

Investigation of Conductivity Characteristics of Nitrile Butadiene Rubber Vulcanizates Filled with Semiconducting Carbide Ceramic

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Received 7 October 2005; accepted 3 July 2006

DOI 10.1002/app.25077

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: SiC- and B₄C-filled NBR rubber composites were prepared with various volume fractions of filler by a conventional roll-mill method. The morphological structures of the NBR–SiC and NBR–B₄C composites were analyzed by scanning electron microscopy. The dependence of room-temperature volume resistivity (ρ_v) on the concentration of filler in the two systems was studied. In addition, variation in the number of current carriers (n), mobility carriers (μ), dielectric constant (ϵ), and dielectric loss factor ($\tan \delta$) on filler concentration in the two systems were investigated in detail. The applicability of composites as negative temperature coefficient (NTCR) linear thermistors was studied by the dependence of volume resistivity on temperature. The

resistivity showed negative temperature dependence and changed linearly with temperature parallel. The conduction mechanism of the conductivity of the two composites was analyzed in terms of the computed activation energy and hopping energy. Change in volume resistivity as a function of frequency for the two systems was also investigated. Finally, the dependence of volume resistivity on applied pressure and possible real applications of these composites as transducers in pressure sensors were also studied. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2158–2165, 2007

Key words: sensors; activation energy; conducting polymers; dielectric properties, rubber

INTRODUCTION

Conductive polymeric composites have been extensively studied in recent years because of their potential applications in light-emitting devices, batteries, electromagnetic shielding, antistatic, corrosion resistant coatings, self-heating element, thermistors, and other functional applications.^{1,2} Polymers are used as insulators,³ but with suitable fillers their conductivity may be changed in a very wide range. In some cases the polymer matrix and the filler have a specific influence on composite conductivity.^{4–6} In recent years composites with resistances close to those of metals have been produced by compounding with high conductive fillers (carbon black, graphite, metal powder). But until now polymer composites possessing semiconducting properties comparable to characteristic features of inorganic semiconductors have not been developed. It is known there is a theoretical possibility of producing such kinds of materials, but problems from the inevitable contaminations and structural imperfections have arisen, making the

transport of current carriers uncontrolled.⁷ These disadvantages probably could be eliminated and compensated for by mixing the polymer matrix used with filler, but much experimentation is needed to find the most suitable filler. At the same time polymer-based composites possessing the properties of the inorganic semiconductors will be successfully developed because their production is not costly and very easy, requiring only simple technology. Of the non-oxide ceramics, boron carbide and silicon carbide stand out for their technological importance as a result of their mechanical properties, elevated thermal conductivity, thermal shock, and oxidation resistance. Nitrile butadiene rubber (NBR) has semiconducting properties, high resistance to environmental degradation, excellent resistance to acids and bases, good adhesion to metal, glass, and concrete, and good thermal stability.^{8–11} In this article, we report the preparation of NBR-filled SiC and B₄C composites by a conventional roll-mill method, and the potential application of these composites in NTC thermistors and pressure sensor applications. Moreover, the effect of filler content on the microstructure was examined by scanning electron microscopy. The electrical conductivity and dielectric properties were determined and are discussed as functions of filler content in order to extend the application of prepared composites in NTC thermistors. The effect of

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Contract grant sponsor: National Research Council, Ministry of Education and Science, Bulgaria.

TABLE I
Compound Formulations of Materials Used

Ingredient (phr) ^a	NBR0	NBR10	NBR15	NBR20	NBR25	NBR30	NBR35	NBR45	Mixing time (min)
NBR	100	100	100	100	100	100	100	100	5
ZnO	5	5	5	5	5	5	5	5	3
Stearic acid	2	2	2	2	2	2	2	2	3
SiC	0	10	15	20	25	30	35	45	6
B ₄ C	0	10	15	20	25	30	35	45	6
PBN	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	3
ZDC	1	1	1	1	1	1	1	1	3
MBT	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	3
Sulfur	2	2	2	2	2	2	2	2	3

^a Parts per 100 parts of rubber by weight.

hydrostatic pressure on the electrical resistivity of particulate silicon carbide- and boron carbide-filled NBR rubber composites is also reported.

EXPERIMENTAL

Materials

Nitrile butadiene rubber (NBR) with a 40% content of nitrile groups was supplied by Bayer (Germany). Silicon carbide (SiC) with a particle size of 1 μm, and boron carbide (B₄C) with a particle size of 2.2 μm were prepared by Wako Chemical Company (Toyo, Japan). Other chemicals used were zinc oxide as an activator to enhance the action of organic accelerators; stearic acid as a coactivator and dispersion agent; zinc-diethyl dithiocarbamate (ZDC) as an ultra-accelerator (Vulkacit LDA, produced by Bayer); 2-mercaptobenzothiazole as an accelerator (MBT; Vulkacit Merkaptol, produced by Bayer); sulfur as a vulcanizing agent; and *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine (PBN) as an antioxidant (Vulkanox 4010-NA, produced by Bayer).

Sample preparation

The materials used and compound formulations are given in Table I arranged in the order in which they were added during preparation. The rubber compounds were prepared on a two-roll mill with a carefully controlled temperature, mixing time, and gap between rolls. The vulcanization process of the rubber compounds was carried out in an electrically heated hydraulic press (Karl Kolb, Germany) using a special homemade steel mold at temperature of 160°C for 10 min under a pressure of 12 MPa. Samples in sheet form (90 × 60 × 2 mm) were obtained as the final result. These vulcanization sheets were allowed to mature at room temperature for 48 h before testing.

Sample testing

The volume resistivity (ρ_v) of the NBR-based composites was measured by a Terraohmmeter Teralin III

(made in Germany) as a function of temperature and pressure.⁶ Resistivity to alternating current was obtained with an RLC Bridge (3535 Z Hitester, Hioki, Japan). The number of current carriers (n) and their mobility (μ) were estimated by the Hall effect technique (type 102, Hitachi, Tokyo, Japan) using the following equations:⁸

$$n = \frac{BI_H}{qhV_H} \quad (1)$$

$$\mu = \frac{\sigma}{ne} \quad (2)$$

where B is the applied magnetic field; q is the charge per current carrier; h is the sample thickness, I_H and V_H are the Hall current and voltage, respectively; e is the elementary electron charge; and σ is the electrical conductivity. The dielectric constant (ϵ) and dielectric loss factor ($\tan \delta$) were determined by the Hewlett-Packard 4994-A technique. The structure of the NBR composites was observed by scanning electron microscopy (SEM; Hitachi, Tokyo, Japan) at an accelerating voltage of 25 kV.

RESULTS AND DISCUSSION

Effect of filler content on volume resistivity

The dependence of volume resistivity of NBR composites on the filler concentration at 25°C and a pressure of 10 kPa is depicted in Figure 1. The resistivity increased with increasing filler concentration. It is clear that the increased concentration of the fillers led to more thin rubber layers among the particles. As a result, the number of places for localization of the current carriers and the number of carriers decreased. This led to decreasing transport intensity of the current carriers through the macromolecular net of the composites. The formation of a thin rubber layer among conductive particles could be further verified by the resistivity-frequency behaviors of the two composites. The change in composite volume resistivity as a function of electric field frequency is

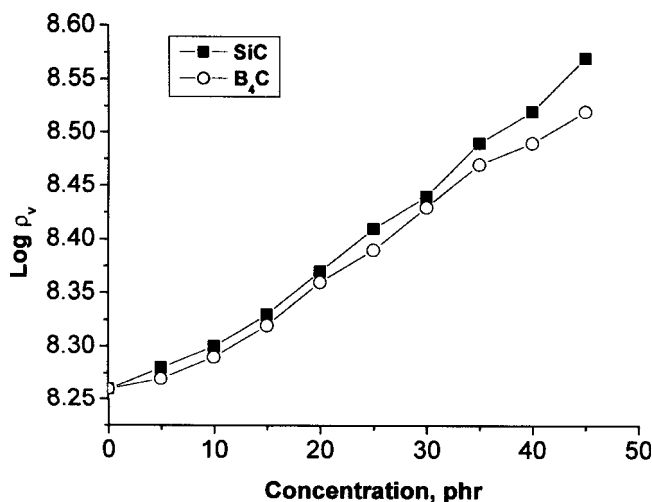


Figure 1 Volume resistivity change (ρ_v , Ωm) as a function of fillers concentration in NBR-SiC and NBR-B₄C composites at $T = 25^\circ\text{C}$ and $P = 10$ kPa.

shown in Figure 2. It can be seen that in the 0–6 kHz region composite resistivity showed a plateau whose width increased with increasing filler concentration. For all composites, in the 6–10 kHz region the smallest charged kinetic units entered in resonance and thus contributed to decreasing resistivity. With filler concentration increasing the number of oscillators decreased because the filler particles blocked them. Their oscillation became quiet, and resistivity increased. The influence of electric field frequency on resistivity shows there were kinetic units of a dipole-segmental type in the composites. They were strongly connected with the macromolecule chains and may have only oscillated without participating

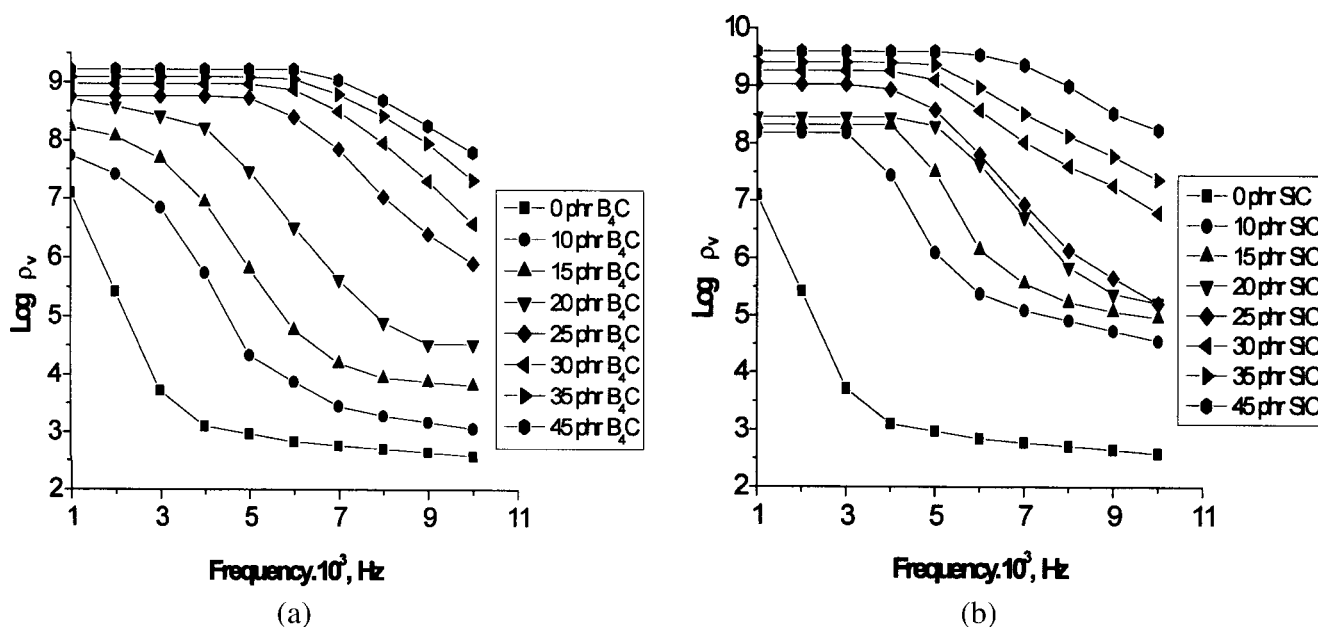


Figure 2 (a) ρ_v -Frequency dependence of NBR-B₄C composites; (b) ρ_v -frequency dependence of NBR-SiC composites.

in current carrier transport. They formed so-called removing currents. Electrons and ions with little mass were responsible for current carrier transport. They had resonance at high frequency and under the influence of alternative electric field may have passed from one macromolecule to another, which is why lower resistivity was measured in alternative current.

Hall characteristic, dielectric, and morphological investigations

The dependence of the number of the current carriers and their mobility on filler concentration is depicted in Figure 3. It was found that current carrier mobility was a more sensitive parameter to filler concentration than current carrier number. The barriers formed between the polymer matrix and the filler particles and their role as a screening shield were the reasons mobility decreased with increasing concentration of filler in the composites. The effect was more clearly observed with SiC than with B₄C because of their different volume resistivities ($2.3 \times 10^9 \Omega\text{m}$ for SiC and $1.3 \times 10^8 \Omega\text{m}$ for B₄C measured at a pressure of 10 kPa). It may be concluded from these results that current carrier transport may be accomplished through both rubber matrix and filler particles.

The values measured for dielectric constant (ϵ) and dielectric loss factor ($\tan \delta$) as a function of filler concentration are depicted in Figure 4. It can be seen that both SiC and B₄C increased the composite dielectric properties, decreasing the values of the above-mentioned parameters. The effect was more

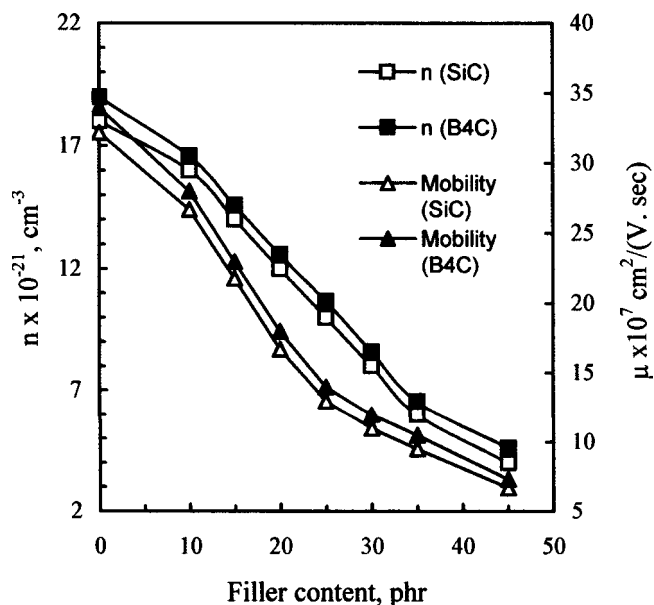


Figure 3 Number of current carriers and their change in mobility as a function of filler concentration for NBR-SiC and NBR-B₄C composites.

clearly observed for B₄C. The difference between SiC and B₄C may be connected with the bigger oscillations of SiC particles, consuming a bigger amount of electric field energy than B₄C particles. When the concentration increased, their standing in one another's way decreased the oscillations and the respective $\tan \delta$ values. The values of dielectric constant decreased because of the unfavorable influence of the fillers on the current carrier transport.

The assumption that the adhesive interaction between the rubber macromolecules and the filler particles influenced the ϵ and $\tan \delta$ values was confirmed by the structures observed by SEM. Figure 5 shows the SEM micrographs of NBR-SiC⁴⁵ and NBR-B₄C⁴⁵ samples, from which difference in the absorption properties of SiC and B₄C can be observed. At a higher concentration (45 phr) the SiC particles were separated from one another, with their surfaces in relief containing well-detached contours. This configuration showed that the surface did not have adsorbed macromolecules and that the interactions with the elastomer matrix were very weak. The interaction between the B₄C particles and the elastomer was considerably stronger with an association with sizable dimensions. They had plump conterminous surfaces formed by adsorbed elastomer film.

Dependence of volume resistivity on temperature and pressure

The dependence of NBR-SiC and NBR-B₄C composite volume resistivity on temperature is shown in Figure 6. It can be seen that with increasing temperature

the volume resistivity of all samples decreased, but the volume resistivity values of the sample without filler and the sample containing 45 phr of filler were quite close to each other. It is worth mentioning that for the composites investigated a temperature hysteresis was not observed. This suggests that the incorporation of filler into the rubber matrix increased the thermal stability of the composites. The same matrix and close values of SiC and B₄C resistivity are the reasons for the very close results obtained for the temperature dependence of the resistivity of the composites. The lower values for B₄C samples may be explained by their having better current carrier emission than the SiC samples. The resistivity temperature characteristics shown in Figure 7 confirmed this. The B₄C curve was below the SiC curve, which explains its more favorable influence on composite electrical conductivity. One of the important parameters characterizing the electrical properties of the composites is the temperature coefficient of resistivity (α). It was determined by the equation:⁶

$$\alpha = \rho_{T2} - \rho_{T1} / (\rho_{T1}T_2 - \rho_{T2}T_1) \quad (3)$$

where ρ_{T1} and ρ_{T2} are the volume resistivity at temperatures T_1 and T_2 , respectively.

The obtained values for the fillers used were $\alpha_{\text{SiC}} = -6.97 \times 10^{-3} \text{ K}^{-1}$ and $\alpha_{\text{B4C}} = -6.85 \times 10^{-3} \text{ K}^{-1}$.

In accordance with the straight parts of the curves shown in Figure 6(a,b), two values for α could be calculated for each composite, one for the temperature range 20°C–80°C and the other for the tempera-

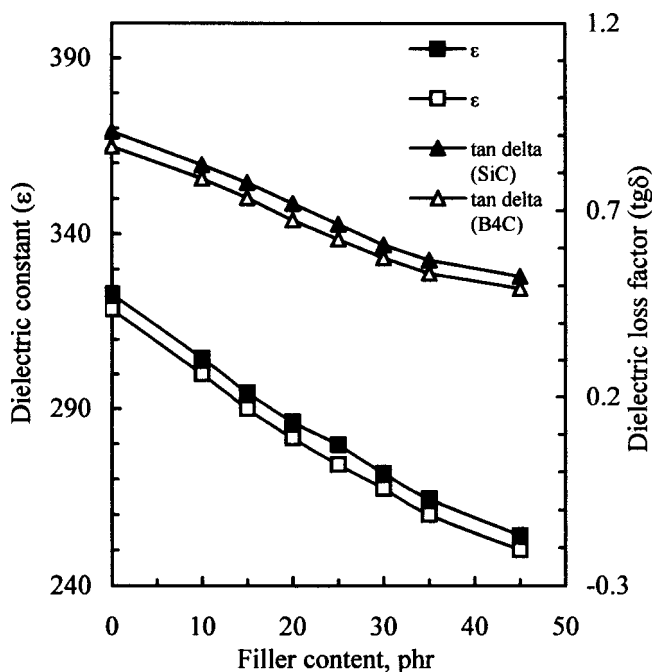


Figure 4 Changes in ϵ and $\tan \delta$ as a function of filler concentration at 1 kHz for NBR composites.

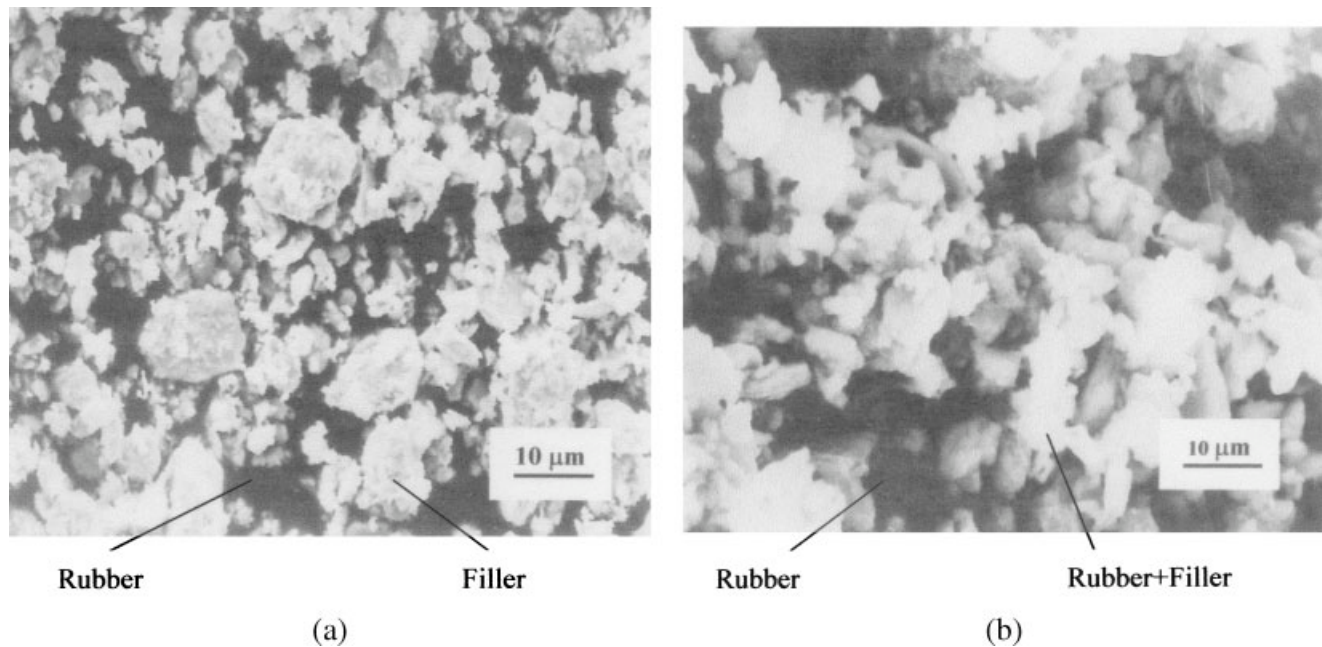


Figure 5 (a) SEM picture of NBR-SiC composite; (b) SEM picture of NBR-B₄C composite.

ture range 80°C–140°C. The values determined were $\alpha_{20-80} = -1.25 \times 10^{-2} \text{ K}^{-1}$ and $\alpha_{80-140} = -6.49 \times 10^{-3} \text{ K}^{-1}$ for the unfilled NBR composites; $\alpha_{20-80} = -1.24 \times 10^{-2} \text{ K}^{-1}$ and $\alpha_{80-140} = -6.56 \times 10^{-3} \text{ K}^{-1}$ for the SiC-filled NBR composites; and $\alpha_{20-80} = -1.25 \times 10^{-2} \text{ K}^{-1}$ and $\alpha_{80-140} = -6.52 \times 10^{-3} \text{ K}^{-1}$ for the B₄C-filled NBR composites.

The amount of filler did not influence the slope of the curves, and as a result the coefficients were identical depending on the filling. The results obtained show that the composites investigated may be classified as negative thermistors. The B₄C was more sensitive to

temperature changes than was the SiC. The properties of the elastomer matrix strongly influenced the composite temperature coefficient of resistivity.

Compression as a factor changing material volume resistivity was applied on the composites investigated. The ρ_v values at 25°C depending on pressure are presented in Figure 8. All curves had an identical slope, equal to the slope of the unfilled NBR composite. This confirmed the rubber matrix had the predominant role. Their scandent situation (increasing the volume resistivity with the filler content) depending on filling was provoked by the rubber layers among the

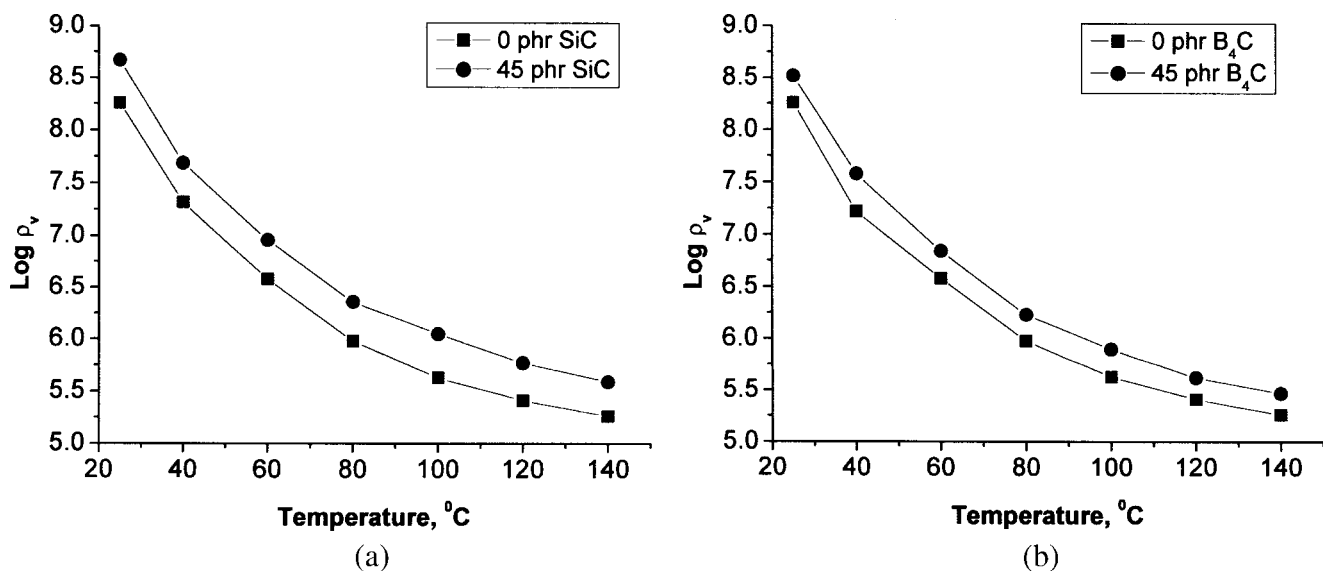


Figure 6 (a) ρ_v -Temperature dependence of NBR-SiC composites; (b) ρ_v -temperature dependence of NBR-B₄C composites.

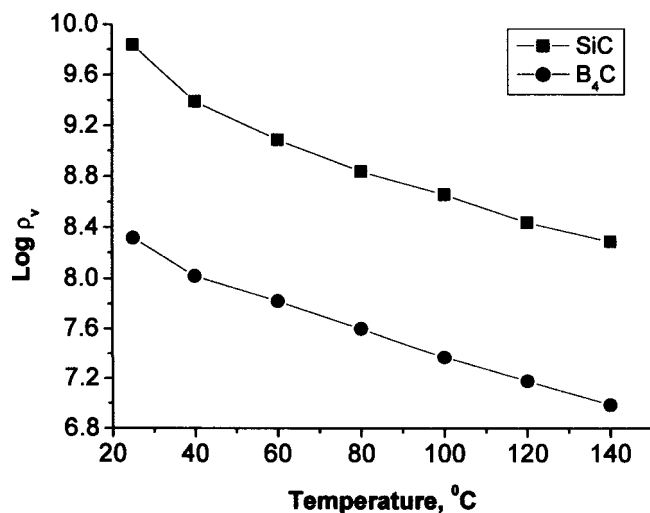
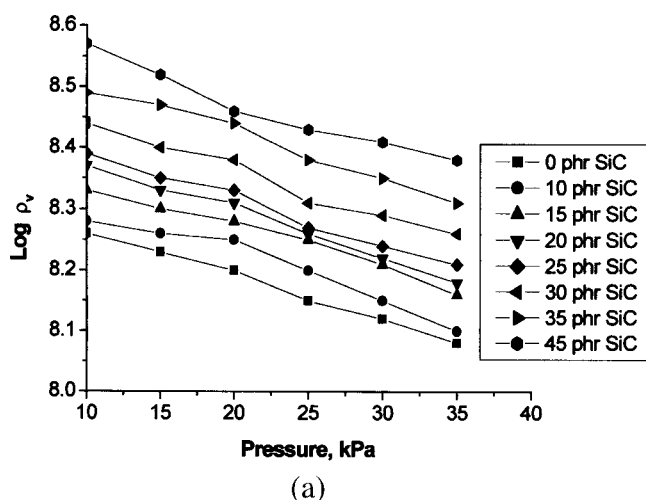


Figure 7 ρ_v -Temperature dependence of SiC and B₄C.

particles that became thinner with increasing filler concentration, thus making current carrier transport more difficult. The descending trend in resistivity with increasing applied pressure may be explained by the rubber layer congestion, which made the transitions of the current carriers from one structural unit to another easier. These facilitating transitions were possible if the current carriers were only electrons. If the carriers were ions, because of their bigger size, their transitions through a more dense structure would be difficult, and as a result the resistivity increased with increasing applied pressure. The composite electron conductivity was also shown by the thermosonde method. The linear trend of decreasing composite volume resistivity with increasing applied pressure showed that the NBR composites investigated may be successfully used as pressure sensors.



The compression coefficient of the volume resistivity (PC_ρ) was determined by the equation¹¹

$$PC_\rho = \left(\frac{\Delta\rho}{\rho_0} \right) \left(\frac{1}{\Delta P} \right) \quad (4)$$

where $\Delta\rho$ is the change in volume resistivity and ΔP is the change in pressure.

The values of PC_ρ as a function of filler concentration are shown in Figure 9. The PC_ρ , like the temperature coefficient of resistivity (α) was negative because of the decreasing values of ρ_v . It increased with increasing filler concentration; the sensibility to compression influences also increased. PC_ρ values were bigger for NBR-B₄C vulcanizates than for NBR-SiC. Their "sensibility" was also bigger. The observed increasing of composite "sensibility" to compression influence with increasing filler concentration may be explained by the coordinating role of the filler particles on the macromolecules. During the compounding process the particles penetrating among the macromolecule chains "disentangled" them and arranged them parallel one to another. This more perfect (than globular) structure made the contacts among the macromolecules easier when an external pressure was applied to the composite. This is why the PC_ρ increased when the amount of filler increased. The B₄C had better coordinating properties because of its higher adhesion to the macromolecules (Fig. 5), which explains the NBR-B₄C composites having higher PC_ρ values than the NBR-SiC composites.

Current carrier transport

The resistivity of the composites investigated and their changes define them as materials with semiconducting properties. The chemical composition and

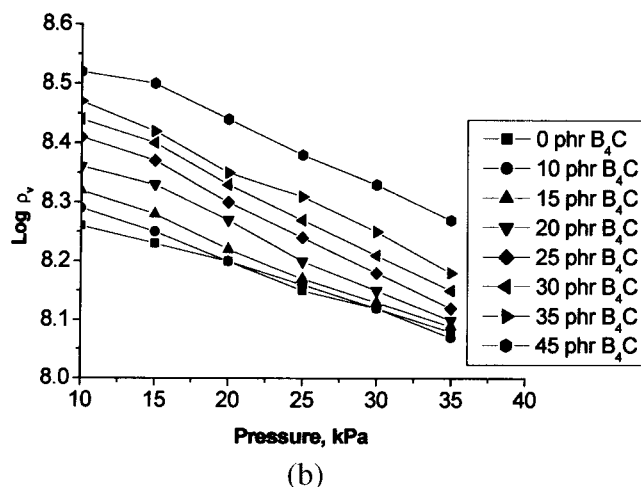


Figure 8 (a) ρ_v -Pressure dependence of NBR-SiC composites at 25°C; (b) ρ_v -pressure dependence of NBR-B₄C composites at 25°C.

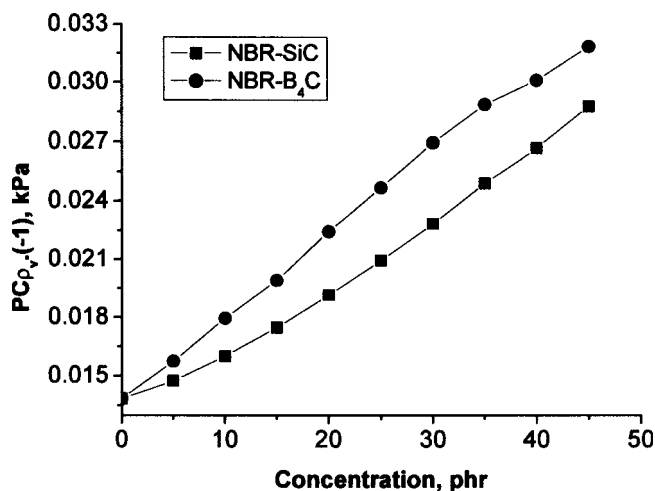


Figure 9 PC_p as a function of filler content for NBR-SiC and NBR-B₄C composites.

conformations of the matrix macromolecules, specific features of the fillers, the ingredients participating in the vulcanization process, and other casual impurities influenced the origin, the type of current carriers, and their transport through the mass of the vulcanizates. Despite the available theoretical interpretations of the conductivity mechanisms, there is not a fully complete theory explaining the electrical properties of these types of composites. The exponential dependence of the conductivity on temperature may be used as a basis to apply the zone theory, which explains the semiconducting properties of the inorganic semiconductors. But the small mobility of the carriers, less than $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, is not in correspondence with the requirements of the zone theory and restricts its applicability for polymer materials. The small mobility of the current carriers may be connected with their localization in some places where they stay longer than the continuance of the pauses in the moving of the electrons and holes in the inorganic semiconductors. That is why in investigations concerning polymer-based composite semiconductors, the so-called theory of hopping transport of carriers is often used. In accordance with this theory, the dependence of the electrical conductivity on temperature is also exponential, but the activation (hopping) energy is higher than the energy in zone transitions because of the larger distance among the places for localization and spatial hindering caused by macromolecular micro-Brownian motion. In zone theory activation energy (E_a) may be calculated by the well-known exponential dependence of conductivity on temperature:¹²

$$\sigma = \sigma_0 e^{-E_a/2KT} \quad (5)$$

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, and T is the temperature on the absolute scale.

The hopping activation energy (E_h) of the composites may be calculated by the equation¹³

$$\sigma\sqrt{T} = \sigma_0 e^{-E_h/KT} \quad (6)$$

The calculated activation energy values of the carriers at the zone transitions of carriers were $E_a^{\text{SiC}} = 0.62 \text{ eV}$ and $E_a^{\text{B}_4\text{C}} = 0.53 \text{ eV}$.

It is evident that the energy for SiC was higher, which corresponded with the volume resistivity of SiC and B₄C.

The dependence of activation energy at zonal and hopping transitions (E_a and E_h) of current carriers on the filler concentration for NBR-based composites is presented in Figure 10, from which it may be concluded that the activation energy for current carrier transport in NBR-SiC composites was higher than that in NBR-B₄C composites. The energy increased with increasing filler concentration. E_h was higher than E_a for all samples. The higher activation energy for rubber matrix (0 phr, Fig. 10) than for SiC and B₄C shows that the current carrier transition through it occurred predominantly by hops; at the same time the transitions through the filler particles were zonal. The dependence of E_a and E_h on the degree of filling confirmed this assumption. When the amount of filler increased, the E_a of the filler particle transition stayed almost constant because the structure and properties of SiC and B₄C did not change. At the same time E_h increased because of the decreasing thickness of the rubber layers among the particles and the increasing distance between the places exchanging current carriers. Thus the values of E_a increased under the influence of the dominating

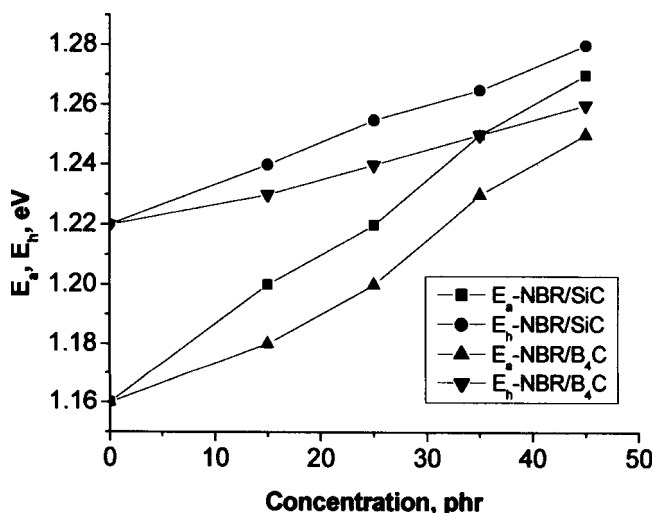


Figure 10 E_a and E_h as a function of filler content for NBR-SiC and NBR-B₄C composites.

values of E_h . The influence of the polymer matrix on composite conductivity was greater than the influence of the fillers. If the filler influence on composite conductivity were predominant, the influence of the zonal transition would also be higher and the total E_a would decrease with increasing filler concentration. As a result, the curves shown in Figure 10 would have to be descending, but this was not observed. Another result confirming the predominant role of the matrix and the hopping mechanism of conductivity is the ρ_v values measured in the alternative electric field. In accordance with Mott and Towse,¹⁴ when the current carrier transport occurred by hops, the resistivity measured in the alternative current had to decrease with increasing frequency, in correspondence with the results shown in Figure 2.

CONCLUSIONS

Polymer composites consisting of NBR and SiC/B₄C, in selected ratios may be characterized as semiconducting materials. Resistivity decreased considerably with increasing temperature and pressure. This makes it possible for these polymers to be used as good negative thermoresistors (NTCR linear thermistors) and strain transducers in pressure sensors. The amount of current carriers and their mobility, determined by Hall, decreased with increasing filler con-

centration. The current carriers were predominantly electrons. In correspondence with the results for the resistivity measured in alternative current and E_a and E_h , the activation energy values, determined as a function of the filling, it is clear that current carrier transport occurred predominantly by hops realized by the dominant role of the elastomer matrix.

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