PROSPECTIVE ROBOTIC TACTILE SENSORS Elastomer-Carbon Nanostructure Composites as Prospective Materials for Flexible Robotic Tactile Sensors

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Keywords: Flexible, pressure sensor, polyisoprene, carbon black, CNT.

Abstract: Our recent achievements in the design, processing and studies of physical properties of elastomer – nanostructured carbon composites as prospective compressive strain sensor materials for robotic tactile elements are presented. Composites made of polyisoprene matrix and high-structured carbon black or multi-wall carbon nano-tube filler have been designed and manufactured to develop completely flexible conductive polymer nano-composites for tactile sensing elements. Electrical resistance of the composites as a function of mechanical strain and pressure is studied.

1 INTRODUCTION

Sensors of strain and pressure are important in many fields of science and engineering. One of the main confines of the existing conventional sensors is being discrete-point, fixed-directional and inflexible. For design of pressure sensors the most often used material is piezoelectric ceramics made separated from the material or structure being monitored. There is a demand for new flexible large-area sensors that can be embedded, for example, into the flexible skin material of robotic fingers and used for sensing multiple locations. Due to increasing application in the machine-building, especially in aerospace industry, polymer - carbon black composites are most actively studied materials (Manson, 1976; Sichel, 1982). Such composites are mostly used as the so-called inactive materials in electrical heating elements, resistors, and antistatic charge materials or shields of electromagnetic radiation (Wessling, 1986). Conductive rubber composites produced using carbon black, are still attracting attention as active materials due to the effectiveness in applications such as strain and pressure sensors, temperature sensors and selective gas sensors (Aneli, 1999; Zhang, 2000; Das, 2002;

Job, 2003; Knite, 2002; Knite, 2004; Dohta, 2000; Dharap, 2004). New interesting properties are expected in case the composite contains dispersed nano-size conducting particles. If the size of carbon particle and specific surface area of carbon black are between 60 to 200 nm and 16-24 m²/g, respectively (low-structure carbon nano-particles (LSNP)), the electrical resistance of natural rubber composites slowly decreases with applied pressure (Job, 2003). The effect is explained by the increasing number of conductive channels due to the increase of external pressure.

Resistance of polyisoprene – carbon nanocomposites grows very rapidly and reversibly for both – tensile and compressive strain when highstructured carbon nano-particles (HSNP) (specific surface area 950 m²/g, mean diameter 25 nm) are used as the filler (Knite, 2002; Knite, 2004).

In this paper our recent success in the design, processing and studies of physical properties of polymer – nano-structured carbon (PNC) composites is presented with regard to prospective flexible compressive strain and pressure-sensing materials for soft robotic tactile elements.

Superior mechanical and electrical properties of carbon nano-tubes offer attractive possibilities for new sensors. So far most studies have been related to mechanical deformation and change of nano-scale electrical properties. An attempt to use the strain sensing capability of single-wall carbon nano-tubes (SWCNT) on the nano-scale level in a macro-scale strain sensor was made by Dharap et al.. We present in this paper an attempt to use the multi-wall carbon nano-tubes (MWCNT) to devise a flexible composite for macro-scale pressure indicators (relative pressure difference sensors) or robotic tactile elements.

2 DESIGN PRINCIPLES OF THE STRUCTURE OF MATERIALS

On the basis of the results of other authors (Aneli, 1999; Zhang, 2000; Das, 2002; Job, 2003) we have developed the following principles designing the structure of materials to obtain most sensitive multifunctional elastomer–carbon nano-composites:

1) Polyisoprene (natural rubber) of the best elastic properties has to be chosen as the matrix material;

2) High-structured carbon nano-particles (HSNP) providing a fine branching structure and a large surface area (better adhesion to polymer chains compared to LSNP) should be taken as the filler. Because of a higher mobility of HSNP compared with LSNP the electro-conductive network in the elastomer matrix in this case is easily destroyed by very small tensile or compressive strain. We suppose this feature makes the elastomer–HSNP composite an option for more sensitive tactile elements in robots.

3) The highest sensitivity is expected in the percolation region of a relaxed polyisoprene composite. The smallest mechanical strain or swelling of the composite matrix remarkably and reversibly increases resistance of such a composite. From the thermodynamic point of view the sensing of strain is based on the shift of percolation threshold, for example, under tensile strain as shown in Figure 1 (Knite, 2002; Knite, 2004).

As seen from Fig. 1, the shift of the percolation threshold at less than 30% strain changes electric resistance of the composite with 10 mass parts of HSNP filler more than 10^4 times. The highest strain sensitivity is expected in the percolation region (9-10 mass parts of the HSNP filler) of a relaxed PNC composite. Thus, the maximum sensitivity of PNC composite materials to thermodynamic forces is supposed to occur near the percolation threshold of electric conductivity.

To obtain completely flexible tactile sensing elements of large area (relative to rigid piezoelectric sensors) a layer of the active PNC composite is fixed between two conductive rubber electrodes by means of a special conductive rubber glue.

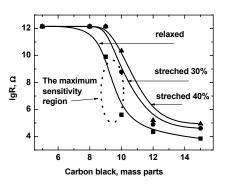


Figure 1: Shift of the percolation threshold in polyisoprene – high-structured carbon nano-particle composite under tensile strain (Knite, 2002; Knite, 2004).

3 PREPARATION OF SAMPLES AND ORGANISATION OF THE EXPERIMENT

The polyisoprene – nano-structured carbon black (PNCB) composite was made by rolling highstructured PRINTEX XE2 (DEGUSSA AG) nanosize carbon black and necessary additional ingredients – sulphur and zinc oxide – into a Thick Pale Crepe No9 Extra polyisoprene (MARDEC, Inc.) matrix and vulcanizing under 30 atm pressure at 150 °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.

The polyisprene - carbon nanotube (PCNT) composites containing dispersed multi-wall carbon nanotubes (MWCNT) were prepared as follows. The size of MWCNT: OD = 60-100 nm, ID = 5-10 nm, length = $0.5-500 \mu m$, BET surface area: 40- $300 \text{ m}^2/\text{g}$. To increase the nano-particles mobility and to obtain a better dispersion of the nanoparticles within the matrix the matrix was treated with chloroform. The prepared matrix was allowed to swell for ~ 24 h. The MWCNT granules were carefully grinded with a small amount of solvent in a china pestle before adding to the polyisoprene matrix. Solution of the polyisoprene matrix and the concentrated product of nano-size carbon black was mixed with small glass beads in a blender at room temperature for 15 min. The product was poured into a little aluminum foil box and let to stand for ~ 24 h,

dried at 40 °C and vulcanized under high pressure at 160°C for 20 min.

Discs of 16 mm in diameter and 6 mm thick were cut from the vulcanized PNCB composite sheet. Conductive polyisoprene – HSCB (30 mass parts) composite electrodes were prepared and fastened to the disc with special conductive adhesive (BISON Kit + 10 mass parts of HSCB) as shown in Figure 2.



Figure 2: Picture of completely flexible strain sensing element made of PNCB composite with conductive rubber electrodes.

Aluminum electrodes were sputtered on opposite sides of the sensing element $(20 \times 11.5 \times 2.4 \text{ mm})$ made of the PCNT composite as shown in Figure 3.



Figure 3: picture of a strain sensing element made of PCNT composite with sputtered Al electrodes.

Electrical resistance of samples was measured vs mechanical compressive strain and pressure on a modified Zwick/Roell Z2.5 universal testing machine, HQ stabilized power supply, and a KEITHLEY Model 6487 Picoammeter/Voltage Source all synchronized with an HBM Spider 8 data acquisition logger. Resistance R of the composites was examined with regard to compressive force F and the absolute mechanical deformation Δl in the direction of the force. Uniaxial pressure and relative strain were calculated respectively.

4 EXPERIMENTAL RESULTS AND DISCUSSION

The percolation thresholds of PNCB and PCNT composites were estimated in the first place. Of all the composites examined, the best results were obtained with samples containing 14.5 mass parts of MWCNT and 10 mass parts HSCB, apparently belonging to the region slightly above the percolation threshold. Dependence of electrical resistance on uniaxial pressure first was examined on a PNCB composite disc without the flexible electrodes. Two brass sheets 0.3 mm thick and 16 mm in diameter were inserted between the disc and electrodes of the testing machine.

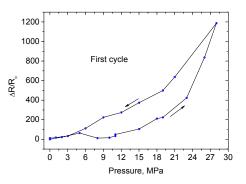


Figure 4: Electrical resistance (in relative units) of an element (without flexible electrodes) of PNCB composite containing 10 mass parts of HSCB as function of pressure. T = 293 K.

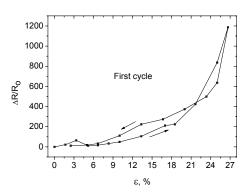


Figure 5: Electrical resistance (in relative units) of an element (without flexible electrodes) of PNCB composite containing 10 mass parts of HSCB as function of compressive strain ε . T = 293 K.

The piezoresistance effect in PNCB composite is reversible and positive $((\Delta R)/R_0>0)$ (Figure 4 and Figure 5).

As a next the measurements of the piezoresistance effect observed in an element of PNCB composite with flexible electrodes attached is illustrated in Figure 6 and Figure 7 showing that the piezoresistance effect decreases approximately 10 times but remains positive.

The positive effect can be explained by transverse slippage of nano-particles caused by

external pressure leading to destruction of the conductive channels.

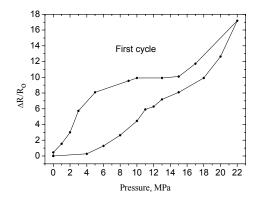


Figure 6: Electrical resistance (in relative units) of an element (with flexible electrodes) of PNCB composite containing 10 mass parts of HSCB as function of pressure. T = 293 K.

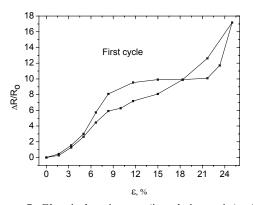


Figure 7: Electrical resistance (in relative units) of an element (with flexible electrodes) of PNCB composite containing 10 mass parts of HSCB as function of compressive strain ε . T = 293 K.

As seen from Figures 8, 9 and 10, the electrical resistance of the sensing element of PCNT composite decreases monotonously with uniaxial pressure and compressive strain. In this case the piezoresistance effect is considered as negative $((\Delta R)/R_0<0)$. Compared with a sensing element of the PNCB composite with flexible electrodes the piezoresistance effect – the absolute value of $(\Delta R)/R_0$ of a sensing element of the PCNT composite (Figure 7 and Figure 9) is more than 10 times smaller. Thus, the PNCB composite is more sensitive to mechanical action than the PCNT composite. The latter exhibits a more monotonous dependence of electrical resistance on compressive strain.

Moreover, only insignificant changes of disposition of the curve were observed during 20

cycles (Figure 10). We explain the negative piezoresistance effect by formation of new conductive channels of MWCNT under external pressure.

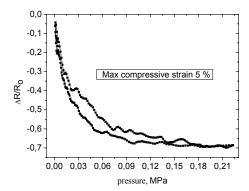


Figure 8: Electrical resistance (in relative units) of an element (with Al electrodes) of PCNT composite containing 14.5 mass parts of MWCNT as function of pressure. T = 293 K.

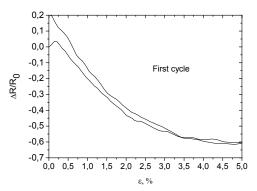


Figure 9: Electrical resistance (in relative units) of an element (with Al electrodes) of PCNT composite containing 14.5 mass parts of MWCNT as function of compressive strain ε . T = 293 K.

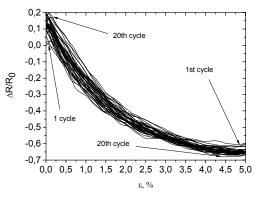


Figure 10: Electrical resistance (in relative units) of an element (with Al electrodes) of PCNT composite containing 14.5 mass parts of MWCNT as function of compressive strain ε . 20 loading cycles. T=293 K.

Consequently, the PNCB composite could be a prospective material for pressure-sensitive indication while the PCNT composite can be considered as a prospective material for pressure sensors.

5 CONCLUSIONS

Completely flexible sensing elements of polyisoprene - high-structured carbon black and polyisoprene – multi-wall carbon nanotube composites have been designed, prepared and examined. The first composite having a permanent drift of its mean electrical parameters is found to be a prospective material for indication of pressure change. The other composite has shown good pressure sensor properties being capable to withstand many small but completely stable and reversible piezoresistive cycles.

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