Mechanical Pressure Induced Capacitance Changes of Polyisoprene/Nanostructured Carbon Black Composite Samples

K Ozols and M Knite
Riga Technical University, Institute of Technical Physics, Riga, Latvia
E-mail: kozols@ktf.rtu.lv

Abstract. Polyisoprene/nanostructured carbon black (PNCB) composite samples with different amount of carbon black (CB) filler were prepared. Investigations of mechanical pressure induced relative capacitance changes (RCC) depending on frequency (20 Hz – 2 MHz) were conducted. It was found that PNCB samples show pronounced and rather complex RCC effect, which depends on frequency, amount of filler (1 – 10 phr of CB) and pressure (from 0 to 234 kPa). At a certain frequency and a certain filler amount RCC effect changes its sign. Pressure induced capacitance changes at least for low CB filler concentrations are caused by piezopermittivity property of the PNCB composite.

1. Introduction
PNCB composites show pronounced resistance change effect when subjected to mechanical deformation [1]. This effect has been used to develop flexible mechanical pressure and organic solvent vapor sensors [2]. Mechanisms of electroconduction [3] and emergence of dielectric constant [4] for such composites in static regime have been explained. Change of electroconduction under mechanical influence [1,2] is in general rather well understood. Recently it was found that PNCB composites show a piezocapacitance effect as well [5]. To advance the composites for sensor and, possibly, other applications further dielectric spectroscopy studies of PNCB samples influenced by mechanical pressure should be conducted. The current work is dedicated mostly to capacitance change measurements of PNCB composite samples while mechanical pressure is applied.

2. Samples and experiments
2.1. Development of samples
Development of PNCB composite samples is as follows. SWR-3L polyisoprene rubber is used as a matrix due to its high elastic properties. Carbon black (high structure Degussa™ Printex™ EX-2 carbon black, the average particle size is 30 nm, surface area 950 m²/g) is used as electroconductive filler. First, a liquid solution of matrix is obtained by dissolving polyisoprene with curing ingredients in chloroform. Then, colloidal solution of CB in chloroform is prepared whereby CB nanoparticles are dispersed in chloroform using ultrasonication (5 min, specific power 1 W/ml). The CB solution is added to the matrix solution and the obtained mixture is stirred for 24 h. Further, the mixture is poured out into Petri dishes to evaporate chloroform. After evaporation of chloroform the obtained dry, raw PNCB mixture is processed in Two-Roll Mills (LabTech Engineering Company, model “Scientific”, cold processing mode used) to disperse CB nanoparticles again. After processing with roll mills a raw
PNCB mixture (Figure 1a) is ready to be used for sample creation during vulcanization. A piece of a raw PNCB mixture is put into a press form together with brass electrodes (thickness of electrodes is 0.05 mm).

The press form is then put into a hot press (Rondol™, curing temperature 150°C, pressure 3 MPa) for 15 minutes. As an additional result of vulcanization of the PNCB mixture, the electrodes are attached tightly to the PNCB composite. After cooling the press form finished PNCB composite sample is removed (Figure 1b). The thickness of the whole sample is 1.1 mm, (1 mm is for the composite), the diameter of the sample is 18 mm. Samples with different CB concentrations were created, from 0.5 phr CB (0.5 mass parts of CB per 100 parts of rubber) to 10 phr of CB. Testing of samples was conducted no less than 24 h after samples were created.

2.2. Measurements
Dielectric spectroscopy measurements were conducted using an Agilent E4980A Precision LCR meter (frequency range 20 Hz - 2 MHz). The mechanical pressure was applied using weights with different mass. During measurements the weights were isolated from the samples with a teflon spacer.

3. Results and Discussion

3.1. Measurement results

According to Knite et al [1] in the case of DC conductivity, as mechanical pressure is applied, PNCB samples show the largest conductivity change when the concentration of the electroconductive filler fits to a region of percolation transition. For samples used in this work percolation transition would correspond to CB concentrations approximately from 3 to 6 phr (Figure 2a). RCC (i.e. ΔC/C₀) effect depending on frequency and applied different values of mechanical pressure for PNCB sample
containing 3 phr of CB is shown in Figure 2b. As it can be seen on the graph the maximum RCC effect for the given sample is small - around 2%. The effect is negative - the capacitance is decreasing at all applied pressures and at all measured frequencies. Measurement results for the lowest frequencies are not shown, because the capacitance of the sample is too small (~12 pF at low frequency) for precise low frequency readings on the LCR meter. The DC conductivity of the sample containing 3 phr of CB is just on the limit of percolation transition and therefore in the case of piezoconductivity the effect caused by mechanical pressure also would be small. The largest RCC effect (20% at maximum pressure) is found for the next sample, containing 4 phr of CB (Figure 3a). Conductivity of this sample ($10^{-7}$ S/m) resides at the lower part of percolation transition. The sign of the RCC effect is negative, too, but in this case large frequency dependence is observed. At 2 MHz maximum RCC effect is only 4%.

![Graphs](image1)

**Figure 3.** Graphs: a) The RCC effect depending on pressure for sample containing 4 phr of CB, b) The RCC effect depending on pressure for sample containing 6 phr of CB.

Further increase of CB leads to decrease of RCC effect while at the same time it shifts the RCC maximum frequency to higher values (see Figures 3a and 3b). Adding more CB to the matrix (7 phr of CB) introduces a change in sign of RCC effect at different frequencies (Figure 4a).

![Graphs](image2)

**Figure 4.** Graphs: a) The RCC effect depending on pressure for sample containing 7 phr of CB, b) The RCC effect depending on pressure for sample containing 10 phr of CB.

At frequency around 200 Hz compression of the sample increases the capacitance of the sample up to around 8% (at maximum pressure), at 4 kHz RCC effect equals zero for all pressures applied, but at higher frequencies, negative RCC effect is observed with a maximum effect around 300 kHz (max RCC around 9% at 234 kPa). Measurement results for the lowest frequencies are not shown, because
dielectric loss in the composite becomes too large (tan δ = 600 at 100 Hz) for precise capacitance readings on the LCR meter. Further CB amount increase in PNCB sample (10 phr of CB, Figure 4b) shifts a zero-change frequency up to around 650 kHz. Well expressed positive RCC effect can be observed (around 10% at 234 kPa, at 2 kHz). On the contrary, maximum negative RCC effect is just around 1%.

3.2. Proposed mechanism of capacitance change

The observed RCC effect is rather challenging to explain since the effect changes its value and sign depending on the CB concentration and frequency. The electroconductive channels in the PNCB composites are formed between CB aggregates by means of tunneling barriers [1,3], where tunneling currents can flow. A network of these electroconductive channels are responsible for the piezoresistance effect [1,2]. Conductive nanoparticle aggregates form microcapacitors [4]. Conductivity percolation at least for polymer/CNT composites is tightly bound to permittivity percolation [6]. Based on these facts, we conclude that the same network of electroconductive channels, which is responsible for piezoresistance effect in the PNCB composite, does form a network of capacitive channels (microcapacitor chains), which mostly determine the overall capacitance of the sample and are responsible for the RCC effect. It should be noted that piezoconductance effect (figures not shown in this paper) for the same samples, same frequency range and for all the concentrations of CB mentioned here is always negative. That means that the compression of PNCB sample, at least for CB concentrations up to 10 phr and pressures up to 234 kPa, always leads to interruptions in conductive and, simultaneously, capacitive channels. Since the underlying physics of conductance and capacitance are different, that could explain why the RCC effect is not always negative. Currently this phenomenon is not entirely clear to us.

Since in our case PNCB samples represent capacitors with an elastic dielectric layer between electrodes and these samples show a decrease of capacitance while being compressed (this is true at least for PNCB samples with low CB filler amount) then it confirms, that piezocapacitance effect of the samples is based on piezopermittivity property of the PNCB composite.

4. Conclusions

The measurements conducted showed, that both negative and positive RCC effects in PNCB composite samples exist. It has been found that inversion of sign of the RCC effect depends on the CB filler concentration and partially on the AC frequency. The explanation for observed effects is based on the concept, that PNCB composite represents an electrical circuit consisting of a large amount of microscale resistive and capacitive elements, which not only form a network of electroconductive channels but simultaneously form a network of capacitive channels. Compression of PNCB samples leads to a change of parameters of resistive and capacitive elements in the composite. Thus, the overall capacitance (and conductance) of the sample is changed. The observed effects simultaneously confirm the piezopermittivity property of the PNCB composite (at least for the cases with low filler concentrations). In PNCB and similar composites, which could be compressed or stretched, RCC effects together with conductivity change effects may help to explain the structure of composites and provide information about the movement of nanoparticles during mechanical influence.

5. Acknowledgements

This work is financially supported by the Council of Science of Latvia and by Latvian National Research Program in Materials Science.

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