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DEVELOPMENT OF PERCOLATIVE STRUCTURE IN PIEZORESISTIVE POLYISOPRENE-NANOSTRUCTURED CARBON COMPOSITE

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Certain attention has been converted to polyisoprene-nanostructured carbon composites (PNCC) as prospective piezoresistive materials for use in pressure sensing applications or as a tactile element in robotics [1]. Recent research approved that vulcanization process has an important role in process chain to obtain material with necessary mechano-electric properties [2].

In current article we present an original attempt to investigate the development of percolative electroconductive structure of PNCC during vulcanization. The "in situ" measurements of electric conductivity have been performed to evaluate the change of materials electric resistivity directly during the vulcanization process. Samples with different vulcanization times have been evaluated using high frequency AC measurements as well as SEM analysis on fractured surfaces. The dependence of conductance G and capacitance C_p on AC frequency for PNCC samples with different vulcanization times confirmed the development of conductive grid during vulcanization process. The results have been presented and evaluated to make certain conclusions.

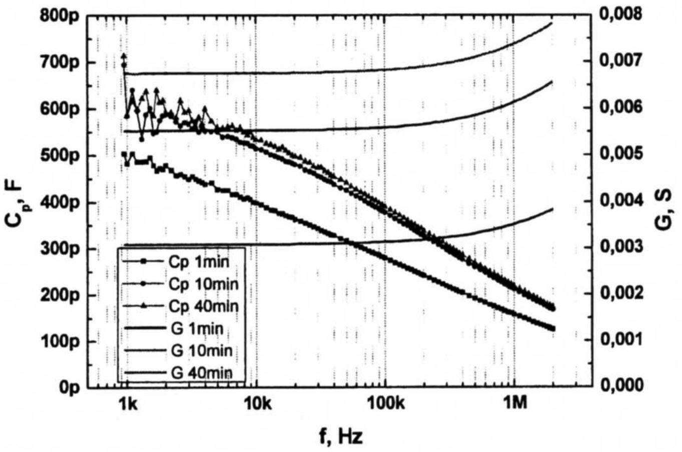

Fig.1 The dependence of conductance G and capacitance Cp on AC frequency for PNCC samples with different vulcanization times.

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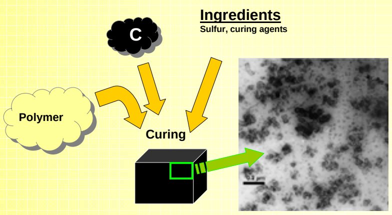

Fig.1 The illustrative schematics of the sample making of PNCBC.

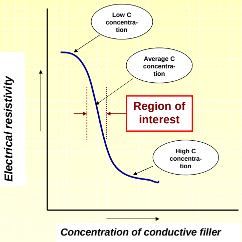

Fig.2 The illustration of the percolation treshold for PNCBC.

INTRODUCTON Broad use of compressive and strain sensors requires new materials to be designed for particular application. Usually pressure and strain sensor are rigid structures leading to difficulties to integrate the sensor into structure being monitored. Attempts were made to design a flexible pressure and strain sensors made of filled polymer or elastomer. But these structures exhibited the lack of reversibility and linearity. Recent research approved polyisoprene-nanostructured carbon black composite (PNCBC) to be a prospective material for current needs. At certain concentrations of conductive filler PNCBC shows remarkable reversible tenso and piezorezistive effect [1]. This is explained by sharp change of tunelling currents between filler particles, caused by mechanical deformation. In this work we present an original attempt to make an in-situ investigation of composites electrical properties during vulcanization. The dependence of composites DC and AC properties on the curing time are investigated. The SEM investigation of liquid nitrogen fractured surfaces is done as well. We believe that our research will lead to a new kind of functional sensor composite material, which could be used for intelligent sensing in robotics and other smart structures.

THE SAMPLES The piesoresistive polyisoprene – nanostructured carbon composite (PNCBC) is made from polyisoprene natural rubber, necessarry curing ingredients and high structure carbon black (HSCB) (Fig.1). All components are mixed into polyisoprene matrix using cold rolls. Research has approved, that the mixing method could be slightly different, like wet mixing into solution or mixing using closed type banbury mixer. According to concept of piesoresistivity, in the sharpest region of the percolation treshold the composite should be more sensitive to external mechanical action (Fig.2). The extremely high structure of the carbon black filler plays critical role in development of piesoresistive properties of PNCBC. Previous results approved, that composite with 10 mass parts of extra conductive Degussa Printex XE2 carbon appears to be in the middle of percolation treshold and shows remarkable reversible tenso and piesoresistive effect [1].

EXPERIMENTAL The original method was developed to investigate composites electrical properties during vulcanisation. The raw sample was placed into specially shaped isolative mould consisting of teflon and polyimide films (Fig.3) to avoid electrical short cirquit. The brass foil extended electrodes were put on both sides of the sample to make electrical connection. The resulting "sandwich" was put into hot press for 30 minutes to vulcanise. The electrical resistivity of the sample during vulcanisation was logged using Agilent A34970A digital multimeter/multiplexer.

For AC and DC measurements disk shaped samples were made, using different discrete vulcanisation times 1, 2, 3, 4, 5, 10, 15 and 20 minutes. The resulting samples was tested for piesoresistivity using ZwickRoell Z2.5 universal material testing machine, coupled with Agilent A34970 digital multimeter/multiplexer.

To investigate the development of the percolative structure in PNCBC, the DC electrical resistivity of samples with different vulcanisation times were measured.

To investigate the percolative structure in PNCBC, samples with different vulcanisation times were put under AC test measurements using Agilent A4980 20Hz-2MHz precision LCR meter.

To investigate the percolative structure in PNCBC, samples with different vulcanisation times were broken in liquid nitrogen and investigated using SEM afterwards.

EVALUATION OF THE RESULTS The "in-situ" resistivity measurements (Fig.5) and comparison of piesoresistive properties (Fig.4) of PNCBC samples with different discrete vulcanisation times concluded, that the piesoresistive properties noticeably depends on the vulcanisation level of the composite. The experimental data of DC and AC conductivity measurements versus vulcanization time (Fig.6-7) could be explained in our opinion by two main processes that affect the formation of percolation structure of CB in PNCBC during vulcanization time: 1) the flow of raw composite mass produced by molding and 2) the crosslink formation by arousing of number of both S – S and C – C covalent bonds.

In the first moments of vulcanisation moulding flow damages the HSCB structure and results to increase the resistivity. This process is determinative approximately in the time interval (1<t<2 min) of vulcanization (Fig.6, 7) when the AC and DC conductance decrease.

The crosslinking promotes the development of three-dimensional percolation structure of CB due to agglomeration of carbon nanoparticle aggregates. This process predominates at curing times t>2min (Fig.5,6) when the resistivity (abruptly) drops.

So the crosslinking occurs all the vulcanization time. The flow dominates at time interval 1min<t<2min (Fig.7,8).

From our previous work [1] is known, that tunneling currents between carbon aggregates is the main conductance mechanism in PNCBC (10 phr CB). That means there are insulating polymer matrix nanoscale interfaces between carbon aggregates in case of percolation. So, the enhancement of conductivity in time interval t > 2 min we explain due to exponential rise of tunneling current I_{tun} versus reciprocal distance *s* between adjacent carbon nanoparticle aggregates [1]:

$$I_{tun} \sim exp[-\gamma s]. \qquad (1)$$

Constant γ is calculated as:

$$\gamma = 4\pi(2m\phi)^{0.5}/h, \qquad (2)$$

where *m* is the electron mass, *h* - Plank's constant and ϕ - the height of potential barrier between adjacent particles. Obviously, the distance *s* between adjacent carbon aggregates diminishes at vulcanization time 2<t<5 min because of agglomeration of HSCB aggregates (SEM pictures in Fig.11) and as result the DC as well as AC conductivity rise (Fig.5, 6).

The experimental AC curves $\sigma(f)$ *(Fig.9)* and $C \sim (f)$ *(Fig.10)* can be described assuming a random distribution of conductor particles in the insulating matrix and modelling the composite as a network of randomly distributed capacitors and resistors. Wilkinson and al. [2] have obtained fundamental expressions for σ and ε as functions of AC frequency *f* in the vicinity of the percolation threshold:

$$\sigma \sim f^x \qquad (3)$$

$$C \sim f^{-y} \qquad (4)$$

Critical indices *x* and *y* are related by general scaling:

$$x + y = 1 \qquad (5)$$

Theoretical considerations suggest that relations (3) and (4) are determined by one of two independent effects:

1) polarisation of the matrix between conductor clusters (*the model of intercluster polarisation*) [2] and 2) anomalous diffusion of charge carriers within clusters (*the model of anomalous diffusion*) [3]. In case of a three-dimensional ($d = 3$) matrix the first effect provides critical indices $x = 0.72$ and $y = 0.28$, the latter – $x = 0.58$ and $y = 0.42$. So the experimental values of *x* and *y* provide information on the electrodynamic processes near the percolation threshold.

(In case of polyisoprene composite with the HSCB concentration closest to the percolation threshold has been found (our previous work [4]) critical index x = 0.685 (linear correlation coefficient R = 0,9988) that is in good agreement with the model of inter-cluster polarisation that provides critical index x = 0.72 in relation $\sigma \sim f^x$.

In general, the frequency dependence of conductivity may be presented as:

$$\sigma(\omega) = \sigma(0) + A\omega^x,$$

where $\sigma(0)$ is the specific DC-conductivity, A – a constant.

The critical index y = 0.292 (R = 0.997) calculated for the same 10 mass parts HSCB composite [4] is also in good agreement with the model of inter-cluster polarisation providing critical index $y = 0.28$ for relation $\varepsilon \sim f^{-y}$.

Thus, in the case of polyisoprene- HSCB composite, the general scaling relation ($x + y = 1$) of the percolation theory is consistent with the experimentally obtained values (0,685 + 0.292 = 0.977).)

The rise of capacity C with vulcanisation time can be explained due to agglomeration of HSCB because of decreasing of distance *s* between adjacent carbon aggregates:

$$C \sim 1/s$$

Additionally to that an asymmetric and branching shapes of particle aggregates cause strong local electric fields in the matrix between clusters providing additional contribution to the dielectric permittivity.

AKNOWLEGMENTS
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Fig.3 The picture of specially moulded PNCBC sample for "in-situ" resistivity measurements during vulcanisation.

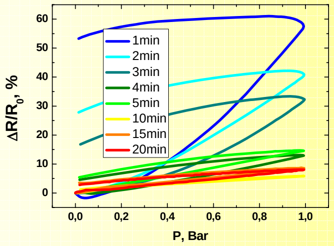

Fig.4 The piezoresistive effect comparison for PNCBC samples with different vulcanisation times.

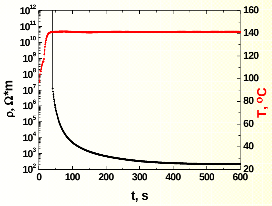

Fig.5 The DC resistivity of PNCBC sample (black line) as a function of vulcanisation time. The red line represents the actual temperature of the mould.

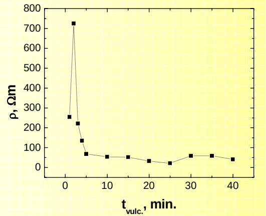

Fig.6 The DC resistivity as a function of vulcanisation time for PNCBC with 10 mass parts of HSCB filler.

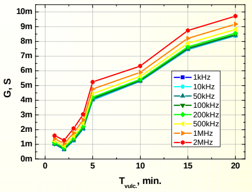

Fig.7 The AC conductance as a function of vulcanisation time for PNCBC with 10 mass parts of HSCB filler.

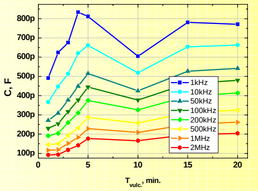

Fig.8 The AC capacitance as a function of vulcanisation time for PNCBC with 10 mass parts of HSCB filler.

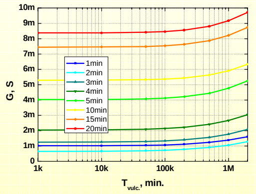

Fig.9 The conductance as a function of AC frequency for PNCBC with 10 mass parts of HSCB filler and different $t_{vulc.}$.

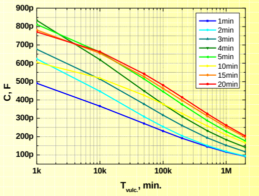

Fig.10 The capacitance as a function of AC frequency for PNCBC with 10 mass parts of HSCB filler and different $t_{vulc.}$.

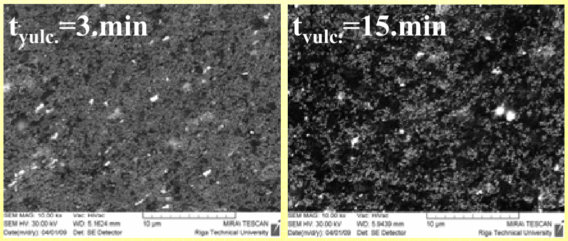

Fig.11 The SEM pictures of a liquid nitrogen broken PNCBC samples. The white indexes represents vulcanisation time of each current sample.