Hyper-elastic Pressure Sensors

Temperature Dependence of Piezoresistivity of Polyisoprene – Nanostructured Carbon Composite

Juris Zavickis, Maris Knite, Artis Linarts and Raimonds Orlovs

Institute of Technical Physics, Riga Technical University, Azenes Street 14/24-322, Riga, Latvia

Keywords: Temperature Dependence, Piezoresistivity, Polyisoprene, Carbon Black, Composite.

Abstract: Our previous efforts revealed polyisoprene-nanostructured carbon composite as prospective sensitive material for elaboration of entirely hyper-elastic piezoresistive pressure sensor element. In this article we investigate the temperature dependence on initial electrical resistivity as well as piezoresistive properties of such material and self-elaborated hyper-elastic pressure sensing element. Certain conclusions about the effect of temperature on electroconductive structure and piezoresistivity are made.

1 INTRODUCTION

Pressure sensing in various ambient conditions may play important role in modern industrial applications. Recent attempts show polyisoprene – nanostructured carbon composite (PNCBC) as a prospective piezoresistive material for elaboration of hyperelastic pressure sensors (Zavickis, 2011). These sensors can be made in various sizes and shapes so they can be easily tailored to specific applications. If functional multi layer approach is used, hyper-elastic pressure sensor can be easily realised (Knite, 2009; Knite, 2008). These sensors are proved to be functional for pressures up to 1 MPa and can be successfully used in different industrial and engineering applications, like civil security, industrial monitoring, robotic skin (Huang, 2011), medical (Chang, 2012), traffic surveillance and many more. Additionally to that PNCBCs show multifunctional sensing properties (Knite, 2007). Hence polymer matrix composites are mostly linked with comparably large coefficients of thermal expansion and their mechanical properties typically have strong temperature dependence, it's anticipated, that operational temperature will have noticeable effect on PNCBCs electrical and piezoresistive properties. All forementioned branches may cover significantly large interval of operating temperatures, therefore it's very important to know the permissible operational temperature range of the PNCBC sensor element as well the dependence of output of sensors electrical parameter on operational temperature.

In our work we determine the temperature dependence of single PNCBC element, as well we elaborate layered hyper-elastic pressure sensor element (LHPS), consisting only of PNCBC structural parts. In the end we measure the time dependence of piezoresistivity of ready-made LHPS element.

2 SAMPLES AND EXPERIMENTAL

Previously known composition was used to elaborate piezoresistive composite (Knite, 2004): Natural polyisoprene caoutchouc was mixed with necessary curing ingredients (sulphur, zinc oxide, stearic acid and N – Cyclohexyl – 2 - Benzothiazole Sulfenamide) and various concentrations of high structure carbon black (HSCB) (Degussa Printex Xe2 with average primary particle diameter 30nm, DBP absorption 380ml/100g, specific surface area of 950m^2/g) in Baltic Rubber factory (BRF) using roll mixing. The concentration of the fillers was expressed in mass parts per hundred rubber (p.h.r.). The raw composition was vulcanized between two parallel brass foil inserts under pressure in hot steel mould using Rondol thermostated press for 15 minutes under 30 atmospheres of pressure at 150°C to obtain finished polyisopene – nanostructured carbon black composite (PNCBC). The brass foil

inserts were used to provide good electrical connection to the samples. We acquired cylindrical shape samples with 18 mm in diameter and 1 mm in height. The vulcanization conditions were determined at BRF using Monsanto 100 dynamic rheometer. Before any measurements were made the samples were shelf aged at room temperature for at least 24 hours. To determine electrical properties of each PNCBC sample the electrical resistivity was measured using a Keithley 6487 Picoammeter/Voltage source. Temperature dependent resistivity measurements were conducted using temperature control system Linkam THMSE 600 coupled with data acquisition unit Agilent 34970A. Mechano-electrical properties of the samples were determined using Zwick/Roell Z2.5 universal material testing machine coupled with Agilent 34970A data acquisition/switch unit. Samples whose initial electrical resistivity was higher than 10^8 Ω were not tested for piezoresistivity due to technical limitation of measuring equipment. Based on these results certain raw rubber compositions were chosen to elaborate a LHPS. The piezoresistive response of LHPS under 1 atmosphere of pressure in different ambient temperatures was determined using Zwick/Roell Z2.5 materials testing machine additionally equipped with temperature chamber and coupled with Agilent 34970A data acquisition/switch unit. Test temperatures have been chosen according to ASTM D1349-99 standard "Standard practice for rubber-standard temperatures for testing".
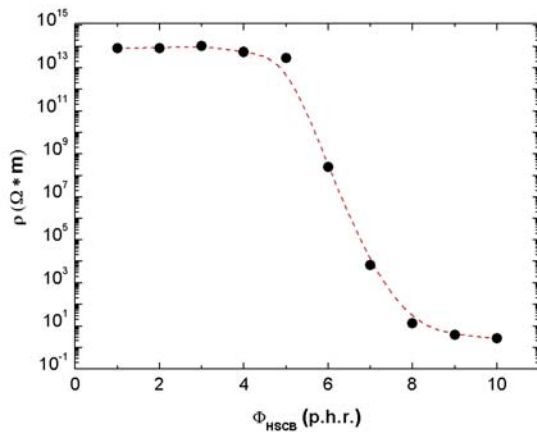
2.1 Selection of Materials for LHPS.

Figure 1: The specific electrical resistivity as a function of the HSCB fraction.

To select the most suitable PNCBC compositions for LHPS elements a series of tests

was performed. The electrical resistivity of PNCBC samples was measured at first. Figure 1 displays the electrical percolation threshold of PNCBC depending on the HSCB concentration.

As it is seen from Figure 1 the percolation transition appears to be in the region from 5 to 9 p.h.r. of HSCB. According to the concept of piezoresistivity, the composites are most sensitive to external force if the concentration of conductive filler is maintained within the range of percolation (Balberg, 2002). The piezoresistive properties of PNCBC samples with 7 to 9 p.h.r of HSCB under external pressure for up to 1 MPa are shown in Figure 2.
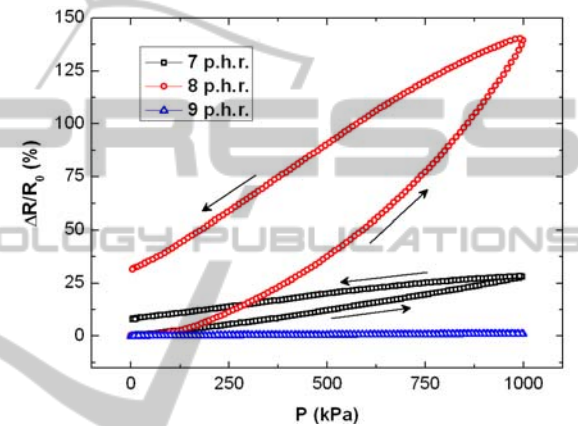

Figure 2: Piezoresistive behaviour of PNCBC with different concentrations of electroconductive filler for up to 1 MPa of uniaxial pressure.

Initial resistivity of PNCBC with lower HSCB fractions was too high to successfully perform this test. The speed of loading and unloading was kept constant at 10 kPa/s. The maximal piezoresistive response was observed for PNCBC samples containing 8 p.h.r. of HSCB.

2.2 Elaboration of LHPS

LHPS prototype was elaborated consisting of outer shell of non-conductive natural rubber and multiple functional layers of PNCBC with two HSCB concentrations. The pressure sensitive layer was made from PNCBC with 8 p.h.r. of HSCB since the piezoresistivity of this composition was found to be highest – relative change of electrical resistivity observed under operational pressure of 1 MPa was more than 100 %. PNCBC with 10 p.h.r. of HSCB was used to produce hyper-elastic electrode layers on both sides of sensitive layer. All three layers were connected in series and incorporated into non-conductive natural rubber shell without CB filler.

Two small wires with end soldered brass foil extensions were added to electrode layers to connect the LHPS to measuring equipment. All structural elements (layers) were semi-vulcanized under pressure of 3 MPa at 140 °C for 7 minutes just enough so they could maintain their shape. During final vulcanization all elements were assembled together in necessary configuration and cured under pressure of 3 MPa at 150 °C for 11 minutes.
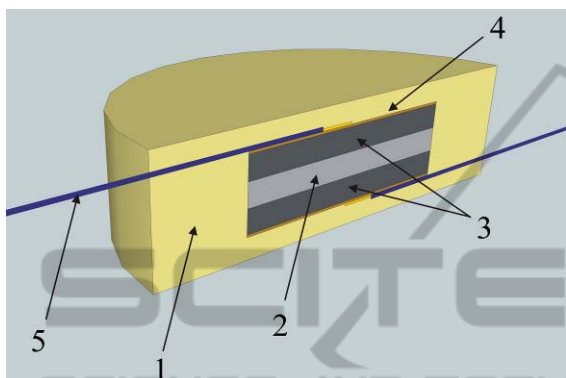

Figure 3: The schematic cross-cut of LHPS, consisting of: 1 – non conductive outer shell, 2 – piezoresistive PNCBC, 3 – electroconductive PNCBC, 4 – brass foil electrode, 5 – wires.

Figure 3 shows schematic construction of LHPS consisting of 3 active layers with wires incorporated into protective rubber shell. Figure 4 shows the picture of functional prototype of LHPS.
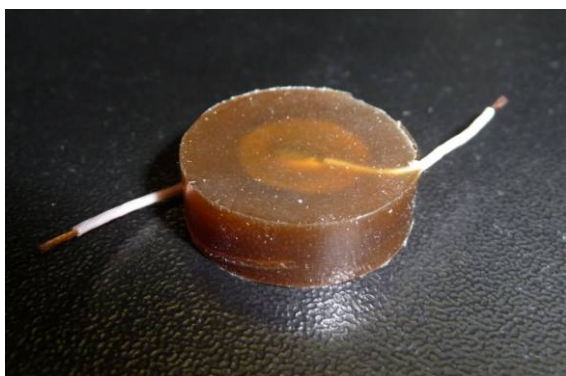

Figure 4: The image of ready-made LHPS element.

3 TEMPERTURE DEPENDENCE OF THE ELECTRICAL RESISTIVITY AND PIEZORESISTIVE EFFECT

As it can been seen in Figure 1, the PNCBC exhibits sharp and distinct percolation transition in the range of 5 to 9 p.h.r. of HSCB. According to theory (Knite, 2004), the composition belonging to the middle of percolation should exhibit most extensive piezoresistivity. The determination of piezoresistive effect was done for PNCBC samples with 7, 8 and 9 p.h.r of HSCB and samples with 8 p.h.r of conductive filler appeared to be the most sensitive to applied external pressure (Figure 2). Based on these results, the piezoresistive layer for LFHPS was elaborated with 8 p.h.r. of HSCB.

First of all the temperature dependence of specific electrical resistivity was determined for PNCBC sample containing 8 p.h.r. of HSCB. Figure 5 shows positive thermal coefficient of resistivity (PTC) that can be explained with large difference in thermal expansion coefficients of polymer matrix and carbon nanostructure filler (Balberg, 2004). Therefore the thermal expansion of the elastomer matrix leads to the partial reorganization of electroconductive network increasing the overall electrical resistivity of the composite. The large coefficient of thermal expansion causes the sufficient broadening of tunnel junctions existing in the composite (Knite, 2004) with subsequent exponential rise of resistivity versus temperature.
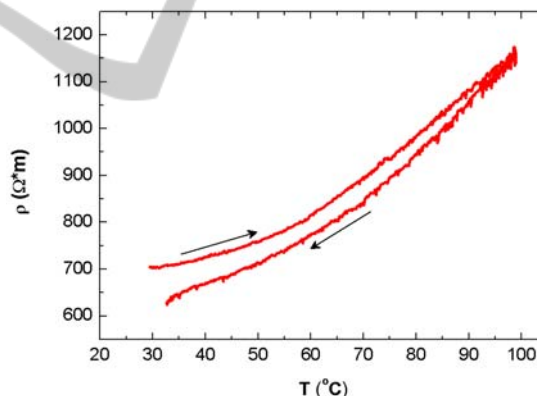

Figure 5: The temperature dependence of specific electrical resistivity of PNCBC with 8 p.h.r. of HSCB at elevated temperatures.

The piezoresistivity of LHPS under 0,1 MPa of pressure was determined in various ambient temperatures (23, 40, 55, 70 and 85 °C) which were chosen according to standard ASTM D1349-99. LHPS was tested for mechano-electrical properties after it was kept and stabilized in each regime of elevated temperature for at least 1 hour. Temperature inside the chamber was monitored using thermocouple.

Figure 6 shows gradual increase of piezoresistive sensitivity with the increase of operating

temperature. This can be explained with decrease of elastic modulus, as the sensor becomes softer thus increasing the cross-deformation under similar operational pressures and providing greater structural mobility of particles of electro-conductive filler at elevated temperatures.
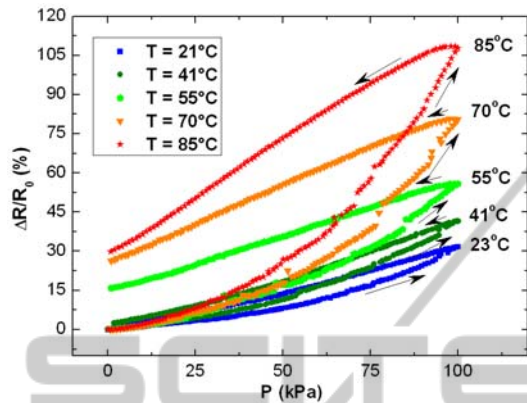

Figure 6: Comparison of piezoresistive behaviour of LHPS in various ambient temperatures for 1st loading cycle.
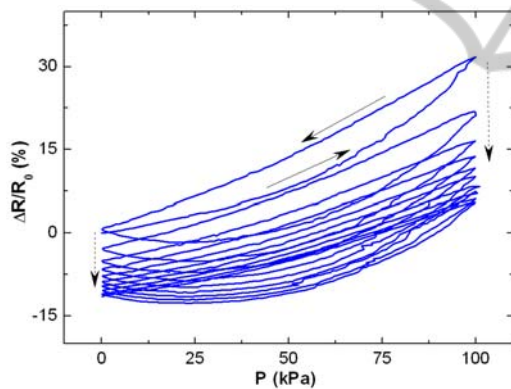

Figure 7: The relative change of electrical resistivity of LHPS under cyclic operational pressure up to 100 kPa at 23 °C.
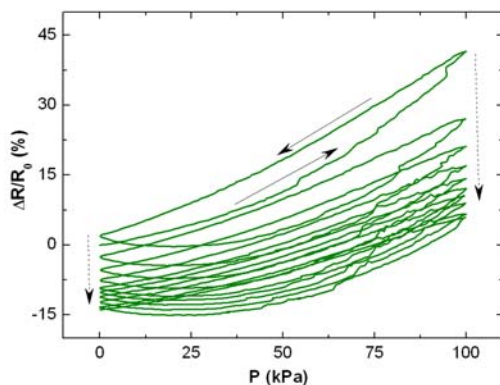

Figure 8: The relative change of electrical resistivity of LHPS under cyclic operational pressure up to 100 kPa at 40 °C.
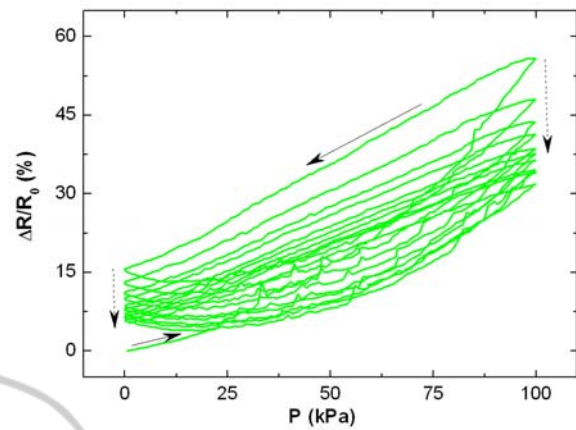

Figure 9: The relative change of electrical resistivity of LHPS under cyclic operational pressure up to 100 kPa at 55 °C.
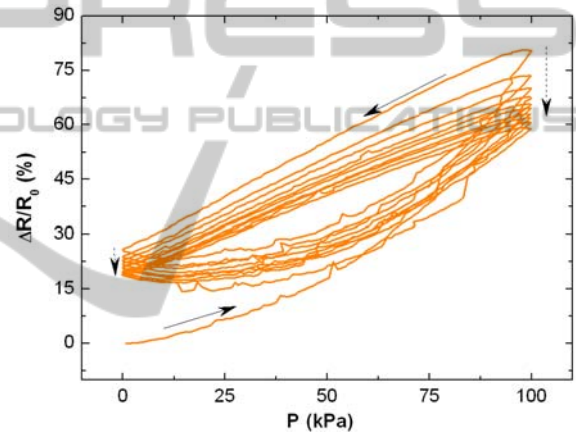

Figure 10: The relative change of electrical resistivity of LHPS under cyclic operational pressure up to 100 kPa at 70 °C.
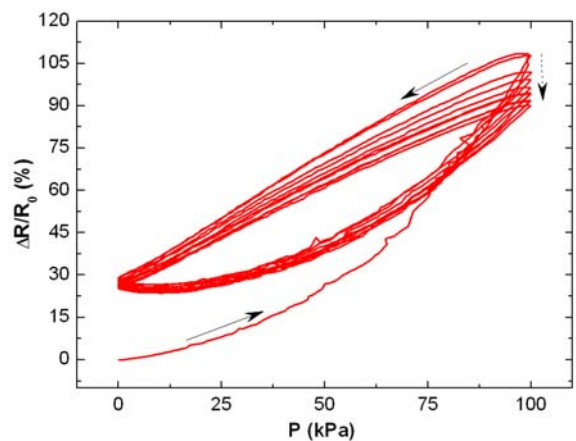

Figure 11: The relative change of electrical resistivity of LHPS under cyclic operational pressure up to 100 kPa at 85 °C.

In the same time from Figures 7-11 it can be seen, that the increase of operating temperature has positive effect on repeatability of the piezoresistive effect during cyclic loading. The noticeable decrease of the initial electrical resistivity at the start of each loading cycle is observed only for operating temperatures of 55 °C and below as the initial resistivity for repeated cycles shifts lower. If the operating temperature was at least 70 °C or higher, only negligible drift of initial resistivity was observed. Thus it can be seen, that LHPS performs considerably better at elevated temperatures which can be attributed to better mobility of filler particles allowing the more rapid mechanical modification and sequencial recombination of electroconductive network of HSCB particles to occur.

4 CONCLUSIONS

The observed positive thermal coefficient of resistivity (PTC) for PNCBC with 8 p.h.r. of HSCB could be explained with large difference in thermal expansion coefficients for both: polymer matrix and HSCB filler causing the sufficient broadening of tunnel junctions with subsequent exponential rise of electrical resistivity versus temperature.

Behaviour of LHPS at evaluated operating temperatures has been successfully investigated.

It has been found out that the sensitivity of LHPS enhances gradually with the increase of operating temperature. The increase of the operating temperature improves the repeatability of the piezoresistive cycles due to greater mobility of particles of electroconductive filler and better partial destruction/recombination of electroconductive structure in the PNCBC.

ACKNOWLEDGEMENTS

REFERENCES

Zavickis, J., Knite, M., Podins, G., Linarts, A., Orlovs, R., 2011. Polyisoprene-nanostructured carbon composite – A soft alternative for pressure sensor application. *Sensors and Actuators A: Physical*. V171, 38-42

Knite, M., Zavickis, J., Podins, G., Orlovs, R., Ozols, K., 2009. Prospective Elasto-plastic Pressure Sensors: All-elasto-plastic polyisoprene/ nanostructured carbon pressure sensing element. In *Proceedings of 6th International Conference on informatics in Control, Automation and Robotics*. 409-412

Knite, M., Podins, G., Zike, S., Zavickis, J., Tupureina, V., 2008. Elastomer – carbon nanostructure composites as prospective materials for flexible robotic tactile sensors. In *Proc. of 5th International Conference on Informatics in Control, Automation and Robotic*. 234-238

Huang, Y., Lu, W., Zhao, X., Lian, C., Ge, Y., 2011. Design and experiment of flexible multi-functional tactile sensors for robot skin. *Jiqiren/Robot*. V 33, 347-353

Chang, F.-Y., Wang, R.-H., Lin, Y.-H., Chen, T.-M., Lee, Y.-F., Huang, S.-J., Liu, C.-M., 2011. Flexible sensing arrays fabricated with carbon nanofiber composite thin films for posture monitoring. *Japanese Journal of Applied Physics*. V 50, N 6-2, 06GE081-06GE084

Knite, M., Klemenok, I., Sakale, G., Teteris, V., Zicans, J., 2007. Polyisoprene-carbon nano-composites for application in multifunctional sensors. *Journal of Alloys and Compounds*. V 434-435, 850-853

Knite, M., Teteris, V., Kiploka, A., Klemenoks, I., 2004. Reversible tenso-resistance and piezo-rezistance effects in conductive polymer-carbon nanocomposites. *Advanced Engineering Materials*. V 6, 742-746

Balberg, I., 2002. A comprehensive picture of the electrical phenomena in carbon black–polymer composites. *Carbon*. V 40, 139-143

Balberg, I., Azulay, D., Toker, D., Millo, O., 2004. Percolation and tunnelling in composite materials. *International Journal of Modern Physics B*. V 18, 2091-2121