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Enhanced piezoresistivity in Ni–silicone rubber composites*

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This paper reports that the nickel–silicone rubber composites with enhanced piezoresistivity were synthesized with much reduced nickel concentration. A large piezosensitivity of 0.716/kPa and a gauge factor of 600 have been obtained for a composite sample with filler-polymer ratio of 2.7:1 by weight. Measurements of resistance as a function of uniaxial force reveal that the piezoresistance arises predominantly from the internal heterogeneity of the material and the effect of geometrical changes of samples under pressure is neglectably small. The nonlinear current–voltage characteristic of the composite depends strongly on the filler content, the initial compression and the electrical current flowing in the sample. Ohmic behaviour has been observed only in the highly compressed samples. The breakdown strength decreases with increasing filler content of the composite. Both $I-V$ and $R-f$ characteristics indicates that the resistivity of the composites decreases with electrical field, suggesting that the composite may also be used to make voltage sensitive resistors for protecting circuits. All the experimental results favour a quantum tunnelling mechanism of conductivity. It finds that the concept 'negative resistance', often used to describe the phenomena that current decreases with increasing voltage, is not appropriate and should be avoided.

Keywords: piezoresistivity, quantum tunnelling, $I-V$ characteristics, voltage sensitive resistors
PACC: 6000, 6140K, 7000, 8160H

1. Introduction

Highly piezosensitive polymer composites have been a research focus for the last two decades.[1−8] Apart from the fundamental physical problems associated with them, these materials have large number of potential applications in electromechanical sensors, tactile sensors for robotics, touchable sensitive screens and the like. Recently a metal-polymer composite (market name QTC$^{\rm TM}$) with unusual properties has been reported.[6] The most distinct difference between QTC$^{\rm TM}$ and the other composites is the morphology of the filler particles in the composite. The nickel particles used have an extremely spiky morphology with numerous sharply pointed protrusions and ridges, which are claimed to be crucial to the high pizoresistivity of the QTC$^{\rm TM}$ composites.[6] As a result, careful mixing of filler and precursor monomer is desired to avoid damaging the surface feature of nickel filler particles. The powders incorporated at loadings of metal to polymer ratio of between 4:1and 6:1 by weight (400–600phr).

Using a newly developed processing technique, we have prepared Ni–silicone rubber composites with much enhanced piezoresistivity and improved electrical characteristics. The content of nickel powder in the composite has been reduced significantly, resulting in a much flexible material with much lower density. A direct consequence is that the manufacturing cost can be reduced since the price of the metal powder is normally more expensive. The relatively low density makes the composites more suitable for aerospace applications. In addition, less metal fillers increase the electrical breakdown strength of the composite, a crucial parameter to the developments of electrical and electronic devices. The much simplified manufacturing process also contributes to a reduced price and large scale industrial production of the material. Here we report the electrical characteristics of this newly developed composite.

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2. Experimental

Samples were prepared by a patented process[9] with nickel powders dispersed in silicone rubber. Nickel powders were chosen due to its high resistance to surface oxidation. Silicone rubber with various grades is widely available in the market. Silastic®3496 mould making base & 81-T curing agent (Dow Corning) was used in preparing the samples. Apart from its high elasticity, it is chemically stable across a relatively wide temperature range in the vicinity of room temperature. Biocompatibility of silicone rubber also makes the resulting composite a potential candidate for applications such as artificial skin and possible pressure sensors which could be implanted in human bodies. The nickel powders used in this work are commercial products (Taizhou Minghua Metallurgy Powder Factory, China) whose particle diameter is graded as less than 74 μm. However, scanning electron microscopy (SEM) study of the composites showed that the real size of the particles ranges from several micrometres down to sub-micrometre. A SEM image for a typical composite sample is shown in Fig.1.

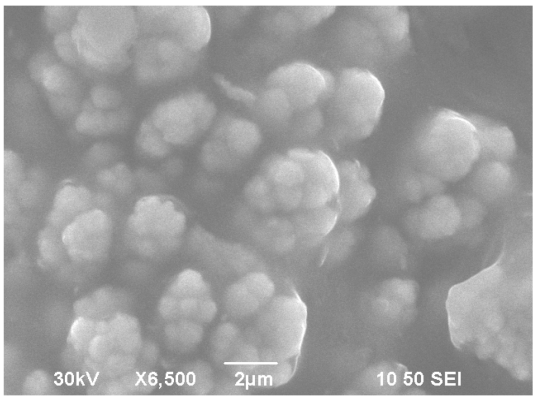


Fig.1. A SEM image of a silicone –nickel composite sample (2.5:1 Ni/polymer by weight).

The powders and the elastomeric matrix were mixed at a ratio ranging from 1.5:1 to 3:1 (150-300 phr) by weight, notably lower than that for QTC materials.[6] We found this percentage of metal powder is adequate to produce a high piezoresistivity. Further increase of metallic filler content leads to higher rigidity and reduced sensitivity to external pressure. To investigate the effect of surface morphology of filler particles on the electrical properties of the composite, samples were also prepared by milling the Ni powders for two hours, before mixing them with the liquid monomers. Subsequent tests showed that there is no detectable difference between samples with and without pre-milling. Contradicting to that of QTC composite, the electrical properties of our samples is not sensitive to the surface nature of the filler particles and the extra measure to retain them in the mixing process is not necessary. Samples with dimensions 4×4×1 mm were cut from composite sheets with a sharp knife. Table 1 gives the details of the samples used in this work. It shows that the density of the composite increases and the resistivity decreases with increasing filler content as expected.

Table 1. Nickel to polymer ratio by weight, density and resistivity of undeformed composite samples, the resistance (Ω)-force (gram) function and the correlation coefficient R-Square obtained by least square fit.

Sample No.	Nickel/polymer	Density/g·cm^{-3}	Resistivity/Ω·m	$R-f$ function	R-Square
1 (2601#)	2.55:1	2.756	2.544×10^{9}	R=$10^{11}\mathrm{e}^{-0.0295f}$	0.9853
2 (2702#)	2.7:1	2.909	5.424×10^{8}	R=$2\times10^{10}f^{-3.6252}$	0.9948

The resistance of uncompressed samples was measured by a ZC36 high resistance tester capable of carrying out resistance measurements up to $10^{17}\Omega$. A Hewlett Packard 3457A digital multimeter was used to measure the resistance of composite samples under uniaxial compression. Using two electrodes of copper plate in direct contact with the composite sample, we measured the resistance in the direction parallel to the compression. Uniaxial pressure was produced and monitored with a Sundoo force gauge with digital output. Current–voltage curves were obtained by using a conventional set up consisting of a D.C. voltage source, two multimeters and an adjustable resistor.

3. Results and discussions

Figure 2 shows the resistance as a function of applied uniaxial force for two composite samples with different Ni contents. Because the thickness and cross-section of the composite samples change under external stress, experimental data are given in terms of resistance rather than resistivity for samples of defined

composition and initial dimensions [6]. This is reasonable since resistance matters in most of practical applications.

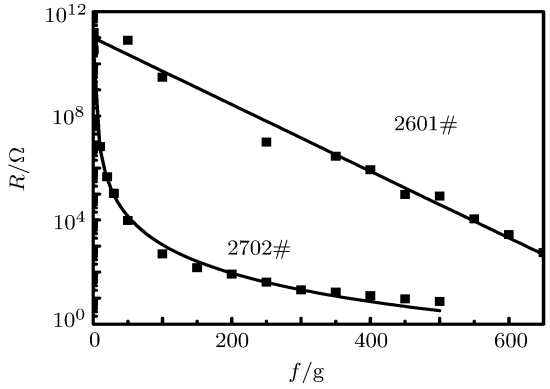


Fig.2. Comparison of piezoresistance for samples with different Ni content. The solid lines are the least square fits to the data.

It can be seen that both samples are very sensitive to external force. For sample 2 (2702#), a small force of 500 gram reduces the resistance from over $10^{11}\Omega$ down to a value less than 10Ω, a change of 10 orders of magnitude. This sensitivity to force depends strongly on the filler loading. When the nickel content is reduced to 2.55:1 (sample 1 (2601#)), the resistance of the composite becomes less sensitive to external force, it decreases only 6 orders of magnitude under the same force of 500 gram. A least square fit of the data in Fig.2 has been carried out for both samples 1 and 2 and the fitting results are also included in the last two columns of Table 1.

Apparently, external stress changes the dimensions of a composite sample, which in turn makes a contribution to the force dependence of resistance in Fig.2. In general, resistance R is proportional to the length l and inversely proportional to the cross section area A of a sample. The derivative of $\ln R$ against force f is given by

$$\frac{\mathrm{d}\ln R}{\mathrm{d}f} = \frac{\mathrm{d}\ln\rho}{\mathrm{d}f} + \frac{\mathrm{d}\ln l}{\mathrm{d}f} - \frac{\mathrm{d}\ln A}{\mathrm{d}f}. \qquad (1)$$

Below the yielding stress of the material, the third term on the right hand side of Eq.(1) is normally much smaller than the second term and may thus be ignored. The value of $\mathrm{d}(\ln R)/\mathrm{d}f$ has been obtained from Fig.2 to be –0.030/gram for sample 1 (2601#) and –0.439/gram for sample 2 (2702#) at low stress. We have measured the compression of both samples 1 and 2 as a function of uniaxial force and found that the absolute value of $\mathrm{d}(\ln l)/\mathrm{d}f$ for both samples is less than 0.001/gram. Thus for a good approximation, Eq.(1) can be simplified to

$$\frac{\mathrm{d}\ln R}{\mathrm{d}f} = \frac{\mathrm{d}\ln\rho}{\mathrm{d}f}. \qquad (2)$$

Equation (2) reveals that the piezoresistance is dominated by the resistivity change of the material and the effect of geometrical changes of the sample under pressure can be neglected without losing much accuracy. Piezosensitivity of a material may be defined as

$$S_{\mathrm{p}} = -\frac{\mathrm{d}\rho}{\rho \mathrm{d}P} = -A\frac{\mathrm{d}\rho}{\rho \mathrm{d}f} = -A\frac{\mathrm{d}\ln R}{\mathrm{d}f}, \qquad (3)$$

where P is the uniaxial pressure and A the cross section area of the sample. The piezosensitivity S_{p} of sample 1 thus calculated is 0.049/kPa. For sample 2, the value of S_{p} is calculated to be 0.716/kPa in the low uniaxial force range. These values of piezosensitivity can be compared with that of field-structured-composites of Au-coated Ni particles in epoxy:[7] 0.0036/kPa for samples at room temperature, which is much smaller than those of our materials.

The strain sensitivity of a piezoresistor is normally indicated by gauge factor (GF):[8]

$$GF = \frac{1}{R}\frac{\mathrm{d}R}{\mathrm{d}\varepsilon}, \qquad (4)$$

where $\varepsilon = \Delta l/l$ is the uniaxial compression strain. A plot of $\ln R$ versus strain has been carried out and the gradient gives a GF of 196 for sample 1. For sample 2, the value of GF decreases with increasing strain and a value of ∼600 has been obtained at a strain of 0.78%. These values are much higher than that reported for QTC materials (∼105)[6] but smaller than that for Au-coated Ni-epoxy composite (∼723).[7]

A common feature for the two samples is that the resistance decreases rapidly with increasing force up to a point depending on the Ni content and then decreases with a slower rate. A possible reason for the observed piezoresistive behaviour is that the conduction mechanism in the composite material at low stress may not be exactly the same as that when the stress is high. The sharp decrease in resistance at low stress suggests that there might be processes of both percolation and quantum tunnelling presented in the material. Normally, the Poisson ratio of a solid rubber is less than 0.5, leading to decrease of volume under uniaxial stress. Consequently, the volume fraction of nickel particles increases initially with increasing uniaxial force. If this volume fraction is in the vicinity of

percolation threshold, the resistivity or the conductivity will be very sensitive to the applied external force. Otherwise, a lower sensitivity will be observed. Further increase in the uniaxial force would eventually bring the volume fraction of nickel particles above the percolation threshold, resulting in a saturated low resistivity.

The experimental results presented above reveal clearly that the piezosensistivity of the composite depends strongly on the content of metallic fillers. When the filler content is well below the percolation threshold, the resistance of the sample decreases exponentially with applied force according to the quantum tunnelling mechanism. In the vicinity of the percolation threshold, the resistivity of the composite is determined by percolation as well as quantum tunnelling processes, resulting in a power-law behaviour of resistance-force relation. Therefore, the resistance range and the sensitivity of the composite may be tuned to suit applications for variety of purposes by varying the filler content.

The current–voltage characteristics of undeformed nickel–silicone rubber composite sample 1 and sample 2 are shown in Fig.3. For Sample 1 where the nickel content is relatively lower (2.55:1 by weight), the current increases exponentially with applied voltage, leading to a resistance decrease with increasing voltage. This current–voltage behaviour is often observed in pure insulating polymers,[10] but is rather different from the linear ohmic feature reported by Bloor *et al.*[11] The current–voltage characteristics of the composite depend strongly on the nickel content. For sample 2, in which the nickel-polymer ratio is increased to 2.7:1 by weight, the current increases with voltage following a power-law rather than an exponential trend (Fig.3), similar to that found in some multiferroic ceramics.[12] Table 2 gives the fitting parameters of current–voltage data for the two samples. Non-ohmic behaviour of the current–voltage characteristics has been observed at atmospheric pressure for all the composite samples with different filler content. Samples with less nickel content show an electrical feature similar to that of base polymer matrix, while the electrical behaviour of composites with high nickel content gradually approaches that of a conductor.

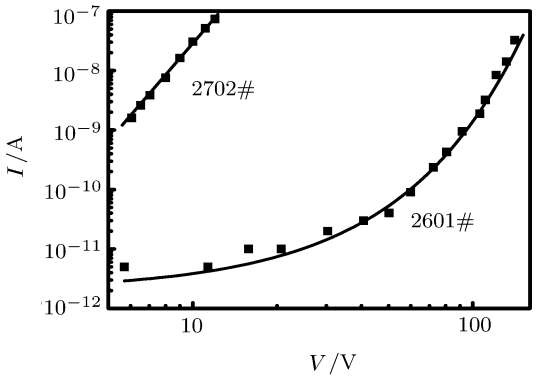


Fig.3. Current–voltage characteristics of undeformed composite samples.

It is interesting to note that both the current–voltage and resistance-force characteristics are exponential for sample 1, but become power-law for sample 2, indicating a possible correlation between the $I-V$ and $R-f$ features observed for these composites. In fact, both Figs.2 and 3 suggest that the resistivity of the composites decreases exponentially or by power-law with increasing electrical field. The electrical field is varied by changing the voltage in the case of current–voltage testing, whereas in the resistance-force measurements the electrical field is increased by reducing the thickness of the samples while keeping the voltage constant.

Table 2. Current–voltage fitting parameters for Ni–silicone rubber composites..

Sample No.	Uniaxial force/g	Increasing(↑)/decreasing (↓) V	Formula	R-square
1 (2601#)	0	↑	$I = 2 \times 10^{-12} \mathrm{e}^{0.0655\ V}$	0.9942
2 (2702#)	0	↑	$I = 6 \times 10^{-14} V^{5.6624}$	0.9988
	0	↓	$I = 4 \times 10^{-11} V^{2.9896}$	0.9994
	500	↑	$I = 0.1156\ V^{1.0665}$	0.9934
	500	↓	$I = 0.0993 V^{0.9735}$	0.9993

The data presented in Fig.3 were obtained with increasing voltage. In fact, the current–voltage characteristic of the composites with increasing voltage is rather different from that with decreasing voltage. Figure 4 shows the current–voltage characteristic of sample 2 with increasing as well as decreasing voltage. It can be seen that the current decreases with voltage following a power–law rather than an ohmic curve but with a much smaller power component (∼3) in comparison with the value of ∼5.7 obtained with increasing voltage (Table 2). This means that the value of current is not uniquely dependent on the applied voltage but associates with the voltage sweeping history. The sample has smaller resistances when measured with decreasing voltage i.e. the sample becomes less resistive after the initial voltage ramping. This hysteresis observed in the composite with increasing and decreasing voltage is similar to that of a pure polymer, but is markedly different from those of similar QTC materials reported by Bloor *et al.*[6,11] Very likely the relatively smaller hysteresis observed in this study is due to the lower testing current, while the extremely large and rather complex hysteresis observed with QTC may be due to the effect of positive temperature coefficient of the resistance, caused by the relatively large current.

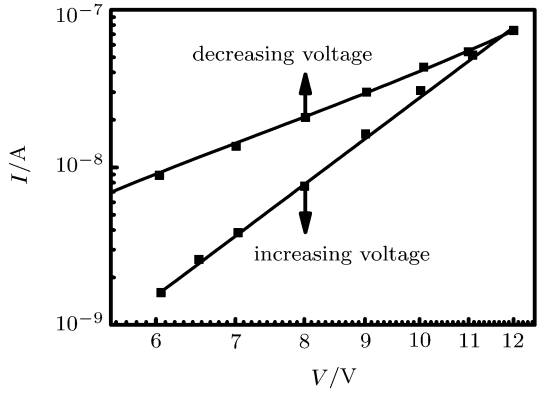


Fig.4. Hysteresis curve for undeformed sample 2 (2702#).

Throughout this paper, Ohm's law $I = V/R$ has been used to calculate the resistance of the composite, although the current–voltage characteristic of the sample shows a non-ohmic behaviour. There have been several papers, in which $R = \mathrm{d}V/\mathrm{d}I$ instead of $R = V/I$ was used to calculate the resistance of a sample.[6,11] Apparently, both equations are correct and make no difference if the material behaves ohmic. However, if non-ohmic materials such as polymers and composites are concerned, one may still use Ohm's law $R = V/I$ to define and calculate resistance but not the formulae $R = \mathrm{d}V/\mathrm{d}I$ because V/I and $\mathrm{d}V/\mathrm{d}I$ have, in general, different values. Physically, using R=dV/dI often leads to contradictions as well as confusions such as the so-called 'negative resistance'.[6,11] In Fig.4, larger currents are obtained when decreasing voltage, indicating that the material is less resistive. However, because the slope of the curve is smaller with decreasing voltage, a larger resistance would be obtained if $R = \mathrm{d}V/\mathrm{d}I$ is used for calculation. This is unreasonable!

To investigate the effect of mechanical stress on the current–voltage characteristic of the composite, the electrical current in sample 2 under an uniaxial force of 500 grams has been measured as a function of voltage and the result is given in Fig.5. To minimize the effect of Joule heating, relatively small voltages have been applied to the sample. The current increases linearly with voltage showing a typical ohmic behaviour as expected. The distance between the nickel particles gets closer when the sample is subjected to an external uniaxial stress, resulting in more physical contacts between the metallic particles and hence a metallic feature in electrical response. At the same time, the hysteresis becomes much smaller than that for the undeformed sample, indicating that the hysteresis observed in these composite materials arises essentially from the space charge distribution in the polymer matrix.

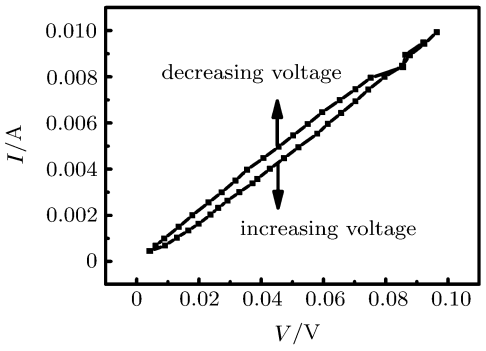


Fig.5. Hysteresis curve for sample 2 (2702#) compressed by 500 gram uniaxial force.

As mentioned in the previous sections, the current increases initially with increasing voltage until reaching a critical voltage. At this critical point, a very sharp increase in the current is observed, indicating an electrical breakdown of the composite. The electrical breakdown field is then determined by dividing the voltage with sample thickness. Figure 6 shows the electrical breakdown behaviour of sample 2 (2702#).

If the voltage on the sample is reduced before the material is burned out, a perfect linear current–voltage relation i.e. ohmic behaviour with a resistance of $10^5\Omega$, is obtained. Once again, this current–voltage characteristic is markedly different from that of QTC.[6] To find the possible reason for this apparent discrepancy, measurement was repeated with a much smaller limiting resistance ($< 30\Omega$) in the circuit to allow high current flow. Indeed, current–voltage characteristics similar to those reported for QTC were observed. This observation strongly suggests that the abnormal large hysteresis observed in QTC may well be due to the effect of Joule heating. Further measurements show that the breakdown strength of the composite depends strongly on the nickel content, it decreases with increasing nickel content.

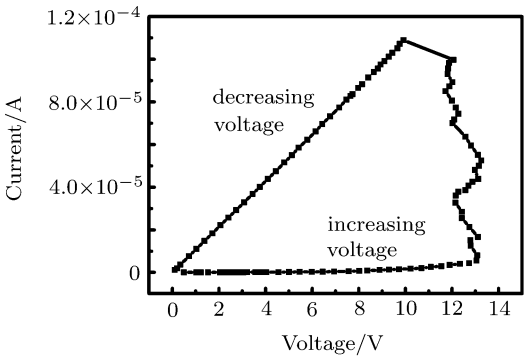


Fig.6. Electrical breakdown behaviour of undeformed sample 2 (2702#).

The breakdown behaviour, together with the current–voltage characteristics discussed in the previous sections, indicates that the resistivity of the composite is sensitive not only to mechanical stress but also to the electrical voltage. The composite material may therefore be used to make voltage sensitive resistors to protect electronic equipment from damaging caused by transient electrical voltage such as lightning, with an adjustable resistance by application of pressure.

4. Conclusions

In summary, we have prepared a Ni–silicone rubber composite with enhanced piezoresistivity. The metallic filler content has been reduced more than 50% by weight in comparison with similar products reported in the literature, resulting in a composite with smaller density, larger piezoresistivity and higher dielectric strength. The piezosensitivity and gauge factor of the composite depend strongly on the filler content. An extremely large piezosensitivity of 0.716/kPa and a gauge factor of 600 have been found for a composite sample with a filler-polymer ratio of 2.7:1 by weight. The current–voltage characteristics of the composite depend on the filler content, the applied stress and the maximum electrical current flowing in the sample. Electrical current varies nonlinearly with voltage and shows a hysteresis for all the samples at atmospheric pressure. An ohmic behaviour has only been observed in the highly compressed composite. We found the concept 'negative resistance', often used to describe the phenomena that current decreases with increasing voltage, is not appropriate. It is the resistance increase rather than the 'negative resistance' that results in the decrease in current. At a critical voltage, the current increases sharply, i.e. the resistance of the sample decreases rapidly, this effect signals a dielectric breakdown. The dielectric strength is found to decrease with increasing filler content in the composite. On the basis of the current study, it is possible to design composite materials with desired resistivity, piezosensitivity, dielectric strength and working pressure range by varying the metallic filler concentration and, perhaps selecting appropriate type of filler material and polymer matrix.

References

[1] Azulay D, Eylon M, Eshkenazi O, Toker D, Balberg M, Shimoni N, Millo O and Balberg I 2003 *Phys. Rev. Lett.* **90** 236601
[2] Tibrewala A, Peiner E, Bandorf R, Biehl S and Lüthje H 2006 *J. MicroMech. Microeng* **16** S75
[3] Yasuoka T, Shimamura Y and Todoroki A 2005 *Nihon Kikai Gakkai Nenji Taikai Koen Ronbunshu* **1** 395
[4] Somani P R, Marimuthu R, Mulik U P, Sainkar S R and Amalnerkar D P 1999 *Synthetic Metals* **106** 45
[5] Carmona F, Canet R and Delhaes P 1987 *J. Appl. Phys.* **61** 2550
[6] Bloor D, Donnelly K, Hands P J, Laughlin P and Lussey D 2005 *J. Phys.* D **38** 2851
[7] Martin J E Anderson R A, Odenic J, Adolf D and Williamson J 2003 *Phys. Rev.* B **67** 094207
[8] Papakostas T V and White N M 2000 *J. Phys.* D **33** L73
[9] Henan Normal University *China Patent* (200710054951.7)
[10] Chang F G and Li T 2006 *J. Material Science* **41** 377
[11] Bloor D, Graham A, Williams E J, Laughlin P J and Lussey D 2006 *Appl. Phys. Lett.* **88** 102103
[12] Chang F G, Song G L, Fang K and Wang Z K 2007 *Acta Phys. Sin.* **56** 6068 (in Chinese)