Effect of Carbon Nanotube Content on Electromagnetic Shielding Performance of Carbon Nanotube-Cellulose Composites: Postprint

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Abstract

Using graphitized carbon nanotubes as conductive fillers and cellulose fibers as the matrix, carbon nanotube-cellulose fiber composites were prepared via vacuum filtration and characterized by scanning electron microscopy, four-point probe resistivity measurement, vector network analyzer, and other techniques. The influence of carbon nanotube content on the electromagnetic shielding performance of carbon nanotube-cellulose composites was investigated. The results demonstrate that the samples exhibit controllable shape and resistance, along with good flexibility, electrical conductivity, and electromagnetic shielding performance. Carbon nanotubes are adsorbed onto the fibers, forming an effective conductive network. As the carbon nanotube loading increases from 10% to 71%, the electrical conductivity and shielding performance of the carbon nanotube composite paper are significantly enhanced, with the electrical conductivity increasing from 9.92 S/m to 216.3 S/m, and the shielding effectiveness in the 175 MHz-1600 MHz frequency range improving from 15 dB to 45 dB.

Full Text

Preamble

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Effect of Carbon Nanotube Content on Electromagnetic Interference Shielding Performance of Carbon Nanotube-Cellulose Composite Materials

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Abstract

Carbon nanotube-cellulose fiber composite sheets were prepared by vacuum filtration using graphitized carbon nanotubes (CNTs) as conductive filler and cellulose fibers as matrix. The composites were characterized by scanning electron microscopy, four-point probe resistivity measurements, and vector network analysis to investigate the effect of CNT content on electromagnetic interference (EMI) shielding performance. The results demonstrate that the composite sheets exhibit controllable geometry and electrical resistance, along with excellent flexibility, electrical conductivity, and EMI shielding effectiveness. The CNTs adsorbed onto the cellulose fibers formed an effective conductive network. As the CNT loading increased from 10% to 71%, the electrical conductivity of the composite paper rose from 9.92 S/m to 216.3 S/m, while the shielding effectiveness in the 175 MHz–1600 MHz frequency range improved from 15 dB to 45 dB.

Keywords: composite materials, carbon nanotubes, electromagnetic interference shielding, flexible, cellulose fibers, conductive paper

Introduction

Carbon nanotubes (CNTs) possess exceptional physical, chemical, and mechanical properties that make them highly effective for enhancing the electromagnetic shielding and microwave absorption capabilities of composite materials. Due to their excellent electrical conductivity, CNTs create significant electromagnetic wave reflection at their surfaces. Additionally, their small size effect and large specific surface area contribute to superior EMI shielding performance.

Conductive composite paper represents a functional material with broad applications in anti-static packaging, electromagnetic shielding, new energy systems, electrochemical devices, planar heating elements, and sensing materials. CNT-cellulose fiber composites can be fabricated into conductive papers with promising electrical and shielding properties. Previous studies have reported notable results: Anderson et al. achieved conductivity of 3 S/m in single-walled CNT-cellulose paper; Seok et al. developed bacterial cellulose-CNT conductive paper with resistivity of 14 S/m at 9.6% CNT content; and Bunshi et al. demonstrated cellulose-CNT composite paper with shielding effectiveness of -40 dB at 35 GHz with 8.32 wt% CNT loading. These conductive papers retain the flexibility and adsorptive properties of cellulose while offering controllable geometry and thickness.

However, conventional "wet-laid" processing suffers from significant CNT loss (over 80%) during filtration, making precise content control difficult and reducing experimental reproducibility. This study employs vacuum filtration for CNT-cellulose composite formation to systematically investigate the relationship between CNT content and shielding performance while exploring the underlying shielding mechanisms.

Experimental Methods

Materials and Composite Preparation

Materials: Multi-walled carbon nanotubes, ethanol (C_2H_5OH, $ $99.7% purity), carboxymethyl cellulose, sodium dodecyl sulfate (SDS), distilled water, tributyl phosphate, and native softwood pulp.

CNT Graphitization: CNTs were placed in a graphite crucible and heated in a graphitization furnace under high-purity argon atmosphere. After vacuum extraction, the furnace was slowly heated to 2800°C, held for 30 minutes, then cooled to yield graphitized CNTs. The graphitized CNTs were ground into fine powder and ball-milled at 250 r/min for 2 hours to obtain uniform, high-purity material.

CNT Dispersion: SDS was dissolved in deionized water and sonicated for 2 hours to prepare a dispersing agent. Graphitized CNTs were wetted with ethanol, added to the dispersant, and subjected to high-shear dispersion at 10,080 r/min for 3 hours, followed by 2 hours of ultrasonication. Tributyl phosphate was added to eliminate bubbles, yielding a stable CNT dispersion.

Cellulose Suspension Preparation: Native softwood pulp fibers were initially beaten, then carboxymethyl cellulose was added. The mixture was high-shear dispersed at 4,000 r/min for 3 hours, settled for 6 hours, and the supernatant was removed to obtain a uniform cellulose fiber suspension.

Composite Formation: The CNT dispersion was added to the cellulose suspension and high-shear dispersed at 4,000 r/min for 3 hours to ensure uniform adsorption of CNTs onto cellulose fibers, forming a conductive cellulose suspension. Vacuum filtration removed water, depositing conductive cellulose fibers uniformly onto 14 mm diameter filter paper to create a dense, smooth fiber mat. After drying at 50°C for 12 hours and calendering, CNT-cellulose composite paper was obtained.

Using 1 g of native softwood pulp fiber as the matrix, CNTs were added at 0.11 g, 0.25 g, 0.5 g, 1 g, 1.5 g, 2 g, and 2.5 g to produce composite papers with CNT mass fractions of 10%, 20%, 33%, 50%, 60%, 66%, and 71% (samples 1#-7#) as detailed in Table 1.

Material Characterization

Morphology was examined using an FEI Quanta 200 environmental scanning electron microscope and a JEM-2100 high-resolution transmission electron microscope. EMI shielding effectiveness was measured with an AV3620 vector network analyzer. Electrical resistivity and conductivity were characterized using a St2258C multifunctional four-point probe tester. Phase composition was analyzed with an XRD DI SYSTEM multifunctional X-ray diffractometer.

Results and Discussion

2.1 CNT Microstructure Characterization

Figure 1 [Figure 1: see original paper] presents SEM and HRTEM images of the CNTs. The SEM image (Fig. 1a) shows straight, non-entangled CNTs with high aspect ratios and smooth surfaces, indicating good dispersibility and electrical performance. HRTEM reveals that before graphitization (Fig. 1b), the atomic arrangement is disordered with low crystallinity. After graphitization (Fig. 1c), the CNTs exhibit regular, dense atomic ordering with a perfect graphite structure.

The XRD patterns in Figure 2 [Figure 2: see original paper] show that the preferred orientation is the (002) crystal plane, with a diffraction peak near 26°. Following graphitization, this peak becomes stronger and sharper, shifting to higher angles. This confirms that graphitization effectively improved the crystalline structure, consistent with HRTEM observations. Perfect CNTs have resistivity one order of magnitude lower than defective CNTs, offering superior conductivity and mechanical properties.

2.2 Composite Morphology

The prepared CNT-cellulose paper is shown in Figure 3 [Figure 3: see original paper]. Cross-sectional SEM images in Figure 4 [Figure 4: see original paper] reveal that cellulose fibers form a three-dimensional network structure, creating numerous interfaces. At higher magnification (Fig. 4b), CNTs are observed to uniformly coat the cellulose fibers, leveraging the superior adsorption properties of cellulose to establish excellent conductivity.

Surface SEM images of samples 1#–7# are presented in Figure 5 [Figure 5: see original paper]. The fibrous network corresponds to cellulose fibers, while the fine powder-like structures are CNTs. As CNT content increases, the fibrous network becomes progressively filled with CNTs, expanding coverage and forming dense conductive networks between fibers. When CNT loading reaches 60%, the surface is completely covered, and further increases produce no significant morphological changes, indicating that the conductive network is fully established.

2.3 Physical Parameter Characterization

Table 2 summarizes the physical properties of composite papers with varying CNT loadings. Due to fixed forming area, increased mass leads to greater thickness. The dominant factor affecting resistance is CNT content. As CNT loading increases from 10% to 71% (samples 1#-7#), sheet resistance decreases progressively. Specifically, from 10% to 60% CNT content, surface resistivity drops from 360.2 Ω/sq to 4.4 Ω/sq, while conductivity rises from 9.92 S/m to 204.9 S/m. Above 60% CNT loading, resistance reduction becomes negligible, with conductivity stabilizing around 215 S/m. This occurs because the conductive network becomes fully formed at ~60% CNT content; additional CNTs no longer improve conductivity, consistent with SEM observations.

2.4 EMI Shielding Performance Analysis

Figure 6 [Figure 6: see original paper] shows the shielding effectiveness of samples across 175 MHz–1600 MHz. Shielding performance improves with increasing CNT content. At 10% CNT loading, effectiveness is approximately 14 dB, rising steadily to 45 dB at 60% CNT content, after which it saturates.

Figure 7 [Figure 7: see original paper] illustrates the relationship between CNT content and both conductivity and shielding effectiveness at 1500 MHz. The trends are consistent: as CNT loading increases from 10% to 60%, conductivity improves from 9.92 S/m to 204.9 S/m, while shielding effectiveness increases from 15 dB to 43 dB. Beyond 60% CNT content, both parameters plateau, with shielding effectiveness stabilizing at ~45 dB, demonstrating a direct correlation between conductivity and shielding performance.

Shielding effectiveness (SE) comprises three components: reflection loss (R), multiple reflection/transmission loss (B), and absorption loss (A). When electromagnetic waves encounter the shielding material, partial reflection occurs at the surface (R), while the transmitted portion undergoes multiple internal reflections (B) and absorption (A) by the material.

Due to their high conductivity and loss tangent, CNTs generate reflection loss through electronic and interface polarization. Their small size effect and large surface area facilitate multiple scattering. At sufficient CNT loading, the complete conductive network provides numerous scattering sites, causing continuous reflection and transmission that progressively attenuates electromagnetic waves. Additionally, the three-dimensional conductive network acts as electric dipoles under alternating electromagnetic fields, establishing eddy currents that convert to thermal losses and generate absorption. However, increasing CNT content cannot continuously enhance the loss tangent because rising conductivity reduces skin depth, limiting absorption loss. Consequently, shielding performance improves with CNT loading but eventually saturates.

Conclusions

This study demonstrates that CNT-cellulose composite paper forms an effective three-dimensional conductive network, exhibiting excellent electrical conductivity and EMI shielding performance. As CNT loading increases from 10% to 60%, composite conductivity rises from 9.92 S/m to 204.9 S/m, with shielding effectiveness improving from 15 dB to 43 dB. Beyond 60% CNT content, the conductive network is fully established, and both conductivity and shielding effectiveness stabilize. At 71% CNT loading, the composite achieves conductivity of 216.3 S/m and shielding effectiveness of approximately 45 dB. The material' s superior electromagnetic properties and network structure make it a promising candidate for flexible EMI shielding applications.

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Note: Figure translations are in progress. See original paper for figures.