



IEGULDĪJUMS TAVĀ NĀKOTNĒ!



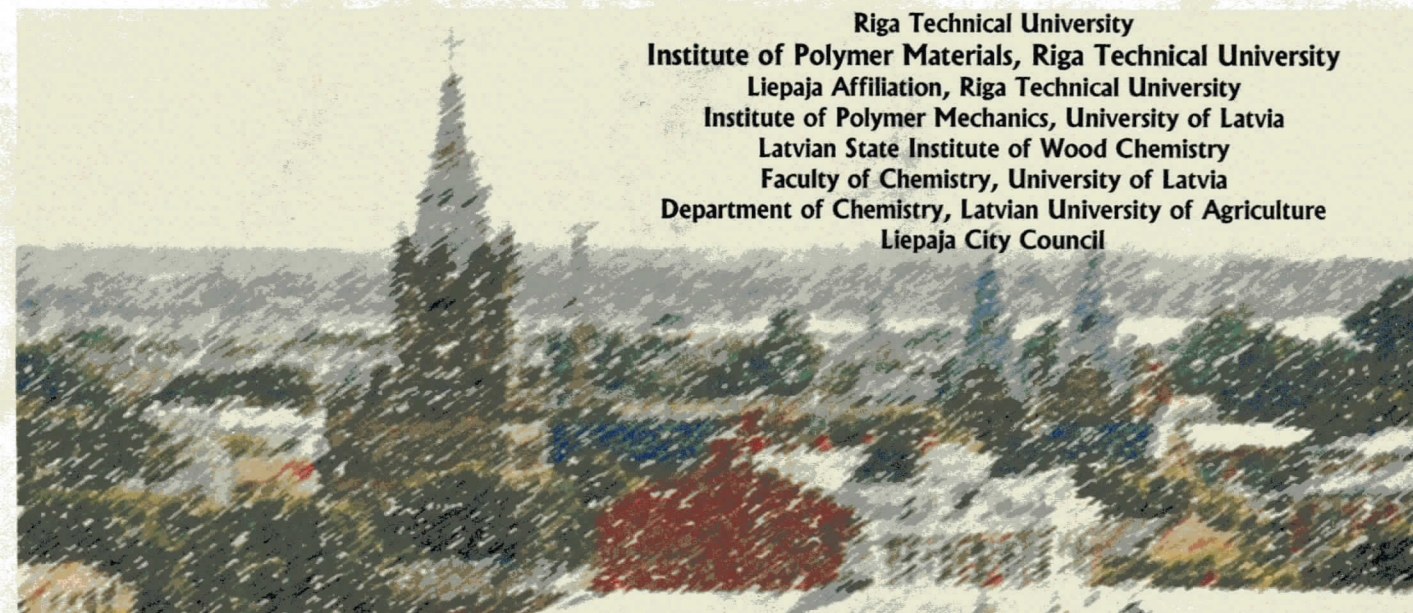
# BALTIC POLYMER SYMPOSIUM 2012

*Liepaja, Latvia*

*September 19-22*

## PROGRAMME AND PROCEEDINGS

Riga Technical University  
Institute of Polymer Materials, Riga Technical University  
Liepaja Affiliation, Riga Technical University  
Institute of Polymer Mechanics, University of Latvia  
Latvian State Institute of Wood Chemistry  
Faculty of Chemistry, University of Latvia  
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Liepaja City Council



## TIME DEPENDENCE OF PIEZOREZISTANCE ON RUBBER/NANOSTRUCTURED CARBON COMPOSITES

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Electro-conductive carbon black filled polyisoprene rubber shows large reflexive piezoresistive effect – electrical resistivity changes due to applied pressure. The reason for this holds three dimensional electro-conductive net, which restructures in time – inter-particle separation changes at low applied pressure and electro-conductive channels disrupt at higher pressures [1].

Reflexive abilities of piezoresistive effect mostly depend on mechanical properties of polyisoprene rubber matrix. When loading/unloading the composite, polyisoprene macromolecules change their conformation in space, promoting the motion of filler particles in rubber matrix, hence decreasing overall electric resistivity of composite. Rubber exhibits viscoelastic properties as creep, recovery and stress relaxation, so this implies time dependence of piezoresistance [2]. One of the main aspects is the recovery of electrical resistance after unloading, which we call the relaxation of piezoresistance. These relaxation processes can be described by following exponential equation:

$$R = R_{\infty} + R_1 e^{-\frac{t}{\tau_1}} + R_2 e^{-\frac{t}{\tau_2}} + R_3 e^{-\frac{t}{\tau_3}},$$

where  $R$  is electrical resistivity of rubber composite,  $t$  is time,  $R_{\infty}$  is electrical resistivity at time  $t_{\infty}$ ,  $R_1$ ,  $R_2$ ,  $R_3$  are constants and  $\tau_1$ ,  $\tau_2$ ,  $\tau_3$  are corresponding exponential decay constants, which represents three corresponding relaxation processes in rubber composites. The possible three piezoresistance relaxation mechanisms have been discussed in comparison with relaxation of mechanical deformation.

### References

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2. Wang L., Ding T. and Wang P.. Effect of instantaneous compression pressure on electrical resistance of carbon black filled silicone rubber composite during compressive strain relaxation// *Compos. Sci. Technol.*- 2008.- Vol. 68- P. 3448-3450.



# TIME DEPENDENCE OF PIEZOREZISTANCE ON RUBBER/NANOSTRUCTURED CARBON COMPOSITES



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## ABSTRACT

Electro-conductive carbon black filled polyisoprene rubber shows large reflexive piezoresistive effect – electrical resistivity changes due to applied pressure. The reason for this holds three dimensional electro-conductive net, which restructures in time – inter-particle separation changes at low applied pressure and electro-conductive channels disrupt at higher pressures. Reflexive abilities of piezoresistive effect mostly depend on mechanical properties of polyisoprene rubber matrix. When loading/unloading the composite, polyisoprene macromolecules change their conformation in space, promoting the motion of filler particles in rubber matrix, hence alters the overall electric resistivity of composite. Rubber exhibits viscoelastic properties as creep, recovery and stress relaxation, so this implies time dependence of piezoresistance. In this work primary goal was to investigate piezoresistive effect at creep-recovery tests, particularly scoping on recovery processes, which includes both: strain and resistivity relaxation [1-3].

## THEORY

As pressure sensing of our composite is based on piezoresistive effect, it is important to determine the behavior of resistivity at constant loadings (stress). It is established that resistivity at small stress changes in fashion:

$$\ln R = \ln R_0 + \ln(1 + \epsilon) + A_0 \epsilon$$

where,  $R_0$  is initial composite resistivity;  $\epsilon$  is engineering strain and  $A_0$  is proportional to potential barrier between two adjacent particles [1,2].

Above we introduced with rubber matrix viscoelastic properties, which implies nonlinear relationship between stress and strain and hysteresis phenomena. At constant stress, when rubber is loaded instantaneously, strain follows equation:

$$\epsilon = \frac{\sigma}{E_e} + \frac{\sigma}{E_{ve}} \left(1 + \exp\left[-\frac{t}{\tau}\right]\right)$$

where,  $\sigma$  is engineering stress,  $E_e$  is modulus of elastic region of deformation,  $E_{ve}$  is viscoelastic modulus,  $t$  is time and  $\tau$  corresponds to relaxation time of strain at viscoelastic region at macroscopic level and at microscopic level,  $\tau$  can be interpreted as  $\alpha$  – relaxation processes time in rubber matrix. Equally, at zero stress, when composite is unloaded instantaneously, expression above can be written as:

$$\epsilon = -\frac{\sigma}{E_e} + \frac{\sigma}{E_{ve}} \exp\left[-\frac{t}{\tau}\right]$$

It is obvious, that resistivity behavior can be predicted by these equations. Particularly at viscoelastic region of strain, at zero stress, resulting resistivity can be described as:

$$R = R_{\infty} + R_0 \exp\left(-\frac{t}{\tau}\right)$$

where,  $R_{\infty}$  is constant,  $R_0$  is resistivity at  $t=0$  and  $\tau$  is resistivity relaxation time [3, 4].

## EXPERIMENTAL

The composite is made from SWR-3L (Standart Vietnam Rubber) natural polyisoprene rubber. For nanofiller we chose high structure Printex XW2 carbon black. Components were mixed with cold roller. Curing agents were added, for further vulcanization. For our study we chose composite with 7 wt% filler concentration. Our choice was based on percolation curve of polyisoprene-carbon black composition. Most prominent piezoresistive effect is observed at percolation transition. 7 wt% of carbon black corresponds to percolation transition lower end with respect to conductivity.

Two kinds of geometrical form samples were made. Strip like samples (fig. 2.) with dimensions: 100mm – 20mm – 1mm, for tensile test and cylinder like samples with dimensions: 9 mm in radius and 1mm/4mm in height for compression test (fig. 1). Experiments were performed on universal material testing machine "Zwick/Roell" for tensile test and specially prepared testing device for manual instantaneous compression loadings. Brass electrodes were attached to samples for resistivity measurements. Resistivity was measured by "Agilent" data logger. Obtained data were processed with data analyzing program "Origin Pro". Great deal of work has been devoted to experimental data fitting to theoretical equations.

Compression tests were performed, using force acting upon a sample for a short period of time, measuring strain and resistivity response. Full creep-recovery test were performed only within tensile tests.



Fig.1. Two samples, for compression tests, with different heights

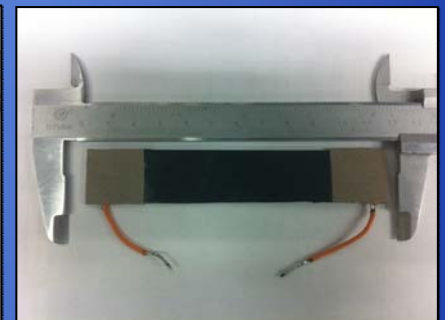


Fig.2. Sample for tensile tests

## RESULTS

As it was predicted, composite shows time dependent piezoresistive effect, when instantaneously loaded with a constant stress and when unloaded in the same fashion.

After sample has been loaded for a brief moment, strain and resistivity recovery follows, that is relaxation process (fig. 3.). It is important to note, that real polymer have relaxation time distribution. In this case both strain and resistivity relaxation curves were fitted with exponential equations, with three different relaxation constants [5]:

$$y = y_0 + A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp\left(-\frac{t}{\tau_3}\right)$$

Compression test revealed mean relaxation constants for strain:  $\tau_1 = 0,4$  s,  $\tau_2 = 3,5$  s,  $\tau_3 = 38$  s. And for resistivity:  $\tau_1 = 0,45$  s,  $\tau_2 = 355$  s,  $\tau_3 = 13500$  s. There is clearly mismatch between strain and resistivity relaxation, in way that strain is ahead of resistivity.

From tensile tests we obtained full creep-recovery graph (fig. 4.), data shows exactly the same mismatch between strain and resistivity at recovery part of test. Even more, creep of the polyisoprene matrix (strain gradually increases) cause, what seems to be exponential decrease of resistivity (fig. 5.).

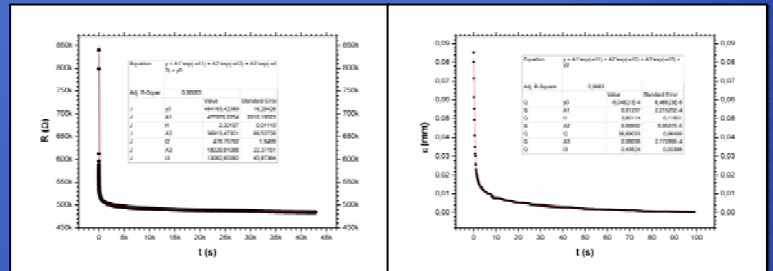


Fig. 3. Resistivity and strain relaxation after unloading

## CONCLUSIONS

The investigation was dedicated to introduce ourselves with time dependence of piezoresistive effect and to reveal some flaws in existing theoretical model, with respect to instantaneous loading of composite.

Both strain and resistivity recovery can be described by exponential equation with three different relaxation constants, but strain relaxation constant values are smaller than resistivity relaxation constants in order of magnitude. It means, that strain recovers faster than resistivity. This phenomenon can be explained by fact that, filler particle motion in matrix holds twofold effect – electro conductive channels can form or disrupt. So resulting resistivity change is sum of both processes.

Creep tests showed unexpected resistivity behavior, which is exponential decrement over time, when strain is increasing and stress is held constant. This may indicate a tendency of resistivity to relax when stress is held constant, even if strain is increasing.

## REFERENCES

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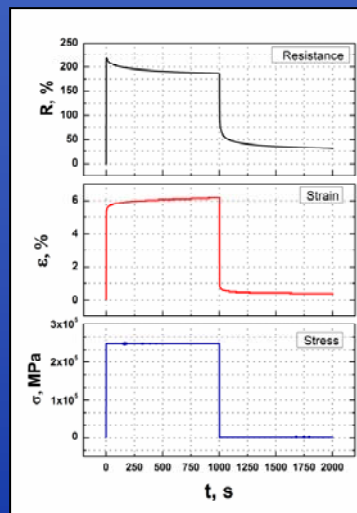


Fig. 4. Creep-Recovery test

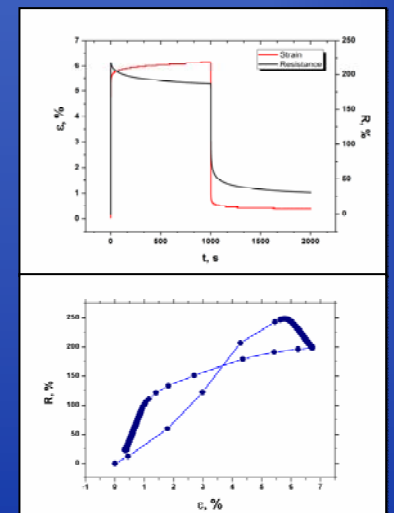


Fig. 5. Relative resistivity as function of strain, and both strain and resistivity functions of time (top)