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Polyisoprene–carbon nano-composites for application in multifunctional sensors

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Abstract

Two simultaneously existing giant effects – strain sensing and gas sensing – were found and investigated in polyisoprene–carbon nano-composites. Sensitivity to any kind of deformation was found depending on the time of vulcanization. High-structure carbon nano-particle filler was chosen as guaranty of manifestation of polyisoprene composites as multifunctional sensors with high reversibility and rapidity of sensing effects.

Keywords: Elastomer nano-composites; Mechanochemical processing; Electronic properties; Strain sensing; Gas sensing

1. Introduction

One of well-known methods to obtain a conductive polymer composite is adding carbon black to a polymer matrix or to a polymer blend. Most often such polymer composites are used as inactive thermodynamic materials in electric heating elements and resistors [1].

New interesting properties are expected in case the composite contains dispersed nano-size conducting particles. If the carbon particle size and specific surface area are between 60 and 200 nm and 16–24 m^2/g, respectively (low-structure carbon nano-particles (LSNP)), the electric resistance of natural rubber composites decreases weakly with the applied pressure [1]. The effect is explained by increase of the volume concentration of conductive carbon particle channels under pressure. The resistance of polyisoprene–carbon nano-composite grows rapidly and reversibly with both tensile and compressive strain when high-structured carbon nano-particles (HSNP) (specific surface 950 m^2/g, mean diameter 25 nm) are used as filler [2]. In this case the electro-conductive network is easily destroyed by very small tensile or compressive strain because the HSNP have a higher mobility in the elastomer matrix compared with LSNP. We suppose that this feature of the elastomer–HSNP composite can be used for very sensitive and rapid detection of different chemical compounds—liquids and vapours. In case high-structured carbon nano-particles (HSNP) are used as the filler in a polyisoprene–carbon nano-composite (PCNC), a giant reversible growth of resistance is obtained with either tensile or compressive strain [3]. The highest sensitivity is expected in the percolation region (9–11 mass parts of the HSNP filler) of relaxed polyisoprene composite. Resistance of such composite increases remarkably and reversibly due to swelling of the composite matrix.

Certainly, this phenomenon is already well known and has received the name “electronic nose”. A number of studies (see [4,5]) are concerned with applications of the effect (environmental and food-quality monitoring, medical diagnostics). However, the time of reaction of the “electronic nose” to any chemical compounds (according to published data) is 20 min or more. The purpose of the present study is finding a material that would react to presence of organic solvents much faster. Electrical resistance of PCNC as a function of deformation on stretching or compression is studied in composite samples for different times of vulcanization.

Vapours of different chemical substances differ by the rate they change the resistance is. Results are presented here.

2. Experimental

The principle of sensing is based on a shift of percolation threshold under thermodynamic forces, for example, under tensile strain, as shown in Fig. 1. The highest sensitivity is expected in the percolation region (samples of 9–11 mass fractions of carbon nano-particles) of a relaxed polyisoprene composite [3]. For that reason further research was performed on samples

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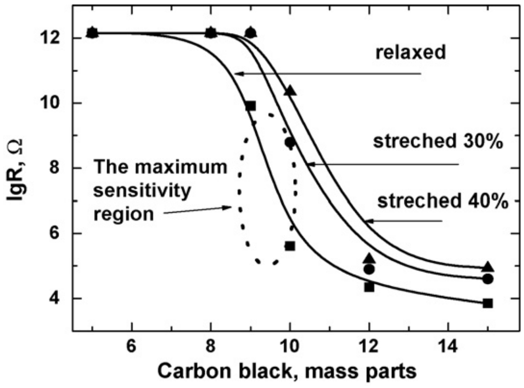

Fig. 1. Electrical resistance *R* of nano-composite (under tensile strain) as function of different amount of carbon black.

of polyisoprene composite containing 10 mass parts of carbon black. The PCNC was made by rolling highly structured PRINTEX XE2 (DEGUSSA AG) nano-size carbon black and necessary additional ingredients – sulphur and zinc oxide – 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 m^2/g. Samples cut from the sheets to the size of 70 mm × 5 mm × 1 mm were used in the experiments. Schematic illustration of the experimental set-up is shown in Fig. 2. The change of the electric resistance of the sample exposed to vapour of organic solvent is measured.

3. Results and discussions

3.1. Mechanical strain sensing effects

To obtain maximum response speed of the smell sensor, maximum reversible change of electric resistance induced by the presence of vapourized organic solvent, a natural polymer of high elasticity was chosen as the matrix. Maximum sensitivity of the composite, as mentioned above, is expected at 10 mass parts of the HSNP filler. Sensitivity to any kind of deformation also depends on the time of vulcanization. Electric resistance vs. stretching for different durations of vulcanization of PCNC containing 10 parts of carbon nano-particles is shown in Fig. 3. Resistance as function of deformation under pressure of the same samples are given in Fig. 4.

As seen in Figs. 3 and 4, the most sensitive nano-composites are obtained at a rather short vulcanization time (5 min). In this case fewer cross-bonds are formed in the polymer matrix and the nano-particles move more easily between the polymer molecules. However, reversibility of the effect in this sample is not so good, which may be explained by rather poor elasticity due to insufficient vulcanization. At longer vulcanization (15 min), sensitivity of the material decreases since mobility of the nano-particles is hindered because of too many cross-bonds. Therefore, 10 min is the optimum time of vulcanization for this particular composite (10 mass parts of carbon).

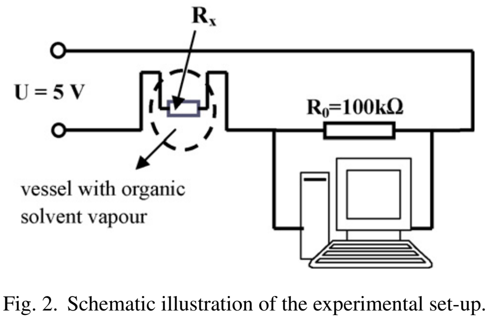

Fig. 2. Schematic illustration of the experimental set-up.

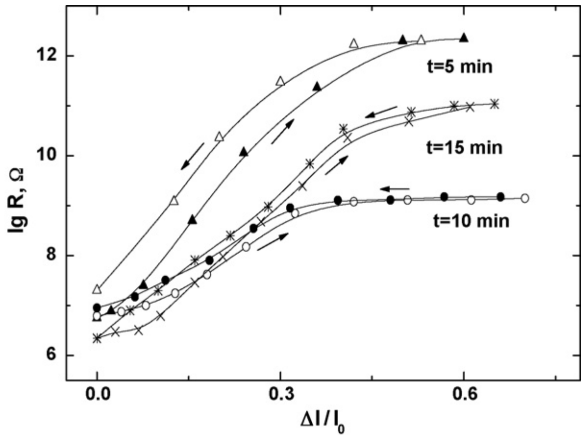

Fig. 3. Electric resistance vs. stretching for different duration of vulcanization of PCNC containing 10 parts of carbon nano-particles.

3.2. Sensing vapours of organic solvents

To perform chemical sensing experiments the carbon–polymer nano-composite samples were placed for 30 s in a vessel with saturated vapour of organic solvent. After that the sample was redrawn and left in air (at normal atmospheric pressure and temperature $T = 294$ K) for 5 h and the experiment was repeated for 5 days in row.

Resistance R_x of the sample evolved off under the following formula:

$$R_x = \left(\frac{5V}{U_0} - 1\right) R_0, \quad R_0 = 100\,\mathrm{k}\Omega$$

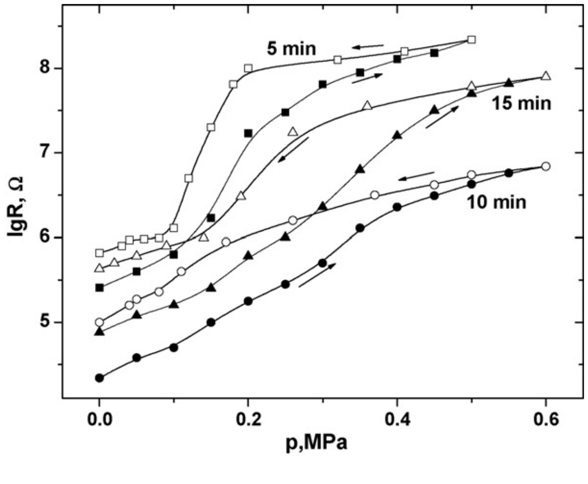

Fig. 4. Resistance as function of deformation under pressure for different durations of vulcanization of PCNC containing 10 parts of carbon nano-particles.

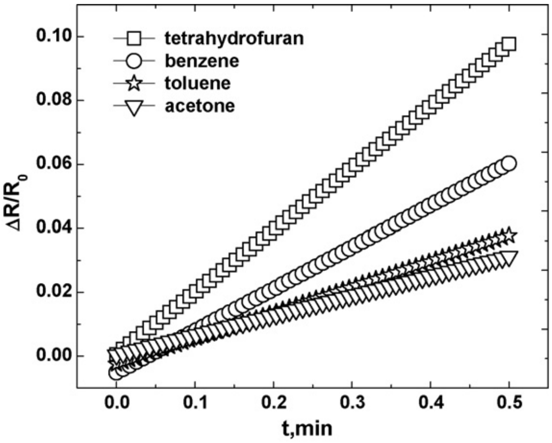

Fig. 5. Relative change of resistance vs. time when sample is held in vapour of different solvents.

The voltage V applied to measure resistance is read out and stored automatically by a computer and the relative change of resistance versus time the sample is held in the vapour of a solvent ($\Delta R/\mathrm{R}) = f(t)$ is constructed. Results of one of the series of experiments are shown in Fig. 5.

Resistance of relaxing sample as a function of time $R_x = f(t)$ is shown in Fig. 6.

The experimental curves have been investigated mathematically by means of a computer software. The experimental curves are found to be well described by the equation:

$$R = R_0 + A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$$

parameter values of which depend on the solvent as given in Table 1.

As seen from the mathematical equation, a fast and a slow process are involved in relaxation of the resistance. The values of τ_1 and τ_2 are different for various solvents, since the size of solvent molecules is different. The chemical interaction of solvent vapour with polyisoprene–carbon nano-composite (that, in turn, is connected with carbon nano-particles) is also different for various solvents. Resistance of the samples practically returned to the initial value after 5 h of relaxation. Therefore, the effect may be considered to be reversible.

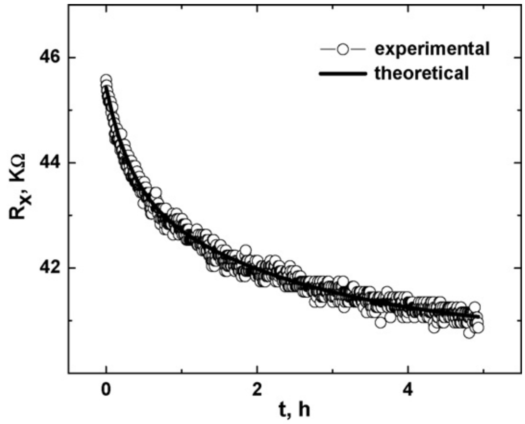

Fig. 6. Relaxation of the sample (5 h) in air after being held for 30 s in benzene vapour.

Table 1
Values of factors in the equation describing the changing resistance depending on the organic solvent

Organic solvents	A_1	A_2	τ_1	τ_2
Acetone	1356	1197	0125	1876
Benzene	2719	3801	0450	4107
Tetrahydro-furan	2831	3727	0366	2834

The explanation of the effect is as follows. The matrix of polymer soaks up the solvent molecules (solvent molecules are absorbed) and carbon nano-particles are separated from each other. As a result, the tunneling current between nano-particles in thin layers of the matrix decreases.

During relaxation in air, in our opinion, the change of the sample resistance is determined 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 relaxation of a volumetric lattice of the electro-conductive carbon nano-particles.

In future manufacturing and experimental testing of thinner samples is planned. A faster response to presence of organic solvents in the ambient atmosphere and faster relaxation of the sample are expected.

4. Conclusions

The most sensitive nano-composites are obtained at a rather short vulcanization time (5 min). In this case fewer cross-bonds are formed in the polymer matrix and the nano-particles move more easily between the polymer molecules. However, reversibility of the effect in this sample is not as good, which may be explained by rather poor elasticity due to insufficient vulcanization. At longer vulcanization (15 min) sensitivity of the material decreases since mobility of the nano-particles is hindered by too many cross-bonds. Therefore, 10 min is the optimum time of vulcanization for the particular composite (10 mass parts of carbon).

The chemical interaction of solvent vapour with polyisoprene–carbon nano-composite (that, in turn, is connected with carbon nano-particles) is different for various solvents. Resistance of the samples practically returned to the initial value after 5 h of relaxation. Therefore, the effect may be considered to be reversible.

The explanation of the vapours sensing effect is seen as following. The matrix of polymer soaks up the solvent molecules (solvent molecules are absorbed) and carbon nano-particles are separated from each other. As a result, the tunneling current between nano-particles in thin layers of the matrix decreases. During relaxation in air, to our opinion, the change of the sample resistance is thought to follow three processes: diffusion of solvent molecules from internal layers of the matrix to the surface, relaxation of cross-section connections of the polymer, and relaxation of a volumetric lattice of the electro-conductive carbon nano-particles.

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