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Natural Rubber Filled SiC and B_4C Ceramic Composites as a New NTC Thermistors and Piezoresistive Sensor Materials

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A novel electrically conductive composite for NTC thermistor and piezoresistive sensor was successfully fabricated by homogeneously dispersing conductive SiC and B_4C in an insulating natural rubber (NR) matrix. The morphology of the composites was investigated by means of scanning electron microscopy, cross linking density (*n*), volume fraction of rubber (V_r), and interparticle distance among conductive phases (r_p). The influence of the filler concentrations on the mechanical properties such as modulus of elasticity (*E*); hardness shore A (*H*), and elongation at break (*EB*) were studied in details. The dependences of volume resistivity of NR based composites filled with B_4C and SiC as a function of fillers concentration was investigated. Temperature dependencies of volume resistivity were also measured to examine the possible application of the composites to polymer linear negative temperature (NTC) thermistors. Furthermore, the temperature dependencies of dielectric constant of the composites were studied. For practical application, the thermal stability of the composites was examined by means of resistivity temperature and pressure hysteresis cycle. In parallel, the conduction mechanism of conductivity of the composites was interpreted in terms of the computed the activation and hopping energy. The applicability of the composites to piezoresistive sensor was examined too. The good mechanical properties and thermal stability of NR composites behavior can be utilized for fabricating various electronic devices as NTC thermistors and piezoresistive sensor (i.e. transducers in pressure sensors). POLYM. COMPOS., 00:000–000, 2006. © 2006 Society of Plastics Engineers

INTRODUCTION

Electrically conductive polymer composites (ECPC) are obtained when conductive particles are implanted into an insulating polymer matrix [1–3]. Recent efforts have been focused on active ECPC the conductivity of which would strongly depend on external thermodynamic parameters such as pressure, temperature, and others [3–9]. Metal carbides are a group of ceramic materials with outstanding and attractive properties for technological applications. Among these materials, SiC and B_4C has unusual physical and chemical properties such as high hardness, superior wear resistance, high modulus, low density, high melting temperature, high corrosion resistance, high electrical conductivity [1]. Polymer composites filled with metal carbides are of interest for many fields of engineering. This interest arises from the fact that the electrical characteristics of such composites are close to the properties of filler themselves. The properties of these composites are mainly varied as a function of conductive phase loading. At very low conductive loading, the electrical resistivity of these composites is very close to that of a polymer matrix. The temperature coefficient of resistance may be positive (PTC), negative (NTC), or zero depending upon the volume fraction of filler and the nature of the polymer and the type of filler [10–14]. NTC thermistors are found in an ever-increasing number of elec-

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TABLE 1. Formulation of mixes.[a]

Ingredients	NR0	NR10	NR15	NR25	NR35	NR45
NR	100	100	100	100	100	100
ZnO	4	4	4	4	4	4
Stearic acid	2	2	2	2	2	2
MBZ	3	3	3	3	3	3
IPA	1.5	1.5	1.5	1.5	1.5	1.5
Glycerol	5	5	5	5	5	5
Sulfur	1	1	1	1	1	1
B_4C	0	10	15	25	35	45
SiC	0	10	15	25	35	45

[a] All the ingredients are in phr (weight per hundred weight of rubber).

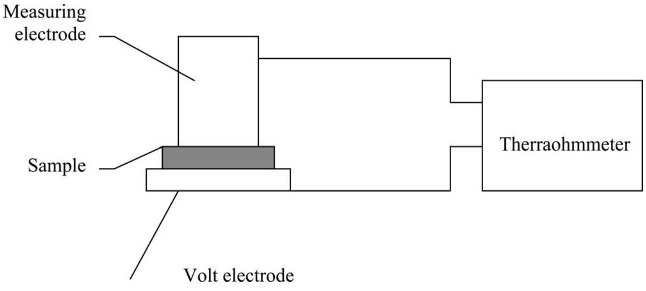

FIG. 1. Circuit used to measure the change in resistivity with applied pressure.

trical and electronic products. Commercial utilization of NTC sensors began in 1930's in telecommunication circuit compensation and temperature measurements. Later, they were introduced in aerospace and cryogenic applications, liquid level sensing, vacuum and pressure gauges, etc [14–20]. In general, the electrical resistivity of ECPC decreases gradually with an increasing filler loading and finally drops sharply at some critical threshold. However, in practical applications such as pressure sensor and NTC thermistors, the sharp fall of resistivity of the composites is not desirable [6]. To overcome these problems, in the present article, we succeed to fabricate a new NTC thermistors and piezoresistive sensor from natural rubber (NR) filled SiC and B_4C composites. The effects of filler content on the room temperature volume resistivity, microstructure, and mechanical properties of the composites were investigated. The effect of temperature on electrical volume resistivity and dielectric constant of the composites has also been reported. For practical application, the thermal stability of the composites was examined by means of resistivity temperature and pressure hysteresis cycle. The applicability of the composites as piezoresistive sensor was tested too.

EXPERIMENTAL

Natural rubber (NR) grade (SMR L) was supplied by Bayer, Germany and used as a polymer matrix. SiC with particle size 1 μm, and B_4C with particle size 2 μm, were used as conductive and reinforcing fillers obtained from Wako Chemical Company, Toyo, Japan. Zinc oxide, strearic acid, glycerol, and sulphur were of commercial grade. Other chemicals such as 2-mercaptobenzothiazole (Vulkacit Merkapto) and *N*-isopropyl-N^1-phenyl-*p*-phenilendiamine (Vulkanox 4010-NA) were from Bayer, Germany. All the chemicals/reagents were used as such without further purification. The materials used and compound formulations are given in Table 1. These materials were arranged in an order in which they were added during the preparation. The rubber compounds were prepared on a two-roll mill at a 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 (Karl Kolb, Germany), using a special home-made steel mould at temperature 155°C for 10 min under pressure of 12 MPa. Samples in a sheet form ($90 \times 60 \times 2$ mm^3) were obtained as a final result. These vulcanization sheets were allowed to mature at room temperature for 48 h before testing. The modulus of elasticity and elongation at break was determined using Shimatzo universal testing machine, with a load cell of 2 KN at a crosshead speed of 300 mm min^{-1}. The test was done at 20°C. The hardness of the specimen was also measured, according to ASTM D 2240–81 using Shore A type durometer. The room temperature resistivity was calculated from the measured resistance, electrode area, and sample thickness. The evaluation of the volume resistivity –temperature characteristics was performed by introducing a specimen into a small control-temperature chamber and raising the temperature of the chamber from 20 to 140°C, and then measuring the DC resistance at that point using Terraohmmeter Teralin II (made in Germany). The dielectric constant was measured using RLC bridge, (3532-Z Hitester, Hioki, Japan) at 1 kHz. A JOEL scanning electron microscopy (SEM) was used to observe the microstructure of the composites. The surface of the samples was coated by carbon ink to ovoid electrostatic charge. The circuit used to display the change in volume resistivity with applied pressure is depicted in Fig. 1. The cross linking density (n) is determined by equilibrium solvent swelling methods: the samples were swelled in ethanol for 48 h until equilibrium swelled volume reached. The molecular weight between crosslinks M_c is related to degree of crosslinking by the following relation 1:

$$n = \frac{\rho_r}{M_c} \tag{1}$$

where ρ_r is the elastomer density and M_c is calculated by the following equation:

$$M_c = \frac{\rho_r V_s \left(\frac{V_r}{2} - V_r^{1/3} \right)}{\ln(1 - V_r) + V_r + \chi V_r^2} \tag{2}$$

where V_s solvent molar volume, χ polymer–solvent interaction parameter, which was 0.42 for NR-ethanol at room temperature [18] and V_r is the equilibrium volume fraction of elastomer and is given by [6]:

$$V_r = \frac{\rho_s M_r}{\rho_s M_r + \rho_r M_s} \tag{3}$$

where ρ_s is the solvent density and M_r and M_s are the weights of dry rubber and absorbed solvent, respectively.

The interparticle distance among conductive particles (r_p) is calculated as follows [18]:

$$r_p = \left(\frac{\pi D^3 \rho_c}{6w}\right)^{\frac{1}{3}} - 1 \tag{4}$$

where ρ_c is the specific gravity of the composites and was measured using the Archimedes method, D is the filler particle diameter and w is the weight fraction of the filler. The drift mobility (μ) of the samples has been calculated using the equation [16]:

$$\mu = \frac{1}{Ne\rho_v} \tag{5}$$

where e is the charge on electron, ρ_v is the composite volume resistivity, N is the concentration of charge carriers, which can be calculated from the following equation:

$$N = \frac{N_A \rho_c N_f}{M_n} \tag{6}$$

where N_A is the Avogadro's number, N_f is the number of filler atoms in the composites, and M_n is the molecular weight of filler.

RESULTS AND DISCUSSION

Relationship Between the Static Volume Resistivity and the Network Structure

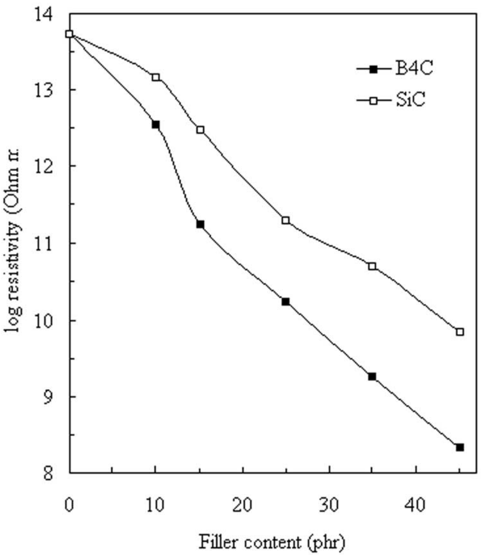

FIG. 2. Dependence of volume resistivity on filler concentration for two composites.

The dependences of volume resistivity of NR/B_4C and NR/SiC composites on the fillers concentration at 20°C is depicted in Fig. 2. The volume resistivity decreases with the increasing of the fillers concentration for both two systems. The volume resistivity values of NR/B_4C composites are lower than these of NR/SiC composites because SiC are intrinsically less conductive than either B_4C. However, the decrease of resistivity with increasing filler volume fraction is due to the formation of conductive network by the dispersion of SiC and B_4C filler in the NR matrix. Upon further increase in filler content, there is more and more increase in the conducting paths along with a gradual decrease in interparticle distance, resulting in a decrease in resistivity of the two elastomer composites. This is supported by the fact that the interparticle distance among conductive phases (r_p) of the composites decreases with increasing filler content as shown in Fig. 3. Interestingly, the observed linear relations between the log resistivity and the volume fraction of fillers content allow one to simply predict the composites resistivity for any desirable utilization electronic technology. However, the dependencies of cross linking density (n) and volume fraction of rubber (V_r) of composites vs. volume portion of the filler are depicted in Fig. 3. The cross linking density is found to be increase with increase in content of filler in the elastomer composites. This is associated to the

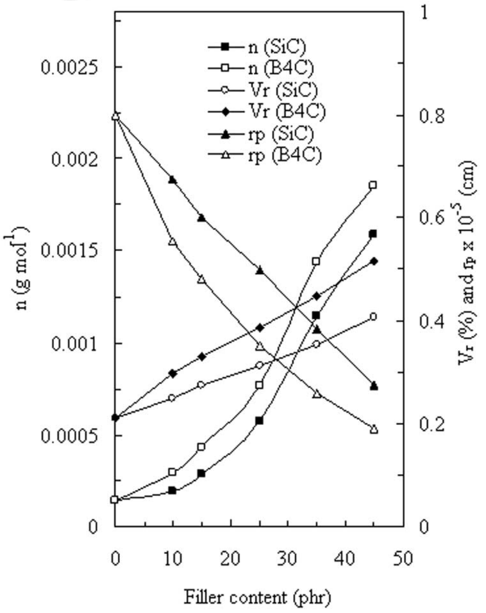

FIG. 3. Cross linking density, volume fraction of rubber and average particle among conductive phases as a function of filler content.

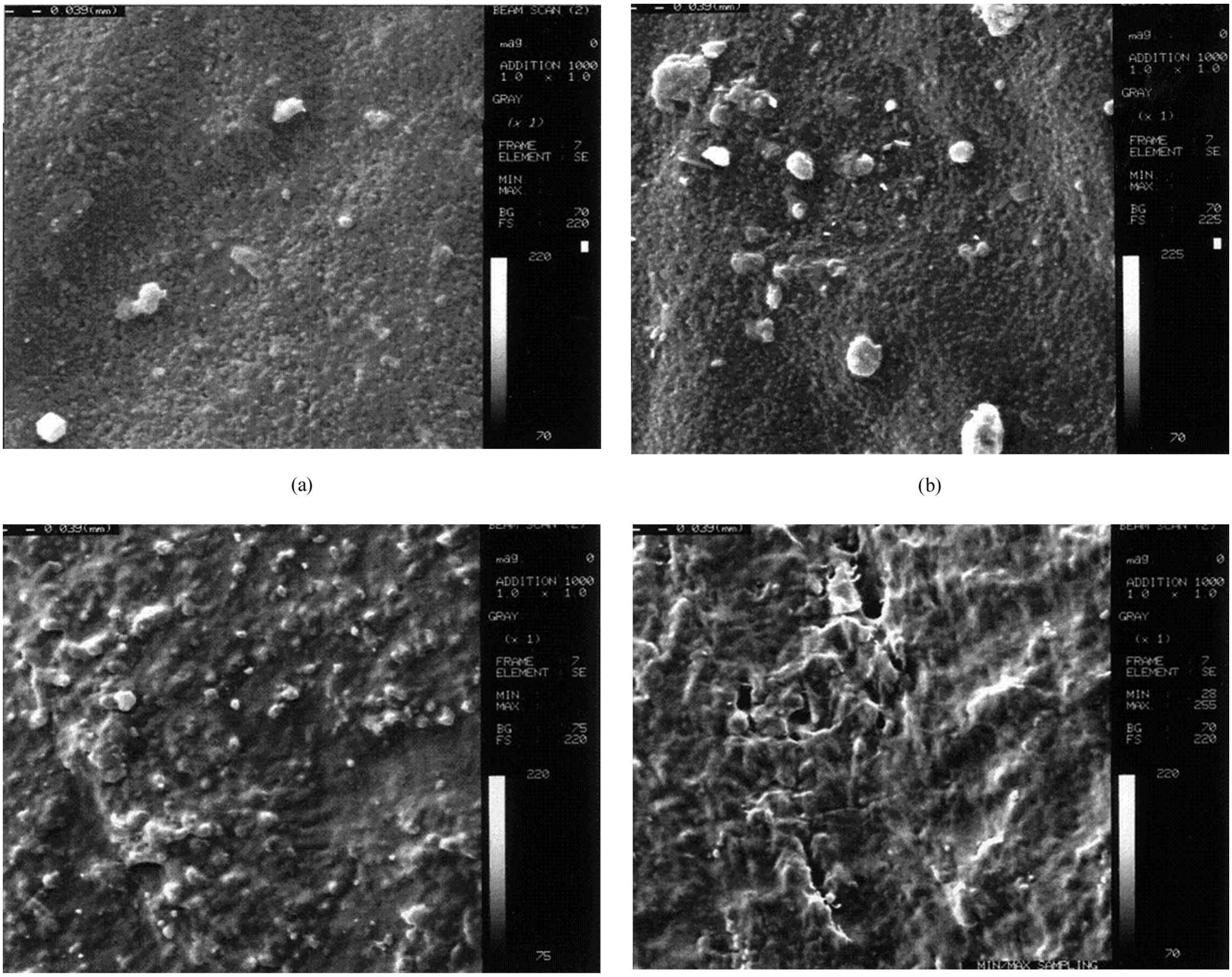

FIG. 4. SEM micrographs for (a) NRS10 samples, (b) NRB10 sample, (c) NRS45sample, and (d) NRB45 sample.

increase of the intermolecular forces among rubber chains and filler particles. This is supported by the fact that the rubber volume fraction in the composites increases with increasing filler content as shown in Fig. 3. That means that the free volume between rubber molecules is reduced leading to increase of cross linking density with increasing filler content as confirmed by the SEM. The dispersion of filler particles can be deduced by analysis of the SEM images. SEM micrographs for NRS10 and NRB10 samples are shown in Fig. 4a and 4b, respectively. It is clear that the composites structure consists of conductive fillers separated by rubber layers, and there are a weak interface adhesion between matrix and filler. In other words, the network formation has not formed because of the increase of the interparticle distance among conductive particles. On the contrary, an SEM micrograph for NRS45 and NRB45 samples in Fig. 4c and 4d, respectively, shows the good distribution and interaction among filler and matrix. This may result in a lower separation between conductive phases thus increasing the possibility of electron tunneling by percolation, in turns leads to a resistivity decrease as confirmed above.

Mechanical Properties

To get more information on the effect of fillers on the network structure, we studied the mechanical properties such as modulus of elasticity (*E*), hardness (*H*) and elongation at break (*EB*) of elastomer composites. Figure 5 depicts the modulus of elasticity, hardness, and elongation at break as a function of filler concentration for two systems. It is clear that modulus of elsticity increases with an increase in filler content for two elastomer composites. This fact is associated with the higher interfacial adhesion and cross linking density among filler and matrix with increasing filler loadings. We believe that, the high interface adhesion increases the effectiveness of the stress transfer from rubber chains and work requires deforming the composites. Shore

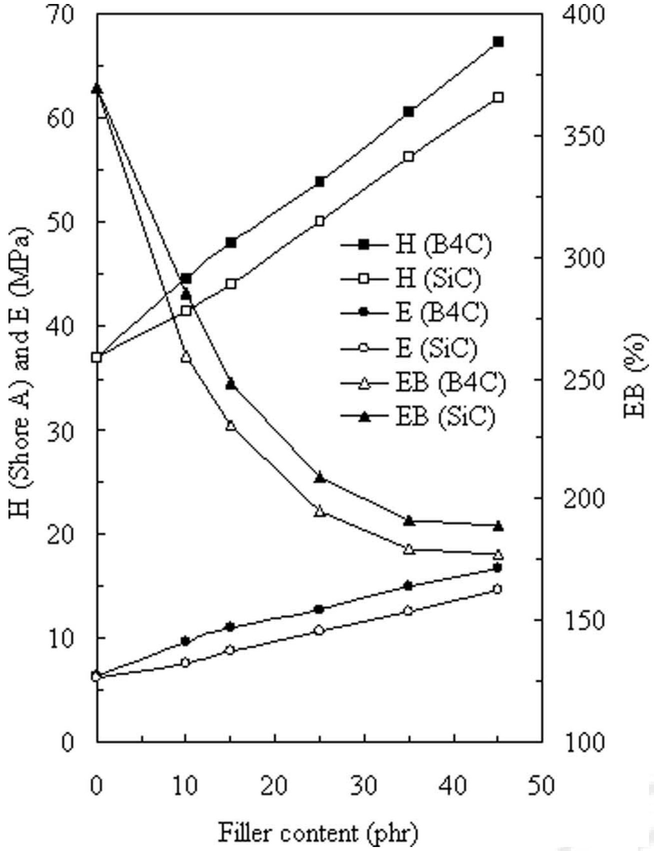

FIG. 5. Modulus of elasticity (*E*), hardness (*H*) and elongation at break (*EB*) of elastomer composites versus volume fraction of fillers.

A hardness of elastomer composites are presented in Fig. 5. It is seen that hardness increases with increase in content of fillers. The reason is that filler included into the elastomer matrix behaves like physical cross linking points and restrict the movement of rubber chains. The improvement in both *E* and *H* may be caused by the strong interactions between rubber matrix and filler, which leads to good dispersion of filler in the composites. These well dispersed filler may have an effect of physical cross linking points, thus increase both the *E* and *H*. On the other hand, we observed a steady decrease of *EB* with an increase in filler content for two elastomer composites. This can be attributed to for two reasons. First, the inclusion of filler in the rubber matrix acts as a reinforcing effect, and also in a formation of sites of stress concentration. The other possible reason is due to the cross linking networks (chemical bonding) between flexible rubber matrix and stiff filler or between the rubber intermolecular chain [3, 10].

NTC Thermistors

F6

The dependences of volume resistivity on the temperature for NR/B_4C and NR/SiC composites are presented in Fig. 6a and 6b, respectively. The resistivity of all tested samples increases with the increase of temperature, i.e., a negative coefficient of temperature NTC effect has been noticed. There are three possible reasons for increasing resistivity with temperature. First, the flocculation of con-

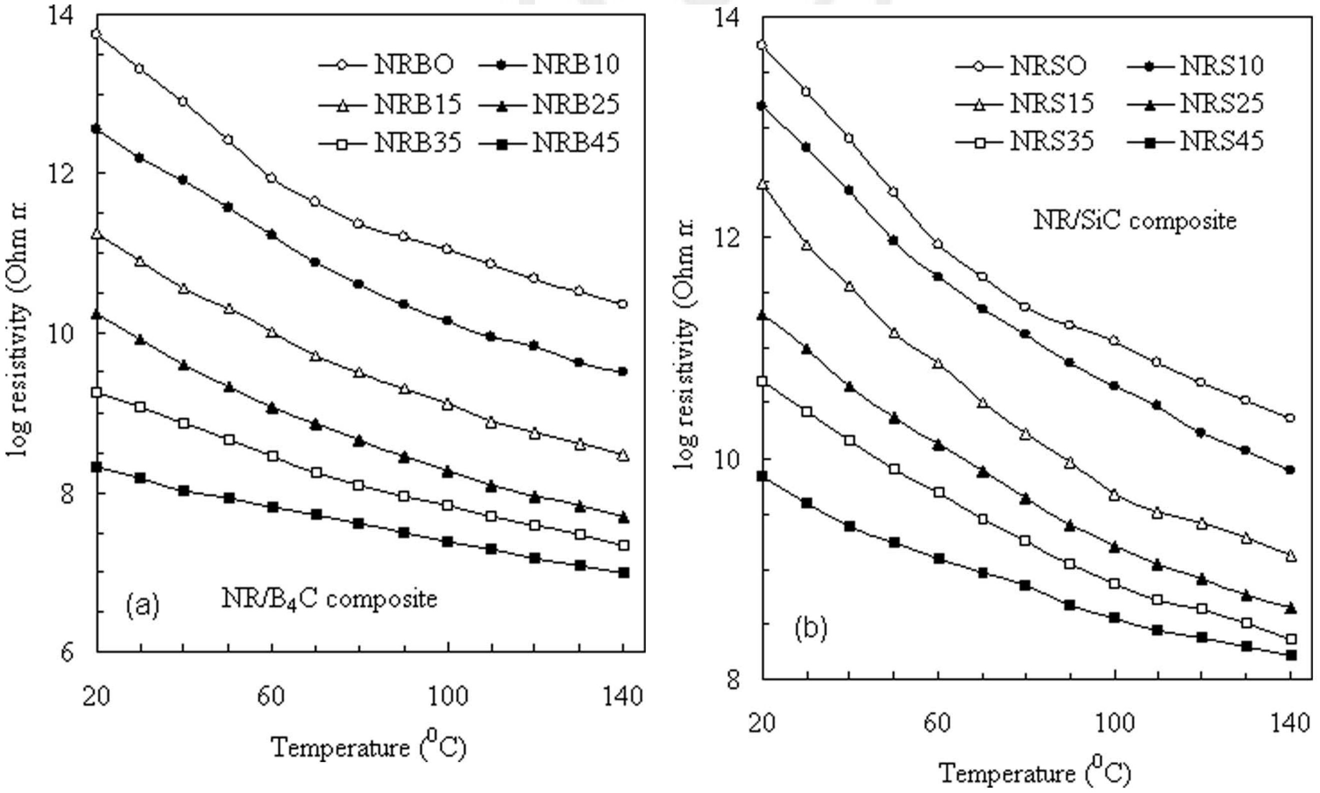

FIG. 6. volume resistivity–temperature dependence (a) for NR/B_4C composites and (b) for NR/SiC composites.

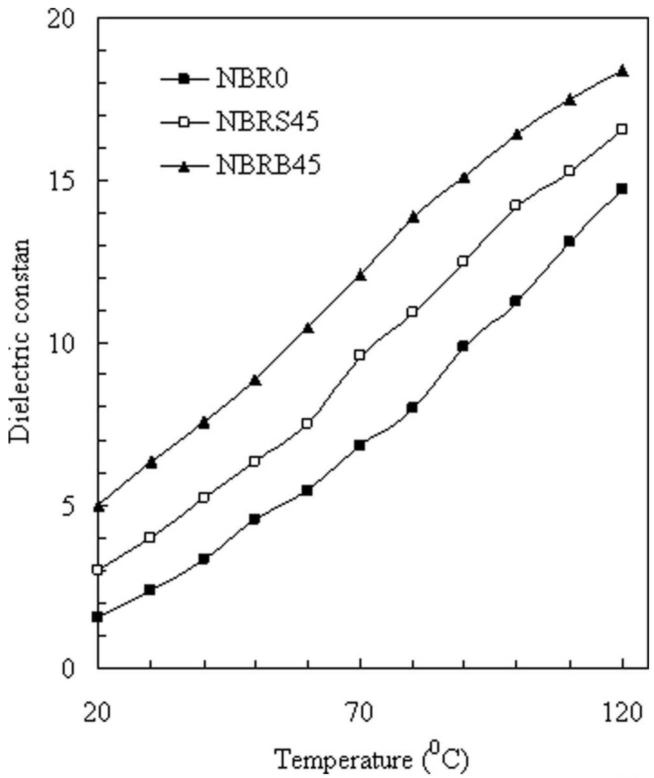

FIG. 7. Dependencies of dielectric constant (ε) of the elastomer composites with temperature.

ductive SiC and B_4C particles leads to formation of additional conductive filaments during heating. Second, electron emission between two filler aggregates increases with increasing temperature. Third, the polar groups due to the air oxidation at high temperature increase [8]. The formation of polar group at high temperature can be further verified by the dielectric behavior. The dependencies of dielectric constant with temperature of the NR0, NRB45, and NRS45 F7 samples are presented in Fig. 7. It was found that the dielectric constant increases with the increase of temperature and loading level. The increase dielectric constant is attributed to the agglomeration of conductive particles in NR matrix and the enhanced polarization from the dipole–dipole interaction of closely packed filler particles. This finding suggests that the adhesion between the rubber matrix and filler particles is very good at high loading level as confirmed before by SEM photos.

To understand the conduction mechanism of conductivity in these composites, we calculated the activation and hopping energies. The activation energy (E_a) in zone theory may be calculated by the well known exponential dependence of the resistivity on the temperature [4]:

$$\rho = \rho_0 e^{\frac{E_a}{KT}} \tag{7}$$

where ρ_0 is the resistivity at total dissociation of electrons when $T \to \infty$, K is the Boltzmann constant and T is the temperature on the absolute scale.

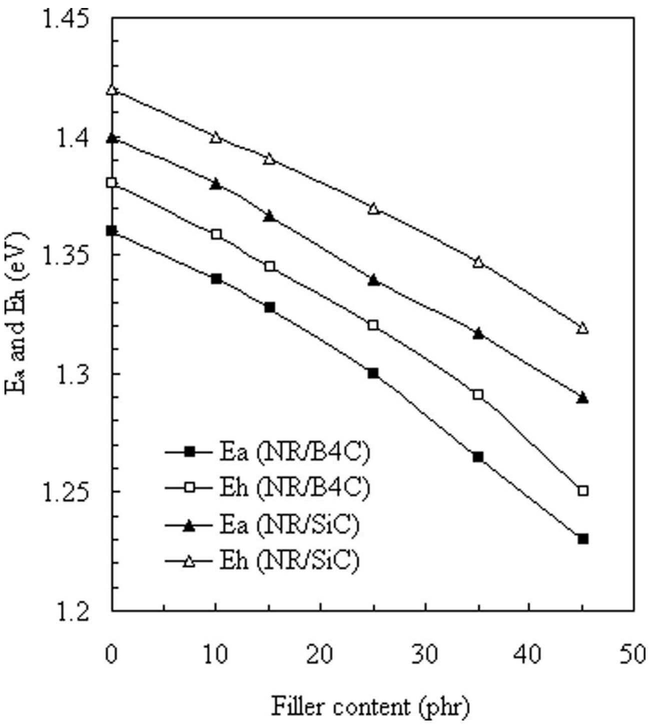

FIG. 8. The estimated values of activation and hopping energies at zone transitions of carriers for the two systems.

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

$$\rho \sqrt{T} = \rho_0 e^{\frac{E_h}{KT}} \tag{8}$$

The estimated values of E_a and E_h at zone transitions of carriers for the two elastomer composites are depicted in Fig. 8. From Fig. 8, it was found that E_a and $E_h$decrease F8 monotonically; one may conclude that the increase of filler loading increases the charge carriers mobility, in turn leads to the decrease of resistivity with increasing filler loadings.

It is worthy to mention that the values of E_h are higher than E_a for all samples. This reflects that the conduction mechanism of conductivity of these composites is governed by hopping mechanism [1].

For practical applications as NTC thermistors, some thermal parameters such as temperature coefficient of resistivity (α) and the sensitivity index (β) are highly essential. The temperature coefficient of resistivity (α) in the range from 20 to 140°C is determined by the equation [2]:

$$\alpha = (\rho_{T2} - \rho_{T1})/(\rho_{T1}T_2 - \rho_{T2}T_1) \tag{9}$$

where ρ_{T1} and $\rho_{T2}$are the volume resistivity at temperature T_1 and T_2 respectively.

The sensitivity index (β) of the composites in the temperature range from 20 to 140°C is determined by the equation [9]:

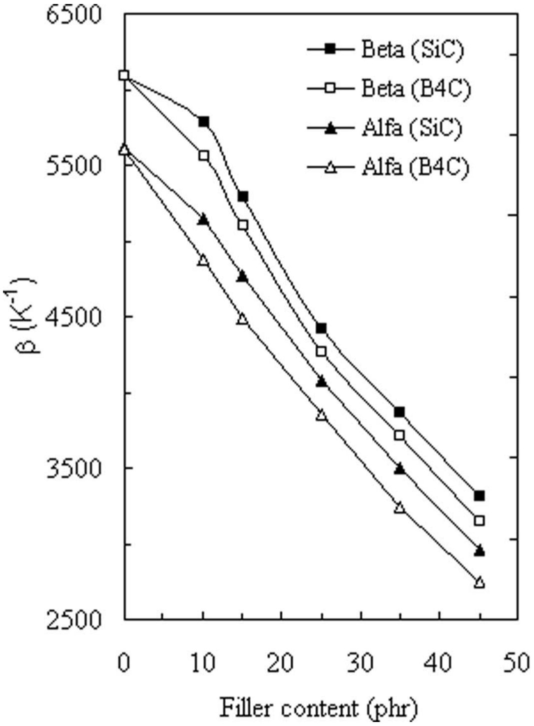

FIG. 9. The computed values of α and β as a function of filler concentration for two systems.

$$\beta = \frac{(\ln \rho_{T1} - \ln \rho_{T2})}{(1/T_1 - 1/T_2)} \qquad (10)$$

The computed values of α and β as a function of filler concentration for two elastomer composites are depicted in F9 Fig. 9. It is observed that α decreases with increasing filler content. This is attributed to the fact that the adhesion force between filler and rubber matrix increase, in turn leading to decease in the temperature coefficient of resistivity. From Fig. 9, the values of β also decreased with decreasing resistivity (i.e. increasing filler content). This result indicates that, in spite of high resistivity, both composites have NTC thermistor characteristics. Moreover, the sensitivity index is also very high for both two systems, which reflect that the proposed composites are very useful as NTC thermistors materials.

Thermal Stability of the Composites

The reproducibility of NTC characteristic of composites and behavior of these composites in different thermal cycles are two other important issues in view of their potential applications. The stability of the NR0, NRS45, and NRB45 samples have been investigated in terms of the temperature–resistivity hysteresis in one thermal cycle are depicted in F10 Fig. 10. As can be seen, for NR0 sample, the very large change of resistivity in the hysteresis cycle is noticed, which can be associated with the relaxation of the accumulated thermo-mechanical stress left over in the NR matrix during the heating run [16, 17]. It can be also be seen in Fig. 10, the resistivity vs. temperature are kept in almost the same shape in both heating and cooling procedures for NRB45 and NRS45 samples. We suppose that the good reversibility of resistivity for NRB45 and NBRS45 samples is due to the strong adhesion force between filler and rubber matrix. As a result, these composites are appropriate as a practical to be used in a high polymer NTC thermistor with good thermal stability.

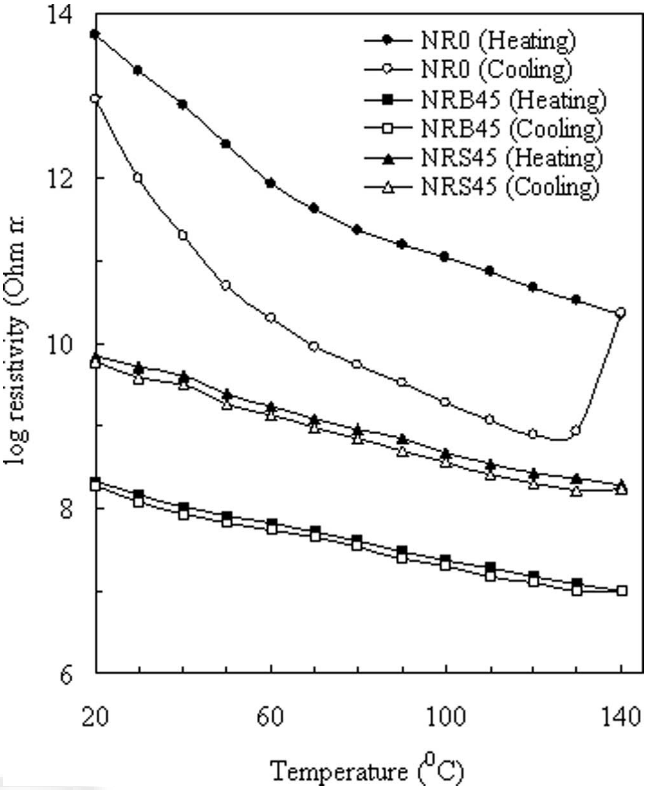

FIG. 10. Variation of volume resistivity with increasing and decreasing the temperature for NR0, NRS45, and NRB45 samples.

Sensing of Pressure

Variation of volume resistivity with applied pressure of NR/B_4C and NR/SiC composites from 0 to 0.35 MPa at 25°C are presented in Fig. 11a and 11b, respectively. For F11 both two types of composites, the increase of resistivity with applied pressure is observed. This is due to the fact that the conductive networks, which is formed by filler particles in the rubber matrix, breaks down with increasing applied pressure. Thereof, the conductive networks in the elastomer matrix are easily destroyed, because of the creep of rubber chains and the deformation of the rubber composite perpendicular to the direction of pressure force [10]. Thereat, the number of conductive paths and the current density decrease with raising the applied pressure leads to the increase of resisitivity. To confirm the above facts, the numbers of mobile charge carriers (N) and drift mobility (μ) of NRB45 and NRS45 samples as a function of applied pressure are

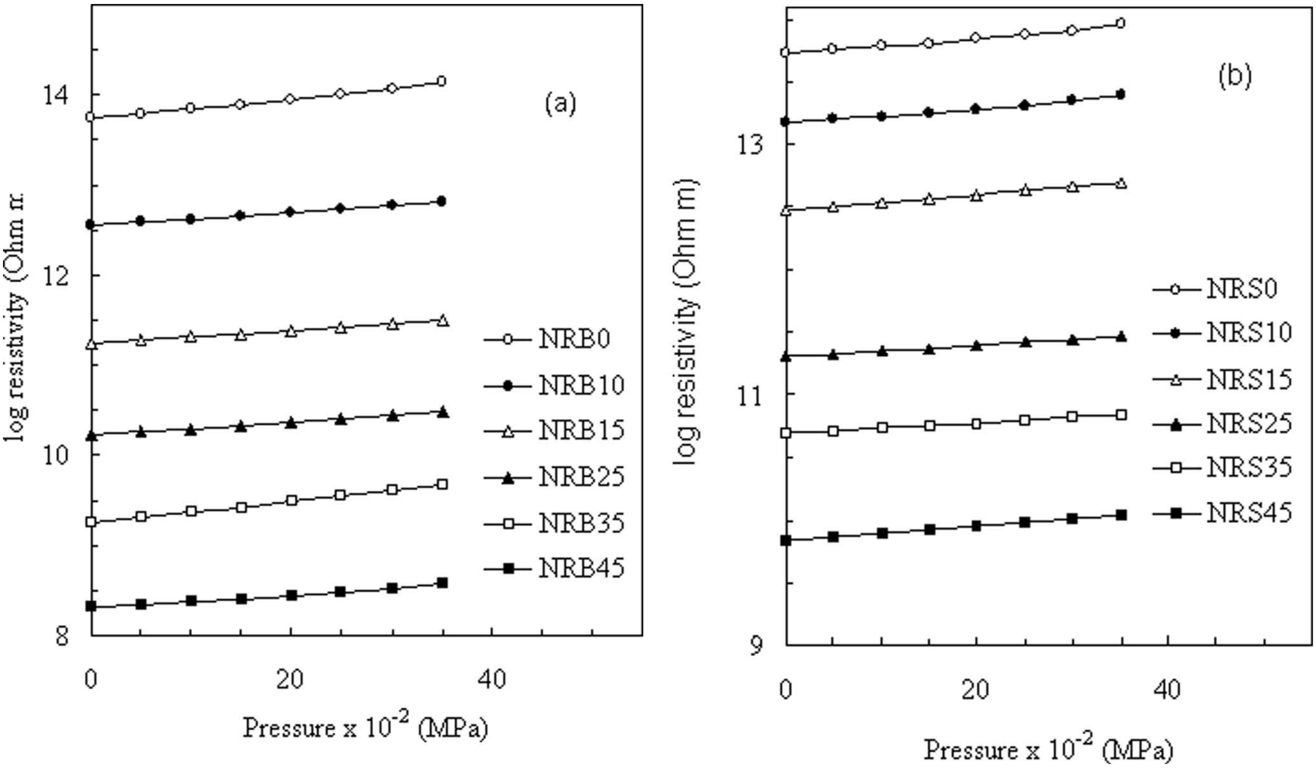

FIG. 11. ρ_v–pressure dependence (a) for NR/B_4C composites and (b) for NR/SiC composites.

F12 depicted in Fig. 12. It is observed from the graph that by increasing applied pressure, both mobility and the concentration of charge carriers decreases. It may be due to the fact that the charge carriers stop hopping from one chain to another as pressure increases [13]. This strong clue reveals that the applied pressure breaks down the conductive network and increases the activation volume between conductive phases into the composites, in turn leading to an increase of resistivity. The breakdown of conductive networks can be further verified by the estimation of activation volume under applied pressure. To estimate the activation volume in the composites, the resistivity dependence of pressure follows the power law [1]:

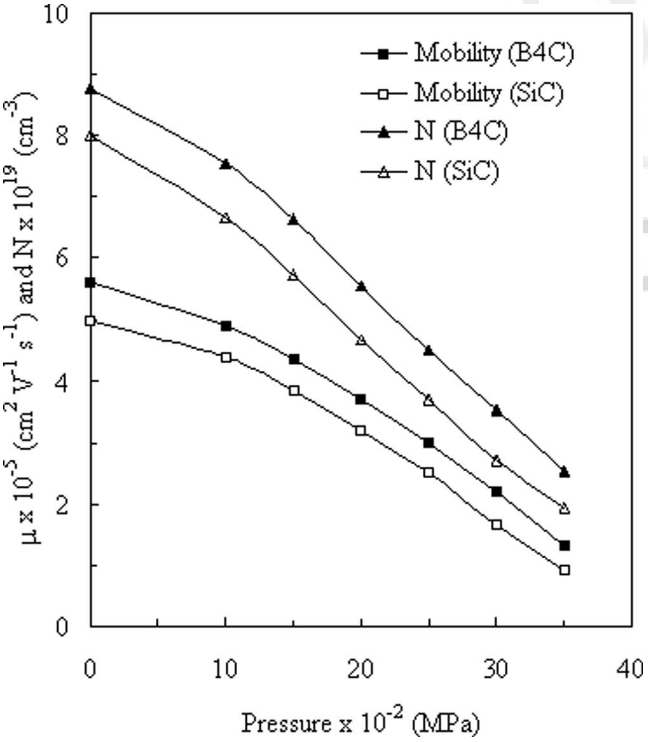

FIG. 12. Numbers of mobile charge carriers and (*N*) drift mobility (μ) of NRB45 and NRS 45 samples as a function of applied pressure.

$$\rho = Ae\frac{W}{KT} \tag{11}$$

where A is a constant depending on time, temperature, pressure, and microstructure, W is the mechanical work and is given by:

$$W = PV_a \tag{12}$$

where V_a is the activation volume (i.e. the volume variation of the composites during compression and is accomplished with the region of the space when the conduction process takes place) and P is the applied pressure.

Equations 11 and *12* was used for the estimation of the activation volume by plotting ln ρ vs. P at constant testing temperature. The calculated values of activation volume as a function of applied pressure for two composites are depicted in Fig. 13. It is clear that the activation F13

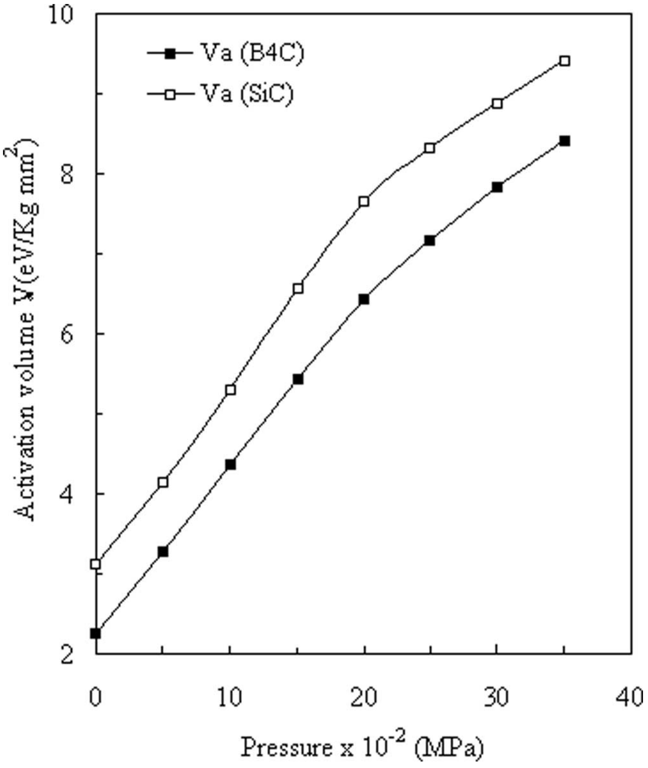

FIG. 13. Activation volume against pressure for NR composites.

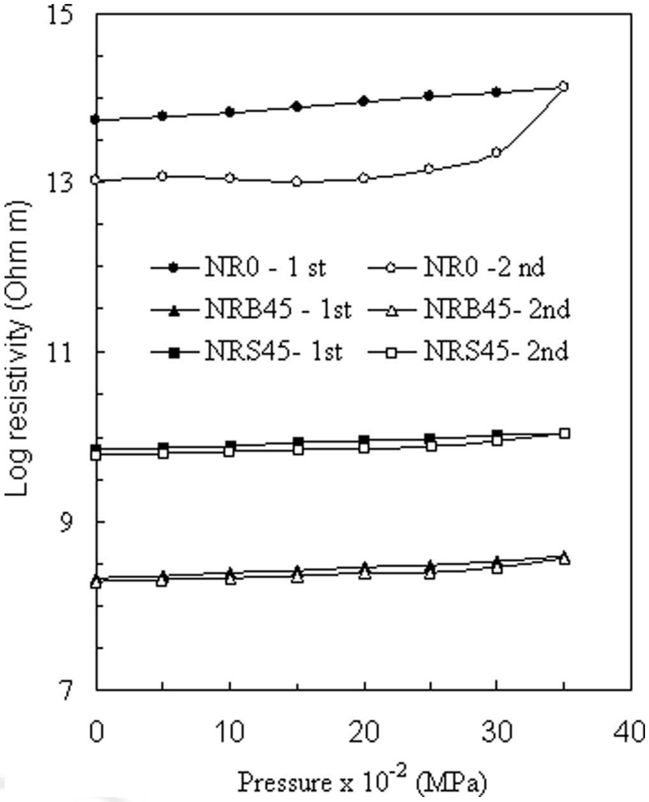

FIG. 14. Resistivity as a function of pressure for two hysteresis cycles.

volume increases with applied pressure. This means that the increase in applied pressure leads to increase the dimensionality among conductive particles and a decrease in transport of charge carrier's mobility in turn leads to an increase in resistivity as confirmed before.

Figure 14 depicted the change in resistivity in successive cycles of compression with applied pressure from 0 to 0.35 MPa for NR0, NRB45, and NRB45 samples. It is clear that there is a large difference in resistivity between first and second measurement for NR0 sample (i.e. unfilled sample). This is mainly due to the creep of NR matrix and the slow in elastic response of the composites under applied pressure [4]. On the other hand, for NRB45 and NRS45 samples, the resistivity is overlap for first and second run. This is ascribed to the good dispersion and interface adhesion of fillers into elastomer matrix and relative stiffness of the composites itself [21, 22].

The compression index (CI) of the volume resistivity was determined by the equation [3, 22]:

$$CI = \left(\frac{\Delta\rho}{\rho_0}\right)\left(\frac{1}{\Delta P}\right) \tag{13}$$

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

The values of compression index as a function of fillers concentration for two composites are depicted in Fig. 15. From the figure, it can be found that the compression index is positive values for two systems. Furthermore, the compression index for both types of composites decreases with

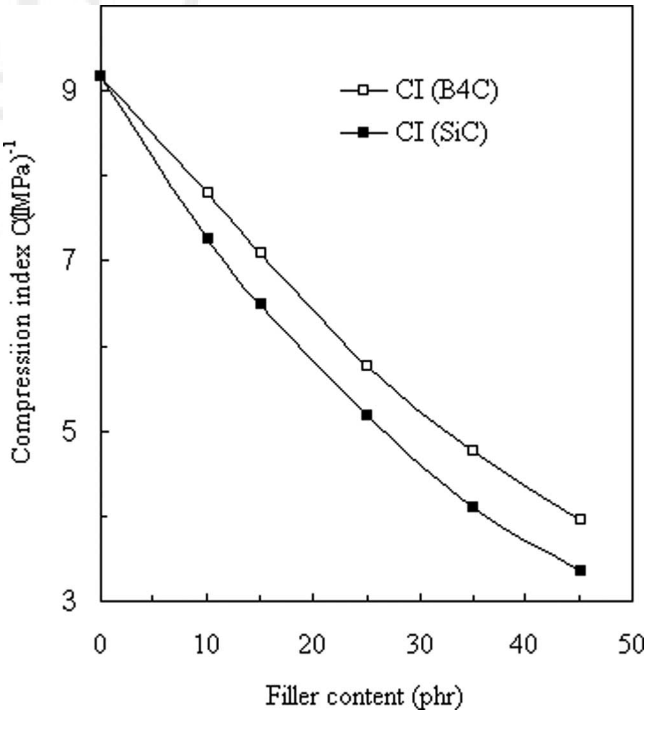

FIG. 15. CI as a function of fillers content for two NR composites.

the increasing of fillers concentration. This indicates that the sensibility of the composites as a transducer in pressure gauge increases with increasing filler concentration for two composites. In conclusion, the linearity of log resistivity variation with the pressure increase and the absence of hysteresis loop make these two elastomer composites well for application as pressure sensors.

CONCLUSIONS

(1). The incorporation of the SiC and B_4C contributed to increase the crosslinking density and interface adhesion of the NR composites. The modulus of elasticity and hardness of the NR composites was significantly enhanced by filling with SiC and B_4C. This is explained by the strong interface adhesion and crosslinking density of rubber composites.

(2). The log volume resistivity of the composites decreases linearly with filler content increasing. This allows one to simply predict the composites resistivity for any desirable utilization electric and electronic technology.

(3). The resistivity decreases considerably with temperature increasing. With increasing volume fraction of filler, the resistivity stability of the composites increases. These electro-polymer composites display high resistivity and, above all, high sensitivity index, and should accordingly find interesting industrial applications as NTC thermistors.

(4). The dielectric constant increases with temperature increases for two composites. The increase in dielectric constant is attributed to the agglomeration of conductive particles in NR matrix and the enhanced polarization from the dipole–dipole interaction of closely packed filler particles.

(5). Volume resistivity of the composites increases with the applied pressure. This can be explained as a result of destruction of the structure of conductive network and increases of the activation volume of the composites with increasing applied pressure. The compressive index decreases with increasing filler concentrations for two composites. This makes the proposed composites very useful for piezoresistive sensor (i.e. transducer in pressure sensor).

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