Novel Metal Nanowire/Polymer Nanocomposites for Electromagnetic Interference Shielding

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ABSTRACT

Well-dispersed metal nanowire/polymer nanocomposites with low electrical percolation threshold and improved surface electrical resistivities on the order of 1×10^{-2} - 1.0×10^{2} Ohm·cm have been prepared. Nanowire/polystyrene nanocomposites were prepared by hot-compression for electromagnetic interference shielding characterization, and the effect of Cu nanowire concentration (0.2 – 3.0 vol. %) on the EMI shielding effectiveness was studied. The EMI shielding effectiveness was correlated with the dc electrical conductivity of the nanocomposites. Cu-nanowire/polystyrene nanocomposites show outstanding performance compared to composites prepared using traditional fillers (eg. stainless steel, metal plated C-fibers) or nanofillers (eg. carbon nanofibers, nanotubes). Thin specimens of these low filler concentration nanocomposites are an alternative to thicker specimens of conventional filled composites used for EMI.

Keywords: nanowires, electrical conductivity, nanofiller, polymer nanocomposites, electromagnetic interference

1 INTRODUCTION

Metal nanowire/polymer nanocomposites are emerging materials with potential applications in electromagnetic interference shielding (EMI), electrostatic dissipation (ESD), conductive adhesives, sensors, catalysis, etc. The use of electrically conductive and high aspect-ratio metal nanoparticles enables significant changes in the electrical properties of nanocomposites at much lower concentrations than those required with conventional fillers (i.e. carbon black, carbon fibers, metal and stainless steel fibers). We have reported low electrical percolation thresholds (< 1.0 vol. %) of copper and silver nanowires (25 nm diameter with average aspect ratios of 50-75) in polymer nanocomposites.[1] The thresholds for electrical percolation of metal nanowires are comparable to those of carbon nanotube-based polymer nanocomposites.[2-6] However, the strong agglomeration of the nanoparticles still prevents harnessing their significant potential in performance enhancement of polymer nanocomposites. For instance, in previous studies, we observed nanowire-agglomerates with dimensions in the order of tens of micrometers, which prevents electrical percolation at lower concentrations.[1,7]

Electromagnetic interference (EMI) is the generation of undesired signals in an electrical or electronic device due to the interaction between external electromagnetic radiation and internal electrical signals. Electromagnetic interference (EMI) shielding refers to the ability of materials to prevent electromagnetic radiation to penetrate or be emitted from an electronic device and prevent malfunction of electronic equipment. The miniaturization of electronics introduces high requirements for EMI shielding and new materials with improved performance are required.[8] The EMI compounds presented in this work comprise novel electrically-conductive metal nanowires dispersed in non-conductive polymers. Metal nanowires with high aspect ratios form electrically conductive networks at low concentrations, which result in compounds with high EMI shielding effectiveness, improved processability and light weight.

Current technologies available for EMI shielding include:[9,10] (1) Conductive coatings such as metallic coatings, conductive paints, and coatings from vacuum metallizing. Although conductive coatings are the most conventional technology for EMI shielding, they have disadvantages such as high cost of manufacturing, multistep manufacturing, leakage of radiation in final products, and difficulties for recycling. (2) Polymer composites that comprise polymers filled with electrically conductive materials such as stainless steel fibers, Ni-plated C-fibers, Ag-coated glass fibers, Ni-coated graphite. These materials contain fibers with dimensions in the range of microns in diameter, which require high loadings to be effective and affect the processibility of the composite. Alternative and emerging technologies for EMI shielding materials include: carbon nanotube-filled polymers[11-15] and intrinsically conductive polymers (ICPs).[16-18] The low purity, high price of nanotubes, and the diverse range of electrical properties (semiconducting to conducting behavior) have prevented the commercial development of nanotube-based polymers. ICPs such as polyaniline possess limitations such as aging, poor mechanical properties and poor processability. Metals are the most preferred and promising materials for the development of high-performance EMI shielding compounds. Metal nanowire/polymer composites can be very competitive to current and alternate EMI shielding technologies.

2 EXPERIMENTAL

2.1 Materials and Methods

Synthesis of nanowires. Copper nanowires were prepared using porous alumina templates prepared in-house. The alumina templates are prepared by two-step anodization process of Al foil in 0.3 M sulfuric acid (H_2SO_4) solutions at 25 V. Al electrodes of 25×10×0.1 cm in size were utilized. Copper was electrodeposited in the pores of the alumina templates using ac electrodeposition and then released using 1.0 M Sodium hydroxide (NaOH) solutions. In the final step, CuNWs are transferred to methanol and dispersed using ultrasound (135 W average power, 38.5-40.5 KHz). Copper nanowires in methanolic suspensions were used to prepare polymer nanocomposites by a solution technique as explained below.

Preparation of polymer nanocomposites. Polymer solutions were prepared in methylene chloride (CH_2Cl_2). Polystyrene (Styron 666D, M_w 200,000 g/mol, MFI 7.5, Tg 100 ^oC) was kindly provided by Dow Chemical. CuNW-filled PS nanocomposites were prepared using a solution method. Measured amounts of 3.3 mg/ml CuNW/methanol solution were mixed with 20.0 mg/ml PS/CH_2Cl_2 solution to yield 2.9 vol.% Cu/PS nanocomposites (final concentration of nanowires was measured using thermogravimetric analysis). The mixture was prepared by mechanical mixing and sonication for 10 minutes in an ultrasound bath (135 W average power, 38.5-40.5 KHz). The sonicated mixture was then placed in an evaporation dish for 16 hours. After that, the evaporation dish was transferred to a vacuum oven for 2 hr at 40 ^oC to remove all remaining solvents from the composite powder. CuNW/PS nanocomposites containing different concentrations of Cu were prepared by dry-mixing with pristine PS. Dry nanocomposite powders were processed in a Carver compression molder to carry out EMI Shielding effectiveness, electrical resistivity and morphology characterization. Nanocomposites were annealed at 250 ^oC, for 30 min to produce films 210 μm in thickness, 2.5 cm in width and 4.2 cm in length.

Characterization of polymer nanocomposites. Thermogravimetric analysis (TGA) of CuNW/polymer nanocomposites were carried out using a Perkin Elmer Thermogravimetric Analyzer (Pyris1TGA) to determine the concentration of CuNWs in the composites produced by solution processing. The analysis was performed by heating 10 mg of the CuNW/PS composite from 25 ^oC to 650 ^oC in a nitrogen environment at a rate of 20 ^oC/min. The sample was maintained at 650 ^oC for 10 min before cooling down to room temperature. The morphology of nanocomposites was characterized using JEOL 6301F field emission SEM operated at 20 kV. Backscattered images of fractured samples at different magnifications were obtained. Samples were coated with chromium to facilitate SEM imaging.

2.2 Electrical conductivity and EMI shielding characterization

Electrical resistivity measurements were carried out according to ASTM 257-75 using a Loresta GP resistivity meter and ESP four point probe.

EMI SE in the X-band frequency was measured using the setup indicated in Figure 1. The setup consists of an HP 8757D scalar network analyzer, HP 8375A sweep oscillator, three HP 11664A detectors, coaxial to waveguide adapters and two HP X752C wave directional couplers. In Figure 1, A measures the reflected wave, B the transmitted wave, R the incident wave. The directional couple opening is 22.5 mm × 10 mm. The dynamic range of the setup is 50 dB. EMI SE is defined as the logarithm of the ratio of the incident power to the transmitted power (Equation 1).

$$\text{EMI SE} = 10\ \text{Log}_{10}\ (P_I/P_T)$$

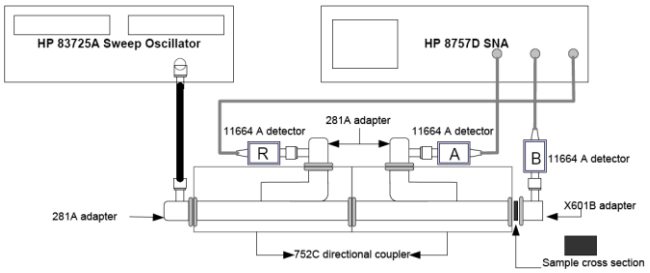

Figure 1: Schematic illustration of setup used for to measure the EMI shielding effectiveness of nanocomposites.

3. RESULTS AND DISCUSSION

Individual copper nanowires produced by our template-directed synthesis methods are 25 nm in diameter and several microns in length. The average length of individual nanowires is 1.29 μm.[19] Figure 2 shows an SEM image of a representative sample of Cu nanowires used for nanocomposite preparation. Bundles of several nanowires as well as individual nanowires can be observed. Results of surface composition (XPS), X-ray diffraction, thermogravimetric analysis and aspect ratio characterization of these nanowires have been published previously.[19,20] Other metal nanowires (eg. Ag, Fe, Ni, Au, Pt) can be produced in gram amounts using similar methods.[1] In our previous publications, Cu and Ag nanowires were used in a powder form and then dispersed in polymer solutions. Electrical percolation thresholds of < 1.0 vol. % were observed despite some degree of agglomeration.[1]

In this work we have developed a method of preparation of nanocomposites that enables us to produce well dispersed polymer nanocomposites. The method is based on the mixing of nanopartice suspensions and

polymer solutions in a miscible solvent mixture; the solvent ratio is then modified to decrease the solubility of the polymer leading to the precipitation of nanocomposites, which are easily separated from the solvent mixture. We believe that this miscible mixing and precipitation method can be applied to different polymer nanocomposite systems. Thus, suspensions (eg. Colloidal) of nanoparticles such as nanowires, nanorods, nanoclays, nanotubes can be all processed using a similar technique to produce well dispersed polymer nanocomposites. Efforts in our laboratories are being focused in this direction. These nanocomposites can then processed by polymer processing techniques to manufacture parts (eg. compression molding) or can be further processed by melt processing (eg. Masterbatching).

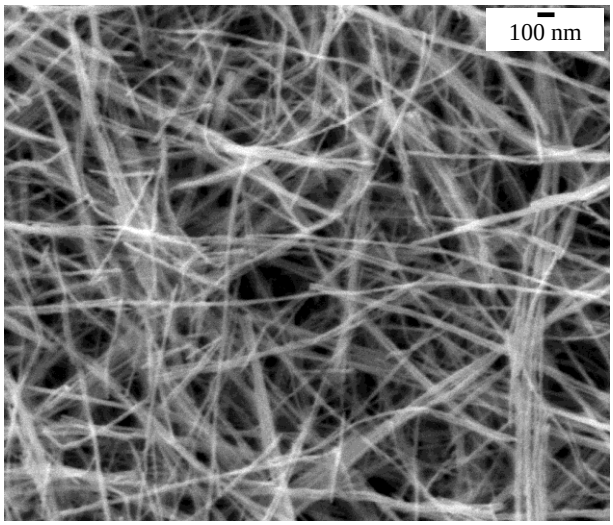

Figure 2: SEM image of CuNWs prepared in porous alumina templates. Bundles and individual NWs are observed. The high aspect ratio of the nanowires (25 nm diameter and microns in length) can be observed.

CuNW/PS nanocomposites have been prepared with different concentrations of metal. In this work, we present the results of polymer nanocomposites prepared by dilution of a concentrated sample using dry mixing technique. A sample containing 2.9 vol. % Cu was produced using our solution process. PS powder was mixed with 2.9%CuNW/PS in different ratios. It is worth mentioning that other efforts have been focused in using solution process and results will be published elsewhere. Figure 3 shows the electrical resistivity of nanocomposites prepared by dry-mixing method. The electrical resistivity of pristine PS was significantly modified (18 orders of magnitude) from 10^{16} Ohm.cm to 10^{-2} Ohm.cm with a concentration of 2.9 vol. % Cu. The percolation threshold of the composites (i.e. concentration at which first electrically conductive network forms) occurs between 0.1 and 0.25 vol.%Cu. By fitting of the data to a power law equation, we determine the percolation threshold is 0.24 vol. % Cu (Figure 3). Beyond the percolation threshold, the electrical resistivity of the composites decreased gradually.

Figure 4 shows the results of EMI SE characterization of CuNW/PS nanocomposites of 210 µm in thickness versus the metal concentration and frequency within the X-band. The EMI shielding of the composites increases with the concentration of metal nanowires. If a material shows EMI SE of 30 dB, it means that it is capable of shielding 99.9 % of incident radiation. PS nanocomposites containing 1.3 vol. % of nanowires showed an EMI SE of ~ 27 dB with a thickness of only 210 µm. Our results indicate that CuNW/PS nanocomposites show outstanding EMI performance compared to thicker materials (1.0 - 5.5 mm thickness) with higher filler concentrations reported in literature (Table 1).

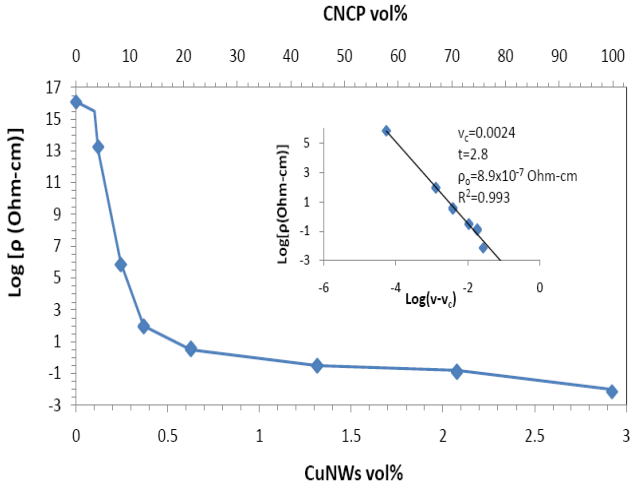

Figure 3: Electrical percolation of CuNW/PS nanocomposites prepared by dry-mixing process. (CNCP: conductive nanopowder)

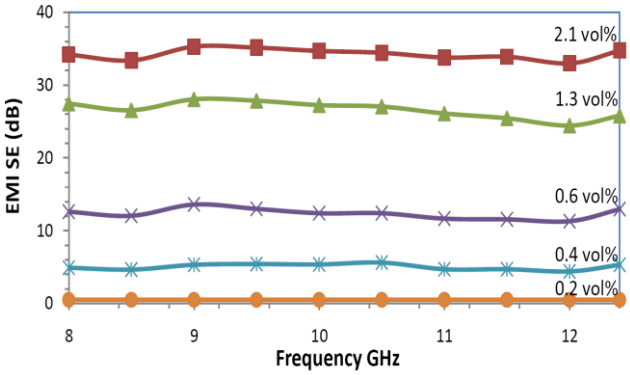

Figure 4: X-band EMI SE of CuNW/PS nanocomposites as a function of frequency and CuNW concentration. A sample containing 2.9 vol. %Cu exceeded the dynamic range of the setup (50dB).

Figure 5 shows the morphology of CuNW/PS nanocomposites containing 1.3 vol. % Cu at different magnification. Backscattered electrons enable us to determine the distribution of copper in the sample. Figure 4(a) shows a low magnification backscattered SEM image that shows the non-uniform distribution of the nanowires in the composite provided by dry-mixing of pristine PS and

CuNW/PS. The low magnification image shows individually dispersed CuNWs in the sample forming electrically conductive networks responsible for EMI SE.

Table 1: Average EMI shielding effectiveness (SE) in the range of frequency 8.2-12.4 GHz for polymer composites containing different fillers reported in literature.

Filler	Polymer	Filler Conc. (wt.%)	Thickness (mm)	Average EMI SE (dB)
SWCNT[14]	PU	20	2.0	17
SWCNT[13]	Epoxy	15	2.0	16
SWCNT[11]	EVA	15	2.5	22
MWCNT[15]	PS	7	1.0	19
VGCNF[21]	PS	20	1.0	20
CB[12]	EPDM-rubber	50	5.5	6 - 12

MWCNT: Multi-walled carbon nanotube, SWCNT: Single-walled carbon nanotube, PU: Polyurethane, EVA: Ethylene vinyl acetate, PS: Polystyrene, EPDM: Ethylene propylene diene monomer rubber, VGCNF: Vapor grown C-nanofiber, CB: Carbon black.

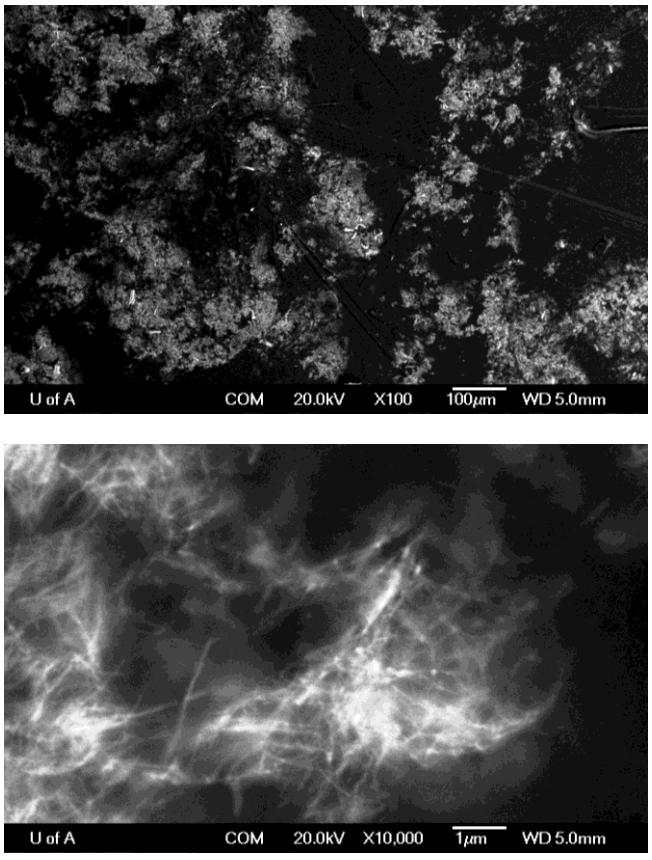

Figure 5: Backscattered SEM image of a CuNW/PS nanocomposite containing 1.3 vol. % Cu. (a) low magnification shows morphology obtained by dry-mixing method, and (b) high magnification image shows individually dispersed NWs in PS.

4. CONCLUSIONS

In this work, novel metal nanowire/polymer nanocomposites with high EMI Shielding effectiveness at low nanofiller concentration have been presented. These materials show great potential and better performance than nanotube-based polymer nanocomposites reported in literature.

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