.*
- [6] Connor M.T., Roy S., Ezquerro T.A., Baltá Calleja F.J. *Broadband ac conductivity of conductor–polymer composites//Physical Review B - 1998 – Nr.57 – 2286.–2294.lpp.*
- [7] Zavickis J., Linarts A., Knite M. *The Electrical Percolation Shift in Polyisoprene - Nanostructured Carbon Composite //Conference of Young Scientists on Energy Issues: Conference Proceedings, Lietuva, Kauņa, 27.-28. maijs, 2010 - 408.-415. lpp.*
- [8] Zavickis J., Linarts A., Knite M. *The downshift of electrical percolation threshold in polyisoprene-nanostructured carbon composite//Energetika – 2011 – Nr.1 – 44-49.lpp*
- [9] Brandrup J., Immergut E.H. *Polymer handbook 3rd edition. – New York: John Wiley&Sons Inc., 1989. – V7.-V8.lpp.*
- [10] Vieth W.R. *Diffusion in and through polymers. – New York: Oxford University Press, 1991 – 22.-29.lpp.*
- [11] Crank J., Park G.S. *Diffusion in polymers. – New York: Academic Press, Inc., 1968 – 15. -16. lpp.*
- [12] Neogi P. *Diffusion in Polymers. - New York: Marcel Dekker, Inc. , 1996 – 184.–185.lpp.*
- [13] Yang Y., Huang Y., Wang D., Liu H., Hu C., *Sorption and diffusion of ethanol vapour polybutadiene/acrylonitrile, polybutadiene/styrene and polybutadiene based polyurethanes//Eur. Polym. J. – 2004 – Nr.40 – 855.–863.lpp.*
- [14] Knite M., Kiploka A., Teteris V., Kaupuzs J. *Polyisoprene-Carbon Black Nanocomposites as Tensile Strain and Pressure Sensor Materials // Sensors and Actuators A – 2004 – Nr.110 - 142.-149. lpp.*
- [15] Luheng W., Tianhuai D., Peng W., *Influence of carbon black concentration on piezoresistivityfor carbon-black-filled silicone rubber composite// CARBON – 2009 – Nr.47 – 3151. –3157.lpp.*

LIST OF PUBLICATIONS

SCI journal papers

- 1) The investigation of sensing mechanism of ethanol vapour in polymer-nanostructured carbon composite. G.Sakale, M.Knite, V.Teteris, V. Tupureina, S.Stepina; E.Liepa. Central European Journal of Physics, 2011, 9, 307-312.
- 2) Polyisoprene-nanostructured carbon composite (PNCC) organic solvent vapour sensitivity and repeatability. G.Sakale, M.Knite, V.Teteris. Sensors and Actuators A: Physical, 2011, 171, 19-25.
- 3) Diffusion, swelling and electrical properties of polyisoprene/multiwall carbon nanotube composites in organic solvent vapours. G.Sakale, M.Knite, V.Teteris. Journal of nanoscience and nanotechnology, 2012, doi:10.1166/jnn.2011.4519 (*in print*)

SCI publications in conference proceedings

- 1) Polyisoprene – nanostructured carbon composite (PNCC) material for volatile organic compound detection. Sakale G., Knite M., Teteris V., Tupureina V. International Conference on Biomedical Electronics and Devices, 2009. January, Portugal, Porto. – Porto: INSTICC PRESS, 2009, 117.-122.
- 2) Atmosphere control by chemoresistive polymer composites. Sakale G., Knite M., Novada M., Liepa E., Stepina S., Tupureina V. Proceedings of the 8th International Conference on Informatics in Control, Automation and Robotics, Netherland, Noordwijkerhout, July, 2011, 370.-375.
- 3) Polymer nanomaterials for novel sensing systems: Nanocomposites for chemical sensing. A. Sternberg, I.Muzikante, R.Dobulans, D.Millers, L.Grigorjeva, K.Smits, M.Knite, G.Sakale. NATO Advanced Research Workshop NATO ARW CRB.NUKR.ARW 984333 Nanodevices and Nanomaterials for Ecological Security 2012, (*in print*).

Results of doctoral dissertation are presented in the following international conferences

1. International Conference on Biomedical Electronics and Devices, Porto, Portugal, January, 2009. Oral presentation: G.Sakale, M.Knite, V.Teteris, V.Tupureina. Polyisoprene – nanostructured carbon composite (PNCC) material for volatile organic compound detection.
2. International conference “Functional materials and nanotechnologies” Riga, Latvia, April, 2009. Oral presentation: G.Sakale, M.Knite, V.Tupureina, V.Teteris. PNCC electric resistance versus organic solvents vapour characteristics.
3. 11th International conference-school “Advanced materials and technologies”, Palanga, Lietuva, 27.-31. Augusts, 2009.
4. Baltic Polymer Symposium 2009, Septembris, Ventspils, Latvija, 22. Septembris – 25.septembris, 2009. Stenda referāts: Sakale G., Knite M., Teteris V., Klemenoks I.,

- Tupureina V. Elaboration of Miniature Polyisoprene-Nanostructured Carbon Composite for Volatile Analyte Detection.
5. Rigas Technical university 50th International scientific conference, Riga, Latvia, October, 2009. Oral presentation: M.Knite, V.Teteris, G.Šakale. Organic solvent vapour induced electric resistance, mass and longitude change in-situ measurements for polyisoprene-nanostructured carbon composite.
 6. International conference “Functional materials and nanotechnologies”, Riga, Latvia, March, 2010. Oral presentation: Sakale G., Knite M., Teteris V. The investigation of organic solvent vapour sensing mechanism on polymer-nanostructured carbon composite.
 7. 20th Anniversary World Congress on Biosensors 2010, Glasgova, Unied Kingdom, May, 2010. Poster presentaion: Sakale G., Knite M., Teteris V. Sensing element performance analyses using in-situ measurements of electric resistance, mass and the sample length change.
 8. European Materials Research Society Spring Meeting 2010, Strastbourg, France, June, 2010. Poster presentaion: Sakale G., Knite M., Teteris V., Zavickis J. Polyisoprene-nanostructured carbon composite (PNCC) organic solvent vapour sensitivity and repeatability.
 9. The 9th International Conference on Global Research and Education, Riga, Latvia, August, 2010. Oral/poster presentation: Sakale G., Knite M., Teteris V. Filler dispersion method effect on polyisoprene-nanostructured filler composite (PNFC) vapour sensitivity. (Presentation has been awarded with Young researchers award).
 10. Rigas Technical university 51st International scientific conference, Riga, Lavtia, October, 2010. Oral presentation: G.Šakale, M.Knite, V.Tupureina, S.Stepiņa, E.Liepa Matrix material selection for organic solvent vapour sensitive nanostructured composite production.
 11. International conference Functional materials and nanotechnologies, April, 2011, Riga, Latvia. G.Sakale, M.Knite, V.Teteris. Poster presentation: Evaluation of analyte vapour diffusion in polymer-nanostructured carbon composite.
 12. 8th International Conference on Informatics in Control, Automation and Robotics, Netherland, Noordwijkerhout, July, 2011. Šakale G., Knite M., Novada M., Liepa E., Stepiņa S., Tupureina V. Oral presentation: Atmosphere control by chemoresistive polymer composites.
 13. Rigas Technical university 52nd International scientific conference, Riga, Latvia. October, 2011. G.Šakale, M.Knite. Oral presentation: Evolution of polyisoprene-nanostructured carbon composite structure and properties during vulcanization.
 14. 9th International conference on Nanosciences & Nanotechnologies, Griekija, Thessaloniki, July, 2012. Sakale G., Knite M., Aulika I., Jakovlevs D. Oral presentation: Percolation phenomena and chemoresistivity study of polyisoprene-MWCNT composite.

Participation in international summer schools:

1. 1st COST COINAPO Summer School “Characterisation Work Group: from Functional Nanomaterials to Composites” July 25-27, 2011, Oxford, United Kingdom.
2. 21st Jyväskylä Summer School August 8-19, 2011, Jyväskylä, Finland. During the summer school following courses have been passed:
 - a. Introduction to Micro- and Nanorobotics.
 - b. Processing of High Dimensional Data.
 - c. Nonlinear microscopy - Four wave mixing (FWM) imaging techniques and their applications - from nanomaterials to biological application.