

POLYISOPRENE – NANOSTRUCTURED CARBON COMPOSITE (PNCC) MATERIAL FOR VOLATILE ORGANIC COMPOUND DETECTION

Gita Sakale, Maris Knite, Valdis Teteris

Institute of Technical Physics, Riga Technical University, Azenes iela 14/24, Riga, Latvia

Velta Tupureina

Institute of Polymer Materials, Riga Technical University, Riga, Latvia

Keywords: Polymer-high structured carbon black composite, Volatile organic compound sensors.

Abstract: Our scientific group has chosen the elaboration of conductive composite material, which could be useful for volatile organic compound detection, as one of research areas. It was found out that the most sensitive composite material consists of polyisoprene and 10 mass parts of nanostructured carbon black. The electric resistance changes of the composite in presence of 10 different saturated organic solvents vapour were measured. Results obtained from our mass-sorption experiments indicated that electrical resistance of the composite increases because of volatile organic compound (VOC) molecule absorption in the composite matrix material. We also evaluated VOC compatibility with PNCC matrix material and estimated how the PNCC resistance change velocity (v_R) versus organic solvent vapour molecule diameter varies.

1 INTRODUCTION

Available statistical data evidence about people exposed to organic solvent daily at their workplaces, but there are no monitoring devices used to control VOC concentration in the room. There is also a necessity to protect environment and equipment from exposure to VOC. Above mentioned denotes that there is an urgent need for VOC sensor materials.

Devices (sorbent polymer films, metal oxide semiconductors, quartz microbalance (quartz resonator), laser gas sensors ect.) in the market can not still be compared with mammal's olfactory system. Scientists are trying to design a prototype of sensor which in sensing capability of different gases could be close to mammals olfactory system and even could be improved for practical applications.

We think that the desirable result of VOC detection can be achieved by using polymer – carbon black composites as gas sensor materials because polymer matrix can be selected for direct volatile compound detection and identifying.

In our opinion a candidate sensor material for gas sensing should fulfil the following criteria: not

expensive constituent materials; simple production; fast and reversible response; in-situ control of VOC; small dimensions of sensing element and ability to function for a long period of time.

The mechanism how polymer – carbon black composite detects VOC is as follows: i) the sample of the composite material is exposed to VOC, molecules of VOC adsorb on the surface of composite and diffuse into the matrix material; ii) intermolecular chains in the polymer matrix weaken and form intermolecular chains between VOC molecules and macromolecules of matrix material; iii) the matrix material swells; iv) electroconducting pathways break down because distance between carbon black aggregates increases; v) at the same time tunnelling currents between carbon aggregates in thin layers of matrix decreases and the electrical resistance of the composite increases.

2 EXPERIMENTAL

Polyisoprene – nanostructured carbon composite material was made by rolling highly structured nano-size carbon black PRINTEX XE2 (specific surface

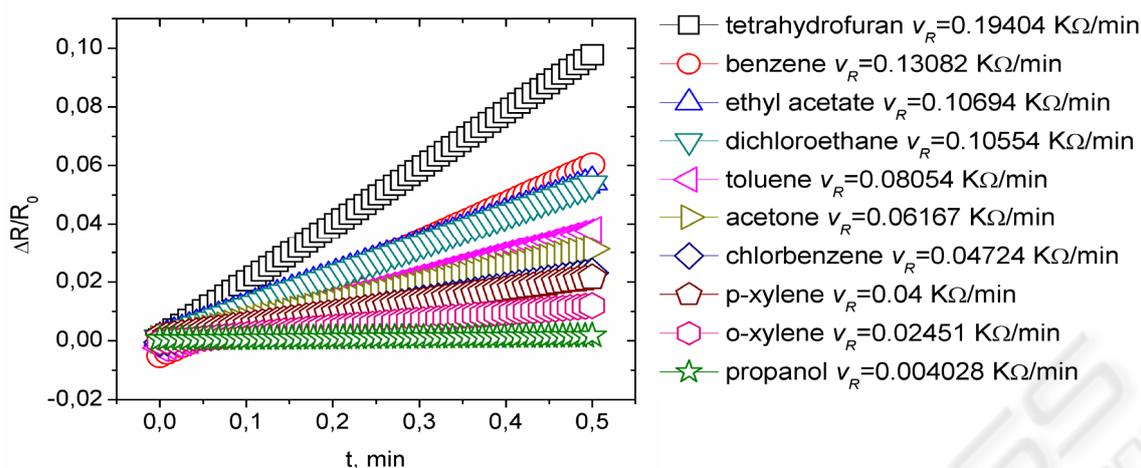


Figure 1: The change of relative resistance vs. time for the sample, held in saturated vapours of different solvents.

950 m²/g, mean diameter of primary particles 25 nm, DBP absorption 380 ml/100g) and necessary additional ingredients – sulphur and zinc oxide – into a Thick Pale Crepe No 9 Extra polyisoprene matrix using cold rolls. Then follows vulcanization process (under 30BAR pressure at 150°C for 15 minutes) when not only sulphur crossbonds form but also possibly chemical bonds between carbon black nanoparticles and matrix macromolecules form. As better carbon black particle electroconductive grid is connected with polyisoprene macromolecules as better sensing element to any kind of deformation is achieved.

Preparation of samples and schematic illustration of the experimental set-up is described in (Knite, 2007).

2.1 The Change of PNCC Electrical Resistance Due to VOC Presence

Samples were exposed to vapour for 30 seconds and then held in open air for relaxation processes to let go on until the composite material reaches its initial resistance R_0 . Then the measurement was repeated. Composite material response to different saturated organic solvents vapour can be seen in Fig. 1. In the figure v_R denotes electrical resistance change velocity (KΩ/min). It is obvious that the largest resistance change velocity is obtained when PNCC is exposed to tetrahydrofuran vapour followed by benzene, ethylacetate and dichloroethane ect. In the case of propanol vapour PNCC resistance did not change at all. The composite can not sense the presence of propanol vapour. In these experiments PNCC samples with dimensions 50 x 5 x 1 mm (length x width x thickness) were used.

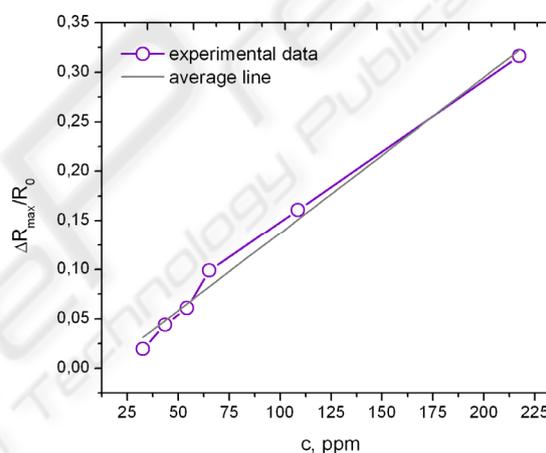


Figure 2: Resistance change of PNCC vs. toluene vapour concentration.

We carried out experiments with PNCC samples with dimensions 50 x 5 x 0,25 mm also. The composite capability to sense different toluene vapour concentrations were tested (Fig. 2.). Resistance of PNCC increases proportionally to toluene vapour concentration. Here we would like to mention that PNCC can sense concentrations which are equal to or lower than TWA limits (TWA indicates a time-weighted average concentration for up to a 8-hour workday during a 40-hour workweek) (<http://www.cdc.gov>). In the case of toluene vapour TWA limit is 200 ppm.

2.2 The Relaxation Process of PNCC Electrical Resistance

After samples were subjected to saturated organic solvents vapour electrical resistance relaxation

process in air were carried out. Typical PNCC sample with thickness 1mm relaxation process is shown in Fig.3.

Experimentally obtained data were fitted with theoretical curve which can be characterised by equation:

$$R = R_0 + A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (1)$$

, where

R_0 – initial electrical resistance

R – transient electrical resistance

A_1, A_2 – constants

τ_1, τ_2 – relaxation time (h).

From equation (1) we calculated relaxation time τ_1 and τ_2 . For all tested organic solvent vapour the relaxation process can be divided into fast and slow processes.

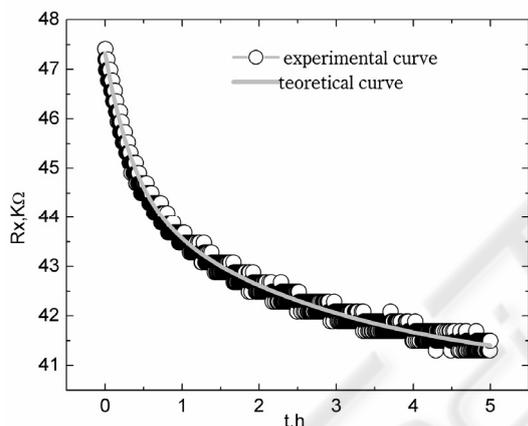


Figure 3: Electrical resistance relaxation of specimen in open air. The sample was exhibited to tetrahydrofuran for 30s.

In the case of 250 μ m thick samples electrical resistance relaxation process is about one hour if the sample has been exposed to 108,7 ppm toluene vapour concentration.

2.3 Mass – sorption Experiments

Experiments of the change of the sample mass as a function of time the sample is kept in organic solvent vapour were used to find out the mechanism of the change of resistance. For example, specimens of pure polyisoprene, PNCC, and a pellet of compressed high-structured carbon black powder were held in toluene vapour for ~ 48 hours and a mass as a function of time (sorption curve) was recorded (Fig. 4.). Sorption of vapour in carbon filler in the initial period (first 15 min) is approximately

three times (approximately 1,5 times after up to 104 min) as big as that of pure polyisoprene rubber. Yet the sorption of vapour in PNCC material in the initial period is around 1,3 times shorter if compared with pure polyisoprene rubber, although it seems that carbon filler should increase the vapour sorption in the PNCC material. That can be explained, firstly, by the fact that in the PNCC composition there are only 10 mass parts of carbon and, secondly, in processing (mixing and vulcanizing) the PNCC compounds insulating polyisoprene layers are formed between the carbon nano-particles. So, even near the percolation threshold (10 mass parts of carbon), when electro-conductive channels are formed, very thin polyisoprene intermediate layers between the nano-particles still exist and tunnelling currents may emerge between the channels.

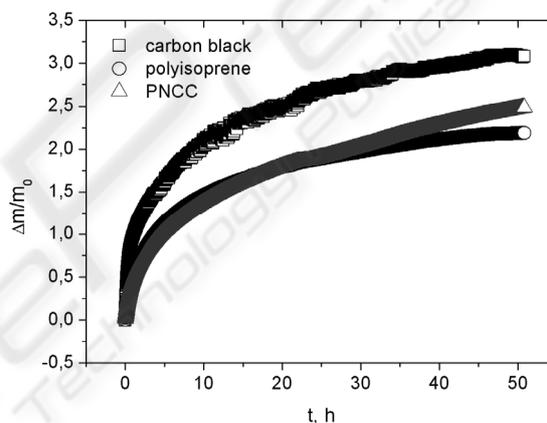


Figure 4: The change of mass for three materials (polyisoprene rubber, HSCB and its composite) as functions of the time of exposure to toluene vapour.

Only after approximately 28 h the sorption of vapour by the PNCC material noticeably exceeds the sorption by polyisoprene rubber, which indicates that only after this period of time the sorption in the filler begins to play substantial role. Consequently, 1) the obtained result indirectly proves the existence of quantum effect – tunnelling currents in the PNCC material, 2) sorption of vapour in the polyisoprene matrix plays absolutely uppermost role in effect of gas sensing (due to sorption of vapour molecules and swelling of the matrix the distance between carbon nano-particles increases and tunnelling currents rapidly decrease) (Knite, Shakale 2007).

3 DISCUSSION

3.1 Electrical Resistance as a Function of VOC Molecule Diameter

Previously we have made positron annihilation lifetime spectroscopy measurements for PNCC in collaboration with scientists from Monash University in Australia (Knite, 2006). The purpose of these experiments was to evaluate free volume cavities dimensions in the composite material when it is stretched and in normal (unloaded) state. As it can be seen from Fig. 5 free volume mean radius for PNCC containing 10 mass parts of carbon black in normal state is 3,305Å. Then diameter of free volume cavities is 6,61Å. When molecule diameters of VOC are smaller than the diameter of free volume cavities in the composite material then there is no need for extra activation energy for molecule diffusion into the matrix material.

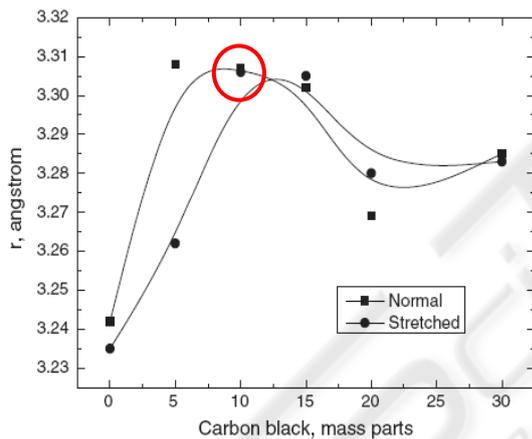


Figure 5: Mean radius of free volume cavities in PNCC as a function of carbon black content in normal and stretched ($\Delta l = 15$ mm) states measured by PALS.

Molecule volume of VOC was calculated using equation (Askadcli, 1983):

$$\sum_i \Delta V_i = \frac{k \cdot M}{N_A \cdot \rho} \quad (2)$$

, where

k – Atoms packing density

N_A – Avogadro number, mol^{-1}

$\sum_i \Delta V_i$ – Van der Valse volume of VOC molecule,

which consists of discrete atom volume sum, cm^3

M – Molar mass of VOC, g/mol

ρ – Density of VOC, g/cm^3 .

After calculation of VOC molecule volume we accepted approximation that all molecules take the form of sphere. Finally we calculated diameters of VOC molecules. We suppose with increasing molecule diameter of organic solvent vapour the maximum PNCC electrical resistance change $\Delta R_{\max}/R_0$ should be decreased.

In Fig. 6 we can see that above mentioned realizes only partly. $\Delta R_{\max}/R_0$ increases with increasing molecule diameter starting from acetone vapour until tetrahydrofuran vapour. In our opinion this means that $\Delta R_{\max}/R_0$ is not dependent only from organic solvent vapour molecule dimensions.

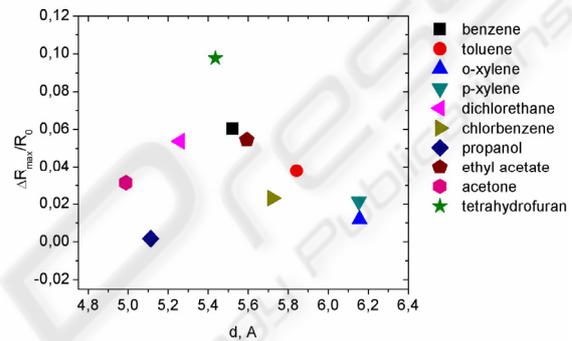


Figure 6: Electrical resistance change of PNCC vs. organic solvents vapour molecule diameter.

$\Delta R_{\max}/R_0$ decreases with increasing molecule diameter of organic solvents vapour in Fig. 6 from tetrahydrofuran vapour until o- and p-xylene vapour. In the case of toluene and chlorobenzene an exception has to be made. Toluene vapour causes greater $\Delta R_{\max}/R_0$ change than chlorobenzene vapour, while molecule diameter of toluene molecule is larger than that of chlorobenzene.

3.2 VOC Compatibility with Polymer Matrix Material

The law “like dissolves the like” is already well enough known. Polar solvents dissolve in polar solvents and analogous non-polar dissolve in non-polar solvents. This also can be attributed to organic solvents and polymer materials.

To evaluate organic solvents compatibility with polyisoprene matrix material we compared solvents dielectric permeability (ϵ) values to polyisoprene ϵ value. As ϵ value of organic solvents is closer to polyisoprene ϵ as the matrix material better absorbs solvent molecules and then greater V_R change is observed.

From literature data (Brandrup, 1989) we know

that polyisoprene dielectric permeability value is 2,68. Organic solvent vapour dielectric permeability values are summarized in Table 1.

Table 1: VOC dielectric permeability values.

Substance	ϵ	Type of solvent
P-xylene	2,2	Non-polar
Benzene	2,3	
Toluene	2,3	
O-xylene	2,5	
Chlorobenzene	5,6	Weakly polar
Ethyl acetate	6	
Tetrahydrofuran	7,4	
Dichloroethane	10,6	Polar
Propanol	20,1	
Acetone	20,7	

From Fig. 7 we can see that PNCC resistance response to organic solvent vapour is concentrated into three groups. First let us begin with polar organic solvents group. As we can see in this group small electric resistance change is observed while molecule dimensions of these solvents are the smallest from all tested organic solvents. It can be explained by acetone, propanol and dichloroethane vapour non-compatibility with the composite matrix material. Thus, we can conclude that resistance change in this group is more dependent of organic solvents vapour compatibility with the composite matrix material.

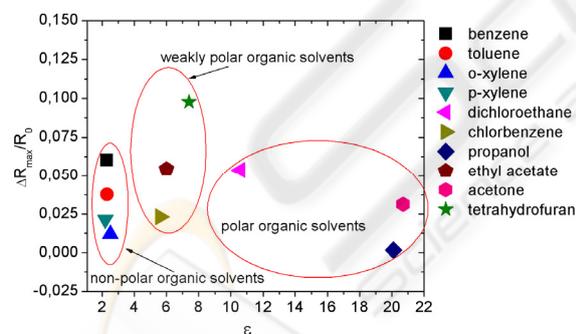


Figure 7: PNCC resistance change vs. organic solvents dielectric permeability values.

We will continue discussion with weakly polar and non-polar solvents group. From Fig. 6 and Fig. 7 we can see that in these groups molecule dimensions and dielectric permeability compensate each other and both affect the composites response to organic solvents vapour. For example, tetrahydrofuran vapour molecule diameter is the smallest from these two groups and the largest $\Delta R_{max}/R_0$ value is obtained, while ϵ value is 7,4.

Above we compared toluene and chlorbenzene vapour caused electrical resistance change versus vapour molecule dimensions. If we look at Fig. 7 then we can see that chlorbenzene belongs to weakly polar solvents group. Chlorbenzene vapour is less compatible with the composite matrix material. For that reason PNCC resistance change in chlorbenzene vapour is smaller then in toluene vapour. If we compare mass of molecule for toluene and chlorbenzene then for toluene it is $15,30 \cdot 10^{-23}$ g and for chlorbenzene it is $18,69 \cdot 10^{-23}$ g. From kinetic-molecular theory we know that for molecules with smaller mass the motion velocity is higher. This also explains why resistance change of PNCC is larger in the case of toluene vapour.

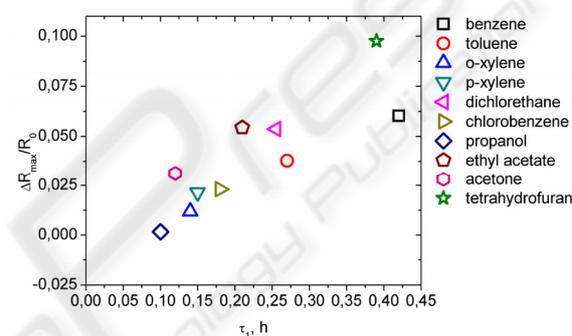


Figure 8: Relaxation time τ_1 vs. resistance change in organic solvents vapour.

Composites organic solvent vapour sensing mechanism is based on matrix swelling, which causes increased distance between carbon black aggregates and resistance change of the composite. As larger is value $\Delta R_{max}/R_0$ as larger is amount of organic solvent vapour molecules the composite has absorbed and as longer should be relaxation process. According to afore said relaxation time τ_1 and τ_2 should be proportional to $\Delta R_{max}/R_0$ change. Concerning Fig. 8 we can say that τ_1 are nearly proportional to $\Delta R_{max}/R_0$, but there are also some exceptions which are related to previously described molecule dimensions and organic solvents compatibility with polymer matrix material. But from Fig. 9 we can not find any mathematical relationship between $\Delta R_{max}/R_0$ change and τ_2 values.

We conclude that fast relaxation processes (τ_1) are determined by vapour molecule diffusion from swelled matrix interior layers to the surface and crosslinked macromolecule relaxation. Slow relaxation processes (τ_2) are related to electroconductive grid relaxation made of carbon black particles.

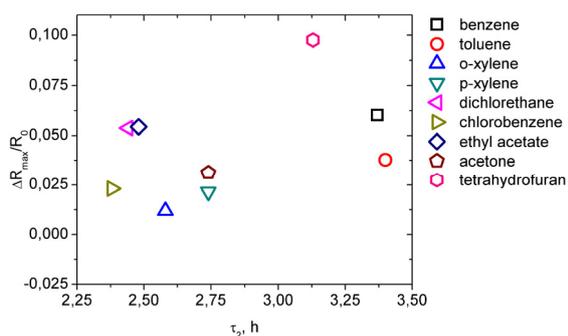


Figure 9: Relaxation time τ_2 vs. resistance change in vapour of organic solvents.

4 CONCLUSIONS

In conclusion we can say that for the production of PNCC we used not expensive and available materials. The production of the composite is rather simple if the production procedure is strictly performed. When PNCC is exposed to VOC the electrical resistance of the composite increases rapidly and the effect is reversible. Electric resistance change velocity is dependent of both VOC molecule diameters and VOC compatibility with PNCC matrix material.

Better sensitivity PNCC exhibits when it is exposed to non-polar or weakly polar solvent vapour. So, we can declare that PNCC sensing of VOC is selective.

Further, in our work, we are going to try to decrease relaxation time of electrical resistance to couple of minutes or even seconds. We suppose that PNCC can be used for VOC detection with some improvements, for example, reducing dimensions of the composite to optimal size. Else, functioning of PNCC needs to be evaluated in long time period.

REFERENCES

- Knite, M., Klemenok, I., Shakale., G., Teteris, V., and Zicans, J., 2007. *J. Alloys Comp.*
- Knite, M., Shakale, G., Klemenoks, I., Ozols, K., Teteris, V., 2007. *Journal of Physics: Conference Series* 93, 012031.
- Askadcli, A. A., Matveev, J. I., 1983. *Chemical structure and physical characteristics of polymers*, Kimija: Moscow.
- Knite, K., Hill, A.J., Pas, S.J., Teteris, V., Zavickis, J., 2006. *Materials Science & Engineering C*, V 26.
- Brandrup, J., Immergut, E.H., 1989. *Polymer handbook*, John Wiley&Sons: New York, Chichester, Brisbane, Toronto, Singapore, 3rd edition.