# Piezoresistivity of Silicone-Rubber/Carbon Black Composites Excited by AC Electrical Field

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**ABSTRACT:** Flexible conductive composites were prepared using liquid silicone rubber as a matrix and conductive carbon black (CCB) as a filler, and the filler loading was varied from 1 to 15 phr in mass ratio. The surface conductivity was studied as a function of CCB concentration (1, 5, 10, 15 wt %), frequency in the range from DC to 1 MHz. The AC resistivity of the composites with low CCB concentration was found to be frequency dependent, whereas the composites with high CCB concentration was almost frequency independent. The resistance/impedance drift of the composites with time decreases sharply with the increase of frequency of applied electrical field. The piezoresistivity of the composite with 5 wt % CCB concentration (the upper percolation limit) was studied. It is found that the composite exhibits prominent positive piezoresistivity coefficient effect through the measurement frequency, and the sensitivity becomes steeper with the increase of exciting frequency. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 337–341, 2009

**Key words:** conducting polymers; composites; silicone; rubber; AC conductivity; piezoresistivity

## INTRODUCTION

Conductive rubber has been known since the latter part of the 19th century,[1] and it has been widely used in many fields such as electrostatic dissipation of charge,[1] pressure sensors, tactile sensors,[2,3] gas sensors,[4,5] and so on because of its many advantages such as ease of shaping, low density, wide range of electrical conductivities, low thermoconductivity, and corrosion resistance.[1] In general, conductive rubber is formed by the compounding of conductive filler particles in an insulating rubber polymer. The resistivity of the conductive rubber is a function of many parameters such as the concentration of filler, the radius and structure of filler particle, the type of matrix and the processing condition,[6] and so on. The insulator to conductor transition is governed by the laws of percolation theory, and a critical volume fraction of the filler is necessary for the onset of electrical conduction.[7]

$$\sigma \sim (P - P_c)^{\alpha} \qquad (1)$$

where $P_c$ is the percolation threshold and $\alpha$ is the critical exponent.

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The AC electrical properties of conductive rubber has been reported in the literature.[6,8,9] To the best of our knowledge, no work is available where the resistance/impedance drifting with time and piezoresistivity excited by AC electric field are studied.

This work gives an equivalent circuit to analyze the AC properties of the composites in macroscopic way and reports the findings of an experimental investigation on the frequency dependence of the resistance/impedance drifting rate, i.e., the frequency dependence of piezoresistivity.

## DERIVATION OF THE EQUIVALENT CIRCUIT

In DC case, the total resistance of the conductive composites is a function of both the resistance of through each conducting particle and the polymer matrix.[10] A DC equivalent circuit has been given out in 1982.[11] In this article, a modified equivalent circuit has been given out for the composites with two electrodes as shown in the Figure 1 aiming to explain the performances both in DC and AC cases.

In Figure 1, $R_{ps}$ and $C_{ps}$ are contact resistance and contact capacitance between electrode and sample, respectively, $R_{sc}$ is the resistance of continuous conductive paths in the sample, $R_s$ is the resistance of separated clusters apt to form conductive paths, whereas $C_s$ is the capacitance between them, $C_p$ is the coupling capacitance of the electrodes. Among them, the $C_{ps}$ is formed by ionic conduction, and the

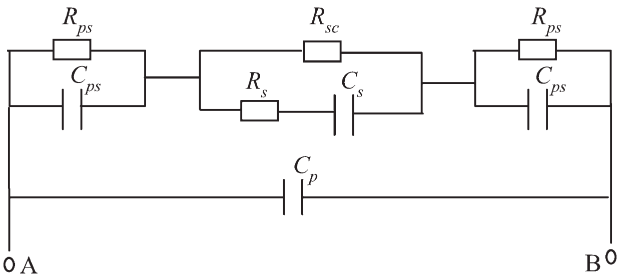


**Figure 1** Equivqlent circuit of the composites with two electrodes.

$C_s$ is formed by the separations of the conducting clusters or aggregates in the sample.

## MATERIALS AND EXPERIMENTS

### Materials

Room-temperature vulcanized liquid silicone rubber (107#) was bought from Beijing Hangping Organic Silicone Plant, Beijing, China. Conductive carbon black (CCB) SL-20 was provided for free by Carbon Black R&D Institute, Zigong, China. The properties of the rubber matrix and carbon black found in the manufacturer literature are shown in Table I.

Hexane, analytically pure grade, was procured from Beijing Modern Eastern Finechemical, China. Di-n-butyltin Dilaurate Compound (ZT-102) and Vinyltriethoxysiline (KH-151) were bought from Beijing Stable Chemical, China, and Nanjing Capatue Chemical, China, respectively. Other compounding ingredients were of chemically pure grade procured from standard suppliers. The formulation used for the preparation of the composites is given in Table II.

### Sample preparation

Rubber and various ingredients were mixed in a beaker at temperature of 30°C for about 1.5 h by following the formulation given in Table II, and mechanical stirring (2000 r/min) and ultrasonic vibrating (200 W) were used for better particle dispersion. The mix was then molded by compression at room temperature for at least 24 h into plates of about 4 mm thick. Square samples of 10 × 10 mm were cut from the molded plates for piezoresistivity test and rectangle samples of 10 × 15 mm for surface-resistivity measurement.

**TABLE I**
**Properties of CCB and Silicone Rubber (taken from manufacturer's literature)**

| | Specific surface area ($m^2/g$) | Resistivity (Ωcm) | Young's modulus (MPa) | Density ($g/cm^3$) |
|---|---|---|---|---|
| CCB | 140 | 0.5 | $1 \times 10^5$ | |
| Rubber | | $9.0 \times 10^{14}$ | 6 | 0.96 |

**TABLE II**
**The Formulation Used for the Preparation of the Composites**

| Ingredient | Loading (phr) |
|---|---|
| 107# | 100 |
| SL20 | 1,5,10,15 |
| ZT-102 | 1 |
| Ethyl silicate | 1.5 |
| KH-151 | 1 |
| Hexane | Appropriate |

### Measurement

DC resistivities were measured with 3458A multimeter (HEWLETT PACKARD) using 2-probe method. AC impedances were measured with 4284A precision LCR meter (Hewlett Packard, 20–1 MHz). The piezoresistivity experiments in the range of 0–1 MPa were conducted using the system composed of electric JSV-500D work table (Algol, Japan), HF-50 force gauge (Algol), computer, and two devices mentioned earlier, all data were read into the computer and recorded automatically. Interdigital electrodes (copper lines sprayed with soldering tin) of 5 × 7 mm were used for the surface piezoresistivity tests and two rectangle electrodes (copper plate) of 4 × 7 mm were used for volume piezoresistivity tests. All the experiments were conducted in the condition of room temperature (about 20–25°C) and humidity (40–60%) in May at Beijing.

## RESULTS AND DISCUSSION

### Surface resistivity of the composites

The variation of surface electrical resistivity of the composites as a function of mass percent of CCB is studied and shown in Figure 2. The data can be fitted with the relation eq. (2).

$$\log \rho = 2.042 * (P - 0.8)^{-0.2748} \quad (2)$$

where ρ is the surface resistivity of the composites and $P$ is the concentration of CCB. From eq. (1), it can be considered that the percolation threshold is 0.8 phr in mass ratio.

It is seen that a relatively considerable drop in resistivity occurs when the CCB concentration is in the range of 0.8–5 phr. The resistivity value for composite with 15 wt % CCB is about three orders of magnitude less than the composite with 1 wt % CB, unlike volume resistivity presented in other literature,[9,12] the resistivity difference between the conductive and the semiconductive is about 10 orders of magnitude. This is because of fewer continuous conductive paths

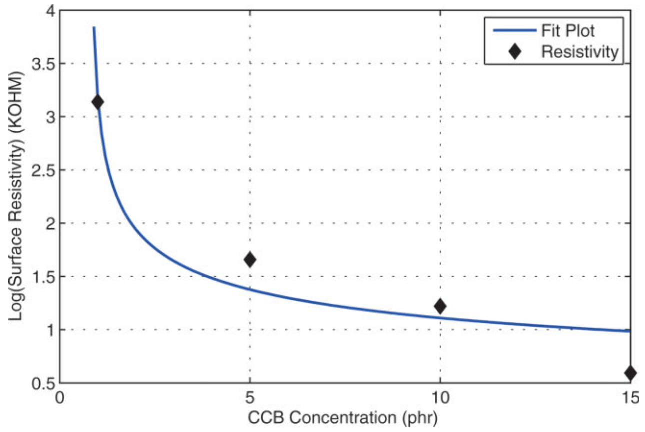


**Figure 2** CCB concentration dependence of the surface resistivity. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

taking part in the transportation of charge carriers in surface than that in volume.

### Frequency dependence of the impedance

The effect of frequency on the surface impedances (namely resistivity) have been studied and shown in Figure 3. From the plot it is observed that the composites near the percolation limit (containing 1, 5, and 10 phr of CCB) show a strong frequency-dependent region (<200 kHz) and an almost frequency-independent region (>200 kHz) of AC impedance. The AC impedance of the composites above the percolation (containing 15 phr of CCB) exhibits almost frequency-independent nature in measurement frequency range. In the composites with 1 and 5 phr of CCB, the frequency dependence of AC impedance can be attributed to the existing capacitances between the CCB aggregates or particles filled with host medium. In the vicinity of percolation region, the number of continuous conductive networks is very few, a large number of conductive aggregates and particles are in a critical status in which their separations are so small that any excitation such as thermo, electrical field, pressure, etc., can affect the conductance of the composites. So at relatively high frequencies, more electrons are sufficiently excited off the surface of CCB particles and transmitted along the direction of the applied electrical field.[7] Other reasons maybe that effective increase of dipolar contributions,[8] possible increase in the number of conduction paths created between the CCB particles aggregates in the composite in addition to a decrease in the width of potential barriers within the bulk regions of conductivity.[13] The result of this is that the current density between electrodes becomes higher and the AC impedance gets lower. While for the composites with high concentrations of CCB, sufficient numbers of continuous conductive paths have formed, a few or no tunnels for electrons to hop, so the current charge carriers prefer to flow along these continuous paths and the overall performance of the composites is resistive. From Figure 3, a strange phenomenon can be found that the impedance of the composites near the percolation (10 phr) begins to be lower than the impedance of the composites above percolation (15 phr) when the frequency is above 200 kHz, it can be interpreted that at relatively high frequencies, the electron hopping becomes very dominant or that the formation of a continuous conductive network minimizes the effect of the electron hopping.[6]

From the macroscopic point of view, referring to the equivalent circuit in Figure 1, when the composites are excited by DC, the total resistance is $R_{sc} + 2R_{ps}$, when the frequency of applied AC field is sufficiently high, the total impedance is approximately equal to $R_{sc}//R_s//Z_p$ ($Z_p$ is the AC impedance of $C_p$, which is very small), when the frequency of applied AC field is relatively low (<200 kHz), the total resistance is$\{2(R_{ps}//Z_{ps}) + [R_{sc}//(R_s + Z_s)]\}//Z_p$ ($Z_{ps}$ and $Z_s$ are AC impedances of $C_{ps}$ and $C_s$, respectively). $C_p$ is very small when measuring the surface impedance, so it will play a more important role when frequency is very high.

### Time dependence of resistance/impedance of the composites

Ions incontestably exist in polymers because of various chemical products added during manufacture and slow decomposition of every ingredient. These ions seem to be responsible for the slow evolution for the current.[11] One of the results of the current variation is the drift of resistance/impedance with time. The frequency dependence of the resistance/impedance drift of the composites has been studied and shown in Figure 4.

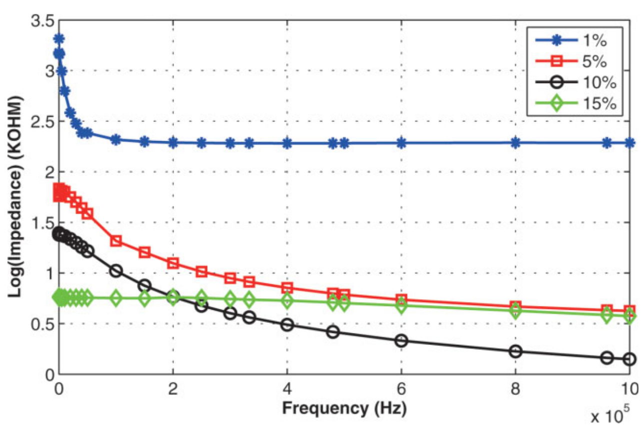


**Figure 3** Frequency dependence of resistance/impedance. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

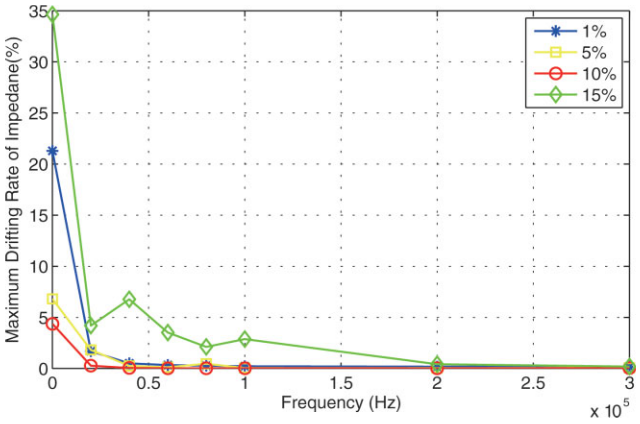


**Figure 4** Frequency dependence of resistance/impedance drift. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

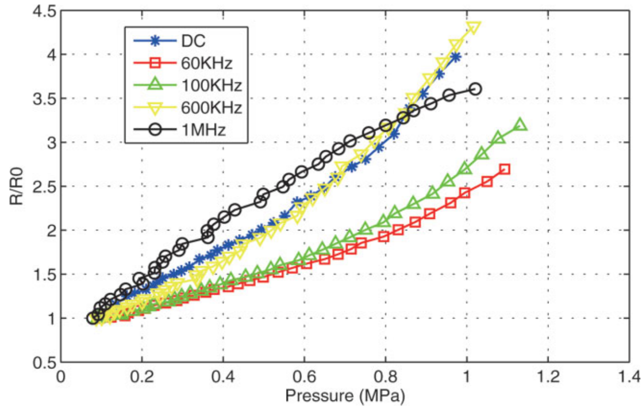


**Figure 5** Piezoresistivity of volume resistance. $R_0$ is the original resistance before press. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

In Figure 4, each point is the rate of maximum resistance/impedance drift to the mean value of the resistances measured every 2 min during half an hour at certain frequency (0–300 kHz) for every composite with different CCB concentrations.

$$R_{\max} = 100^{*}(D_{\max} - M)/M \quad (2)$$

where $R_{\max}$ is the maximum drifting rate of impedance (%), $D_{\max}$ is the maximum drift from mean value, and $M$ is the mean value of the impedance in half an hour, $M\sum_{i=1}^{15} R_i/15$, $R_i$ is the impedance at certain time.

It can be observed that the drifting rates decrease sharply in the frequency range of DC to 50 kHz and stay in a very low level in higher frequency. In other words, the impedance is becoming more stable in high frequency range than in DC and low frequency, this property must be beneficial to the applications in sensor field such as electronic nose, stress sensor, and so on. At the same time, the drifting rate decreases with the increase of CCB's concentration except that of the 15 wt %. The reason maybe that the effect of capacitance including ionic conduction, interfacial polarization, etc., is eliminated with the increase of frequency. The case of 15 wt % could not be understood to our knowledge till now.

## Piezoresistivity in the process of continuous loading

The volume and surface piezoresistivity of the composite with 5 wt % CCB has been studied in the frequency range of DC to 1 MHz, loading speed is constant, 4.7 mm/min. The result is shown in Figures 5 and 6, respectively. It can be observed that the composite performs positive piezoresistivity coefficient effect except the surface piezoresistivity at 20 kHz, the sensitivity increases with the increase of frequency, the sensitivity of the volume piezoresistivity is nearly two times that of the surface, the response of the composite to the pressure becomes more linear with the increase of frequency. On the other hand, the DC response of the composite is similar to that of the high frequencies for both the surface and volume piezoresistivity.

The reason for these phenomena can be explained using the equivalent circuit of the composite shown in Figure 1. When the composite is excited with DC and high frequency AC field, the piezoresistivity of the composite is the result of construction and destruction of resistive current paths so they have high sensitivity.[10,14,15] When the composite is excited with relatively low frequency electric field (<200 kHz), the resistive and capacitive current paths wok together at

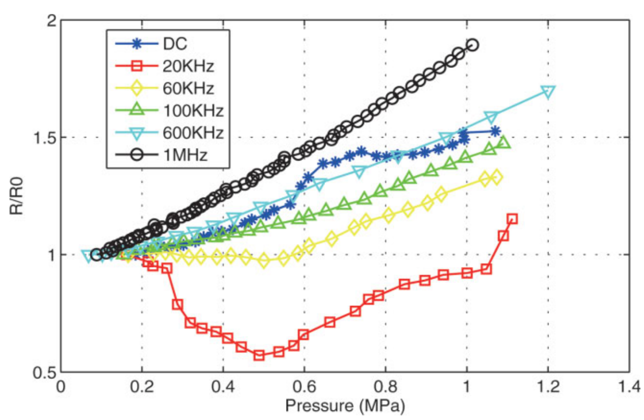


**Figure 6** Piezoresistivity of surface resistance. $R_0$ is the original resistance before press. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the same time, whereas the capacitance in the composite distributes more randomly than the resistance, so the piezoresistivity is averaged and the sensitivity becomes less obvious.

As to the difference between surface and volume, it may be understood in the aspect of the number of conducting paths.

## CONCLUSIONS

The surface AC resistivity of low CCB-loaded composites (in the vicinity of percolation threshold) exhibits a strong frequency-dependent nature, whereas that of the high CCB-loaded composites is frequency independent because of the increased contribution of DC conductivity. The maximum drifting rate of resistance/impedance decreases with the increase of frequency because of the less effect of polarization and electron "hopping." The sensitivity of the piezoresistivity increases with the increase of the frequency.

## References


1. Norman, R. H. Conductive Rubbers and Plastics; Elsevier: London, 1970; p 3.
2. Shimojo, M.; Namiki, A.; Ishikawa, M.; Makino, R.; Mabuchi, K. IEEE Sens J 2004, 4, 589.
3. Yuji, J.; Shida, K. IEEE Trans Instrum Meas 2000, 49, 1091.
4. Kim, Y. S.; Ha, S. C.; Yang, Y.; Kim, Y. J.; Cho, S. M.; Yang, H.; Kim, Y. T. Sens Actuators B 2005, 108, 285.
5. Lei, H.; Pitt, W.; McGrath, L.; Ho, C. Sens Actuators B 2007, 125, 396.
6. Mohanraj, G. T.; Chaki, T. K. J Appl Polym Sci 2007, 104, 986.
7. Psarras, G. C.; Manolakaki, E.; Tsangaris, G. M. Compos Part A 2003, 34, 1187.
8. Rao, R. V.; Shridha, M. H. Mater Lett 2002, 55, 34.
9. Singh, V.; Tiwari, A. N.; Kulkarni, A. R. Mater Sci Eng 1996, 41, 310.
10. Zhang, X.; Pan, Y.; Zheng, Q.; Yi, X. J Polym Sci Part B: Polym Phys 2000, 38, 2739.
11. Jean-pierre, R. In Carbon Black-Polymer Composites; Sichel, E. K., Ed. Marcel Dekker: New York, 1982; p 92.
12. Wei, Z.; Blackburn, R. S.; Abbas, D. S. Scr Mater 2007, 57, 949.
13. Elimat, Z. J Phys D: Appl Phys 2006, 39, 2824.
14. Knite, M.; Teteris, V.; Kiploka, A.; Kaupuzs, J. Sens Actuators A 2004, 110, 142.
15. Das, N.; Chaki, T.; Khastgir, D. Polym Int 2002, 51, 156.