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Rubber based nanocomposites applicable as sensors in smart tires

Omar A.Al-Hartomy[1,2], **Ahmed Al-Ghamdi**[2], **Nikolay Dishovsky***[3], **Petrunka Malinova**[3],
Farid El-Tantawy[4]
[1]Department of Physics, Faculty of Science, University of Tabuk, 71491 Tabuk, (SAUDI ARABIA)
[2]Department of Physics, Faculty of Science, King Abdulaziz University, 21589 Jeddah, (SAUDI ARABIA)
[3]Department of Polymer Engineering, University of Chemical Technology and Metallurgy, 1756 Sofia, (BULGARIA)
[4]Department of Physics, Faculty of Science, Suez Canal University, Ismailia, (EGYPT)
E-mail : dishov@uctm.edu

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ABSTRACT

This work reports on the preparation of titanium diboride filled composites based on different in chemical nature elastomers (natural rubber, nitrile butadiene rubber and siloxane rubber). The studies on the dependences of volume resistivity on pressure and of resistance on deformation were carried out with regard to the application of such composites as pressure and deformation sensors. It has been found out that titanium diboride used as a filler at certain concentrations, has a very valuable property that a number of fillers do not possess, i.e. to linearize (to make linear) the dependences of volume resistivity and resistance on pressure and on deformation (varied in a wide range). The composites comprising that filler are also sensitive to slight changes in outside factors and those with an optimal filler amount have no hysteresis. The prepared elastomer based composites first of all those based on siloxane rubber could be used as transducers in pressure and deformation sensors. The elastomer nature of the composites and the possibility for an easy incorporation of the sensing element into tires, certainly after carrying out some additional investigations, is an especially interesting aspect of application of such type of composites in so called smart tires.

KEYWORDS

Rubber;
Nanocomposites;
Sensors;
Smart tires.

INTRODUCTION

Recent advances in computers, sensors and other related technology have contributed to the improved reliability of vehicles. Safety in acceleration, braking, steering and cornering all depend on a relatively small area of road contact, i.e. on the tires - the only parts of the vehicle which are in contact with the road. For reducing the economic and personal costs of fatalities and serious injuries on the roads in the European Union, starting 2012, all new models of passenger cars must be equipped with a tire-pressure monitoring system (TPMS). Sensors which are embedded into the tire material are one of the advance options for a TPMS. The main innovation is in developing a wireless sensor that will transmit data about pressure load and wear[1] and will allow manufacturing of the so called 'smart tires'. The sensors needed might operate by two alternative mechanisms: they may be either pressure sensors responsive to changes in the pressure of the tire, or deformation sensors which are irresponsive to pressure changes but react to a deformation of the tire sidewall resulting from pressure[2]. Therefore much attention has been paid to the potential utilization of conductive composites based on rubber and different fillers as a sensing element incorporated into the tires.

The major requirements that the materials for elastomer based pressure and deformation sensors should meet are:

1. The dependence between the volume resistivity and the applied pressure or deformation should be linear in a wide range of changes in pressure and deformation;

2. The change in the volume resistivity with changing pressure and deformation should be great enough in order to guarantee that the changed value is not in the error range of the adopted method for measuring the pressure and deformation;

3. The electric parameters of the composite should not change with time, i.e. the properties of the dielectric matrix, as well as those of the conductive phase should remain constant for a long time.

4. The change in the environment temperature should have a negligible effect upon the sensor resistivity, if compared to the effect that pressure or deformation has.

Vulcanizates based sensors should not be used when[3];

1. The conductive phase migrates from the matrix volume to its surface and worsens the surface properties of the composite;

2. The possibility for a contact between the conductive particles changes with the temperature of the matrix;

3. The rubber matrix does not deform at the needed degree and resistivity values do not change notably with pressure and deformation, i.e. the sensitivity is not enough.

The thesis of this study is that the introduction of an appropriate quantity of a suitable conductive phase into the rubber matrix could ensure that the mentioned above specific electric properties (especially volume resistivity) of vulcanizates, thus obtained, could meet the requirements set for sensing materials and may be used, respectively, for the production of pressure and deformation sensors. On the other hand, the conductive composite material sensitive to pressure and deformation should be elastic, containing a small filler quantity and having not too complicated composition.

This work reports on the preparation of composites based on elastomers of different chemical nature (natural rubber, nitrile butadiene rubber and siloxane rubber) filled with titanium diboride. The studies on the dependences of volume resistivity on pressure and deformation were carried out with regard to the application of such composites as pressure and deformation sensors.

EXPERIMENTAL

Materials

Natural rubber (SMR 10) was purchased from North Special Rubber Corporation of Hengshui, Hebei Province, China. High temperature cure siloxane rubber paste with hardness of 30 Shore A was purchased from the same company. Nitrile butadiene rubber, containing 33 % ACN (Krynac 3345F, produced by Lanxess) was also used.

TiB_2 used as conductive filler was with particle size of ~50 nm and received from Wako Chemical Company, Tokyo, Japan.

TABLE 1 : Formulations of NR based nanocomposites filled with TiB_2

Ingredients	phr					
NR	100	100	100	100	100	100
ZnO	4	4	4	4	4	4
Stearic acid	2	2	2	2	2	2
TiB_2	0	10	15	25	35	45
IPPD[1]	1.5	1.5	1.5	1.5	1.5	1.5
MBT[2]	3	3	3	3	3	3
Sulphur	1	1	1	1	1	1

[1]IPPD – N-isopropyl-N'phenyl-p-phenyldiamine (Vulkanox 4010-NA, produced by Lanxess); [2]MBT - 2-mercapto benzothiazole (Vulcacit Merkapto, produced by Lanxess).

TABLE 2 : Formulations of siloxane rubber based nanocomposites filled with TiB_2

Silicon rubber paste	100	100	100	100	100	100
TiB_2	0	10	15	20	30	45

TABLE 3 : Formulations of NBR based nanocomposites filled with TiB_2

Ingredients	phr					
NBR	100	100	100	100	100	100
ZnO	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
TiB_2	0	10	15	25	35	45
IPPD[1]	1.5	1.5	1.5	1.5	1.5	1.5
ZDEC[2]	1	1	1	1	1	1
MBT[3]	0.5	0.5	0.5	0.5	0.5	0.5
Sulphur	2	2	2	2	2	2

[1]IPPD – N-isopropyl-N'phenyl-p-phenyldiamine (Vulkanox 4010-NA, produced by Lanxess); [2]ZDEC – zinkdiethylcarbamate (Vulkacit LDA, produced by Lanxess); [3]MBT - 2-mercaptobenzothiazole (Vulkacit Merkapto, produced by Lanxess).

The formulations of the compound prepared (in phr) were as follows (TABLE 1-3):

Preparation and vulcanization of rubber compounds

The rubber compounds were prepared on an open two-roll laboratory mill (L/D 320õ360 and friction 1.27) according to the requirements for processing natural rubber, nitrile butadiene rubber and siloxane rubber[4]. The speed of the slow roll was 25 min^{-1}. The experiments were repeated for verifying the statistical significance. The ready compounds in the form of sheets stayed 24 hours prior to their vulcanization.

The optimal curing time was determined by the vulcanization isotherms, taken on an oscillating disc vulcameter MDR 2000 (Alpha Technologies) according to ISO 3417:2002. The vulcanization of the rubber compounds was carried out in an electrically heated hydraulic press at 160°C for nitrile butadiene rubber (NBR) composites and at 155°C for the composites of natural rubber (NR), under pressure of 12 MPa. The sample sheets of siloxane rubber based composites were vulcanized at 195°C and under pressure of 15 MPa. The obtained samples with a size of 200 x 200 x 2 mm were used for further investigations.

Characterization and Measurements

Volume resistivity measurement

Volume resistivity (ρ_v, *Ω.m*) was measured using two electrodes (2-terminal method) and calculated by the equation:

$$\rho_v = R_v . S / h \qquad (1)$$

where:

R_v - measured ohmic resistance between the electrodes, Ω;

S – cross sectional area of the measuring electrode, m^2;

h – sample thickness between the electrodes, m.

Determining the volume resistivity as a function of the pressure

The equipment presented schematically on Figure 1 was used to determine the volume resistivity as a function of the applied pressure. The pressure in the range of 5-35 kPa was changed by varying the mass of the measuring electrodes. The samples were subjected to pressure of 5, 10, 15, 20, 25, 30 and 35 kPa, respectively. Our previous investigations give grounds to consider that the dependence of specific volume resistivity on pressure within the above interval should be of a near-linear scale.

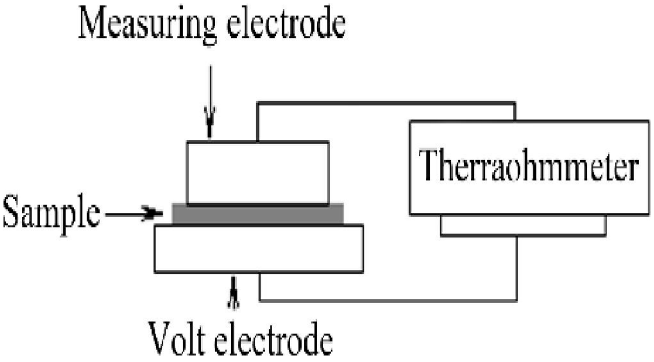

Figure 1 : Scheme of laboratory equipment for volume resistivity measurement

The resistance was measured on a therraohmmeter Teralin III (produced in Germany), using direct current.

The current voltage was 100 V. The measurements were performed on samples 2 mm thick 1 min after the current was switching on, so that the resistance values could stabilize. The measurements were carried out at ambient temperature increasing and decreasing the pressure in order to determine the presence or absence of hysteresis.

Determining the compression coefficient of volume resistivity ($PC\rho_v$)

The compression coefficient of volume resistivity

($PC\rho_v$) was determined[5] by equation (2).

$$PC\rho_v = \frac{\Delta\rho}{\rho_0}\cdot\frac{1}{\Delta P} \qquad (2)$$

where:

- $\Delta\rho$ – the change of the volume resistivity;
- ρ_0 – the volume resistivity of the unfilled sample at pressure of 10 kPa;
- ΔP - the change of the pressure, kPa.

Determining the volume resistivity as a function of the deformation

A simple experiment was carried out regarding the eventual use of the vulcanizates as tensotransducers in deformation sensors. For the purpose we invented a method for simulating the working conditions in a tensotransducer of mechanic values into electric ones.

The experimental tensotransducers were 79 x 20 x 2 mm belts cut from the investigated vulcanizates. Copper foil was glued to the upper surface of the tensoelement using electro-conductive glue. Then the tensotransducer was glued to a 190 x 25 x 0.37 mm steel belt (Figure 2). The arching carrying element thus constructed was connected to the therraohmmeter by conductors. The radius of the arch was regulated by a stopping rack.

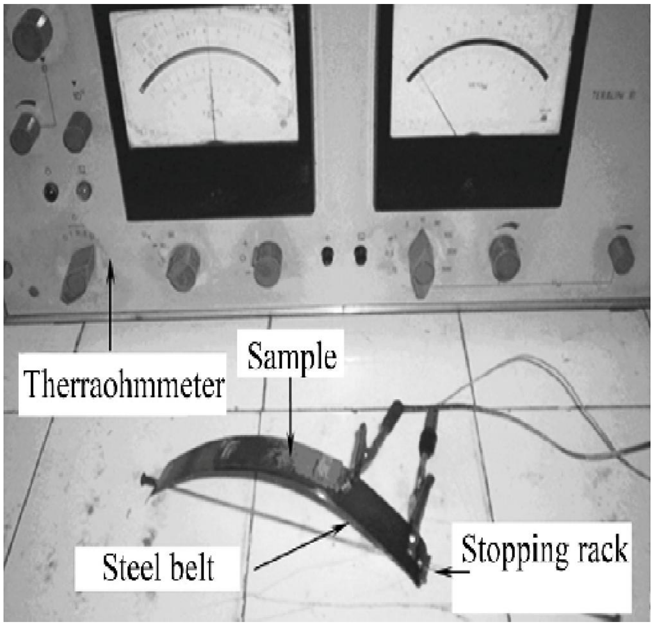

Figure 2 : Laboratory equipment for measurement of resistance R (in Ω) depending on applied deformation

The chosen initial radius was 100 mm. The deformation in percentage was calculated by the following formula[6]:

$$\delta = \frac{r_0 - r}{r_0}\cdot 100,\% \qquad (3)$$

where δ is the bending and r_o and r are the initial and the current radius, respectively, at different degrees of deformation.

RESULTS AND DISCUSSION

Figures 3-5 present the dependences of volume resistivity (ρ_v) on applied external pressure and filler quantity for titanium diboride filled composites based on nitrile butadiene, natural and siloxane rubber.

A decrease of volume resistivity with the increasing applied pressure and filler concentration has been observed for all the composites investigated. However, the volume resistivity of the non-filled samples of natural and siloxane rubber (0 phr TiB_2) increases slowly with the increasing pressure. This effect could be explained by the fact that mainly ions are current carriers in the non-filled composites based on natural and siloxane rubber, i.e. the latter exhibit ionic conductivity and with congestion of the rubber structures under applied pressure, the transitions of ions is hampered. In the filled composites, as the filler content and the applied pressure increase, the rubber layers among the filler particles become thinner, which leads to lower volume resistivity.

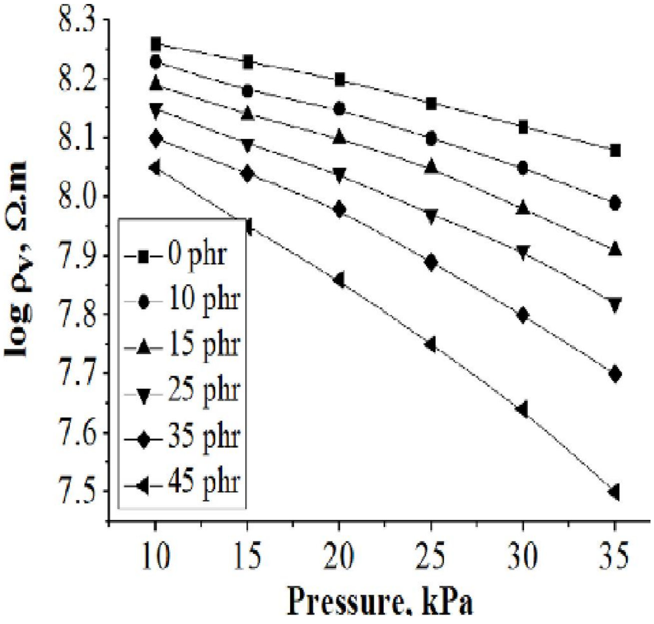

Figure 3 : Dependence of ρ_v on pressure and filler quantity for composites on NBR basis

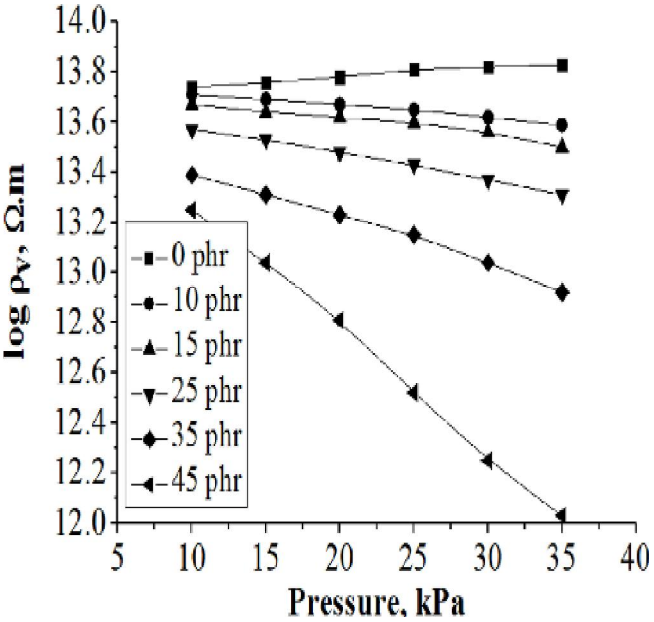

Figure 4 : Dependence of ρ_v on pressure and filler quantity for composites on NR basis

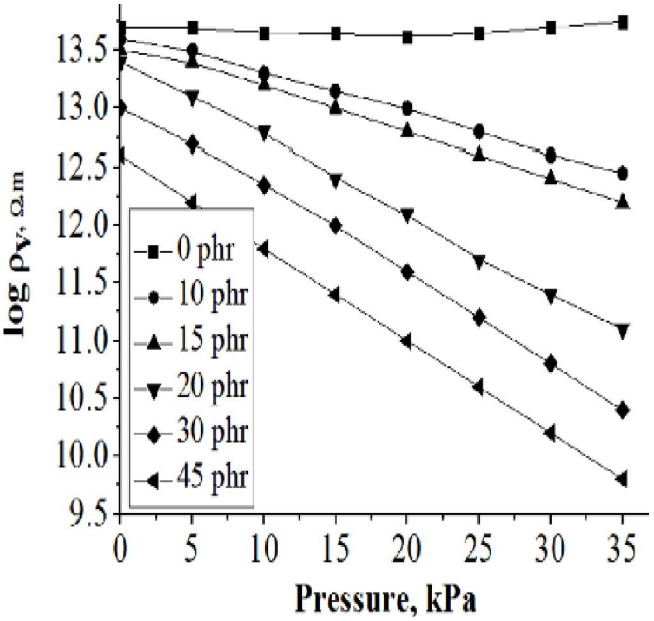

Figure 5 : Dependence of ρ_v on pressure and filler quantity for composites on siloxane rubber basis

The effect is more pronounced for samples with higher filler content (30-45 phr). The larger amount of TiB_2 particles enhances the electroconductivity of the composite and has a negative effect upon its volume resistivity. This decrease of the volume resistivity is due to the fact that following the increase in titanium diboride amount, the current carriers become predominantly electrons.

As seen from Figures 3, 4 and 5 in the interval from 0 to 35 kPa the volume resistivity (ρ_v) changes as pressure increases in a linear scale, i.e that type of materials could be used as pressure sensors. Furthermore, the siloxane rubber based composite containing TiB_2 at 45 phr is the most sensitive to changes in the resistivity caused by pressure, hence it is the most suitable material for sensor applications. The use of such composites as sensors has another advantage – the siloxane rubber based vulcanizates are distinguished by very high ozone stability, resistance to thermal aging in air, frost resistance[7]. Our results prove that along with mentioned properties reveal the capacities of the composites as materials suitable for production of sensors too. Figures 3-5 also show how the chemical nature of the elastomer matrix affects the values of volume resistivity. These values for vulcanizates based on nitrile butadiene rubber are several orders lower because that matrix may principally be referred to polymer semiconducting materials and not to dielectrics as natural and siloxane rubber are. The resistivity value changes upon varying the pressure are the slightest for the non-filled composites. There is no increase in volume resistivity of non filled NBR based samples with higher pressure applied (Figure 3) as it has been observed for the other two rubbers investigated (Figures 4 and 5). It is considered that the electron type of conductivity prevails in the nitrile composites[8, 9].

The compression coefficients of specific volume electric resistivity for composites based on nitrile butadiene, natural and siloxane rubber have been determined as a function of titanium diboride content (Figure 6).

As Figure 6 shows the compression coefficients of volume resistivity $PC\rho_v$ are negative. That means the resistivity decreases with the increasing pressure. This change in $PC\rho_v$, reveals how specific volume electric resistivity varies with pressure. ”Sensitivity” to compression impacts improves with the increasing of TiB_2 content, too. The Figure also shows that vulcanizates based on siloxane rubber posses the highest compression coefficients values almost in the entire investigated range, i.e. their sensitivity to compression impacts is the highest. This is other evidence that these composites are the most suitable for pressure sensors, while the sensitivity of nitrile butadiene rubber based composites is the lowest.

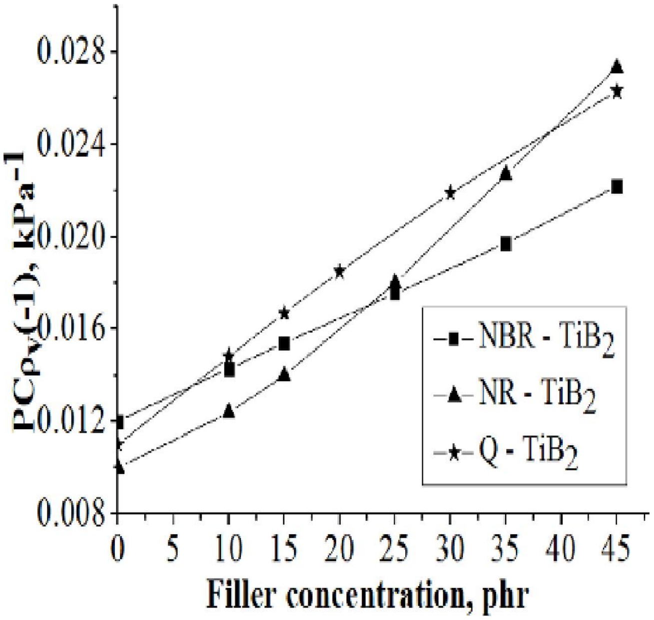

Figure 6 : PCρ_v as a function of TiB$_2$ content for composites on nitrile butadiene, natural and siloxane rubber basis

A tensoeffect has been established when applying deformation impact on the samples of titanium diboride filled composites based on nitrile butadiene, natural and siloxane rubber. Figures 7, 8 and 9 present the results from resistance (R, Ω) measurements carried out according to the bending of the steel belt to which the composite specimens were fixed.

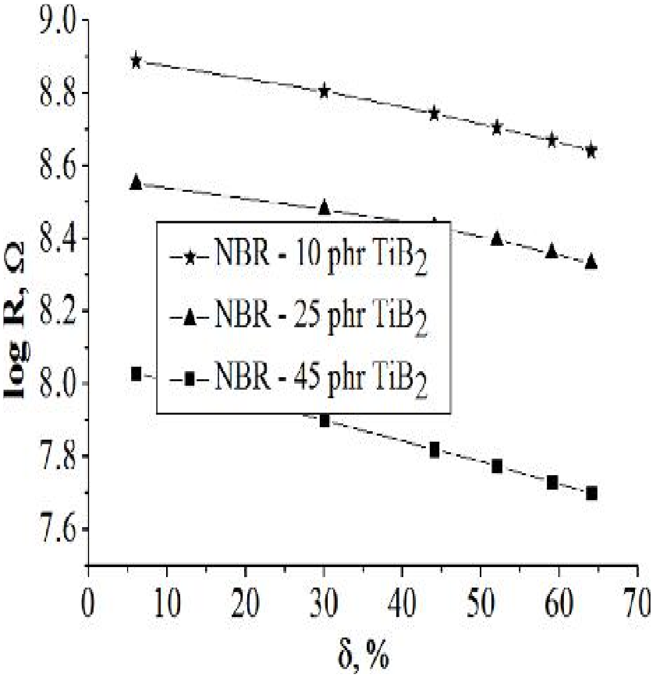

Figure 7 : Change of resistance depending on applied deformation and filler content for composites on nitrile butadiene rubber basis

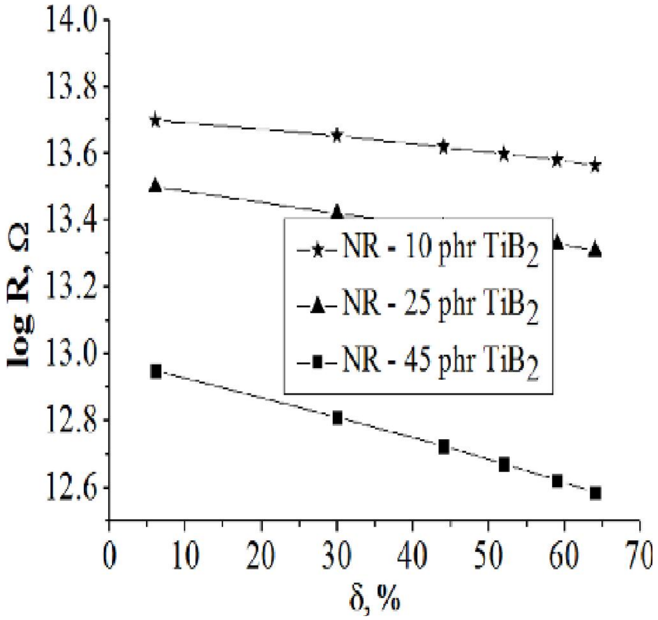

Figure 8 : Change of resistance depending on applied deformation and filler content for composites on natural rubber basis

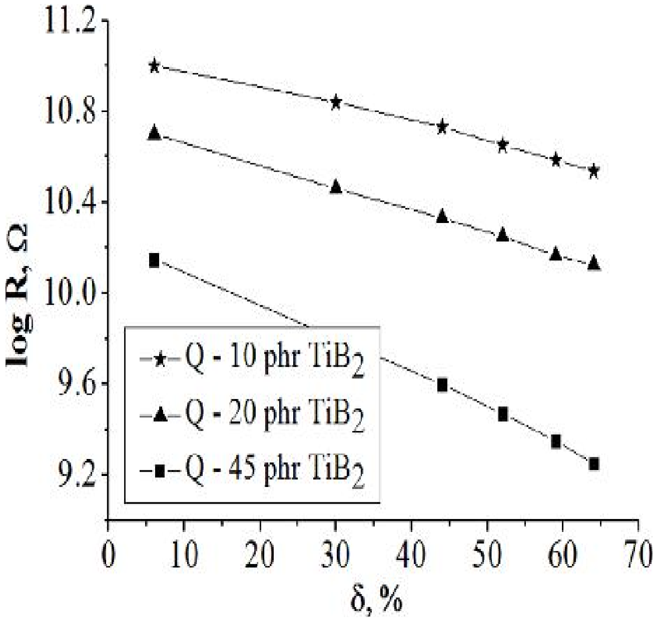

Figure 9 : Change of resistance depending on applied deformation and filler content for composites on siloxane rubber basis

As seen the tendency of resistance R changing (Figure 7-9) and that of the change in volume resistivity with pressure, shown on Figures 3-5 are the same for composites investigated The tendency of a linear resistance vs. deformation function opens opportunities to use these composites as deformation sensors. The composites based on nitrile butadiene rubber are the most insensitive to deformation changes, i.e the most unsuitable for deformation sensors. The bending process leads to creeping of composite layers and successive orientation of the structure. That to a certain extent fascinates the transport of current carriers and lowers the resistance values, respectively. The electroconductive glue used improves the contact between the sample, the copper foil and steel belt what is a prerequisite for obtaining lower resistance values. It is obvious from the results that the elastomers investigated are prone to high deformations without a danger of breaking unlike the traditional (inorganic) materials used as sensors which are brittle, fragile and with deformability up to 1%[6].

The experiment has proven that a relatively easy technology for a rubber matrix and type of filler selection can yield various and simple pressure and deformation sensors for a wide range of applications.

Figure 10 shows the dependence of volume resistivity on consecutive pressure increase and decrease for composites based on siloxane rubber, containing 45 phr titanium diboride (TiB_2). As seen from the Figure hysteresis does not occur upon pressure increasing and decreasing. That is also a prerequisite that those composites can find application as pressure sensors. The natural rubber based composites filled with titanium diboride exhibit a similar behavior.

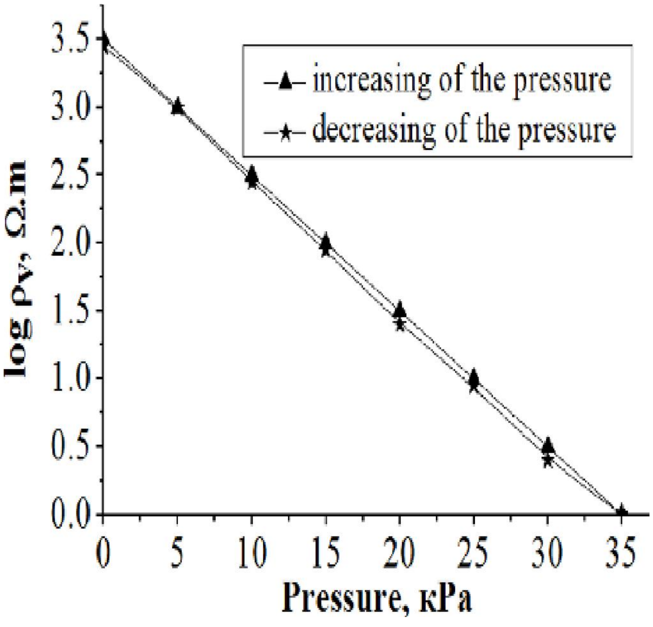

Figure 10 : Change of volume resistivity of composite on siloxane rubber basis, containing 45 phr titanium diboride upon consecutive pressure increase and decrease

Noteworthy is the fact that while a hysteresis is observed in the case of non-filled composites, it decreases with the increasing filler quantity and practically disappears at a 45 phr filler content.

The experiments carried out have demonstrated that the titanium diboride in quantities from 20 to 45 phr (with appropriate selection of an elastomer matrix, mainly siloxane rubber) is suitable filler for development of composites with eventual application as pressure and deformation sensors in the future production of smart tires. The advantages of those composite materials with optimal filling in view of such an application are:

- sensitivity to slight changes in pressure and deformation;
- linear volume resistivity *vs*. pressure and resistance *vs*. deformation dependences in wide intervals;
- absence of hysteresis upon increasing and decreasing of pressure and deformation
- possibilities to embed the element into the tire.

FUTURE INVESTIGATIONS

One of the future research areas is the optimization of sensors size regarding the application of the prepared composites as sensors in the production of smart tires. The composites behavior upon multiple cyclic loads, the changes in their properties occurring cycle by cycle should be also studied, as well as the creep influence on the exploitation characteristics of the composite. The influence of temperature on the possibilities for composites application as sensors should be clarified as well. Further investigations should be carried out, e.g. how the signal from the sensor will be processed and sent that information to the vehicle's computer; how the sensor will be embedded into the tire (for example –in sidewall), and how the problem of the power supply to the sensor will be solved.

CONCLUSIONS

1. The influence of nanosized titanium diboride on the volume resistivity of composites based on nitrile butadiene, natural and siloxane rubber and their response to environment effects, in particular to pressure and de-

formation has been investigated. It has been established that volume resistivity and resistance decrease in all cases with the increasing filler quantity and with the intensity of outside impacts. These effects are more pronounced at higher filler amount.

2. It has been established that titanium diboride used as a filler at certain concentrations has a very valuable properties that a number of fillers do not possess, i.e. under its influence the dependences of volume resistivity and resistance on outside impacts (pressure, deformation) in a wide interval become linear. The composites comprising that filler are also sensitive to slight changes in outside factors and those with an optimal filler amount have no hysteresis.

3. The elastomer based composites, mostly those based on siloxane rubber and filled titanium diboride could be used as transducers in pressure and deformation sensors. Their elastomer nature and the ability to incorporate them easily into the tires are a particularly interesting aspect of their application in the production of tire-pressure monitoring systems. Certainly for the purpose the discussed composites should undergo more specific investigations in the near future.

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