Conductivity and Piezoresistivity of Conductive Carbon Black Filled Polymer Composite

Peng Wang, Tianhuai Ding

State Key Laboratory of Precision Measurement Technology and Instruments, Department of Precision Instruments and Mechanology, Tsinghua University, Beijing 100084, People's Republic of China

Received 17 April 2009; accepted 26 October 2009
DOI 10.1002/app.31693

ABSTRACT: Dispersing conductive carbon black (CCB) particles into silicone rubber (SR), we studied the conductivity and piezoresistivity of particles filled polymer composite. The experimental results show that the conductive percolation threshold and shape exponent of composite are effected on by filler's size and reduce with filler's size decreasing. The electrical resistance and Young's model of composite have different critical filler volume fraction to fall or increase. The compressing deformation is the main reason of the piezoresistivity of composite, but the piezoresistivity is more obvious when particles have larger size or polymer matrix has smaller Young's Model. A research was done to explain the piezoresistivity through comparing CCB/SR with CCB/high density polythene (HDP). The other interesting find is that the electrical resistance of composite decreases with time under an invariant load, showing "electrical resistance creep" behavior, which is due to the composite's compressing strain creep under uniaxial pressure. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 2035–2039, 2010

Key words: conducting polymer; composites; rubber; sensors; compression

INTRODUCTION

In the past several years, some polymer composites containing dispersed conducting 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 a composite critically depends on the volume fraction of the conducting filler particles that is well explained by the percolation theory.[7,8] Usually, general effective media (GEM) theory was used to optimize fitting of resistivity as a function of filler fraction such that the resistivity at any chosen filler fraction can be predicted. Mclanchlan et al.[9] explained their findings of pressure-resistivity in conductive particles filled polymer system by GEM theory. Hussain et al.[10] researched the fabrication process and electrical behavior of a novel pressure-sensitive polymer composites filled by carbon black. Wang et al.[11,12] presented the effects of compression cycles and precompression pressure on the repeatability of piezoresistivity for carbon black filled silicone rubber (SR) composite.

However, in the process of investigation, we found that the conductivity and piezoresistivity of conductive carbon black (CCB) filled polymer composites would be effected on by the filler particle's size and polymer's elastic properties. Interestingly, some composites presented a time dependence of electrical resistance under uniaxial pressure, which is similar to an "electrical resistance creep" behavior. So, in this article, attention has been paid to these phenomena and some rules were obtained.

MATERIALS AND EXPERIMENTS

CCB powders (SL-10, SL-20, SL-30, SL-32, SL-36, Carbon Black R&D Institute, China) were dispersed respectively in room-temperature-vulcanized liquid SR (QD234, Beijing Chemical Plant, China) and high density polythene (HDP) (PE602D, Maoming Chemical Plant, China) used as insulating matrix. The volume ration of carbon black to polymer was from 0.05 : 1 to 0.60 : 1. The properties of carbon black and polymer found in manufacturer's literature are shown in Table I. Hexane was used as solvent to mix the fillers with the polymer, ethyl silicate was used as crosslinker, and nano-sized alumina powder was used as dispersant. Mechanical stirring along with ultrasonic vibration was also used for better particle dispersion. After 4 h of vigorous mixing, the

---

Correspondence to: P. Wang (peng@mail.tsinghua.edu.cn).
Contract grant sponsor: National Nature Science Foundation of China; contract grant number: 60702001.
Contract grant sponsor: State Key Laboratory of Transducer Technology of China; contract grant number: skt0707.

Journal of Applied Polymer Science, Vol. 116, 2035–2039 (2010)

TABLE I
Properties of Carbon Black and Polymer

CCB	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
SL-20	140	7.0	1.0	0.5	1.0×10^5
SL-30	320	6.8	2.0	0.4	1.2×10^5
SL-32	430	7.0	2.0	0.4	1.2×10^5
SL-36	780	6.3	3.0	0.2	1.5×10^5
Polymer	Dielectric constant	Electrical resistivity (Ω cm)	Dielectric strength (KV/mm)	Density (g/cm^3)	Solid Young's modulus (MPa)
QD234	3.3	9.0×10^{14}	13	0.96	6.0
PE602D	4.0	8.2×10^{13}	20	0.94	100

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 minutes.

A compression apparatus used for measuring the samples' body electrical resistance change with uniaxial pressure is described in Figure 1. Two steel plates contacting the samples were used as electrodes. In cases, pressure was applied in a direction parallel to the electrical current flow using 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 has interfaces with the multimeter and dial indicator, was used to record the data at preconcerted times. All the results reported here were obtained from fresh samples.

RESULTS AND DISCUSSION

Percolation threshold of composites

In this article, five kinds of CCB particles have different specific surface area, which is inverse to the particle size. We dispersed these CCB particles into SR from 0.05 : 1 to 0.60 : 1 and measured the initial electrical resistance of composites without compressing. It is found from the results shown in Figure 2 that the electrical resistance of composite falls at a critical volume fraction, which is variable with CCB particle size. Generally, Bruggeman effective media and percolation theory is used to explain this type of phenomena and its mathematic expression is as[7,10]

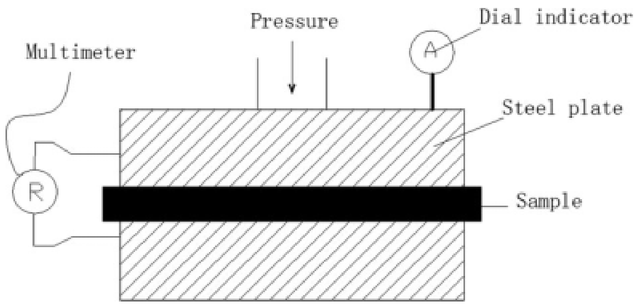

Figure 1 Scheme of sample measurement under uniaxial pressure.

$$\frac{(1-\phi)(\rho_l^{-1/w}-\rho^{-1/w})}{\rho_l^{-1/w}-A\rho^{-1/w}}+\frac{\phi(\rho_h^{-1/w}-\rho^{-1/w})}{\rho_h^{-1/w}-A\rho^{-1/w}}=0 \qquad (1)$$

where $A = (1-\varphi_c)/\varphi_c$, φ is the volume fraction of the CB particles, and φ_c is the critical volume fraction of the percolation threshold. Here ρ_l is the resistivity of the polymer matrix, ρ_h is the resistivity of the CB, ρ is the resistivity of the composite itself, and w is a shape exponent. Because the electrical resistivity of SR is so largest that it can be assumed to approach infinite, i.e. $\rho_l \to \infty$, a simplified solution of eq. (1) can be acquired as:

$$\rho = \rho_l\left(\frac{1-\phi_c}{\phi-\phi_c}\right)^w \qquad (2)$$

For solving the critical volume φ_c and shape exponent w, suppose $\rho_n (n = 1,2,\ldots,8)$ is the

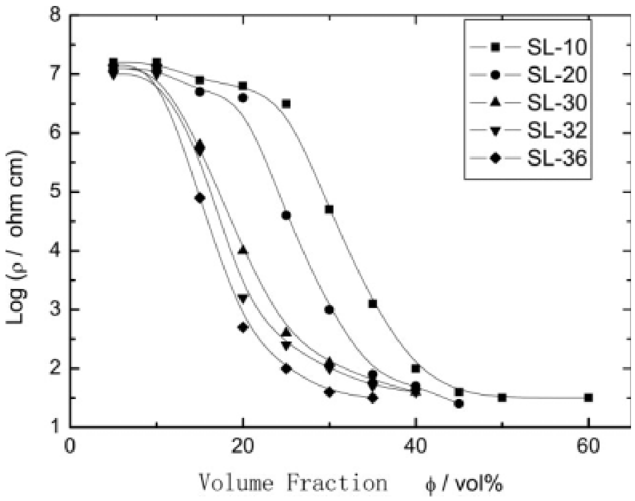

Figure 2 Percolation threshold of CCB/SR composites.

TABLE II
Critical Volume Fraction and Shape Exponent of Composites

CCB	Critical volume fraction (φ_c/vol %)	Shape exponent (w)
SL-10	28	2.2
SL-20	22	2.1
SL-30	19	1.9
SL-32	18	1.7
SL-36	17	1.7

theoretical expression from eq. (2) and ρ_n' is the experimental value as the volume fraction is φ_n. Then, we can design an optimization function: $\min f(\phi_c, w) = \sum_n |\rho_n - \rho_n'|$. For every CCB particle style, eight experimental values from Figure 2 were input into the optimization function. Considering φ_c and w as variables, the Newton method was used to solve this function and Solving results are shown as Table II. It can be concluded from these results that the critical volume and shape exponent of CCB filled polymer composites are effected on by CCB particle size and reduce with filler size decreasing.

Piezoresistivity of composites

We dispersed SL-10, SL-20, and SL-36 into SR near to their critical volume fraction respectively. In the process of piezoresistivity test, the electrical resistance was read as pressure was loading. To compare with different composites, the relative electrical resistance change is used to describe the test results, as shown as Figure 3. The R_0 is the initial resistance of sample without load. In the area of percolation threshold, the electrical resistance decrease of composites with pressure increasing, which is a negative piezoresistivity. Especially, a useful conclusion is that the SL-10 filled composite, which has the biggest shape exponent, presents the most obvious electrical resistance change.

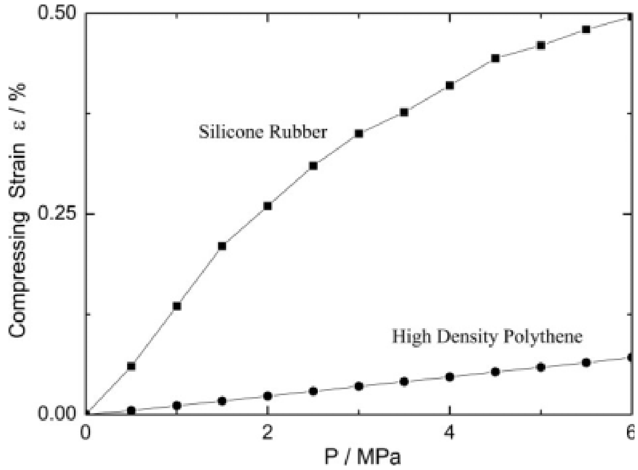

Figure 4 Compressing strains of CCB/SR and CCB/HDP composites.

To explain this piezoresistivity phenomenon, HDP was selected as a reference polymer matrix. Using SR and HDP as polymer matrix respectively, two kinds of composite samples (SL-10, 35 vol %) were fabricated. Firstly, the mechanical deformation of samples was detected during compression process. The results are shown in Figure 4. It can be seen that the compressing deformation of CCB/SR is bigger than CCB/HDP in the range of 0–3 MPa because the Young's model of SR is smaller than HDP. Secondly, the piezoresistivity of samples was detected during compression process. The results are shown in Figure 5. It can be seen that the piezoresistivity of CCB/SR composite is more obvious than CCB/HDP composite in the range of 0–3 MPa. In addition, through comparing Figure 4 with 5, the deformations of both samples presented negative correspondence to the resistivity of both samples. In other

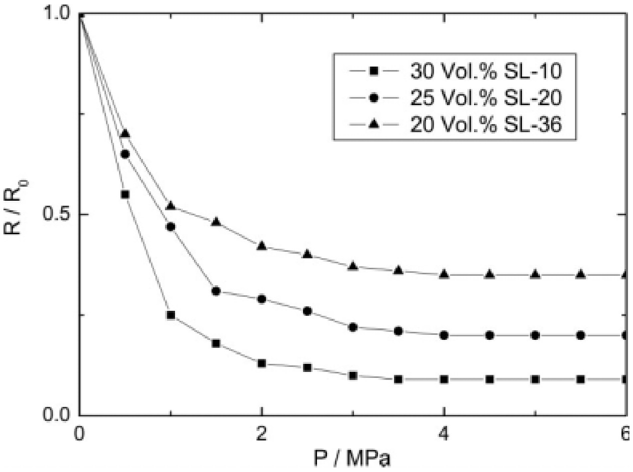

Figure 3 Piezoresistive curves of CCB/SR composites (SL-10, SL-20, SL-36).

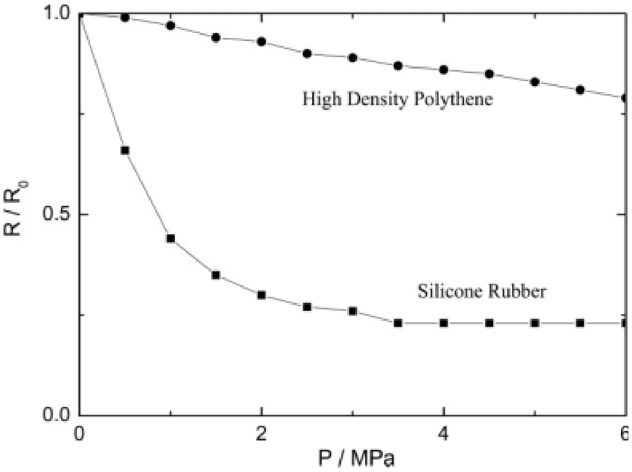

Figure 5 Piezoresistive curves of CCB/SR and CCB/HDP composites.

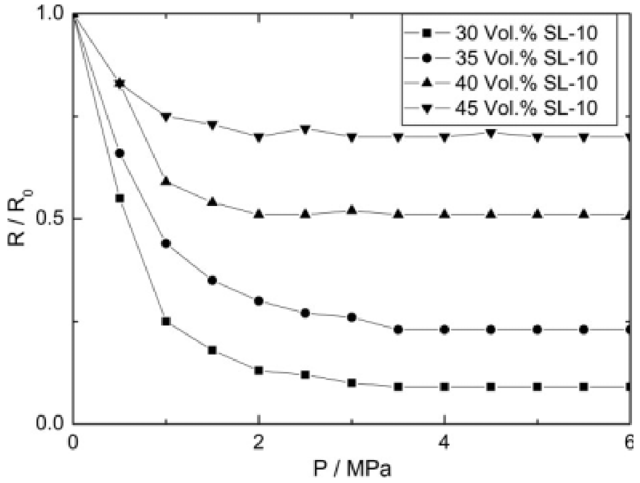

Figure 6 Piezoresistive curves of SL-10 CCB/SR composites (30, 35, 40, 45%).

words, the resistivity of sample decreased with the deformation increasing. So, we believe that the compressing deformation is the main reason of the piezoresistivity of particles filled conductive composites.

However, we also found that in the range of 3–6 MPa the piezoresistivity of CCB/SR composite disappeared gradually. For studying farther, we disperse SL-10 into SR with different volume fraction and tested their piezoresistivity. The results are shown in Figure 6. It can be seen that the composite near to percolation threshold, 30 vol %, has the most obvious piezoresistivity and others far from percolation threshold is imperfect. Then, we can conclude a clear process to explain piezoresisitivity of CCB filled polymer composite as follow as:

Firstly, the volume fraction of conductive particles increases because the volume of composite decreases when composite is compressed.

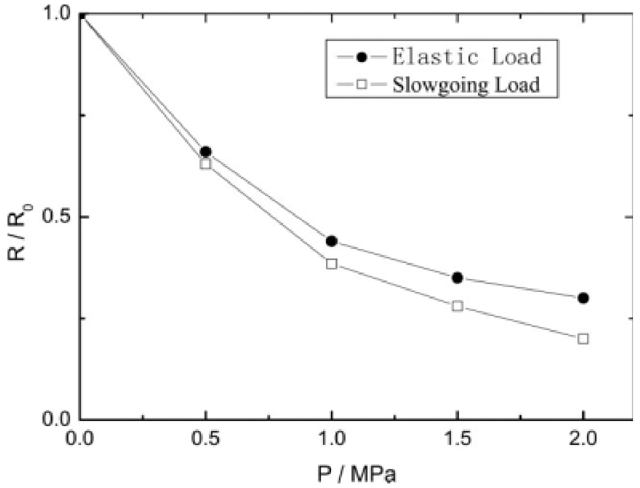

Figure 7 Piezoresistive curves of CCB/SR composite (SL-10, 35%) under different loads.

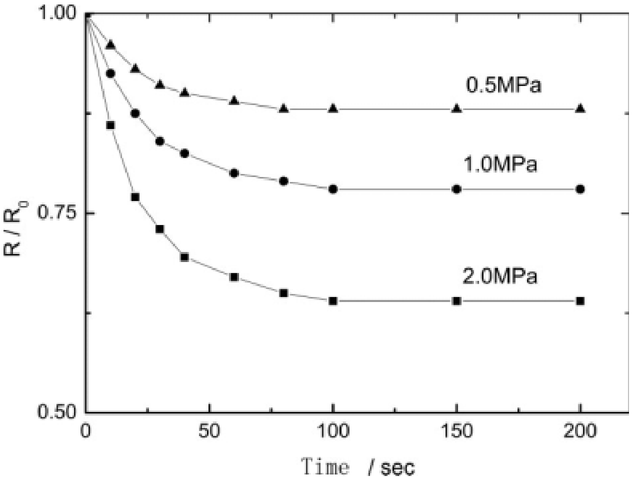

Figure 8 Electrical resistance creep behavior.

Secondly, if the volume fraction of CCB particles is in the area of percolation threshold, the particles are easy to contact each other and form new conductive networks with the volume fraction increasing, which has been proved by the above experiment. Then, the electrical resistivity of composite will fall. However, before the area of percolation threshold, the CCB particles are difficult to contact each other. After the area of percolation threshold, most CCB particles have contacted each other and it is difficult to form new conductive networks. These also can be seen from the experimental results in Figure 2.

Electrical resistance creep behavior of composites

Using CCB/SR (SL-10, 35 vol %) as sample, we increased the pressure from 0 to 2 MPa by the slowgoing load and the elastic load respectively. Slowgoing load was obtained through compressing samples to a given pressure slowly at speed of 0.1 MPa/min. Elastic load was obtained through

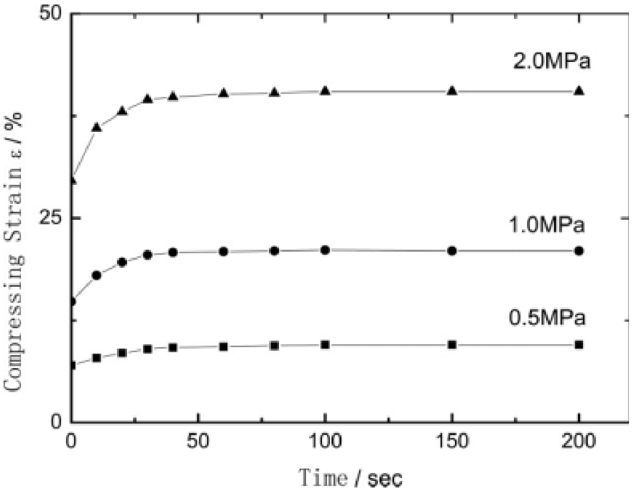

Figure 9 Compressing strain creep behavior.

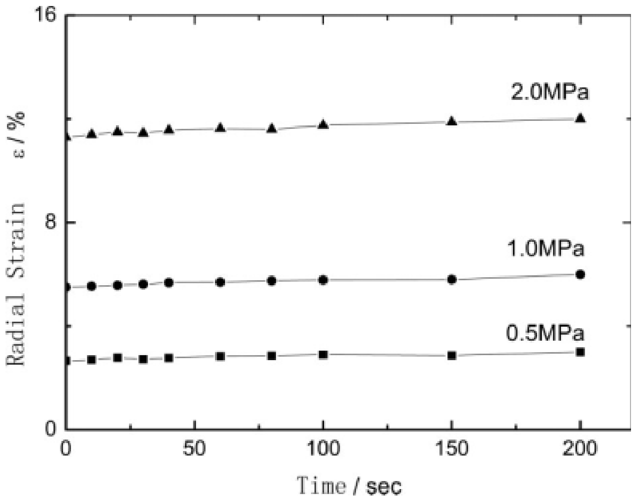

Figure 10 Radial strain creep behavior.

compressing samples to a given pressure immediately. Under both loads, resistance would be detected when the load arrived at the given pressure immediately. An interesting result can be found that the piezoresistivity of sample under slowgoing load is different with that under elastic load, as shown as Figure 7. This phenomenon presents that the piezoresistivity of particles filled conductive composites has time dependence.

To analyze deeply, a further experiment designed is to put sample under several invariable pressures for 200 s and test the piezoresistivity, compressing strain and radial strain at the same time. The results are shown as Figures 8, 9, and 10. It can be seen that the radial strain of composite keeps mostly invariable, but the electrical resistance and compressing strain all present creep behavior. Especially, the decrease of electrical resistance is fast in the period of 0–30 s, slow in 30–100 s and mostly unchanged after 100 s and the increase of compressing strain is also fast in the period of 0–30 s, slow in 30–100 s and mostly unchanged after 100 s. This is because there exists molecular motion of the polymer matrix under uniaxial pressure, which results in strain creep behavior in the composite. With the strain creeping process, the volume of composite sample decreases gradually. Then, the distance between adjacent fillers is reduced and more adjacent fillers contact each other. More conductive paths may occur not only parallel to the stress direction but also perpendicular to the stress direction. As a result, the orientation constraint of conductive paths is broken. There generates a new conductive network inside the composite sample. Then, the electrical resistance decreases with time under an invariant load, showing "electrical resistance creep" behavior.

CONCLUSIONS

Based on a series of experiments, we analyzed the conductivity and piezoresistivity of particles filled polymer composite with different filler particle's size and polymer's elastic property. Some conclusions can be obtained as (1) the conductive percolation threshold and shape exponent of CCB filled polymer composites are effected on by CCB particle size and reduce with filler size decreasing; (2) In the area of conductive percolation threshold, the composite has obvious negative piezoresistivity and more obvious with bigger shape exponent; (3) the compressing deformation is the main reason of the piezoresistivity of particles filled conductive composites. These are very useful to apply in the design and fabrication of polymer sensors. The other interesting phenomenon is that the electrical resistance of composite decreases with time under an invariant load, showing "electrical resistance creep" behavior. However, this will bring negative affect on sensors' dynamic respondence. So, we will focus on this creep behavior in the future work.

References

1. Yi, X. S.; Wu, G. Z.; Pan, Y. J Mater Sci Lett 1997, 16, 1381.
2. Shimojo, M.; Namiki, A.; Ishikawa, M.; Makino, R.; Mabuchi, K. IEEE Sens J 2004, 4, 589.
3. Zhu, S.; Zheng, Q.; Zhou, J. F.; Song, Y. H.; Zhang, M. Q. Acta Polym Sin 2006, 1, 82.
4. Busfield, J. J.; Thomas, A. G.; Yamaguchi, K. J Polym Sci Part B: Polym Phys 2005, 43, 1649.
5. Yuji, J.; Shida, K. IEEE Trans Instrum Meas 2000, 49, 1091.
6. Lei, H.; Pitt, W.; Mcgrath, L.; Ho, C. Sens Actuators B 2007, 125, 396.
7. Mclanchlan, D. S. J Phys C: Solid State Phys 1987, 3, 865.
8. Fan, Z. Y. Acta Metall Mater 1985, 1, 43.
9. Mclanchlan, D. S.; Blasziewicz, M.; Robert, E. J Am Ceram Soc 1987, 8, 2187.
10. Hussain, M.; Choa, Y. H.; Niihara, K. Composites A 2001, 4, 1689.
11. Wang, L. H.; Ding, T. H.; Wang, P. Sens Actuators A 2007, 135, 587.
12. Wang, L. H.; Ding, T. H.; Wang, P. J Polym Sci Part B: Polym Phys 2008, 46, 1050.