The Dependence of Piezoresistivity of Elastomer/Nanostructured Carbon Composites on Dynamic Mechanical Load Frequency

Artis Linarts, Imants Barons and Maris Knite
Institute of Technical Physics, Rigas Technical University, Paula Valdena 3, Riga, Latvia

Keywords: Dynamic Mechanical Loading, Piezoresistivity, Nanostructured Carbon Composites, Sensor Materials, Piezoresistive Sensor.

Abstract: The aim of this article is to determine piezoresistive sensitivity of elastomer nanostructured carbon composites at dynamic loading tests and show the piezoresistive effect correlations to various frequencies of applied mechanical force in a manner that could provide a parameter of the highest detectible dynamic load frequency. This parameter is crucial when determining sensor's usability in possible applications. There are only few articles on conductive polymer composite sensitivity in dynamic mechanical loading tests.With this article we are trying to estimate the values of dynamic loading frequencies in which sensor would be functional.

1 INTRODUCTION

Rapid detection of mechanical forces in tactile sensing devices is very important for precise and cautious automation. Electrically conductive polymer composites (CPCs), being stretchable, bendable, light weight, low cost, and soft, offer several key advantages soft compared to their solid state alternatives. Applications of CPCs are now widely used in different research fields such as stress/strain sensors (Knite et al., 2004), mechanical damage self-monitoring materials (Nanni et al., 2011), gas sensors (Knite et al., 2007), health control (Sebastian et al., 2014), and tactile sensing skin for human robotic application (Canavese et al., 2014).

If insulating polymer matrix is filled with electrically conductive fillers like carbon nanotubes (Wang and Cheng, 2014), carbon blacks (Zhou et al., 2008; Wang et al., 2011; Knite et al., 2004; Nanni et al., 2011; Aldraihem et al., 2009), metallic particles (Jung et al., 2013), or hybrid fillers (Zavickis et al., 2011) at concentrations just above percolation transition also known as critical volume fraction, piezoresistive effect in CPCs can be observed (Zhou et al., 2008). Piezoresistive effect in general describes the electrical conductivity variation upon an influence of external force. Conductivity of the piezoresistive CPCs can be easily tuneable by changing the content of the nanoparticles. However it should be noted that the critical volume fraction as well as piezoresistive sensitivity critically depends on the efficiency of filler dispersion method used to produce these composites (Zha et al., 2014). Piezoresistive CPCs are starting to become one of the most widely researched materials for possible sensor manufacture because of simple and low cost preparation, simple electronics and low power consumption (Stassi et al., 2014). For example, tactile sensing skin for human robotic application was made from nickel particles and poly-dimethylsiloxane rubber. Particle size was from 3.5 micrometers to 7 micrometers in diameter. On particle surfaces were sharp spikes ranging under hundred nanometers in height. Results of this study revealed that this metal–polymer composite is capable of sensing pressure deformations with speeds from 2.5 up to 250 mm/s (Canavese et al., 2014).

Structural health monitoring for observations of other structural materials in buildings is another field where CPC`s would be very helpful. These systems were made from glass fibers with conductive carbon tubes as spikes on their surface in the insulating matrix of epoxy. Strain deformation experiments revealed that these systems could sense different types of deformation including longitudinal, transverse and off-axis orientated (Sebastian et al., 2014).

Linarts A., Barons I. and Knite M..
The Dependence of Piezoresistivity of Elastomer/Nanostructured Carbon Composites on Dynamic Mechanical Load Frequency.
DOI: 10.5220/0005121704160420
In *Proceedings of the 11th International Conference on Informatics in Control, Automation and Robotics* (ICINCO-2014), pages 416-420
ISBN: 978-989-758-039-0

Conductive polymer composite with 10 parts by weight carbon black embedded in a polyurethane matrix was tested to confirm the usage of these sensor materials for paint sensors. These sensors could be applied to structures as paint and observe structural stresses as well as noise levels in towns. The experiments were conducted using compression deformation with oscillation frequency under 100 Hz (Aldraihem et al., 2009).

In our Institute conductive polymer composites are made from natural rubber as matrix and carbon black is mostly used as the conductive filler. The piezoresistive effect for this sensor material is stable in temperatures from 20 to70 degrees Celsius. Knite et al. have investigated polyisoprene nanostructured carbon composites as sensor materials in quasistatic loading tests where the loading happens once and after it the relaxation is observed. Relaxation and its velocity are strongly connected to dynamic loading, so these studies were the base from which this research was developed (Knite et al., 2004).

2 PREPARATION OF SAMPLES AND THE EXPERIMENT

In our case CPCs were made by roll mixing of extra-conductive carbon black (CB) Printex XE2 (specific surface area 950 m2/g, average primary particle diameter 30 nm, DBP absorption 380 ml/100 g) together with natural raw rubber – polyisoprene (Pi) and necessary vulcanization ingredients. Raw rubber chemical composition expressed in parts per hundred rubbers (p.h.r.) is shown in Table 1.

Table 1: Chemical composition of raw rubber composite.

Component	Content, p.h.r.
Natural polyisoprene	100
Sulfur	3,5
Cyclohexyl-benzothiazolesulfonamide	0,8
Zinc oxide	5
Stearic acid	1
Carbon black	8

The electrical conductivity of these composites is highly dependent on the conductive filler concentration and external influences like pressure, tension, temperature. Since this CPCs has got a positive piezoresistive effect (the electrical resistivity increases on external influence) then concentration of conductive filler should be slightly over percolation threshold so that it would be easier to monitor resistivity during testing. In this study to achieve relatively low electrical resistivity we used concentrations of 8 p.h.r. CB (further in text refered to as PiCB8). To get an excellent electrical contact for resistivity monitoring brass electrodes with thickness of 0.05 millimetres where chemically bound to both sides of the sample during vulcanization. After curing, the samples were shelf aged at room temperature for at least 24 hours before any measurements were made.

Equipment for creating high frequency dynamic loading was specially made for this research to study the piezoresistivity of our sensor materials. Device produces oscillating movements with frequency from 3 to 45 Hz and the amplitude of movement differentiates from 3 to 40 mm giving deformation from 4.3 to 57.1% of samples length.

Device is electrically powered from the 220 V AC grid. Rotation frequency of an electric motor is controlled manually with a transformer that changes electric voltage. The rotation frequency is monitored using stroboscope. The electric motor has a gear at the end of the shaft which is connected to an eccentric part by timing belt. The eccentric part is round and has a T-shape channel on its surface. Through it a T-shape figure is moved to differentiate the amplitude of the clamp movement. A connecting rod is bolted to the T-shape figure which can be fixated in different positions. The other end of the connection rod is cylindrical and is gliding through a pipe-like control channel, which turns the eccentric movement in to linear movement. A clamp for holding a sample is permanently connected to this end of the connecting rod and is moving during the experiment. The other clamp for holding the sample is electrically insulated from all the other components and stays static during the experiment.

Electrical resistivity is calculated from voltage measured by an''HBM Spider8'' data acquisition system capable of 4,8 kHz reading frequency on 4 parallel channels which is connected to the sample and a personal computer where data is stored. Resistivity measurements where conducted with 1.2 kHz frequency. Data acquisition system is connected to the sample as is shown in figure 1.

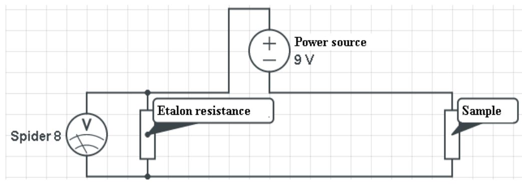

Figure 1: Circuit diagram for sample monitoring.

Two resistances– our sample and an etalon resistor are in series with a nine volt voltage source which produces the current for the circuit. Data acquisition system ''Spider 8'' is connected in parallel to the etalon resistance to measure the voltage drop when our sample is deformed. For more precise measurements, the etalon resistance is almost matched to the sensor's resistance. Electrical resistivity of the sample is at least one order higher than the wire and contact resistances combined therefore they are not taken in to account. The same is true for the measuring equipment resistances. Resistivity of the sample is calculated from the formula:

$$R_x = \left(\frac{U_0}{U_1} - 1 \right) \times R_e, \qquad (1)$$

where U_0 is the power source voltage and U_1 – the voltage measured by Spider, R_x is the resistance of sensor sample and R_e is the etalon resistance.

The piezoresistive effect at slow loading frequency tests (0.005-0.1 Hz) was determined using a Zwick/Roell Z2.5 universal material testing machine coupled with an Agilent 34970A data acquisition/switch unit. Images of the loading equipment are shown in Figure 2.

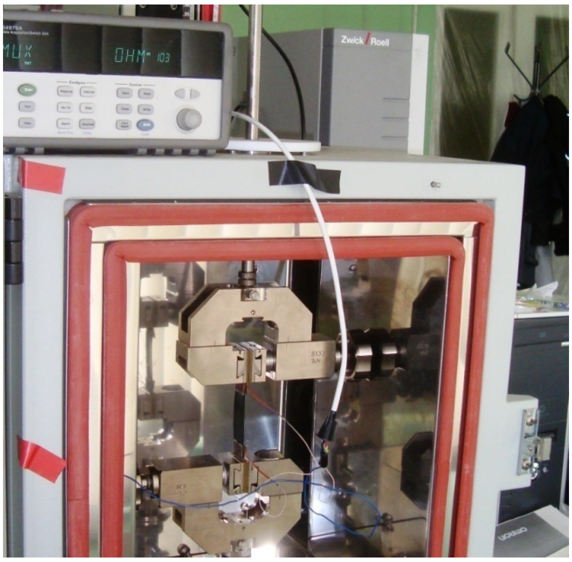

Figure 2: Equipment used for dynamic mechanical loading for low (top) and high (bottom) frequencies; where 1 – electric motor; 2 – eccentric sheave; 3 – sample; 4 – stroboscope; 5 – HBM spider 8.

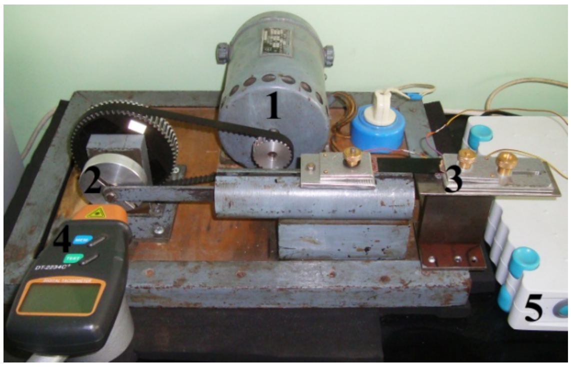

Figure 2: Equipment used for dynamic mechanical loading for low (top) and high (bottom) frequencies; where 1 – electric motor; 2 – eccentric sheave; 3 – sample; 4 – stroboscope; 5 – HBM spider 8. (cont.)

3 RESULTS AND DISCUSSION

Mechanical loading frequency influence on the CPC piezoresistivity were conducted in room temperature at 0 to 6.6%deformationfrom 0,005 to 45 Hz. For deformation frequencies higher than 3 Hz the desired loading frequency is manually set using the transformer and the stroboscope. After at least 5 minutes of mechanical loading the change of sample resistivity is measured in time.

The same was done for frequencies lower than 3 Hz, however in this case automated frequency control was used. PiCB8 piezoresistive effect at 0.01, 3 and 40 Hz loading frequencies in 0 to 6.6% deformation are shown in Figure 3.

The observed piezoresistive effect can be explained by transverse slippage of nanoparticles in the composite structure caused by external strain leading to disarrangement of the conductive channels. When the frequency is increased the minimal and maximal resistivity values or resistance at zero and 6.6 % deformation increases as well, however the overall piezoresistivity tends to decrease with increasing frequency as shown in figure 4.

When the sample is deformed the average distance between particles in the strain direction increases leading to an increase in overall resistivity of the sample, however at constant deformation in time the polymer macromolecules reconfigure (process known as strain relaxation) in strain direction leading to a decrease of average layer thickness between conductive particles and subsequent increase of tunnelling current or decrease of overall resistivity.

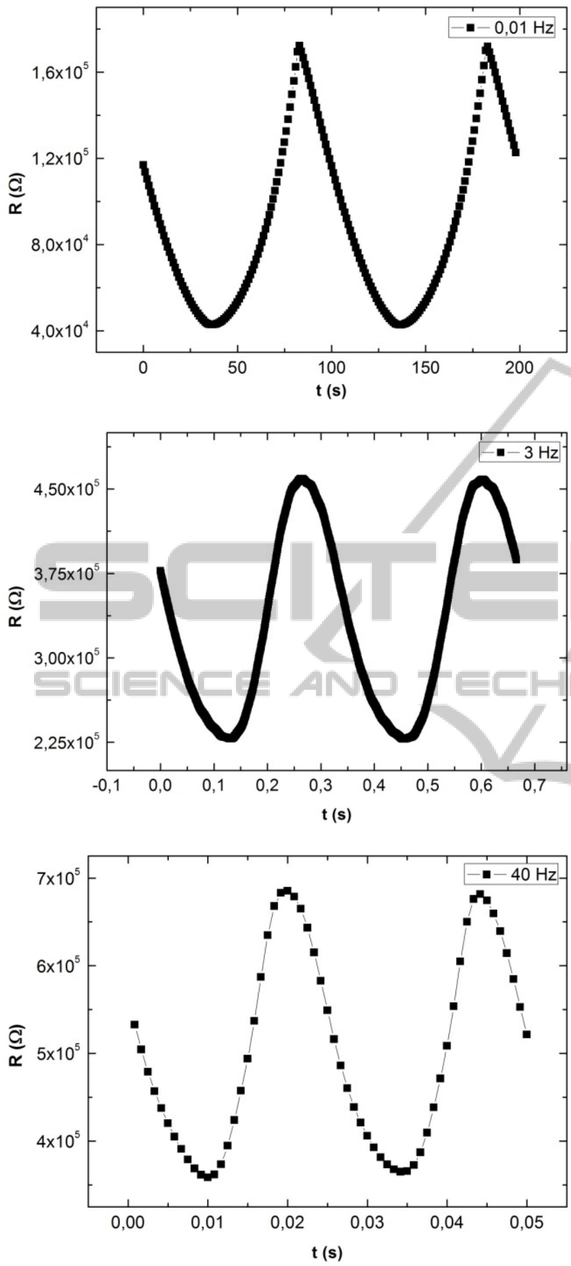

Figure 3: Change of resistivity in 0.01; 3 and 40 Hz deformation frequencies.

To explain these results the relaxation of sample's resistivity at constant 6.6% strain deformation was carried out in room temperature (Figure 5). At constant deformation the decrease of resistivity in time can be explained as fallows. The 3D conductive grid throughout the composite structure is composed from carbon black particles which mostly are separated by a thin layer of polymer. The conductivity in this case is ensured by tunnelling currents between particles.

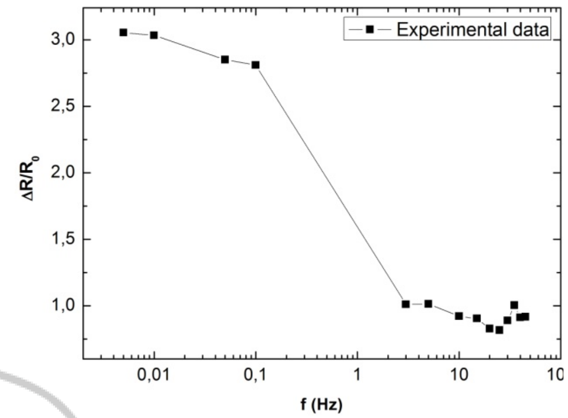

Figure 4: The dependence of piezoresistive sensitivity versus loading frequency.

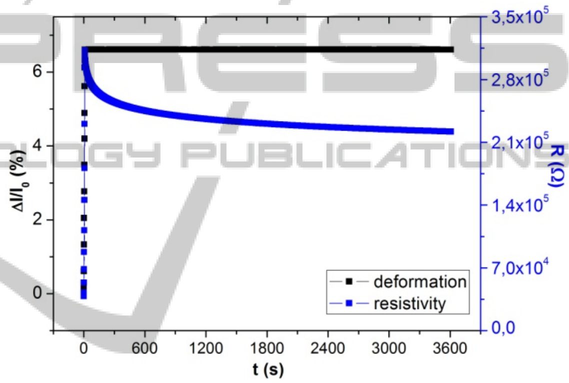

Figure 5: Change of resistance in time at constant 6.6 % strain deformation.

Luheng Wang et.al (14) described the change of resistivity in time using a mathematical model similar to stress relaxation in time:

$$R(t) = R(\infty) + \sum_{i=1}^{m} R_i * \exp\left(-\frac{t}{\tau_{Ri}}\right) \qquad (2)$$

The exponents in equation (2) represent the resistance relaxation times related to the movement of the polymer composites constituent parts. We found the best fitting of experimental curve using in equation (2) three exponents i = 3 with three mean relaxation times τ_1 = 1754, τ_2 = 197, and τ_3 = 22s that could represent relaxation of carbon nanoparticle aggregates, polymer chains, and chain segments respectively.

Based on the additional investigation of relaxation processes (Figures 5 and 6) and analysis of the acquired values of relaxation time τ_1, τ_2, and τ_3 we explain the strain sensitivity $\Delta R/R_0$ dependence on load frequency f as follows. At very low tension load frequencies both the macromolecular chain and the CB nanoparticle

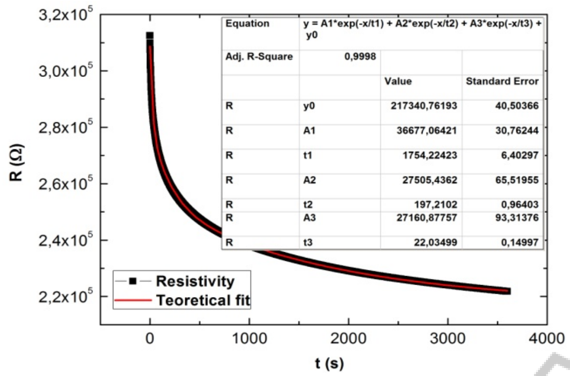

Figure 6: Fitting of experimental curve of change of resistance in time at constant 6.6 % strain deformation with equation (2) taking into account three mean relaxation times: $\tau_1 = 1754$, $\tau_2 = 197$, and $\tau_3 = 22$s.

aggregates have enough time to relax, therefore R also relaxes with time when the mechanical loading and the strain sensitivity is the highest. At higher (>1Hz) frequencies CB aggregates have a difficulty to follow the macromolecular chains during loading, so the strain sensitivity decreases versus frequency.

4 CONCLUSIONS

It was shown that the polyisoprene high structure carbon black composite samples can be used for periodically changed mechanical load or mechanical vibration testing. The maximal and minimal values of resistivity increase with mechanical load frequency while the piezoresistivity effect decreases. These can be explained by analysing the experimentally determined values of relaxation times of carbon black aggregates and polymer chains. The limiting factors for use of the developed sensors at higher mechanical load frequencies are the rise of maximal and minimal resistivity as well as the decrease of piezoresistivity versus frequency.

ACKNOWLEDGEMENTS

This study was supported by ESF Grants Nr. 1DP/1.1.1.2.0/13/APIA/VIAA/021.

REFERENCES

Knite, M., Teteris, V., Kiploka, A., Kaupuzs, J. 2004.Polyisoprene-carbon black nanocomposites as strain and pressure sensor materials, *Sensors & Actuators A: Physical*, *Volume 110, Issue 1-3*, pp. 142-149

Nanni, F., Ruscito, G., Puglia, D., Terenzi, A.,Kenny, J.M., Gusmano, G.2011.Effect of carbon black nanoparticle intrinsic properties on the self-monitoring performance of glass fibre reinforced composite rods, *Composites Science & Technology*, *Volume 71, Issue 1*, pp. 1-8

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

Sebastian, J., Schehl, N., Bouchard, M.Boehle, M., Li, L., Lagounov, A., Lafdi, K. 2014. Health monitoring of structural composites with embedded carbon nanotube coated glass fiber sensors**.** *Carbon*, *Volume 66*, pp. 191-200

Canavese, G., Stassi, S.,Fallauto, C.,Corbellini, S., Cauda, V.,Camarchia, V., Pirola, M.,Pirri, C. F. 2014.Piezoresistive flexible composite for robotic tactile applications. *Sensors & Actuators A: Physical*, *Volume 208*, pp. 1-9

Wang, L., Cheng, L. 2014. Piezoresistive effect of carbon nanotube silicone-matrix composite. *Carbon*, *Volume 71*, pp. 319-331

Zhou, J.F., Song, Y.H., Zheng, Q., Wu, Q., Zhang M.Q.2008. Percolation transition and hydrostatic piezoresistance for carbon black filled poly(methylvinylsilioxane) vulcanizates. *Carbon*, *Volume 46, Issue 4*, pp. 679-691

Wang, L., Ma, F., Shi, Q., Liu, H., Wang, X. 2011. Study on compressive resistance creep and recovery of flexible pressure sensitive material based on carbon black filled silicone rubber composite. *Sensors and actuators*, *Volume 165, Issue 2*, pp. 207-215

Aldraihem, O., Akl, W., Baz, A. 2009. Nanocomposite functional paint sensor for vibration and noise monitoring**.** *Sensors & Actuators A: Physical, Volume 149, Issue 2*, p233-240

Jung, J., Kim, M., Choi, J.K., Park, D.W., Shim, S.E. 2013.Piezoresistive effects of copper-filled polydimethylsiloxane composites near critical pressure. *Polymer*, *Volume 54*, pp. 7071-7079

Zavickis, J., Linarts, A., Knite, M. 2011. The downshift of the electrical percolation threshold in polyisoprene–nanostructured carbon composites. *Energetika*, *Volume 57, Issue 1*, pp. 44-49

Zha, J. W., Li, W. K., Zhang, J., Shi, C. Y., Dang, Z. M. 2014. Influence of the second filler on the positive piezoresistance behavior of carbon nanotubes/silicone rubber composites**.** *Materials Letters*, *Volume 118*, *Issue 1,* pp. 161-164

Stassi, S., Cauda, V., Canacese, G., Pirri, C.F. 2014. Flexible tactile sensing based on piezoresistive composites: A review. *Sensors*, *Volume 14*, pp.5296-5332

Wang L., Ding T., Peng Wang P. 2008. Effects of instantaneous compression pressure on electrical resistance of carbon black filled silicone rubber composite during compressive stress relaxation, *Composites Science & Technology, Volume 68,* pp.3448-3450