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Improving the Electrical Conductivity of Composites Comprised of Short Conducting Fibers in a Nonconducting Matrix: The Addition of a Nonconducting Particulate Filler

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The addition of a second discontinuous filler (silica fume) that is essentially nonconducting to a composite with a comparably nonconducting matrix (cement) and a conducting discontinuous filler (carbon fibers) was found to increase the electrical conductivity of the composite when the conducting filler volume fraction was less than 3.2%. The maximum conducting filler volume fraction for the second filler to be effective was only 0.5% when the second filler was sand, which was much coarser than silica fume. The improved conductivity due to the presence of the second filler is due to the improved dispersion of the conducting filler. The silica fume addition did not affect the percolation threshold, but the sand addition increased the threshold.

Key words: Carbon fibers, conducting composite, electrical conductivity

INTRODUCTION

Nonconducting or essentially nonconducting materials (such as polymers and ceramics) can be rendered electrically conducting by the addition of an electrically conducting filler, which is usually discontinuous for the sake of convenience in composite fabrication by injection molding, slurry casting, or other techniques. These composites are widely used in electronic packaging as die attach adhesives, solder replacement, interconnections, and electromagnetic interference shields. The development of these composites has been centered around the choice of the conducting filler or fillers, with particular attention given to the composition(s), size(s), shape(s), and volume fraction(s) of the filler(s).[1–3] Much less attention has been given to the choice of the nonconducting matrix or the nonconducting filler that may coexist with the conducting filler. In the case of composite fabrication using a mixture of the matrix powder and the discontinuous conducting filler(s), attention has been given to the size of the matrix particles relative to that of the conducting filler, as a smaller relative size of the filler decreases the critical filler volume fraction needed for conduction via percolation;[4,5] in the subcase that the polymer is a thermoplast, attention has also been given to the effect of the viscosity of the polymer during composite fabrication on the electrical conductivity of the resulting composite.[6] In contrast, in this paper, attention is given to the effect of an essentially nonconducting coexisting filler on the electrical conductivity of the composite. Both the matrix and the additional filler (of unit size much smaller than that of the conducting filler) were essentially nonconducting, but the presence of the additional filler was found in this work to significantly increase the electrical conductivity of the composite. This effect is attributed to the improvement in the conducting filler dispersion due to the presence of the additional filler. Low conducting filler volume fractions are often used in practical composites because of

- the lower cost,
- in the case of a ductile-matrix composite, the higher ductility, and

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- in the case of a composite with poor filler-matrix adhesion and/or filler induced porosity, the higher strength.

Therefore, it is practically useful to increase the conductivity of the composite without increasing the conducting filler volume fraction. This work shows that the addition of a second filler of small unit size is effective for achieving this objective, even if the second filler is nonconducting like the matrix.

EXPERIMENTAL

The conducting filler used was carbon fibers of diameter 10 μm and nominal length 5 mm, as kindly provided by Ashland Petroleum Co. (Ashland, KY) as Carboflex. The volume electrical resistivity of these fibers is 3×10^{-3} Ω.cm, as shown in Table I together with other properties.

The matrix used was Portland cement, Type I, from Lafarge Corporation (Southfield, MI). The mean particle size was between 0.1 and 0.2 μm. The electrical resistivity of the cement paste (with a water/cement ratio of 0.32, corresponding to a slump of 150 mm) at seven days of curing was 1.49×10^5 Ω.cm. The second filler was silica fume (Elkem Materials, Inc., Pittsburgh, PA; EMS 960; average particle size 0.15 μm, particle size range 0.03–0.5 μm; 94% SiO_2) used in the amount of 0.15 of the cement weight.[7] The addition of silica fume to the cement paste (with the water/cement ratio increased to 0.35 in order to maintain the slump at 130 mm) slightly increased the resistivity to 2.32×10^5 Ω.cm when the fibers were absent. This implies that the second filler and the matrix were about the same in resistivity, i.e, they were both essentially nonconducting compared to the fibers. However, when the fibers were present, the addition of silica fume decreased the resistivity of the composite, as described below.

Table I. Properties of Carbon Fibers

Filament diameter	10 μm
Tensile strength	690 MPa
Tensile modulus	48 GPa
Elongation at break	1.4%
Electrical resistivity	3.0×10^{-3} Ω.cm
Specific gravity	1.6 g cm^{-3}
Carbon content	98 wt%

Because the dispersion of the fibers is greatly enhanced by the addition of a very small amount (0.4% of the weight of the cement) of methylcellulose (Dow Chemical Corp., Midland, MI; Methocel A15-LV), methylcellulose was used whenever the fibers were present, whether or not the silica fume was present.[7] The defoamer always used along with methylcellulose was Colloids 1010 (Colloids, Inc., Marietta, GA) in the amount of 0.13 vol.%. For the sake of assessing the effect of methylcellulose on the resistivity when the fibers were absent, cement pastes without fibers were made with and without methylcellulose. The resistivity was found to be 1.49×10^5 Ω.cm when methylcellulose was present and 1.50×10^5 Ω.cm when methylcellulose was absent. Thus, the methylcellulose had no effect on the resistivity when the fibers were absent, as expected since the proportion of methylcellulose used was very small.

In order to investigate the effect of the particle size of the second filler on the effectiveness of this filler in increasing the conductivity of the composite, sand (coarser than silica fume) was used in place of silica fume in some composites. The sand was natural sand (100% passing 2.36 mm sieve, 99.91% SiO_2). The addition of sand to the cement paste (without silica fume or fibers) was associated with an increase of the water/cement ratio from 0.32 to 0.475, a resulting increase of the slump from 150 to 180 mm, and essentially no change in the resistivity of the compos-

Table II. Mix Proportions of the Composites Studied

	Water/Cement Ratio		WR/Cement (%)		Slump (mm)	
Fiber vol.%	**With M**	**With M+SF**	**With M**	**With M+SF**	**With M**	**With M+SF**
Without Sand:						
0	0.32	0.35	0.5	3	150	130
0.53	0.32	0.35	1	3	130	125
1.06	0.32	0.35	3	3	140	120
2.12	0.33	0.35	3	3	130	110
3.18	0.36	0.37	3	3	110	100
4.24	0.40	0.40	3	3	77	77
With Sand:						
0	0.475	0.475	1	2	180	200
0.35	0.475	0.475	1	2	160	160
0.70	0.475	0.475	2	3	155	140
1.40	0.475	0.475	3	3	140	120
2.10	0.475	0.48	3	3	110	100
2.80	0.475	0.485	3	3	77	105
3.50	0.475	0.51	3	3	77	77
4.20	0.475	0.55	3	3	77	77

Note: M = methylcellulose; SF = silica fume; WR = water reducing agent.

ite. Thus, the resistivity of the sand was essentially the same as that of the cement paste matrix.

Both types of second filler were the same as the cement matrix in resistivity. Thus, the situation allowed study of the effect of the second filler addition on the dispersion of the first (conducting) filler via resistivity measurement.

The water/cement ratio and water-reducing-agent/cement ratio were chosen to increase with increasing fiber volume fraction in order to maintain the slump in the range from 77 to 200 mm. The water reducing agent was TAMOL SN powder (Rohm and Haas), which contained 93–96% sodium salt of a condensed naphthalenesulfonic acid. Table II gives the mix proportions for all the composites studied.

Mixing was conducted by using a Hobart mixer with a flat beater. Methylcellulose was dissolved in water and then the fibers and the defoamer were added and stirred by hand for about 2 min. Then this mixture, cement, water, and the water reducing agent (and sand and/or silica fume, if applicable) were mixed in the Hobart mixer for 5 min. After pouring the mix into oiled molds, a vibrator was used to decrease the amount of air bubbles.

Table III and Fig. 1 give the volume electrical resistivity of the various composites at seven days of curing. Six specimens of each type were measured by the four-probe method, using silver paint for electrical contacts. The DC current used ranged from 0.1 to 4 A. The specimen size was 140 × 40 × 40 mm. The distance between the voltage (inner) probes was 58 mm. Varying the specimen cross-sectional area had little effect on the resistivity, indicating that the resistivity had negligible contribution from surface conduction. The resistivity decreased much with increasing fiber volume fraction, whether a second filler was present or not. When sand was absent, the addition of silica fume decreased the resistivity at all carbon fiber volume fractions except the highest volume fraction of 4.24%; the decrease was most significant at the lowest fiber volume fraction of 0.53%. When sand was present, the addition of silica fume similarly decreased the resistivity, such that the decrease was most significant at fiber volume fractions below 1%. When silica fume was absent, the addition of sand decreased the resistivity only when the fiber volume fraction was below about 0.5%; at high fiber volume fractions, the addition of sand even increased the resistivity due to the porosity induced by the sand.[7] Thus, the addition of a second filler that was essentially nonconducting (as the matrix) decreased the resistivity of the composite only at low volume fractions of the conducting filler and the

Table III. Volume Electrical Resistivity of the Composites Studied

	Volume Electrical Resistivity (Ω.cm)	
Samples	**With M**	**With M+SF**
Without sand		
Plain	1.50×10^5	1.50×10^5
+M or +M+SF	1.49×10^5	2.32×10^5
+0.53 vol.% F	2.53×10^4	2.14×10^3
+ 1.06 vol.% F	26.1	13.9
+2.12 vol.% F	16.9	5.02
+3.18 vol.% F	7.82	3.88
+4.24 vol.% F	2.84	3.58
With sand		
Plain	1.46×10^5	1.46×10^5
+M or +M+SF	1.47×10^5	2.09×10^5
+0.24 vol.% F	8.33×10^4	3.19×10^3
+0.37 vol.% F	—	—
+0.49 vol.% F	8.51×10^3	680
+0.73 vol.% F	—	—
+0.98 vol.% F	1.62×10^3	25.6
+1.46 vol.% F	447	11.6
+1.50 vol.% F	—	—
+1.95 vol.% F	78.4	8.49
+2.19 vol.% F	—	—
+2.44 vol.% F	27.2	7.26
+2.92 vol.% F	—	—
+2.93 vol.% F	14.1	5.01
+3.65 vol% F	—	—
+4.38 vol.% F	—	—

Note: M = methylcellulose; SF = silica fume. Sand/cement = 1.5 for both M and M+SF.

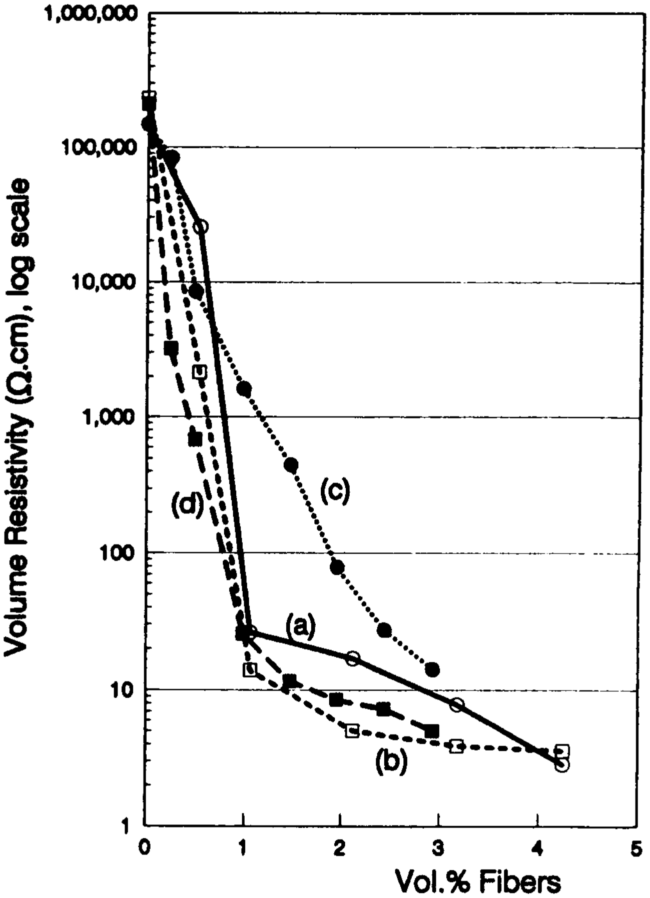

Fig. 1. Variation of the volume electrical resistivity with carbon fiber volume fraction: (a) without sand, with methylcellulose, without silica fume; (b) without sand, with methylcellulose, with silcia fume; (c) with sand, with methylcellulose, without silica fume; and (d) with sand, with methylcellulose, with silica fume.

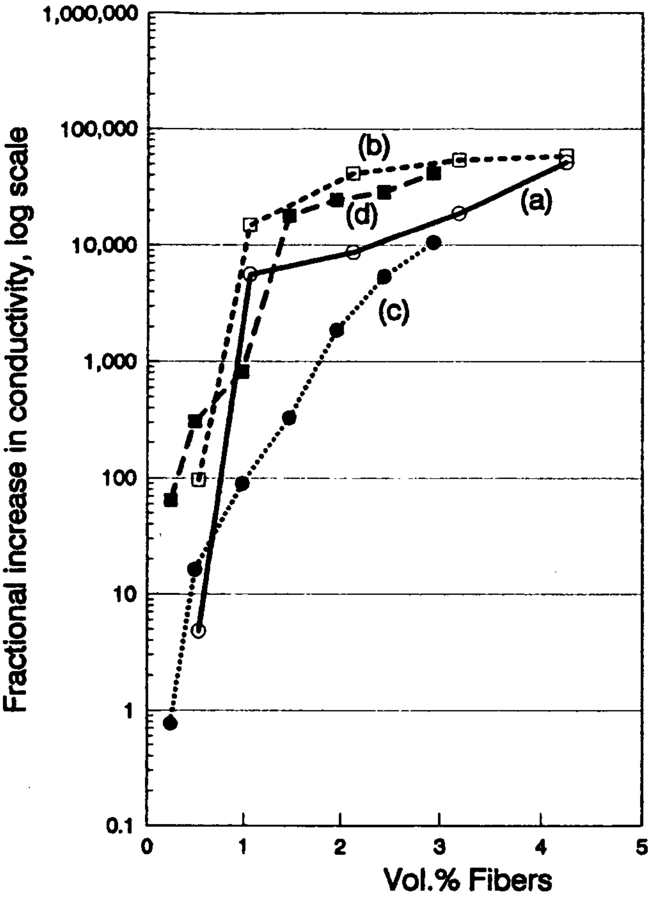

Fig. 2. Variation with the carbon fiber volume fraction of the fractional increase in volume electrical conductivity due to the carbon fibers alone: (a) without sand, with methylcellulose, without silica fume; (b) without sand, with methylcellulose, with silcia fume; (c) with sand, with methylcellulose, without silica fume; and (d) with sand, with methylcellulose, with silica fume.

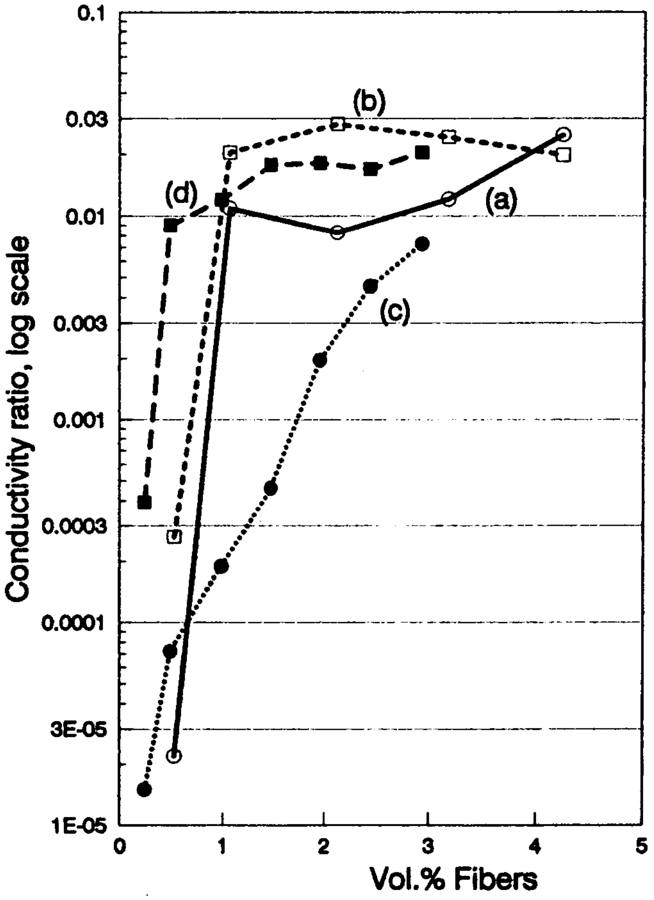

Fig. 3. Variation with the carbon fiber volume fraction of the ratio of the measured volume electrical conductivity to the calculated value obtained from the Rule of Mixtures by assuming that the fibers were continuous and unidirectional along the axis of conductivity measurement. The matrix conductivity used in the calculation was the measured conductivity for the case without fibers but containing the corresponding additives, i.e., either methylcellulose or methylcellulose plus silica fume: (a) without sand, with methylcellulose, without silica fume; (b) without sand, with methylcellulose, with silcia fume; (c) with sand, with methylcellulose, without silica fume; and (d) with sand, with methylcellulose, with silica fume.

maximum conducting filler volume fraction for the resistivity to decrease was larger when the particle size of the second filler was smaller. The resistivity decrease is attributed to the improved fiber (conducting filler) dispersion due to the presence of the second filler. Consistent with the improved fiber dispersion was the increased flexural toughness and strength due to the presence of the second filler, as found in a companion study.[7]

DISCUSSION

Figure 2 shows the fractional increase in conductivity (reciprocal of resistivity) due to the fibers alone. At a given fiber volume fraction, the fractional increase was higher when silica fume was present, whether sand was present or not. At fiber volume fractions above 1%, the use of silica fume but no sand gave the highest fractional increase, while the use of sand but no silica fume gave the lowest fractional increase. At fiber volume fractions below 1%, the use of both sand and silica fume gave the highest fractional increase, while the use of no sand nor silica fume gave the lowest fractional increase.

Figure 3 shows the measured conductivity as a fraction of the calculated value obtained from the Rule of Mixtures by assuming that the fibers were continuous and parallel along the axis of the conductivity measurement. This fraction provides an indication of the degree of fiber dispersion. At a given fiber volume fraction, it was higher when silica fume was present, whether sand was present or not. When sand was absent, the use of silica fume did not affect the percolation threshold volume fraction (1%), but increased the fibers' effectiveness. When sand was present, the use of silica fume greatly diminished the percolation threshold volume fraction. On the other hand, the addition of sand without silica fume greatly increased the threshold.

The use of both silica fume and sand resulted in an electrical resistivity of 3.19×10^3 Ω.cm at a carbon fiber volume fraction of just 0.24 vol.%. This is an outstandingly low resistivity value compared to those of polymer-matrix composites with discontinuous conducting fillers at similar volume fractions. For example, from companion work, a composite with polyether sulfone as the matrix and 3 mm long carbon fibers (of the same type as this work) in the amount of 5 vol.% as the conducting filler exhibited a resistivity of 6 × 10^3 Ω.cm;[8] a composite with polyimidesiloxane as the matrix and 0.8–1.35 μm size silver particles in the amount of 1.3 vol.% as the conducting filler exhibited a resistivity of 2.4 × 10^8 Ω.cm.[5] Though these polymers themselves had resistivities higher than cement, the high resistivities of the polymer-matrix composites is partly due to the poor dispersion of the conducting fillers in the polymers. We know this because, in companion work, the addition of latex (polystyrene butadiene) to the carbon fiber reinforced cement at a fixed fiber volume fraction led to an observed large fractional increase of the resistivity of the composite with increasing latex/cement ratio; in contrast, the addition of latex to cement without fibers led to a relatively small fractional increase of the resistivity with increasing latex/cement ratio.[9] The low resistivity of the carbon fiber filled cement makes this structural material a candidate electronic material. The room temperature processing of this composite adds to its attractiveness compared to glass-metal composites and many polymer-matrix composites, which require heating in their fabrication. The paste form of the carbon fiber filled cement during processing allows fabrication into thick films (coatings) as well as bulk forms.

The effectiveness of the second (nonconducting) filler addition increased with decreasing volume fraction of the first (conducting) filler and increased with decreasing unit size of the second filler. Its dependence on the volume fraction of the second filler had not been studied.

The two types of second filler used were silica fume and sand. In spite of the smaller proportion of the silica fume (silica fume/cement ratio of 0.15) compared to the sand (sand/cement ratio of 1.5), the silica fume was much more effective. This is attributed to the smaller particle size of the silica fume compared to sand. Due to the small diameter of the carbon fibers, a dispersion enhancer with a smaller particle size is more effective.

CONCLUSION

The addition of a second discontinuous filler that is essentially nonconducting to a composite with a comparably nonconducting matrix and a conducting discontinuous filler was found to increase the electrical conductivity of the composite at low volume fractions of the conducting filler, such that the highest conducting filler volume fraction for the second filler to be effective was higher when the unit size of the second filler was smaller. This effect is attributed to the improved dispersion of the conducting filler when the second filler was present. For the case of short carbon fibers in cement, the addition of silica fume as the second filler increased the conductivity of the composite at fiber volume fractions up to 3.2%, while the addition of sand (coarser than silica fume) as the second filler increased the conductivity of the composite at fiber volume fractions up to 0.5%. The silica fume was much smaller in particle size than the fiber diameter, whereas the sand was much larger in particle size than the fiber diameter. Thus, the unit size of the second filler is preferably smaller than that of the conducting filler in order for the second filler to be highly effective in improving the dispersion of the conducting filler. The second filler does not affect the percolation threshold if it is small in unit size, but increases the threshold if it is large in unit size. Even when the threshold is not affected, the second filler still improves the conducting filler's effectiveness. In the presence of a third nonconducting filler which is large in unit size, the presence of the second filler which is small in unit size decreases the threshold.

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