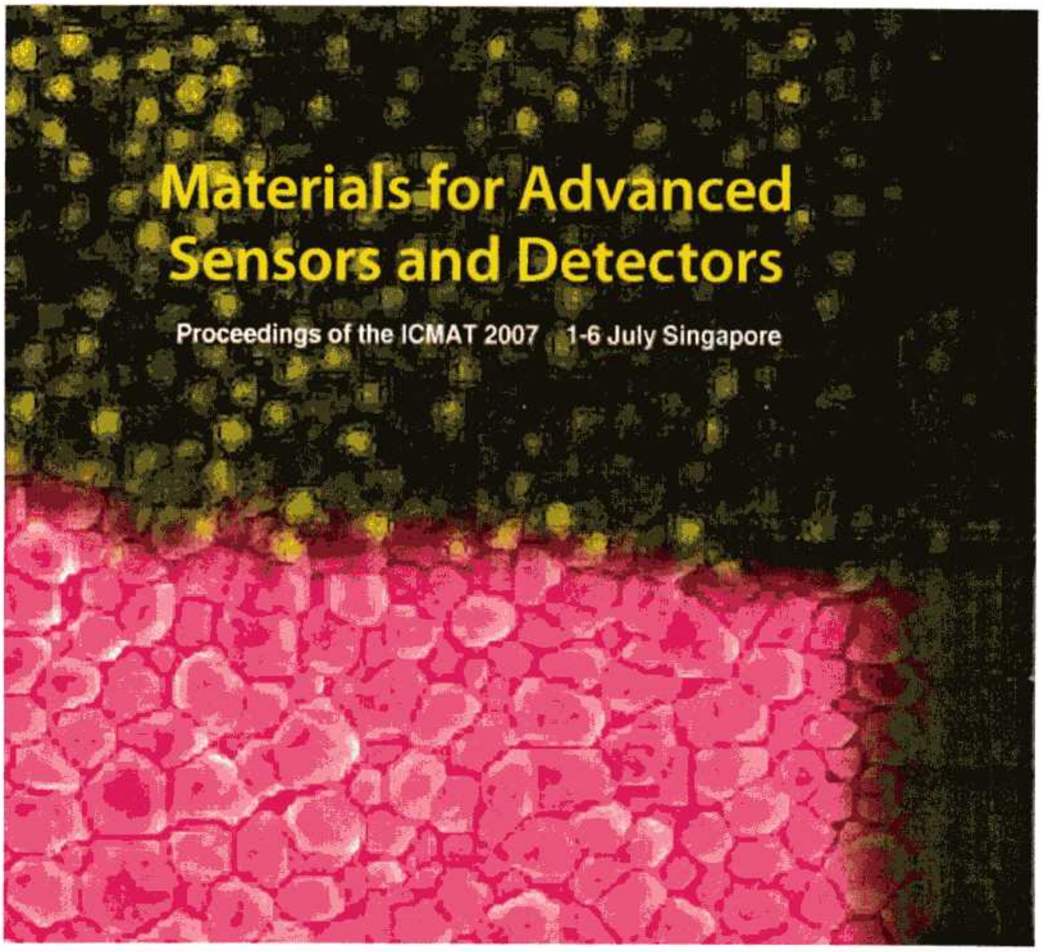

Materials for Advanced Sensors and Detectors

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ELASTOMER – CARBON NANOTUBE COMPOSITES FOR COMPRESSIVE STRAIN AND PRESSURE SENSING

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Carbon nanotubes offer attractive possibilities for developing new sensors because of superior mechanical and electrical properties. So far most studies relate the mechanical deformation to the change of nano-scale electrical properties. We present an attempt to use multi-wall carbon nanotubes (MWCNT) to develop a new flexible composite for macro-scale pressure sensors. Elastomer composites containing dispersed nano-size particles, for example, polyisoprene - multi-wall carbon nanotube composites,(PMCNTC) were prepared by treatment of the composite matrix with chloroform providing an increase of mobility and better dispersion of the nano-particles within the matrix. MWCNT with a small amount of solvent was carefully ground in a china pestle before adding to the polyisoprene matrix. Both the polyisoprene matrix solution and concentrated MWCNT solution were mixed in a mixer with small glass beads at room temperature for a certain time. The product was then dried and vulcanized under high pressure at 160ºC for 20 min.PMCNTC shows attractive pressure sensing properties. The highest sensitivity has been reached in the region slightly above the percolation threshold of the composite. The results are compared with the polyisoprene and high structure carbon black composites (PHSCBC) elaborated and prepared by a similar technology. A mechanism of the sensing effect is being discussed

1. Introduction

Pressure and strain sensors as well as tactile sensors for robots are important in many fields of science and engineering. One of the main limitations of existing conventional sensors is that they are discrete point, fixed directional and not flexible sensors, and are separate from the material or structure that is being monitored. There is a need to develop new flexible large-area sensors that can be embedded into the material and can be used for multiple location sensing.

Polymer – electro-conductive particle composites for strain sensing can be obtained when particles of good conductors (carbon black, graphite powder, carbon fibres, particles of metals) are implanted into an insulating polymer matrix [1-5]. A continuous insulator-conductor transition is observed in two-component systems at gradual increase of the number of randomly dispersed conductor particles in an insulator matrix. Most often such transitions, called percolation transitions, are described by the model of statistical percolation [6-7]. In the vicinity of the percolation transition, the electrical conductivity σ of the composites changes under a 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.

An 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 interesting properties are expected in case the composite contains dispersed nano-size conducting particles [8-13]. Polymer – electro-conductive nanostructure composites offer attractive alternatives for developing new generation of flexible large-size sensors because of their superior mechanical and electrical properties.

Carbon nanotubes in itself change their electrical properties when subjected to strain. Farajian at al [14] calculated theoretically the I-V characteristics and showed that the current in carbon nanotube with metallic conductivity (properties) decreases with increased bending, while that of tube with semiconducting conductivity increases. A possible application to nano-electro-mechanical sensors and switches is discussed [14].

An attempt to use the strain sensing capability of single-wall carbon nanotubes (SWCNT) on the nanoscale to develop a strain sensor on the macroscale was made by Dharap at al [15]. A carbon nanotube film has been produced by mixing unpurified SWCTNs with 0.25 mg/ml N,N-dimethylformamide (DMF). The film (10 μm thick) was composed of mechanically entangled randomly oriented nanotube bundles, to which it has isotropic electronic properties [15]. The carbon nanotube film was attached to a brass plate with a PVC film between them. A four point probe was used to measure voltage changes in the carbon nanotube film. The brass specimen was subjected to tension as well as compression cycles. It can be concluded that there is a nearly linear relationship between the measured change in voltage and the strains in the carbon nanotube films [15].

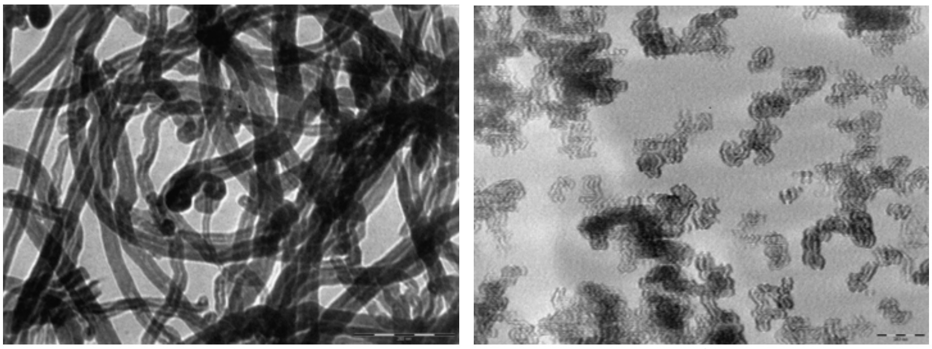
The purpose of our paper was the design, elaboration and investigation of polyisoprene and multiwall carbon nanotube (MWCNT) composites for application in compressive strain (pressure) sensors as well as to compare them with the polyisoprene and high structure carbon black composites elaborated and prepared by the same technology.

2. Samples and experimental procedure

The experimental work was done at the Institute of Technical Physics of Riga Technical University. Polyisoprene composites containing dispersed nano-size particles, in our case two types, multiwall carbon nanotubes (MWCNT) Aldrich 636835 as well as highly structured carbon black (HSCB) Printex XE2 were prepared by a "solution method" as follows. The matrix composition was treated with chloroform providing: 1) an increase of the nano-particles mobility and 2) better dispersion of the nano-particles within the matrix. The prepared matrix composition was allowed to stand for swelling ~ 24 h. Nano-size carbon black is carefully grinded with a small amount of solvent in a china pestle before addition to the polyisoprene matrix. The polyisoprene matrix solution and the nano-size carbon concentrated solution were mixed in a mixer with small glass beads at room temperature for 15 min. Then the product is poured out into a little aluminium foil box and standing ~ 24 h, dried at 40 ºC for more than12 h and vulcanized under high pressure at 160ºC for 20 min.

The size of MWCNT: OD = 60-100 nm, ID = 5-10 nm, length = 0.5-500 μm, BET surface area: 40-300 m^2/g. A TEM image (Figure 1) shows the entangled structure of MWCNT. The average particle diameter of HSCB is 30 nm and its dibutyl phthalate (DBP) absorption is 380 ml/100g. Its surface area is 950 m^2/g.). A TEM image (Figure 2) shows the high structure of Printex XE. A Philips TEM-301 transmission electron microscope equipped with Keen View II CCD camera was used for nanoscopic investigation of the fillers.

To study compressive strain and dependence of the electrical resistance of composites on the compressive force, samples of the size of 12 mm × 12 mm × 1.5 mm were cut from the vulcanized sheets with HSCB and samples of the size of 20 mm × 11.5 mm × 2.4 mm from the vulcanized sheets with MWCNT respectively. To avoid contact effects thin vacuum deposited Al electrodes were used. The electrical properties of the samples were measured using a custom modified Zwick/Roell Z2.5 universal testing machine, HQ stabilized power supply as well as a KEITHLEY Model 6487 Picoammeter/Voltage Source all synchronized with the HBM Spider 8 data acquisition logger.



a) b)

Figure 1. TEM image of the multi wall carbon nanotube Aldrich 636835 (a) and the high structured carbon black nanoparticle Printex XE2 (b). Scale mark is 200 nm.

3. Results and discussion

To estimate roughly the percolation threshold, a series of PMCNTC were prepared with 6.1, 8.3, 10.9, 12.1 and 14.5 mass parts (m.p.) of MWCNT added to 100 m.p. of polyisoprene. The PHSCBC with 6.6, 7.7, 8.8, 9.35, 9.9 and 11 m.p. of HSCB added to 100 m.p. of polyisoprene were prepared for confrontation with PMCNTC using the same preparing procedure. The 8.3 m.p. PMCNTC and 8.8 m.p. PHSCBC appeared to be within the region of percolation threshold (Figure 2). Samples with 6.6, 7.7 and 11 m.p. of HSCB as well as samples with 6.05, 12.1 and 14.5 m.p. of MWCNT were obviously outside the region of percolation threshold. The samples with 6.6 and 7.7 m.p. of HSCB were practically insulators, while the samples with 9.9 and 11 m.p. of HSCB were good conductors. The percolation threshold in the case of MWCNT composites was not as sharp as in the case of HSCB composites. For HSCB composites prepared by the "solution method" the percolation threshold is slightly shifted to lower values of the HSCB concentration than for HSCB composites made by the "rolling in" method used in our

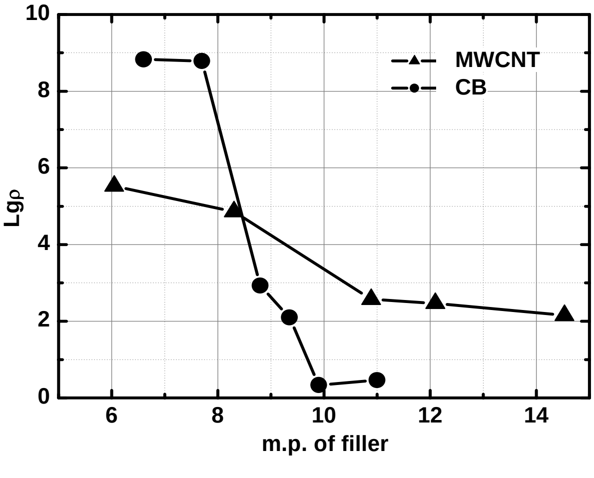


Figure 2. Electric resistivity ρ of the polyisoprene – MWCNT composite and polyisoprene – HSCB composite vs. concentration (mass parts) of the corresponding filler (percolation curves).

previous investigations (the composite was made by rolling highly structured nano-size carbon black (Printex XE2, DEGUSSA AG) and the necessary additional ingredients (S, ZnO) into a polyisoprene matrix and vulcanizing under high pressure at 140ºC for 15 min.) [12]. The difference mentioned above can be explained due to better dispersion of HSCB in polyisoprene matrix by the "solution method".

Furthermore, the resistance R of the composites was examined with regard to the compressive force and the absolute mechanical deformation Δl in the direction of the force. In this paper we report resistance changes at small compressive strains. No variation in the electric resistance was found for composites with 7.7 m.p. HSCB and 3.63 m.p. MWCNT. From all composites examined, the best results were obtained for samples with 12.1 and 14.53 m.p. MWCNT as well as 10 m.p. HSCB which apparently belonged to the region slightly above the percolation threshold. The resistance of these samples decreased about 20% upon a 2% compressive strain for the 12.1. m.p. MWCNT composite (Fig.3) and about 60% for the 14.53 m.p. MWCNT composite (Fig.4). After the samples were released, the resistance of the MWCNT composite practically returned to its previous value, that means, reversible piezoresistive effect curves were observed. Each piezoresistive effect curve has a minimum value of compressive strain that could be defined as critical compressive strain. If the compressive strain is less than the critical strain, the resistance is monotonic decreasing. If the compressive strain is more than the critical strain, the resistance is monotonic increasing. In order to explain the experimental results mentioned above we base on a model derived in [2]. The total electrical resistance of a conductor-filled polymer composite is a function of both the resistance of each conducting carbon nanotube and the polymer matrix. Since the conductivity of a carbon nanotube is very large compared with that of the polymer matrix, the resistance of the nanotube may be neglected. When nanotubes are separated far enough from each other, no current flows through the composite. If the distances separating particles are small, tunnelling currents may arise.

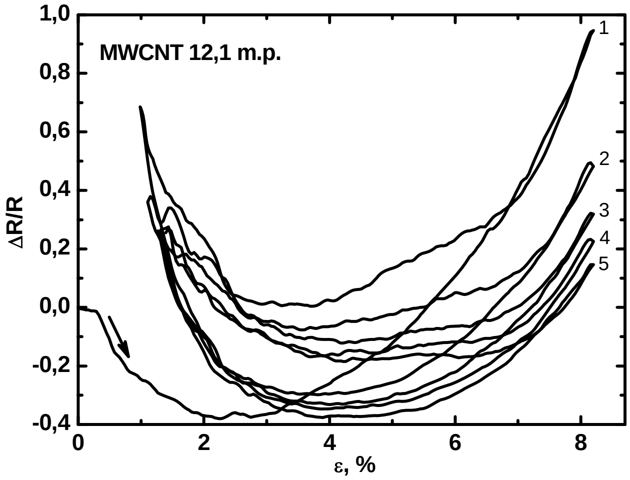


Figure 3. Relative change of the electrical resistivity as a function of relative compressive strain for the polyisoprene composite containing 12.1 mass parts of the multi wall carbon nanotubes during sequential pressure loading cycles. Numbers in the graph correspond to the respective cycles.

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

$$R=\left(\frac{8\pi hs}{3a^2\gamma e^2}\right)\left(\frac{L}{N}\right)\exp(\gamma s) \tag{1}$$

where *L* is the number of carbon 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 tunneling, *e* – the electron charge, and γ is calculated as:

$$\gamma=\frac{4\pi(2m\Phi)^{0,5}}{h} \tag{2}$$

where *m* is the electron mass and Φ the height of the potential barrier between adjacent particles. Equation (1) shows that the decrease of s caused by the external pressure leads to a decrease of the resistance of PMCNTC, that is, the external pressure makes the polymer gaps between MWCNT smaller decreasing the resistance of one individual conductive

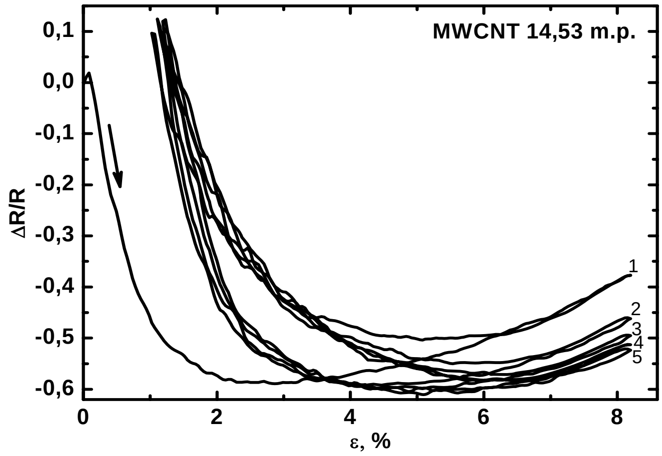


Figure 4. Relative change of the electrical resistivity as a function of relative compressive strain for the polyisoprene composite containing 14.53 mass parts of the multi wall carbon nanotubes during sequential pressure loading cycles. Numbers in the graph correspond to the respective cycles.

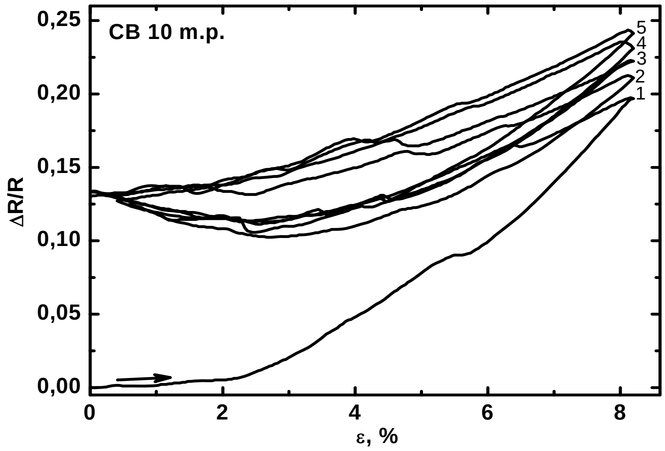


Figure 5. Relative change of the electrical resistivity as a function of relative compressive strain for the poliisoprene composite, containing 10 mass parts of the high structured carbon black during sequential pressure loading cycles. Numbers in the graph correspond to the respective cycles..

channels. On the one hand the external pressure makes the gaps between nanotubes smaller, leading to the formation of new conductive channels. On the other hand, the transverse slippage of MWCNT, caused by external pressure, leads to the destruction of conductive channels. If the formation effect plays a main role, the number of conductive channels increases. If the destruction effect plays a main role, the number of the conductive channels decreases. Therefore the change in the number of conductive channels is the main reason to cause the experimental results that the composite resistance decreases first and then increases in the process of compression.

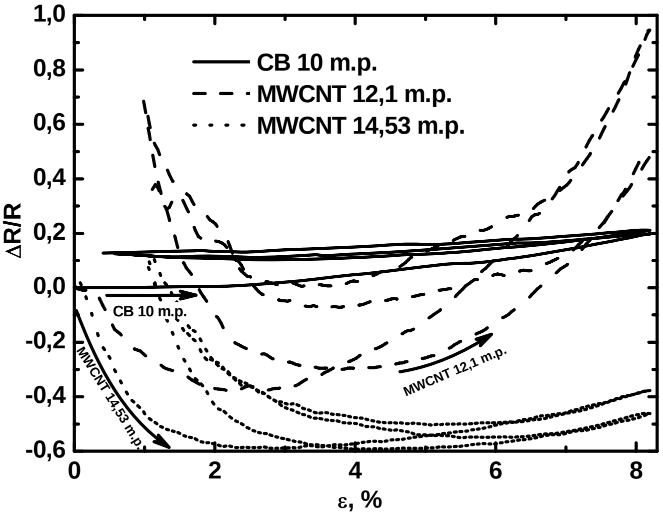


Figure 6. Relative change of the electrical resistivity as a function of relative compressive strain for the polyisoprene composite samples with 12.1 and 14.53 mass parts of the multi wall carbon nanotubes and 10 mass parts of the high structured carbon black during repeated pressure deformation up to 8% for the first 2 cycles.

In case of greater strain a relatively large hysteresis of R(ε) (Fig. 3 and Fig. 4) was observed. It can be explained by the entangled structure of MWCNT as well as due to the high stiffness of nanotubes. As it is seen in Fig.3 and Fig.4 a slight "sinking" of resistance of the compressed sample during cycling (see cycles number 1-5 on Fig.3 and Fig. 4) can be explained due to raise of the number of conductive channels in the process of cycling of the compression.

The electrical resistance response to approximately the same compressive strain for composites of 10 m.p. HSCB is shown in Fig. 5. In this case the decrease of resistance is inconspicuous for small (2%) deformation. The resistance increase (no conductive channel formation occurs) and the absolute value of piezoresistance effect is remarkably weaker for 8% compressive strain than in case of PMCNTC (Fig.6). It could be explained due to the high mobility of HSCB nanoparticles in the polyisoprene matrix during strain change.

4. Conclusions

The maximum change of the resistivity at compressive strain for both types of composites were observed near the percolation threshold or slightly above it.

Polyisoprene – multiwalled carbon nanotube composites are preferable for small (up to 2%) compressive strain sensing comparing to polyisoprene – high structure carbon black composites.

The tunneling conductance model is qualitatively consistent with the experimental piezoresistivity characteristics of the polyisoprene – multiwalled carbon nanotube composites and high structure carbon black – polyisoprene composites.

The change in the number of conductive channels is the main reason to cause the experimental results that the composite resistance decreases first and then increases in the process of compression.

The hysteresis of piezoresistivity characteristics of polyisoprene – multiwalled carbon nanotube composite at large stretch we explain with entangled structure of nanotube.

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6. References

1. J.N. Aneli, G.E. Zaikov, I.M. Khananashvili, *J. Appl. Polymer Sci.* **74**, 601 (1999).
2. X.W.Zhang, Y.Pan, Q.Zheng, X.S.Yi, J. *Polymer Sci.* **38,** 2739 (2000).
3. N.C.Das, T.K.Chaki and D.Khastgir, *Polymer International* **51**, (2002) 156
4. T.M.Wu, J.C.Cheng, *J. Appl. Polymer Sci.* **88,** 1022 (2003).
5. T.M. Wu, M.C. Yan and J.C.Cheng, *Polymer* **44**, (8) 2553 (2003).
6. D.Staufer and A.Aharony, *Introduction in to percolation theory* (Taylor. Francis, Washington, DC, 1992).
7. V.I. Roldughin, V.V. Vysotskii, Progr. *Org. Coatings* **39**, 81 (2000) .
8. L. Flandin, A. Chang, S. Nazarenko, A. Hiltner, E. Baer, *J. Appl. Polymer Sci.* **76**, 894 (2000).
9. L.Flandin, Y.Brechet, J.Y.Cavaille. *Comp. Sci. Technol.* **61**, 895 (2001).
10. M.Knite, V.Teteris, B.Polyakov, D.Erts, *Mater. Sci. Eng. C* **19**, 15 (2002).
11. M.Knite, V.Teteris, A.Kiploka, *Mater. Sci. Eng. C*, **23**, 787 (2003).
12. M.Knite,Valdis Teteris, Aleksandra Kiploka, Jevgenijs Kaupuzs, *Sensors and Actuators A: Phys.* **110**, 142 (2004).
13. M.Knite, V.Teteris, I.Aulika, H.Kabelka, A.Fuith, *Adv. Eng. Mater.* **6**, 746 (2004),.
14. Farajian A.A., Yakobson B.I., Mizuseki H., Kawazoe Y, *Phys. Rev. B* **67**, 205423-1 (2003).

[15] Dharap P., Li Z., Nagarjaiah S., Barrera E.V, *Nanotechnology* **15**, 379 (2004).