Mingguang Zhu

D. D. L. Chung

Composite Materials Research Laboratory,
State University of New York at Buffalo,
Buffalo, NY 14260

Nickel Fiber Silicone-Matrix Composites as Resilient Electrical Conductors[1]

Short nickel fiber silicone-matrix composites containing 3-12 vol. percent fibers were fabricated by the impregnation of silicone into a nickel fiber preform. The composites exhibited volume electrical resistivity ranging from 4.5×10^{-4} to 2.8×10^{-3} ohm.cm, contact electrical resistivity (with copper at a pressure >0.1 MPa) ranging from 0.0090 to 0.0155 ohm.cm^2, permanent set one percent after compression to a stress of 0.4 MPa and a strain up to 13.5 percent for 7 days, and electromagnetic interference (EMI) shielding effectiveness >50 dB at 1.0-2.0 GHz. The volume and contact resistivities were essentially not affected after heating in air at 130-150°C for 7 days. The coefficient of thermal expansion was 27.5×10^{-6} °C^{-1} for a composite containing 8.2 vol. percent nickel fibers. These resilient electrically conducting composites are useful for electrical contacts and for gaskets for EMI shielding.

1 Introduction

Elastomeric electrical conductors are technologically useful for electrical contacts (and possibly thermal contacts too) in the form of electrical connectors, contact pads and the like in electronic packages. They are also useful for electrical contacts in biomedical electrodes used for stimulating nerves or muscles. For these applications, the electrical contact materials must have a low volume electrical resistivity and a low contact electrical resistivity. In particular, for applications in electronic packaging, it is important for the volume and contact electrical resistivities to remain low after heating, as high-density electronics tend to generate considerable heat. Moreover, for both lines of applications, it is desirable for the electrical contact materials to be resilient, as the resilience facilitates the formation of an intimate contact, which means a lower contact resistivity.

Elastomeric electrical conductors are also used for gaskets for electromagnetic interference (EMI) shielding. Such gaskets are needed for EMI shielded rooms and electronic housings.

Silicone filled with silver particles or carbon particles is commonly used as an elastomeric electrical conductor. Silver particles are attractive because of their very low electrical resistivity, which gives rise to a resistivity of the order of 10^{-4} ohm.cm in the silicone composite [1, 2]. Carbon particles are not as conductive, but they have no oxide film on them and are much less expensive. Copper particles, though low in electrical resistivity, have the drawback of being easily oxidized, even at room temperature. In general, particles (as opposed to fibers of a similar diameter) as fillers have the disadvantage in the need to use the particles at a relatively high volume fraction in order to achieve a low electrical resistivity. A higher filler volume fraction makes the composite less resilient and more expensive.

Flavia et al. [3] have used nickel fibers as a filler in silicone. By using ≤ 4.3 vol. percent nickel fibers, an electrical resistivity $\geq 8.8 \times 10^{-2}$ ohm.cm was achieved in the composites. This resistivity is much higher than that achieved by using silver particles as a filler. Moreover, the resistivity of the nickel fiber composites did not vary smoothly with increasing filler volume fraction, as shown in Table 1 [3]. Such large scatter in the data in the plot of resistivity versus fiber volume fraction was probably due to the non-uniformity in the fiber distribution in the composites.

In this paper, we have extended the work of Flavia et al. [3] by using nickel fibers in the amount of 3-12 vol. percent. By using this higher fiber content, we have achieved an electrical resistivity down to 4.5×10^{-4} ohm.cm—comparable that of silver particle filled silicone containing ~35 vol. percent silver particles [1]. Moreover, by using a different method of composite fabrication, we have been able to distribute the fibers uniformly, thereby fabricating composites of various

Table 1 Volume electrical resistivity of nickel fiber silicone composites of [3]

Ni vol.%	Resistivity (ohm.cm)
3.1	0.595
3.3	0.278
3.5	0.376
3.7	0.113
3.9	0.440
4.1	0.088
4.3	0.166

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filler contents with resistivity values that have very little scatter in the data. Our fabrication method involved the impregnation of a silicone resin into a nickel fiber preform. In contrast, the fabrication method of Flavia et al. [3] involved forming a slurry of nickel fibers in the silicon resin. Furthermore, we provide in this paper data on (i) the contact electrical resistivity and its dependence on pressure, (ii) the effect of heating on the electrical resistivity, (iii) the compressive mechanical properties, and (iv) the coefficient of thermal expansion. Such data are absent in [3] and are highly relevant to the applications of these composites.

2 Materials

The nickel fibers used were short fibers with non-circular (dumpbell-shaped) cross-section of size 20–25 μm, length 0.5–3.0 cm and nominal aspect ratio 1000. They are kindly provided as Fibrex RL/20 by National-Standard Co. in Mishawaka, Indiana. The fibers were essentially the same as those of [3].

The elastomer used was RTV 511 silicon rubber of General Electric Co.

3 Composite Fabrication

The composites were fabricated by first preparing a nickel fiber preform and then impregnating the preform with silicone.

The preform was prepared by spreading (without deliberate compression) a weighed amount of fibers to form a rectangular blanket of thickness 2–3 mm, and then rolling the blanket up to form a cylinder, which was the preform. After rolling, the individual layers in the roll could not be distinguished, as the layers had clung together very strongly.

The impregnation was achieved by partially inserting a preform into a mold containing the resin and then applying pressure. The composite was removed from the mold after the resin had cured at room temperature.

4 Results

4.1 Volume Electrical Resistivity. The volume electrical resistivity of single nickel fibers was measured by the four-probe method, using silver paint for all four electrical contacts. The measured value was 9.3 ± 0.2 μΩ.cm, based on data taken on two samples. This value is higher than the value 6.844 μΩ.cm of nickel given in the Metals Handbook [4], partly due to the presence of unreduced oxide in the nickel fibers provided by National Standard Co. Based on the measured fiber resistivity, the volume electrical resistivity of the composites was calculated using two models, as shown in Table 2. Model 1 assumes that the conducting filler is continuous and unidirectional, and it uses the Rule of Mixtures (ROM), which yields the lower limit to the resistivity ($\rho_{\min}$) that can be reached for a composite with a filler volume fraction ϕ, a filler resistivity ρ_f, and a matrix resistivity ∞. This limit is

$$\rho_{\min}=\frac{\rho_f}{\phi}. \tag{1}$$

Model 2 assumes that the conducting filler is in the form of short, straight, discontinuous, randomly oriented and intersecting fibers, and it yields the resistivity ρ_c of a composite of filler volume fraction ϕ and filler resistivity ρ_f [5]:

$$\rho_c=\frac{3\pi}{2\phi}\rho_f \tag{2}$$

The volume electrical resistivity of the composites was measured by the four-probe method, using silver paint for the outer current contacts and metal needles going through the sample as the inner voltage contacts. Three samples of each composition were tested. Table 2 and Fig. 1 show the measured values in comparison with the calculated values. The measured values were much higher than the corresponding calculated values based on both models, such that the ratio of the measured value to the calculated value decreased with increasing nickel fiber volume fraction. This effect is attributed to the high electrical resistance at the junctions between fibers and the fact that the electrical connection between the fibers improves as the fibers are more densely packed. Model 2 gave calculated resistivity values that are much closer to the corresponding measure values than Model 1 did, as expected. The difference between the measured values and the corresponding calculated values based on Model 2 is partly due to the fact that the nickel fibers in the composite were not straight, and partly due to the contact resistance between the fibers.

Table 2 Volume electrical resistivity of composites

Ni vol.%	Resistivity (10^{-3} ohm.cm)			Resistivity ratio (Measured/calculated)	
	Measured	Calculated			
		Model 1	Model 2	Model 1	Model 2
3.31	2.75 ± 0.10	0.281	1.324	9.79	2.08
4.53	1.96 ± 0.04	0.205	0.967	9.56	2.03
6.43	1.37 ± 0.04	0.145	0.683	9.45	2.00
8.19	0.95 ± 0.03	0.113	0.533	8.41	1.78
9.15	0.80 ± 0.06	0.102	0.481	7.79	1.66
10.35	0.64 ± 0.04	0.0898	0.424	7.13	1.51
11.46	0.45 ± 0.01	0.0811	0.382	5.55	1.18

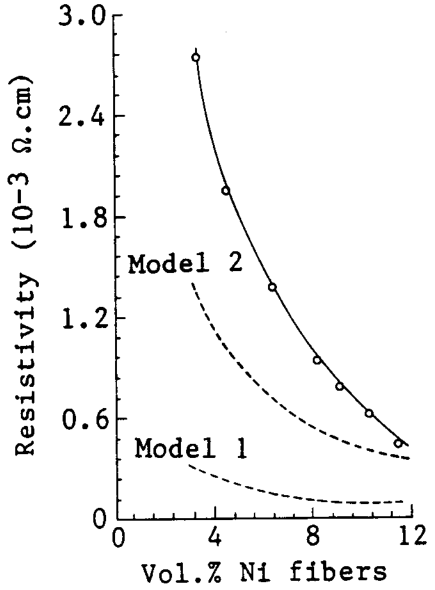

Fig. 1 Volume electrical resistivity as a function of nickel fiber volume fraction. The solid line gives the measured values; the dashed lines give the calculated values based on Model 1 and Model 2.

The effect of heating on the composite resistivity was investigated. Table 3 shows the resistivity before and after heating the composites in air at 130–150°C for 7 days. The heating increased the resistivity very slightly.

4.2 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. Two samples of each composition were tested.

Table 3 Volume electrical resistivity before and after heating at 130-150°C for 7 days

Ni vol.%	Resistivity (10^{-3} ohm.cm) Before heating	 After heating
3.31	2.75±0.10	2.82±0.05
4.53	1.96±0.04	2.09±0.07
6.43	1.37±0.04	1.49±0.20
8.19	0.95±0.03	0.99±0.03
9.15	0.80±0.06	0.83±0.06
10.35	0.64±0.04	0.67±0.01
11.46	0.45±0.01	0.46±0.02

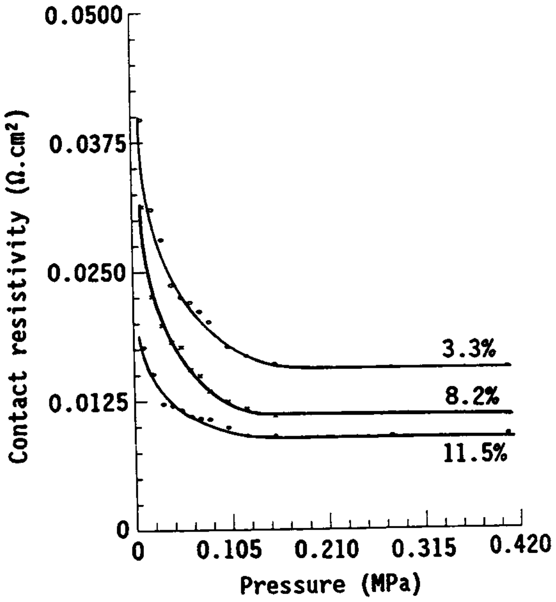

Fig. 2 Contact resistivity (with copper) as a function of pressure for composites containing various volume fractions of nickel fibers

Figure 2 shows the contact resistivity (per contact) as a function of pressure for composites of three different filler volume fractions. The contact resistivity for each composite decreased with increasing pressure, but leveled off at about 0.10 MPa. The leveled-off or stable value decreased with increasing volume fraction of nickel fibers. For the highest nickel content of 11.5 vol. percent, the stable value was 0.009 Ω.cm².

The composites were heated in air at 130-150°C for 7 days. Figure 3 shows the contact resistivity as a function of pressure for the composite containing 8.2 vol. percent nickel before and after heating. The heating had essentially no effect on the stable value of the contact resistivity or the minimum pressure required for the contact resistivity to become stable.

4.3 Electromagnetic Interference (EMI) Shielding Effectiveness. The EMI shielding effectiveness was measured at 1.0-2.0 GHz by using the coaxial cable method. The sample was in the form of an annular disk. The outside diameter and the inside diameter were 97.4 and 28.8 mm, respectively. In order to get a continuous metallic contact between the sample and the steel shielding tester chamber, conductive silver paint was applied to the inner surface of the center hole of the sample and the outer rim of the annular disk. Two compositions were tested, namely 5.9 and 11.6 vol. percent nickel fibers. Three specimens of each composition were tested. The specimen thickness was 2.55-2.78 mm for specimens containing 5.9 vol. percent nickel fibers and was 2.95-3.20 mm for specimens containing 11.6 vol. percent nickel fibers. The set-up allowed the shielding effectiveness to be measured up to 50 dB only. For all specimens of either composition, the shielding effectiveness was thus found to be >50 dB at all frequencies from 1.0 to 2.0 GHz.

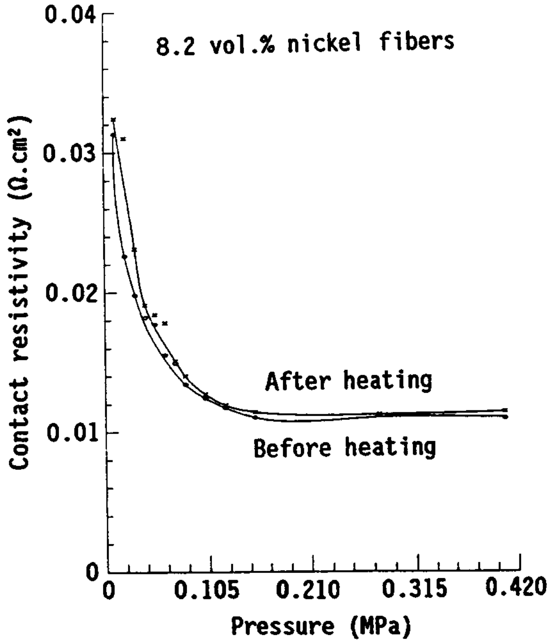

Fig. 3 Contact resistivity (with copper) of composites containing 8.2 vol. percent nickel fibers before and after heating

4.4 Coefficient of Thermal Expansion (CTE). The linear CTE was measured by using the Mettler TMA40 thermal mechanical analyzer operated by scanning from 30 to 110°C at 5°C/min, with a force of 0.05 N applied at the quartz probe resting on the sample surface. The mean CTE at 35-95°C was 292×10^{-6} and 27.5×10^{-6} °C^{-1} for the plain silicone and a composite containing 8.2 vol. percent nickel fibers, respectively. Hence, the CTE was dramatically decreased by the nickel fiber addition. The calculated CTE for a composite containing 8 vol. percent parallel continuous Ni fibers is 12×10^{-6}/°C along the fiber direction, based on the rule of mixture. Hence, the measured value is reasonable. The decreased CTE value is closer to the CTE values of copper (16.6×10^{-6} °C^{-1}), aluminum (25×10^{-6} °C^{-1}) and other metals used for electrical contacts. The effectiveness of the small volume fraction of nickel fibers in lowering the CTE gives further attraction for the use of the composites of this work in electronic packaging.

4.5 Mechanical Properties. Compression testing was performed using a Vishay Bench Top Testing Machine (Model BT-1000). Figure 4 shows the compressive stress-strain curves of composites containing 0, 5.1, 6.6 and 11.5 vol. percent nickel fibers. The curve for 0 vol. percent nickel fibers exhibits a concave shape, which is typical of an elastomer. The slope (related to the modulus) increased with increasing nickel fiber volume fraction. The onset of cracking was observed during compressive testing in composites containing 6.6 and 11.5 vol. percent nickel fibers only and it occurred at 1.2 and 0.9 MPa, respectively; the cracking caused the curve to decrease in slope.

Table 4 shows the permanent sets remaining in the composites after compression to a stress of 0.4 MPa for either 30 s or 7 days. The permanent set was up to 0.6 percent after 30 s and up to 1.3 percent after 7 days. Two to three samples were tested for each composition. The permanent sets were determined by measuring using a micrometer the change in distance between the two parallel needles that went through the sample.

The fracture surfaces after compressive failure were examined under a scanning electron microscope (SEM), as shown in Fig. 5. Much fiber pull-out was observed, indicating poor bonding between the nickel fibers and the silicone matrix. The

Table 4 Permanent sets after compression to a stress of 0.4 MPa for different lengths of time

Time	Ni vol.%	Permanent set (%)
30 s	3.3	0.45±0.04
	4.5	0.56±0.01
	6.4	0.61±0.10
	8.2	0.27±0.05
	11.5	0.42±0.04
7 days	7.9	1.06±0.20
	11.1	1.26±0.20

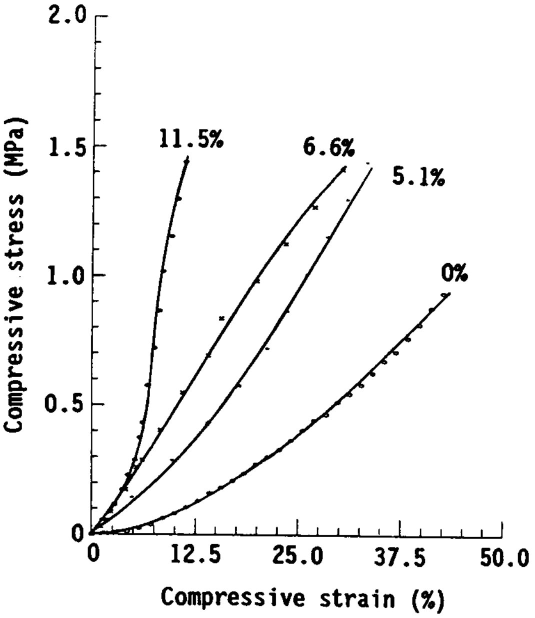

Fig. 4 Compressive stress-strain curves for composities containing various volume fractions of nickel fibers

Fig. 5 SEM photograph of the compressive fracture surface of the composite containing 8.2 vol. percent Ni fibers

debonding between the fibers and the matrix was partly due to the fibers cutting through the matrix.

5 Discussion

The volume electrical resistivity of the nickel fiber silicone-matrix composites of this work are orders of magnitude lower than that of the composites of [3]. This is due to the higher fiber volume fraction used in this work.

The reproducibility of a composite of a given fiber volume fraction (associated with a certain value of the volume electrical resistivity) is better in this work than in [3], as shown by comparing the variation of the resistivity with fiber content in Tables 1 and 2. This is attributed to the difference in composite fabrication method between this work and [3]. It is easier to obtain a uniform fiber distribution using the preform impregnation method (this work) than using the slurry casting method [3]. It is also easier to obtain composites with a high fiber content using the preform impregnation method than using the slurry casting method.

As the nickel fiber composites of this work are comparable to silver particle composites in the volume electrical resistivity, the composites of this work are useful for electrical contacts. The main drawback of the composites of this work lies in the impossibility of using these composites for screen printing, due to the fact that the nickel fiber preform cannot flow.

A particular attraction of the composites of this work lies in the excellent thermal stability, as shown by the very little effect of heating (130-150°C for 7 days) on the volume and contact electrical resistivities. Another attraction lies in the low CTE, which makes the composites compatible with metals used as electrical contacts.

The EMI shielding effectiveness of the composites of this work is comparable to or better than that of the composites of [3]. However, it should be noted that the frequency range was 1.0-2.0 GHz in this work and was 0.2-1.0 GHz in [3]. Hence, the composites of this work are useful for gaskets for EMI shielding.

An increase in the nickel fiber content increases the compressive stress needed per unit compressive strain. However, the resilience of the composites (as shown by the small values of the permanent sets after compression to a stress of 0.4 MPa and a strain of up to 13.5 percent) is maintained up to the highest nickel fiber content of 11.5 vol. percent. A pressure of just 0.10 MPa was required for achieving a minimum (stable) contact resistivity with copper. This resilience is valuable for applications as electrical contacts and as gaskets for EMI shielding.

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