Ethylene vinylacetate copolymer and nanographite composite as chemical vapour sensor

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Abstract. Polymer-nanostructured carbon composite as chemical vapour sensor is described, made by the dissolution method of a non-conductive polymer, ethylene vinylacetate copolymer, mixed with conductive nanographite particles (carbon black). Sensor exhibits relative electrical resistance change in chemical vapours, like ethanol and toluene. Since the sensor is relatively cheap, easy to fabricate, it can be used in air quality monitoring and at industries to control hazardous substance concentration in the air, for example, to protect workers from exposure to chemical spills.

1. Introduction

In nowadays scientific development has increased amount and the variety of used chemicals in manufacturing [1], therefore there is need to investigate and create sensor which can detect different kind of chemicals and warn factory workers about potential leakage of chemicals.

Ethanol and toluene are most popular chemicals. Ethanol is polar solvent and is used in factories to produce large amount of goods, like alcohol, perfume, in disinfectants. Toluene is non-polar solvent used to produce paint, paint thinners, adhesives and nail polishers.

Still these two chemicals are not the only ones. There are a wide range of hazardous chemicals in manufacturing and consequently in the human environment. Although there are several methods described (photo/flame-ionization detectors, mobile gas chromatographs, semiconductor based gas sensors) to detect different chemicals vapours, however there is still no ideal device invented. That is why in the present work we developed a chemical vapour sensor, whose active layer is a thin film of a non-conductive polymer – ethylene vinylacetate copolymer – mixed with conductive nanographite particles, in order to develop new sensor device. With the term “nanographite” can be marked following fillers: extra-conductive highly structured carbon black (EHSCB), carbon nanotubes (CNT), thermally exfoliated graphite (TEG) as well as recently discovered graphenes because all of them have a sp²-hybridized crystal structure like graphite, but at least one dimension of nanographite is smaller then 100 nm. In this research we used EHSCB as composite filler. Their primary nanoparticles are like polyhedron of mean size 30 nm whose faces are made of graphite platelets. Therefore this kind of carbon black has very high conductivity and is named as “extra-conductive”.
2. Materials and Methods

2.1. Materials

To produce composite ethylene vinylacetate copolymer (Sigma Aldrich; figure 1) is used as matrix. It is known that amount of vinylacetate impacts the copolymer crystallization degree and flexibility. In this case we used ethylene vinylacetate copolymer with 40 % vinylacetate content. Copolymer consists of ethylene and vinylacetate repeating units, where ethylene unit is non-polar and vinylacetate – polar. Copolymer complex structure indicates that the sensor could detect both polar and non-polar organic solvent vapours.

Nanographite particles (EHSCB: PRINTEX XE-2) with average particle size 30 nm are used as conductive filler. Particles specific surface: 950 m$^2$/g and DBP (dibutyl phthalate) adsorption: 380 ml/100 g. PRINTEX XE-2 as mentioned before has high electrical and it has been used in many electrical rubber creation. This type of carbon black has no additional surface treatment as mentioned in [2].

![Figure 1. Structure of ethylene vinylacetate copolymer](image)

2.2. Composite production

Sensor production is based on dissolution method, where ethylene vinylacetate copolymer was dissolved in chloroform solution. Then different mass parts of EHSCB were homogenized in chloroform using ultrasonic homogenizer. The obtained carbon black suspension was added to polymer solution and stirred on magnetic stirrer for 2 hours. After that obtained homogenous composite mixture spotted on epoxy laminate plate with cooper electrodes by dip-coating method.

2.2.1. Sensing mechanism

Ethylene vinylacetate-nanostructured carbon composites (EVA-NCC) chemical sensoreffect can be explained on the basis of conductive filler percolation theory in the matrix. In the vicinity of the percolation threshold, the electrical conductivity $\sigma$ of the composite changes according to:

$$\sigma = \sigma_0 / \Phi - \Phi_C / t,$$

where $\sigma_0$ is scaling factor, $\Phi_C$ is critical concentration or percolation threshold and $t$ is the critical index [3]. In our previous studies [4] we have shown the existence of tunnelling conductivity between two adjacent conductive nanoparticle aggregates. We also showed the best sensitivity of such kind composites in the vicinity of the percolation threshold [4,5]. Absorption of the solvent vapour molecules by polymer induces polymer matrix swelling and the distance between carbon nano-particle aggregates increases. Consequently, the tunnelling currents between carbon aggregates decreases and the electrical resistance of the composite increases.
3. Results and discussions

![Figure 2](image1.png)  
**Figure 2.** Conductivity of EVA-NCC as function of CB concentration in the composite

![Figure 3](image2.png)  
**Figure 3.** Approximation of EVA-NCC experimental data with percolation scaling law

In order to start testing sensoreffect, there is necessary to determine the percolation threshold of the EVA-NCC, because the percolation threshold transition predicts the most sensitivity of chemicals sensor. Experimentally measured percolation curve is shown on Figure 2. Theoretical fit of experimental data by equation (1) is shown on Figure 3. From approximation (Figure 3) of EVA-NCC experimental data with percolation scaling law one can decide, that critical concentration is 7.75 mass parts of carbon black. This fitting result correlates with ethanol vapour sensing experiments (Figure 4) where sensoreffect of each obtained composite sample was measured.

Figure 5 show how the polarity of VOC affects EVA-NCC VOC sensoreffect. For example, the EVA-NCC with 8 mass parts of EHSCB presents remarkably better sensitivity to nonpolar VOC.

![Figure 4](image3.png)  
**Figure 4.** Maximal relative electrical resistance change of EVA-NCC versus carbon black concentration in the composite. Samples were exposed to ethanol vapours (9069 ppm) for ... seconds. Thickness of the samples 70 μm.

![Figure 5](image4.png)  
**Figure 5.** EVA-NCC electrical resistance change versus time in toluene and ethanol vapours. EVA-NCC contains 8 mass parts of carbon black. Vapour concentration was 500 ppm.

Experimental data (Figure 6) shows that EVA-NCC is able to detect VOCs at elevated relative humidity. It was found that at the water-ethanol mixture ratio 70:30 changes the composite response mechanism to vapour: the contribution of proton conductivity of the water layer on the surface of EVA-NCC sample overcomes the contribution of tunnelling currents inside of composite.
4. Conclusions
There are investigated EVA-NCC percolation threshold, volatile organic compounds (VOC) sensoreffect and its influencing factors.
EVA-NCC ethanol vapour sensoreffect has been determined. The highest relative electrical resistance change in vapour is observed at 7 mass parts.
Experimental data shows that EVA-NCC is able to detect VOCs in high relative humidity. It was found that at the water-ethanol mixture of 70:30 ratios the composites electrical response mechanism varies from tunelling conductivity to the proton conductivity.

5. Acknowledgements

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