Investigation of mechanism of organic solvent vapours sensing effect in polyisoprene-high structure carbon black composite

M Knite, G Shakale, I Klemenoks, K Ozols and V Teteris
Institute of Technical Physics, Riga Technical University, 14/24 Azenes str., LV-1048, Riga
E-mail: knite@latnet.lv

Abstract. A study of detecting organic vapour environments of nine different solvents by polyisoprene-high structured carbon composite (PHSCBC) sensors is reported. The electric resistance of the composite is found to be increased as soon as it contacts the vapour and to return to the initial value after being removed from the environment. To reveal the mechanism of the effect, simultaneous measurements of electrical resistance, elongation, and changes caused by sorption of organic solvent molecules in the bulk of PHSCBC samples were made in real time. From sorption experiments it has been found that the increase of electric resistance is generally dominated by absorption of solvent molecules in the matrix material, subsequently swelling it up and increasing the distance between conductor particles. The experiments prove that a remarkable and rapid change of the resistance could be explained by change of the tunnelling currents between adjacent carbon nano-particles.

1. Introduction
Electrically conductive polymer composites with different sensing properties [1-5] can be obtained when particles of good conductors (carbon black, graphite powder, carbon fibre, microparticles of metals) are implanted into an insulating polymer matrix. Such materials may become the basis for a new generation of cheap large-size sensors.

A continuous insulator-conductor transition is observed in two-component systems at gradual increase of the number of conductor particles randomly dispersed in an insulator matrix. Most often such transitions (called percolation transitions) are represented by the model of statistical percolation [6, 7]. In the vicinity of the percolation transition, the electrical conductivity \( \sigma \) of the composites changes under the smallest deformation of the matrix manifesting the strain. The change of the electrical resistance under strain on the microscopic level can be explained as the result of destruction of the percolation structure of the network of conductive particles.

Irreversible change of the electrical resistance at deformation by stretch or pressure has been found in the case of micro-size particles of good conductors [1-3].

New properties are expected in case the composite contains dispersed nano-size conducting particles [8-15]. If the carbon particle size and specific surface area of carbon black are between 60 to 200 nm and 16-24 m\(^2\)/g, respectively (low structure carbon black (LSCB)), the electrical resistance of natural rubber composites slightly decreases with the applied pressure [10]. The effect is assumed to be a result of increasing bulk concentration of conductive carbon particle channels under pressure. If high structure carbon black (HSCB) (specific surface 950 m\(^2\)/g, mean diameter 25 nm) are used as the
filler, the electrical resistance of the polyisoprene-carbon nanocomposite grows extremely and reversibly with both tensile and compressive strain [11-13]. Since the HSCB in the elastomer matrix have a higher mobility compared with LSCB, the electro-conductive network in this case is easily destroyed by very small tensile or compressive strain. We expect this feature of the elastomer – HSCB composite can be used for a very sensitive and rapid detection of different chemical compounds – liquids and vapours. The highest sensitivity is expected in the percolation region (9-11 mass parts of the HSCB filler) of relaxed polyisoprene composite. Due to swelling of the matrix, resistance of such composites should increase remarkably and reversibly.

2. Experimental

The PHSCBC was made by rolling highly structured PRINTEX XE2 (DEGUSSA AG) nano-size carbon black and necessary additional ingredients – zinc oxide and sulphur – into a Thick Pale Crepe No9 Extra polyisoprene (MARDEC, Inc.) matrix and vulcanizing under high pressure at 140 °C for 15 min. The mean particle size of PRINTEX XE2 is 30 nm, DBP absorption – 380 ml/100 g, and the BET surface area – 950 m²/g. Samples cut from the sheets to the size of 70 mm × 5 mm × 1 mm were used in the chemical sensor experiments. Using special glue and method, electrodes with the size of 10 mm × 5 mm were fixed to both ends and sides of sample. As electrode material epoxy laminate covered with 105 μm copper alloy was used. Schematic illustration of the experimental set-up is described in [14]. The simultaneous change of both the electrical resistance and the elongation of the sample exposed to vapour of organic solvent were possible to be measured. The elongation of sample was photographed with digital camera, after that printed on transparent to be measured under optical microscope (relative error was 1% for the largest elongation (Δl/l₀ = 0.1)).

For sorption experiments 0.55 mm thick polyisoprene and polyisoprene-carbon black composite samples were cut to have diameter of ~15 mm. A pellet (d = 10 mm) of carbon black powder was pressed at 60 bar.

A KEITHLEY 6487 picoammeter combined with a computer were used to take readings and make data processing. Data were recorded as \( R = f(t) \). The sample was located in a locked vessel (volume 5 l) containing the vapour of the corresponding solvent.

In the case of the mass change of the sample it was held in the solvent vapour in a specially equipped enclosure, measurements were taken by KERN ALS 124-4 electronic weights connected to a computer (error ± 0.2 mg).

3. Results and discussion

To perform chemical sensing experiments, carbon-polymer nanocomposite samples with 10 mass parts of HSCB were placed for 30 s in a vessel with saturated vapour of the organic solvent to be detected. After that the sample was taken out and left in air (at normal atmospheric pressure and temperature \( T = 294 \) K) for 5 h, and the experiment was repeated five days in row. The results of one of the experimental series are shown in figure 1. Resistance of the samples practically returned to the initial value after five hours of relaxation, so that the effect may be considered reversible. During relaxation in air, in our opinion, the change of the sample resistance is defined by three factors: diffusion of solvent molecules from internal layers of the matrix to the surface, relaxation of cross-section connections of the polymer, and recovery of the network of electro-conductive carbon nanoparticles.

Experiments of the change of the sample mass as a function of time the sample is kept in organic solvent vapour were also used to find out the mechanism of the change of resistance. For example, specimens of pure polyisoprene, PHSCBC, and a pellet of compressed HSCB powder were held in toluene vapour for ~ 48 hours and mass as function of time (sorption curve) was recorded (figure 2). Sorption of vapour in extruded carbon filler in the initial period (first 15 min) is approximately three times (approximately 1,5 times after up to 10⁴ min) as big as that of pure polyisoprene rubber. Yet the sorption of vapour in PHSCBC material in the initial period is around 1,3 times smaller compared with
pure polyisoprene rubber, although it seems that carbon filler should increase the vapour sorption in the PHSCBC material. That can be explained, firstly, by the fact that in the PHSCBC composition there are only 10 mass parts of carbon and, secondly, in processing (mixing and vulcanizing) the PHSCBC compounds insulating polyisoprene layers are formed between the carbon nano-particles. So, even near the percolation threshold (10 mass parts of carbon), when electro-conductive channels are formed, very thin polyisoprene intermediate layers between the nano-particles still exist and tunnelling currents may emerge between the channels. Only after approximately 28 h the sorption of vapour by the PHSCBC material noticeably exceeds the sorption by polyisoprene rubber, which indicates that only after this period of time the sorption in the filler begins to play substantial role. Consequently, 1) the obtained result indirectly proves the existence of quantum effect – tunnelling currents in the PHSCBC material, 2) sorption of vapour in the polyisoprene matrix plays absolutely uppermost role in effect of gas sensing (due to sorption of vapour molecules and swelling of the matrix the distance between carbon nano-particles increases and tunnelling currents rapidly decrease).

The fit of the sorption curve of toluene vapour in PHSCBC (see figure 3) is shown by the one-dimensional diffusion equation [16] (based on Fick’s second law)

\[ \frac{m_t}{m_e} = \frac{4}{l} \left( \frac{D t}{\pi} \right)^{1/2}, \]  

(1)

where \( m_t \) – mass of the sample at time \( t \), \( m_e \) – mass of the sample at \( t \to \infty \), \( l \) – thickness of the sample, \( D \) – diffusion coefficient and \( t \) – time. Two diffusion processes – a slower and a comparatively faster can be distinguished in figure 3. The faster diffusion begins to dominate at \( t > 10^3 \) s. Simultaneous measurements of the electrical resistance (figure 3) prove the above discussed sorption processes (figure 2), i.e., 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. At the same time diffusion into the HSCB aggregates begins to dominate.

To obtain a comprehensive picture of the mechanism of the organic solvent vapour effect, simultaneous measurements of elongation and electrical resistance of the polyisoprene nanocomposite sample were made in real time. Some results obtained with toluene vapour are shown in figure 4. It is seen that in case of a relatively longer time the elongation growth is approximately linear while the resistance shows an exponential growth. It seems that the tunnelling current between nanoparticles in thin layers of the matrix decreases because the polymer matrix absorbs the solvent molecules separating the carbon nanoparticles from each other. The circumstantial evidence of the existence of

**Figure 1.** The change of relative resistance vs. time for the sample, held in saturated vapours of different solvents.

**Figure 2.** The change of mass of three materials (polyisoprene rubber, HSCB and its composite) samples as functions of the time of exposure to toluene vapour.
tunnelling currents in the polyisoprene – high structure carbon nanoparticle composites is also given by AC reported earlier [15].

4. Theoretical model of the changes of electrical resistance caused by swelling of the composite

To explain the reversibility of the vapour sensing effect at the nanoscale level the bonds between the nanostructure agglomerates of carbon black and the elastomer chains are assumed to be stronger compared with the bonds between themselves. Possibly, they are bonded by free radicals of the chains thermally activated during vulcanisation. As the composite swells, the carbon agglomerates are pulled apart and remaining chemically bonded to the polymer chains are dragged along by the latter. In the case of poorly structured nano-size or micro-size filler the bonding between carbon particles and polymer chains is weak; at deformation the filler makes irreversible (rigid and rather immobile) clusters in the insulating matrix. In our case the polymer chains return to (“remember”) original positions as the adsorbed molecules evaporate and contacts between the carbon agglomerates are restored.

The total electrical resistance of a conductor-filled polymer composite is a function of both the resistance of each conducting particle and the polymer matrix. Since the conductivity of a conducting particle is very large compared with that of the polymer matrix, the resistance of the particle may be neglected. When particles are separated far enough from each other, no current flows through the composite. If the distances separating particles are small, tunnelling currents may arise.

According to the model derived in [2], the total electrical resistance $R$ of the composite is calculated as:

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

where $L$ is the number of particles in a single conducting path, $N$ - the number of conducting paths, $h$ - Plank’s constant, $s$ - the least distance between conductive particles, $a^2$ – the effective cross-section of tunnelling, $e$ – the electron charge, and $\gamma$ is calculated as:

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

where $m$ is the electron mass and $\Phi$ - the height of the potential barrier between adjacent particles.
If the swelling of a composite matrix occurs, the resistance will be altered due to particle separation. Assuming that under swelling of matrix the particle separation changes from $s_0$ to $s$, the relative resistance ($R/R_0$) is given by

$$
\frac{R}{R_0} = \left( \frac{s}{s_0} \right) \exp[\gamma (s - s_0)],
$$

(4)

where $R_0$ is the initial resistance, and $s_0$ - the initial particle separation. In case of elastomer composite the separation $s$ under swelling of matrix is calculated as

$$
s = s_0 (1 + \varepsilon) = s_0 \left[ 1 + \left( \frac{\Delta l}{l_0} \right) \right],
$$

(5)

where $\varepsilon$ is the relative elongation of matrix during swelling, $\Delta l$ – elongation of the composite sample, and $l_0$ – initial length of the sample. Substitution of eq. (5) into eq. (4) yields

$$
\ln R = \ln R_0 + \ln \left( 1 + \frac{\Delta l}{l_0} \right) + A_0 \left( \frac{\Delta l}{l_0} \right)
$$

(6)

where $A_0 = \gamma s_0$.

The experimental data obtained on samples of the composite containing 10 mass parts of HSCB is compared with eq. (6) in figure 5 (solid line). It is seen that the model of tunnelling currents quite well describes the experimental data at small deformations $\Delta l/l_0 < 0.1$ with $A_0 = 47.17$ (the approximation $\ln \left[ 1 + (\Delta l)/l_0 \right] \approx 0$ being made in eq. (6)).

5. Conclusions

Different organic solvent vapours can be detected and distinguished by polyisoprene and high structure carbon black nanocomposite sensors.

Mass sorption experiments indicate that organic solvent vapour molecules are mainly absorbed into the matrix material (for which reason the electric resistance increases) and by the carbon black nano-particle aggregates. Sorption of the vapour molecules in carbon black does not affect electric resistance of the composites.

The interaction of solvent vapour with polyisoprene–high structure carbon nanoparticle composite is different for different solvents. The polymer matrix absorbs the solvent molecules in different ways and the carbon nanoparticles separate from each other at different velocities. The mechanism of the effect is seen in the change of thickness of the insulating polymer layer between the carbon nanoparticles as the polymer matrix swells up absorbing the solvent molecules. The tunnelling conductance model is consistent with the experimental data on electrical resistance measured with respect to swelling-caused elongation of the composite.

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