Piezoresistive Properties of Multi-Walled Carbon Nanotube/Silicone Rubber Composites under Cyclic Loads with AC Excitation

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Abstract. Multi-walled carbon nanotube (MWCNT)-filled silicone rubber (SR) composites were prepared as piezoresistive materials for pressure sensing applications, with MWCNT concentrations from 0.5 wt% to 6.5 wt%. Samples were compressed under successive loading–unloading cycles with alternating current (AC) excitation, and electrical admittances were measured using interdigital electrodes. Then the piezoresistive properties were obtained and explored. Experiment reveals negative piezoresistivities with exponential performance characteristics for all concentrations. Furthermore, piecewise polynomial approximations of the performance characteristics are established to simplify the design of circuits. As the MWCNT concentration increases, the proper measurement range broadens, and the sensitivity in this range increases. However, the repeatability and hysteresis appear relatively poor far above the percolation threshold; both show minimums near the percolation threshold, with values of 2.3% and 16.1% respectively. The repeatability and the hysteresis varying with the MWCNT concentration are interpreted as the recovery capabilities of the conducting networks varying with the distribution densities of nanotubes. Achieved results serve to guide the development of piezoresistive nanocomposite sensors.

1. Introduction
Piezoresistive polymer composites have recently been developed for force and pressure sensing applications [1-6]. Piezoresistivity refers to the behavior in which the electrical conductivity of the composite changes with the applied load [7,8]. Since the mechanism of the electrical conductivity is the formation of conducting paths inside the matrix [9], both direct current (DC) and AC conductivities are expected to vary with load. However, most previous studies have focused on the DC piezoresistive properties of polymer composites [10-14], while only a few investigations have addressed the properties under AC excitation. Kilbride et al. [15] fully discussed the experimental observation of scaling laws for the AC conductivities in nanotube/polymer composite thin films, yet the relationship between the pressure load and the AC conductivity was not explored by the authors. Wang et al. [16] qualitatively studied the piezoresistivity of carbon black/silicone rubber composites excited by AC electrical field. They observed piezoresistivity in the continuous loading process and found out that the sensitivity increased with increasing frequency. Further study is needed to quantitatively evaluate the performance of sensing materials under cyclic loads.

In this work, MWCNT/SR nanocomposites have been prepared with concentrations from 0.5 wt% to 6.5 wt%. Sensing elements with interdigital electrodes were compressed under successive loading–
unloading cycles, and AC responses were measured at a frequency of 1MHz. Based on the experimental data, the relationship between the pressure load and the AC conductivity during loading–unloading cycles was discussed. The conventional performance indexes of sensing materials are quantitatively evaluated, such as sensitivity, proper measurement range, repeatability and hysteresis. Furthermore, the dependence of the repeatability and the hysteresis on MWCNT concentrations is interpreted in terms of recovery capabilities of the conducting networks varying with the distribution densities of nanotubes.

2. Experiments
MWCNTs (Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences, China) were dispersed into SR (Beijing Hangping Organic Silicone Plant, China) solution by ultrasonic and magnetic stirring at 50 ℃ for 30 min, and cross linker and catalyzer were then added to help vulcanize the nanocomposite. The mixture was deposited by drop coating onto 4 mm × 7 mm tinned copper interdigital electrodes, with the film thickness of nanocomposite around 0.3 mm. The nanocomposite materials together with interdigital electrodes made up a pressure sensing element for test. Samples prepared in this work contained MWCNT concentrations of 0.5 wt%, 2.0 wt%, 2.9 wt% and 6.5 wt%.

Each sample was compressed under successive loading–unloading cycles to investigate the piezoresistive properties. The rate of pressure change was approximately 36 kPa/s, and the time interval between two cycles was 5 min. The pressure was recorded by HP-500 digital force gauge (Yueqing Handpi Instruments Co. Ltd., China), and the admittance was measured by a HP 4284A Precision LCR Meter with an exciting voltage of 1V at 1MHz, using two-point measuring method at room temperature.

3. Results and discussions
3.1. Sensitivity to pressure under AC excitation
Fig. 1 shows the relative changes in admittance magnitudes during the first loading process. It is obvious that samples of different concentrations exhibit negative piezoresistivity with distinguishable characteristic plots. The characteristic plot in the full scale can be well fitted by an exponential function in the form

\[ \frac{\Delta|Y|}{|Y_0|} = r_1 \exp\left(-\frac{p}{t}\right) + r_2 \]

where, \( p \) is the pressure, and \( r_1, r_2, t \) are calibrated parameters. Adjusted R-Square values obtained are greater than 0.98 for all three concentrations. Note that the slope of characteristic curve reflects the sensitivity to the input [10]. Thus the sensitivity, the slope at each point on the fitting curve, is decreasing with the increasing pressure in the full scale.

The exponential characteristic curve and varying sensitivity describe the sensing performance with a high accuracy. However, in many applications low-order polynomials are preferred in the fitting process of sensing characteristic to achieve significant complexity reduction in electronic circuit design, despite a slight loss of accuracy. Accordingly, characteristic plots are divided into distinct regions. Fig. 2 demonstrates three regions: the linearly ascending region under relatively low pressures (Region I), the linearly creep region under relatively high pressures (Region III) and the transition region between them (Region II).

In Region I and Region III, the plot section can be well fitted by a straight line in the form

\[ \frac{\Delta|Y|}{|Y_0|} = k_1 p + k_2 \quad (p_l \leq p \leq p_h) \]

where, \( k_1 \) is the slope of the fitting line, \( k_2 \) is the intercept value, \( p_l \) is the low limit of the region, and \( p_h \) is the high limit. Adjusted R-Square values obtained are in the range of 0.91–0.99. The fitting lines in these two linear regions are illustrated in Fig. 2, and the slopes of these lines are presented in Table...
1. For all three concentrations the sensitivity in Region III is an order of magnitude less than that in Region I. Moreover, the sensitivity in Region I increases distinctly with increasing concentration.

In Region II, the plot section is nonlinear, and it can be fitted by a quadratic function in the form

$$\frac{\Delta |Y|}{|Y_0|} = s_1 p^2 + s_2 p + s_3 \quad (p_{tl} \leq p \leq p_{th})$$

(3)

where, \(s_1, s_2, s_3\) are calibrated parameters, \(p_{tl}\) is the low limit of the transition region, and \(p_{th}\) is the high limit. Adjusted R-Square values are greater than 0.98 for all three concentrations, and the fitting curves are also illustrated in Fig. 2. The sensitivity in this nonlinear region is variable, decreasing with the increasing pressure from a maximum value approaching the sensitivity in Region I down to a minimum value approaching that in Region III.

Considering the moderate sensitivity, we extend the proper measurement range of the sensing element from Region I to Region II, excluding Region III. The specific ranges are listed in Table 1. Clearly, this range broadens with increasing concentration. Furthermore, the linear region, Region I, shortens with increasing concentration, while the nonlinear region, Region II, is quite the opposite.

Figure 1. Changes in admittance magnitudes during the first loading process.

Figure 2. Experimental and fitting results for samples with MWCNT concentrations of (a) 0.5 wt% and (b) 2.0 wt% and (c) 2.9 wt%.
Table 1. Slopes of fitting lines and proper measurement ranges.

| MWCNT concentration (wt%) | Slope of the fitting line in Region I (kPa⁻¹) | Slope of the fitting line in Region III (kPa⁻¹) | Proper measurement range (kPa) |
|---------------------------|---------------------------------------------|-----------------------------------------------|-------------------------------|
| 0.5                       | 1.49E-05                                    | 1.45E-06                                      | 200~1.20E+03                  |
| 2.0                       | 3.58E-05                                    | 3.09E-06                                      | 200~1.40E+03                  |
| 2.9                       | 5.39E-05                                    | 2.60E-06                                      | 200~1.60E+03                  |

3.2. Repeatability under cyclic loads

Fig. 3 depicts the relative changes in admittance magnitudes under successive loading processes. Repeatability is defined as the ratio of standard deviation of measured results to the full-scale output [17]. As Fig. 3a and Table 2 reveals, the repeatabilities are good for samples with MWCNT concentrations from 0.5 wt% to 2.9 wt%. Especially, for samples with MWCNT concentrations of 2.0 wt% and 2.9 wt% the calculations are quite low, typically less than 3.0%. Note that, as previous studies have shown [9], the percolation transition lies right within the concentration range of 2.0 wt% ~ 2.9 wt%, with an estimate of the percolation threshold at 2.45 wt%. Hence, it suggests that the repeatability shows a minimum value of 2.3% near the percolation threshold, or rather slightly below the percolation threshold. As for the sample with a MWCNT concentration far above the percolation threshold, the repeatability appears relatively poor compared to those of samples with lower concentrations, directly demonstrated in Fig. 3b. Referring to the conducting paths theories [9], such behaviors can be interpreted as follows.

The electroconductibility of nanocomposite relies on the cooperation of resistive and capacitive conducting paths inside the matrix. Current passes through the resistive paths as conduction current and through the capacitive paths as displacement current. The resistive paths do not appear until the concentration reaches the percolation threshold, at which concentration the neighbouring nanotubes become close enough for electron hopping or tunnelling to occur [18]. Near or below the percolation threshold the relatively large distance between neighbouring nanotubes makes it difficult to constitute a resistive network, and the admittance is dominated by the capacitive network. Besides, the small quantity of fillers helps maintain the elasticity of the composite. Therefore after the load is removed the capacitive network configuration reverts to the original state, and during the next loading period the configuration deforms in a similar way. As a result, samples exhibit good repeatabilities. On the other hand, far above the percolation threshold the nanotubes distribute densely in the matrix to form numerous resistive and capacitive paths, constituting a conducting network throughout the composite. Moreover, the great amount of fillers decreases the elasticity of the composite. Consequently the conducting network deforms irreversibly each time the sample is compressed, resulting in relatively poor repeatability.
Figure 3. Changes in admittance magnitudes under successive loading processes for samples with MWCNT concentrations of (a) 0.5 wt%, 2.0 wt% and 2.9 wt% and (b) 2.9 wt% and 6.5 wt%.

Table 2. The repeatability of samples.

| MWCNT concentration (wt%) | Repeatability (%) |
|---------------------------|-------------------|
| 0.5                       | 5.6               |
| 2.0                       | 2.3               |
| 2.9                       | 2.9               |

3.3. Hysteresis under cyclic loads

Hysteresis is defined as the maximum difference in output between the loading and unloading processes, compared to the full-scale output [17]. As Fig. 4 reveals, samples at all concentrations tested exhibit hysteresis during loading–unloading cycles, for the nanocomposite always tends to maintain the previous state due to the viscoelasticity of the polymer. Furthermore, the calculations in Table 3 indicate that the hysteresis shows a minimum value of 16.1% near the percolation threshold, or rather slightly above the percolation threshold, while the sample with a MWCNT concentration far above the percolation threshold shows a more remarkable hysteresis effect. Similar to the reason for
poor repeatability at this concentration, this is due to the irreversible deformation resulting from the dense distribution of nanotubes.

Figure 4. Changes in admittance magnitudes under loading-unloading cycles for samples with MWCNT concentrations of (a) 0.5 wt% and (b) 2.0 wt% and (c) 2.9 wt% and (d) 6.5 wt%.

Table 3. The hysteresis of samples.

| MWCNT concentration (wt%) | Hysteresis (%) |
|---------------------------|----------------|
| 0.5                       | 28.1           |
| 2.0                       | 32.4           |
| 2.9                       | 16.1           |
| 6.5                       | 75.9           |

4. Conclusions
MWCNT/SR nanocomposite pressure sensing elements have been prepared with concentrations from 0.5 wt% to 6.5 wt%. Samples exhibit negative piezoresistivity under loading–unloading cycles with AC excitation. The experimental plots of change in admittance magnitude vs. pressure are divided into three regions according to the sensitivity characteristics: the linearly ascending region, the nonlinear transition region and the linearly creep region. Plot sections are independently fitted by low-order polynomials, yielding reduction of complexity in the circuit design. Considering the moderate
sensitivity, we extend the proper measurement range through the former two regions. Especially, in the linearly ascending region the sensitivity approaches a constant value and increases rapidly with increasing concentration.

While the sensitivity and proper measurement range are generally improved as the concentration increases, the repeatability and hysteresis properties behave dissimilarly. Both the repeatability and hysteresis exhibit minimum values of 2.3% and 16.1% respectively when the MWCNT concentration is near the percolation threshold, while the repeatability and hysteresis show larger values when the MWCNT concentration is far above the percolation threshold. These results are interpreted in terms of different recovery capabilities of the conducting networks due to different distribution densities of nanotubes.

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