

Effect of the Second Filler which Melted During Composite Fabrication on the Electrical Properties of Short Fiber Polymer-Matrix Composites*

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This paper presents a method for greatly enhancing the electrical conductivity and electromagnetic interference shielding effectiveness of short conducting fiber filled polymers. This method involves the addition of a small proportion of metal particles as a second filler to the fiber polymer-matrix composite. The key to the method is that the metal particles melt during the composite fabrication, so that the metal electrically connects the metal-coated carbon fibers to a certain degree, thereby resulting in a partially connected three-dimensional network. By adding 2 vol% tin-lead particles to 20 vol% short nickel-coated carbon fiber filled polyether sulfone, the electrical resistivity was decreased by a factor of 2000, while the shielding effectiveness at 1 GHz was increased from 19 to 45 dB. No such improvement was found for the same volume fraction of tin-lead particles added to an uncoated carbon fiber composite. This difference is due to the superior wetting of solder with nickel compared to that of solder with carbon, as shown by contact angle measurements.

Key words: Composite, carbon fiber, nickel coating, particles, metal, tin-lead, electrical resistivity, electromagnetic interference shielding

1. INTRODUCTION

Carbon fiber polymer-matrix composites have attractive electrical and mechanical properties due to the high electrical conductivity and high tensile modulus of carbon fibers.^{1,2} The use of short carbon fibers in these composites is desirable due to the convenience of molding by extrusion, injection molding or other processing methods. Electromagnetic interference (EMI) shielding is an important area of application for these composites.³

Metal-coated carbon fibers are superior to uncoated carbon fibers in providing polymer-matrix composites of high electrical conductivity, since the electrical conductivity of a carbon fiber is lower than that of a metal. The use of metal-coated carbon fibers also provides composites with greater EMI shielding effectiveness.^{4,5}

The addition of a second filler to a polymer is another technique for enhancing the electrical properties of a composite. This technique is particularly effective when the melting temperature of the second filler is below the composite fabrication temperature, as demonstrated for the case of Sn-Pb particles as a second filler in a polymer containing metal particles or flakes.⁶ In this paper, by using fibers instead of particles or flakes as the first filler, we have greatly increased the effectiveness of this technique. Furthermore, this paper shows that the first filler must be wetted by the molten second filler in order for the technique to be effective.

In this work, tin-lead alloy (60 Sn-40 Pb) was cho-

sen for the second filler because its melting temperature (183–188° C) was lower than the composite fabrication temperature (310° C for the case of polyether sulfone as the matrix of the composite). In addition, for the sake of comparing with the case in which the second filler did not melt during composite fabrication, nickel particles were used instead of Sn-Pb particles. Nickel was chosen also for its good oxidation resistance. For the sake of comparing the case of the first filler being wetted by the molten second filler with the case of the first filler not being wetted by the molten second filler, metal-coated carbon fibers and bare carbon fibers were separately used as the first filler.

2. EXPERIMENTAL METHODS

Materials and Samples Preparation

The polymer used was polyether sulfone (PES), a thermoplastic (Victrex PES 4100P of ICI). The properties of this polymer are shown in Table I.

The carbon fibers prior to metal coating were isotropic, short, pitch-based and unsized, of diameter 10 μm and nominal length 400 μm , and provided by Ashland Petroleum Co. (Ashland, KY, USA) as Carboflex P-400. The fibers had been carbonized by Ashland Petroleum Co. at $\sim 1000^\circ\text{C}$, so they were amorphous in structure. Nickel coating was performed in SUNY/Buffalo by electroplating using a nickel anode, a nickel sulfate electrolyte and a proprietary process. The crystalline nickel coating was uniform around the fiber. The density of the fiber increased from 1.6 to $2.50 \pm 0.05\text{ g/cm}^3$ after nickel

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Table I. Properties of Polyether Sulfone Polymer

T_g (glass transition temperature)	220–222° C
Density	1.37 g/cm ³
Particle size	100–200 μ m
Tensile strength	45.93 \pm 1.12 MPa
Tensile modulus	2.64 \pm 0.19 GPa
Elongation at break	(3.1 \pm 0.3)%
Electrical resistivity	>10 ¹⁰ Ω cm
Coefficient of thermal expansion	55 \times 10 ⁻⁶ /K

coating. The thickness of the Ni coating was about 0.34 μ m; the volume fraction of Ni in the Ni-coated carbon fiber was 12.3%. The measured electrical resistivity of the Ni-coated fiber was 7.4×10^{-5} Ω cm, which is much lower than the measured value of 3.5×10^{-3} Ω cm for the bare carbon fiber.

The tin-lead was powdered solder of composition 60 wt% Sn, 40 wt% Pb (more exactly 59.5–61.5 wt% Sn, balance Pb, max. 0.40 wt% Sb), obtained from Taracorp Industries, Inc. The particle size distribution was as follows: max. 0.5–1% of 200 mesh size, 10% of 200–235 mesh size, 50% of 325–400 mesh size and 30–50% of 400 mesh size.

The nickel particles had a spherical shape, a rough surface, and a particle size of 1–5 μ m. They were provided by Atlantic Equipment Engineers (Bergenfield, NJ, USA).

Composites were fabricated by mixing the polymer powder, fibers and metal powder for 4 h by using a ball mill and then heating the mixture in a matched metal die at 310° C and 6.51 MPa for 20 min, unless stated otherwise. In one case, a pressure of 4.90 MPa was used instead of 6.51 MPa, but the resulting composite exhibited higher electrical resistivity and lower EMI shielding effectiveness than that fabricated at 6.51 MPa. The composites studied contained 20 vol.% fibers (whether metal-coated or not) and 1–4 vol.% Sn-Pb solder particles.

Electrical Testing

Electrical resistivity measurements were made on composite materials which had been cut into bars. The four-probe method was used. Four specimens of each composition were tested. Four data points were obtained for each specimen.

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 disc. The outside diameter and the inside diameter were 97.4 and 28.8 mm, respectively. The thickness ranged from 2.34 to 2.70 mm. 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 disc. Two specimens of each composition were tested. The setup was capable of measuring attenuation up to 50 dB only.

Mechanical Testing

The specimens were tested mechanically using standard methods and a servo-hydraulic load frame.

A personal computer and a data acquisition board were used for the data collection. Strain gages were applied on the specimens to measure the strain during the tensile testing. Four specimens of each sample type were tested. After tensile fracture, the fracture surfaces were examined under a scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

Electrical Properties

The electrical resistivity and EMI shielding effectiveness of the various composite materials are listed in Table II. The thickness of all EMI samples was 2.50 ± 0.20 mm. The electrical resistivity of 20 vol.% Ni-coated carbon fibers (400 μ m) composite with an addition of 2 vol% Sn-Pb particles (Row 2) was a factor of 2000 lower than that of the corresponding composite without Sn-Pb particles (Row 1). The EMI shielding effectiveness at 1 GHz also increased from 19 dB (Row 1) to 45 dB (Row 2). A comparison of the 20 vol% Ni-coated carbon fiber composite (Row 1) and the composite with an addition of 2 vol% Ni particles (Row 3) shows that the Ni particle addition to the composite decreased the resistivity only slightly and increased the shielding effectiveness slightly, although Ni has a lower electrical resistivity than Sn-Pb. The main difference between Sn-Pb and Ni was that Sn-Pb particles melted at the fabrication temperature of 310° C, whereas Ni did not. Thus, it appears that the melting of Sn-Pb particles helped to enhance the electrical properties of the composite greatly.

For electrically conductive composites, in order to reach a low electrical resistivity and a high EMI shielding effectiveness, either a high volume fraction or a large aspect ratio of the conductive filler is needed in the composites. For both Ni-coated and bare carbon fiber composites, the critical volume fraction was 13 vol%, based on the experimental result of Ref. 7 on wood fibers as a model filler. When the volume fraction of the randomly oriented fibers in the composite is higher than the critical volume fraction, the electrical resistivity is given by $3\pi\rho/2\phi$, where ρ is the resistivity of the fiber and the ϕ is the volume fraction of the fiber.⁸ For 20 vol% bare and coated carbon fiber composites, the calculated resistivities are 8.2×10^{-2} Ω cm and 1.7×10^{-3} Ω cm, respectively. However, the measured resistivity values (Table II) are several orders of magnitude higher than the calculated ones. This implies that the degree of connection between the fibers was actually limited.

The electron transport mechanism near the critical volume fraction of the filler is governed by the tunnelling of electrons from one fiber (or particle) to the next across gaps of a few nanometers.⁹ When the gap between the fibers is large, the electrons cannot jump from one fiber to another. This will result in a high electrical resistivity of the composite, even when the concentration of the conductive fi-

Table II. Electrical Properties of Uncoated Carbon Fiber and Ni-coated Carbon Fiber PES-matrix Composites

Row	Fillers	Sample Thickness for EMI (mm)	EMI Shielding Effectiveness (dB)										Electrical Resistivity (Ω cm)	
			Frequency (GHz)											
			1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9		2.0
1.	Ni-coated carbon fiber	2.70	19.0	17.7	17.1	16.4	16.2	16.0	17.8	20.8	22.4	23.0	22.5	$(6.12 \pm 1.12) \times 10^2$
2.	Ni-coated carbon fiber + 2 vol% Sn-Pb particles	2.34	45.0	49.0	44.0	37.0	35.5	35.5	35.5	37.5	38.0	39.0	37.0	(0.33 ± 0.15)
3.	Ni-coated carbon fiber + 2 vol% Ni particles	2.64	26.6	27.0	26.9	26.1	25.5	26.6	26.7	29.2	31.1	32.1	32.0	$(3.31 \pm 0.35) \times 10^2$
4.	Carbon fibers (without coating)	2.60	17.6	17.3	16.0	14.8	15.6	14.8	16.8	19.4	20.9	22.0	21.8	$(3.06 \pm 1.68) \times 10^3$
5.	Carbon fibers (without coating) + 2 vol% Sn-Pb particles	2.56	22.6	24.1	24.4	23.9	23.1	23.2	24.2	26.2	28.8	29.6	29.5	$(4.87 \pm 1.04) \times 10^2$
6.	Carbon fibers (without coating) + 2 vol% Sn-Pb particles*	2.67	12.4	13.9	14.1	13.7	14.1	14.3	15.1	17.3	18.9	20.2	20.1	$(6.13 \pm 0.56) \times 10^3$

Fiber volume fraction: 20%

*composite fabricated at 4.90 MPa

bers is higher than the critical volume fraction. Therefore, the contact efficiency needs to be improved in order to reach a low electrical resistivity. Calleja *et al.*¹⁰ and Radhakrishnan¹¹ reported that carbon black could be a second filler to improve the electrical properties of carbon fiber composites. However, the improvement was small because the gaps between the fibers still existed after the addition of the second filler. For the Ni-coated carbon fiber composite of this work, when 2 vol% Ni particles were added to the composite, the electrical properties only improved slightly. The small effect of carbon black and Ni particles as the second filler resulted because these fillers did not melt at the fabrication temperature and thus would not fill the gaps well, even though they could supply more contact points, which resulted in slightly improved electrical properties.

Comparison of Rows 4 and 5 of Table II shows that the Sn-Pb particle addition to the bare carbon fiber composite decreased the resistivity by a factor of 6 and increased the shielding effectiveness. Thus, the Sn-Pb addition to the composites with Ni-coated fibers was much more effective than that to composites with bare carbon fibers for improving the electrical behavior. Figures 1 and 2 show that the electrical conductivity of 20 vol% Ni-coated carbon fiber composites containing 1–4 vol% Sn-Pb particles (Fig. 2) was much higher than that of the bare carbon fiber counterpart (Fig. 1), especially when the content of Sn-Pb was ≥ 2 vol%. Optical microscopy of polished sections of the PES composites containing 20 vol% Ni-coated carbon fibers and 2 vol% Sn-Pb particles showed that the Sn-Pb coated the Ni-coated carbon fibers (Fig. 3(b)) and connected some of the fibers. None of the Sn-Pb remained as dis-

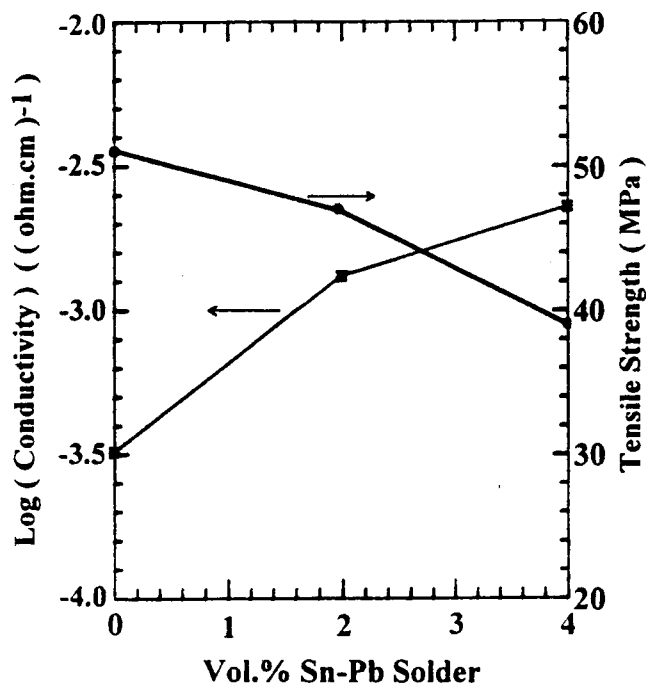


Fig. 1 — Variation of the electrical conductivity and tensile strength of 20 vol% bare carbon fiber composites with the Sn-Pb volume fraction.

crete particles in the composites, as all of the solder adhered to Ni-coated carbon fibers. Therefore, more electrically conductive bridges were formed by the melted Sn-Pb, which filled the gaps between adjacent Ni-coated carbon fibers. In contrast, for 20 vol% bare carbon fiber composites containing 2 vol% Sn-Pb particles (Fig. 3(a)), the Sn-Pb particles remained as discrete particles in the composites and

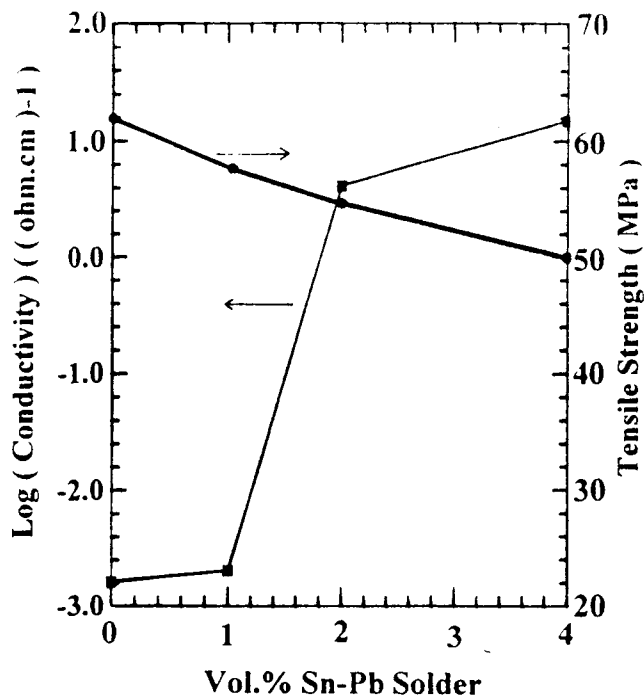


Fig. 2 — Variation of the electrical conductivity and tensile strength of 20 vol% Ni-coated carbon fiber composites with the Sn-Pb volume fraction.

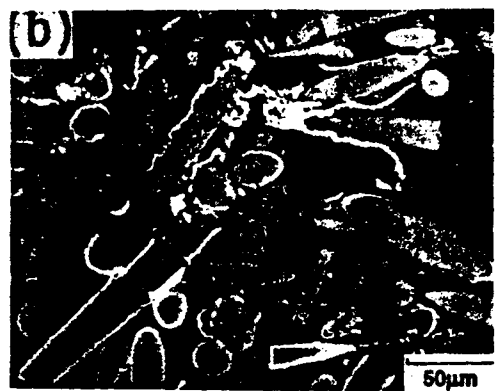
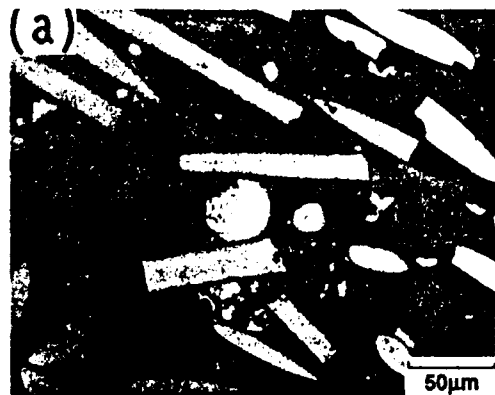


Fig. 4 — Optical microscope photographs showing the wetting angle of (a) Sn-Pb with carbon, and (b) Sn-Pb with Ni-coated copper.

some of them agglomerated to form larger particles. This difference can be explained by the difference in the wetting properties of Sn-Pb with carbon and of Sn-Pb with Ni. Figure 4 shows polished sections revealing the wetting angles of these pairs of materials, as explained below.

The wetting angle (θ) (contact angle) is governed by the surface energy of the materials. The liquid will completely wet ($\theta = 0$) the solid surface if the two new surfaces formed have less energy than the original solid-vapor interface. A complete lack of wetting ($\theta = 180^\circ$) occurs when the converse applies.¹² Actually, non-wetting rarely corresponds to θ being exactly equal to 180° and wetting never corresponds to θ being exactly equal to 0° . From Fig. 4(a), it can be seen that the Sn-Pb solder did not wet the surface of carbon, as θ was much larger than 90° ($\theta \approx 150^\circ$). In contrast, Sn-Pb wetted the surface of Ni-coated copper well, as θ was less than 90° ($\theta \approx 70^\circ$) (Fig. 4(b)). Therefore, the solder wets the Ni surface and does not wet the carbon surface. This is why Sn-Pb is much more effective in filling the gaps between the fibers in the Ni-coated carbon fiber composites than those in the bare carbon fiber composites.

Comparison of Rows 5 and 6 of Table II shows that a decrease of the composite fabrication pressure from 6.51 MPa (Row 5) to 4.90 MPa (Row 6) degrades the electrical properties quite signifi-

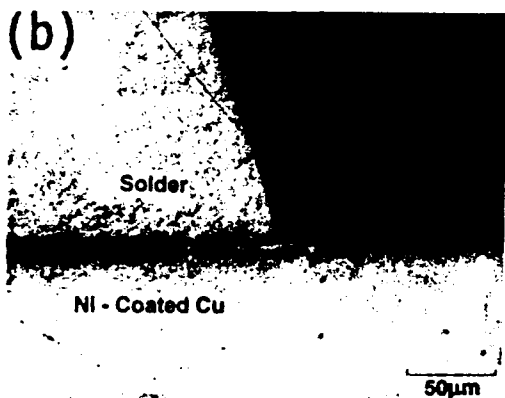
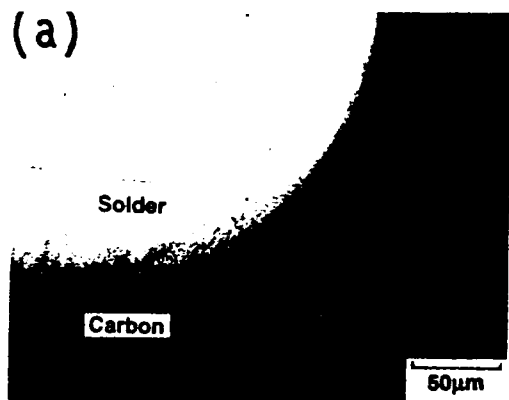


Fig. 3 — Optical microscope photographs of polished surfaces of 20 vol% fiber filled PES composites containing 2 vol% Sn-Pb. (a) Bare carbon fibers. (b) Ni-coated carbon fibers.

Table III. Comparison of Ref. 6 and This Work

	Ref. 6	This Work
Polymer	76.9 vol% pellets	78 vol% powder
First filler	15.4 vol% Fe powder	20 vol% Ni-coated CF
Second filler	7.7 vol% Sn-Pb	2 vol% Sn-Pb
Processing method	Injection molding	Compression molding
Electrical resistivity	$2 \times 10 \Omega \text{ cm}$	$3 \times 10^{-1} \Omega \text{ cm}$

cantly for the case of bare carbon fibers. This is because a higher pressure was needed to cause the melted Sn-Pb to squeeze in between the carbon fibers so as to electrically connect the fibers.

Comparison of Rows 1 and 4 of Table II shows that, without Sn-Pb, the presence of a metal coating on the carbon fibers improved the electrical properties of the composites only marginally. Therefore, a second filler was needed in order to improve the contact between the fibers (the first filler) for the purpose of achieving a low electrical resistivity in the composite.

The electrical conductivity of the Ni-coated carbon fiber composites increased abruptly at a Sn-Pb content of about 2 vol%, as shown in Fig. 2. This means that 2 vol% was the critical Sn-Pb volume fraction for the filling of the gaps between the fibers by the melted Sn-Pb.

Assuming that the nickel-coated carbon fibers were continuous and unidirectional in the PES-matrix composite, the electrical resistivity of the composite was calculated by the rule of mixtures to be $3.7 \times 10^{-4} \Omega \text{ cm}$, which is orders of magnitude lower than the measured value of $0.3 \Omega \text{ cm}$ for the PES-matrix composite containing both Ni-coated carbon fibers and Sn-Pb particles (Row 2 of Table II). This means that the Sn-Pb particles did not electrically connect all the Ni-coated carbon fibers well, though a certain degree of connection must be present. Assuming that the Sn-Pb and Ni-coated carbon fibers were both continuous and unidirectional and not electrically connected at all, the rule of mixtures indicates that the Sn-Pb addition decreases the resistivity from 3.7×10^{-4} to $1.8 \times 10^{-4} \Omega \text{ cm}$ —a rather small effect. However, the observed effect of the Sn-Pb addition on the resistivity was large—orders of magnitude decrease in the resistivity. Thus, the observed effect of the Sn-Pb addition cannot be explained by ignoring the connectivity of the short carbon fibers due to the Sn-Pb addition. This notion that the Sn-Pb particles helped connect the fibers indeed was supported by optical microscopy (Fig. 3). Due to the complexity of the short fiber composites, no model can exactly predict the electrical resistivity of the composites. Usually, the predicted results are orders of magnitude lower than the experimental results. Therefore, it is difficult to quantify the degree of connection of the fibers due to the Sn-Pb solder in the composites.

Table III is a comparison of the composite of Ref. 6 and that of this work. Both composites used Sn-

Pb as the second filler, but a large difference in the electrical resistivity exists between the two composites. This difference is because the filler used in this work was metal-coated fibers, whereas that used in the Ref. 6 was iron powder. It is easier to form an electrically conducting network in a fibrous composite than in a particulate composite, because of the larger aspect ratio of the fibers. The larger aspect ratio of fibers or flakes will enhance the connectivity and hence increase the conductivity. On the other hand, the processing method and the shape of the conductive and polymer materials are other factors that affect the electrical properties of the composite materials.

Mechanical Properties

The tensile properties of the composites are listed in Table IV. The 20 vol% Ni-coated carbon fiber composite had the highest tensile strength among all the composites studied. The tensile strength decreased gradually with increasing Sn-Pb content (Fig. 1 and 2). This is a result of the weak bonding between the Sn-Pb and the PES matrix, as shown by the tensile fracture surface.¹³ Figure 5 shows SEM photographs of the fracture surfaces of (a) uncoated and (b) coated carbon fiber composites, both containing 2 vol% Sn-Pb particles and 20 vol% fibers. Discrete solder particles remained in the fracture surface of the uncoated carbon fiber composite, but were not observed in the fracture surface of the coated fiber composite. The tensile strength of the bare carbon fiber composite was lower than that of the Ni-coated carbon fiber composite with the same volume fraction of Sn-Pb (Figs. 1 and 2), because without the nickel the solder particles act as initiation sites for fracture.

The addition of 2 vol% Ni particles to the 20 vol% Ni-coated carbon fiber composite only decreased the tensile strength slightly (Table IV). This effect is caused by the rough surface of the Ni particles which enhances the good bonding between the Ni particles and the polymer.¹⁴

4. CONCLUSION

This paper provides a new method for enhancing the electrical conductivity and EMI shielding effectiveness of short conducting fiber filled polymers. This method involves the addition of a small proportion of metal particles as a second filler to the fiber polymer-matrix composite. For a fiber content of 20 vol%, a metal particle content of 2 vol% is effective. The key to the method is that the metal particles melt during the composite fabrication, so that the metal electrically connects the fibers to a certain degree, thereby resulting in a partially connected three-dimensional conductor network. The method does not require modification of the conventional composite fabrication procedure, as the hot pressing was performed in one step at a temperature above the melting temperature of the metal particles. As the volume fraction of metal particles

Table IV. Mechanical Properties of Uncoated Carbon Fiber and Ni-coated Carbon Fiber PES-matrix Composites

Row Fillers	Fiber Volume Fraction (%)	Tensile Strength (MPa)	Modulus (GPa)	Elongation (%)
1. Ni-coated carbon fibers	20	61.85 ± 2.06	5.02 ± 0.20	1.36 ± 0.05
2. Ni-coated carbon fibers + 2 vol% Sn-Pb particles	20	55.04 ± 0.16	4.99 ± 0.16	1.15 ± 0.09
3. Ni-coated carbon fibers + 2 vol% Ni particles	20	57.84 ± 3.26	5.03 ± 0.42	1.21 ± 0.15
4. Carbon fiber (without coating)	20	51.12 ± 2.23	4.89 ± 0.33	1.21 ± 0.17
5. Carbon fibers (without coating) + 2 vol% Sn-Pb particles	20	47.10 ± 1.17	4.61 ± 0.25	1.25 ± 0.11
6.* Carbon fiber (without coating)	20	46.80 ± 4.16	4.50 ± 0.32	1.16 ± 0.17

*composite fabricated at 4.90 MPa

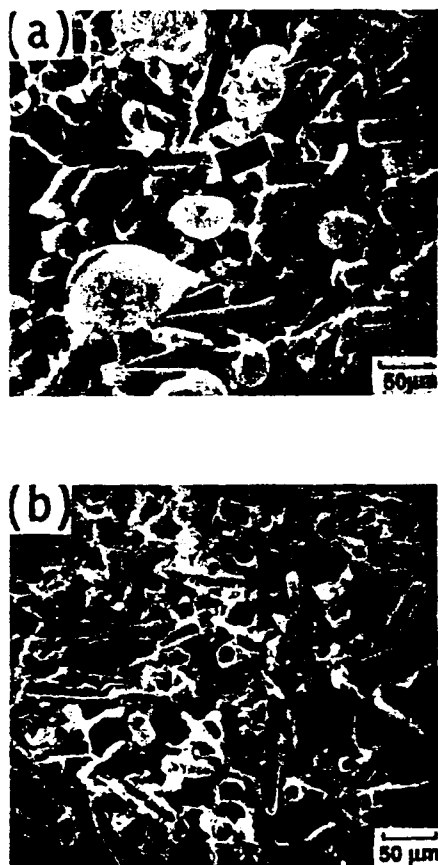


Fig. 5 — SEM photographs of the tensile fracture surfaces of 20 vol% fiber filled PES composites containing 2 vol% Sn-Pb. (a) Bare carbon fibers. (b) Ni-coated carbon fibers.

is low, the effect of the metal particle addition on the mechanical properties and density is very small compared to the effect on the electrical properties. For this method to be effective, the fibers should be wettable by the liquid metal particles. For the case of carbon fibers, sufficient wettability was observed when metal-coated carbon fibers were used instead of bare carbon fibers. In this work, the metal coating was electroplated crystalline nickel, though other metals are also possible for the coating.

By the addition of 2 vol% Sn-Pb particles (of mean particle size 25 μm) to a PES composite containing

20 vol% short Ni-coated carbon fibers, the electrical resistivity of the composite was decreased by a factor of 2000, while the EMI shielding effectiveness at 1 GHz was increased from 19 to 45 dB. If bare carbon fibers were used instead, the electrical resistivity was decreased by a factor of only 6 and the shielding effectiveness was increased from 18 to 23 dB only.

The presence of a nickel coating on the carbon fibers decreased the electrical resistivity of carbon fiber PES-matrix composites (without metal particles added) by a factor of 5 and increased the EMI shielding effectiveness at 1 GHz from 18 to 19 dB only. Thus, the addition of the metal particles was far more effective than just using a metal coating on the carbon fibers in improving the electrical behavior of carbon fiber polymer-matrix composites, because the low-melting-temperature metal particles could fill the gaps and form electrically conductive bridges between the fibers.

The main requirement for the metal particles is that they melt at the composite fabrication temperature. Thus, other than Sn-Pb, numerous alloys with low melting temperatures can be used.

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