A three-dimensionally interconnected metal-spring network in a silicone matrix as a resilient and electrically conducting composite material

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Isotropic, highly resilient and electrically conducting composites in the form of a copper-spring three-dimensional network embedded in a silicone matrix were developed for use as electrical and thermal contact materials. The springs were made from 63 μm diameter copper wires and were coated and interconnected by Sn–Pb solder. The springs used were long coils, intersecting and interconnected to one another to form a three-dimensional network. Composites were fabricated by infiltration of a silicone resin into a preform of springs. A volume resistivity of 5×10^{-4} Ω cm, a contact resistivity with copper of 0.016 Ω cm^2 at $\geqslant$ 0.03 MPa, and a permanent set of 0.6% after compresssion at 0.4 MPa were achieved in a silicone-matrix composite containing 3.1 volume% Cu springs and 2.9 volume% solder (i.e., 6.00 volume% total filler); the volume resistivity was not affected by heating in air at 130–150°C for 7 days, nor by immersion in water for 7 days. The volume resistivity values of composites containing from 4.17 to 6.00 volume% total filler were equal to three times the corresponding calculated values for composites containing unidirectional and continuous fibres, indicating that the filler was indeed a continuous three-dimensional network.

Key words: *composite materials; volume electrical resistivity; contact electrical resistivity, three-dimensional interconnected network; copper springs; tin-lead solder; silicone matrix*

Resilient electrical contact materials are required in electronic packaging (in the form of connectors, interconnections, die attach adhesives, etc.) and biomedical electrodes (such as those for transcutaneous electrical stimulation). The resilience is attractive for minimizing the electrical contact resistivity by compensating for tolerance variability between surfaces needing to be contacted. Conducting elastomers, such as silicone filled with silver particles or carbon particles, are most commonly used for these applications. The lowest volume resistivity is about 10^{-4} Ω cm, as obtained in silicone containing 80 weight% (wt%) (~35 volume% (vol%)) silver particles[1], which is used in electronic packaging. For silicone filled with carbon particles, the volume resistivity is much higher—of the order of 1 Ω cm for a typical carbon-filled silicone used in biomedical electrodes. In order to achieve a volume resistivity of about 10^{-4} Ω cm, the use of silver particles at large volume fractions is necessary, even though silver is expensive and large volume fractions of the filler reduce the degree of resilience of the composite.

Elastomeric thermal interface materials are used in electronic packages as thermal contacts to enhance heat dissipation. Such materials may be placed between a heat sink and the door of the electronics cabinet[2], between a heat sink and a thermal module cap[3], or in general for interfacing heat sinks[4,5]. Silicone filled with silver particles[1], silver-coated wires[2] or metal fibres[6,7] are most commonly used for this purpose.

Conducting fibres are more effective than particles (of size similar to the fibre diameter and of the same

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composition) in rendering a composite material with an insulating matrix electrically conducting. This is because fibres ensure better chance of having a continuous conducting phase by minimizing the total number of contact points within a given distance. The longer the length of the fibres, the greater the tendency for the fibres to contact one another. Ideally, continuous fibres are preferred. However, dispersing long fibres uniformly in such a way that the composite is three-dimensionally isotropic is quite difficult, especially when the volume fraction of fibres in the composite is low. Moreover, a large fibre volume fraction lowers the resilience of the composite. Even more preferred than mechanically-contacting long fibres is the case of electrically interconnected fibres, as such interconnections will decrease the electrical contact resistance between the fibres and result in a continuous network. However, for a resilient composite material, the network must not be too rigid. For this purpose, the density of interconnections in the composite should be relatively small, though sufficient for forming a continuous three-dimensional network. Since short fibres require a high density of interconnections in order to form a three-dimensional network, they are not desirable. Long fibres are preferred, but dispersing them uniformly such that their orientations are random is difficult. However, this dispersion problem can be alleviated by the use of fibres in the form of coils or springs. The springs can be allowed to bend and mechanically interlock. If electrical contacts are further made at the points of interlocking, a three-dimensionally interconnected and isotropic spring network can be formed. This indeed has been achieved in this paper, which thus provides a new class of isotropic and conducting elastomers.

In this work, copper was used for the metal springs due to its low electrical resistivity, while tin–lead solder was used for the interconnections. Coating of the copper springs with the solder also had the advantage of greatly enhancing the oxidation resistance of the contact points between the springs, so that the electrical resistivity of the composite was not affected after heating at 130–150°C for 7 days or after immersion in water for 7 days. With only 3.1 vol% Cu and 2.9 vol% Sn–Pb, a silicone-matrix composite of resistivity $5.4 \times 10^{-4}\,\Omega$ cm was obtained. This resistivity is comparable to that of 35 vol% silver particle silicone-matrix composite[1]. The low filler volume fraction of the composites of this work allowed the composites to be highly resilient.

The composite fabrication method used in this work, namely silicone liquid infiltration, is simple and inexpensive. The infiltration occurred particularly readily for composites containing up to 8 vol% springs.

The low materials cost for the composites of this work is most attractive compared with the silver-powder-filled silicone on the market. An additional advantage is related to the low filler volume fraction in our composites, which makes them highly resilient. The main disadvantage is that our composites can only be made in bulk form; they cannot be used in screen printing as silver-powder-filled silicone can.

EXPERIMENTAL

Materials

The springs were made from bare soft-temper alloy 172 Cu–Be (1.86 wt% Be) wires of diameter 63 μm, kindly provided by R&F Alloys, Fairfield, NJ, USA. The interconnection material was solder (Sn–Pb, 63 wt% Sn); it was in the form of a solder paste provided by Electro-Science Laboratories, Inc (type 3702). The silicone used was a low temperature two-part silicone, namely RTV511 silicone rubber compound, together with dibutyl tin dilaurate as a catalyst, both provided by General Electric Co.

Spring fabrication

The springs were made by winding the Cu–Be wire (single or multiple) from a spool on to a horizontal steel wire (1.6 mm in diameter and 400 mm in length) rotated by a variable speed motor. The winding started at one end of the steel wire and gradually proceeded to the other end as the Cu–Be wire spool was moved at a controlled speed. When the winding had reached the other end, the Cu–Be wire was cut from the spool and the spring was allowed to loosen from the steel wire and then removed from one end of the steel wire. The springs used in this work had a diameter of 2.5 mm, a length of 400 mm, and had 5–20 windings per mm. They were highly flexible. The softness of the alloy made disentanglement of groups of springs crossed to one another all but impossible without pulling out the coil set.

Coating the springs with solder

After washing the springs with acetone (for degreasing), acid (for oxide removal) and water, an organic binder and the solder paste were applied on the springs by mixing.

Spring preform fabrication

An isotropic spring preform was prepared by mixing the springs randomly and compacting them into a cylinder of inside diameter 10–12 mm. A preform consisted of numerous, bent, randomly oriented and intersecting springs. By controlling the degree of compaction, the volume fraction of springs was varied. Fig. 1 shows scanning electron microscope (SEM) photographs of spring preforms (without solder) containing 6 and 10 vol% springs. The higher magnification photographs of each composition shows that each spring intersection involves the close knitting of a number of wires.

The spring preform (with solder) was then heated to melt the solder particles. Fig. 2 shows the spring preform (with solder) before and after heating. The bright particles in Fig. 2(a) (before heating) are the solder particles, which are not visible after heating (Fig. 2(b)). The connections between the springs are clearly seen in Figs 2(a) and 2(b). After reflow, the soldered spring preform was washed with acetone to remove the flux remaining on the springs.

Composite fabrication

The preform in a cylinder of inside diameter 10–12 mm was infiltrated with liquid silicone resin by using the

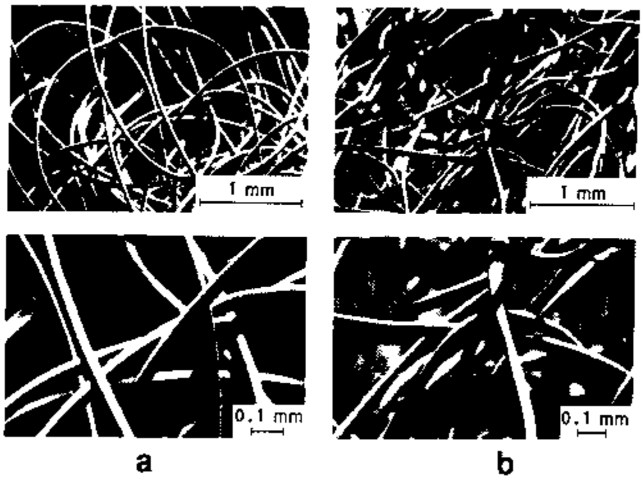

Fig. 1 SEM photographs of spring preforms (without solder) containing: (a) 6.1 vol% Cu; and (b) 10.1 vol% Cu. Two magnifications are shown for each volume fraction

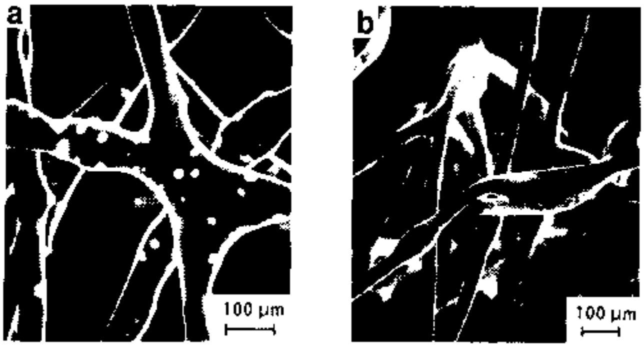

Fig. 2 SEM photographs of spring preforms with solder: (a) before melting the solder; and (b) after melting the solder

cylinder as a piston, which was fitted with a seal to a slightly larger cylinder containing silicone liquid. The pressure applied to the piston was 0.5–50 MPa during infiltration of the preform. The springs in the preform were essentially not compressed during infiltration for composites containing < 10 vol% springs, but they were compressed by 10–15 vol% for composites containing > 10 vol% springs. The degree of compression may be decreased by decreasing the piston speed. After infiltration had been completed, the pressure was released. When the silicone had hardened, the composite was pushed out of the cylinder.

Fig. 3 shows SEM photographs of the composites containing 6.1 and 7.9 vol% springs (without solder) after cutting with a knife. The cut surface was not smooth, as wires protruded out of it. The distribution of springs was more uniform in the composite containing 7.9 vol% springs than in that containing 6.1 vol% springs. In general, the lower the spring volume fraction, the less uniform was the spring distribution in the composite.

Mechanical testing

Compression testing was performed using a Vishay bench top testing machine (model BT-1000). Fig. 4 shows the compressive stress/strain curves of composites (without solder) containing 0, 4.1, 6.1, 7.9 and 11.2 vol% springs. All the curves exhibit a concave shape which is typical of an elastomer, although the slope (related to the modulus) increases with increasing spring volume fraction. The fracture point of each composite is not shown, as it was off scale.

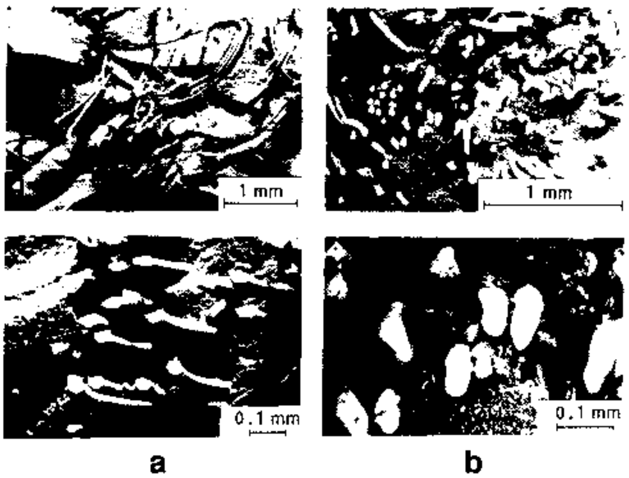

Fig. 3 SEM photographs of composites (without solder) containing: (a) 6.1; and (b) 7.9 vol% Cu after cutting with a knife. Two magnifications are shown for each volume fraction

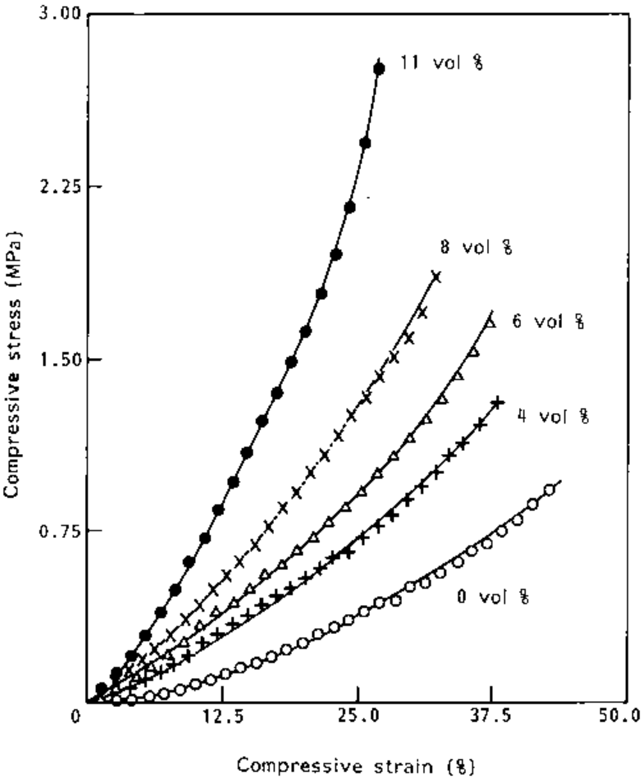

Fig. 4 Compressive stress/strain curves of composites (without solder) containing 0, 4.1, 6.1, 7.9, and 11.2 vol% Cu

Fig. 5 shows the compressive stress/strain curves of composites with and without solder, such that the total filler volume fraction was 4% in both cases. The composite with solder contained 2.10 vol% Cu and 2.07 vol% solder. The slope of the stress/strain curve is lower for the composite with solder than for that without solder. This means that the lower volume fraction of Cu springs in the composite with solder enables the composite to be softer.

Table 1 shows the permanent sets remaining in the

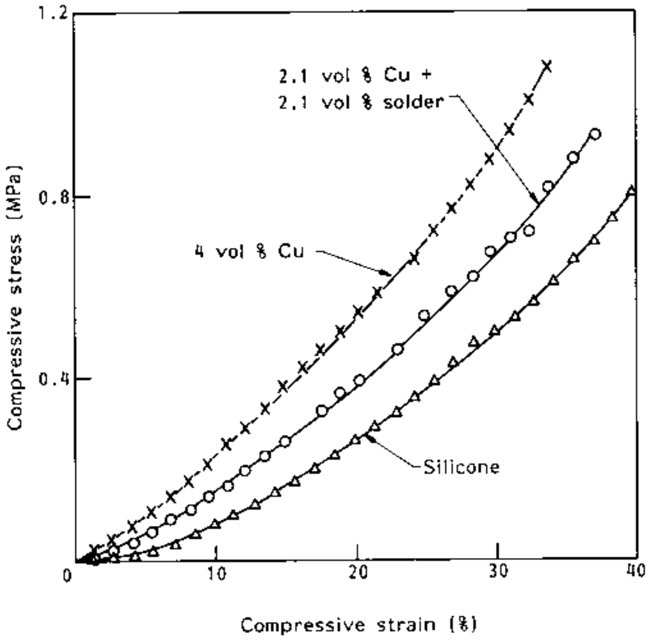

Fig. 5 Compressive stress/strain curves of: (a) plain silicone; (b) composite containing 2.10 vol% Cu and 2.07 vol% solder; and (c) composite containing 4 vol% Cu (without solder)

Table 1. Permanent sets of composites without solder after compression by 0.4 or 0.8 MPa

Volume fraction springs (%)	Permanent offset (%)	
	0.4 MPa	0.8 MPa
0	0 ± 0.04	0 ± 0.04
4.71	0.05 ± 0.01	0.33 ± 0.06
7.94	0.61 ± 0.04	1.38 ± 0.40
8.31	0.80 ± 0.04	1.42 ± 0.15
10.75	0.40 ± 0.02	0.78 ± 0.20

Table 2. Permanent sets of composites with solder after compression by 0.4 MPa

Total filler (vol%)	Cu (vol%)	Solder (vol%)	Permanent set (%)
4.17	2.10	2.07	0.37 ± 0.03
4.90	2.30	2.60	0.46 ± 0.03
5.56	2.70	2.86	0.44 ± 0.02
6.00	3.10	2.90	0.59 ± 0.04

composites (without solder) after compression to a stress of 0.4 or 0.8 MPa for 30 s. The permanent set increased with increasing spring volume fraction up to 8.31 vol%, but decreased upon further increase to 10.75 vol%. All the sets were less than 1.5%. One sample was tested for each composition. The permanent sets were determined by measuring using a micrometer the change in distance between two parallel needles that went through the sample.

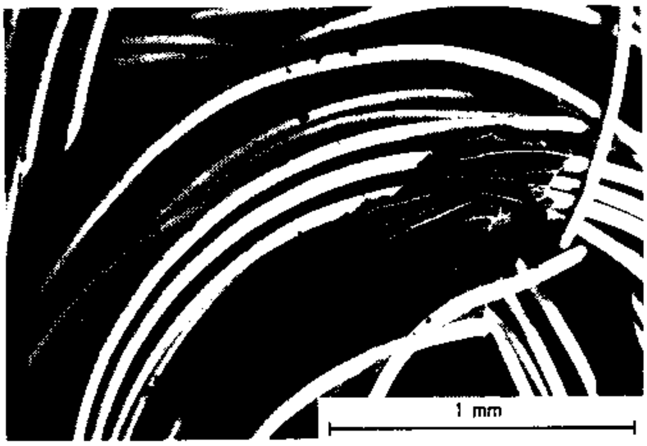

Fig. 6 SEM photograph of the tensile fracture surface of the composite (with solder) containing 7.9 vol% Cu

Table 2 shows the permanent sets remaining in the composites (with solder) after compression to a stress of 0.4 MPa for 30 s. Three samples were tested for each composition. The permanent sets increased with increasing filler content (Cu + solder) and with increasing Cu spring content. Comparison of the composite containing 4.71 vol% Cu (without solder, Table 1) with that containing 4.9 vol% filler (with solder, Table 2) shows that the solder interconnections increased the permanent set, causing the composite to be less resilient. Nevertheless, the permanent sets were only at most 0.6% for the composites with solder.

Fig. 6 shows an SEM photograph of the tensile fracture surface of the composite containing 7.9 vol% springs. In order to fully separate the two parts of a sample after fracture, the springs still connecting the two parts had to be cut by scissors. Fig. 6 shows that some springs were pulled out, dragging some silicone along with them.

Volume electrical resistivity

The volume resistivity was measured by the four-probe method, using silver paint for the current (outer) probes and needles pushed into the sample as the voltage (inner) probes.

Two models were used to obtain the calculated values of the volume resistivity. In both models, the spring resistivity was taken to be 10.53 μΩ cm (which is the measured value of the resistivity of the bare copper wire used in this work) and the solder resistivity was taken to be 14.7 μΩ cm. Model 1 assumes that the conducting fillers are continuous and unidirectional, and uses the rule of mixtures (ROM) to yield the lower limit to the resistivity (ρ_{min}) that can be reached for a composite containing a volume fraction ϕ_1 of filler of resistivity ρ_1, a volume fraction ϕ_2 of filler of resistivity ρ_2, and a matrix of infinite resistivity. This limit is:

$$\frac{1}{\rho_{min}} = \frac{\phi_1}{\rho_1} + \frac{\phi_2}{\rho_2} \qquad (1)$$

Model 2[8] assumes that the conducting fillers are in the form of short, straight, discontinuous, randomly oriented and intersecting fibres, and it yields the resistivity ρ_c of a composite with a volume fraction ϕ_1 of filler of resistivity ρ_1, a volume fraction ϕ_2 of filler of resistivity ρ_2 and a matrix of infinite resistivity:

Table 3. Volume electrical resistivity of composites without solder

Volume fraction Cu springs (%)	Resistivity (mΩ cm)			Resistivity ratio (measured/calculated)	
	Measured	Calculated			
		Model 1	Model 2	Model 1	Model 2
4.1	1.391 ± 0.154	0.257	1.272	5.41	1.09
4.7	1.097 ± 0.019	0.224	1.056	4.90	1.04
6.1	0.744 ± 0.071	0.173	0.815	4.31	0.91
7.9	0.534 ± 0.0412	0.134	0.631	3.99	0.85
11.2	0.353 ± 0.0202	0.094	0.443	3.76	0.80

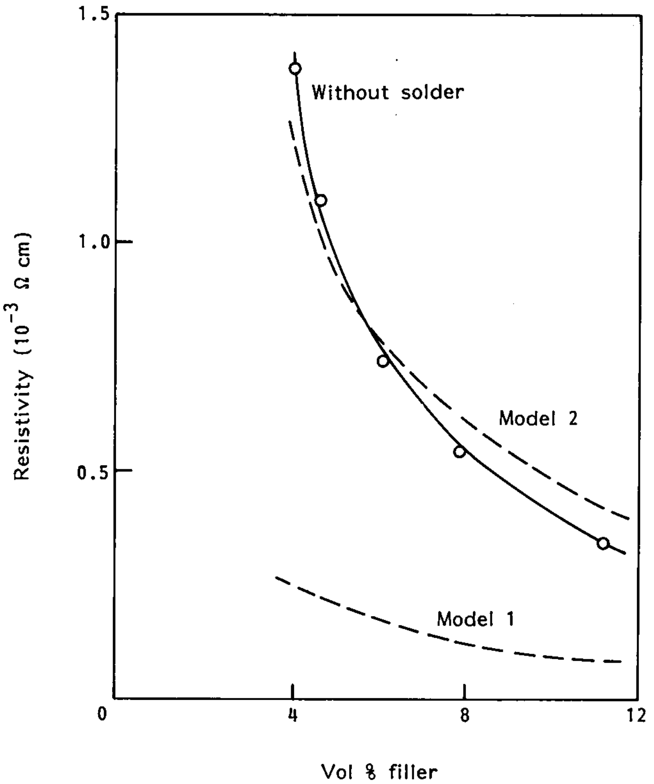

Fig. 7 The electrical volume resistivity of composites without solder as a function of the filler volume fraction. The solid line gives the measured values; the dashed line give the calculated values based on Models 1 and 2

$$\frac{1}{\rho_c} = \frac{2}{3\pi}\left[\frac{\phi_1}{\rho_1} + \frac{\phi_2}{\rho_2}\right] \qquad (2)$$

Table 3 and Fig. 7 show the measured and calculated values of the volume resistivity of composites without solder; Table 4 and Fig. 8 show those of composites with solder. Two samples were tested for each composite composition. The resistivity decreased with increasing spring content (whether with or without solder). Moreover, for the case without solder, the ratio of the measured resistivity to the calculated resistivity (based on Model 1 or Model 2) decreased with increasing spring volume fraction. This is reasonable since a contact resistance exists at the intersection of one spring with another (whether with or without solder), and the volume resistivity will be reduced by a larger number of intersections, which is the case when the spring volume fraction is larger. That the frequency of intersections increases with spring volume fraction is a fact that is separately confirmed by visual observation.

The measured resistivity values for the case without solder were similar to those predicted by Model 2, but higher than those predicted by Model 1. The measured values for the case with solder were lower than those for the case without solder for the same total filler content, which is shown by the horizontal axis in Fig. 8. The effect of the solder is significant, particularly considering that copper (springs) has a lower resistivity than solder. This effect is because the solder connected the intersecting springs to form a three-dimensional network. The measured resistivity values for the case with solder were lower than those predicted by Model 2, but higher than those predicted by Model 1. The ratio of the measured resistivity to the calculated resistivity based on Model 1 was three for all filler volume fractions (Table 4). As Model 1 is for the case of continuous and unidirectional fibres, the factor of three means that the composite with solder had a conductor in the form of a continuous but three-dimensional network. That the measured resistivity for the case with solder was lower than the calculated value based on Model 2 is consistent with this interpretation.

A composite (without solder) containing 9.07 vol% Cu springs was heated in air at 130–150°C for 7 days. The volume electrical resistivity, as determined by measuring three samples, was 0.337 ± 0.045 mΩ cm before heating and 13.7 ± 1.5 mΩ cm after heating. Thus the heating greatly increased the resistivity, most probably due to oxidation of the copper springs (without solder).

Table 5 shows the effect of heating (in air at 130–150°C for 7 days) on the volume electrical resistivity of composites with solder. Two samples were tested for each composition. Heating had no effect on the resistivity, in sharp contrast to the large effect of heating on the resistivity of composites without solder. Thus the solder greatly reduced the effect of oxidation on the electrical resistance of the composites.

Table 6 shows the measured resistivity of composites without solder before and after immersion in water for 7 days. The resistivity increased by 7.6–39.8% after immersion, the fractional change increasing with increasing spring volume fraction. However, for a spring volume fraction of 8.3% or less, the fractional change was 15% or less. This trend indicates that the springs rather than the silicone were responsible for the

Table 4. Volume electrical resistivity of composites with solder

Total filler (vol%)	Cu (vol%)	Solder (vol%)	Resistivity (mΩ cm)			Resistivity ratio (measured/calculated)	
			Measured	Calculated			
				Model 1	Model 2	Model 1	Model 2
4.17	2.10	2.07	0.814 ± 0.010	0.294	1.385	2.77	0.587
4.90	2.30	2.60	0.765 ± 0.010	0.253	1.192	3.02	0.642
5.56	2.70	2.86	0.613 ± 0.015	0.222	1.046	2.76	0.585
6.00	3.10	2.90	0.535 ± 0.010	0.203	0.957	2.63	0.554

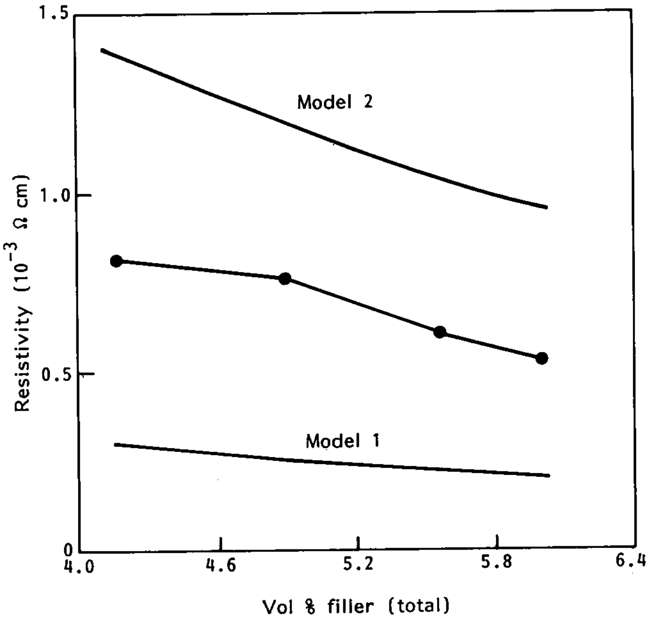

Fig. 8 The electrical volume resistivity of composites with solder as a function of the total filler volume fraction: —●—, measured values; and calculated values based on Models 1 and 2

degradation, which may be due to oxidation of the spring surfaces.

Table 7 shows the measured resistivity of composites with solder before and after immersion in water for 7 days. The resistivity was not affected by the water immersion. Comparison of Tables 6 and 7 shows that the solder improved the water resistance (related to the oxidation resistance) of the composites.

Contact electrical resistivity

The contact electrical resistivity was measured by sandwiching a cylindrical composite sample disc (10–12 mm in diameter, 10–12 mm in height) between two copper sheets, applying pressure on the sandwich in the direction perpendicular to the sandwich layers, applying a voltage between the two copper sheets and measuring the current flowing across the sandwich, which comprised two copper–composite contacts. As the contribution of the volume resistivity of the composite to the measured resistance is orders of magnitude less than the measured resistance, it was neglected in calculating the contact resistivity.

Fig. 9 shows the contact resistivity (for the composites without solder) as a function of pressure. The contact resistivity for each composite decreased with increasing pressure, but levelled off at about 0.10 MPa. The levelled-off or stable value decreased with increasing volume fraction of springs. For the highest spring content of 11 vol%, the stable value was 0.01 Ω cm^2. The experimental error of each data point for the composite containing 4.1 vol% springs was ± 0.0005 Ω cm^2; that for 6.1 vol% springs was ± 0.0011 Ω cm^2; that for 7.9 vol% springs was ± 0.0004 Ω cm^2; and that for 11.2 vol% springs was ± 0.0004 Ω cm^2.

The composites without solder were immersed in water at room temperature for 7 days. Fig. 10 shows the contact resistivity as a function of pressure for the composite containing 6 vol% springs (without solder) before and after water immersion. The stable value of the contact resistivity was increased by up to 25% after water immersion, as shown also in Table 8. In particular, for the composite containing 11.2 vol% springs, the stable value of the contact resistivity was not affected at all by the water immersion. More samples of each composition need to be run in order to ascertain whether the water resistance indeed depends on the spring volume fraction.

Figs 11 and 12 show the contact resistivity as a function of pressure for composites of two compositions, both with solder, before and after immersion in water for 7 days. The water immersion had no effect on the stable value of the contact resistivity nor the pressure required for the contact resistivity to be stable. Comparison of Figs 11 and 12 shows that the stable value of the contact resistivity is 0.0180 Ω cm^2 for the composite containing 2.1 vol% Cu + 2.1 vol% solder, and is 0.0160 Ω cm^2 for that containing 3.1 vol% Cu and 2.0 vol% solder. That a higher filler content corresponds to a low contact resistivity is consistent with the trend depicted in Table 7. The contact resistivities of composites with solder and those without solder are quite similar. However, the pressure required for the contact resistivity to be stable is 0.025 MPa with solder and 0.1 MPa without solder. The solder greatly decreased this pressure, because solder is softer and more oxidation resistant than copper.

DISCUSSION

This paper provides a new class of isotropic conducting elastomers, namely a three-dimensionally interconnected metal-spring network in a silicone matrix.

The closest prior art is an anisotropic conducting

Table 5. Effect of heating (in air at 130–150°C for 7 days) on the volume electrical resistivity of composites with solder

Total filler (vol%)	Cu (vol%)	Solder (vol%)	Resistivity (mΩ cm)	
			Before heating	After heating
4.17	2.10	2.07	0.814 ± 0.010	0.818 ± 0.010
4.90	2.30	2.60	0.765 ± 0.010	0.770 ± 0.010
5.56	2.70	2.86	0.613 ± 0.015	0.610 ± 0.010
6.00	3.10	2.90	0.535 ± 0.010	0.536 ± 0.010

Table 6. Volume electrical resistivity of composites without solder before and after immersion in water for 7 days*

Volume fraction springs (%)	Volume resistivity (mΩ cm)		Fractional change in resistivity due to immersion (%)
	Before	After	
4.7	1.097 ± 0.019	1.180 ± 0.040	7.6
7.9	0.415 ± 0.027	0.475 ± 0.015	14.5
8.3	0.351 ± 0.019	0.404 ± 0.020	15.1
10.7	0.256 ± 0.01	0.358 ± 0.012	39.8

*Samples of this table were prepared by a procedure slightly different from that described in the text. The springs, after fabrication and before preform preparation, were washed with acetone and then 25% HCl acid for surface cleaning. Comparison between Tables 3 (without acid wash) and 6 (with acid wash) shows that the acid wash decreased the resistivity by 22% for the same composition of 7.9 vol% springs

Table 7. Volume electrical resistivity of composites with solder before and after immersion in water for 7 days

Total filler (vol%)	Cu (vol%)	Solder (vol%)	Resistivity (mΩ cm)	
			Before immersion	After immersion
4.9	2.3	2.6	0.610 ± 0.010	0.612 ± 0.010
5.6	2.7	2.9	0.770 ± 0.010	0.767 ± 0.010

elastomer composite containing a parallel array of S-shaped (not spiral) springs such that the two ends of the letter S emerge at the two opposite surfaces of the composite. Such composites are used as pressure-mated interconnections in electronics and are produced by Rogers Corporation (Rogers, CT, USA) under the trademark Isocon[9]. The distance from one spring to the next is ⩾ 1.270 mm in Isocon.

The next closest prior art is a spring energized elastic metal gasket consisting of a helical core spring wrapped with a soft metal envelope[10].

The novel aspect of the composites of this paper lies in the use of long, bent, intersecting and interconnected spiral springs. The intersecting springs tend to mechanically lock on to one another and the frequency of intersections increases with increasing spring volume fraction. The collection of intersecting and interconnected springs can be viewed as a three-dimensional spring network. Moreover, the springs inherently have a low spring constant, so they do not interfere with the highly resilient nature of the elastomeric matrix.

The diameter and length of the springs were 2.5 mm and 400 mm respectively in this work. However, the same technology may be applied for springs of smaller or larger dimensions, provided that the spring wire is not too stiff (making it hard to make springs with a small diameter) or too soft (making it hard to loosen the spring from the steel wire after winding). Springs of smaller dimensions would be more attractive for applications in electronic packaging.

This work used Cu–Be (1.86 wt% Be) springs, but springs made from Cu or Cu–Be plated with silver, gold or nickel may be used instead for superior environmental resistance. On the other hand, the solder coating already helps the environmental resistance greatly.

The effects of the solder addition on the composites of this work include greatly improved temperature resistance, improved corrosion resistance, greatly decreased pressure needed to achieve a stable contact resistivity, decreased volume electrical resistivity, decreased resistivity ratio (measured/calculated) and increased permanent set after compression. The last effect is the only negative one, but it is acceptable since the solder allows the spring volume fraction to decrease greatly without increasing the volume resistivity and the permanent set tends to increase with increasing filler content. At the small filler contents needed for

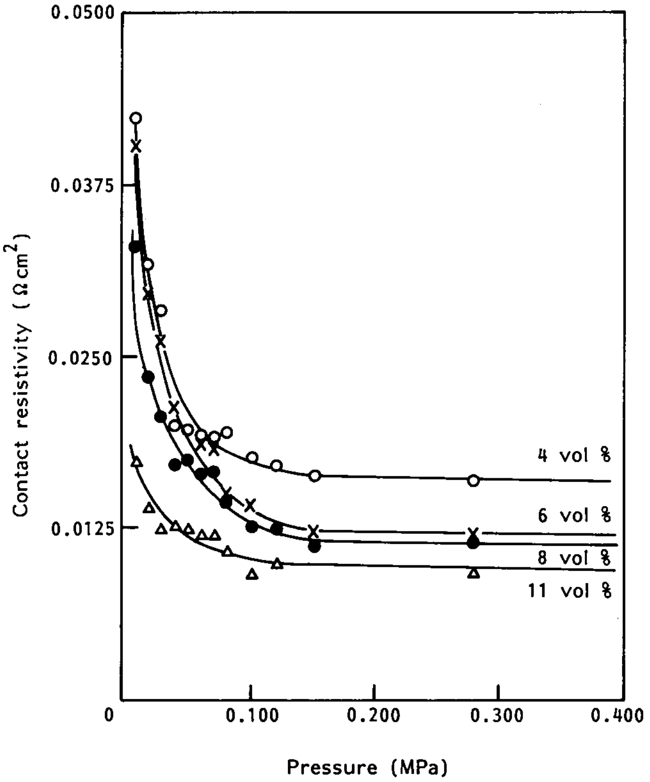

Fig. 9 The contact resistivity as a function of pressure for composites (without solder) containing 4.1, 6.1, 7.9 and 11.2 vol% Cu

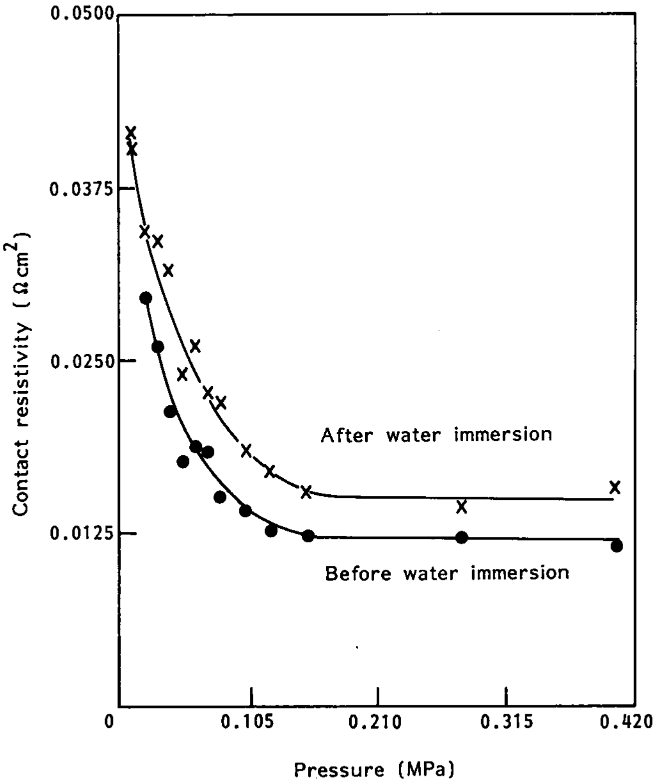

Fig. 10 The contact resistivity as a function of pressure for a composite (without solder) containing 6.1 vol% Cu before (●) and after (x) immersion in water for 7 days

composites with solder, the permanent sets are all quite small, as seen by comparing Tables 2 and 1.

CONCLUSION

Isotropic silicone-matrix copper-spring three-dimensional network composites were fabricated by infiltration of a silicone resin into a solder-coated preform of springs, which were long, bent, intersecting and interconnected to one another. The interconnections were made by the solder. Highly resilient and electrically conducting composites were fabricated. The volume resistivity decreased with increasing filler content. A value of 0.54 mΩ cm was obtained in a composite containing 3.1 vol% Cu and 2.9 vol% solder. The solder served to electrically connect the springs, decrease the volume electrical resistivity for the same total filler volume fraction, decrease the pressure for achieving a stable contact resistivity from 0.10 to 0.03 MPa, and increase the oxidation resistance, but it slightly decreased the resilience of the composites. The solder addition allowed a small spring volume fraction (2.1–3.1%) to yield a low composite resistivity, thereby maintaining the resilience at the level without solder. With solder, the volume resistivity of the composites was not affected by heating in air at 130–150°C for 7 days; a 400% increase of the resistivity was observed after the heating for the case without solder. With solder, both the volume resistivity and the contact resistivity were not affected by immersion in water for 7 days; a 7.6–39.8% increase of the volume resistivity and a 0–25% increase of the contact resistivity were observed after the immersion for the case without solder. With solder, the volume resistivity was lower than that calculated for the case of discontinuous and randomly oriented fibres; without solder, it was close to the corresponding calculated value. In particular, the volume resistivity of composites with solder was equal to three times that calculated for the case of continuous and unidirectional fibres, indicating the three-dimensional and continuous nature of the filler.

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REFERENCES

1 **Lutz, M.A. and Cole, R.L.** *39th Electronic Components Conf* (IEEE, 1989) pp 83–87
2 **Fulton, J.A., Horton, D.R., Moore, R.C., Lambert, W.R., Jin, S., Opila, R.L., Sherwood, R.C., Tiefel, T.H., Mottine, J.J.** *39th Electronic Components Conf* (IEEE, 1989) pp 71–77
3 *IBM Technical Disclosure Bulletin* **27** No 10A (1985) p 5558
4 **Fick, H.J.** *US Patent 4 842 911* (1989)
5 **Fick, H.J.** *US Patent 4 602 678* (1986)
6 **Reilly, J.J., Thoman, S.J., and Lin, W.W.** *SAMPE J* **23** No 1 (1987) pp 22–27

Table 8. Stable contact resistivity and the pressure required for stability for the composites without solder

Volume fraction springs (%)	Stable contact resistivity (Ω cm²)	
	Before water immersion*	After water immersion†
4.1	0.0160 ± 0.0005 (≥ 0.10 MPa)	0.0200 ± 0.0010 (≥ 0.12 MPa)
6.1	0.0120 ± 0.0010 (≥ 0.12 MPa)	0.0150 ± 0.0020 (≥ 0.15 MPa)
7.9	0.0118 ± 0.0005 (≥ 0.12 MPa)	0.0145 ± 0.0010 (≥ 0.15 MPa)
11.2	0.0100 ± 0.0005 (≥ 0.10 MPa)	0.0100 ± 0.0005 (≥ 0.15 MPa)

*Two samples tested for each composition
†One sample tested for each composition

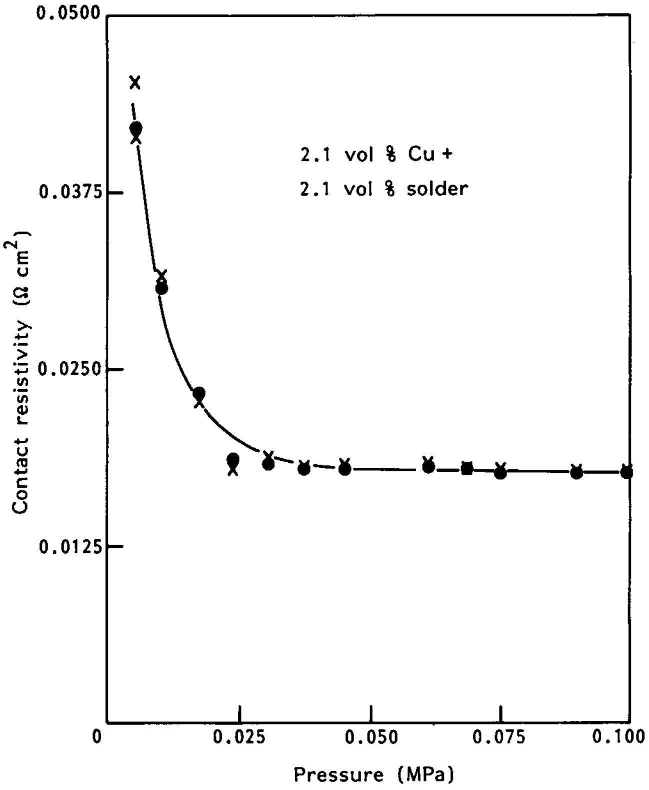

Fig. 11 The contact resistivity as a function of pressure for a composite containing 2.1 vol% Cu and 2.1 vol% solder before (●) and after (x) immersion in water for 7 days

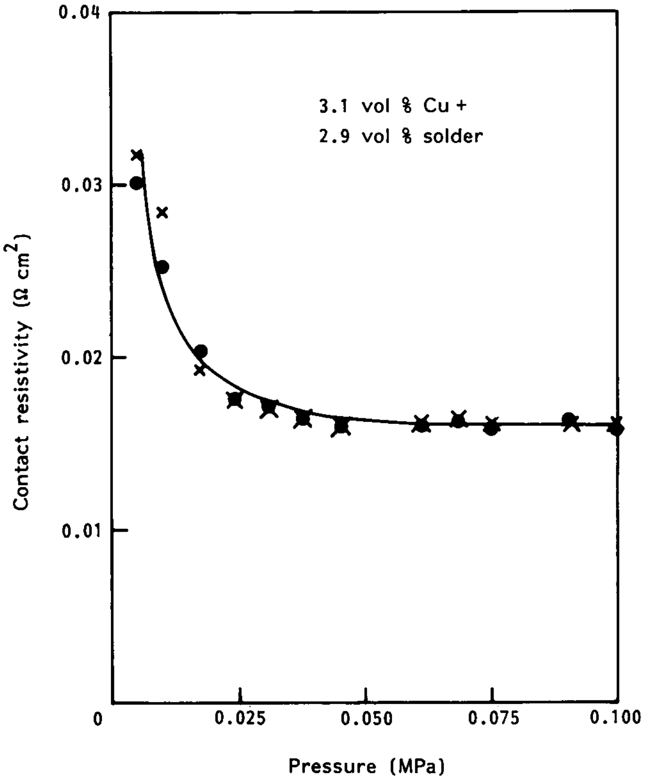

Fig. 12 The contact resistivity as a function of pressure for a composite containing 3.1 vol% Cu and 2.9 vol% solder before (●) and after (x) immersion in water for 7 days

7 **Bigg, D.M. and Bradbury, E.J.** *Org Coat Plast Chem* **43** (1980) pp 746–752
8 **Blythe, A.R.** *Electrical Properties of Polymers* (Cambridge University Press, UK, 1980) p 126
9 **Mersereau, J.M., Gordon, H.B. and Simpson, S.S.** *Proc Tech Conf IEPS, Fourth Ann Int Electronics Packaging Conf* (Int Electronics Packaging Soc, Glen Ellyn, IL, USA, 1984) pp 43–53
10 **Nishida, T.** *SAE Special Publication SP-697* (SAE, Warrendale, PA, USA, 1987) pp 23–27

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