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Conductivities of Graphite Fiber Composites with Single-Walled Carbon Nanotube Layers

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The present study investigates the potential of air-spraying method in enhancement of electrical and thermal conductivities. Single-walled carbon nanotubes (SWCNTs) functionalized with carboxylic acid groups were air-sprayed on the surface of carbon fiber prepreg. The prepregs were stacked up and processed to carbon fiber laminates with SWCNTs layered between plies. From scanning electron microscopy, it was discovered that SWCNTs formed thin bands between carbon fiber layers and did not transport deep into the thickness direction due to low resin flow during cure. As it was hypothesized prior to experiments, the electrical conductivity was significantly enhanced by using a higher concentration of SWCNTs, while no amelioration for thermal conductivity was observed.

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1. Introduction

Carbon nanotubes (CNTs) have been used to improve electrical and thermal conductivities of polymers. Due to high aspect ratios and high electrical conductivity of CNTs, CNT/epoxy composites showed very low percolation threshold (< 0.1 wt%) for electrical conductivity.[1] In comparison with other polymer matrices that were near complete insulation, the electrical conductivity of CNT/polymer composites was increased to 10^{-3} S/cm by using less than 1.0 wt% CNTs.[1-5] The electrical conductivity of CNT/polymer composites relies on formation of electrical pathways which are promoted by fillers with a high aspect ratio such as CNTs.[2]

Theoretically, thermal conductivity of single-walled carbon nanotubes (SWCNTs) is predicted up to 6600 W/m K.[6] Although well accepted theories in the field predict a linear increase in thermal conductivity with nanotube loading for low concentrations of randomly arranged nanotubes within polymer matrix,[7] it is previously reported in the field that there is a distinct increase in thermal conductivity at the critical percolation threshold.[8] Most of prior studies reported in the field only describe a modest improvement in thermal conductivity for CNT/epoxy composites.[2,3,7] Biercuk et al, for instance, had reported that the addition of SWCNTs to an epoxy matrix had led to only a small increase even above the percolation concentration of filler (125% at 1wt% filler concentration).[9] It is evident that for thermal conductivity, interface resistance between CNTs and polymer matrix plays a critical role for phonon transport. Hence, large interface areas with CNTs do not lead to a significant increase in thermal conductivity as predicted by theories.[2,3,7]

Also, CNT-reinforced polymer matrices have been investigated as matrix systems of fiber composites. Compared with the advanced in-plane properties of carbon fiber composites which fully utilize high mechanical and electrical properties of carbon fibers, the out-of-plane properties of carbon fiber composites are desired to be enhanced further. The out-of-plane properties of carbon fiber composites are dominated by a matrix system. Also, the out-of-plane electrical and thermal conductivities can be enhanced by improving the properties of polymer matrices. As reported in a prior study, it was shown that electrical conductivity of carbon fiber composites was ameliorated by two-fold with electrophoretic deposition of 0.25-wt% SWNTs on carbon fibers.[10] Also, thermal conductivity in the fiber direction of carbon fiber/phenolic resin composite with 7-wt% MWCNTs was increased by approximately 55%.[11]

Most of effective CNT-incorporation methods for the out-of-plane property enhancement of fiber composites use aligned carbon nanotubes between fiber layers. However, this processing method clearly is costly and has limitation in mass production. In present study, SWCNTs were incorporated by a scalable air spray method and the composites were characterized for electrical and thermal conductivities.

2. Experiments and Results

2.1 Processing

SWCNTs were provided by Carbon Solutions (Riverside, California). They were synthesized by an electric arc discharge method. Then, they were purified and functionalized with carboxylic acid groups (-COOH). SWCNTs usually exist in the form of bundle and the nominal length and diameter of SWCNT bundles are 1~5 μm and 3~5 nm, respectively. IM7/977-2 unidirectional prepregs from Cytec Engineering Co. were used in this study. IM7 is an intermediate modulus carbon fiber and 977-2 is a toughened epoxy resin. The prepreg has 65% fiber volume fraction.

The process starts with the preparation of a dilute suspension. A bath-type sonicator (Branson, 75 W power) was used for SWCNT dispersion. Ethanol was chosen as the solvent for its non-toxic character and rather good dispersion result. 0.5 mg/ml SWNT/ethanol concentration was used for spray solution since it was the highest concentration that a reasonable dispersion of SWCNTs was achieved at. An airbrush was used to spray the dispersion of SWCNTs on the prepreg. SWCNTs were sprayed so that each side of the prepreg has the same amount of SWCNTs. Spraying is repeated until the pre-measured amount of solution is used up. During air spray, the prepreg is placed on a hot plate (70 ^{o}C) to promote faster solvent evaporation.

SWCNT-deposited prepreg layers were laid up and cured in an autoclave in accordance with the manufacturer's cure cycle. A silicone rubber dam tightly surrounded the lay-up of prepregs to prevent resin bleeding. A lay-up sequence used for this study was $[0/90]_S$, Fig. 1.

2.2 Electrical and thermal conductivity measurement

Two-point and four-point methods were used for measuring the out-of-plane and in-plane electrical conductivities, respectively. In case of the out-of-plane conductivity, both surfaces were silver-painted. Copper plate electrodes were pressed onto the silver-painted surfaces by using a vise. For the in-plane measurement the electrodes were copper plated to ensure good contact with the fibers.

In collaboration with Air Force Research Lab (Dayton, Ohio), thermal conductivity in the thickness direction (κ_z) of the composites was measured. After heat capacities (C_p) and thermal diffusivity (h) of the testing specimens were measured by Netzsch laser flash diffusivity system, LFA 457, thermal conductivity was calculated by $\kappa_z = \rho\ C_p\ h$ with ρ being density of the specimen. ASTM E1461-92, "Standard Test Method for Thermal Diffusivity of Solids by the Flash Method" was used as a reference to this instrument and procedure. In present study, three specimens were tested in each direction for electrical conductivity and in the out-of-plane direction for thermal conductivity.

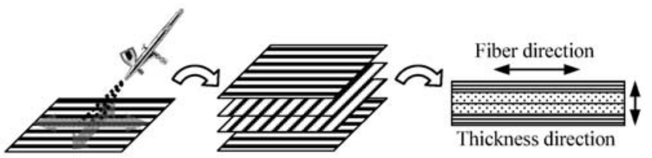

Fig. 1 Schematic of lay-up sequence of the SWCNT-sprayed prepregs

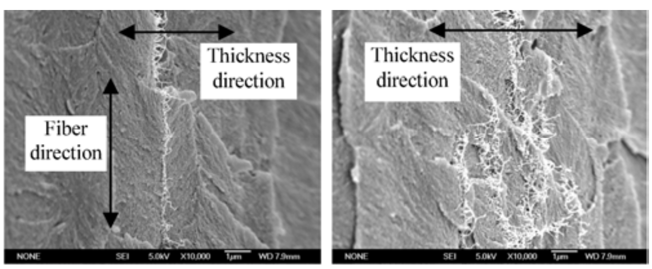

Fig. 2 SWCNTs on cross-sections of laminates with 1.0-wt% (left) and 2.0-wt% (right)

2.3 Microstructure

It was originally anticipated that the SWCNTs sprayed on the prepreg surface would penetrate into the individual plies during curing. However, there is no indication of SWCNTs dispersed throughout the thickness possibly due to the entanglement and little flow of resin through the thickness. Figure 2 shows the SWCNT distribution on cross sections of laminates with 1.0 wt% and 2.0 wt%, respectively. In comparison with 1.0-wt% SWCNTs, 2.0-wt% SWCNTs show more presence of SWCNTs in the thickness direction of the composite similar to what had been previously reported.[12]

2.4 Electrical conductivity

Table 1 shows large increases in the out-of-plane electrical conductivity resulting from the addition of SWCNTs. Although the SWCNTs sprayed on the surfaces of the prepreg plies were not distributed well in the thickness direction, they can still provide conductive path between adjacent carbon fiber plies and the out-of-plane electrical conductivity of carbon fiber composites, which is

Table 1 Electrical conductivity results

SWCNT wt%	Out-of-plane conductivity (S/m) (STDEV)	In-plane conductivity (S/m) (STDEV)
0	0.75 (0.085)	14682 (322)
1.0	1.04 (0.021)	14499 (1375)
2.0	1.83 (0.325)	14402 (817)

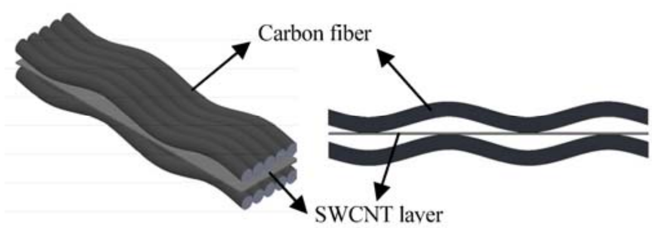

Fig. 3 Schematic of current path in fiber composites: Thin SWCNT layer can help formation of electrical current path between adjacent carbon fiber layers

Table 2 Thermal conductivity results

SWCNT wt%	C_p (J/g K)	Diffusivity (mm^2/s)	Conductivity (W/m K) (STDEV)
0	0.942	0.476	0.701 (0.016)
1.0	0.942	0.469	0.682 (0.001)
2.0	0.942	0.488	0.704 (0.017)

controlled by the number of contact points between carbon fiber plies as shown in Fig. 3.[13] Also, a high concentration of SWCNTs leads to their eventual distribution in the thickness direction as well, and hence results in a high conductivity, Fig. 2. The in-plane electrical conductivity of graphite fiber/epoxy composites is governed mostly by the electrical conductivity of the graphite fibers since the electrical conductivity of graphite fiber is 17 or 18 orders of magnitude higher than that of the epoxy matrix. Thus, not much improvement is expected from the addition of SWCNTs in agreement with the observed result in Table 1. Evidently, experimental result for both in-plane and out-of-plane properties agree well with previously reported finding.[12]

2.5 Thermal conductivity

Table 2 summarizes results of the out-of-plane thermal conductivity experiment. Unlike the out-of-plane electrical conductivity, a significant increase in the out-of-plane thermal conductivity of carbon fiber composites with SWCNTs was not observed. Two probable reasons for no increase in the out-of-plane thermal conductivity in this study are: 1. Difference in thermal conductivity between SWNT filler and epoxy matrix is much less than that in electrical conductivity (4 vs. 18 orders of magnitude). 2. Interfacial thermal resistance between SWCNTs and epoxy matrix is large to have any enhancement by addition of few contact points due to SWCNT layers between carbon fiber plies.[2]

3. Conclusions

SWCNTs were incorporated into carbon fiber composites by air spraying SWCNTs onto the surfaces of carbon fiber prepregs. SWCNTs in the composites did not show good distribution in the thickness direction (the out-of-plane direction), however, the out-of-plane electrical conductivity of the composites with SWCNTs increased despite the poor distribution. Thermal conductivity by using SWCNTs did not show much of improvement.

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