

**RIGA TECHNICAL UNIVERSITY**  
Faculty of Material Science and Applied Chemistry  
Institute of Technical Physics

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**THE FEATURES OF PERCOLATION  
AND PIEZORESISTIVE EFFECT IN  
POLYISOPRENE – NANOSTRUCTURED  
CARBON COMPOSITES**

Summary of Doctoral thesis

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The doctoral dissertation for the Doctoral degree in physics will be defended in public at 14:00 o'clock on September 9 2011 at Riga Technical University, Faculty of Material Science and Applied Chemistry, Riga Azenes street 14/24, Room Nr. 272.

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APPROVAL

With following I approve that I've elaborated current doctoral dissertation, which is submitted to be reviewed in Riga Technical University to qualify for Doctoral degree in physics and doctoral dissertation is not submitted anywhere else to qualify for scientific degree.

Juris Zavickis \_\_\_\_\_ (signature)

Date 31.04.2011.

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I would like to thank all, who directly or indirectly have assisted to accomplish the presented study; the supervisor of my thesis paper, professor Māris Knite, in the first place for generously directing my research efforts and elaborating the subjects of it in previous years, defining the general outlook of the main problems, as well as for helpful advice interpreting the physical terms and publishing results. I am thankful to my advisor for bringing me into excitingly interesting world of science that presently has become the primary domain of my activity.

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Riga, year 2011

J.Zavickis

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## **OVERALL REVIEW OF THE THESIS**

### **Introduction**

Many different pressure sensors and equal devices are known. They include piezoelectric ceramics, piezoresistive silicon, capacitive, inductive and optical pressure sensors. Majority of them has disadvantages, such as expensive process of manufacture, complicated structure, and need for sophisticated electronic components. Many of the sensors are brittle and do not endure rough handling or sharp impacts. Recently polymers, filled with electro conductive particles are proposed as a cheap and simple alternative to conventional pressure sensors. Their electrical resistivity depends on the rate of deformation. If such behavior is observed under compression, the property is called piezoresistivity. Depending on properties of the ingredients, such composites can be made with desired sensitivity and mechanical properties. Recently focus has been set on elastomer composite systems, filled with highly disperse electro-conductive components. Such systems possess positive piezoresistivity, when under any kind of deformation the increase of the electrical resistivity is observed. Research at the RTU Institute of Technical Physics has established that such sensitive composites can be acquired by filling natural polyisoprene rubber with highly structured carbon particles. The polyisoprene-nanostructured carbon composites (PNCC) acquired in this way exhibit remarkable sensitivity, they are hyper-elastic and rather easy to make. Although PNCC belonging to so called group of “smart” materials are interesting from the viewpoint of application they are more of scientific interest. At the same time, natural rubber and its vulcanized derivatives have long since proved themselves as being popular for consumption, easy and cheaply acquirable materials with wide branches for application.

The main aim of the study has been set to find out, how vulcanization, the chosen filler, its concentration, and the method of dispersing affect the electrical percolation threshold and piezoresistive properties of the PNCC, as well as to elaborate the functional prototype of completely hyper-elastic pressure sensitive element based on PNCC and to evaluate its practical applications.

### **The state of art**

The piezoresistivity of PNCC is well known, and such are the electrical properties of similar polymer systems depending greatly on the type of filler and the method of dispersing used. The characteristic piezoresistive properties of PNCC appear only after the composite is vulcanized. At the same time, there is no unambiguous information concerning dependence of mechano-electrical properties of PNCC on composition and production techniques of the composite.

The research of electrical properties of PNCC is believed to hold significant information about its microstructure.

### **Aims**

- 1) To estimate the effect of vulcanization on electrical conductivity and piezoresistivity of PNCC;
- 2) To explore the effect of filler type and the method of dispersion on electrical percolation threshold and piezo-resistivity of PNCC;
- 3) To devise and to test techniques to monitor the change of electrical resistivity of PNCC during vulcanization;
- 4) To derive a theoretical model describing the positive PR effect;
- 5) To design a hyper-elastic pressure sensor element of PNCC and to make a functional prototype.

### **Scientific novelty**

- 1) An innovative methodology has been developed to measure electrical resistivity of PNCC *in-situ* during vulcanization;
- 2) A theoretical model has been derived based on available literature and originally used to describe the change of electrical resistivity of PNCC under uni-axial compression;
- 3) A completely hyper-elastic pressure sensor element has been designed and an original functional prototype made.

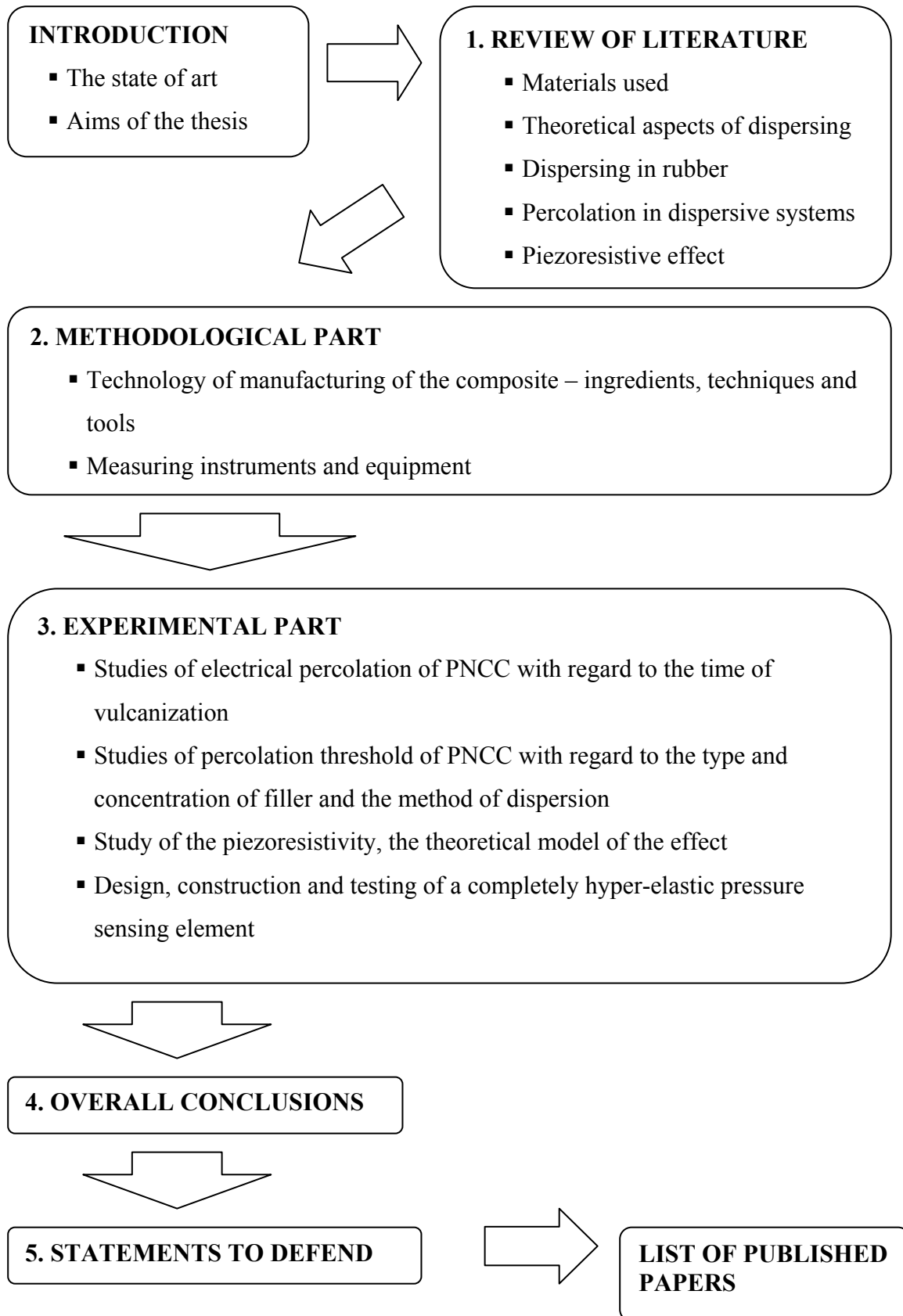
### **Composition and volume of the thesis**

The 128 pages of the thesis paper including 102 pictures and 6 tables comprises introduction and 5 chapters: a review of literature, methodological part, experimental part, overall conclusions and the statements to defend, the list of papers published by the author, and list with 72 references.

### **Approbation and publication of the thesis**

Results presented in thesis paper are approbated in 7 full text articles (4 of them SCI), one monograph, 11 conference proceedings and have been covered with 1 LV patent.

## Structure of thesis





## CONTENTS OF THE THESIS

### Review of literature

The section includes analysis of available published reports, a short synopsis of subjects considered in the theses, and a review of the structure, specific properties and origin of the materials used to make PNCC.

The first chapter tells about materials used in the study. Polyisoprene (PI) caoutchouc and its vulcanizates, used fillers – high structure carbon black (CB) and multi-wall carbon nanotubes (MWCNT) are considered in separate sub-chapters. The basic methods used to obtain natural and synthetic rubber vulcanizates and properties the latter being discussed.

In the second and third chapters theoretical aspects of dispersing nano-particles and traditional methods of dispersing fillers in natural rubber are reviewed, the classical stabilization diagram of suspension being analyzed and the dependence of potential interaction energy on distance between particles and the essence of quasi-statistical state of colloidal suspension explained. The main technological issues faced dispersing nano-particles in viscous media are highlighted.

The fourth chapter is dedicated to analysis of electrical percolation in disperse systems, to determining and their physical interpretation of critical parameters, and to explaining significance of tunneling currents to electrical conductivity of PNCC. According to Killbride et al. [1], statistical percolation theory predicts dependence of the conductivity on the filler fraction of a composite filled with disperse electro-conductive particles to be expressed by:

$$\sigma = \sigma_0 |\Phi - \Phi_c|^\tau, \quad (1)$$

where  $\sigma$  – electrical conductivity of the composite,  $\sigma_0$  – constant,  $\Phi$  – actual concentration of filler,  $\Phi_c$  – critical concentration of filler,  $\tau$  – the critical index of percolation. The current theoretical expression is further used to describe the critical parameters electrical percolation of different PNCC. According to Balberg [2], the critical index can also be interpreted as a statistical average of the number of contacts each electro-conductive particle has with its neighbors and thus describes the structural complexity of the particles.

The basic principles of piezoresistive (PR) effect and best published papers available since 1946 and related to piezo- and tenzoresistive effects are considered in the final section of the review. Bulgins [3] and Wack et al. [4] are the first to describe the increase of the electrical resistivity of rubber filled with carbon black under stretch. They try to explain the effects observed by breakdown or rearrangement of the electro-conductive chains of conductive particles caused by deformation. It is interesting that the first of the articles already at the time it was published includes in the explanation the hopping of electrons between closely distributed particles still separated by a thin dielectric

layer. The explanation quantitatively corresponds to theories based on tunneling effect by Simmons and Zhang et al. 20 and 60 years later [5, 6]. Hassan et al. [7] describe improvement of electrical conductivity observed in the direction parallel to elongation of highly filled sample of electro-conductive rubber. The phenomenon is explained by deformation of the material in cross direction to the strain axis causing modulation of the electro-conductive structure. Pramanik et al. [8, 9] have studied dependence of PR effect on filler concentration of elastomers filled with carbon particles and short carbon fibers. In major cases the decrease of PR effect is observed at increasing the concentration of the electro-conductive filler. The authors have found a higher PR sensitivity in composite systems filled with disperse carbon compared with similar system filled with short fibers. Kijuro et al. [10] have acquired patent describing PR rubber filled with disperse metal particles. Such materials possess negative PR effect and are proposed as hyper-elastic current switches. Knite et al. [11] propose using natural polyisoprene (PI) matrix and extremely high structure carbon black as filler to obtain extremely sensitive PR and tenzoresistive composite material. Due to hyper-elasticity of the chosen matrix and high structure of filler particles, the obtained composite can be characterized as a material of positive PR effect, high sensitivity and reversibility of the changes of resistivity. By using dielectric spectroscopy Knite et al. [12] demonstrates the duality of conductive mechanism and importance of tunneling currents in such type of conductive composites. Luheng et al. [13] have studied composites of carbon-filled silicone rubber and their PR effect depending on concentration of the conductive filler. They have succeeded to observe inversion of the PR effect, when under gradual increase of the filler concentration the effect turns from negative into positive.

The analysis of available reports helped to chose the right components for the materials being studied, to develop the methods of obtaining samples and to set the main objectives of the research. It made possible to identify the current trends in research of similar materials and to make conclusions based on experience of other authors as well.

## Methods

In the first chapter the PNCC is described in details with special attention to its chemical composition, technology of manufacture and methods, tools, and equipment used to prepare the samples. The basis of PNCC is natural PI rubber. The other components and proportions are shown in Table 1. According to the accepted methodology, the concentration of components is expressed as mass parts per 100 mass parts of PI caoutchouc (p.h.r.).

Table 1

Chemical composition of raw rubber

Component	Concentration, m.p.
Natural PI caoutchouc	100
Sulfur	3,5
Cyclohexyl-benzothiazolyl sulfenamide	0,8
Zinc oxide	5
Steric acid	1

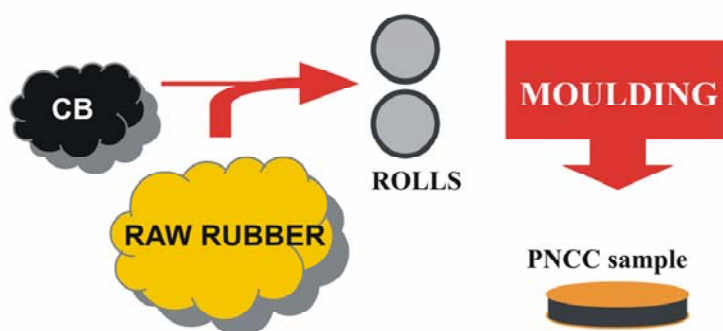


Fig. 1.

Schematic diagram of PNCC manufacturing by dispersing the electro-conductive phase in raw rubber using cold rolls (dry mixing)

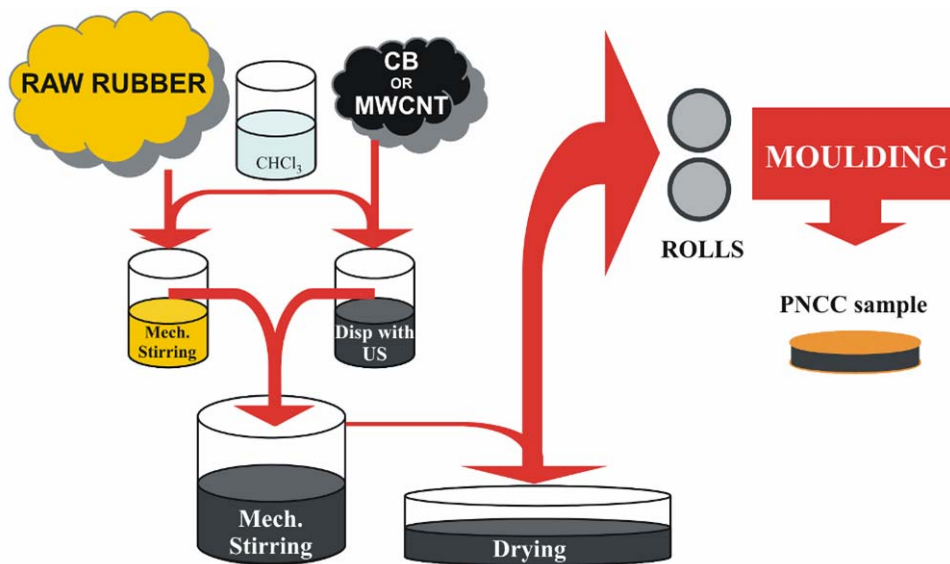


Fig. 2.

Schematic diagram of the PNCC manufacturing by US dispersion of the electro-conductive phase in cloroform and mechanical mixing with dissolved raw rubber (wet mixing)

To obtain PNCC the electro-conductive fillers has to be dispersed into raw rubber. In the first case the high structure carbon black (CB) Printex XE2<sup>TM</sup>

produced by Degussa<sup>®</sup> were used. Their primary particle size – 30 nm, dibutylphthalate absorption – 380 ml/g and specific surface area – 950 m<sup>2</sup>/g. For second case the multiwall carbon nanotubes (MWCNT) produced by SigmaAldrich<sup>®</sup> were used. Their outer diameter – 40-60 nm, average length – 0,5-500 µm. Two principally different methods were used to disperse the electro-conductive filler – dry mixing by rolling (Figure 1) and wet mixing by ultrasound in chloroform (Figure 2), followed by mixing into raw rubber in chloroform solution.

Technological nuances used in „Baltic Rubber Factory” Ltd are described and basic calculations presented, both related to obtaining optimal vulcanization regimes and producing the experimental samples of PNCC. The main three types of samples used in the experiments are shown in Figure 3. To obtain good electrical contact for electrical measurements, the brass foil electrodes were incorporated into samples during the vulcanization.

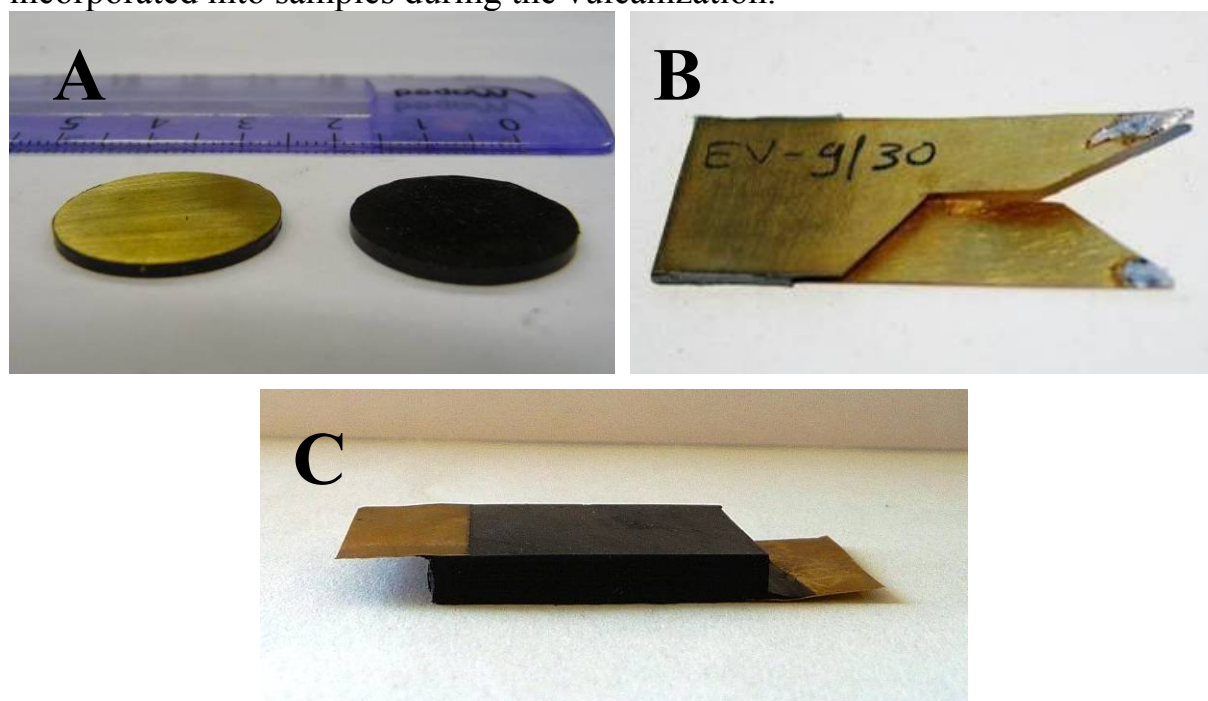


Fig. 3.

PNCC samples, produced and used within the study: A) Cylindrical samples of 18 mm in diameter, 1 mm thick, for measuring piezoresistivity; B) Sample for *in-situ* measurements during vulcanization; c) Complex multi layer PNCC sample with brass foil electrode extensions

In the second chapter the basic measuring equipment used to obtain results are shown and shortly described. Special attention is paid to the self-assembled material testing setup consisting of a modified universal Zwick/Roell Z2.5, an Agilent A34970A digital multimeter, a Keithley 6487 picoammeter and a Spider8 data acquisition and processing module (Figure 4) properly suited to perform mechano-electrical measurements.

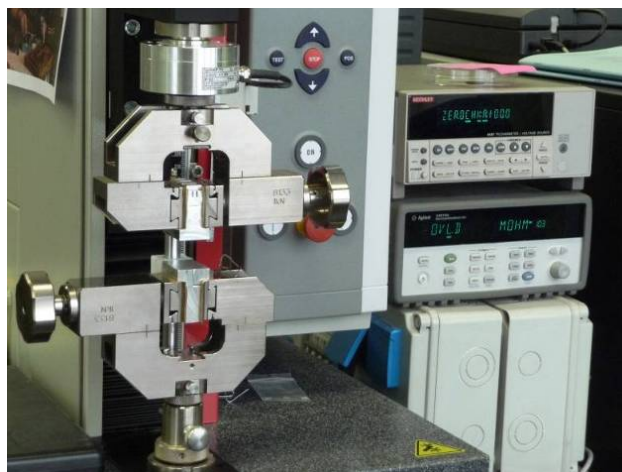


Fig. 4.

The close-up view of the sample holding clamps of the universal Zwick/Roell Z2.5 material testing machine. The instruments for electrical measurements - Agilent A34970A multimeter and Keithley 6487 picoammeter are seen in the background

## Experimental part

**The first chapter** is devoted to the study of the dependence electrical and mechano-electrical properties of PNCC {R1, R6, R7, M1} on vulcanization time. As revealed earlier, only completely vulcanized PNCC possess electrical conductivity typical for composites belonging to the middle region of percolation transition. No electrical conductivity is observed in the raw rubber samples of the same composition.



Fig. 5.

Custom made Teflon mould-frame with polyimide foil shell suitable for measurements of electrical properties *in-situ* during vulcanization. The sample with brass foil electrode extensions is inserted in the mould

The experimental method for direct *in-situ* measurements of electrical resistivity during vulcanization has been developed by using custom-made mould, consisting of Teflon frame and a polyimide outer shell (Figure 5). The

temperature of vulcanization is properly reduced to 140 °C to increase the time of vulcanization improving the time resolution of the experiment.

Experiments are performed with samples of 9 and 10 p.h.r. of CB. According to Knite et al. [11, 12, 15, 16], the samples belonged to the percolation transition region of the studied PNCC. The measurements revealed abrupt decrease of the electrical resistivity of PNCCs just within the first minutes of the vulcanization phase (Figure 6).

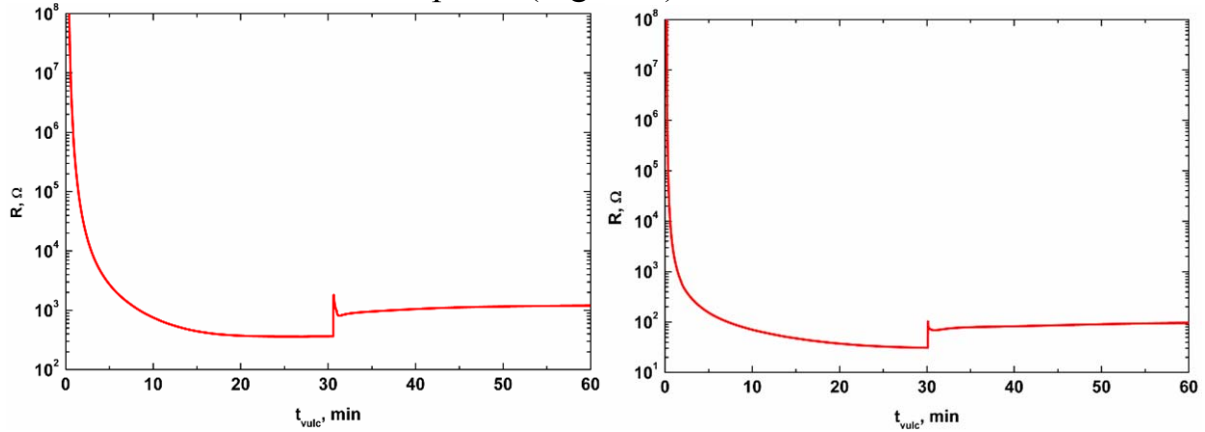


Fig. 6.

Electrical resistivity of PNCC with 9 p.h.r. (left) and 10 p.h.r. (right) of CB as a function of vulcanization time. Temperature of vulcanization – 140 °C. The sharp change of the electrical resistivity at 30 min. are caused by removing the sample from press

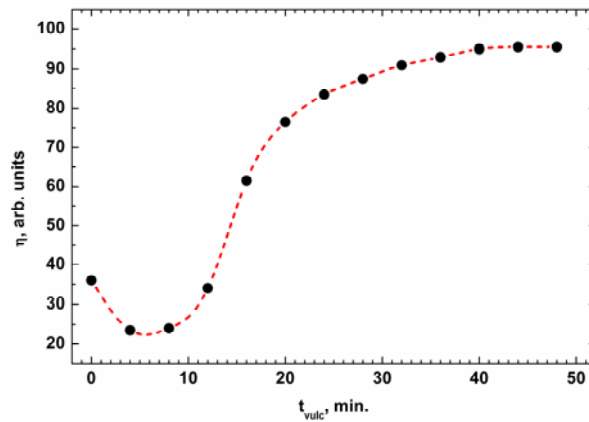


Fig. 7.

Dynamic viscosity of PNCC with 10 p.h.r. of CB as a function of vulcanization time. Temperature of vulcanization – 140 °C

It is interesting, that the sharpest change of electrical properties correlate with the viscosity minimum detected by rheological measurements of vulcanization (Figure 7). Assuming this, the hypothesis was proposed, that firstly the conductive filler particles in raw rubber are well dispersed making formation of any electro-conductive filler structure hardly or not at all possible. The major decrease of the viscosity of the matrix, as well as a high pressure during vulcanization causes significant mass transfer of filler particles. Under such circumstances, the delivered thermal energy incites agglomeration of

particles and builds electro-conductive spatially oriented chains dramatically decreasing the overall electrical resistivity of the PNCC. Such phenomenon has been previously described in literature by Bauhofer et al. [14].

To verify the hypothesis, the PNCC raw rubber samples were made with 9 and 10 p.h.r. of electro-conductive CB dispersed by cold rolling. The samples were vulcanized under pressure of 3 MPa at temperature of 140 °C for 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35 and 40 minutes. Two types of samples were made for each of the respective durations of vulcanization (Figure 8) – with brass foil electrodes to evaluate electrical properties, and without electrodes to be broken in liquid nitrogen to study its microstructure by SEM.

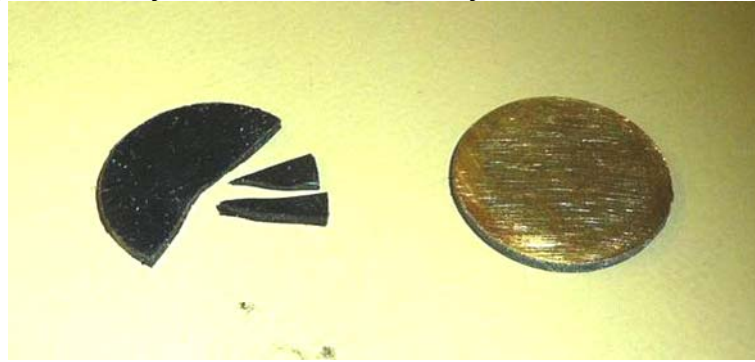


Fig. 8.

Disc-shaped samples of PNCC, 18 mm in diameter, 1 mm thick. On left – without electrodes, broken in liquid nitrogen, on right – with brass foil electrodes

Resulting dependence of electrical resistivity on time of vulcanization are shown in Figures 9 and 10.

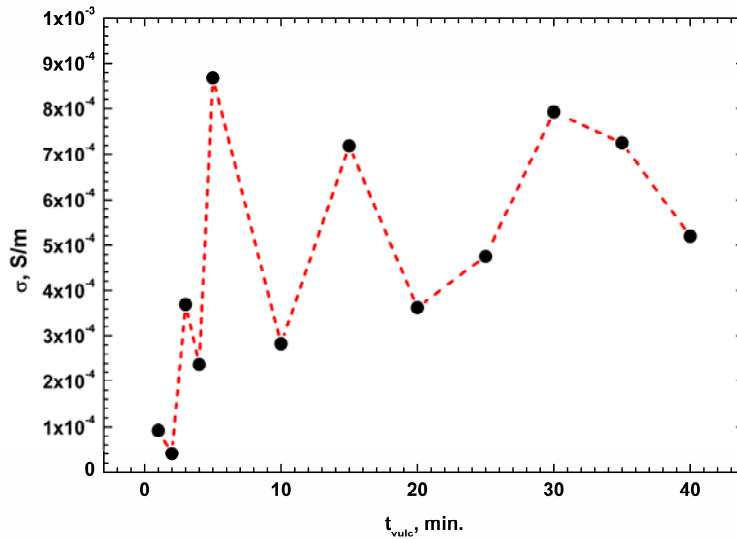


Fig. 9.

Initial conductance of PNCC with 9 p.h.r. of CB as a function of vulcanization time



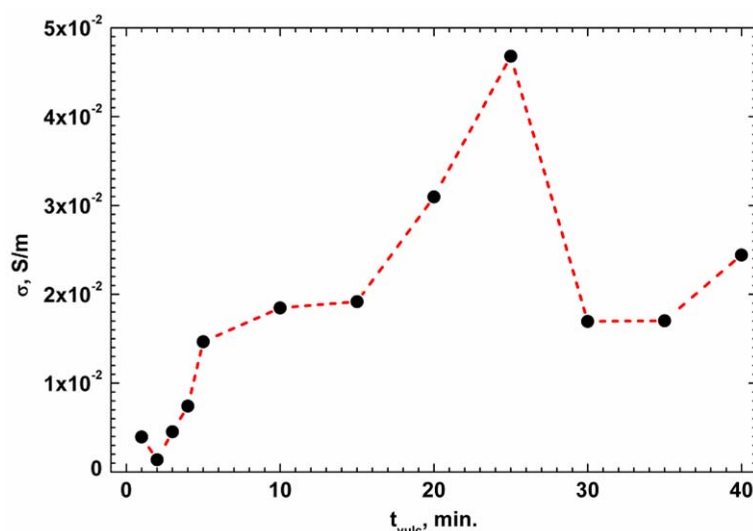


Fig. 10.

The initial conductance of PNCC with 10 p.h.r. of CB as a function of vulcanization time.

The obtained results show a small decrease of electrical conductivity of the PNCC in the first minutes of vulcanization, which is followed by fast increase. There is no obvious increase in conductivity after 10 minutes of vulcanization, and it can be assumed reaching relative saturation.

To visually evaluate the distribution of electro-conductive carbon in the PNCC matrix, the samples were broken in liquid nitrogen and evaluated using SEM. The most representative SEM pictures of PNCC samples with 10 p.h.r. of CB vulcanized for 3, 5, 10 and 15 minutes are shown in Figure 11. The dark background is the polyisoprene matrix, while the pale granular structure appearing on it is the electro-conductive carbon and aggregates of it.

The pictures clearly demonstrate that PNCC samples of small vulcanization times (3 minutes) have comparably good dispersion of carbon particles, the gradual aggregation being observed after increasing of the vulcanization time. (5, 10 and 15 minutes). No further aggregation is observed in samples vulcanized longer than 15 minutes.



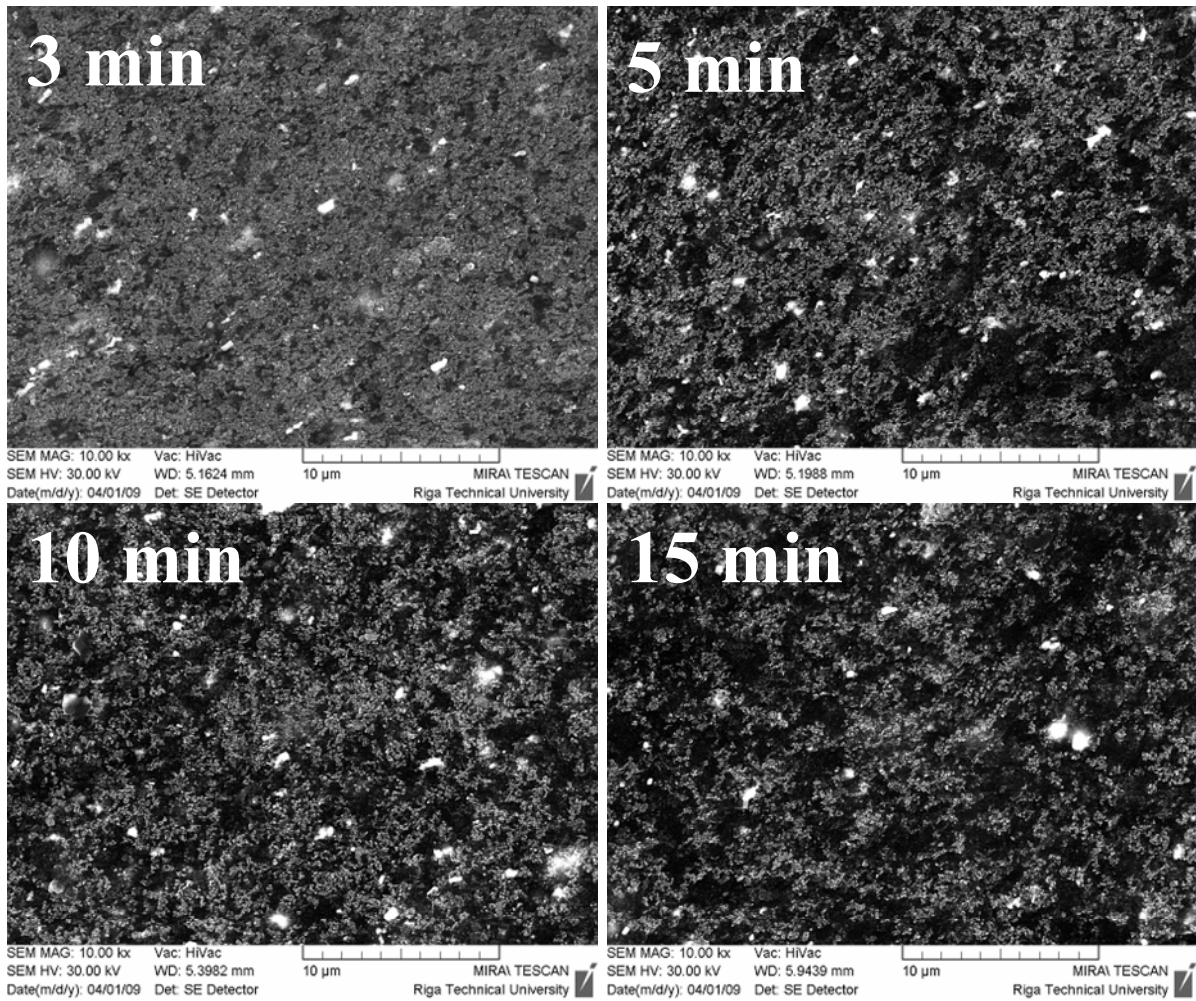


Fig. 11.

SEM images of brittle fracture surfaces of PNCCs samples after vulcanization of different duration indicated on images

The PR properties of the samples were evaluated afterwards (Figures 12 and 13). The major decrease of the PR sensitivity of the PNCC samples and reduction of hysteresis are seen during the first 4 minutes of vulcanization.

Two coexisting processes may be used to explain the observed features: 1) degree of dispersion of the conductive particles being reduced due to kinetic agglomeration and 2) the increase of cross-linking of the matrix during the vulcanization phase increasing the hyper-elastic component of the composite against the viscous-plastic properties.

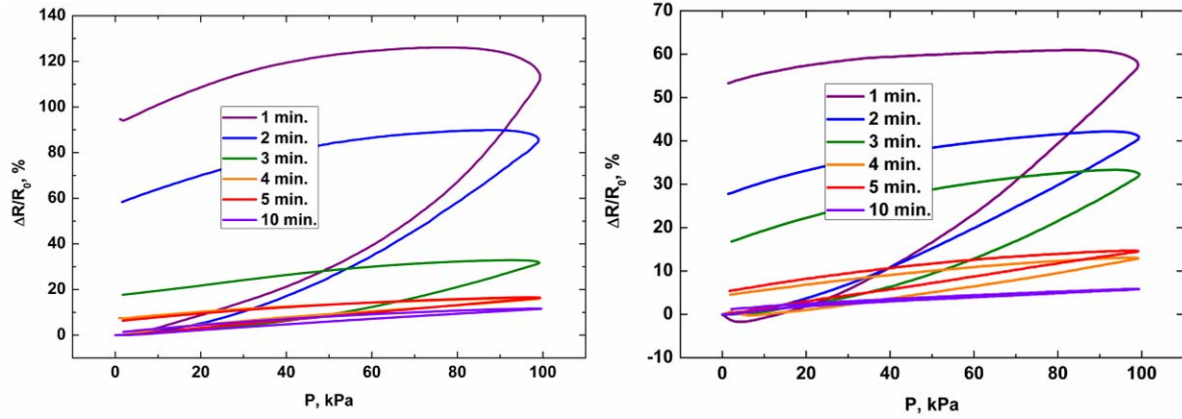


Fig. 12.

The relative change of electrical resistivity of PNCC depending on pressure and different vulcanization time (at 140 °C), indicated by corresponding colors.

Samples with 9 p.h.r. of CB (left) and of 10 p.h.r. of CB (right)

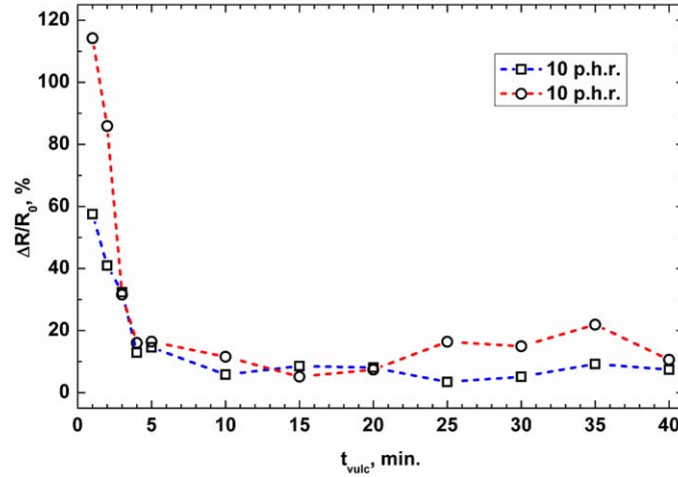


Fig. 13.

The maximum relative change of the electrical resistivity of PNCC under uni-axial pressure of 100 kPa in samples with 9 (red line) and 10 (blue line) p.h.r. of CB depending on vulcanization time. The vulcanization temperature – 140 °C

**The second chapter** is devoted to the study of percolation threshold of PNCC depending on the type and concentration of the conductive filler and techniques used to disperse it {R2, R3, R4}. PNCC samples, filled with high structure electro-conductive CB and MWCNT are compared. Available data on PNCC samples made earlier using Thick Pale Creppe caoutchouc were used as well fresh PNCC samples were elaborated using SWR-3L caoutchouc. Dependence of specific electrical conductivity on concentration of the electro-conductive filler for all samples is shown in Figure 14.

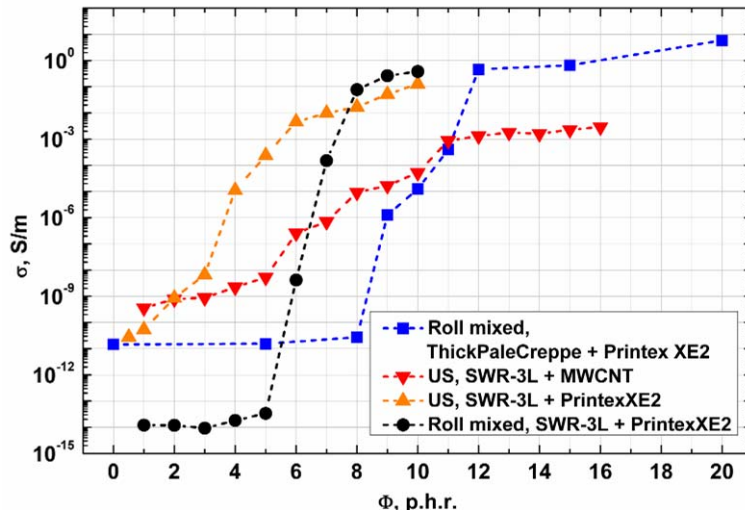


Fig 14.

Specific electric resistance of PNCC samples as function of concentration of the conductive filler

The critical concentrations and indexes of percolation and the relative intensities of tunneling currents determined by analysis of experimental data, in accordance to procedures described in literature [2] are shown in Table 2.

From the results is concluded that:

1) Both – the structure of the filler and the method of dispersing have a noticeable effect on electrical properties of the PNCC in the region of electrical percolation threshold;

2) A 40% decrease of the electrical percolation threshold, 54% decrease of critical electrical percolation index and 14% increase of relative intensity of tunneling currents is observed in PNCC the electro-conductive filler in which is dispersed by US in chloroform compared with PNCC made by cold rolling. The obtained difference proves the structure of filler being strongly reduced (as evidenced by the decrease of the critical index) by US dispersion of the filler distributing the nano-particles more evenly over the bulk of the PNCC (as evidenced by relative increase of the intensity of tunneling currents).

Table 2

Comparison of critical percolation parameters of different PNCCs

Filler used	Matrix	Dispersed by	$\Phi_c$ , p.h.r.	$\tau$	Relative intensity of tunneling currents
OK	Thick Pale Creppe	Rolls	8,1	6,6	0,81
OK	SVR-3L	Rolls	5,49	8,88	0,83
OK	SVR-3L	US	3,3	4,05	0,95
MWCNT	SVR-3L	US	4	5,7	0,97

**The third chapter** is devoted to the study of the PR effect in PNCC, filled with different electro-conductive fillers and prepared using different dispersion techniques {R2, R3, R4, R6, R7}. The PR effects of PNCC samples filled with US dispersed (Figures 15-16) and only roll-mixed CB (Figures 17-18) and US dispersed MWCNT (Figures 19-20) are compared side by side.

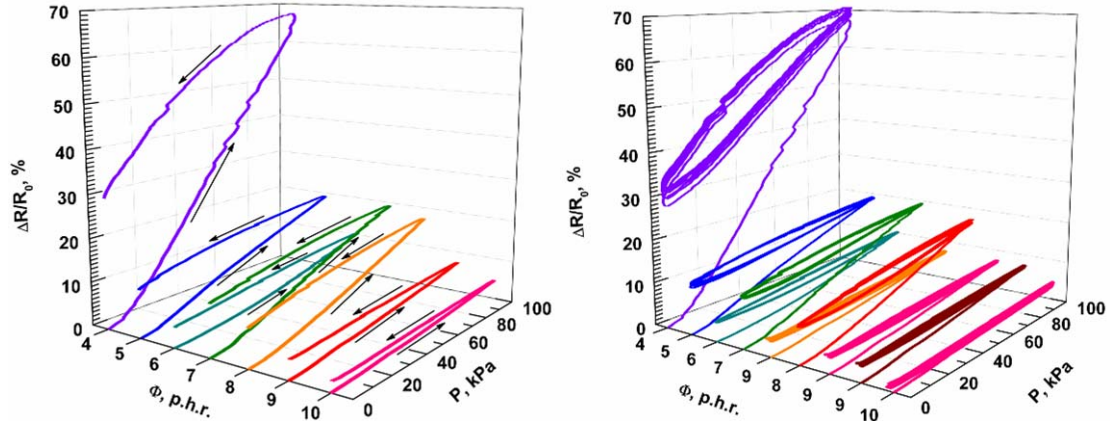


Fig. 15.

The relative change of electrical resistivity of PNCC samples with different concentrations of US dispersed CB in a single (left) and tenfold (right) cycle of pressure of up to 100 kPa

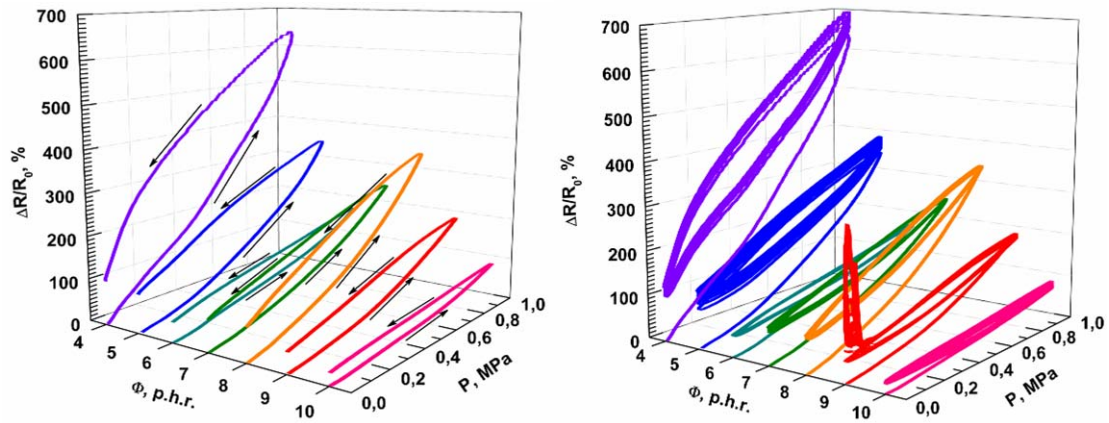


Fig. 16.

The relative change of electrical resistivity of PNCC samples with different concentrations of US dispersed CB in a single (left) and tenfold (right) cycle of pressure of up to 1 MPa

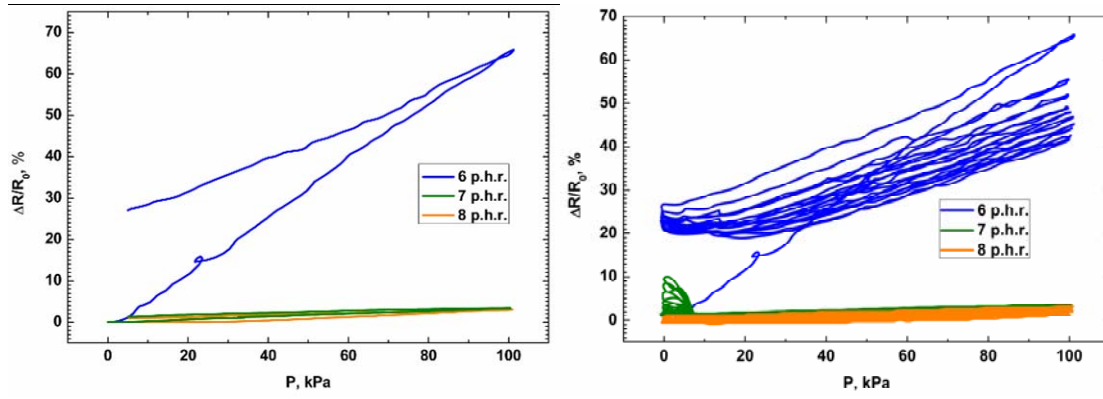


Fig. 17.

The relative change of electrical resistivity of PNCC samples with different concentrations of cold-rolled CB in a single (left) and tenfold (right) cycle of pressure of up to 100 kPa

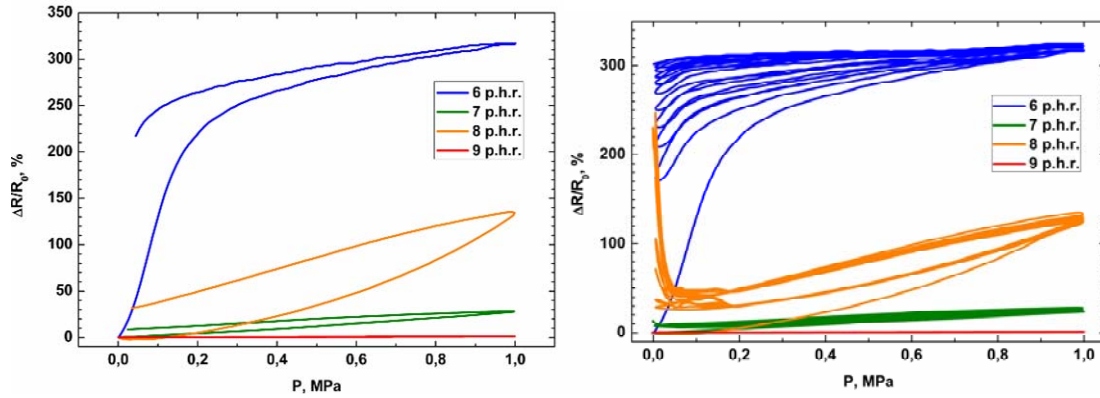


Fig. 18.

The relative change of electrical resistivity of PNCC samples with different concentrations of cold-rolled CB in a single (left) and tenfold (right) cycles of pressure of up to 1 MPa

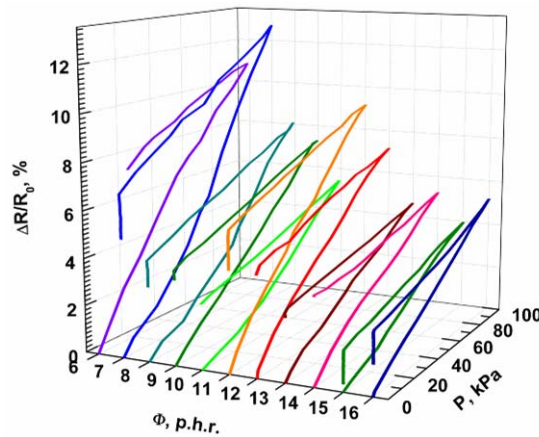


Fig. 19.

The relative change of electrical resistivity of PNCC samples with different concentrations of US dispersed MWCNT in a single cycle of pressure of up to 100 kPa



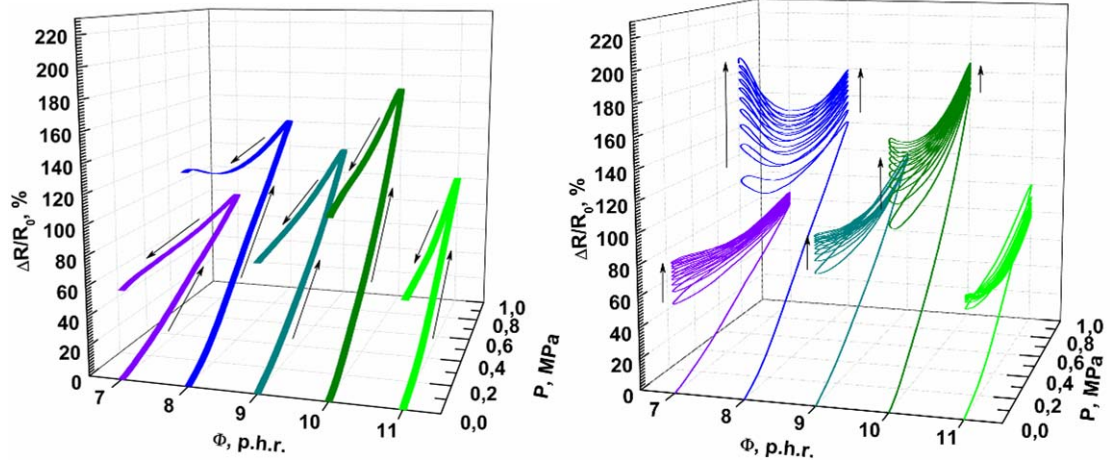


Fig. 20.

The relative change of electrical resistivity of PNCC samples with different concentrations of US dispersed MWCNT in on single (left) and tenfold (right) cycles of pressure of up to 1 MPa

At the end of the third chapter a theoretical model, based on literature and explaining the positive PR effect by positive elongation of PNCC in the direction transversal to the applied force is derived. Zhang et al. [6] have proved that electrical resistivity of similar composites can be expressed by:

$$R = \left( \frac{n}{N} \right) \left( \frac{8\pi h s}{3a^2 \gamma e^2} \right) \exp(\gamma s), \quad (2)$$

where  $n$  – number of particles forming the electro-conductive channel,  $N$  – number of electro-conductive channels,  $h$  – Plank's constant,  $s$  – average distance between two electro-conductive particles,  $a^2$  – effective cross section of the tunneling junction,  $e$  – elementary charge, and  $\gamma$  can be expressed as follows:

$$\gamma = \frac{4\pi(2m_e\phi)^{0.5}}{h}, \quad (3)$$

where  $m_e$  – electron mass, and  $\phi$  is the height of the potential barrier between neighboring particles.

When composite is stretched, the change of the electrical resistivity can be expressed as

$$\frac{R}{R_0} = \left( \frac{s}{s_0} \right) \exp[\gamma(s - s_0)], \quad (4)$$

where  $s_0$  – the primary distance between electro-conductive particles.

Since the matrix of the composite is an elastomer a small deformation of which is generally characterized by Puisseon ratio of 0.5, the distance between electro-conductive particles is equal to:

$$s = s_0(1 + \varepsilon) = s_0 \left[ 1 + \left( \frac{\Delta L'}{L'_0} \right) \right], \quad (5)$$

where  $\varepsilon$  – relative elongation,  $\Delta L'$  – deformation of the sample and  $L'_0$  – length of the sample – all parameters given in the direction transversal to the applied force.

According to this, the change of the electrical resistivity of the composite under small deformation can be expressed as

$$\ln R = \ln R_0 + \ln \left[ 1 + \left( \frac{\Delta L'}{L'_0} \right) \right] + A_0 \left( \frac{\Delta L'}{L'_0} \right), \quad (6)$$

where  $R_0$  – the initial electrical resistivity of the sample in relaxed state and  $A_0 = \gamma s_0$ .

According to Knite et al. [15], the rupture and following decrease of the number of conductive channels start to dominate at increasing the deformation ratio of PNCC. The number of conductive channels  $N$  can be expressed as:

$$N = \frac{N_0}{\exp \left[ A_1 \left( \frac{\Delta L'}{L'_0} \right) + B \left( \frac{\Delta L'}{L'_0} \right)^2 + C \left( \frac{\Delta L'}{L'_0} \right)^3 + D \left( \frac{\Delta L'}{L'_0} \right)^4 \right]}, \quad (7)$$

where  $A_1, B, C$  and  $D$  are constants and  $N_0$  is the initial number of conductive channels.

Combining of the equations provides:

$$\ln \left( \frac{R}{R_0} \right) = \ln \left[ 1 + \left( \frac{\Delta L'}{L'_0} \right) \right] + A \left( \frac{\Delta L'}{L'_0} \right) + B \left( \frac{\Delta L'}{L'_0} \right)^2 + C \left( \frac{\Delta L'}{L'_0} \right)^3 + D \left( \frac{\Delta L'}{L'_0} \right)^4. \quad (8)$$

This expression includes both mechanisms – the change of the thickness of the tunneling junctions and the change of the number, caused by rupture. By taking into account the elastic properties of the rubber under small relative deformations (usually less than 10%), the relative elongation of PNCC, transversal to applied force can be expressed as:

$$\frac{\Delta L'}{L'_0} = - \left( -\nu \frac{\Delta L}{L_0} \right) = \nu \frac{P}{\lambda}, \quad (9)$$

where  $\nu$  - Poisson's ratio,  $\lambda$  – elastic modulus of the matrix,  $P$  – pressure on the sample, and  $-\Delta L/L_0$  is the negative elongation (shortening) in the direction parallel to the applied force.

By joining obtained expressions we acquire that under a small deformation

$$\ln R = \ln R_0 + A'_0 P \quad (10)$$

and

for a larger deformation

$$\ln R = \ln R_0 + A' P + B' P^2 + C' P^3 + D' P^4, \quad (11)$$

where  $A'_0 = A_0 \frac{\nu}{\lambda}$ ,  $A' = A \frac{\nu}{\lambda}$ ,  $B' = B \left( \frac{\nu}{\lambda} \right)^2$ ,  $C' = C \left( \frac{\nu}{\lambda} \right)^3$  un  $D' = D \left( \frac{\nu}{\lambda} \right)^4$ .

The proposed model includes 3 different cases, depending on the magnitude of pressure force applied to the sample:

1) Linear at very small pressures, when the relative elongation of the sample is close to zero and, according to (4), the change of the electrical resistivity is proportional to the applied pressure (Fig. 21. A);

2) Exponential at relatively small and average pressures when, according to (4), the electrical resistivity of the sample mainly depends on the thickness of tunneling junctions and is proportional to the exponent of the pressure applied (Fig. 21. B);

3) Hyper-exponential when the rupture of the electro-conductive channels occurring at relatively higher pressures and larger deformations reduces their number and enhances the change of the electrical resistivity of PNCC (Fig. 21. C).

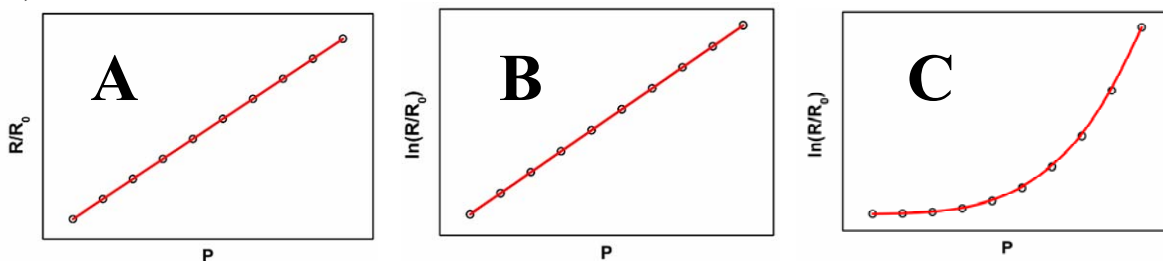


Fig. 21.

Simulated change of electrical resistance of PNCC at very small operational pressures (A), small and average operational pressures (B), and large operational pressures (C)

To verify applicability of the proposed theoretical model to PNCC, it was compared with the experimental data of PR measurements at pressures up to 400 kPa, where linear relationship is found between linear deformation of PNCC and uni-axial operational pressure.

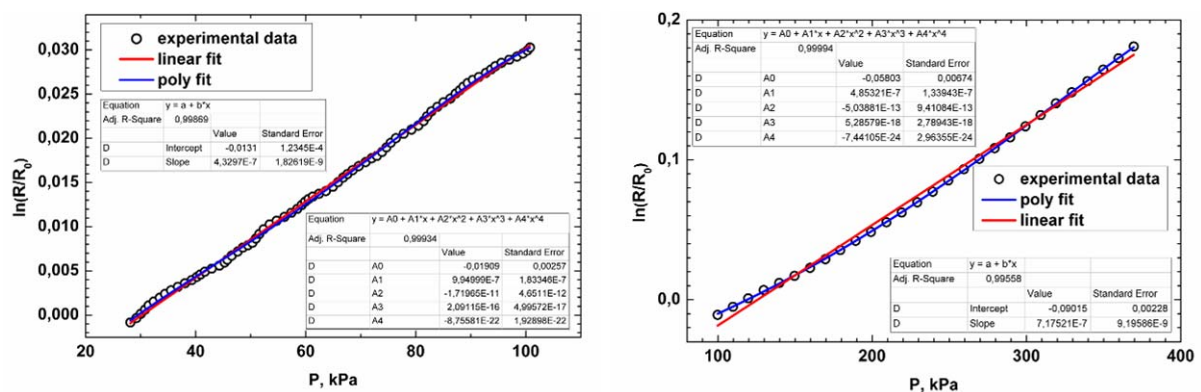


Fig. 22.

The linear (red line) and 4-th order polynomial (blue line) fits of the experimental values of PR effect of a PNCC sample of 8 p.h.r. of CB, dispersed by rolling. Operational pressures – 30-100 kPa (left) and 100-400 kPa (right)



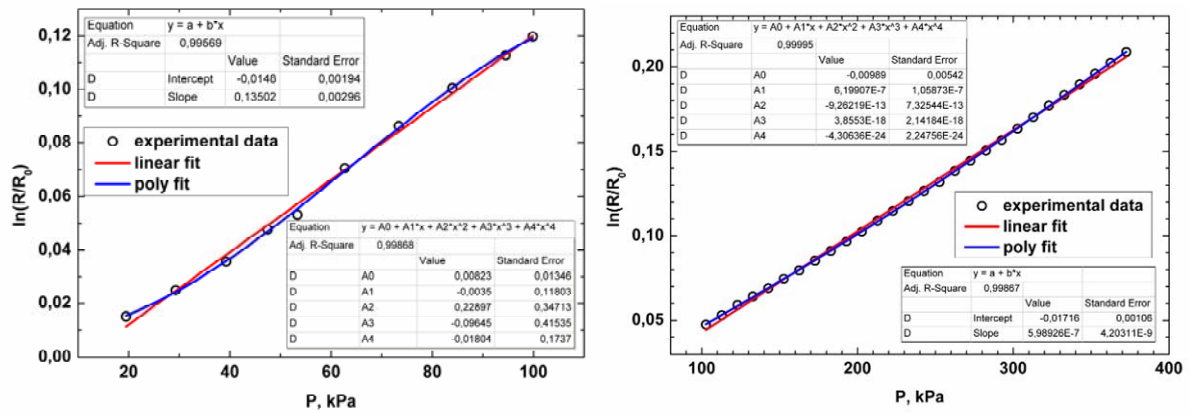


Fig. 23.

The linear (red line) and 4-th order polynomial (blue line) fits of the experimental values of PR effect of a PNCC sample of 7 p.h.r. of MWCNT dispersed by US . Operational pressures – 20-100 kPa (left) and 100-400 kPa (right)

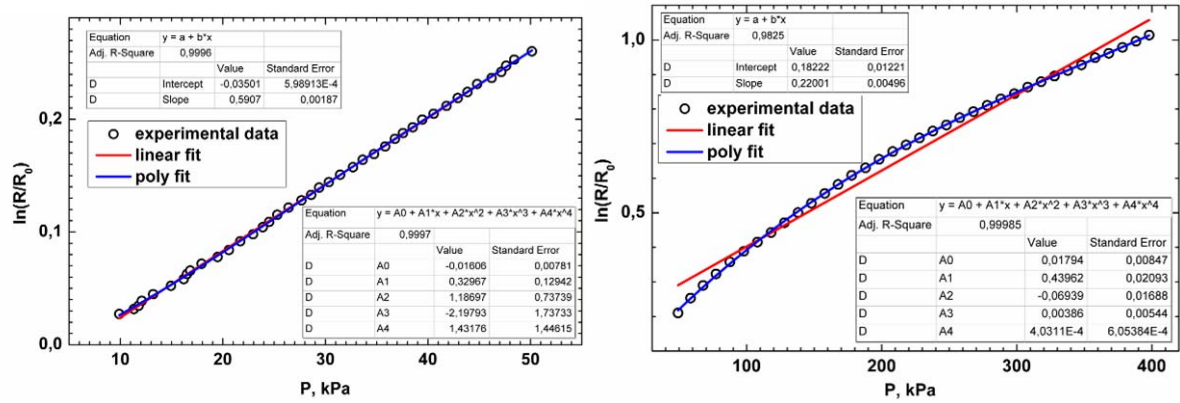


Fig. 24.

The linear (red line) and 4-th order polynomial (blue line) fits of the experimental values of PR effect of the PNCC sample of 4 p.h.r. of CB, dispersed by US . Operational pressures – 10-50 kPa (left) and 50-400 kPa (right)

It was concluded that resolution of the experimental method does not allow testing the case of extremely small deformations. Accordingly the fits are made in the two other cases.

The proposed model perfectly fits only the roll-mixed PNCC, because both – the exponential and the hyper-exponential dependences are observed to comply with the change of electrical resistivity with the uni-axial operational pressure (Figure 22).

An exponential dependence over the whole region of operational pressure is observed in case of PNCC with US dispersed MWCNT filler (Figure 23) giving an evidence of a significant effect of the changing tunneling currents on the resulting piezo-resistivity of the composite. This can be explained by the entangled structure and comparably low mobility of MWCNT limiting the spatial restructuring of electro-conductive formations and subsequent change of the number of electro-conductive channels. At the same time there are tunneling

junctions between separate nanotubes and their bundles in general being responsible for the features of piezoresistivity.

In PNCC with US-dispersed CB the exponential dependence of the electrical resistivity on operational pressure is observed at small pressures. An increase of the operational pressure causes weakening of the PR effect (Figure 24). This is explained with possible restructuring of the filler and appearance of new electro-conductive chains in the direction parallel to the applied force, reducing the overall PR effect.

By summarizing results of the 3-rd chapter, it is concluded that:

1) The character of all PR effects observed in the study depends on the type of electro-conductive filler and techniques it is dispersed with.

2) Almost all CB filled PNCC samples possess reversible PR effect, while in case of the MWCNT filler a significant hysteresis is observed. This can be explained by the high structure and small dimensions of CB particles and aggregates allowing for restructuring and regaining the previous spatial arrangement under de-stress. In its turn, the entangled structure of MWCNT dwarfs restructuring of electro-conductive formations after removal of the load.

3) The largest reversible relative PR effect of 70 % at operational pressure of 100 kPa is observed in both CB filled PNCC. The largest PR effect at operational pressure of 1 MPa is 130 % for roll-mixed PNCC and 700 % for US mixed PNCC.

4) At operational pressures of up to 100 kPa the largest PR effect is been observed in PNCC samples at concentrations of the conductive filler closer to the concentration of the critical percolation. In such a case the electro-conductive network in the composite is unsaturated and no new electrical channels develop in the direction parallel to the applied force to reduce the PR effect.

5) The proposed mathematical model explains the increase of the PNCCs resistivity in the direction parallel to the applied force with elongation and rupture of the structure of electro-conductive filler in the transversal direction. It although distinguishes two mechanisms of PR effect – the change of the thickness of tunneling junctions and following exponential dependence of resistivity on small operational pressures, as well as the change of the number of electro-conductive channels under higher pressure and deformation. The proposed theoretical model is used to describe the experimentally acquired relationships of the PR effect and to explain the type of the filler and the way of dispersing affecting PR properties of PNCC.

**The fourth chapter** is related to design, construction, and possible application of a completely hyper-elastic pressure sensing element {R5, M1, P1}. The most popular conventional widely used pressure sensing elements and the physical principles of their operation are reviewed and the advantages and drawbacks are being analyzed.

Original concept of the hyper-elastic pressure sensing element proposes manufacturing of all the necessary parts (the sensitive element, “electrodes” and an insulating outer shell) exclusively out of PNCC the concentration of CB for each part being different. The parts are partly vulcanized separately, then assembled into the required configuration and the assembly vulcanized to obtain a monolithic structure. For the sensitive layer the concentration of CB of the PNCC is chosen just in the middle of the electrical percolation threshold while the PNCC of electrode layers contains higher concentration of CB. Such an approach allows making sensors consisting of many specific rubber parts joined together in the most reliable way – by vulcanization. The element can be made of rubber only, without any metallic parts, thus it is strongly monolithic and mechanically consistent.

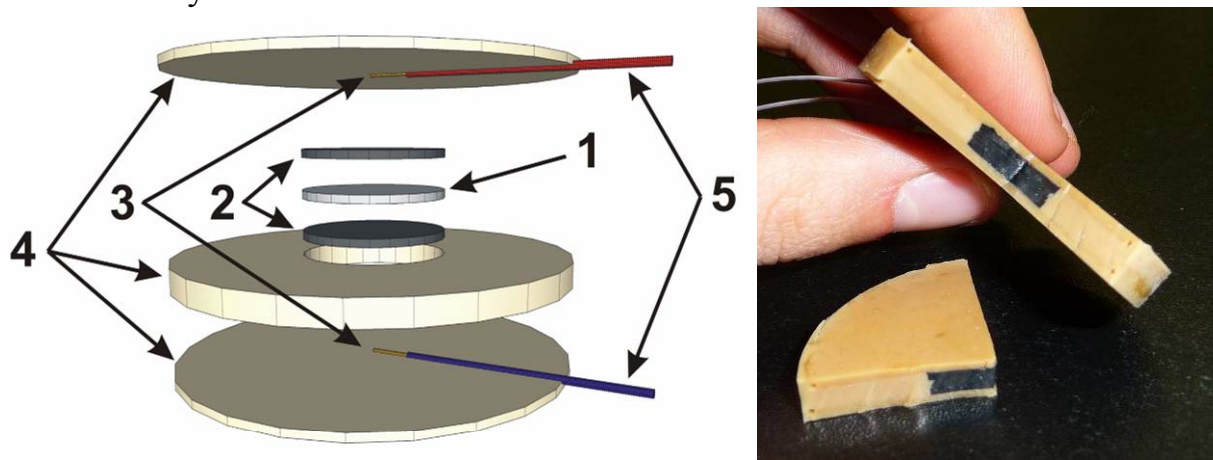


Fig. 25.

Illustration of structural parts of the completely hyper-elastic pressure sensing element (to the left) and its picture with radial cross cut (to the right). The numbers refer to: 1- sensitive element, 2 – electro-conductive elements, 3 – brass wire extensions, 4 – insulating layers, 5 – flexible wires

The sequence of construction of such prototype is described and results of preliminary tests demonstrated in the chapter. Technology of production of the completely hyper-elastic pressure sensing element is outlined, schematic structure and a real functional prototype are shown in Figure 25. The PR sensitivity of the element studied under cyclic loading (Figure 26) and the high-speed measuring capability of it are experimentally evaluated (Figure 27). The results show the sensor reasonably detecting repeated pressure pulses up to 1 MPa resolving separate 10 ms pulses.

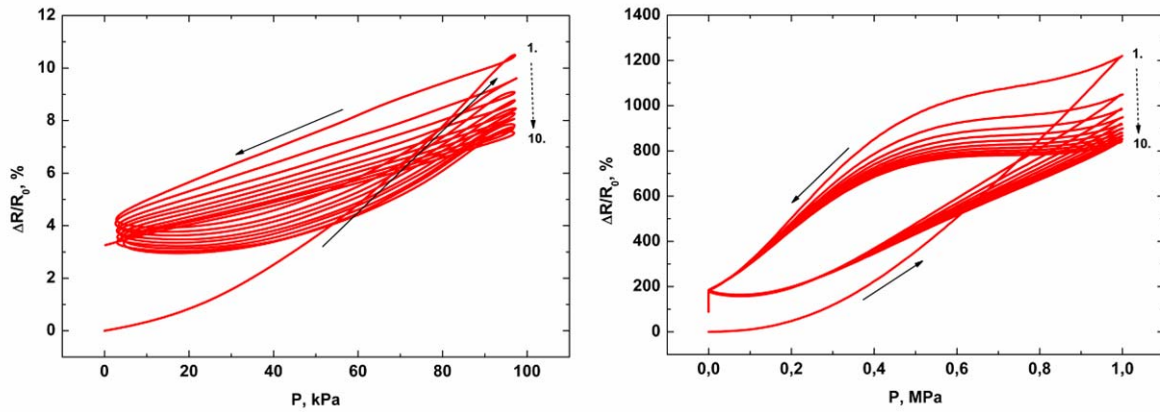


Fig. 26.

Relative change of the electrical resistivity of completely hyper-elastic pressure sensing element prototype (Fig. 25) at cyclic operational pressure of up to 100 kPa (left) and up to 1 MPa (right)

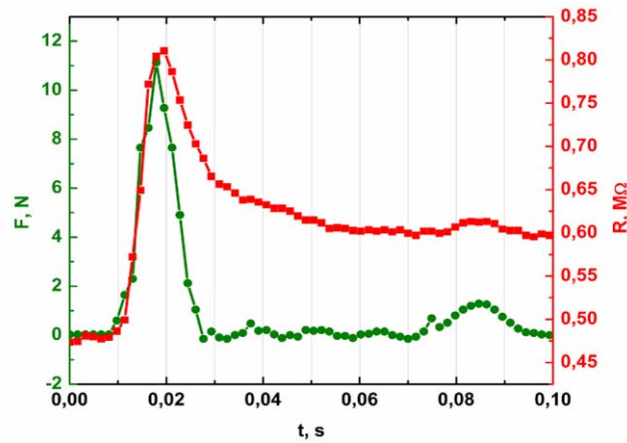


Fig. 27.

Electrical resistivity of completely hyper-elastic pressure sensing element (red curve) and operational pressure (green curve) as functions of time

An obvious hysteresis observed in the sensing element does not allow to use it for determining exact values of operational pressure. Similar sensing elements are suggested for technical application, where simple and cheap registration and, possibly, only rough estimates of the magnitude of pressure pulses is required. Such applications could include:

- security systems, detection of pressure or impact;
- industrial robotics, as tactile sensors for manipulators;
- industrial machinery, as deformation and vibration sensors, incorporated into anti-vibration damping and cushions;
- car industry, as sensing mouldings (“smart bumpers”);
- in systems performing statistical monitoring of pedestrians and traffic on roads.

## Overall conclusions

1. Innovative method using special electro-insulating Teflon mould and polyimide films to measure electrical resistivity of PNCC *in-situ* during vulcanization is proposed and tested. It has allowed measuring the change of the electrical resistivity of PNCC *in-situ* during vulcanization. The electrical conductivity of PNCC is found to increase dramatically just at the beginning of the vulcanization phase corresponding to minimum viscosity of raw rubber.
2. PNCC samples with different durations of vulcanization have been made in work and broken in liquid nitrogen, after what their microstructure was studied using SEM. Images revealed that CB is evenly dispersed and distributed in samples of short durations of vulcanization. The agglomeration of CB and development of a spatially branched percolative electro-conductive structure is observed upon increasing duration of vulcanization and proves kinetic electric percolation occurring in PNCC during vulcanization when dynamic agglomeration of nanoparticles takes place at thermal motion in viscous media. Electrical conductivity of the composite increases not because of the increase of filler fraction, but because of the development of complicated electro conductive structure.
3. Significant hysteresis of the PR effect revealed by the study of PNCC PR properties at incomplete vulcanization is likely due to poor cross-linking of the matrix. Such samples do not retain the initial state after removal of load, or do it very slowly. A smaller PR effect and smaller hysteresis are observed in completely vulcanized PNCC, which can be attributed to stronger cross-linking and better elasticity.
4. The studied dependence of the critical parameters of electrical percolation in PNCC on the method of dispersing CB reveals a remarkable decrease of the electrical percolation threshold and the critical percolation index and slightly increased relative intensity of tunneling currents at US dispersing of CB and mixing it in chloroform solution instead of dispersing by roll-mixing. The decrease of the critical index and increase of the intensity of tunneling currents confirm a decrease of the size of CB formations and a more uniform distribution of the particles over the bulk.
5. The effect of the type, concentration and the method of dispersion of the electro-conductive filler on the PR effect of PNCC have been studied. Results shows a comparatively higher PR sensitivity and better reversibility in CB filled PNCCs compared with MWCNT filled PNCCs what is explained by the entangled structure of MWCNTs used in the study, dramatically decreasing mobility of separate MWCNTs within the matrix.
6. The proposed theoretical model of positive PR effect explains the increase of the electrical resistivity in direction parallel to applied pressure force by elongation of the matrix in the transversal direction increasing the thickness

of tunneling junctions followed by decrease of the tunneling current at small pressures and destruction and decrease of the number of electro-conductive channels at higher pressures.

7. It has been proven that both, the type of the electro-conductive filler and the method of dispersing have a significant effect on the electrical percolation threshold and PR properties of the PNCC.
8. The prototype of completely hyper-elastic pressure sensing element has been elaborated and possible engineering applications have been proposed.

## STATEMENTS TO DEFEND

1. The proposed theoretical model of positive PR effect explains the increase of electrical resistivity of PNCCs in the direction parallel to the longitudinal axis of applied pressure by elongation of the matrix in transversal direction, increasing the thickness of tunneling junctions between the aggregates with a consequent decrease of tunneling currents under small pressures and destructing the electro-conductive channels with a consequent decrease of their number under higher pressures.
2. The so called kinetic agglomeration, or development, of the structure of the electro-conductive filler is proven to occur during vulcanization of PNCC and a percolative electro-conductive CB network being built. Kinetic agglomeration is stimulated by decreasing viscosity and mass transfer of raw rubber, induced by increasing temperature and pressure at the beginning of the vulcanization phase.
3. Electrical percolation of PNCC is proven to depend on the type and the method of dispersing the electro-conductive filler. The fits of experimental values of the electrical percolation thresholds with mathematical equations, confirm that US dispersing of CB in PNCC a) decreases the electrical percolation threshold; b) decreases the critical index of electrical percolation, and c) increases relative proportion of tunneling currents.
4. An original method is developed to detect the change of electrical properties of PNCC *in-situ* during vulcanization.
5. The model and a functional prototype of a completely hyper-elastic pressure sensing element suitable for detecting pressure pulses over a wide range of duration have been developed

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