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Creep of electrical resistance under uniaxial pressures for carbon black–silicone rubber composite

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Abstract A composite comprised of dispersed conductive particles in an insulating polymer matrix is an excellent sensing material and could be used in flexible pressure sensors and tactile sensors. In this study, we investigated the variation of electrical resistance as a function of pressure for carbon black–silicone rubber composite. Samples were fabricated with different carbon black volume fractions. From experimental results, it was found that the composite has not only piezoresistivity but also electrical resistance creep behavior, which illustrates the relationship between electrical resistance and time. To describe and predict the above two phenomena, a mathematical model was established for particles filled polymer composites. When the piezoresistive composite was applied as a pressure-sensing unit, errors were seen due to "resistance creep" behavior. Based on this study, a method to inhibit such errors were investigated, developed, and realized.

Introduction

In the past years, polymer composites containing dispersed conductive particles in an insulating polymer matrix have been studied for applications such as thermistors [1], pressure sensors [2, 3], tactile sensors [4, 5], and gas sensors [6]. The electrical resistivity of such composites depends critically on the volume fraction of the conducting filler particles and this is well explained by the percolation theory [7, 8]. Usually, general effective media (GEM) theory was used to predict resistivity as a function of filler fraction and thereby optimize resistivity. For a composite near the critical threshold, one would expect to see a negative piezoresistive effect below a critical pressure as well as a positive temperature coefficient [PTC] effect and devices (thermistors and overcurrent protection devices [9, 10]) have already been developed based on these principles. Malachlan and Blaszkiewicz [11] explained their findings of pressure-resistivity in conductive particles filled polymer system by GEM theory. Manwar Hussain et al. [12] researched the fabrication process and electrical behavior of novel pressure-sensitive polymer composites filled by carbon black. Luheng Wang et al. [13, 14] presented the effects of compression cycles and precompression pressure on the repeatability of piezoresistivity for a carbon black filled silicone rubber composite.

The time-dependent elastic properties of composites containing randomly dispersed particles in a polymer matrix have also been recently studied [15, 16]. However, in the process of this investigation, we found that the resistance of carbon particle filled polymer composites would decrease with time under an invariant uniaxial pressure, which is similar to a "resistance creep" behavior. A short letter has been published about this phenomenon by authors [17]. In this article, we presented more experimental results and try to explain the theoretical underpinnings of this phenomenon. We also presented a mathematical model to describe and predict the piezoresistivity and time-dependence of electrical resistance for particle filled polymer composites. A series

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of experiments using carbon black–silicone rubber composites are induced to prove the validity and practicability of this model. Moreover, based on these studies, a method to mitigate "resistance creep" behavior is also presented because the behavior could introduce significant error if the piezoresistive composite was used as a pressure-sensing unit.

Experimental

Room temperature vulcanized (RTV) liquid silicone rubber (SR, QD234, Beijing Chem. Plant, China) was used as the polymer matrix in our experiment. Conductive carbon black (CB) powder with an average particle size 6 μm (SL10, Carbon Black R&D Institute, China) was dispersed in the matrix and was between 30 and 45% of total volume. The properties of the carbon black and the polymer from the manufacturer's literature are shown in Table 1. Hexane was used as the solvent to mix the fillers with the polymer and ethyl silicate was used as the crosslinker. Mechanical stirring along with ultrasonic vibration was also used to improve the particle dispersion. After 4 h of vigorous mixing, the solvent was evaporated. The viscous mixture was molded into disks ($25 \times 25 \times 2.5$ mm^3) under 14.7 MPa at 165 °C for 10 min. In some samples, silica white (SW) powder was added to improve the Young's modulus ranging in volume 4% or 6%.

A compression apparatus used for measuring the samples' body electrical resistance change with uniaxial pressure is described in Fig. 1. Two steel plates contacting the samples were used as electrodes. Pressure in the range of 0–4 MPa was applied in a direction parallel to the electrical current flow using a JSV-500D worktable. The electrical resistance was measured directly using a HP-3458A digital multimeter at room temperature. The compression deformations of the samples were obtained by measuring the displacement of the upper steel plate using a digital dial indicator. A computer, which interfaced with the multimeter and dial indicator, was used to record the data at preconcerted times. All results reported here were obtained from fresh samples, i.e., samples exposed to the mechanical field first.

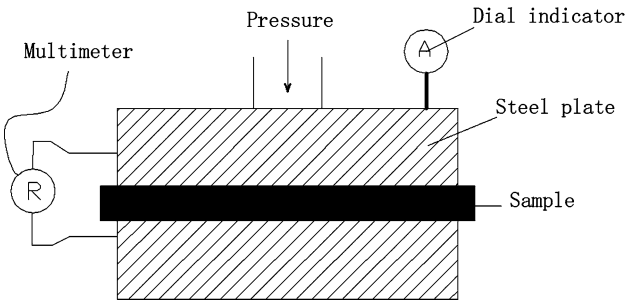

Fig. 1 Schematic of resistance measurement under uniaxial pressure

Results and discussions

Experimental results

Figure 2 shows electrical resistance variation for different CB volume fraction samples (30, 35, 40, and 45%) as a function of uniaxial pressure. The electrical resistance was recorded immediately after each pressure increment of 0.5 MPa. For cross-comparison, the relative electrical resistance change (R/R_0, R is the current resistance, R_0 is the initial resistance) was chosen to describe the test results of conductivity in this article. The piezoresistivity exhibited by our samples when under uniaxial pressure corroborates the findings of Malachlan and Hussain. Especially, significant piezoresistivities occur at 30 and 35% CB volume fraction.

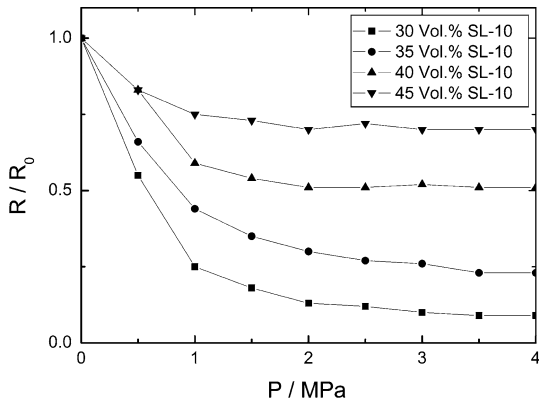

Fig. 2 Piezoresistivity of CB/SR composites

Table 1 Properties of carbon black and silicone rubber

CB	Specific surface area (m^2/g)	pH	Heating loss (%)	Electrical resistivity (Ω cm)	Young's modulus (MPa)
SL-10	58	7.0	1.0	0.8	1.0×10^5
SR	Dielectric constant	Electrical resistivity (Ω cm)	Dielectric strength (kV/mm)	Density (g/cm^3)	Young's modulus (MPa)
QD234	3.3	9.0×10^{14}	13	0.96	6.0

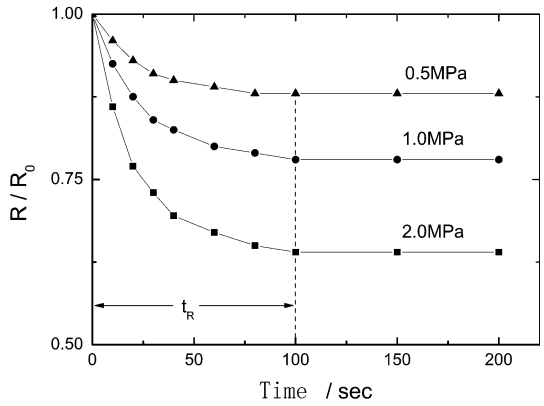

Fig. 3 Creep behavior of electrical resistance (CB, 35%)

However, the time-dependence of electrical resistance, similar to a "resistance creep" was found when the pressure was held constant at 0.5, 1.0, and 2.0 MPa, respectively. The experimental results showing the variation of electrical resistance relative to time are shown in Fig. 3. Although the deformation creep for rubber materials is known, we still measured the time dependence of strain under the same pressure conditions. This allowed us to further analyze the relationship between electrical resistance and strain. The experimental results showing strain variation are presented in Fig. 4. The data represented in Figs. 3 and 4 come from a sample with 35% CB volume fraction composite. t_R is the period time of obvious resistance creep, and t_S is the period time of obvious strain creep. Note that a time lag exists between resistance creep (t_R) and strain creep (t_S). The lag time of the resistance creep is about double that of the strain creep. The relative resistance variation in the period of t_R and the strain variation in the period of t_S were extracted, respectively. These two groups of data are represented in Fig. 5 together for comparison. It can be seen that the variation trend of

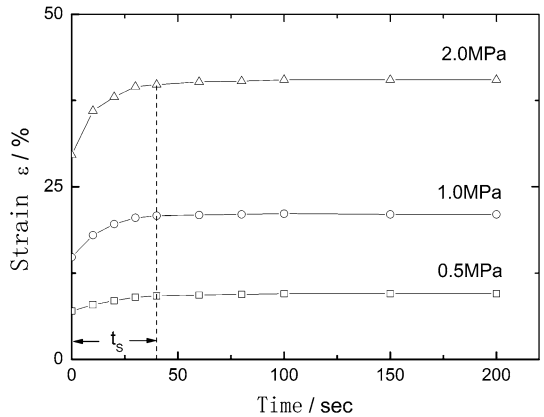

Fig. 4 Creep behavior of strain (CB, 35%)

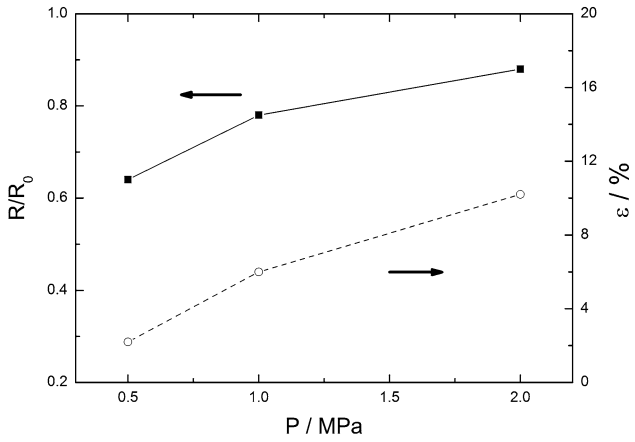

Fig. 5 Creep values of resistance (*filled square*) and strain (*open circle*) under pressures

resistance creep–pressure curve is the same as that of strain creep–pressure curve.

Mathematical model

Based on the percolation theory, the piezoresistive effect, as shown in Fig. 2, can be illustrated as follows. The conductive filler particles are essentially not in contact in the composite just before the critical threshold, giving the composite a high electrical resistance. As stress is applied on the composite, the volume of composite is compressed and the CB volume fraction increases. So, the elastic polymer matrix deforms to the extent that conductive filler particles are forced closer together to form conduction paths, resulting in reduction of resistance. This process may be described by Fig. 6 and the relationship between the electrical resistivity and the CB volume fraction may be expressed by the simplified general medium equation as [12]

$$\rho = \rho_1 \left(\frac{1 - \phi_c}{\phi - \phi_c} \right)^w \tag{1}$$

where ρ is the volume resistivity of composite, ρ_1 is the volume resistivity of CB, ϕ_c is the critical CB volume fraction for percolation, ϕ is the current CB volume fraction, and w is an exponent.

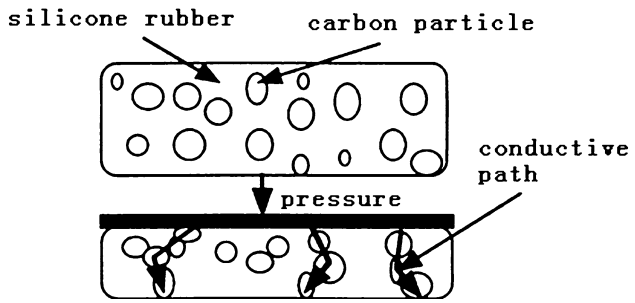

Fig. 6 Formation of conductive paths under pressure

For rubber-based composites, the viscoelasticity theory is applied to describe the deformation under outside pressure. It can be expressed by the Voigt–Kelvin model as [18]

$$\varepsilon(t) = \varepsilon_0 + \varepsilon_e(1 - e^{-t/\tau}) \tag{2}$$

where $\varepsilon(t)$ is the total strain parallel to the pressure direction, $\varepsilon_0 = P/E$ is the elastic strain, P is the uniaxial pressure, E is the Young's modulus, ε_e is the creep deformation coefficient, t is the time, and τ is the creep time coefficient. Divided by P, Eq. 2 can be transformed to

$$J(t) = J_0\left[1 + \beta\left(1 - e^{-t/\tau}\right)\right] \tag{3}$$

where $J(t) = \varepsilon(t)/P$ is the creep compliance, $J_0 = 1/E$ is the elastic compliance, $\beta = \varepsilon_e/\varepsilon_0$ is a balancing coefficient.

Because the composite sample is a rectangular solid, its electrical resistance can be expressed as

$$R = \rho G \tag{4}$$

where R is the resistance, $G = L/S$ is the geometrical factor, L is the length passed by the current, and S is the cross-section area.

Under the applied pressure, the sample becomes deformed. As a result, the volume resistivity and the geometrical factor will both change. First, the change of geometrical factor must be accounted for. Because the structure of the measurement apparatus, shown in Fig. 1, may keep the sample's cross-section area invariable, the deformation induces only the change of length. Thus the change of geometrical factor can be expressed as

$$\frac{1}{G}\frac{\delta G}{\delta P} = -J_0\left[1 + \beta\left(1 - e^{-t/\tau}\right)\right] \tag{5}$$

Through integration, Eq. 5 can be transformed to

$$G = G_0 e^{-J_0\left[1+\beta\left(1-e^{-t/\tau}\right)\right]P} \tag{6}$$

where G_0 is the initial geometrical factor without pressure.

Second, we considered the change of volume resistivity. Under applied pressure, the volume change of composite is

$$\frac{\delta V_m}{V_m} = [1 - \varepsilon(t)] \cdot [1 + \varepsilon'(t)]^2 - 1 \tag{7}$$

where V_m is the volume of composite and $\varepsilon'(t)$ is the lateral strain perpendicular to the pressure direction. Since $\varepsilon(t)$ and $\varepsilon'(t)$ are both less than 1, second-order small quantities can be ignored. Equation 7 divided by P can be transformed to

$$\frac{1}{V_m}\frac{\delta V_m}{\delta P} = \frac{2\varepsilon'(t) - \varepsilon(t)}{\delta P} = 2J'(t) - J(t) \tag{8}$$

where $J'(t)$ is the lateral creep compliance. Because the lateral creep behavior is very weak, only lateral elastic deformation is considered. Then, assuming $J'(t) = vJ_0$ is the lateral electric compliance and v is the Poisson ratio. We transform Eq. 8 to

$$\frac{1}{V_m}\frac{\delta V_m}{\delta P} = \left(2v - 1 - \beta + \beta e^{-t/\tau}\right)J_0 \tag{9}$$

For CB filled composite, the volume fraction ϕ may be expressed by V_i/V_m, where V_i is the volume of CB. Because the Young's modulus of CB is more than that of silicone rubber, the contribution for compressed part comes from silicone rubber mainly. Since V_i can be considered invariable under pressure the change of CB volume faction is

$$\frac{1}{\phi}\frac{\delta\phi}{\delta P} = -\frac{1}{V_m}\frac{\delta V_m}{\delta P} \tag{10}$$

By substituting Eq. 9 into Eq. 10, we can get

$$\frac{1}{\phi}\delta\phi = -\left(2v - 1 - \beta + \beta e^{-t/\tau}\right)J_0\delta P \tag{11}$$

Through integration, Eq. 11 can be transformed to

$$\phi = \phi_0 e^{-\left(2v-1-\beta+\beta e^{-t/\tau}\right)J_0 P} \tag{12}$$

where ϕ_0 is the initial CB volume fraction without pressure. Based on Eqs. 1 and 12, the volume resistivity of composite can also be expressed as

$$\rho = \rho_1(1 - \phi_c)^w\left[\phi_0 e^{-\left(2v-1-\beta+\beta e^{-t/\tau}\right)J_0 P} - \phi_c\right]^{-w} \tag{13}$$

Finally, according to Eqs. 4, 6, and 13, the electrical resistance of composite can be expressed by a mathematical model as

$$R = R_0(\phi_0 - \phi_c)^w \left[\phi_0 e^{-\left(2v-1-\beta+\beta e^{-t/\tau}\right)\frac{P}{E}} - \phi_c\right]^{-w} e^{-\left(1-\beta+\beta e^{-t/\tau}\right)J_0\frac{P}{E}} \tag{14}$$

where R_0 is the initial resistance of composite without pressure. In this mathematical model, not only pressure P but also time t are both variables which induce the change of electrical resistance. On physical level, the former represents the piezoresistivity and the latter represents the resistance creep behavior.

Discussions

For the carbon black (SL-10) and silicone rubber (QD234) used in this article, the critical CB volume fraction ϕ_c is 28%, the exponent w is 2.4, the Poisson ratio v is 0.38, the balance coefficient β is 0.31, and the creep time coefficient τ is 30 s [19]. The Young's modulus of composite is different at given CB volume fractions, for instance, 6.42 MPa at 30% and 6.53 MPa at 35%.

Using Eq. 14, the time dependence of electrical resistance for composite can be computed. In the computational process, the pressure P is set to be 0.5, 1.0, or 2.0 MPa and the initial CB volume fraction ϕ_0 is set to be 35%. For comparison with the experimental results, we plot the

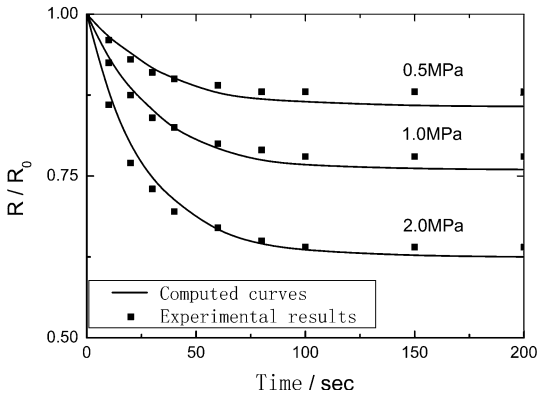

Fig. 7 Computed curves of resistance creep behavior (CB, 35%)

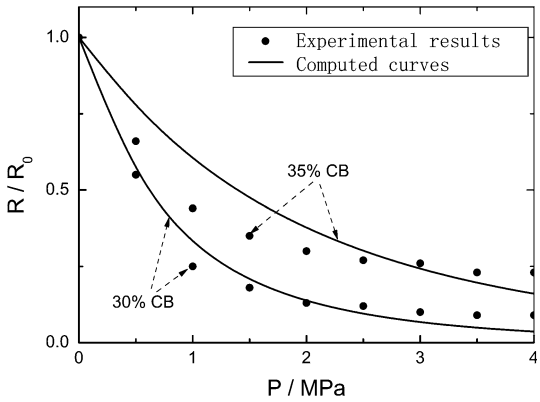

Fig. 9 Computed curves of piezoresistivity (CB, 30% or 35%)

computed curves and the experimental results together, as shown in Fig. 7. It can be seen that Eq. 14 is capable of describing resistance creep behavior of CB filled composite reasonably well.

For verifying the effect of time further, a slow-going load, as shown in Fig. 8a, was applied to the sample. The pressure ranged from 0 to 2 MPa and increased 0.4 MPa every 20 s. The experimental results for changes in electrical resistance are shown in Fig. 8b. There are also two computed curves in Fig. 8b. Importantly, curve I is computed by $t = 0$ and curve II is computed by $t = 20$ s. It can be seen that curve II can describe the experimental results better than curve I because of the electrical resistance creep behavior.

However, when we use Eq. 14 to calculate the piezoresistivity of the composite, computed curves and experimental results deviate significantly as shown in Fig. 9. For the calculations, t is set to zero and the initial CB volume fraction ϕ_0 is set to at either 30 or 35%. This shows that the resistance creep behavior can have a negative effect on piezoresistivity, which is the most important property if the composite is employed as a pressure or force sensor. Clearly methods are needed to inhibit this behavior.

Figure 10 shows a series of curves calculated using different Young's moduli. It can be seen that increasing the Young's modulus inhibits the resistance creep behavior effectively. Although increasing the carbon black fraction can reduce the lag time of resistivity, the piezoresistivity of the composites is also weakened to a certain extent as shown in Fig. 2. To improve the Young's modulus independently, we dispersed silica white fillers prepared by the vapor phase process into the rubber composite and fabricated new samples comprised of 30%CB + 6%SW and 35%CB + 4%SW. Measurements indicate that the Young's modulus of

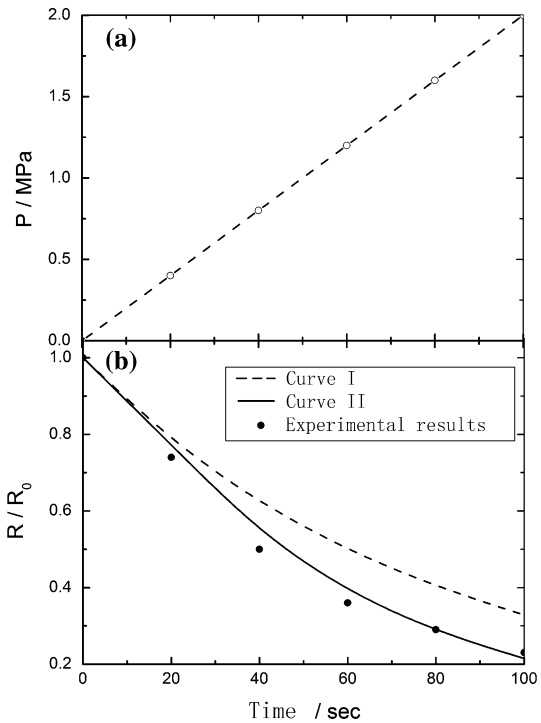

Fig. 8 Change of electrical resistance for composite under slow-going load (CB, 35%)

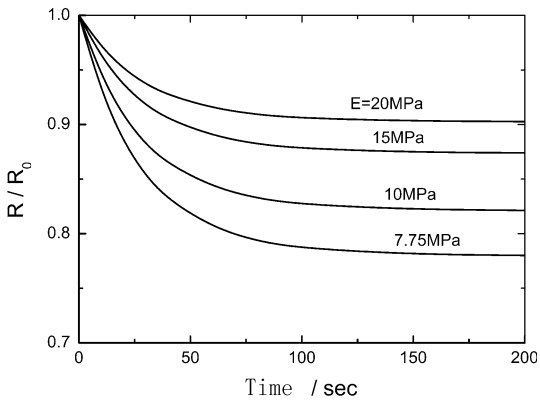

Fig. 10 Computed curves for effect of Young's modulus (1 MPa loading)

the composite increased almost 50%. This suggests that the presence of silica white filler controlled the microstructure and physical properties of the composites [20]. On the surface of silica white particles, there exist abundant unstable Si–O_x structures because the oxygen atoms are used up. The value of x is typically in the range of 1.2–1.6. In the process of vulcanization, the Si–O–Si bond may be formed from the dealcoholization reaction taking place between the vulcanizator and the SiO_x. This chemical bond structure can make the crosslinked reaction more efficient for the silicone rubber. Moreover, silica white particles can adsorb other nearby silicone rubber molecules because of their high surface energy and binding energy. As a result the silica white particle acts as a kind of strengthening filler, which may form not only effective chemical bonds but also physical sorption. In the experiment the mechanical properties of these composites were found to be improved significantly and thus the resistivity creep was effectively dampened. Experiments to elucidate the resistance creep behavior and piezoresistivity of the new samples were conducted. These results are shown in Figs. 11 and 12, respectively. It can bee seen that, for the new samples containing silica white, the resistance creep behavior is significantly abrogated and the piezoresistivity agrees better with the calculated curve. This shows that the silica white filler can improve the piezoresistivity of the composite through inhibition of the resistance creep behavior.

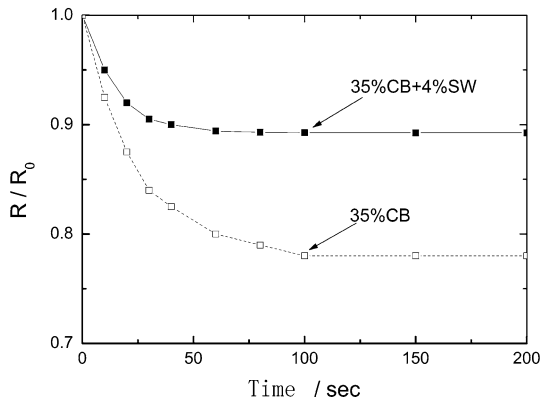

Fig. 11 Creep behavior of electrical resistance for new samples (1 MPa loading)

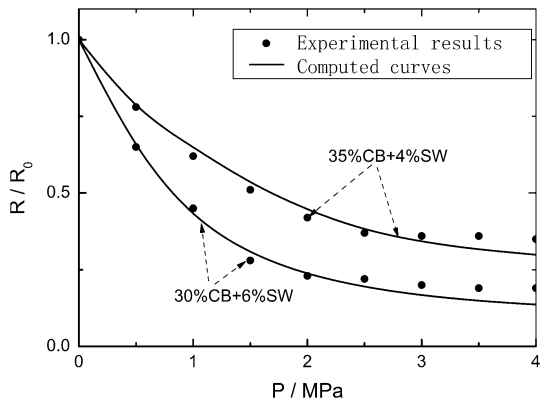

Fig. 12 Piezoresistivity of new samples (35%CB + 4%SW and 30%CB + 6%SW)

Conclusions

In this article, the variation of electrical resistance under uniaxial pressure for carbon black–silicone rubber composite was presented. From experimental results, it was found that the composite has not only piezoresistivity but also electrical resistance creep behavior. The former is a result of the relationship between electrical resistance and pressure, the latter stems from the relationship between electrical resistance and time. Upon further analysis, the deformation of composite was shown to be the main driving force behind the above two phenomena. Also, a mathematical model was established to enable the prediction of piezoresistivity and electrical resistance creep in rubber composites. Experimental results indicate that the model describes the piezoresistivity and resistance creep behavior of CB filled composites reasonably well. Furthermore, the model predicted that increasing the Young's modulus of the composite could overcome resistance creep and this prediction held true in the subsequent experimentation. Thus we developed a novel way to mitigate resistance creep in rubber composites by the inclusion of white silica fillers. This is very useful for the creation of flexible force sensors.

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