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Influence of different carbon allotrope filler on the VOC sensitivity of polymer composite

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Abstract. In this work, both, pristine and hybrid polyisoprene as well as ethylene vinyl acetate copolymer nanocomposites with carbon nanoparticles and carbon nanotubes were developed and studied for their application in toluene sensors. The response to toluene was determined for pristine and hybrid composite samples. Hybrid samples were compared to pristine composite samples and the composite with highest sensing effect is obtained.

1. Introduction

Electrically conductive polymers are subjects of intensive research due to great interest in different technological applications [1,2]. Our research is devoted to the development and studies of hybrid nanocomposites for their application in Volatile Organic compound (VOC) vapour sensors [3]. Detection of VOC vapour including toluene is significant for air quality monitoring. VOCs are believed to be the major contributors to poor indoor and outdoor air quality. For example, toluene is used frequently in many work operations involving paint, metal cleaners, adhesives and other products. In last 50 years, air quality sensor market is dominated by metal oxide gas sensors. Polymer based composite sensors could be a good alternative over metal oxide sensors, having several advantages like low price and functioning at room temperature. Polymer based composites also can be easily produced (dip coating, spin coating, inkjet or screen printing [4]) and the cost of one sensor unit can be comparatively low. Many properties of polymer based composites are described with percolation phenomena[5–8]. However, the results are contradictory and depend on particle dispersion technique, physical characteristics of particles and type of polymer used.

In this work both, binary and hybrid polyisoprene (Pi) or ethylene vinyl acetate copolymer (EVA) with carbon nanoparticles and carbon nanotubes were developed and studied. All elaborated composites were tested for response to toluene vapours because toluene can be found in common household products (paints, paint thinners, adhesives, synthetic fragrances and nail polish), cigarette smoke and even in gasoline at large quantities. Synergetic effect was observed and enhanced sensing properties were achieved for certain composites.

2. Materials and methods

2.1. Materials

Pi was chosen as one of the matrix because it is known as an elastomer with good both gas permeation and elastic properties. Pi was mixed with additives (sulphur, zinc oxide, stearic acid) to enable

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crosslinking during the curing of the raw composite mass. For second set of samples as matrix material EVA (vinyl acetate content 40%) was used. One type of filler, the extra electro-conductive, highly structured carbon black nanoparticles (CB; Printex XE2), was purchased from Degussa Co. CB has mean particle size 30 nm, dibutylphthalate (DBP) absorption - 380 ml/100 g, specific surface area - 950 m2/g. Two types of CNT (carbon nanotubes) were used as filler material as well. First type of CNT was purchased from Sigma Aldrich; the outer diameter of tubes is in range from 40 to 60 nm, inner diameter is in range from 5 to 10 nm, length 0.5-500 μm, and aspect ratio 12500. These comparatively long CNT further will be designated as CNT_l. Second type of CNT were obtained from CheapTubes; outer diameter is in range of 50-80 nm, inner diameter is from 5 to 15 nm, length 0.5-2 μm, maximal aspect ratio 40. Further these short CNT will be designated as CNT_s.

2.2. Sample preparation

Elaboration of the composite samples was performed with liquid mixing (using chloroform as solvent). At first, a solution of the liquid matrix-filler was prepared. The solution was coated on epoxy laminate substrate by dip-coating method. Dip coating procedure was followed by drying at room temperature. Composites with Pi were also cured during compression molding at both temperature of 150 °C and pressure of 30 atm. Composites containing EVA were left air dried without compression molding. More detailed instructions for preparation of the composites are given in our previous work [9]. The dimensions of the obtained samples were 10 mm x 14 mm x 0.05 mm.

2.3. Methods

Keithley picoammeter 6487 was used to measure steady state electrical resistance of composites. KinTek FlexStream™ automated permeation tube system was used for generation of different toluene vapor concentrations in a set with nitrogen as a carrier gas. Special VOCs sensing chamber was originally created for simultaneous testing of 4 composite samples. To minimize the humidity influence on the response of the sensors to definite VOCs concentration, the chamber was designed as a closed flow system connected to KinTek FlexStream™. During sample recovery the chamber was purged with pure nitrogen. Tests of toluene response determination were carried out at the room temperature (23 °C). Agilent data acquisition switch unit 34972A was applied to measure sample electrical resistance during sensing tests for toluene.

3. Results

Based on our previous researches on Pi and EVA composites as VOC sensor materials [10–14], in this work will be researched hybrid composites and its sensing abilities compared with pristine composites made with CNT and CB. If only CNT are used as filler, electro-conductive network is formed from CNT and the distance between adjacent CNT (existence of tunneling currents) determines the CNT contribution in the electro-conductive network. If both CB and CNT are used and the concentration of CNT is larger than CB, main electro-conductive network is formed by CNT, however CB aggregates contribute in electro-conductive network formation due to connection of CNT branches as described by Jan Sumfleth et al. [8]. Some of CB aggregates are settled between CNT branches, additional electro-conductive branches are joined to the electro-conductive filler network and the resistance of the composite decreases. If the CB content in CB composite is equal to or more than 5phr or CB is more than CNT in the hybrid composites, main electro-conductive network is formed by CB, however CNT contribute in electro-conductive network formation due to connection of CB branches. In this case, the electro-conductive network is built from homogenously distributed CB aggregates and can be described by percolation theory.

3.1. Percolation theory

The percolation theory is used [7,15] to characterize electro-conductive network structure in composites. The peculiarities of electro-conductive network structure formed within the polymer are essential to improve the gas sensing properties. According to the percolation theory the dependence of composite conductivity (σ) on filler concentration is represented as follows [7]:

$$\sigma = \sigma_o (f - f_c)^t , \quad (1)$$

where σ_o is conductivity of electro-conductive particles (S/m), f is actual filler concentration, f_c - critical filler concentration and t - critical index.

A fit of experimental percolation curves by statistical percolation scaling law (1) was performed to obtain critical percolation parameters t and f_c. Critical percolation parameter t value for PiCB is 1.078, for $PiCNT_l$ is 4.95 and for $PiCNT_s$ is 4.54 (percolation curves in figure 1). Previously it was reported that t indicates the dimensionality of the electro-conductive network [8]. If value of the t is between 1.33 and 2.00, it means that the electro-conductive network is built in two or three-dimensional network [5,16]. According to classical percolation theory, t is called universal value if it equals 2.00 (the case without both, aggregation and tunnelling junctions between electro-conductive particles). The divergence of t value can be explained by large statistical distribution of the values of distance between adjacent particles or aggregates in the composite [5,7]. According to Balberg's [7] considerations, the non-universal high t values represent large distribution with of the inter-particle distances, while low t values corresponds to the almost-equal small inter-particle distances in composite. It is clear that those network paths, where the distance between adjacent particles is shorter and, subsequently, tunnelling currents are stronger, determine the electrical conductivity of the composite.

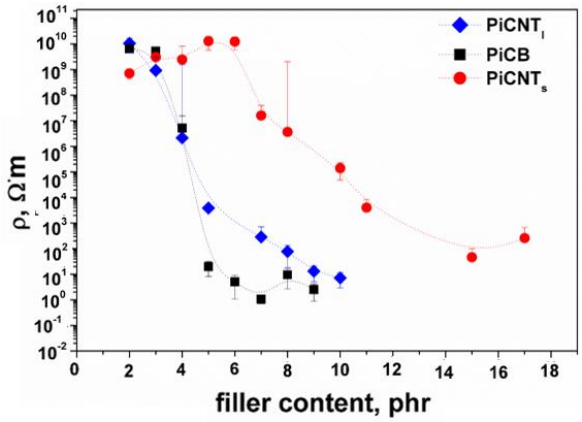

Figure 1. Electrical resistivity as function of filler concentration (parts per hundred rubber - phr) for PiCB, $PiCNT_l$ and $PiCNT_s$ composites

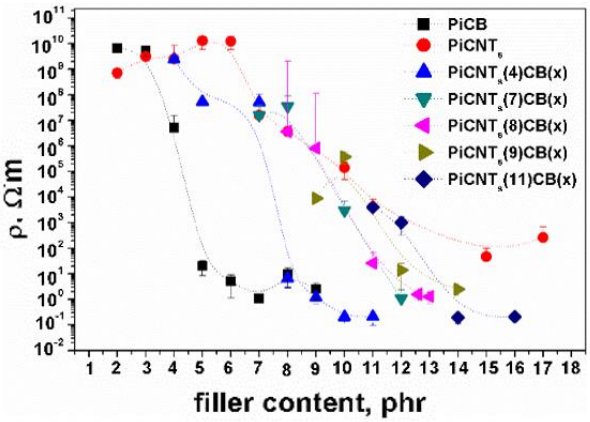

Figure 2. Electrical resistivity as function of filler concentration for PiCB, $PiCNT_s$ and $PiCNT_sCB$ composites, where CB concentration (x) in hybrid composites is varied from 1 to 7 phr.

PiCB composite (Fig.3.) has the lowest percolation critical concentration, f_c = 2.60, followed by $PiCNT_l$ (f_c = 3.40) and $PiCNT_s$ (f_c = 6.13). Hybrid composites were made by adding CB filler to the $PiCNT_s$ with fixed values of CNTs concentration. In Fig.2 the electrical resistivity for hybrid composite $PiCNT_sCB$ versus cumulative sum of electro-conductive filler concentration values (in phr units) is shown.

As can be seen from Fig.2, percolation curves of electrical resistivity for the hybrid composite are located between PiCB and $PiCNT_s$ curves that indicate a synergistic effect of electro-conductive fillers. By substitution certain amount of CNT with much cheaper filler – CB, electrical resistance of a composite is considerably decreased. An addition of at least 3 phr of CB is necessary to reduce electrical resistance values of the $PiCNT_s$ below 100 MΩ.

As it can be seen from the percolation data of PiCB composite (Fig.2), when CB content is of 5 phr, the composite already has considerably low electrical resistance. It means that the main electro-conductive network is formed by CB aggregates. In turn, if hybrid composite is made using CB equal to or more than 5 phr, then the electro-conductive network is generally formed from CB aggregates, where CNT contribute in electro-conductive network as connectors of CB aggregates. As a result, electrical resistance of hybrid composites is decreased even more comparing to pristine PiCB composite. Synergetic effect is expressly remarkable in prepared hybrid composites when short CNT are used. In these composites both, entanglement and folding of CNT, are negligible.

As second set of composites was compared previously investigated [12,14] EVA composites with CNT_s and CB conducting fillers. As well as hybrid composites made by using both fillers at once. For EVA CB composite f_c is 3 phr, but for EVA CNT_s composite f_c is 13 phr. It is necessary to make samples with resistivity below 100 MΩ, so the more simple measuring devices could be used. Accordingly, the best composition was EVA CB composite with 7.75 phr CB and in case of CNT_s it was 30 phr. In hybrid case such were EVA composites with CNT_s content above 10 phr.

3.2. Sensing effect

For application of developed composites in toluene sensing in air, the change of the relative electrical resistance of composites at the presence of toluene vapour has been determined. In Fig.3 the relative electrical resistance change versus toluene concentration for $PiCNT_s(7)CB(5)$, $PiCNT_s(9)CB(5)$ and PiCB(7) composites is shown. The samples were exposed to toluene vapor concentrations 90, 60 and 30ppm. Exposure was done until saturation was reached. After exposure to toluene, the samples were purged with pure carrier gas (N_2) until the initial electrical resistance was reached. No external heating was applied to sensor element during these measurements.

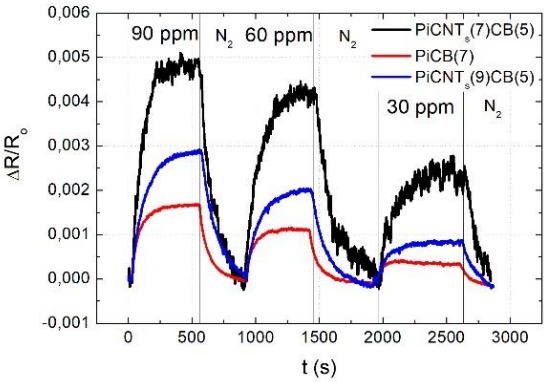

Figure 3. Relative electrical resistance change of $PiCNT_s(7)CB(5)$, $PiCNT_s(9)CB(5)$ and PiCB(7) composite versus time, when samples are exposed to toluene concentrations of 90, 60 and 30ppm.

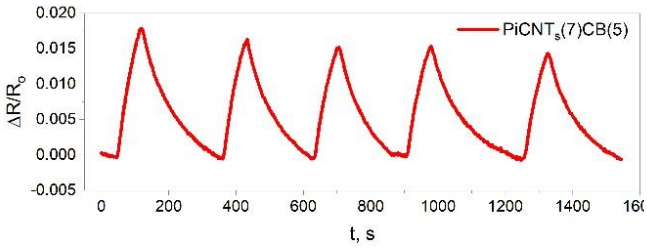

Figure 4. $PiCNT_s(7)CB(5)$ relative electrical resistance change versus time, when samples are exposed to toluene for 60s at 400ppm in five repeated cycles.

The sensing mechanism of the VOCs for this kind of composites was discussed in our previous works [13,17]where the change of the electrical resistance was explained basing on electron quantum tunneling theory:

$$\frac{R}{R_o} = \left(\frac{s}{s_o}\right) \exp[\gamma(s - s_o)], \quad (2)$$

where R_o is the initial electrical resistance, R - electrical resistance after matrix swelling, s_o – initial distance between adjacent particles, s – distance after matrix swelling, and γ is calculated from:

$$\gamma = \frac{[4\pi(2m\Phi)0.5]}{h}, \quad (3)$$

where m is mass of the electron , Φ – the height of the potential barrier between adjacent particles, h – Plank's constant. It has been proved experimentally that VOCs sensing mechanism is based on polymer swelling induced increase of distance between electro-conductive nanoparticles that causes exponential decrease of the tunnelling currents [13,17].

Hybrid samples were exposed to toluene vapour of 400 ppm concentration for time period of 60s in five repeated cycles as can be seen in Fig.4. The sensing effect is repeatable and can be used many times in a row.

Average maximal relative electrical resistance change from five repeated measurements was calculated and the standard deviation estimated (see Fig.5). The $PiCNT_s17$ composites showed the highest sensitivity among the PiCNT composites [9] and PiCB(7) showed the highest sensitivity among the

PiCB composites. Hybrid composites with electro-conductive network built of CNT and CB (Figure 5) show higher sensitivity to toluene, compared with composites where only CNT or CB as filler is used. The highest sensitivity among hybrid composites showed PiCNT$_s$(7)CB(5). Thus, one can conclude that sensitivity of CNT composites can be considerably increased by addition of the carbon black nanoparticles in case of Pi matrix. The diffusion of toluene molecules in composite matrix obviously causes greater changes of width of tunnelling junctions between different types of electro-conductive fillers. In case of EVA matrix it can be clearly seen that EVA CB 7.75 has the highest relative electrical change compared to all created samples, even in comparison with Pi hybrid composite samples. Adding CB to EVA CNT samples gave insignificant increase in relative electrical resistance change. The rise of sensing effect when concentration of short CNTs rises (PiCNT$_s$15 -> PiCNT$_s$17) we explain due to the increase of the number of comparatively easy destroyable and renewable (in case of matrix swelling -> recovering) conductive channels in composite. In contrary, in case of long CNTl (PiCNT$_l$7 -> PiCNT$_l$ 10) the additional conductive channels have a larger reinforcement effect, it means, the conductive channels can be not so easy destroyed due to matrix swelling, so the sensing effect diminishes. More detailed review of EVA composites sensing abilities can be found in our previous studies [11,12,14].

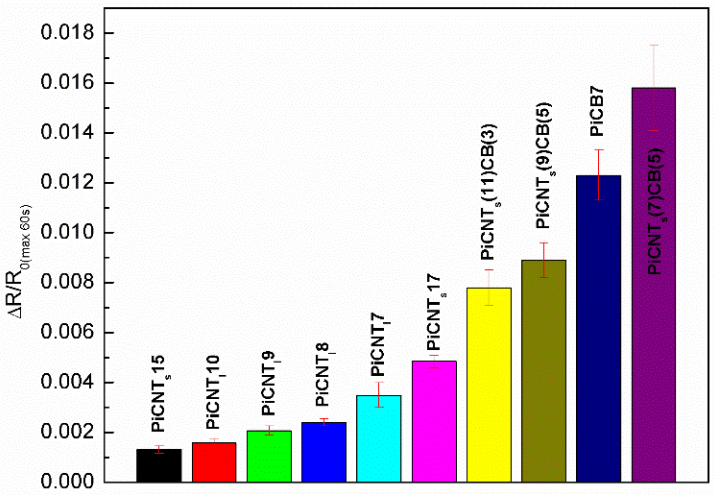

Figure 5. Average maximal relative electrical resistance change in toluene (400ppm) compared for different composite samples with Pi matrix.

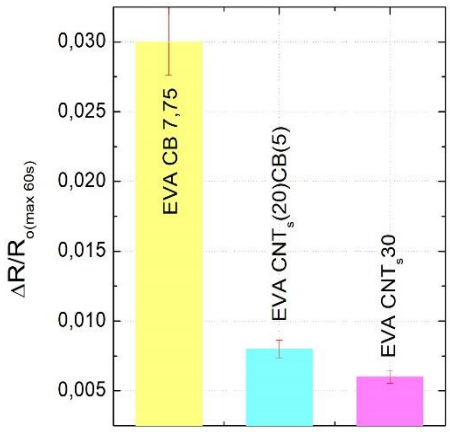

Figure 6. Average maximal relative electrical resistance change in toluene (400ppm) compared for different composite samples with EVA matrix.

4. Conclusions

In this paper hybrid composites of Pi or EVA with carbon black (CB) and carbon nanotubes (CNT) as conductive fillers for the application in VOC sensors were elaborated and studied. The electrical resistance versus the filler concentration was investigated for composites with the CB and CNT fillers separately and in the hybrid case. Electro-conductive network structure for polymer/conductive filler composites for CB and CNT was tested and analysed. Response to toluene vapour of elaborated composites was tested. Because of synergetic contribution of fillers, hybrid polymer nanocomposites show several advantages over composites where only one type of filler is used. Firstly, addition of certain amount of CB to PiCNT composites considerably decreases the composite steady state electrical resistance (that is preferable for possible sensor integration in portable VOC detection system). Secondly, the toluene sensor effect of hybrid Pi composites is greater in comparison to composites, where only CNT or CB is used as electro-conductive filler whereas EVA hybrid composite showed much lower sensing abilities than EVA CB 7.75.

It can be concluded that matrix and filler material can greatly affect composite sensing abilities and even increase relative electrical resistance change more than 10 times (EVA CB 7.75 in comparison to PiCNT$_s$15).

Acknowledgements
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