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Submicron Nickel Filaments Made by Electroplating Carbon Filaments as a New Filler Material for Electromagnetic Interference Shielding

XIAOPING SHUI and D.D.L. CHUNG

Composite Materials Research Laboratory, Furnas Hall, State University of New York at Buffalo, Buffalo, NY 14260-4400

Short nickel filaments of diam 0.4 μm and containing 94 vol% Ni and 6 vol% C were fabricated by electroplating with nickel 0.1 μm diam catalytically grown carbon filaments. The use of these filaments in polyether sulfone in amounts of 3, 7, 13, and 19 vol% gave composites with electromagnetic interference shielding effectiveness at 1–2 GHz of 42, 87, 84, and 92 dB, respectively, compared to a value of 90 dB for solid copper. Less shielding was attained when 0.1 μm diam carbon filaments or 2 or 20 μm diam nickel fibers were used instead.

Key words: Composites, electromagnetic interference, filaments, fibers, nickel, shielding

INTRODUCTION

Electrically conducting polymer-matrix composites are used for electromagnetic interference (EMI) shielding,[1–6] the need of which is increasingly important due to the increasing sensitivity and abundance of electronics. Polymer-matrix components, as opposed to monolithic metals, are attractive due to their moldability. These composites are conducting due to the presence of an electrically conducting filler, which can be discontinuous (such as particles and short fibers) or continuous (such as continuous fibers). Discontinuous fillers are in general less effective than continuous fillers in decreasing the electrical resistivity of the composite. However, unlike electrical conduction, EMI shielding does not require continuity or percolation of the conducting phase, though continuity or percolation helps. Moreover, discontinuous fillers are suitable for composite fabrication by injection molding and, if the discontinuous filler is fine enough in size, even by ink jet printing or screen printing. Due to the lower cost and greater versatility of composite fabrication for discontinuous fillers compared to continuous fillers, discontinuous fillers are widely used for making electrically conducting composites, especially those for EMI shielding.

Discontinuous fillers that have been used in polymer matrices for EMI shielding include metal particles (e.g., Ni particles), metal flakes (e.g., Al flakes), carbon particles, (e.g., graphite and carbon black), carbon fibers, metal fibers (e.g., stainless steel fibers, nickel fibers), metal coated carbon particles, and metal coated carbon fibers (e.g., Ni coated carbon fibers). For any filler, the EMI shielding effectiveness increases with increasing filler volume fraction in the composite, but the maximum filler volume fraction is limited by the poor composite mechanical properties at high filler volume fractions resulting from the poor filler-matrix bonding.

For materials and process cost saving and good mechanical properties, the attainment of a high shielding effectiveness at a low filler volume fraction is desirable. Because electromagnetic waves at high frequencies (such as microwaves) interact with a

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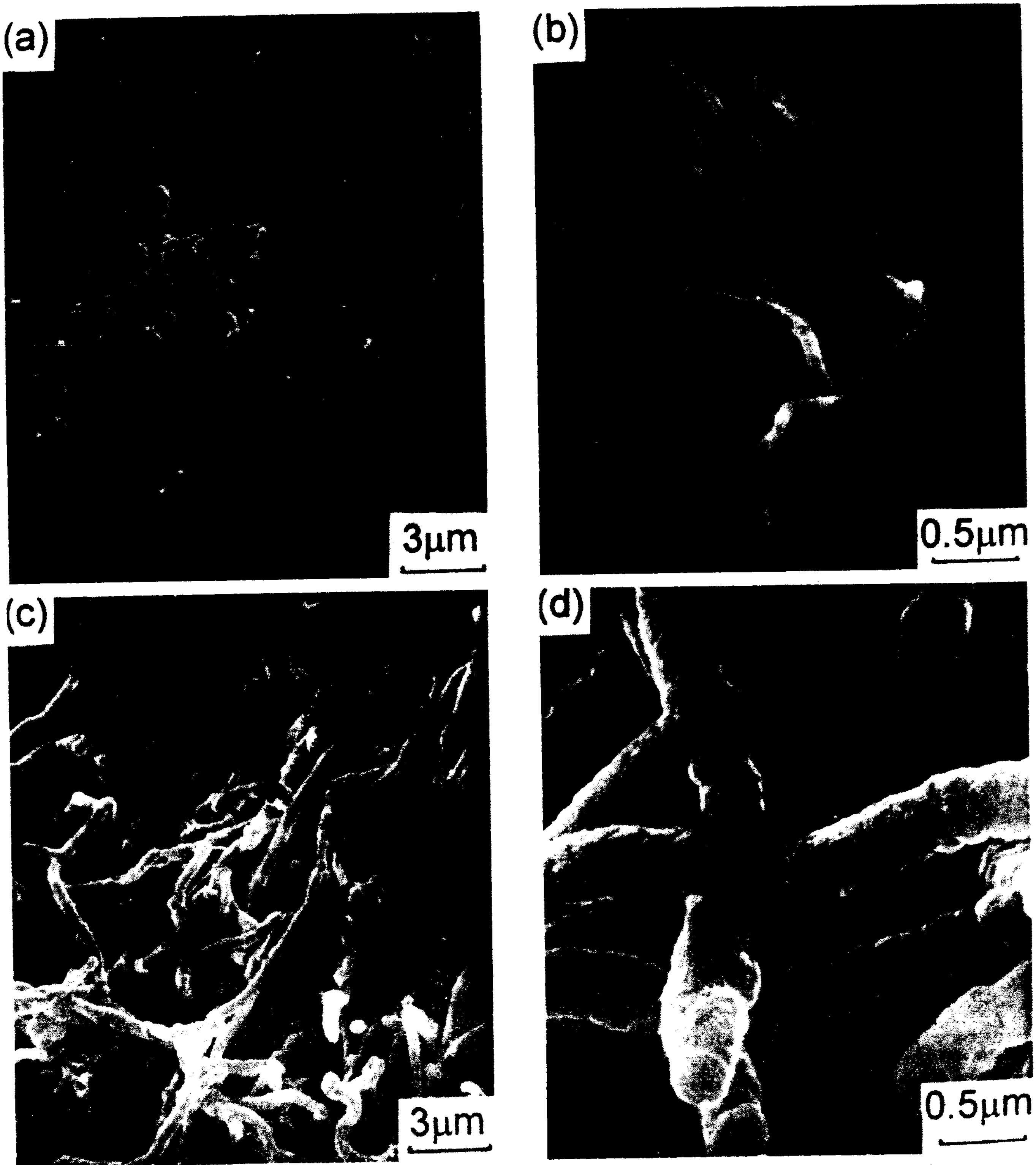

Fig. 1. Four SEM photographs. (a) and (b): carbon filaments at two magnifications; (c) and (d): nickel filaments at two magnifications.

conductor only near its surface, a smaller unit size of the conducting filler enables a higher shielding effectiveness to be attained at the same filler volume fraction. Therefore, this paper emphasizes the development of a submicron diameter filament filler. By "filament," we refer to a fiber of diameter less than 2 μm.

The only submicron diameter filament filler that has been previously used for EMI shielding is carbon filaments (catalytically grown from carbonaceous gases); a shielding effectiveness at 1 GHz of 45 dB was attained at a filler content of 60 wt% (about 45 vol%).[6] The sizes of these carbon filaments are in contrast to those of conventional carbon fibers, which typically have diameter in the range 7–11 μm. The coating of conventional carbon fibers with nickel has been previously shown to greatly increase the shielding effectiveness, so that a shielding effectiveness at 1 GHz of 76 dB was attained.[1] In this work, by coating the submicron diameter carbon filaments with nickel, we have provided a new filler that results in shielding effectiveness at 1 GHz of 90 dB—a value higher than what had been previously achieved by any filler. Due

Table I. Properties of Polyether Sulfone Polymer

T_g	220–222°C
Density	1.37 g/cm^3
Particle size	100–150 μm
Tensile strength	45.93 ±1.12 MPa
Tensile modulus	2.64 ±.0.19GPa
Elongation at break	(3.1 ± 0.3)%
Electrical resistivity	> 10^{10} Ω.cm
Coefficient of thermal expansion	55 ×10^{-6}/K

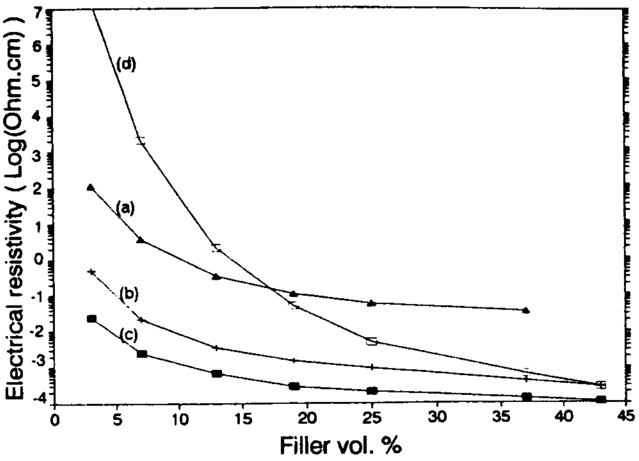

Fig. 2. Variation of the volume electrical resistivity of composites with filler volume fraction: (a) carbon filaments, (b) nickel filaments, (c) nickel fibers of diam 2 μm, and (d) nickel fibers of diam 20 μm.

Table II. Electrical Resistivity of Composites with Different Fillers

	Resistivity of Composites (Ω.cm)			
Filler vol%	**Ni Filaments**	**2 μm Ni Fibers**	**20 μm Ni Fibers**	**C Filaments**
3	5.00×10^{-1}	2.40×10^{-2}	2.20×10^{7}	1.16×10^{2}
7	2.20×10^{-2}	2.50×10^{-3}	2.20×10^{3}	3.78×10^{0}
13	3.50×10^{-3}	6.90×10^{-4}	2.20×10^{0}	3.68×10^{-1}
19	1.50×10^{-3}	2.90×10^{-4}	5.30×10^{-2}	1.16×10^{-1}
25	9.58×10^{-4}	2.10×10^{-4}	5.00×10^{-3}	6.22×10^{-2}
37	4.16×10^{-4}	1.35×10^{-4}	6.60×10^{-4}	3.57×10^{-2}
43	2.81×10^{-4}	1.06×10^{-4}	2.80×10^{-4}	/

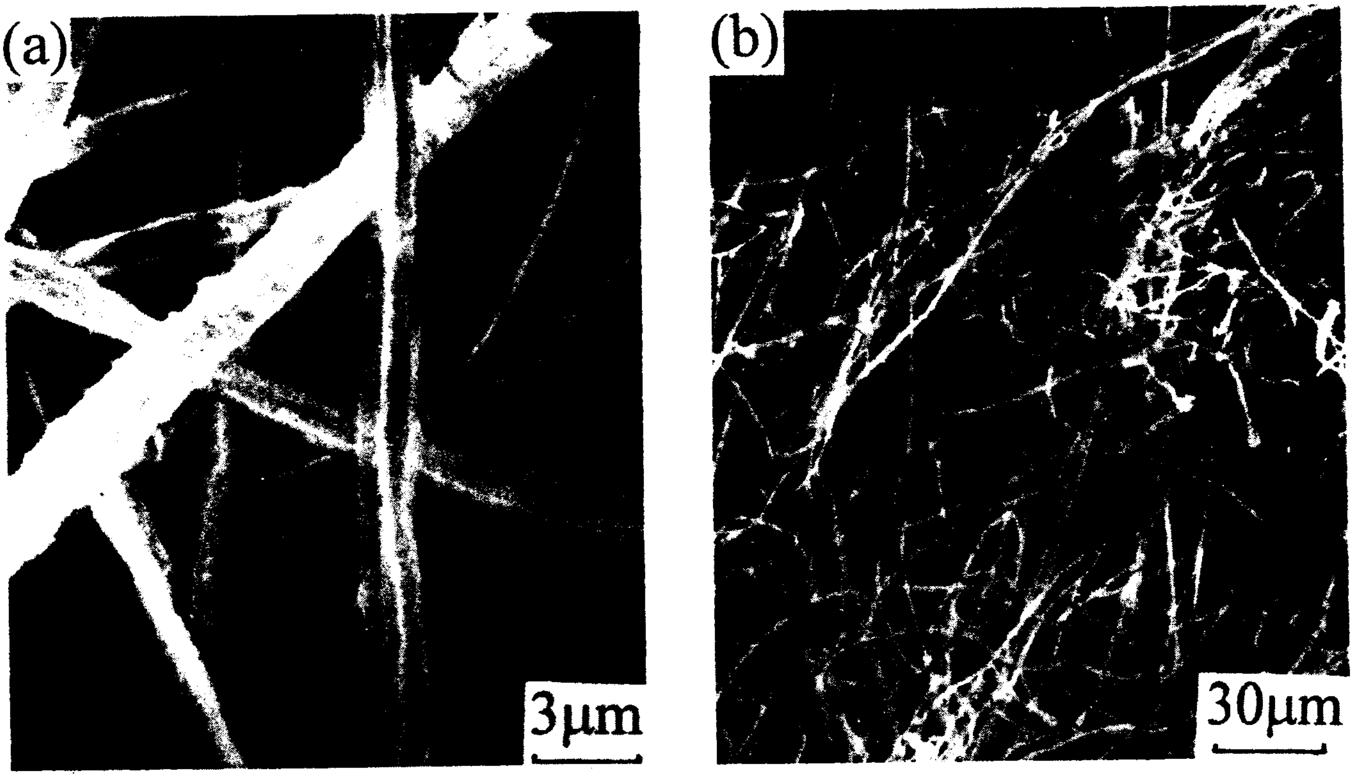

Fig. 3. Scanning electron microscopy photographs of Ni fibers of diam 2 μm at two magnifications.

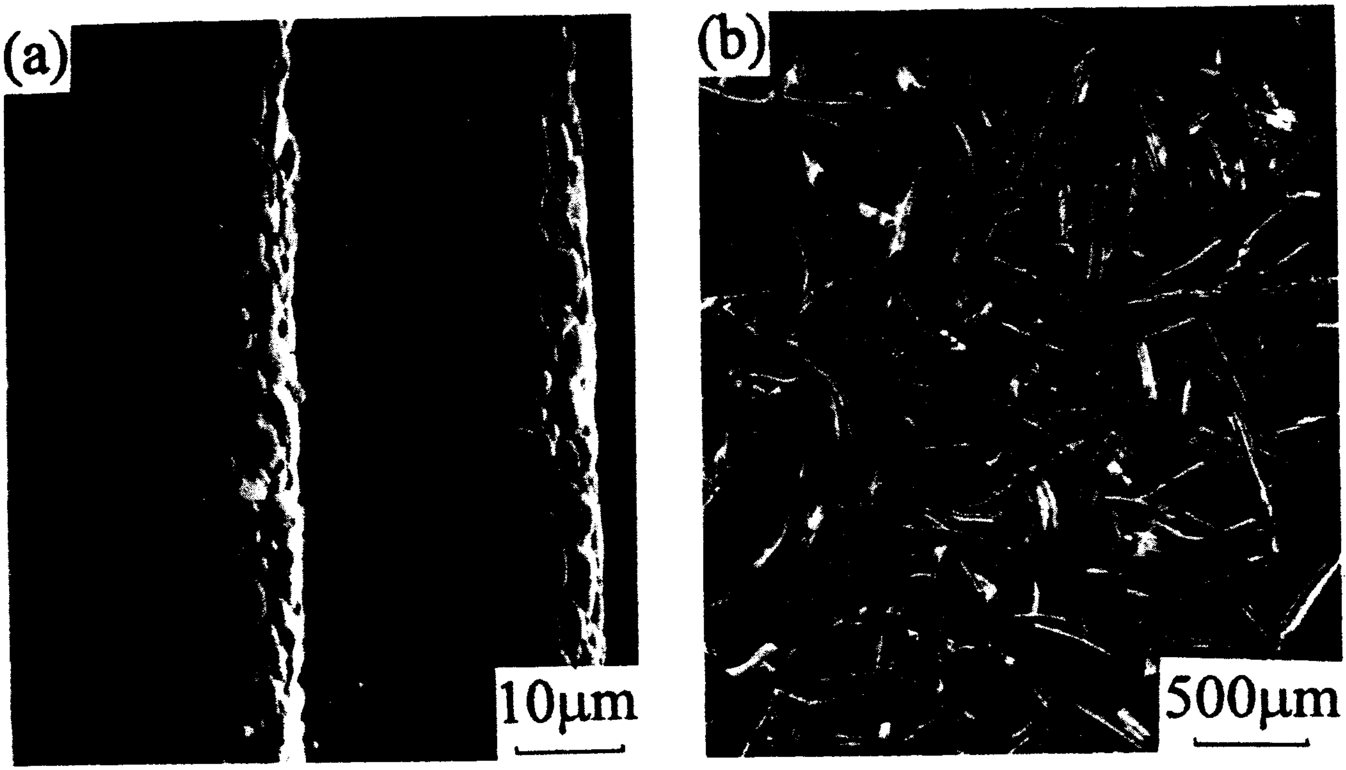

Fig. 4. Scanning electron microscopy photographs of Ni fibers of diam 20 μm at two magnifications.

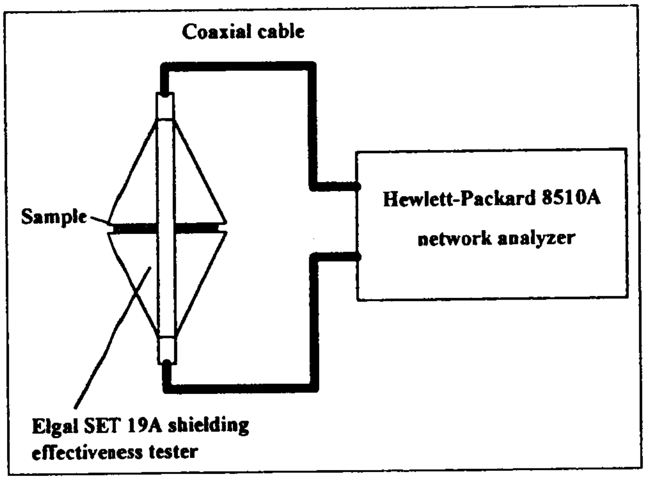

Fig. 5. Experimental setup for measuring the EMI shielding effectiveness.

to the submicron diameter of the new filler, a high shielding effectiveness was attained even at an extraordinarily low filler volume fraction, e.g., 87 dB at just 7 vol% filler.

The new filler of this work contained 94 vol% Ni and 6 vol% C, as the filler diameter was 0.4 μm, compared to a diameter of 0.1 μm for the carbon filaments which form its core. Due to the large proportion of Ni, the new filler is hereby called nickel filaments. They are to be distinguished from the nickel fibers of diam ≥ 2 μm that are made by either deformation processing or melt processing. This paper includes comparison of the shielding effectiveness of the new filler with that of the commercial nickel fibers and that of the carbon filaments.

EXPERIMENTAL

Nickel Filaments

A typical nickel filament measured 0.404 ± 0.022 μm in diameter, and it contained a carbon core of diameter 0.096 ± 0.018 μm. Each nickel filament contained 94.4 vol% Ni and 5.6 vol% C. The carbon core was present because the nickel filaments were fabricated by the electroplating of nickel onto carbon filaments. The carbon filaments were catalytically grown from carbonaceous gases, in contrast to conventional carbon fibers, that are made from pitch or polymers. As a result, the carbon filaments can have diameters much smaller than conventional carbon fibers. Prior to electroplating, the surface of the carbon filaments was treated;[7] without the treatment, the Ni coating was not uniform and resulted in composites orders of magnitude higher in electrical resistivity compared to the case with the treatment.[8] The electroplating was conducted by using a nickel anode and a nickel sulfate electrolyte solution. The nickel in the nickel filaments was crystalline, as shown by x-ray diffraction. Because the carbon filaments were not straight, the resulting nickel filaments were also not straight, as shown in Fig. 1 for both the acetone-washed carbon filaments and the resulting nickel filaments. Due to the bent morphology and large aspect ratio, determination of the exact length of the carbon or nickel filaments was not possible. Nevertheless, a lower limit of the length was found by scanning electron microscopy (SEM) to be 100 μm.

The submicron nature of either nickel or carbon filaments did not allow measurement of the electrical

Table III. Electromagnetic Interference Shielding Effectiveness (dB), averaged in the Range 1–2 GHz

	3 vol%	7 vol%	13 vol%	19 vol%	25 vol%	37 vol%	43 vol%	100 vol%
Ni filaments	42.2 (2.4)	86.6 (5.1)	83.7 (5.3)	91.7 (6.6)				
C filaments	20.6 (1.3)	31.8 (1.7)	53.6 (3.5)	73.9 (5.1)				
2 µm Ni fibers	45.2 (2.5)	58.1 (4.2)	60.3 (3.2)	71.7 (4.6)				
20 µm Ni fibers				4.9 (1.9)	10.5 (2.3)	38.4 (1.9)	73.7 (4.4)	
Copper								90.2 (5.0)
Stainless steel								88.9 (4.0)

Note: The standard deviations are shown in parentheses.

resistivity of single filaments. However, based on resistivity measurements of filament compacts, the resistivity was estimated to be 10^{-3} and 10^{-6} Ω.cm for the carbon filaments and nickel filaments, respectively.

The skin depth of nickel is 4.7 µm at 1 GHz. Thus, nickel fiber/filament diameters less than 4.7 µm are preferred—the smaller the better—for maximizing the EMI shielding effectiveness.

Composite Fabrication

The polymer used for all composites was polyether sulfone (PES), a thermoplastic provided as Victrex PES 41 00P by ICI. Its properties are shown in Table I. The nickel fibers used for comparing with the nickel filaments were

- 2 µm in diam and 2000 µm in length, as provided by Ribtec (Gahanna, Ohio), and
- 20 µm in diam and 1000 µm in length, as provided as Fibrex by National-Standard Co. (Corbin, Kentucky).

Due to the large length of the nickel fibers of diam 2 µm (which resemble cotton wool), the dispersion of these fibers was most difficult. The carbon filaments used for comparing with the nickel filaments were 0.1 µm in diam and > 100 µm in length, as provided as Applied Sciences, Inc. (Cedarville, Ohio).

The composites were fabricated by forming a dry mixture of the polymer powder and the filler and subsequent hot pressing in a steel mold at 310°C (processing temperature for PES, as recommended by ICI) and 13.4 MPa for ~30 min. For the nickel filaments and the 20 µm diam Ni fibers, the mixing was carried out dry in a ball mill. For the carbon filaments, mixing was carried out wet—with water in a blender, and then the wet mix was dried at 120°C. For the 2 µm diam Ni fibers, mixing was performed by hand, as neither the abovementioned dry mixing nor wet mixing was possible.

Electrical Properties of the Composites

The volume electrical resistivity of the composites was measured by the four-probe method, using silver paint as electrical contacts. Figure 2 and Table II give the resistivity vs filler volume fraction for various PES-matrix composites. The Ni filaments were slightly less effective than the Ni fibers of diam 2 µm but much more effective than the Ni fibers of diam 20 µm in providing low resistivity. That the Ni filaments of diam 0.4 µm were slightly less effective than the Ni fibers of diam 2 µm is because the cross-sectional area of the Ni filaments (Fig. 1) is not as uniform as that of the Ni fibers (Fig. 3) and probably also because the resistivity of the Ni filaments is higher than that of the Ni fibers. That the Ni filaments were much more effective than the Ni fibers of diam 20 µm (Fig. 4) is because of their large aspect ratio (250 for Ni filaments and 50 for Ni fibers). The difference in effectiveness for providing composites of low resistivity between the Ni filaments and the Ni fibers of diam 20 µm decreased with increasing filler volume fraction.

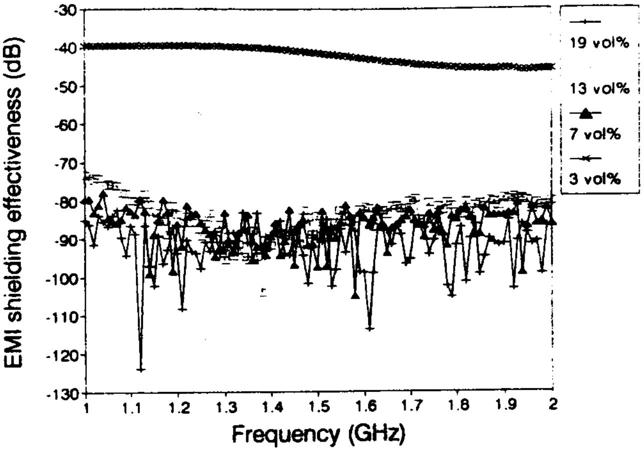

Fig. 6. Electromagnetic interference shielding effectiveness vs frequency for composites containing Ni filaments at various volume fractions.

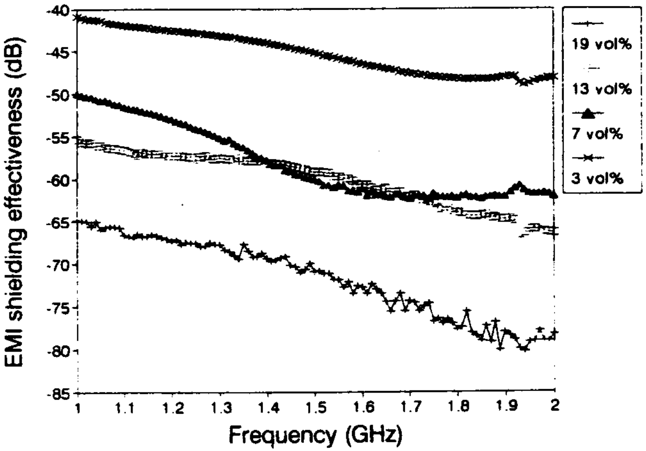

Fig. 7. Electromagnetic interference shielding effectiveness vs frequency for composites containing 2 µm diam Ni fibers at various volume fractions.

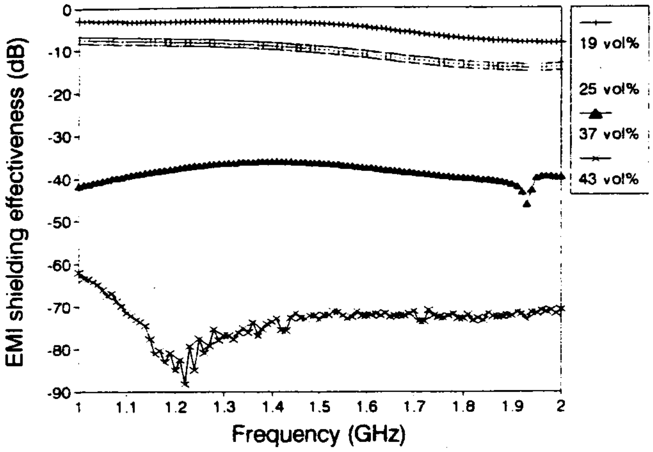

Fig. 8. Electromagnetic interference shielding effectiveness vs frequency for composites containing 20 μm diam Ni fibers at various volume fractions.

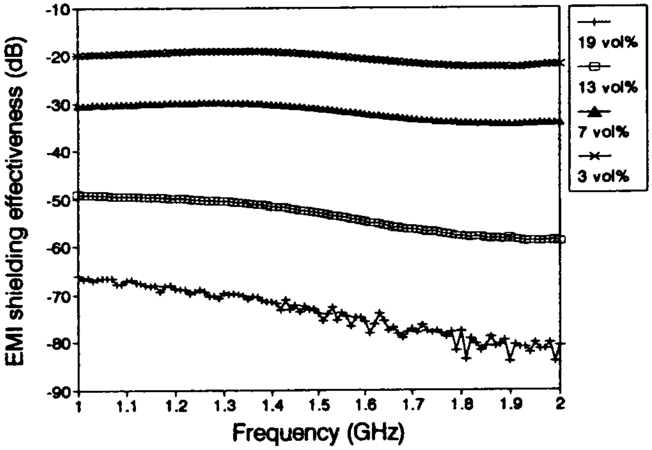

Fig. 9. Electromagnetic interference shielding effectiveness vs frequency for composites containing carbon filaments at various volume fractions.

At all filler volume fractions, the carbon filaments, though smaller in diameter and more uniform in cross-sectional area (Fig. 1), were less effective than the Ni filaments because of the high resistivity of the former.

EMI Shielding Effectiveness of the Composites

The EMI shielding effectiveness was measured in transmission using the commonly used coaxial cable method (Fig. 5). The sample was in the form of an annular ring of outer diam 3.8 in (97 mm) and inner diam 1.25 in (32 mm). The sample thickness was 2.85 mm for all the composites, 3.1 mm for solid copper, and 4.0 mm for solid stainless steel. The frequency was scanned from 1 to 2 GHz such that 101 shielding effectiveness data points were taken within this frequency range. The average of these 101 data for each sample is shown in Table III, together with the standard deviation of these 101 data in parentheses. Figures 6–9 give all the data for each composite sample. The error of each data point was better than ± 1 dB at < 10 dB, and ± 5 dB at > 70 dB; the error increased with increasing attenuation (dB).

Table IV. Electromagnetic Inference Shielding Effectiveness at 1-2 GHz of PES-Matrix Composites with Various Fillers

Filler	Vol%	Effectiveness (dB)	Ref.
Al flakes (15 × 15 × 0.5 mm)	20	26	9
Steel fibers (30–56 μm × 1.6 mm)	20	42	9
Carbon fibers (10 μm × 400 μm)	20	19	9
Ni particles (1–5 μm)	9.4	23	10
Ni fibers (20 μm × 1 mm)	19	5	This work
Ni fibers (2 μm × 2 mm)	7	58	This work
Carbon filaments (0.1 μm × > 100 μm)	7	32	This work
Ni filaments (0.4 μm × > 100 μm)	7	87	This work

Note: Sample thickness ~2.8 mm.

Table III shows that, at the same filler volume fraction, the shielding effectiveness was highest for the Ni filaments. At 7 vol%, the advantage of the Ni filaments compared to the other filaments was most significant. The shielding effectiveness attained by the Ni filaments at 7–19 vol% was comparable to those of copper and stainless steel, which were thicker than the composites. Even at 43 vol%, the 20 μm diam Ni fibers gave lower shielding effectiveness than the Ni filaments at 7 vol%. Even at 19 vol%, the 2 μm diam Ni fibers and the carbon filaments gave lower shielding effectiveness than the Ni filaments at 7 vol%. The high shielding effectiveness associated with the Ni filaments is attributed to the combination of small diameter (smaller than the Ni fibers) and low resistivity (lower than all except the 2 μm diam Ni fibers) of the Ni filaments.

The shielding effectiveness of the composite with 13 vol% carbon filaments is higher than that of the composite with ~ 45 vol% carbon filaments reported in Ref. 6. This difference is attributed to the difference in composite processing and to the difference in the carbon filaments used in this work and in Ref. 6.

Table IV compares the EMI shielding effectiveness at 1–2 GHz of PES-matrix composites with various fillers and with sample thickness 2.8 mm. The shielding effectiveness was all determined by the coaxial cable method. Even at a low filler content of 7 vol%, the nickel filaments provided much greater shielding effectiveness than all the other fillers of Table IV. In the case of the matrix being polyimidesiloxane (PISO) instead of PES, it has been shown that nickel particles of size 1–5 μm provide greater EMI shielding effectiveness at 1–2 GHz than silver particles of size 0.8–1.35 μm.[11] Together with Table IV, this means that the nickel filaments provide greater shielding effectiveness than silver particles.

CONCLUSION

A new electrically conducting filler for polymer-matrix composites was developed. It is nickel filaments of diam about 0.4 μm, length > 100 μm, volume electrical resistivity about 10^{-6} Ω.cm, and containing 94 vol% Ni and 6 vol% C. It was fabricated by electroplating carbon filaments of 0.1 μm diameter with nickel. For providing polymer-matrix composites of low electrical resistivity, the nickel filaments were slightly less effective than nickel fibers of diam 2 μm, much more effective than nickel fibers of diam 20 μm, and much more effective than carbon filaments of diameter 0.1 μm. For providing composites of high EMI shielding effectiveness, at least at 1–2 GHz, the nickel filaments were much more effective than all other fillers including nickel fibers, steel fibers, carbon fibers, carbon filaments, aluminum flakes, nickel particles, and silver particles, due to their combination of small diameter, large aspect ratio, and low resistivity. The shielding effectiveness provided by the Ni filaments at just 7 vol% was comparable to that of copper at 1–2 GHz.

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