Prospective polymer composite materials for applications in flexible tactile sensors

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1. Introduction

The purpose of this paper is to give a review of the polymer composite materials specially developed for application in strain and pressure sensors that can be used for elaboration of flexible tactile sensing systems. Our recent achievements in design, processing and investigation of physical properties of elastomer and nanostructured carbon composites as prospective materials for mechanical (pressure, strain) indicators are also presented.

The material used most often for design of pressure sensors is the 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. High elasticity polymer matrix based materials are still of interest. All polymer-composites materials elaborated for mechanical sensing can be generally classified as electrically active (electronic response) and optically active (photonic response) materials. An example of optically active polymeric composite transducer for tactile sensation is based on optical fiber with Bragg grating embedded in polydimethilsiloxane (Heo et al., 2006). The basic principle of this transducer lies in the monitoring of the wavelength shift of the returned Bragg-signal as a function of the strain or force. Comprehensive picture of current status of micro- and nano-structured flexible optical fiber sensors with particular reference to surface plasma resonance fiber sensors and photonic crystal fiber sensors is given by (Lee et al., 2009).

In present paper we are going to concentrate to electrically active polymer composites. One of well-known methods to obtain an electrically active polymer composite is adding of micro-size and nano-size conductive particles or structures to a polymer matrix. Conductive polymer-composite for strain sensing can be obtained when particles of good conductors (carbon black, graphite powder, carbon fibres or undersized particles of metals) are implanted in to an insulating polymer matrix. 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 (Staufer & Aharony, 1992) (Roldughin & Vysotskii, 2000). The volume concentration of conductor particles V_C at which the transition proceeds is called percolation threshold or critical point. According to the statistical model, conductor particles, in the vicinity of V_C, assemble in

clusters the correlation radius ξ (average distance between two opposite particles of a cluster) diverges as

$$\xi \sim |V-V_C|^{-\nu} \tag{1}$$

upon approaching V_C (ν - critical indices) (Staufer & Aharony, 1992).

In the vicinity of percolation threshold, electric conductivity of the composite changes as:

$$\sigma \sim |V-V_C|^{t}, \tag{2}$$

here t - critical indices (Roldughin & Vysotskii, 2000). If such conductive composite have been mechanically stressed, the ξ and as follows σ would change. This is the reason of tensoresistance (the resistance changes versus tensile strain) and piezoresistance (the resistance changes versus compressive strain) effects. The changes of electric resistance with strain and pressure can be explained on microscopic level as a result of change (destruction or formation of conductive micro-channels) of the percolation structure of conductive particles network.

New interesting properties are expected in case the composite contains dispersed nano-size conducting particles (Yang & Sheng 2000; Wolf, 2004). Polymer – electro-conductive nanostructure composites (PENC) offer attractive alternatives for developing new generation of flexible large-size sensors because of their superior mechanical and electrical properties.

The main task of this paper is to focus directly to the PENC developed for application in strain and pressure sensors. From the thermodynamic point of view the principle of strain sensing is based on the shift of percolation threshold, for example, under tensile strain as shown in Figure 1 (experimental points for construction of curves are taken from our previous works (Knite et al., 2004 a) (Knite et al., 2002)). One can see that due to the shift of percolation threshold under 30% strain the electric resistance changes more than 10^4 times for composite with 10 mass parts of nano-structured carbon black. The best strain sensitivity can be expected in the percolation region (9-11 mass parts of filler) for relaxed PENC. Thus, one may expect the maximum sensitivity of PENC materials to thermodynamic forces near the percolation threshold of electric conductivity.
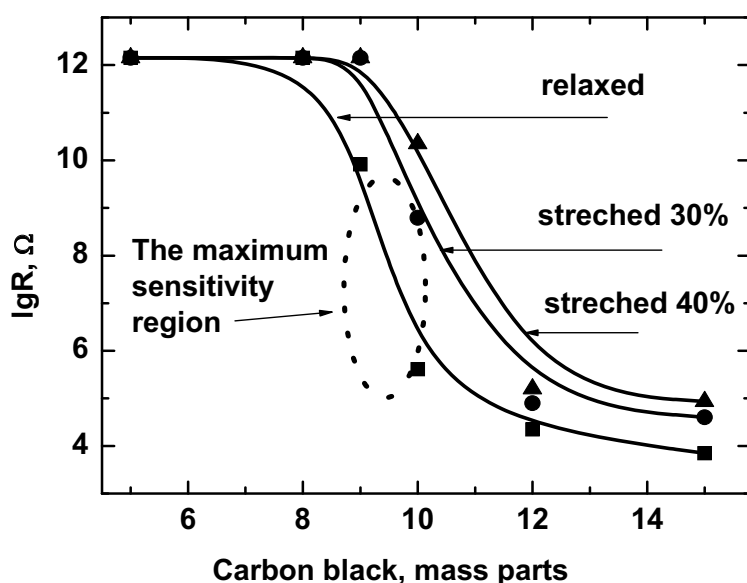
Fig. 1. Shift of the percolation threshold under tensile strain in polyisoprene/high structure carbon nanoparticles composite. The experimental points are taken from the papers (Knite et al., 2002) (Knite et al., 2004 a)

2. Prior work

To date there are several approaches to design PENC for application in strain and pressure sensors. One can subdivide all known such PENC in to composites with insulator matrix and different conducting filler: 1) metal nanoparticles (Ishigure et al., 1999) (Zhang et al., 2000); 2) conductive polymer nanoparticles (Xie & Ma, 2000) (Flandin et al., 2001); 3) carbon microcoils (Yang et al., 2006); 4) graphite nanosheets (Chen et al., 2007); 5) carbon black nanoparticles (Aneli et al., 1999) (Dohta et al., 2000) (Das et al., 2002) (Job et al., 2003) (Flandin et al., 2000) (Knite et al., 2002) (Knite et al., 2003) (Knite et al., 2004 a) (Zavickis et al., 2008); 6) carbon nanotubes (Farajian et al., 2003) (Dharap et al., 2004) (Knite et al., 2007b).

2.1 Composites with insulating polymer matrix and metal filler

Several series of polymer-conductor micro- and nano-composites were prepared from epoxy, silicone rubber, polyethylene, and polypropylene as matrix, and metal, graphite and conducting ceramics as filler materials and examined for applications such as pressure sensor by (Ishigure et al., 1999). Particle size was within 0.1 μm and 600 μm. Particles has different shapes: spherical, plate-like, angular, dendritic, somewhat dendritic and aggregated spherical. Different preparation procedures were used (Ishigure et al., 1999):

1) epoxy composites were prepared by stirring with Cu or Sb-doped SnO_2 filler in acetone and subsequent curing;

2) silicone rubber composites were prepared by hand-mixing with Cu, Ni, Sb-doped SnO_2 or $La_{0.5}Sr_{0.5}CoO_3$ filler, and with a small amount of hardener and subsequent curing;

3) thermoplastic polymer composites were mixed with Sb-doped SnO_2 or graphite filler by laboplastomill at 140 °C for polyethylene, and at 180 °C for polypropylene. The mixture was molded into disk under 20 MPa at 140 °C for polyethylene, and under 100 MPa for polypropylene. Some polymer-conductor composites showed a piezoresistive effect near the critical threshold of the percolation curve. This effect was large in composites prepared from polymers such a silicone rubber having a low Young's modulus. The largest piezoresistive effect was found in silicone rubber composites with 15 vol % fine (100 nm) Sb-doped SnO_2 particles: resistance diminishes about 10^3 times with 5 MPa pressure (Ishigure et al., 1999).

The piezoresistance and its time dependence of conductor-filled polymer composites were investigated also by (Zhang et al., 2000). The conducting fillers were Sn-Pb alloy powder (mean particle diameter 100 nm), Cu powder (200 nm) and Al powder (700 nm). Polyethylene (PE), polystyrene (PS) and epoxy were used as polymer matrixes. Epoxies were modified by adding dibutylphthalate. The addition of this additive was to decrease the compressive modulus of epoxy. For the samples of Sn-Pb/PE, Cu/PE, Al/PE, Sn-Pb/PS, Cu/Ps, and Al/Ps, the conducting filler and polymer powder mixtures were mixed in a satellite ball mill (QM-1SP) at 200 rpm for 11 h, then the powder mixtures were compression moulded in a matched metal die at 170 °C for 20 min to form the 4 mm-thick sheets. For the epoxy matrix samples, the epoxies (added with the hardener and additive) were mixed with the conducting fillers for 10 min by hand, than cured at 90 °C for 3h (Zhang et al., 2000). Mechanical properties, such as the compressive modulus and the creep behaviour were measured. For the convenience of the piezoresistance measurement and to get excellent conductive contact, brass electrodes of 1 cm^2 were adhered at each side by silver paste. The piezoresistance measurements were performed under uniaxial presses. It was found that the relative resistance decreases with an increase of applied stress. Authors (Zhang et al., 2000) suppose that this process is affected by the applied stress, filler particle diameter, filler volume fraction, matrix compressive modulus, and potential barrier height between the adjacent particles. The deformation of polymer matrix under a fixed stress increases with the time, which is the basic reason of time dependence of piezoresistance. The results of (Zhang et al., 2000) show that the increases of applied stress, filler particle diameter, and polymer matrix creep enhances the time dependence of piezoresistance, while the increase of filler volume fraction weakens it.

Authors from the Durham University (Bloor et al., 2005) showed that the nickel particle/silicone matrix composites QTC™ produced by Peratech Ltd has unusual properties, namely a very high resistance even when the quantity of nickel powder incorporated in the composite is above the percolation threshold because the adhering polymer separates the metal particles. The resistance of such composite is found to be extremely sensitive to any mechanical deformation. Thus unlike other PENC the resistance falls when the material is stretched, or bent or twisted. Modest applied forces produce resistance changes of many orders of magnitude. The exponential dependence of sample resistance on deformation indicates that the principal conduction mechanism is determined by carriers tunneling between the filler particles (Bloor et al., 2005).

Conductive nanocomposites prepared using styrene butadiene rubber as the polymer matrix and nanosized powder of cooper-nickel (Cu-Ni) alloy as the filler (Mohanraj et al., 2007) show weak piezoresistance effect (resistance decreases only about one order under pressure 30 kPa). The positive temperature coefficient of resistance (PTC) on the contrary is very high. The DC resistivity changes of 8 orders of magnitude when temperature rises from 300K to 400K. The appreciable PCT effect is explained by the predominant breakdown of the conducting network structure due to higher thermal expansion of rubber matrix compared to the filler (Mohanraj et al., 2007). It is not understandable for us why thermal expansion of matrix affects the percolation structure of conductive particles much more effective than mechanical compression.

Consequently, for composites with insulating polymer matrix and metal filler the piezoresistance effect always is considered as negative ($(\Delta R)/R_0 < 0$). Unique is the negative tensoresistance effect (when the resistance falls if the material is stretched) for nickel particle/silicone matrix composite (Bloor et al., 2005).

2.2 Composites with insulating polymer matrix and conductive polymer nanoparticles

A polyaniline (PAn)/styrene-butadiene-styrene (SBS) triblock copolymer conductive elastomeric composites were recently investigated by (Xie & Ma, 2000). The composites were prepared by *in situ* emulsion polymerization of aniline in the presence of SBS using dodecylbenzene sulfonic acid (DBSA) as an emulsifier and a dopant. The product was melting processed (MP), solution processed (SP), or secondary doped with *m*-cresol (SSP). The results of conductivity measurements showed that for the MP and SP samples conductivity increases with extension, whereas for the SSP sample when PAn content is lower than percolation threshold, conductivity diminishes with increasing extension, but when the PAn content exceeds the percolation threshold value, conductivity followed an empirical equation with a maximum value. All differences are related to their different morphological structures (Xie & Ma, 2000).

New strain sensing materials have recently been processed (Flandin et al., 2001) by mixing an insulating latex of a stryrene-butil acrylate copolymer with a colloidal suspension of intrinsic conducting polymer (polypyrolle) particles. This work has dealt with the AC electrical properties measurements under large strain of composites. A good correlation between electrical conductivity and mechanical stress was measured. The macroscopic conductivity and stress evolution were very smooth, due to the nanoscopic size of the fillers. Real part of the conductivity at low frequency versus deformation is explainable in terms of damage in the percolating network. Imaginary part of the conductivity was found to increase at high frequency for volume fractions close to percolation threshold. Authors (Flandin et al., 2001) related this to the creation of new capacitors with very high values (tiny distance) when the network is broken between two fillers. Different numerical tools have been developed by (Flandin et al., 2001) that may be applied to many composites.

Investigations (Barra et al., 2008) of electrical conductivity and electromechanical properties of a polystyrene- block- poly(ethylene-ran-butylene)- block- polystyrene copolymer (SEBS)/ polyaniline doped with dodecylbenzenesulfonic acid (PAn.DBSA) blends show the insulator – conductor transition not as sharp as those found in carbon black conducting systems and the percolation threshold was lower than 20 wt.% of PAn.DBSA. The effect of conductivity as a function of compression force then was evaluated. For the filler content below the percolation threshold, the conducting PAn domains are separated by a polymer matrix

insulation layer and the electrical conductivity is low, therefore no significant changes in relative electrical conductivity under compressive stress were observed. Above the percolation threshold, the conducting polymer particles are much closer, which contributes to an increase in the electrical conductivity of the blends. Under compressive stress, the contact between the conducting particles increases and, consequently, the relative electrical conductivity of the polymer blend increases significantly. The best compressive stress sensitivity (Barra et al., 2008) have been reached for blends with 30 wt.% of PAn.DBSA, there is a 15-fold increase in the relative conductivity with compressive stress up to 200 MPa, reaching a constant value above this pressure. Thus, the SEBS/PAn.DBSA blend samples (70/30) are prospective active element for future flexible tactile systems (Barra et al., 2008).

2.3 Composites with insulating polymer matrix and conductive spring shaped carbon microcoils

Composites filled with spring shaped carbon microcoils (CMCs) seems to be promising materials for tactile sensing (Yang et al., 2006) (Yoshimura et al., 2007). It's reported (Yang et al., 2006) that until now three kinds of CMCs have been used in tactile sensors: (1) conventional double-helix CMCs: the separation between coil wires are quite small; (2) super-elastic double-helix CMCs: the separation between coil wires are quite large; (3) single-helix CMCs. The electrical properties of these three kinds of CMCs change with the extension or contraction and this property is the foundation of the CMCs tactile sensors (Yang et al., 2006). It was shown (Yang et al., 2006) that polysilicone/single-helix CMCs composites have a higher sensitivity than composites filled with double-helix CMCs. The CMCs with average fiber diameter of 0.7 μm and coil diameter of 5 μm were dispersed into silicone rubber (Shin-Etsu Chemical, KE-1842) matrix by (Yoshimura et al., 2007). The CMCs used in this study were prepared by the chemical vapor deposition process using acetylene as a carbon source at 700-800 ^{0}C (Yoshimura et al., 2007). The mechanism of electrical resistivity change in CMCs/silicone-rubber composites was investigated and discussed in comparison with that in the composites involving vapor grown carbon nanofibers (VGCFs) or carbon blacks (CBs). The carbon content was given as volume fraction, using the density of CMCs (1.9 g/cm^3), VGCFs (2.0) and CBs (1.8) (Yoshimura et al., 2007). The measurements of electrical resistance of test examples were carried out under compressive as well as tensile stress applied using tensile tester (Instron, 4505) at constant speed of 10 mm/min. The values obtained were converted into resistivity under the condition of Poisson's ratio = 0.3. The addition of relatively small amount of CMCs effectively made the material semiconductive. The electrical resistivity of the CMCs/silicone-rubber composites increased with the compressive or tensile strain, and a change in the resistivity was found to be much higher that of the other composites involving VGCFs and CBs. The authors (Yoshimura et al., 2007) have not given any specific data of CBs – only SIGMA-ALDRICH, 05-1530-5. It is believed these CBs to be a low structure microsized CBs because in case of HSCB (Knite et al., 2004) approximately the same strain sensitivity has been achieved as for CMCs/silicone-rubber composites (Yoshimura et al., 2007). The higher sensitivity of CMCs/rubber composites according to the authors (Yoshimura et al., 2007) was attributable to the synergetic effects of the changes in resistivity of the conductive paths and CMCs themselves. We believe that better sensing properties of CMCs/rubber composites (Yoshimura et al., 2007) relate with much higher structure of CMCs compared to CB used.

2.4 Composites with insulating polymer matrix and graphite nanosheets

Novel conductive nanocomposites with low percolation threshold were prepared by adding conductive graphite nanosheets (GNs) to high density polyethylene (Lu et al., 2005). GNs with average sheet diameter 5-20 μm and 30-80 nm in thickness were prepared by ultrasonic powdering technique (Lu et al., 2005). The HDPE and GNs were first wet-mixed to achieve a uniform dispersion and after mixed on a two-roll mill. The compound was further compressed by hot press. The piezoresistivity measurements were performed under uniaxial pressures both at low- and high-pressure range. It reveals that the piezoresititvity strongly depends on the GNs concentration. Authors (Lu et al., 2005) stated that such piezoresistive material could be used as pressure sensor as the electrical component.

A novel pressure sensing nanocomposite with remarkable and reversible piezoresistivity is successfully fabricated by dispersing homogenously conductive GNs in a silicone rubber (SR) matrix (Chen et al., 2007). Authors have used as filler the same GNs with average sheet diameter 5-20 μm and 30-80 nm in thickness and have got super-sensitive positive piezoresistivity under very low pressure, in finger –pressure range. Authors (Chen et al., 2007) described the piezoresistive behaviour by the tunnelling models as well as used the models for change of the number conducting paths that are similar to model developed in (Knite et al. Sensors, 2004) for polyisoprene/high structure carbon black composites. In the same way as (Knite et al., 2004 a) stated for nanostructured carbon black the authors (Chen et al., 2007) made conclusions that stronger adhesion of the GNs to the polymer matrix compared to the cohesion between the nanosheets themselves lead to excellent piezoresistive properties of composite.

2.5 Composites with insulating polymer matrix and carbon black

Electric conductivity measurements of carbon black-filled rubbers under low and high stretching deformations as well as all-round and uniaxial compression at both low and high pressure were carried out by (Aneli et al., 1999). Relaxation processes were also investigated. High-molecular elastomer polymethylvinilmethylsiloxan and low-molecular elastomer polydimethylsiloxan were composed with P357E and P803 carbon black using the additive vulcanization technique. The carbon particle size and specific surface area of carbon black are not given. Electrodes were embedded into sample during vulcanisation of rubbers. It was found that a significant increase of the interaction between macromolecules of the elastomer and filler particles induces a sharp growth of rubber tensoresistivity. The maximum changes of electric resistivity did not exceed 10^2 times under stretching strain till 160 %. The maximum changes of electric resistivity did not exceed 5 times under pressure up to 20 MPa. Addition to that, the changes of resistivity was not reversible – significant hysteresis effects were observed.

Scientists from the Okayama University (Dohta et al., 2000) demonstrate an application of a flexible strain sensor to a pneumatic rubber hand. The flexible strain sensor is composed of the silicone rubber and electro-conductive paints. The electro-conductive paint (FUJICURA Co, Ltd.: DOTITE RA-3) is painted thinly on the rubber of 20 mm in length and 3 mm in width. In order to increase the durability, the electro-conductive paints are coated with thin silicone rubber. The operating principle of the flexible strain sensor is as follows: when the sensor is expanded longitudinally, the density of carbon in the electro-conductive paint increases in the direction of the thickness and lowers in the direction of the length. Consequently the electric resistance increases by 20 kΩ under 100 % strain. Two kinds of

flexible strain sensors are installed in the pneumatic rubber hand. One is a displacement sensor that can detect a bending displacement of soft gripper to confirm the grasping of an object and to recognize a size of this object. The other is a tactile sensor that can detect contact force and contact position to recognize the stiffness and shape of the object. The variation of electrical resistivity of carbon black and short carbon fiber (SCF) filled rubber composites against the degree of constant strain rate have been studied by (Das et al., 2002). Ethylene-propylene-diene rubber (EPDM) and ethylene vinyl acetate copolymer (EVA) was taken as matrix, and conductive carbon black Vulcan XC-72 and Carbon India Ltd. Carbon fibers, grade RK 12 as filler. Chosen matrix and filler were mixed in Brabender plasticorder (PLE-330) under identical conditions of mixing time (5 min), temperature (90 °C) and rotor speed (60 rev.min^{-1}). The mixes were sheeted in a laboratory size two-roll mixing mill. The optimum cure times at 170 °C for these composites were determined using Monsanto rheometer R-100S. The mixes were than cured at 170 °C in an electrically heated press under identitical pressure of 5 Mpa. These cured sheets were kept at room temperature for 24h maturation before testing. The Zwick universal testing machine was coupled with a volume resistivity measurement set up for continuous reading the variation of resistivity of the sample during extension and retraction cycles. Composites (Das et al., 2002) exhibit appreciable irreversibility in the variation of the electrical resistivity against strain during extension-retraction cycles.

An ethylene-octene (EO) elastomer was the matrix in studies of (Flandin et al., 2000). The fillers were a carbon fiber (CF) with diameter 10 μm and aspect ratio 20, a low structure carbon black (LSCB) with particle diameter 300 nm and surface area 8 m^2/g, and two high structure blacks (HSCB) Printex 30 (particle diameter 27 nm and surface area 80 m^2/g) and Condutex 975 Ultra (particle diameter 21 nm and surface area 242 m^2/g) (Flandin et al., 2000). Blending was carried out in Haake Rheomix 600 mixing head. The polymer was mixed without filler for 1 min until melted and the filler was added slowly over a period 10 min. Specimens were deformed in an Instron 1123 testing machine at a strain rate of 0.2 %/min. Electrical properties were measured with a four-terminal technique using a Keythley model 220 as current source and a Keythley model 619 for voltage and current measurements. Composites with CF and LSCB did not maintain good mechanical properties, generally exhibited an increase in resistivity with strain, and exhibited irreversible changes in both mechanical and electrical properties after extension to even low strains. It was found that the composite with HSCB exhibited an unusual decrease in resistivity at low strains and reversibility in the resistivity upon cyclic deformation. For an explanation of the unusual properties of EO with HSCB authors (Flandin et al., 2000) proposed model that incorporates the multifunctional mobile physical crosslinks of the EO matrix and dynamic filler-matrix bonds. For HSCB, rotation and translation, or possibly shape changes of the asymmetric aggregates, can reduce resistivity. Authors (Flandin et al., 2000) imagine that the very small particles of HSCB are less constrained during elongation if they are incorporated into a network of mobile junctions than if the network has fixed junctions. Therefore, deformations can produce new conducting pathways by particle reorientation.

By (Job et al., 2003) a natural rubber (NR) and carbon black (CB) were compounded, aiming the development of composites with good mechanical properties, processability and electrical conductivity for use as pressure sensors. The carbon particle size and specific surface area of carbon black was between 60 to 200 nm and 16-24 m^2/g respectively (LSCB).

Composites were prepared by casting. First, a solution of 25 ml of ammonium hydroxide and CB was prepared under stirring for 15 minutes. After 10 ml of the stabilized latex was mixed to the carbon black solution under stirring for 10 minutes. Finally, composites were prepared by casting the obtained solution onto glass substrate and then heated at 65 °C, for 6 hours, for evaporation of volatile components. A linear dependence of conductivity on the applied pressure is observed for CB contents up to 20 wt % in the pressure range of 0 to 1.6 Mpa, tending to saturation for higher values of pressure. For contents of CB less than 10 % the results are scattered and no clear dependence of the conductivity on the pressure was found.

A polyisoprene/very high structure carbon nanoparticles (surface area 950 m^2/g) composites (PHSCNC) were prepared and investigated by (Knite et al., 2002) (Knite et al., 2004 a). Plates of 12 mm diameter were cut for electrical resistivity vs pressure measurements of 1 mm thick 20 cm x 20 cm sheets vulcanized at high pressure. To study dependence of electric resistance of the PHSCNC on stretching force and stretch deformation 15 cm × 1.5 cm samples were cut. Copper foil electrodes were glued on both sides at the ends and each pair of electrodes was shortcut by copper wiring. On a relaxed sample the distance between electrodes l_0 did not exceed 50 mm. Sandpaper was glued on the electrodes to fasten the samples in the stretching machine. A modified conductive tapping mode AFM Nanoscope III (Dimensions 3000, Digital Instruments) was used to investigate the electrical conductivity on local nano-size spots on the surface of the composites. The AFM cantilever tips were of standard silicon nitride. The AFM tip and cantilever were coated with a 5 nm thick Cr adhesive layer and a 15 nm thick Au layer to get conductive tip. A typical tip radius measured with a transmission electron microscope was 30 nm. A bias of 10 - 1000 mV was applied between the tip and the sample. With a contact mode conductive atomic force microscope authors (Knite et al., 2002) (Knite et al., 2004 a) succeeded in obtaining a topographic picture of the sample surface, as well as a nanoscale map of cross-sections of the electro-conductive channels and an insulating matrix of the same local spot. The current distribution inside the conductive pattern was not uniform. The size of sub-channels was around 30 nm.

Of all the composites examined (Knite et al., 2002) (Knite et al., 2004 a) the best results were obtained for the samples with 10 mass fractions of carbon nanoparticles, which apparently belonged to the region of percolation phase transition. The electric resistance of these samples changed more than 4 orders upon a 40% stretch and more than 3 orders upon a 0.30 Mpa pressure. After the samples were released, the resistance practically returned to its previous value. The reversibility and the giant changes of electric resistance under both tensile and compressive strain were explained due to comparatively higher mobility of high structure nanoparticles compared to low structure particles as well as stronger adhesion of carbon nanoparticles to the polymer matrix compared to cohesion between nanoparticles themselves (Knite et al., 2004 a). The growth of electric resistance with uniaxial stretching and pressure can be explained as a result of destruction of the structure of the carbon electro-conductive nano size channel network. At low stretching deformation the experimental data has good coincidence with model of tunneling conductance (Knite et al., 2004 a). The AC conductivity measurements (Knite et al., 2004 b) also verify the tunneling model of conductance. For description of the experimental results at high deformation both - the destroying of conductive network and decrease of conducting path have to be taken into account. In case of uniaxial pressure destruction of electrically conductive channels is

caused by deformation of the polyisoprene nanocomposite perpendicular to the direction of pressure. The stated fact that the resistance grows rapidly and reversibly with both tensile and compressive strain can be used also for elaboration of chemical sensors (Knite et al., 2007a) based on swelling of the composite matrix in ambience of different chemical substances.

The effect of a plasticizer on the change of the electrical resistance under deformation at stretch were studied in polyisoprene composites containing dispersed nano-size conducting carbon particles at concentrations in the vicinity of the percolation threshold by (Knite at al, 2003) (Knite at al, 2005) (Knite et al., 2006). The addition of plasticizer to the initial materials increases the strain sensitivity of the composite and broadens the carbon concentration interval of the percolation threshold. The observed improvements of the tenso-resistive response are explained by decrease of cohesion forces between carbon nanoparticles and higher mobility of the carbon nano-particles in the elastomer matrix in the presence of the plasticizer.

2.6 Composites with insulating polymer matrix and conductive carbon nanotubes

Carbon nanotubes (CNT) change their electrical properties when subjected to strain. Calculated (Farajian et al., 2003) theoretically the I-V characteristics, showed that the current of metallic tube decreases with increased bending, while that of semiconducting tube increases. Possible application to nanoelectromechanical sensors and switches is discussed.

An attempt to use the strain sensing capability of single-walled carbon nanotubes (SWCNT) on the nanoscale to develop a strain sensor on the macroscale was made by (Dharap et al., 2004). The carbon nanotube film is produced by mixing 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 electric properties. The carbon nanotube film was attached to a brass plate with 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 nearly linear relationship between the measured change in voltage and the strains in the carbon nanotube films (Dharap et al., 2004).

Recently the interest rise about elaboration of polymer/multi-walled carbon nanotube (MWCNT) composites for strain sensing (Knite et al., 2007b) (Bokobza, 2007) (Pham et al., 2008) (Hu et al., 2008) (Li et al.,, 2008) (Knite et al., 2008) (Knite et al., 2009).

The purpose of (Knite et al., 2007b) paper was the design, elaboration and investigation of the polyisoprene/multiwall carbon nanotube (MWCNT) composites for application in strain sensors as well as to compare they with the polyisoprene/high structure carbon black composites elaborated and prepared by the same technology. Polyisoprene composites containing dispersed nano-size particles, in this case two types, multiwall carbon nanotubes (MWCNT) Aldrich 636835 as well as highly structured carbon black (HSCB) Printex XE2 were prepared by "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. 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. Polyisoprene matrix solution and nano-size carbon structure concentrated product was mixed in the mixer with small glass beads at room temperature for 15 min. Product is poured out into little

aluminium foil box and stand ~ 24 h, dried at 40 °C for more than 12 h and vulcanized under high pressure at 160°C for 20 min (Knite et al., 2007b). 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. The average particle size of HSCB was 30 nm and its dibutyl phthalate (DBP) absorption is 380 ml/100g. Its surface area was 950 m^2/g.) (Knite et al., 2007b). It has been shown that the use of high structure carbon nanoparticle as filler of a polyisoprene matrix provided about 6 orders of magnitude a reversible change in the electric resistivity at large (40%) stretch. The use of multiwalled carbon nanotube as filler of a polyisoprene matrix provided about 4 orders of magnitude a non-reversible change in the electric resistivity at large (40%) stretch. The maximum change at stretch for both type of composites were observed near the percolation threshold. The reversible change in electric resistivity of high structure carbon nanoparticle – polyisoprene composite even at large stretch can be explained by the high porosity of carbon agglomerates providing better adhesion to polymeric globules and mobility of nanoparticles, which is not observed in the case of a poorly structured carbon black. The non-reversible change in electric resistivity of multiwalled carbon nanotube – polyisoprene composite at large stretch we explain with entangled structure of the nanotube. Authors (Knite et al., 2007b) stated that polyisoprene/MWCNT composite can be used for small tensile strain sensing but polyisoprene/HSCB composite are preferable for large tensile strain sensing. The compressive strain sensitivity of above mentioned polyisoprene/MWCNT composites were proved in papers (Knite et al., 2008) (Knite et al., 2009).

In the review of (Bokobza, 2007) the mechanical and electrical properties of composite based on styrene-butadiene rubber (SBR) filled with MWCNT which have lengths and diameters in the range of 0.1-5 μm and 10-50 nm, respectively. Electrical measurements carried out under uniaxial stretching deformation display an increase in resistivity as a result of a breakdown of conductive path and an orientation of the filler particles (Bokobza, 2007).

The possibility of using MWCNT films purchased from Nano-Lab Inc. (Newton, MA, USA) as strain sensors have been studied by (Li et al., 2008). Uniaxial load-unload tensile test was carried out to investigate the static sensing property. Results indicated that the change in resistance of the MWCNT film was proportional to the applied strain. It was indicated that MWCNT film is potentially useful for structural health monitoring and vibration control applications (Li et al., 2008).

Researchers from the United States (Pham et al., 2008) report about the development of conductive, MWCNT-filled, polymer composite films that can be used as strain sensors with tailored sensitivity. The films were made from polymethylmethacrylate (PMMA) matrices and MWCNT obtained from Aldrich by two different methods – dry blended film fabrication or solution based fabrication. The electric surface resistivity of the films was measured in situ as the specimen was loaded in tension. The increasing resistivity with increasing tensile strain is explained due to the reduction in conductive network density and increase in inter-nanotube distances induced by applied strain. The highest sensitivity achieved in this study was almost an order of magnitude greater than conventional resistance strain gauges (Pham et al., 2008).

2.7 Summary on prior work

From the available papers regarding polymer/MWCNT composites for strain sensing one can conclude that attention is devoted only to investigations of tensile strain sensing properties. Almost in all papers the report was about the best sensitivity of MWCNT composites in comparison with conventional resistance strain gauges. Thus more attention should be paid to elaboration of polymer/MWCNT composites for compressive strain sensing.

Of all the composites examined, elastomer/(carbon nanostructure) composites shows the best electromechanical properties as flexible large area materials for strain and stress sensing. To reveal the strain sensing mechanisms further investigations of these composites are required. We present in next paragraphs an attempt to use the HSCB as well as MWCNT to devise an all flexible composite for macro-scale pressure indicators (relative pressure difference sensors) or robotic tactile elements.

3. Design principles of the structure of polymer/carbon nanostructure composites for pressure strain sensing

Based on the review of other authors, we have developed four simple principles, which should be obeyed to obtain maximum sensitivity of 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) or MWCNT should be taken as a 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. The sharper is the percolation transition of insulator/conductive particle composite the higher should be the compressive stress sensitivity of sensing element.

4) The investigation of development of percolative structure during curing process could be very suitable for finding out the optimal vulcanization time of the PHSCNC with the best compressive strain sensing properties.

4. The investigation of development of percolative structure in PHSCNC during curing process

To investigate a development of carbon nanoparticle cluster percolative structure during vulcanization process the test samples with different levels of vulcanization were prepared and the character of their piezoresistivity was established and compared. Measurements of mehano-electrical properties as well as SEM investigations were carried out.

First of all PHSCNC samples with 9 and 10 mass parts of filler have been prepared. The mixing was done using cold rolls. To obtain good electrical connection with samples, clean

sandpapered brass foil mould inserts were used on both sides of the samples. The previous research approved them to be the most suitable for this need because brass forms permanent electro-conductive bonding with the PHSCNC during vulcanization. To provide optimal processing parameters, first the optimal complete curing time of the composite was ensured using MonsantoRheometer100 rubber rheometer and appeared to be 40 minutes for current rubber composition. Disk shape PHSCNC samples 18mm in diameter (Figure 2) with 9 and 10 mass parts of filler were made using different curing times in range from 1 to 40 minutes. 40 minutes corresponds to complete vulcanization of PHSCNC and 1 minute was the smallest possible time to obtain the desired shape of the sample. During "pre-research" the original method was developed to measure samples initial electrical resistivity "in-situ" in the curing mould. The results claimed that electrical resistivity of PHSCNC dramatically drops exactly during the vulcanization (Figure 3). This fact made us to assume, that the development of percolative electrocondutive structure of filler nanoparticles is happening during the vulcanisation although.
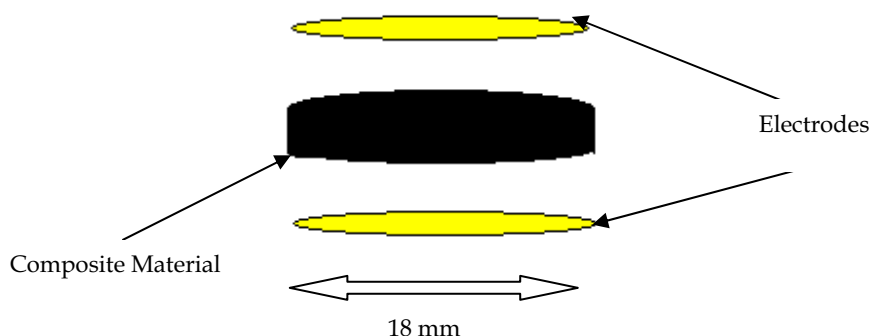

Fig. 2. Schematic structure of the PHSCNC sample with embedded brass foil electrodes
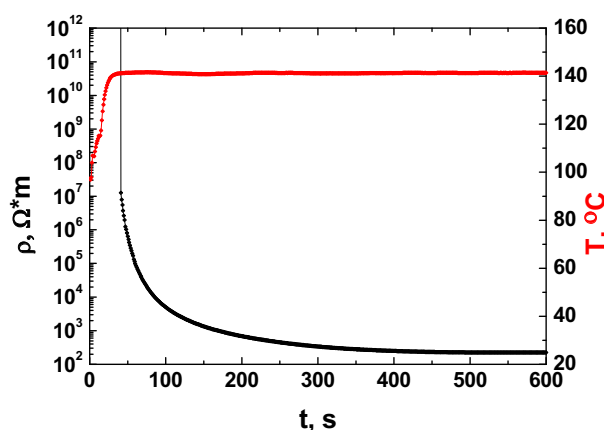

Fig. 3. The change of specific electrical resistivity (black) and temperature (red) as a function of time for PHSCNC sample with 9 mass parts of carbon.
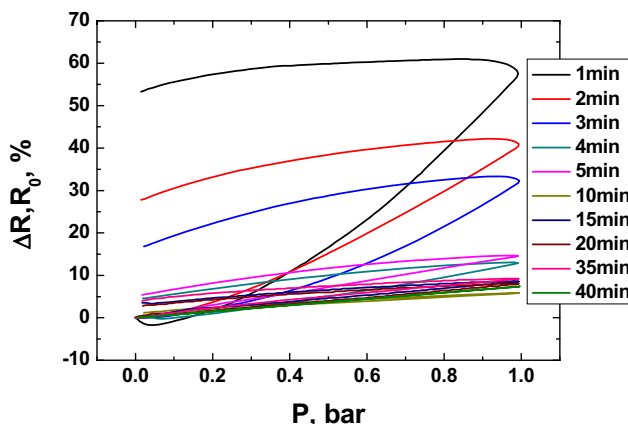
Fig. 4. The piezoresistance of PHSCNC samples with 10 mass parts of carbon black which are made using different curing times from 1 to 40 minutes.

The piezoresistive properties of PHSCNC samples were determined using Zwick/Roell Z2.5 universal material testing machine, equipped with HBM 1kN load cell and HBM Spider8 data acquisition module. This allowed the measurements of mechanical and electrical properties to be taken simultaneously. This testing was done using variable external operational pressure from 0 to 1 bar, with speed of 1×10^{-2} bar·s^{-1}. The piezoresistive properties of samples were determined and evaluated as shown in Figure 4.

To ensure our previous assumption, SEM investigation was made on incompletely vulcanized samples, fractured in liquid nitrogen. Technically, the smallest possible vulcanization time here was 3 minutes from 40 which corresponds to 7,5% of complete vulcanization time. The SEM picture of this sample is shown if Figure 5. It was compared with SEM image of PHSCNC sample cured for 15 minutes, which corresponds to 35,5% of complete vulcanization time shown in Figure 6. Comparing these pictures it can be seen, that sample with less vulcanization time has more uniform structure of conductive filler particles (opaque dots all over the image). On other hand in sample with more vulcanization time the conductive filler particles has formed entangled or forked structure. With reference to (Balberg, 2002), exactly the entangled structure of carbon agglomerates is responsible for unique conductive properties of percolative concentrations in polymer matrices.

The results indicate that the balance between the maximum piezoresistivity and more complete relaxation of initial electrical resistivity of sample is critical. If one of them is greater, the other starts to lack useful dimensions and vice versa. The optimum vulcanization time was found out to be at least the 12% of the time necessary for complete vulcanization.
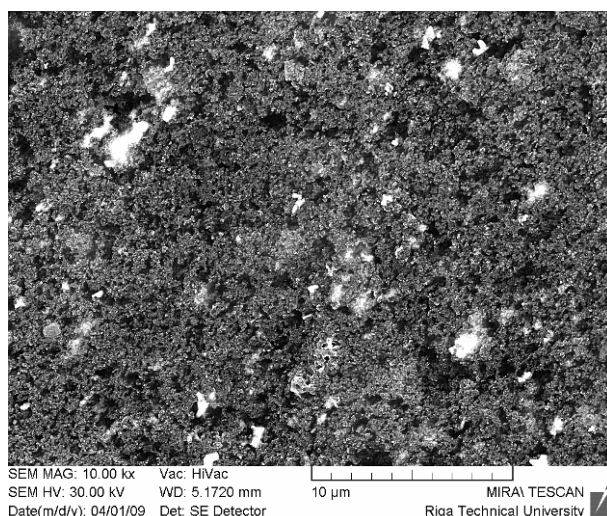
Fig. 5. The SEM image of liquid nitrogen fractured surface of PHSCNC sample with 10 mass parts of carbon black, cured for 7,5% of time necessary for complete vulcanization. No structurization of carbon black aggregates.
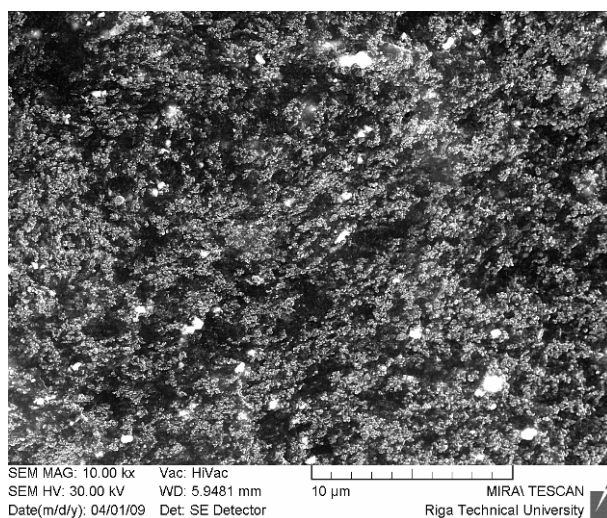

Fig. 6. The SEM image of liquid nitrogen fractured surface of PHSCNC sample with 10 mass parts of carbon black, cured for 35,5% of time necessary for complete vulcanization. The structurization of carbon aggregates (opaque dots) are clearly visible.

5. All-elasto-plastic polyisoprene/nanostructured carbon pressure sensing element with glued conductive rubber electrodes

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

5.1 Preparation of samples and organisation of experiment

The PHSCNC was made by rolling high-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 30 bar 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 polyisoprene – 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 µm, BET surface area: 40-300 m²/g. To increase the nano-particles mobility and to obtain a better dispersion of the nano-particles 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 were mixed with small glass beads in a blender at room temperature for 15 min. The product was poured into a small aluminum foil box and let to stand for ~ 24 h, dried at 40 ºC and vulcanized under high pressure at 160ºC for 20 min (Knite et al., 2008).

Discs of 16 mm in diameter and 6 mm thick were cut from the vulcanized PHSCNC 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 7.
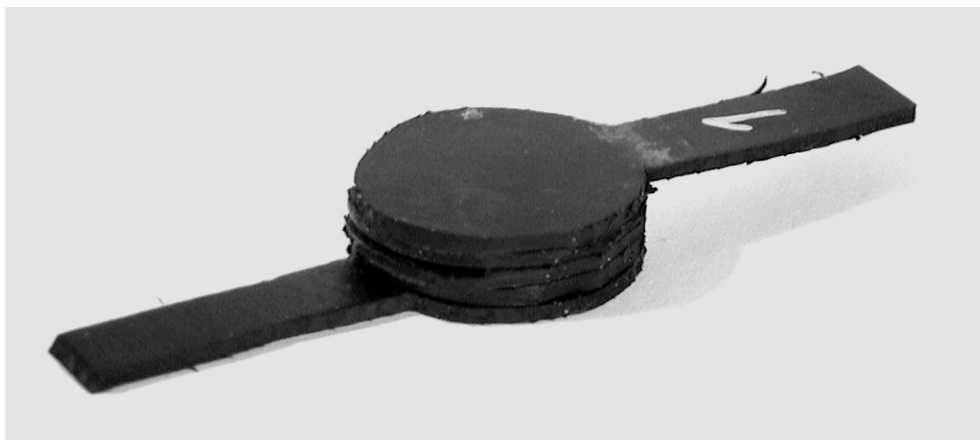

Fig. 7. Picture of completely flexible strain sensing element made of PHSCNC with conductive rubber electrodes.

Aluminum electrodes were sputtered on opposite sides of the sensing element (20 × 11.5 × 2.4 mm) made of the PCNT composite as shown in Figure 8. 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 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.

Fig. 8. Picture of a strain sensing element made of PCNT composite with sputtered Al electrodes.

5.2 Experimental results and discussion
The percolation thresholds of PHSCNC and PCNT composites were estimated at first. 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 PHSCNC 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.

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