Electrical properties of conductive polyisoprene/high structured carbon black composites in the temperature range 90 – 335 K

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This presentation deals with electrical properties study of high structured carbon black/polyisoprene (HSCB/PI) composites of various HSCB concentrations (8, 9, 10 and 11 mass parts) in the temperature range 90K – 335K. The DC electrical resistance of the sample was measured as a function of temperature. Composites exhibit negative temperature coefficient of resistivity (TCR) below the room temperature. The resistivity varies exponentially with temperature similar to a semiconducting behavior. Similar to doped semiconducting materials, composites have two different activation energies. The activation energies decrease with increasing HSCB concentration. Hysteresis of R(T) is not observed.

Above the room temperature composites show positive TCR. Coefficient decreases with increasing HSCB concentration. There is observed small hysteresis of R(T).

The resistance change with temperature in both cases is reversible.

We have found that the investigated composite has wide multifunctional sensor properties. It shows temperature, strain and organic solvent vapor sensing behavior.

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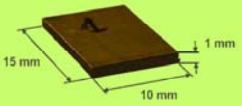
ABSTRACT

The studies of electrical properties of the polyisoprene (PI) matrix/high structure carbon black (HSCB) composites (PCBC) with various concentrations (8, 9, 10 and 11 mass parts) of filler have been carried out in the temperature interval 90K – 335K. All composites exhibit negative temperature coefficient of resistivity (NTCR) at low temperatures and show positive temperature coefficient of resistivity (PTCR) above approximately 280 K. The existence of NTCR and PTCR is explained due to overlapping of two general processes – thermally activated charge transport on the one hand and broadening of tunneling gaps between conductive particles caused by different thermal expansion of matrix and filler particles on the second hand. Mott's variable range hopping (VRH) and near neighbor hopping (NNH) as well as Sheng'sl thermal fluctuation induced tunneling (TFIT) of charge carriers are discussed as possible charge transport mechanisms in PCBC in different temperature regions.

EXPERIMENTAL

PCBC have been made by mixing of extra-conductive HSCB Degussa Printex XE2 together with necessary additional ingredients into raw natural rubber Thick Pale Creppe matrix. In our approach this was done using cold rolls. Many samples with different HSCB concentrations (8, 9, 10, 11 mass parts (m.p.)) has been made. Afterwards the samples were vulcanized in the stainless steel mould, using 50 μm thick brass mould inserts as electrodes, under pressure 30x10^5 Pa at 150^{o}C for 15 minutes. A flat ~1 mm thick sticks of PCBC were made. These sticks were cut into flat pieces with dimensions of 10x15 mm using diamond disk cutter to avoid unnecessary squeezing.

A home made liquid nitrogen thermostat was used for making measurements of resistivity at different temperatures. Thermostat consisted of brass cylinder, where was placed sample and platinum thermo-resistor. Platinum resistor was used to measure temperature change. Measurements were made in helium atmosphere.



RESULTS AND DISCUSSION

The volume resistance R of PCBC was measured in the temperature range of 90 K – 335 K. In figure 1 the experimental data of R(T) for PCBC with 9 m.p. of HSCB are represented. One can distinguish three temperature regions: region I (90 K – 230 K); region II (240 K – 270 K) and region III (280 K – 335 K) with apparently different charge transport mechanisms. The relative resistivity $\Delta\rho/\rho_o$ as function of temperature calculated from the experimental results are given on Figure 2 for all investigated composites. It is seen that character of the resistivity temperature dependence is the same for all samples with different HSCB concentrations. Figure 3 shows a plot of the logarithm of electrical conductivity versus the temperature inverse for all investigated samples.

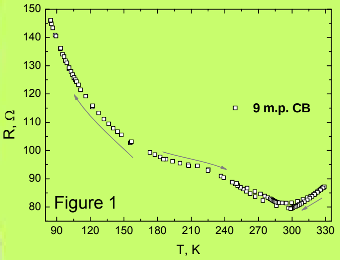


Figure 1

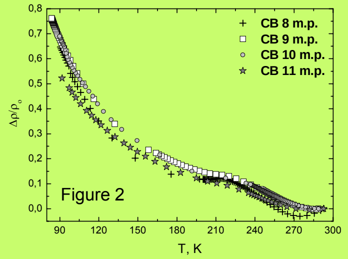


Figure 2

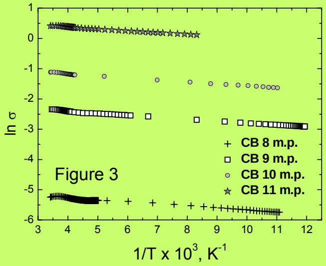


Figure 3

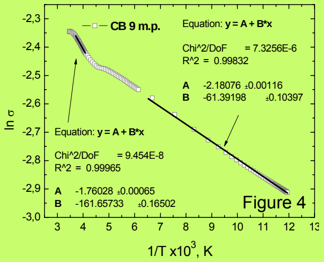


Figure 4

The conductivity of the samples can be analyzed by well-known Arrhenius relation: $\sigma = \sigma_0 \exp\left(-\frac{\Delta E_a}{kT}\right)$

where σ_o is the pre-exponential factor and ΔE_a is the activation energy for conduction. Two different thermally activated charge transport mechanisms can be evaluated from figure 4 where lnσ with (1/T) is given for composite with 9 m.p. of HSCB. The activation energy as well as σ_o values for the two temperature ranges (region I and region II) is given in a Table. E_{a1}, σ_{o1} corresponds to region I and E_{a2}, σ_{o2} to region II. The activation energy decreases with increasing of the HSCB concentration that is similar to most conductive polymer composites with carbon filler content. The decrease in ΔE_a with increasing of HSCB filler concentration, is explained with increasing of impurities concentration, and can be attributed to the increase in the number of the localized states inside the energy gap which causes a shift of the Fermi energy level towards the conduction band or valence band. Next step is to elucidate which thermally induced charge transition mechanism corresponds to the two generally different values of ΔE_a.

The most appropriate charge transport mechanism to region II is believed to be Near Neighbor Hopping. Electron receives energy from a phonon, which enables it to move to a near by state above E_F, conductivity can be expressed:

$$\sigma = \sigma_0 \exp\left(-\frac{\varepsilon_3}{kT}\right)$$

The ε_3 is of the form $\varepsilon_3 \sim 1/N(E_F)a_3$ where a is the distance between nearest neighbours.

For region I the most appropriate charge transport mechanism is believed to be Variable Range Hopping.

$$\sigma = \sigma_0 \exp\left(-\left(\frac{T_0}{T}\right)^n\right)$$

where the parameter σ_o can be considered as the limiting value of conductivity at infinite temperature, T_o is the characteristic temperature that determines the thermally activated hopping and considered as a measure of disorder and the index n is related to the dimensionality d of the transport process: $n = 1/(1+d)$ where d = 1,2,3.

	CB 8 m.p.	**CB 9 m.p.**	**CB 10 m.p.**	**CB 11 m.p.**
E_{a1}, eV	0,0064	0,0056	0,0055	0,0046
E_{a2}, eV	0,017	0,013	0,0125	0,01
σ_{o1}, (S/m)	0,0073	0,12	0,11	1,79
σ_{o2}, (S/m)	0,012	0,16	0,14	2,34

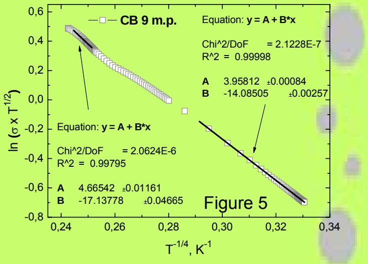


Figure 5

Sheng described a mechanism for tunneling of electrons through a barrier whose height is varying due to local temperature fluctuations. In this model it is assumed that the two conductive particles separated by insulating layer form a junction and charge-carriers tunnel through this junction. Due to random thermal motion of electrons there can be temporary deficit or excess of charge at the tunnel junction surfaces resulting in fluctuation of voltage at the junction known as thermal fluctuation voltage. This mechanism is named as thermal fluctuation induced tunneling (TFIT). In this model, the temperature dependence of the conductivity of sample is governed by the equation

$$\sigma = \sigma_0 \exp[-\frac{T_1}{T+T_0}] \qquad T_1 = \omega A\varepsilon_0^2/8\pi k \qquad T_0 = A\varepsilon_0^2/4\pi^2\chi k$$

where ω is width of tunneling gap, A is the area of the capacitance formed by the junction, k – is the Boltzmann constant, $\varepsilon_o = 4V_o/e\omega$, where V_0 is the potential barrier height, e is the electron charge, and $\chi = (2mV_o/h^2)^{1/2}$, where m is the electron mass and h is Planck's constant. Figure 6 represents a good fit of the experimental results for PCBC composite with 9 m.p. of HSCB.

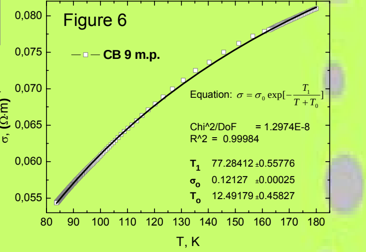


Figure 6

In the temperature range 90–200 K the VRH mechanism and TFIT mechanism take part simultaneously and the resistivity decreases. In the region 210–270 K the thermal fluctuations decrease the potential barrier which results in more tunneling as well as the more carriers are excited into the localized states at the band edges (NNH). Nearly up to 270-280 K the thermal fluctuation dominates over thermal expansion. In the temperature region 270-280 K the resistance shows a minimum value. So there are two effects, one increases conductivity but other decreases it. These two effects act simultaneously. This implies that differential thermal expansion balances the TFIT. Above the 280 K the differential thermal expansion of matrix (α = 225 x 10^{-6} ^{o}C^{-1} at T=20^{o}C) and filler (α ~ 6 x 10^{-6} ^{o}C^{-1} at T=20^{o}C) determines the raising of resistivity as it is shown in Figure 2.

CONCLUSIONS

The electrical conductivity of PCBC has been investigated. It has been found out, that along the temperature range of 90 K-335 K there are multiple mechanisms of conduction involved. One can distinguish three temperature regions: region I (90 K – 230 K); region II (240 K – 270 K) and region III (280 K – 335 K) with apparently different charge transport mechanisms. For region I the most appropriate charge transport mechanism is believed to be Variable Range Hopping. This is proved by analyzing different activation energies for temperature regions I and II. During the same analysis, it has been considered, that Near Neighbor Hopping is dominant during temperature region II. For both these regions Thermally Induced Charge Hopping and Thermal Fluctuation Induced Tunelling is proved to happen simultaneously. This leads to generally negative temperature coefficient of resistivity with different slopes below approximately 280 K. For region III the tunneling intensity has noticeably raised, but as well it is the thermal expansion of matrix, resulting a broadening of tunneling gaps between the high structure carbon black particles and a positive temperature coefficient of resistivity of the composite at the end.