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Sensing element performance analyses using in-situ measurements of electric resistance, mass and the sample length change

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Sensing element made of polyisoprene and nanostructured carbon black particles (mean size: 30nm, specific surface: 950m²/g) for organic solvent vapour (osv) detection have been produced. To create very sensitive and reusable sensor material for the air quality monitoring, we have to analyze possible sensor material osv detection performance. Using in-situ measuring technique we determined absorbed analyte amount by the composite, analyte induced elongation of the sample and electric resistance change(see Fig. 1).

Mass-sorption data is the source for evaluation of sensor material suitability for vapour detection. First, we can calculate analyte diffusion coefficient in to the composite. Second, we can find out diffusion behaviour. From diffusion theory: $\frac{M_t}{M_\infty} = k \cdot t^n$, where M_t is mass uptake

in time t , M_∞ is mass uptake, when time (t) approaches infinity. n and k are constants. If $n=0,5$ then the rate of diffusion is much slower than molecular chain relaxation (Fickian diffusion). When diffusion is very rapid compared with molecular chain relaxation process, then it is called Supercase II and $n \geq 1$. The third one is non-Fickian diffusion ($0,5 < n < 1$) that occurs when the diffusion rate and molecular chain relaxation are comparable [1]. For sensor material with immediate response to vapour the value of n should be within $0,5 \leq n < 1$.

Length and electric resistance measurements let us evaluate resistance change mechanism. We have found out that at short exposure time electric resistance of the composite increases due to tunnelling current decrease in thin layers of matrix between carbon black aggregates (see Fig.2. 1.tunneling). But further exposure of composite to vapour leads to extreme increase of R/R_0 and it is related to destruction of the conducting network (at deformations larger than 0,018). The process can be described by equation (see Fig.2.):

$$\ln R = \ln R_0 + \ln \left[1 + \frac{\Delta l}{l_0} \right] + A \left(\frac{\Delta l}{l_0} \right) + B \left(\frac{\Delta l}{l_0} \right)^2 + C \left(\frac{\Delta l}{l_0} \right)^3 + D \left(\frac{\Delta l}{l_0} \right)^4, \text{ where } R \text{ is}$$

samples electric resistance, R_0 —samples initial electric resistance and $\Delta l/l_0$ —relative elongation of the sample [2].

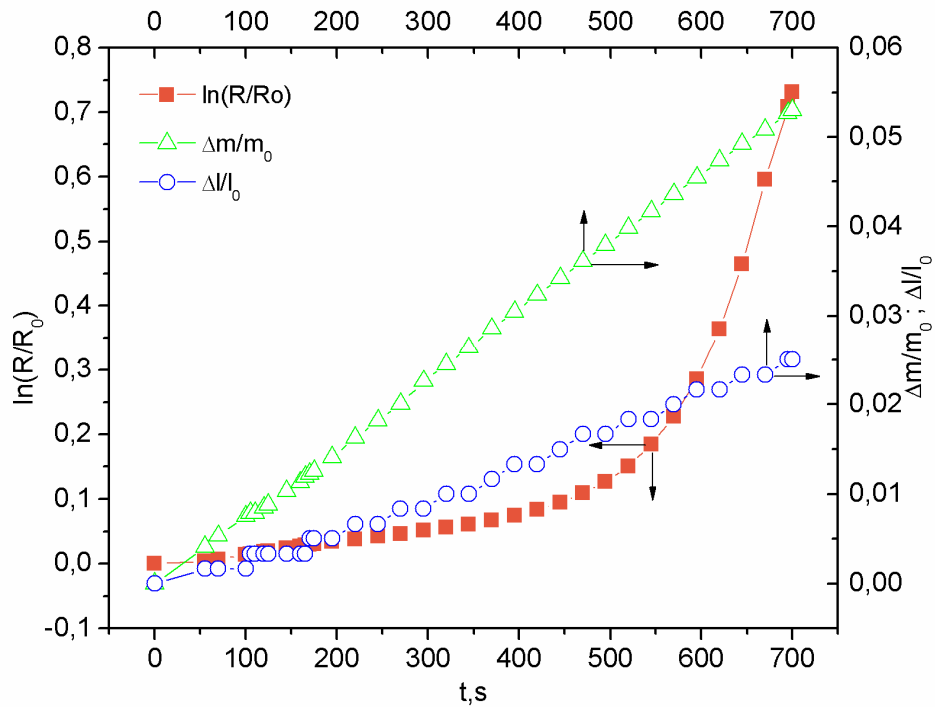


Fig. 1. The composite electric resistance (R/R_0), mass ($\Delta m/m_0$) and longitude change ($\Delta m/m_0$) versus time (t) in toluene vapour.

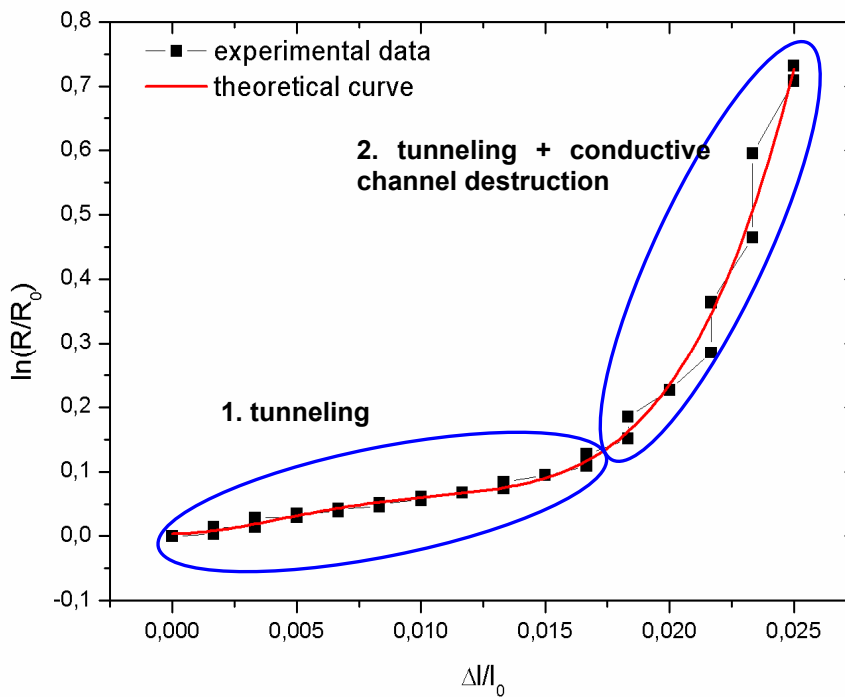


Fig. 2. Electric resistance of the composite versus relative elongation of the composite, when it is held in toluene vapour for 700 seconds.

[1] Y. Yang, Y. Huang, D. Wang, H. Liu, C. Hu, Sorption and diffusion of ethanol vapour polybutadiene/acrylonitrile, polybutadiene/styrene and polybutadiene based polyurethanes, European Polymer Journal 40 (2004) 855-863.

[2] M.Knite, V.Teteris, A.Kiploka, J.Kaupuzs, Polyisoprene-carbon black nanocomposites as tensile strain and pressure sensor materials, *Sensors and Actuators A* 110 (2004) 142–149.

Keywords: diffusion in composite, tunneling current, organic solvent vapour detection

Introduction

Chemoresistive polymer films are promising sensor materials for contaminant detection in the air, air quality monitoring at chemical production sites and process control of chemicals or food production. Here we propose composite film volatile organic compound sensing suitability determination method by measuring simultaneously electrical resistance, mass and sample length change, when the composite is exposed to organic solvent vapour.

Volatile organic compound (VOC) molecule adsorption onto the surface of the composite and succeeding vapour molecule absorption into the composite leads to increase of the composite mass. Mass sorption data are the source for vapour diffusion mechanism evaluation in the composite, which determines the composite response speed to the presence of VOC. Vapour diffusion mechanism into the composite can be described by following diffusion relationships. Fickian diffusion mechanism is observed, when the rate of diffusion is much slower than molecular chain relaxation. As a result fast molecule diffusion can proceed and large diffusion coefficient values are obtained. Anomalous diffusion mechanism occur, when the diffusion rate and molecular chain relaxation are comparable and medium velocity diffusion process can be observed. Case II and Supercase II are diffusion processes, when diffusion is very rapid compared with molecular chain relaxation process and therefore slow diffusion process with lower diffusion coefficient values are obtained. The sample length change is a result of vapour diffusion in to the composite and subsequent composite swelling. As the composite is designed of polyisoprene matrix and nanostructured carbon black nanoparticles, then composite swelling leads to distance increase between carbon black nanoparticles aggregates and tunneling currents decrease. Subsequent composite electrical resistance increase can be observed.

RESULTS

1. Results of mass sorption

Equilibrium sorption for short times can be described by equation [1]

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

, where m_t – mass uptake in time t , m_∞ – mass uptake, when t approaches infinity, l – thickness of the sample, D – diffusion coefficient, t – time.

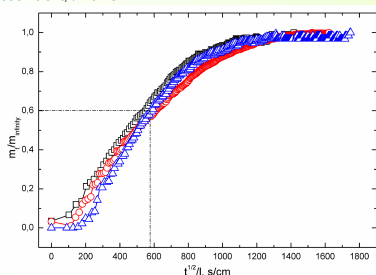


Fig. 3. Ethyl acetate vapour sorption (m/m_{∞}) by polyisoprene-nanostructured carbon composite (PNCC) (square) and pure polyisoprene (triangle) versus square root of time (t) divided by a sample thickness (l). Toluene vapour sorption by PNCC (circle) vs. square root of time (t) divided by a sample thickness (l). m_{∞} denotes mass uptake, when t approaches infinity. Vapour concentration in the chamber 0.3ml/l.

Analyte diffusion behaviour into composite can be determined by equation [2]

$$\frac{m_t}{m_\infty} = k \cdot t^n \quad (2)$$

, where m_t – mass uptake in time t , m_∞ – mass uptake, when t approaches infinity, n and k are constants.

Diffusion mechanism [2,3]:

- 1) Fickian diffusion $n = 0.5$
- 2) Anomalous diffusion $0.5 < n < 1$
- 3) Case II $n = 1$
- 4) Supercase II $n > 1$

Table 1. D and n values of PNCC and polyisoprene

Material	Vapour	D , m ² /s	n
PNCC	ethyl acetate	$2.93 \cdot 10^{-13}$	0.61
Polyisoprene	ethyl acetate	$4.47 \cdot 10^{-13}$	0.67
PNCC	toluene	$2.63 \cdot 10^{-13}$	0.57

2. Results of length and electrical resistance increase

Electrical resistance R of the composite is described by [4]:

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

, where L is the number of particles in a single conducting path, N the number of conducting paths, h the Planck's constant, s the least distance between conductive particles, a the effective cross-section of tunneling, e the electron charge. γ is a coefficient.

Experimental setup



Fig. 1. Sample in the sample holder.

Personal computer

Mass change

Electrical resistance change

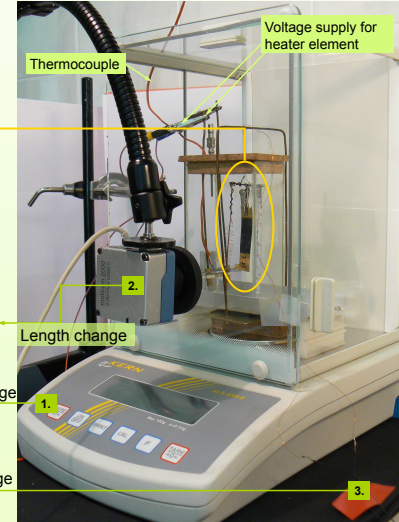


Fig. 2. Experimental setup for simultaneous mass, length and electrical resistance measurements.

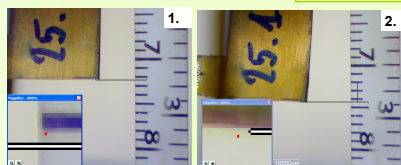


Fig. 4. Photos of end part of the sample at initial state (1.) and after exposure to toluene vapour for ~ 960s (2.).

Charge tunneling into the swelled composite can be described by equation [5]:

$$\ln R = \ln R_0 + \ln \left[1 + \frac{\Delta l}{l_0} \right] + A_0 \left[\frac{\Delta l}{l_0} \right] \quad (4)$$

at deformations $\Delta l/l_0 < 0.1$ tends to 0.
, where R is transient resistance, R_0 – initial resistance, $\Delta l/l_0$ – relative elongation, l_0 – initial length of the sample, A_0 – constant.

Conducting network destruction due to the composite extreme swelling, we describe by [5]:

$$\ln R = \ln R_0 + \ln \left[1 + \frac{\Delta l}{l_0} \right] + A \left(\frac{\Delta l}{l_0} \right) + B \left(\frac{\Delta l}{l_0} \right)^2 + C \left(\frac{\Delta l}{l_0} \right)^3 + D \left(\frac{\Delta l}{l_0} \right)^4 \quad (5)$$

, where A , B , C and D are constants

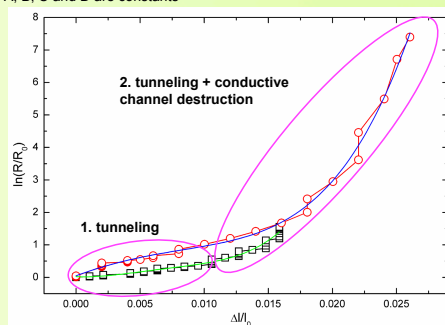


Fig. 6. Electrical resistance increase ($\ln(R/R_0)$) vs. relative elongation ($\Delta l/l_0$) of sample held in toluene (circle) and ethyl acetate (square) vapour. Solid lines denote theoretical fitting of experimental data (line and symbol) by Eq.5.

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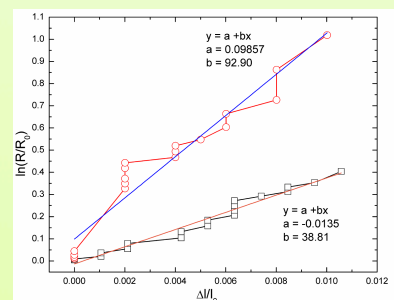


Fig. 5. Electrical resistance increase ($\ln(R/R_0)$) versus relative elongation ($\Delta l/l_0$) of sample held in toluene (circle) and ethyl acetate (square) vapour. Straight, solid line denotes theoretical fitting of experimental data (line and symbol) by Eq.4.

Conclusions

1. Volatile organic compound diffusion into the polyisoprene-nanostructured carbon composite follows anomalous diffusion relationship, which means that VOC molecule diffusion rate are comparable with polyisoprene macromolecule relaxation rate. Therefore immediate PNCC response to the presence of VOC is achieved.
2. The largest diffusion coefficient values are obtained for both pure polyisoprene and PNCC in ethyl acetate vapour. But greater electric resistance increase is observed for PNCC in toluene vapour. We suppose that faster diffusion rate of ethyl acetate vapour in comparison with toluene vapour diffusion rate in PNCC is obtained because ethyl acetate molecules are smaller than toluene vapour molecules. But it is interesting that larger diffusion coefficient does not mean always also larger PNCC swelling and electrical resistance increase of the composite. In our opinion this is observed because ethyl acetate vapour has weaker compatibility with PNCC matrix material – polyisoprene.
3. Obtained results indicate that two electrical resistance change mechanisms in the composite take place. i) At small deformations ($\Delta l/l_0 < 0.010$) predominate the changes of tunneling currents in thin layers of matrix between carbon black nanoparticle aggregates. Due to tunnelling current existence in the composite the great sensitivity to the presence of organic solvents vapour have been observed. ii) At larger deformations the electrical resistance increases extremely and it is related to destruction of the conducting network with decrease of the number of conducting paths.