Polyisoprene-nanostructured carbon thick films as a sensitive non-selective gas indicator material.

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In this work we present filled elastomer-nanostructured carbon based film as a promising material for nonselective gas indicator. The material is made by dispersing nanostructured carbon into the natural polyisoprene raw rubber matrix and vulcanizing afterwards. When the concentration of conductive filler is close to the percolation threshold such composite exhibits sharp changes of its electrical resistance when exposed to certain organic solvent vapor. The absorbed vapor causes the matrix to swell and increases the tunneling gaps between conductive filler particles, thus increasing the electrical resistance of the composite. Similar changes on electrical resistivity are observed due to mechanical interaction on composite, such as strain or external pressure.

Thick film samples by thickness of 1 mm and 200 microns with embedded brass foil electrodes were made to compare their sensitivity to toluone vapor. All samples were weared-in by multi cyclic pre-straining using universal material testing machine. It was found out that decreasing the sample thickness leads to up to 5 times increased vapor sensitivity. This means although, that effective exposure time can be shortened up to 5 times for similar exposure conditions. The sensing intensity is compared and conclusions are made.

POLYISOPRENE-NANOSTRUCTURED CARBON THICK FILMS AS A SENSITIVE NON-SELECTIVE GAS INDICATOR MATERIAL

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European Materials Research Society
Spring Meeting 2008
Strasbourg, France, May 26-30

Abstract. Monitoring of environmental working conditions is very important for many industrial sectors, especially, when poisonous or toxic organic solvents are used in production.

In this work we present filled elastomer-nanostructured carbon based film as a promising material for nonselective gas indicator. The material is made by dispersing nanostructured carbon into the natural polyisoprene raw rubber matrix and vulcanizing afterwards. When the concentration of conductive filler is close to the percolation threshold such composite exhibits sharp changes of its electrical resistance when exposed to certain organic solvent vapor. The absorbed vapor causes the matrix to swell and increases the tunneling gaps between conductive filler particles, thus increasing the electrical resistance of the composite. Similar changes on electrical resistivity are observed due to mechanical interaction on composite, such as strain or external pressure[1].

Thick film samples by thickness of 1 mm and 250 microns with embedded brass foil electrodes were made to compare their sensitivity to toluone vapor. All samples were weared-in by multi cyclic pre-straining using universal material testing machine. It was found out that decreasing the sample thickness leads to up to 5 times increased vapor sensitivity. This means although, that effective exposure time can be shortened up to 5 times for similar exposure conditions. The sensing intensity is compared and conclusions are made.

Samples & Equipment. The polyisoprene-nanostructured carbon thick films were made by mixing 10 mass parts of an extra conductive carbon Printex XE2 and necessary curing ingredients into natural polyisoprene matrix using cold rolls. Afterwards the raw material was cured under pressure into steel mould for 15 minutes at 150°C under pressure. The brass foil mould bolsters were used as integrated electrodes, to eliminate unwanted contact resistance effects. The thick film samples were made within dimensions of 50 x 5 mm with different thicknesses from 0,25 mm to 1 mm and used for electric resistance measurements and test of mechanical properties. The electrical resistance of samples in the exsiccator was measured using Agilent model 34970A multi channel multimeter and data logger. The mechanics were taken using Zwick/Roell model Z2.5 universal testing system, equipped with HMB model Spider8 data acquisition and logging utility. The mass sorption data were taken in-situ in the small atmosphere chamber using self made KERN ALS 124-4 electronic weights system with data logger (see Fig. 4). For mass sorption experiments we used 1mm thick tablet shaped polyisoprene-carbon black composite samples (diameter of ~15 mm).

Fig. 2. The picture of sample alone and in the sample holder set up for electric resistance measurements in vapor atmosphere.

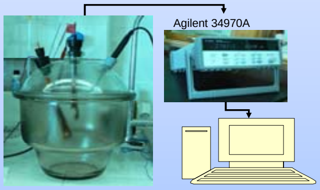

Fig. 3. Schematic illustration of the experimental set-up for sortion-caused resistivity change measurement.

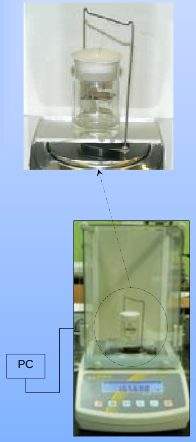

Fig. 4. Schematic illustration of the experimental set-up for mass sorption measurements.

Stand of the problem. We made mass sorption experiments in saturated toluene vapor atmosphere for polyisoprene-carbon black nanocomposite (1 mm thick film were used). We wanted to find out how much toluene vapor should be absorbed by the composite to increase the composites electric resistance. Results can bee seen in Fig. 1. Two diffusion processes – a slower and a comparatively faster can be distinguished. The faster diffusion begins to dominate at $t > 10^3$ s. Simultaneous measurements of the electrical resistance (green curve in Figure 1) prove that at $t > 10^3$ s the tunnelling currents between nano-size channels break up because of remarkable swelling of the polyisoprene interfaces between more distanced adjacent carbon particle aggregates [2].

Obtained mass sorption experiments data we compared with diffusion theories in polymer materials. As the polymer matrix used for fabrication of the nanocomposite is well above T_g and as polyisoprene has high elasticity (it ensures that polymer units need smaller activation energy for penetrant movement inside the matrix), the data should conform with Fickian sorption theory.

According to Fickian theory initial stage for sorption until 60 % or more of M_e should be <u>linear</u> (where M_e is the amount of vapor absorbed per gram of dry polymer until the sorption equilibrium is reached) and is described by equation:

$$\frac{m_t}{m_e} = \frac{4}{l}\left(\frac{Dt}{\pi}\right)^{1/2}$$

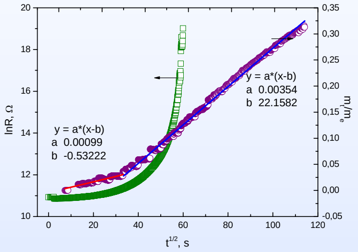

Fig1. Samples mass change and natural logarithm of electrical resistance as a function of time during sorption in saturated toluene atmosphere.

where m_t – mass of the sample at time t,
m_e – mass of the sample at $t \rightarrow \infty$,
l – thickness of the sample,
D – diffusion coefficient and t – time [3].

In the frame of this work we want to find out whether the observed mass sorption anomaly is caused by internal stresses due to anisotropic vapor sorption into the sample.

Experimental and Results. At beginning the change of electrical resistivity of 1 mm and 0,25 mm thick film samples were measured under exposure to different concentrations of toluene vapour. The results showed, that thinner sample is up-to 5 times more sensitive to the same concentration of solvent. This proves, that sensitivity of this composite can be improved simply by reducing the dimensions of the sample.

Stress/strain tests of 1 mm and 0,25 mm thick polyisoprene-carbon black composite samples for 5 % marginal strain with the speed of 5 %/s were made in clear environment (see Fig. 6 - unsaturated). The test was carried out for both directions – straining and releasing of sample, letting the sample to relax between these stages for 5 minutes. After that the samples were held in toluene vapor (concentration 217,4 ppm) and their electric resistance was measured until all conducting carbon black pathways where destroyed by the swelling of the matrix and the composite became insulator. Then mechanical properties of these samples were measured again (see Fig. 7). When calculated in the relatives, the modulus of both samples in the unsaturated state is almost identical, as is the mechanical behavior. We observed the same similarity in the case of saturated samples, only the modulus for both of them was slightly decreased by 21 %. This can be explained my weakening of the physical intermolecular interaction forces between molecule chains. Unfortunately, we weren't able to measure electrical parameters simultaneously due to technical difficulties.

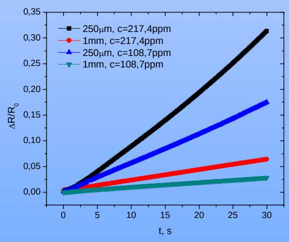

Fig. 5. Polyisoprene carbon black composite samples (thickness 1mm and 0,25 mm) electric resistance change vs. time, held in toluene vapor 30 seconds.

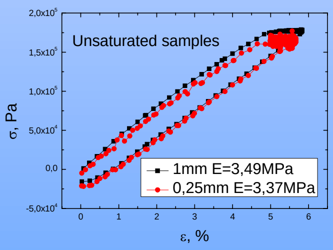

Fig. 6. Charectaristic stress-strain curves for polyisoprene carbon black composite samples (thickness 1 mm and 0,25 mm).

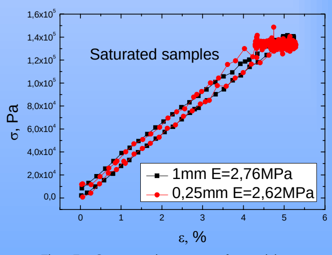

Fig. 7. Stress-strain curves for polyisoprene carbon black composite samples (thickness 1 mm and 0,25 mm), which were held in toluene vapor.

Conclusions.

1. From Fig. 6 and 7 can be seen that Young's modulus for polyisoprene-carbon black composites reduces if samples are saturated with toluene vapor due the weakening of the physical intermolecular interaction.
2. As there is no differences in stress-strain curves for saturated samples (Fig. 7) with thickness 1mm and 0,25 mm, we can say that observed two staged mass sorption is not caused by internal stresses which could form in a film because of its relatively large thickness value.
3. We suppose that sorption curve is not like characteristic Fickian in its initial state because the diffusion coefficient is dependent of concentration.
4. The sensitivity of composite can be improved simply by reducing the thickness of the sensor film. If we compare composites with thickness 1mm and 0,25 mm sensitivity to toluene vapor (217,4 ppm) (see Fig.5), we see that composite with thickness 0,25 mm has about 5 times higher sensitivity than composite with thickness 1mm. This relationship keeps if we reduce vapor concentration from 217,4 ppm to 108,7 ppm.

This work has been partly supported by the European Social Fund within the National Programme „Support for the carrying out doctoral study programm's and post-doctoral researches" project „Support for the development of doctoral studies at Riga Technical University".

The research was supported by the Council of Science of Latvia and by the Latvian National Research Program in Materials Science.

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