

INVESTIGATION OF SOME ELECTRICAL PROPERTIES OF NATURAL RUBBER BASED COMPOSITES CONTAINING AS FILLERS SiC AND B₄C

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ABSTRACT

The dependences of volume resistivity (ρ_v) of natural rubber (NR) based composites, filled with boron carbide (B₄C) and silicon carbide (SiC) as a function of fillers concentration, pressure and temperature are investigated. The results show that the volume resistivity of both NR-B₄C and NR-SiC decreases when increasing the fillers concentration and the temperature, but with pressure increase, the ρ_v values increase. The conduction mechanism of the composites is interpreted by calculation of the activation and hopping energies.

The defined electrical properties classified the investigated samples as polymer composite semiconductors, so the possibilities for application of these composites as linear thermistors and transducers in pressure sensors were studied.

Keywords: Natural rubber, SiC, B₄C, composites, electrical properties, activation energy of current carriers transport.

INTRODUCTION

The electrical properties of polymers and polymer composites have been an object of multilateral studies due to their capabilities for various applications in the contemporary electrical engineering. Usually, they are used as insulators [1] but with suitable fillers their conductivity may be changed in a very wide range. The object of the present investigations are composites of NR with two typical semiconductors: silicon carbide (SiC) and boron carbide (B₄C). Their conductivity is interpreted theoretically and the possibilities for their application as transducers of unelectrical quantities in electrical quantities are studied.

EXPERIMENTAL

The fillers selected (SiC with particle size 1 μ m, B₄C with particle size 2,2 μ m, prepared by Wako Chemi-

cal Company, Toyo, Japan) were introduced into NR. Series of NR-SiC composites and series of NR-B₄C composites were prepared. The composition of the used rubber compounds (in phr - per hundred rubber) was as follows: natural rubber – 100; zinc oxide – 4; stearic acid – 2; 2- mercaptobenzothiazole (Vulkacit Merkapto, produced by Bayer) – 3; sulfur – 1; N-isopropyl-N'-phenyl-p-phenyldiamine (Vulkanox 4010-NA, produced by Bayer)-1,5 and filler (SiC, B₄C): 0, 15, 25, 35 and 45 phr. The rubber compounds were prepared on a two – roll mill at carefully controlled temperature, mixing time and gap between the rolls. The vulcanization process of the rubber compounds was carried out in an electrically heated hydraulic press using a special home – made mold at temperature 155 °C for 10 minutes under pressure of 12 MPa. Samples in a sheet form (90 X 60 X 2 mm) were obtained as a final result.

The volume resistivity (ρ_v) of NR based composites was measured by Terraohmmeter Teralin III

(made in Germany) as a function of temperature and pressure [2].

RESULTS AND DISCUSSION

Changes of ρ_v as a function of carbides concentration

The dependences of the volume resistivity of NR-B₄C and NR-SiC composites on the fillers concentration at 25 °C and pressure of 10 kPa is shown in Fig. 1(a) and Fig. 1(b).

The volume resistivity decreases with the increasing of the fillers concentration for both types of composites. This effect may be explained with the lower volume

resistivities of fillers ($\rho_v^{B4C} = 1,3 \cdot 10^8 \Omega m$, $\rho_v^{SiC} = 2,3 \cdot 10^9 \Omega m$) compared with the rubber matrix resistivity ($\rho_v^{NR} \approx 5,5 \cdot 10^{13} \Omega m$). The ρ_v values of boron carbide composites are lower than those of silicon carbide composites.

Volume resistivity change as a function of applied pressure

The variations of ρ_v values of NR-B₄C and NR-SiC composites with pressure increasing from 10 to 35 kPa at 25°C are presented in Figure 2(a) and Figure 2(b).

For both types of composites increase of ρ_v is observed. This may be explained with the fact that fillers used do not reach their percolation threshold and with the pressure increase, the rubber matrix becomes

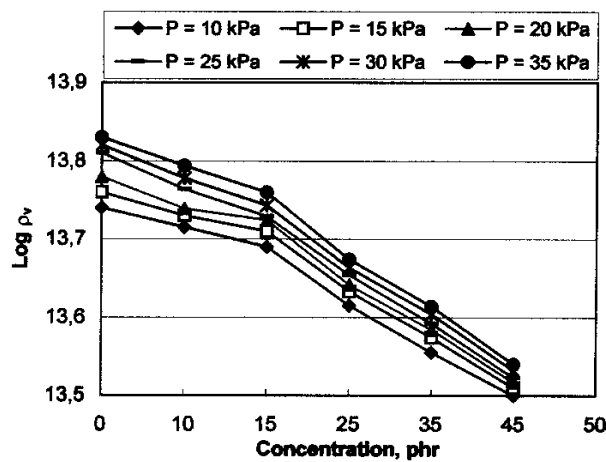


Fig. 1 (a). Volume resistivity change ρ_v , [Ωm] as a function of B₄C concentration in NR.

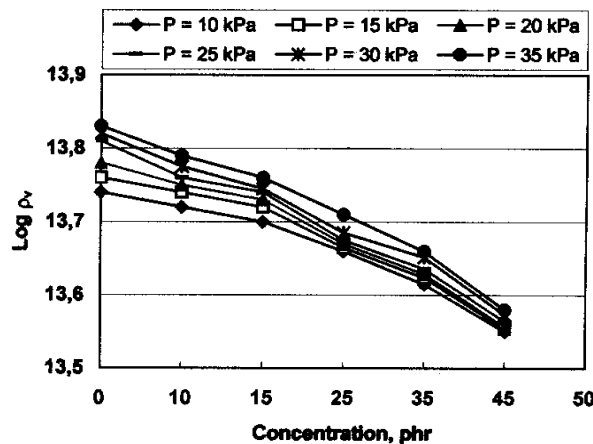


Fig. 1 (b). Volume resistivity change ρ_v , [Ωm] as a function of SiC concentration in NR.

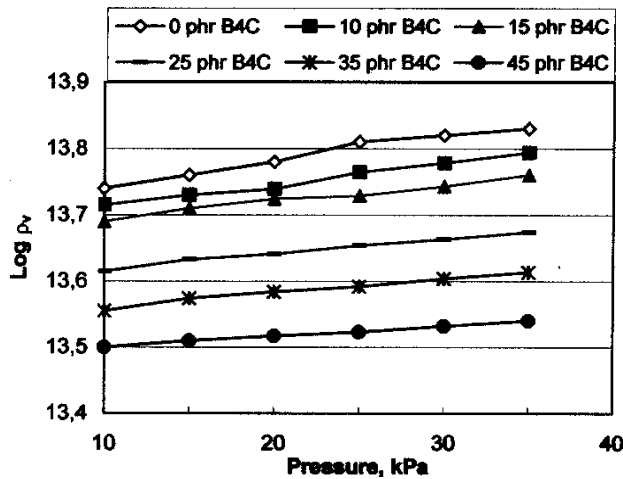


Fig. 2 (a): ρ_v , [Ωm] – pressure dependence for NR- B_4C composites.

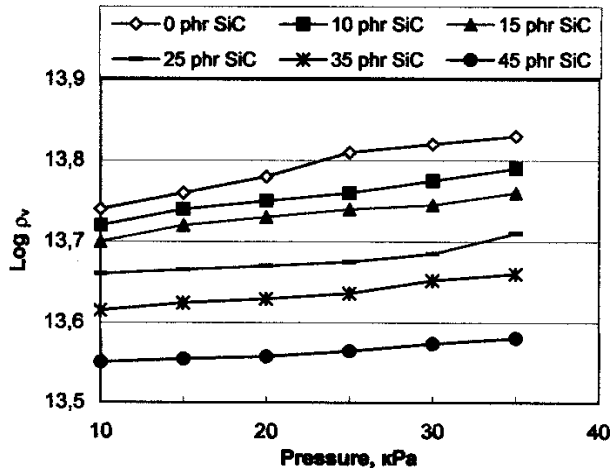


Fig. 2 (b): ρ_v , [Ωm] – pressure dependence for NR-SiC composites.

a denser structure which makes more difficult current carriers (predominantly ions) transport. The ρ_v values of silicon carbide composites are higher due to the higher volume resistivity of SiC than that of B_4C . The linearity of the volume resistivity variation with the pressure increase and the absence of a hysteresis loop identify as suitable the samples investigated for application as pressure sensors.

The compression coefficient of the volume resistivity (PC_p) was determined by the equation [3]:

$$PC_p = \left(\frac{\Delta\rho}{\rho_0} \right) \left(\frac{1}{\Delta P} \right) \quad (1)$$

where $\Delta\rho$ is the change of the volume resistivity, Ωm ; ΔP – the change of the pressure, kPa. The values of

PC_p as a function of the fillers concentration are shown in Fig. 3.

PC_p for both types of composites is positive. It shows that with the increasing of pressure the resistivity increases and with the increasing of the fillers concentration the sensibility to compression influences decreases. The values of PC_p , presented in the Fig. 3, are very close to each other, but they are higher than the relative error $\pm 3\%$ and it allows the two curves to be considered as separated characteristics. PC_p has a little higher values for NR- B_4C vulcanizates than those for NR-SiC. Their sensibility is higher also.

Volume resistivity change as a function of temperature

The dependences of volume resistivity on the temperature for NR- B_4C and NR-SiC composites are presented in Fig. 4a and Fig. 4b.

With the temperature increasing, the volume resistivity for all samples decreases, but the values for the sample without fillers and for the sample containing 45 phr of fillers are quite close. A temperature hysteresis is observed for the unfilled vulcanizate of NR which decreases when increasing the fillers content and at high concentrations (45 phr) there is almost no hysteresis loop. The hysteresis obtained for NR- B_4C composites is smaller than that for NR-SiC composites.

The same matrix and the close values of the SiC and B_4C resistivity are the reasons for the quite close results obtained for the temperature dependence of the resistivity of the composites. The lower values measured

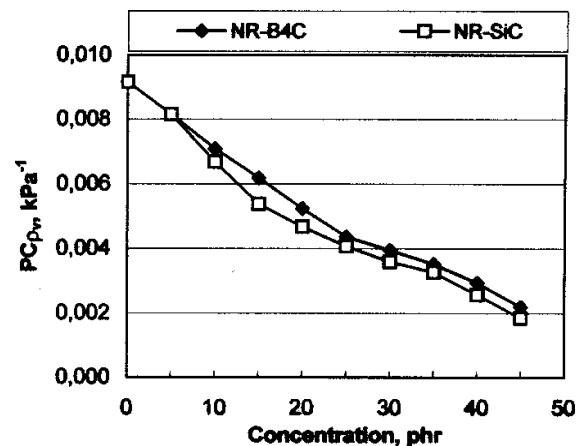


Fig. 3. PC_p as a function of fillers content for NR- B_4C and NR-SiC composites at $\Delta P = 25$ kPa.

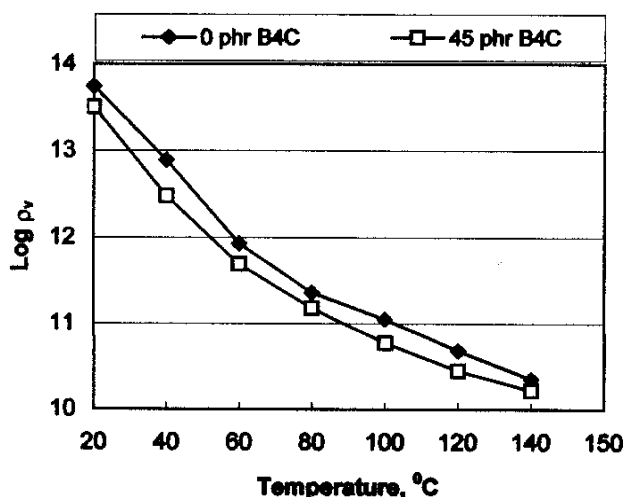


Fig. 4a. ρ_v , [Ωm] - temperature dependence for NR- B_4C composites.

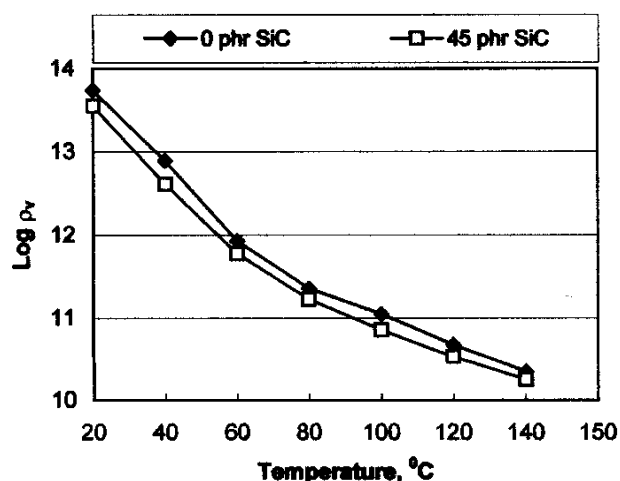


Fig. 4b. ρ_v , [Ωm] - temperature dependence for NR-SiC composites.

for B_4C samples may be explained with a better current carrier emission than that of SiC. The resistivity temperature characteristics (Figure 5) confirm this assumption. The B_4C curve is situated below the SiC curve which explains its more favorable influence on the composites electrical conductivity.

The temperature coefficient of resistivity (α) is determined by the equation [2]:

$$\alpha = \frac{\rho_{T_2} - \rho_{T_1}}{(\rho_{T_1} T_2 - \rho_{T_2} T_1)} \quad (2)$$

where: ρ_{T_1} - volume resistivity at temperature T_1 ; ρ_{T_2} - volume resistivity at temperature T_2 .

From the straight portions of the curves shown in Fig. 4a, b, two values for α may be calculated for each composite - one concerning the temperature range 20 - 80°C and another, concerning the temperature range 80 - 140°C. The determined values were as follow:

- for unfilled NR composite: $\alpha_{20-80} = -1,25 \cdot 10^{-2} \text{ }^\circ\text{C}^{-1}$;
 $\alpha_{80-140} = -6,80 \cdot 10^{-3} \text{ }^\circ\text{C}^{-1}$;
- for NR- B_4C composites: $\alpha_{20-80} = -1,25 \cdot 10^{-2} \text{ }^\circ\text{C}^{-1}$;
 $\alpha_{80-140} = -6,80 \cdot 10^{-3} \text{ }^\circ\text{C}^{-1}$;
- for NR-SiC composites: $\alpha_{20-80} = -1,25 \cdot 10^{-2} \text{ }^\circ\text{C}^{-1}$;
 $\alpha_{80-140} = -6,81 \cdot 10^{-3} \text{ }^\circ\text{C}^{-1}$;
- for B_4C : $\alpha_{20-140} = -6,85 \cdot 10^{-3} \text{ }^\circ\text{C}^{-1}$;
- for SiC: $\alpha_{20-140} = -6,97 \cdot 10^{-3} \text{ }^\circ\text{C}^{-1}$.

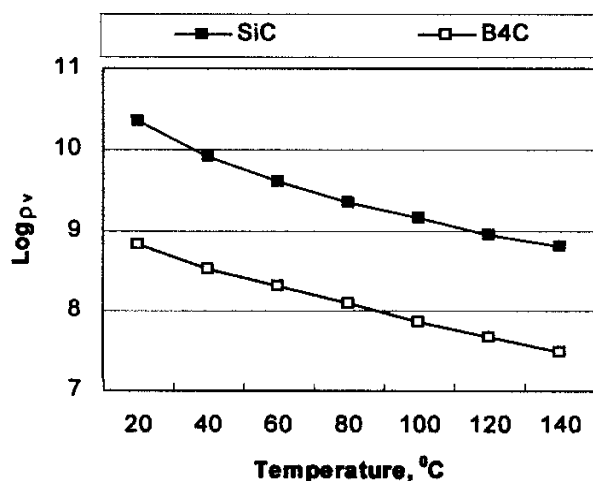


Fig. 5. ρ_v , [Ωm] - temperature dependence for SiC and B_4C .

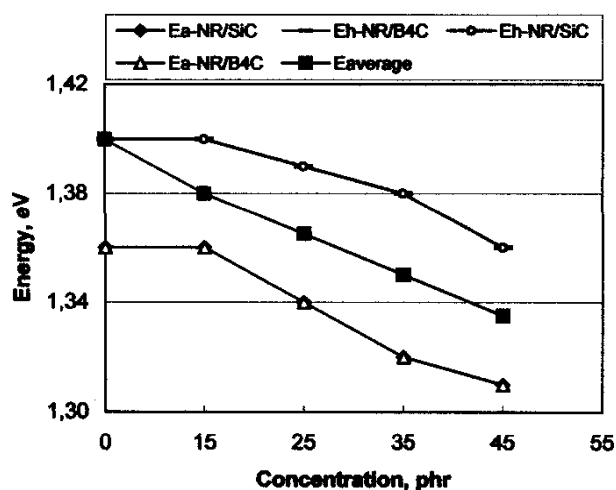


Fig. 6. E_a and E_h as a function of fillers content for NR- B_4C and NR-SiC composites.

The filler amount does not influence the slope of the curves and as a result, the coefficients are identical and not depending on the filling.

The results obtained show that the composites investigated may be classified as negative thermistors. The SiC is more sensitive to temperature changes than B₄C. The properties of the elastomer matrix are strongly influencing the composites temperature coefficient of resistivity.

Current carriers transport

The transport of current carriers can be explained by zonal and hopping mechanisms from their calculated activation energies. The main reason for that is the absence of a theory clarifying the processes of current carriers transport through the systems composed by substances in which the carriers pass through structures with huge differences in the chemical composition and in the degree of ordering of their components. The defining of only one activation energy (E_a or E_h) of the composites investigated does not describe the real energetic levels because of which the carriers pass through the composite. Because of this, it would be better the activation energies characterizing each of the components of the composite to be presented or one average activation energy which shows one global value for the type of composite (Fig. 6) to be calculated.

The activation energy (E_a) in zone theory may be calculated by the well known exponential dependence of the conductivity on the temperature [4]:

$$\sigma = \sigma_0 e^{-E_a/2kT} \quad (3)$$

where σ_0 is the conductivity at total dissociation of electrons when $T \rightarrow \infty$; E_a is the activation energy (energy gap between the valence and conducting zones); k is the Boltzman constant; T is the temperature on the absolute scale.

The hopping activation energy (E_h) of the composites may be calculated by the equation [5]:

$$\sigma_h \sqrt{T} = \sigma_0 e^{-E_h/2kT} \quad (4)$$

The values of activation energies at zone transitions of carriers for the two carbides are as follow: E_a^{SiC}

= 0,62 eV; $E_a^{\text{B}_4\text{C}} = 0,53$ eV. It is evident that the energy for SiC is higher which corresponds to the volume resistivities of SiC and B₄C.

From Fig. 6 it may be concluded that the transition energies decrease when the fillers concentration is increasing. E_h are higher than E_a for all samples. The values of the energies of the two composites are quite close, they are in the error region ($\pm 3\%$) and that is why they are presented with one graphical characteristic only.

The higher activation energy for the rubber matrix (0 phr – Fig. 6) than the SiC and the B₄C energies show that the current carrier transition through it is predominantly by hops; in the same time through the fillers particles the transitions are zonal. With the fillers content increasing the zonal activation energy in the carbides particles stays almost constant because the structure and the properties of B₄C and SiC do not change but the global energy of zonal transition decreases, because of the increasing particles number where this transition is realized. In the same time E_h decreases due to the decreasing of the thickness of the rubber layers among the particles and of the distances between the places of current carriers localization.

CONCLUSIONS

The volume resistivity of the composites investigated (NR-B₄C and NR-SiC) decreases with filler content increasing. The resistivity linearly increases with the pressure increasing but it decreases considerably with temperature increasing. It gives possibilities for their application as negative thermoresistors (NTCR linear thermistors) and strain-transducers in pressure sensors.

On the basis of the volume resistivity dependences on the pressure and on the carbides content the current carriers are presented by both ions and electrons. Two theories are used for the mechanism of their transport: for zonal transition and for transition by hops. According to the received results for the volume resistivity as a function of different parameters, and the activation energies E_a and E_h as a function of fillers filling, the conductivity mechanism of the current carriers transition is mixed and realized under the influence of both carbides and elastomer matrix.

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