

ATMOSPHERE CONTROL BY CHEMORESISTIVE POLYMER COMPOSITES

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Abstract: This work reports about polymer-nanostructured carbon composite (PNCC) and its possible application for relative humidity registration and volatile organic compound (VOC) detection in the air. PNCC have been produced using high structured carbon black (HSCB) nanoparticles and polyisoprene (PI), ethylene-vinylacetate (EVA) copolymer, polyvinylacetate (PVAc), polyethylene glycol (PEG) and polyvinylalcohol (PVA). Matrix material for composite production has been selected with respect to desired analyte to be tested. Composites show selective response to particular species of analytes vapour. It has been found that humidity sensing mechanism changes from proton conductivity to electron tunnelling by addition of HSCB to PVA matrix. Plasticizer effect on PVAc-NCC ethanol vapour sensitivity has been evaluated.

1 INTRODUCTION

In the spotlight of scientific research are different kind of sensor materials for odour detection and inspection. Metal oxide (ZnO, SnO ect.) sensor materials are already proved themselves as good sensing materials for detection of ethanol, CO₂, etc. and are widely utilized (Yang et al., 2009; Trinh et al., 2011). Conductive polymers and chemoresistive polymer composites show multiple VOC selectivity at room temperature (Kang et al., 2010; Wang et al., 2010). The greatest selectivity with possibility to distinguish even individual odour molecules can be obtained by molecularly imprinted polymers and biosensors (Van Dorst et al., 2010). With increasing sensitivity of produced sensor materials, consequently, application field also enlarges from environmental control (VOC leakage detection in chemical and petrochemical industry) to agricultural (diagnosis of plant disease), food industry (food quality, storage life, freshness) and medicine (diagnosis of disease). Mahmoudi (Mahmoudi, 2009) has reported that microbial organisms such as fungi and bacteria can grow and generate VOC including different alcohols, aldehydes, ketones, aromatic compounds, amines, terpenes, chlorinated

hydrocarbons and sulphuric compounds while metabolizing nutrients. It means that VOC can be a biomarker for early stage diagnostic of human diseases or microbial organism discovery in food and wood.

It is already a well known practice to impart to polymer conductivity by dispersing conductive particles in it. When conductive particles are dispersed in isolating matrix, continuous conductive network through matrix is formed either by geometrical or tunnelling contact between particles. If the composite is exposed to VOC, particles aggregate forming conductive network are withdrawn from each other by VOC induced isolating polymer matrix swelling. Consequently, electrical resistance of the composite increases and the presence of VOC can be detected.

Here is presented a polymer/HSCB composite film capability to selectively detect different VOC or register relative humidity of the environment. The influence of structural state of composite matrix material (rubbery, viscoelastic, crystalline) on VOC sensitivity is analyzed. Two different relative humidity sensing mechanisms existing in PVAc-NCC are described. Also attempts to improve PVAc-NCC ethanol vapour sensitivity by addition

of plasticizer are demonstrated.

2 MATERIALS AND METHODS

Polymers for PNCC production were selectively chosen. PI has been selected as highly non-polar matrix with a purpose to detect non-polar VOC. On the contrary PEG, PVAc was selected as highly polar matrix to detect polar VOC like methanol, ethanol, propanol, butanol, formamide, acetone, methyl ethyl ketone etc. PVA was chosen for highly polar solvent vapour presence determination. As EVA copolymer contains non-polar part – ethylene and polar part - 29.7% vinyl acetate, it was picked up to produce composite, which could sense both polar and non-polar solvents.

For all produced composites high structured carbon black PRINTEX XE2 (mean diameter 30 nm, DBP absorption - 380 ml/100 g, BET surface area - 950m²/g) as conductive filler was used. Firstly, HSCB was dispersed in appropriate solvent using Hielscher UP200S ultrasound homogenizer. Specific power 1W/ml was applied for 5 minutes. Secondly, the HSCB dispersion in solvent was added to a polymer solution in the same solvent. Magnetic stirring for 1 to 24 hours were applied. After magnetic stirring polymer-HSCB mixture was coated on epoxy laminate substrate with copper or brass wire (in case of PI-NCC) electrodes. The composite layer on epoxy laminate substrate was obtained by repeated immersion of the epoxy laminate into the mixture and subsequent solvent evaporation from the film. Immersion-evaporation cycles were repeated up to 4 times. PI-NCC after solvent evaporation was cured under 30 atm pressure at 150°C for 15 minutes. Brass wire electrodes were selected for PI-NCC production because at the time of curing chemical bonds between polyisoprene rubber and brass wires are formed, which ensures excellent composite adhesion to electrodes. Produced samples were in size 10x14mm (width x length) and with varying thickness.

For PVA-NCC production slightly different production method was used. Firstly, PVA was dissolved in water for 6h at 80°C. Secondly, HSCB was dispersed in distilled water using Hielscher UP200S ultrasound homogenizer. Specific power 2.5W/ml was applied for 5minutes. Thirdly, HSCB suspension in water was added to 20ml of 10% PVA solution in water. Obtained mixture was stirred with glass beads for 10 minutes. The mixture was purred out in Petri dishes. To obtain hydrogel from the mixture, it was subjected to repeated freezing (12h at

-12°C) and thawing (12h at +25°C) cycles. Cycles were repeated 3 times. Samples with dimensions 5x50x0.3mm were used for measurements. At the time of freezing and thawing hydrogen crosslinks are formed in PVA (Stasko, J., Kalnins, M., Dzene, A., Tupureina, V., 2009). These physical crosslinks prevents PVA from dissolution in water.

HSCB content in PI-NCC was varied form 2.2 to 6.6 phr (parts per hundred rubber). In case of PEG-NCC, PVAc-NCC, EVA-NCC HSCB was held constant 10 parts per hundred polymer (php) and 9php for PVA-NCC, respectively.

3 RESULTS AND DISSCUSION

3.1 Evaluation of Polymer Matrix Structural State

PEG with molecular weight 40000 was used for PEG-NCC production. Hydroxyl end groups in chemical structure of PEG determine it polar nature ($\epsilon = 3.37$), and single polymer backbone without side branches ensures highly crystalline (92%) structure formation.

PVAc with molecular weight 101600 was used for PVAc-NCC production. PVAc has relatively large acetate side groups, which act as steric hindrance for three dimensional structure formation of PVAc. As a result PVAc has amorphous structure. EVA copolymer structure is composed of ethylene and vinylacetate repeating units. Introduction of vinylacetate in ethylene structure leads to reduced copolymer crystallinity.

Differential scanning calorimetry (DSC) was used for matrix material structural state analyzes, when it is pure as well as in composite content. DSC measurements were carried out only for composites indented for detection of polar VOC (see Table 1). Glass transition temperature (T_g) and crystallinity has been chosen as parameters for evaluation because both greatly influence the composite VOC sensitivity. T_g indicate how flexible are polymer macromolecules at room temperature. As lower value of T_g as more rubbery like amorphous polymer is and more flexible are polymer macromolecules. Therefore more rapidly segmental motions of the polymer can be performed by absorption of analyte. VOC molecule absorption and polymer swelling would be more favourable by hyperelastic than by stiff and brittle matrix. Segmental motions can be made more easily in amorphous structure than in closely packed crystalline. It is seen in Table 1, that crystallinity of EVA and PEG decreases, when

HSCB are introduced in polymer matrix. It seems like that electroconductive grid formed by HSCB particles in matrix acts as hindrance for polymer crystallization. Crystallinity of EVA and EVA-NCC has been calculated using heat of fusion of 100% crystalline polyethylene 293.6 J/g (on line data base). Crystallinity of PEG and PEG-NCC has been determined using heat of fusion of 100% crystalline PEG 196.8 J/g (Nalawade, Picchioni, Janssen, 2007). HSCB addition to EVA and PEG has no significant effect on T_g . On the contrary addition of HSCB to PVAc matrix has notable effect on T_g , which changes from 39.07°C to 3.28°C. It means that PVAc chain mobility enhances with addition of HSCB. Similar decrease of T_g by addition of B₂O₃, Al₂O₃ or SiC to polymer have been observed by Sundar and others (Sundar, Selladurai, 2006; Ahmad, et. al 2009; Koo Choi, Hee Shin, 1996).

Table 1: DSC results of pure polymers and composites.

Material	T_g , °C	Crystallinity, %
PVAc	39.07	-
PVAc-NCC	3.28	-
EVA	-25.35	7.4
EVA-NCC	-25.99	1.5
PEG	-60.55	92
PEG-NCC	-59.47	67.5

3.2 Composite Film Thickness Impact on Sensitivity

PI-NCC, PEG-NCC, EVA-NCC and PVAc-NCC electrical resistance response to VOC has been determined (Fig.1). PI-NCC was exposed to non-polar solvent - toluene, but PEG-NCC, EVA-NCC and PVAc-NCC to polar solvent - ethanol vapour. Data available in Fig.1 indicate that the best ethanol vapour sensitivity has PEG-NCC followed by EVA-NCC and PVAc-NCC. It can be seen that PEG-NCC and EVA-NCC change in thickness has greater impact on vapour sensitivity than PVAc-NCC and PI-NCC.

Let us analyze now VOC sensitivity of composites versus thickness regarding its structural state. As determined by DSC the EVA-NCC is slightly crystalline and the PEG-NCC is highly crystalline. Both these composites show greater thickness impact on VOC sensitivity, than amorphous polymer composites like PVAc-NCC and PI-NCC. Explanation could be as follows. If the composite film is rather thick, then larger crystalline structures have been grown during formation of the sample. These larger crystalline structures are harder to dissolve by absorbed VOC. In amorphous

polymer structures exist a lot of free volume cavities, where diffusion of analyte occurs. But in crystalline polymer structures there are remarkably less free volume cavities. Analyte diffusion in the composite can take place only by dissolution of crystalline structure, molecule rearrangement and free volume cavities formation.

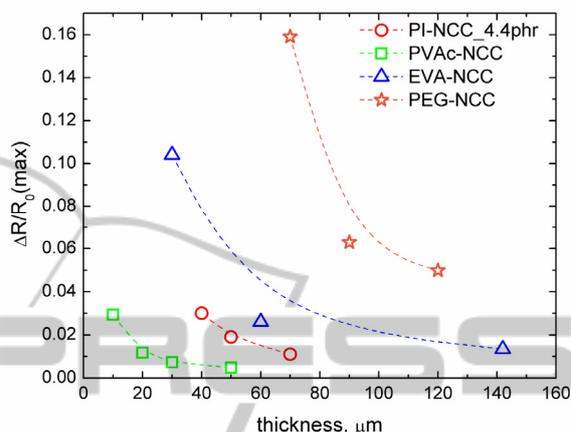


Figure 1: Relative electrical resistance change in VOC versus composite thickness. PI-NCC samples exposed to toluene (0.008ml/l). PVAc-NCC, EVA-NCC and PEG-NCC samples exposed to ethanol (0.1ml/l).

3.3 Selective Detection of VOC

PEG-NCC, PVAc-NCC, EVA-NCC and PI-NCC selectivity to one specific class of solvents (polar or non-polar) has been determined. Relative electrical resistance change of PEG-NCC, PVAc-NCC and EVA-NCC exposed to the same concentration (~9100ppm) of polar (ethanol) vapour and weakly polar (ethyl acetate) vapour is shown in Fig.2 (a, b, c).

Because of PEG-NCC and PVAc-NCC polar matrix nature greater electrical resistance change can be observed, when composites are exposed to ethanol vapour. EVA-NCC shows sufficient sensitivity to both ethanol and ethyl acetate vapour. It is related to dual nature of EVA matrix. Rather great part of EVA is ethylene (70.3%), therefore also good sensitivity to ethyl acetate is observed. In Fig.2 (d) can be seen that PI-NCC has high sensitivity to non-polar VOC, but electrical resistance response to polar VOC is weak and dissipated.

Advantage of our produced composites comparing to other polymer/conductive filler composites is good sensitivity and fast reversibility even if the composite is exposed to quite large VOC concentrations (~9100ppm) (Choudhury, 2009). Obtained results in Fig.2 evidence that greater role plays matrix material compatibility with VOC than the structural state of matrix material. PEG-NCC is

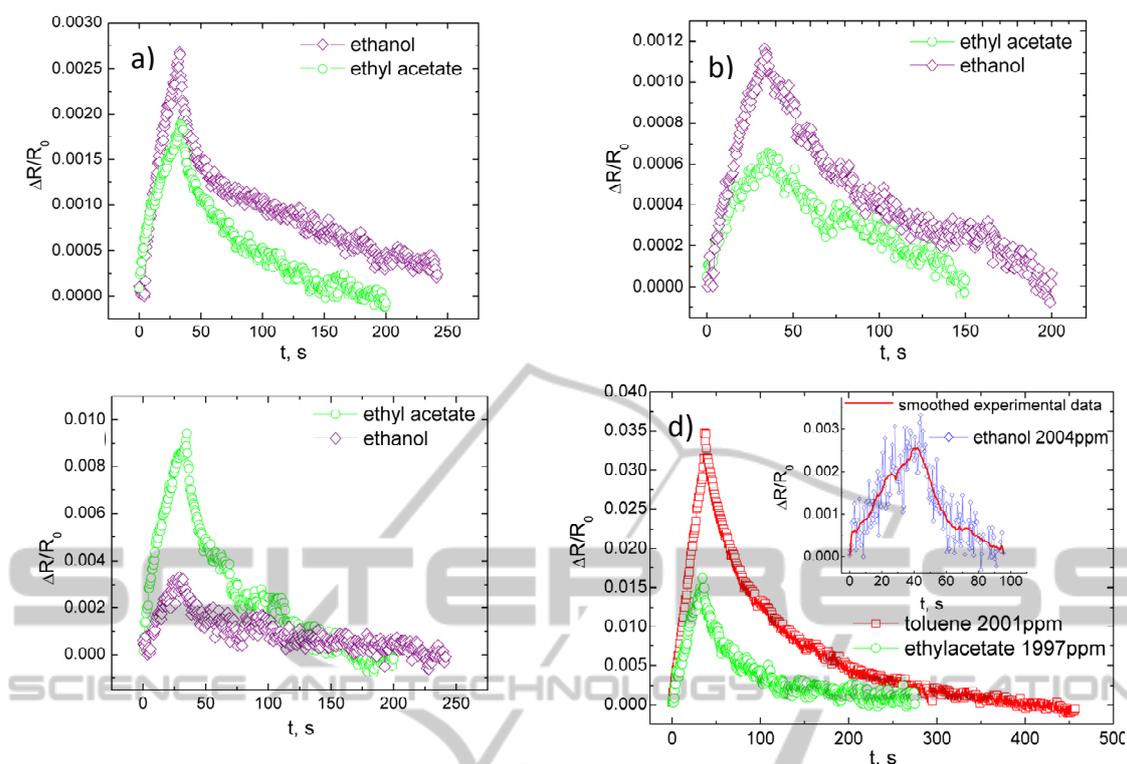


Figure 2: PEG-NCC (a), PVAc-NCC (b), EVA-NCC (c) relative electrical resistance change versus time, when samples exposed to ethanol (9069ppm) and ethyl acetate (9105ppm). PI-NCC (d) relative electrical resistance change versus time, when sample exposed to different VOC. Thickness of tested samples were as follows: PEG-NCC 110 μ m, PVAc-NCC 40 μ m, EVA-NCC 80 μ m and PI-NCC 40 μ m.

the most crystalline of all tested composites, but it shows unexpectedly good VOC sensitivity due to more polar like nature than PVAc-NCC and EVA-NCC.

If we compare PI-NCC and PEG-NCC, PVAc-NCC and EVA-NCC ethyl acetate sensitivity, then we can observe that PI-NCC has greater relative electrical resistance change than PEG-NCC, PVAc-NCC and EVA-NCC. Even the PI-NCC is exposed to reduced ethyl acetate concentration. But electrical resistance relaxation time for PI-NCC is similar to other tested composites. It is a challenge in future to produce sensor material on the base of polymer composite with highest possible sensitivity and with as short as possible relaxation time. Fast recovery of sensor material after analyte detection is very important for alarm systems to exclude delayed warning of VOC leakage. More adequate comparison of PEG-NCC, EVA-NCC, PVAc-NCC and PI-NCC responses will be made, when percolation threshold for PEG-NCC, EVA-NCC, PVAc-NCC will be determined and the most sensitive polymer/HSCB composition found.

3.4 PI-NCC VOC Sensitivity Versus HSCB Content

PI-NCC has been produced varying content of HSCB from 2.2 to 6.6phr. PI-NCC transition from isolator to electro conductive composite is shown in Fig.3. PI-NCC specific electrical resistance decreases with development of percolative HSCB structure. Maximal relative electrical resistance change of PI-NCC exposed to toluene vapour is also displayed in Fig.3. Samples were held in vapour for 30s and then left in the air for electrical resistance relaxation. Maximal relative electrical resistance change is the highest obtained value of $\Delta R/R_0$, when PI-NCC sample exposed to toluene vapour for 30s. PI-NCC response to vapours are immediate, electrical resistance starts to increase at the moment of samples introduction to vapour. VOC sensor effect of PI-NCC is reversible. Electrical resistance of the composite PI-NCC_4.4phr shows the best sensitivity. It is characteristically for polymer/conductive nanoparticle composites to exhibit the highest sensitivity in vicinity of isolator-

conductor transition (slightly above percolation threshold).

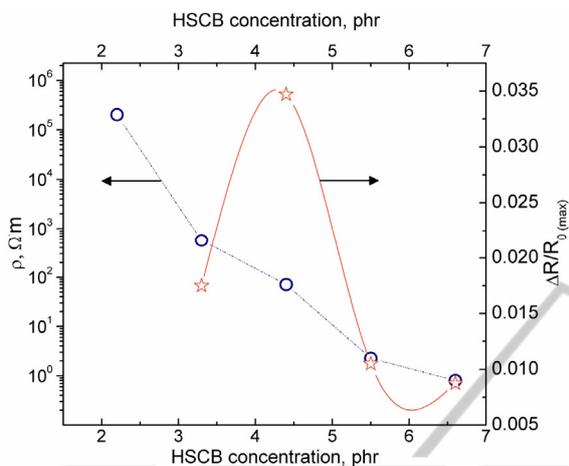


Figure 3: PI-NCC specific resistance versus HSCB concentration and PI-NCC toluene vapour sensitivity ($\Delta R/R_{0(max)}$) versus HSCB loading in the composite. Thickness of samples is 40 μ m. Toluene vapour concentration is 2001ppm.

3.5 Plasticizer Impact on PVAc-NCC Sensitivity

The worst ethanol vapour sensitivity has been determined for PVAc-NCC despite the fact that PVAc-NCC samples were produced with the smallest thickness (Fig.1). It is not clear why EVA-NCC shows better ethanol vapour sensitivity than PVAc-NCC? Copolymer for EVA-NCC production contains only 29.7% vinyl acetate. This can be explained as fallow. When in a flexible (ethylene) backbone stiff units (vinyl acetate) are introduced, the stiff units are able to move, rearrange faster under external influence.

We decided that PVAc still has insufficient polymer chain mobility. Plasticizers can improve it. 1% and 15% of plasticizer di-n-octyl sebacate (DOS) was added to PVAc-NCC and ethanol sensor effect has been determined. Obtained results are summarized in Fig.4. All tested samples were exposed to ethanol vapour for 30s and then left in the air for electrical resistance relaxation. The plasticizer addition to the composite significantly improves PVAc-NCC ethanol vapour sensitivity. But PVAc-NCC electrical resistance reversibility worsens at high plasticizer loadings.

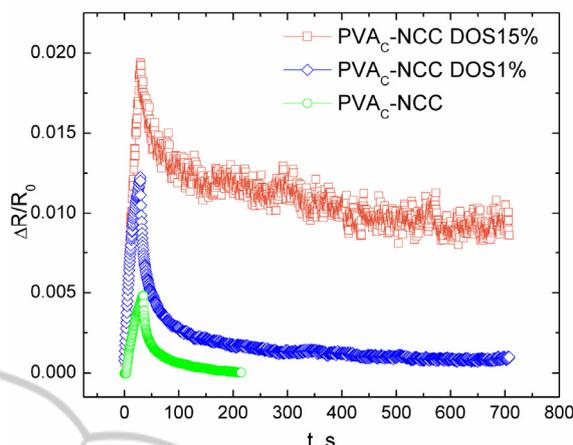


Figure 4: Relative electrical resistance change for PVAc-NCC with different DOS content. Thickness of samples is 50 μ m. Ethanol vapour concentration is 0,11ml/l.

3.6 PVA-NCC Sensitivity to Relative Humidity

Pure PVA and PVA-NCC electrical resistance change was registered sequentially exposing samples to 99% and 10% relative humidity (RH) (Fig. 5). 99% and 10% RH was obtained by using K_2SO_4 and $ZnCl_2$ oversaturated salt solution in water. Electrical resistance of pure PVA decreases, when it is exposed to 99% RH. On contrary, PVA-NCC electrical resistance increases. Totally different RH sensing mechanisms can explain such difference in electrical resistance responses.

PVA consists of $[-CH_2-CH(OH)-]_n$ repeating unit. OH side group attached to the second C atom determines PVA high hydrophilicity. If PVA is exposed to high RH, water molecules adsorb on the surface by bonding to PVA OH side groups. It is known that water normally exists as a mixture of molecules, hydroxide ions (OH^-) and hydronium ions (H_3O^+). The third H^+ ion of hydronium ion can perform hopping between adjacent adsorbed water molecules. As a result proton conductivity is realized in PVA and electrical resistance of pure PVA at elevated RH decreases.

PVA-NCC case is more complicated. It is believed that in PVA-NCC coexist two sensing mechanisms, which counteract to each other. The first sensing mechanism is the same as for pure PVA, that is, proton conductivity. The second sensing mechanism is charge tunnelling. There we should remember that the composite consists of PVA with homogeneously dispersed HSCB. The HSCB nanoparticles form conductive network throughout PVA matrix. When

water molecules are adsorbed by highly hydrophilic PVA, it swells and HSCB aggregates are withdrawn from each other. As a result tunnelling currents in thin layers of PVA between HSCB aggregates decreases and PVA-NCC electrical resistance increases.

For both PVA and PVA-NCC RH sensitivity decreases with each measuring cycle. It can be related to PVA great hydrophilic nature, at the time of electrical resistance relaxation not all water molecules are desorbed from PVA matrix.

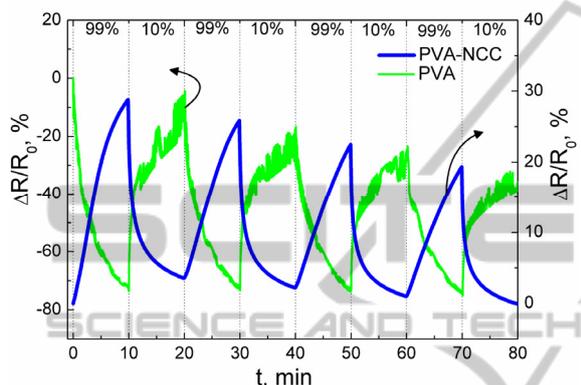


Figure 5: Relative electrical resistance change versus time of pure PVA and PVA-NCC, when samples were sequentially exposed to 99% and 10% RH.

4 CONCLUSIONS

In this work possibility to use polymer chemoresistive composites for VOC detection and RH registration have been presented and following conclusions can be made. Selectivity of the composite can be managed with respect to desired analyte. Sensitivity of the composite with stiff polymer matrix can be greatly increased by addition of plasticizer. The most sensitive VOC sensor material can be obtained by choosing composite with composition at the vicinity of percolation threshold. In PVA-NCC two electrical resistance change mechanisms exist, which compete to each other. Composite matrix compatibility with analyte vapour has greater influence on composite sensitivity than composite material structural state. Future research work would be devoted to percolation transition determination for PEG-NCC, PVAc-NCC and EVA-NCC.

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