Mold Pressure and Filler Concentration Effect on Both - the Percolation Threshold and the Piezo-Resistive Effect of the Polyisoprene-Nanostructured Carbon Black Composites

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Industry demands on cheap, full scale tactile sensors, capable to be embedded into material or structure being monitored. Previous research reported polyisoprene-nanostructured carbon black composite (PNCBC) as a promising material for this use. PNCBC is made when certain concentration of high-structure nano-size extra conductive carbon, close to that of a percolation threshold, is well dispersed into a rubber matrix before vulcanizing. In such case reversible tenso-resistance effect as well as piezo-resistance effect with up to 4 orders of magnitude is observed. During previous research, it was concluded that technological parameters like mold pressure, vulcanizing time and filler distribution have a critical effect on final properties of PNCBC. In this work we have ascertained, how the mold pressure during vulcanizing have an effect on electric properties of PNCBC. Extra conductive carbon black was mixed into polyisoprene matrix by means of cold rolls for 20 minutes at room temperature. Afterwards the raw material was vulcanized using different mold pressures. Specific electric resistance and piezo-resistance effect were determined depending on filler concentration and mold pressure. By evaluating results, conclusions were made, that not always the best conductivity and piezo-resistance effect of PNCBC are gained using typical mold pressures, used in classic rubber industry. The mechanism of the effect of mold pressure on the final sensor properties and the percolative behavior of PNCBC is discussed.

MOLD PRESSURE AND FILLER CONCENTRATION EFFECT ON BOTH - THE PERCOLATION TRESHHOLD AND THE PIEZORESISTIVE EFFECT OF THE POLYISOPRENE-NANOSTRUCTURED CARBON BLACK COMPOSITES

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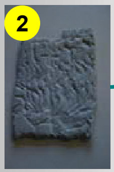

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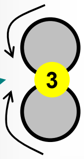

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Introduction. Nanocomposites have played a major role in material science over last decade. Industry demands on cheap, full scale tactile sensors, capable to be embedded into material or structure being monitored. Previous research reported polyisoprene-nanostructured carbon black composite (PNCBC) as a promising material for this need [1,2]. PNCBC is made when certain concentration, close to that of a percolation treshhold, of high-structure nano-sized particles of electro conductive carbon **(Fig.1,2)** are well dispersed into a rubber matrix and vulcanised afterwards. Stable, large and reversible tenso and piezo-resistant effects are observed in such conditions [3,4]. The change of resistance can be explained with destruction and recombination of conductive paths and the change of tunneling currents between closely separated filler particles at the same time [4]. The piezoresistive properties of PNCBN are linked with it's processing parameters, such as vulcanization pressure and mixing conditions [5].

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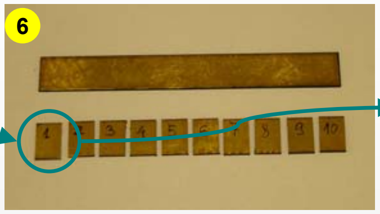

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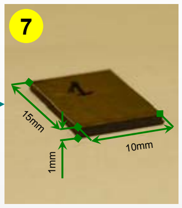

Making of samples. Image series above shows the making of a polymer – nanostructured carbon black composite (PNCBC) step by step . High structure extra conductive carbon black Degussa™ Printex™ EX-2 **(image 1)** was mixed into thick PaleCrepe natural rubber **(image 2)** using cold rolls **(image 3)**. Raw material **(image 4)** with 8, 9, 10 and 11 mass parts (m.p.) of conductive filler was cut into pieces and cured between two 50μm thick brass sheets in hot steel mold using Rondol termostated press **(image 5)**. Curing time used $\tau_{1,5}$ was determined by Monsanto™ Reometer100™. 10 sticks were made for each concentration using mold pressures from 10 to 100 kg/cm^2 by step of 10. Each stick **(image 6)** was cut into 10 to 11 similar slabs using diamond cutter to avoid squeezing sensitive core material. Afterwards the slabs **(image 7)** were cleaned with ethanol from rubber dust and numbered according to their origin in stick and used as a test samples.

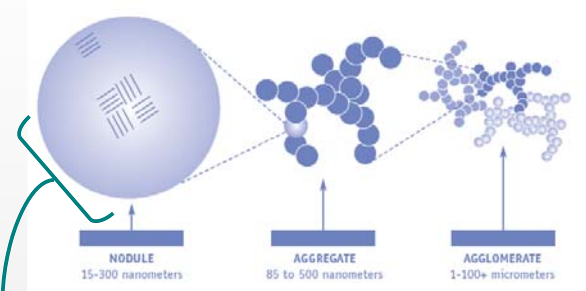

Fig.1 Shematic sequence of structure development of high structure carbon black.

Fig.2 Illustrative example of extremely high structure carbon black particle [W.Hofman, H.Gupta, Kautchuk technology, *Doktor Gupta Verlag*, 2001, p.16]

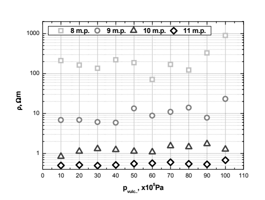

Fig.3 Average specific electrical resistance ($\rho_{average}$) as a function of mold pressure for PNCBC with 8 to 11 mass parts (m.p.) of carbon black.

Experimental. Initial electrical resistance of virgin samples were measured between custom made brass electrodes using Wavetek™ Meterman™ 27XT digital multimeter. Specific resistance has been calculated regarding to slab size. Error values were eliminated using statistics and crude error estimation criteria. The arithmetical averages were calculated from accepted values for each group of samples and were plotted into one graph **(Fig.3)** for comparision. Afterwards the dynamic determination of piezoreziastance was done with samples best matching the average initial resistance for each group. Measurements were made using modified Zwick/Roell Z2.5 universal material testing machine, HBM Spider8 universal data acquisition and visualization module and HQ stabilised power source. As can be seen for used operative pressures, the piezoresistive effect appears to be quasi linear - it can be described by formula: $\Delta\rho/\rho_0=\Pi\cdot p_{oper.}$ where: Π is effective coefficient of piezoresistance, $\Delta\rho/\rho_0$ is the relative change of resistivity and $p_{oper.}$ is the operational pressure applied.

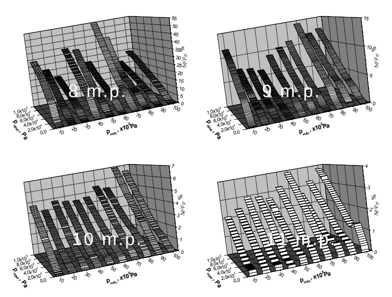

Fig.4-7 The piezoresistive behavior of PNCBC with 8, 9, 10 and 11 m.p. of carbon black (indicated with big white numbers on charts, respectively) depending on vulcanization pressure used.

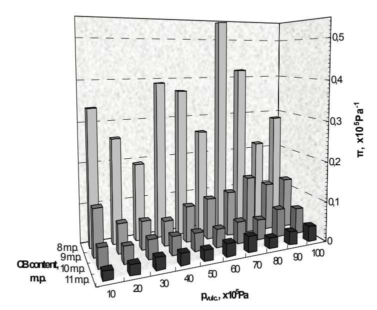

Fig.8 The comparison of effective piezoresistive coefficient Π for different samples of PNCBC, depending on filler content and vulcanization pressure.

Results and discussion. Reliable technology for making PNCBC cells has been developed. PNCBC samples with thickness from 1mm to 100μm has been made using this method. The problem with electrodes has been resolved using brass sheet mold bolsters. As can be seen, PNCBC has a tendency to rise its initial electrical resistivity with increase of mold pressure **(Fig.3)** and it's appears to be reverse we expected. In fact, that eliminates the argument that rise of curing pressure should approximate the filler particles, therefore allowing tunneling currents to flow more easily. Pressure has an inhabiting effect on the formation process of conductive network more likely. Mixing on cold rolls could be extended or replaced by different, more efficient method to gather better results. But too high homogeneity of mixture will result with rise of electrical resistivity of PNCBC and weakening of piezoresistive effect. The piezoresistive effect for current samples and operative pressures appears to be quasi linear (**Fig. 4-7)** and could be described by effective coefficient of piezoresistance - Π. The noticeable greater piezoresistive effect for samples with less filler concentration **(Fig. 8)** can be explained by means of lower density of percolative structure, which leads to more complete destruction of electroconductive channels, using similar mechanical interaction. The noticeable deviation of piezoresistive effect for samples with small filler concentration **(Fig.8)** more likely is caused by incomplete development of percolative structure.

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