RIGA TECHNICAL UNIVERSITY

August 9-12, 2010
Riga, LATVIA

iA inter-academia

The 9th International Conference on Global Research and Education

Inter-Academia 2010

DIGEST

Filler dispersion method effect on polyisoprene-nanostructured filler composite (PNFC) vapour sensitivity

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Summary

Previously polyisoprene-nanostructured carbon composite (PNCC) was prepared by mixing on cold rolls carbon black nanoparticle aggregates into the polyisoprene. The composite organic solvent vapour (*osv*) sensitivity has been evaluated (Fig.1). In this paper we are going to compare *osv* sensitivity of previously made PNCC with PNCC, which is made using sonication for carbon black nanoparticle dispersion into the polyisoprene. The composite *osv* sensitivity as a function of used filler material (carbon black nanoparticles or multi wall carbon nanotubes - MWCNT) also will be presented.

Introduction

Conductive polymer composite films are widely researched because of possible application for hazardous volatile compound detection in the air [1].

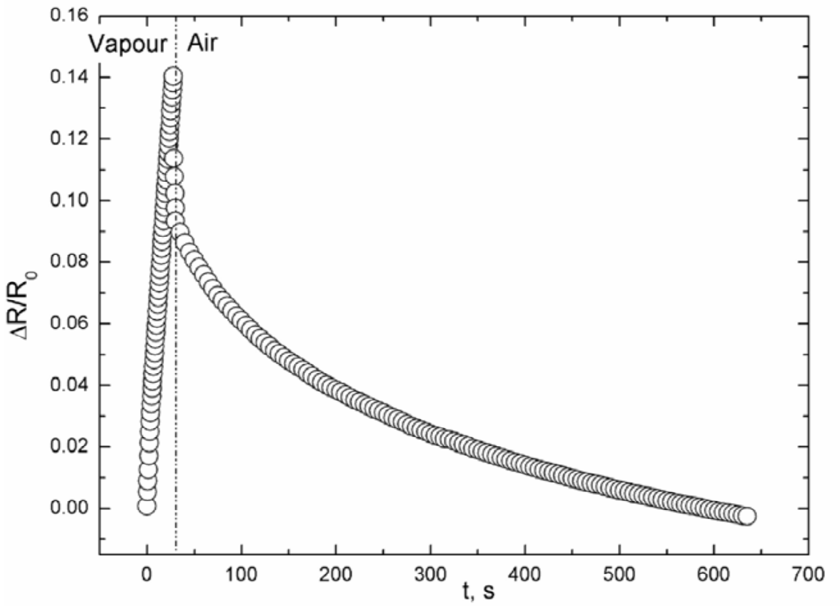

Fig. 1. PNCC (roll mixed) relative electric resistance change versus time, when the sample held in toluene vapour (94mg/l) for 30 seconds and followed by electric resistance relaxation in the air.

PNFC *osv* sensitivity basically determines two circumstances: i) Appropriate matrix material selection for certain vapour detection. It is preferred that substance to be detected is good solvent for matrix material. Also important is matrix material macromolecule super elasticity, which provides immediate matrix swelling as diffusion of analyte in the composite occurs. ii) Dispersion extent of conductive filler and subsequent electroconductive grid formation by filler. It is known from our previous research that determinative electric resistance change mechanism, which is responsible for PNFC *osv* sensing, is tunneling current decrease between carbon black aggregates in thin layers of matrix [2].

Materials and methods

For PNFC production highly structured nano-size carbon black PRINTEX XE2 (specific surface 950 m^2/g, mean diameter of primary particles 25 nm, DBP absorption 380 ml/100g) or MWCNT Aldrich 636835 (outer diameter OD=60–100 nm, inner diameter ID=5–10 nm, length = 0.5–500 nm, BET surface area: 40–300 m^2/g) were used. In the case of first PNCC preparation method carbon particle dispersion was achieved by rolling carbon black and necessary additional ingredients (sulphur and zinc oxide) polyisoprene matrix using cold rolls. Then followed vulcanization process (under 30Bar pressure at 150˚C for 15 minutes) when not only sulphur crossbonds form (between polyisoprene macromolecules) but also possibly chemical bonds between carbon black nanoparticles and matrix macromolecules form. Second carbon black nanoparticle dispersion in matrix material was prepared in polyisoprene and chloroform solution, where sonication was used for carbon black agglomerate destruction. After that magnetic stirring for 24h were applied. Obtained dried film was vulcanized as described above. PNFC samples were prepared with different filler concentrations varying the composite electrical properties from isolator till conductor [3]. For evaluation of *osv* sensitivity composite samples with filler concentration in the vicinity of percolation threshold were chosen.

Conclusion

Obtained results from comparison of PNCC produced by different carbon black dispersion methods and conclusions of the work are going to be presented at the conference presentation.

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Filler dispersion method effect on polyisoprene-nanostructured carbon composite (PNCC) vapour sensitivity

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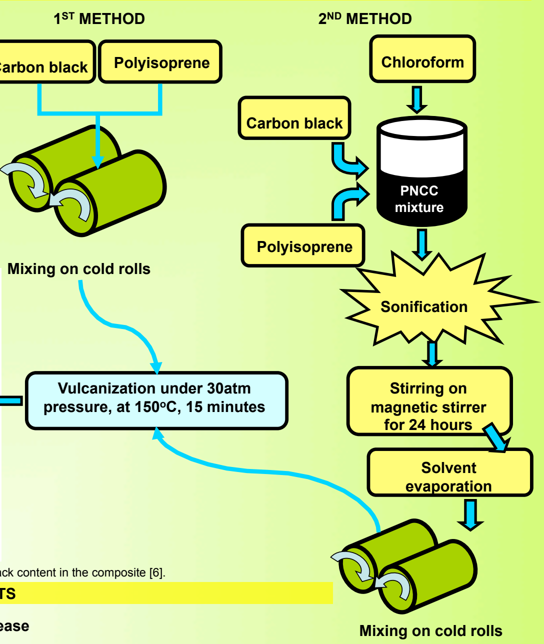
INTRODUCTION

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 is presented polyisoprene-nanostructured carbon composite (PNCC) volatile organic compound sensitivity determination by measuring simultaneously electrical resistance, mass and sample length change. Two different carbon black nanoparticle dispersion techniques in polyisoprene matrix are used. Also PNCC vapour sensitivity as functuon of used filler (carbon black nanoparticles or multi wall carbon nanotubes) is described.

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 fallowing diffusion relationships (Fickian diffusion, anomalous diffusion, Case II and Supercase II). 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.

PNCC PRODUCTION METHODS



1^{ST} METHOD

Carbon black
Polyisoprene
Mixing on cold rolls

2^{ND} METHOD

Chloroform
Carbon black
Polyisoprene
PNCC mixture
Sonification
Stirring on magnetic stirrer for 24 hours
Solvent evaporation
Mixing on cold rolls

Vulcanization under 30atm pressure, at 150°C, 15 minutes

EXPERIMENTAL SETUP

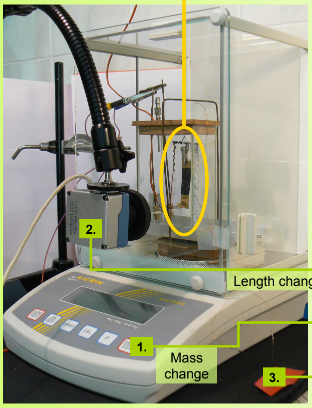


Fig.2. Experimental setup for simultaneous mass, length and electrical resistance measurements.

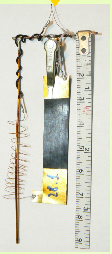


Fig.1. Sample in the sample holder.

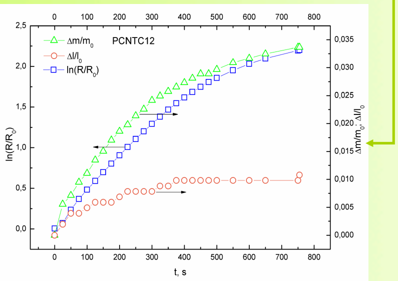


Fig.4. Simultaneous electric resistance ($\ln(R/R_0)$), relative mass ($\Delta m/m_0$) and relative elongation ($\Delta l/l_0$) change in time for PCNTC12. Ethyl acetate vapour concentration (0,297ml/l).

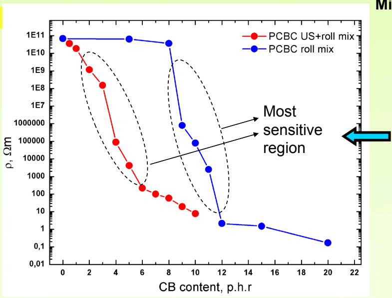


Fig.3. Specific electric resistance of PCBC sample versus carbon black content in the composite [6].

RESULTS

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

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

, 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.

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

$$\frac{m_t}{m_\infty} = k \cdot t^n \tag{2}$$

, where $\boldsymbol{m_t}$ **–** mass uptake in time t, $\boldsymbol{m_\infty}$ – mass uptake, when t approaches infinity. n and k are constants.

Table 1. Ethyl acetate vapour diffusion constants for PCBC, PCNTC and pure polyisoprene.

Material	Diffusion constants		
	D, m²/s	k	n
Pure polyisoprene	$4{,}47\cdot10^{-13}$	-4,803	0,670
PCBC10	$2{,}93\cdot10^{-13}$	-4,144	0,608053
PCBC10U	$3{,}40\cdot10^{-13}$	-4,238	0,73952
PCNTC12	$3{,}86\cdot10^{-13}$	-4,948	0,815
PCNTC13	$4{,}07\cdot10^{-13}$	-4,596	0,748
PCNTC14	$4{,}36\cdot10^{-13}$	-4,775	0,71205

RESULTS

2. Results of length and electrical resistance increase

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

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

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

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

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

, 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.

at deformations $\Delta l/l_0 < 0{,}1$ tends to 0.

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

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

, where A, B, C and D are constants

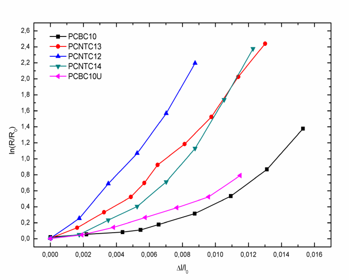


Fig.5. Electric resistance ($\ln(R/R_0)$) change of PCBC and PCNTC versus relative elongation ($\Delta l/l_0$) change in ethyl acetate vapour (0,297ml/l).

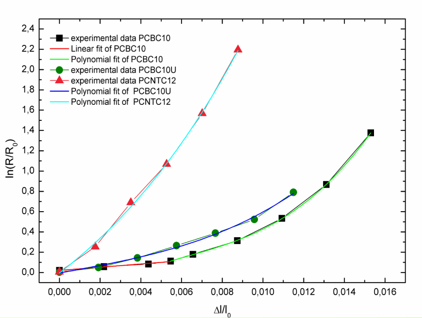


Fig.6. Experimental data (doted lines) of electric resistance ($\ln(R/R_0)$) versus relative elongation ($\Delta l/l_0$) of PCNTC12, PCBC10U and PCBC10. Solid lines represent theoretical fitting of experimental data.

Table 2. Composites PCBC10, PCBC10U and PCNTC12 fitting constants of ($\ln(R/R_0)$) vs. ($\Delta l/l_0$) experimental data.

Material	Function	Constants					Electric resistance increase mechanism
		A_0	A	B	C	D	
PCBC10	Linear	15,86	-	-	-	-	tunneling
	Polynomial	-	212,11	-26100,98	$1{,}63\cdot10^{6}$	$-1{,}96\cdot10^{7}$	tunneling and conductive network destruction
PCBC10U	Polynomial	-	36,95	-339,04	265905,73	-	tunneling and conductive network destruction
PCNTC12	Polynomial	-	155,69	7216,67	403409,67	-	tunneling and conductive network destruction

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

Conclusions

1. **Simultaneous measurements of organic solvent vapour sorption parameters and electrical resistance of composites allows evaluate the role of conductive filler in vapour general diffusion process.**
2. **It was approved that ethyl acetate vapour absorption occur not only in matrix material but at longer exposure times to vapour leads also to vapour absorption by the filler material MWCNT and HSCB. On the one hand filler in the composite material acts as hindrance for vapour diffusion, but one the other hand filler material enhances material diffusion properties at longer exposure times to vapour. Polyisoprene-nanostructured carbon composite material diffusion coefficient values increases with increasing MWCNT content in the composite.**
3. **Organic solvent vapour diffusion mechanism in the composite has been determined as non-Fickian anomalous diffusion, which provides rapid and immediate composite material response to the presence of vapour.**
4. **The developed tunneling – percolation model basing on both pure tunneling current change effect and tunneling conductive path interruption effect well describes the VOC vapour sensing effect in PCNTC and PCBC.**

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