三維碳奈米塗層阻燃和電磁波屏蔽應用

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摘要

這項研究證明了將多種碳奈米材料(奈米碳點、奈米碳管和石墨烯奈米片)嵌入亞矽酸鈉 + 石膏混合物中的 3D 碳塗層的功效。它具有優異的阻燃性和電磁波(EMI)屏蔽性能。應用於木材時，它可以承受 1050°C 的火焰噴射，抑制火焰蔓延，並最大限度地減少碳化。熱重分析顯示大量 800°C 碳殘留物，顯示透過其堅固的 3D 碳結構增強隔熱性能。這些塗層還顯著減少電磁場，由於包含特別添加的碳奈米材料，因此顯示出有效的 EMI 屏蔽。綜上所述，3D 碳複合材料未來可視為阻燃和電磁波吸收建築塗料最希望的材料選項之一。

關鍵字：三維碳材；阻燃性；電磁干擾屏蔽；建築塗料；碳奈米複合材料

Three-dimensional Carbon Nanocoatings for Fire Retardancy and Electromagnetic Wave Shielding Applications

Abstract

This study demonstrates the effectiveness of a three-dimensional carbon coating containing various carbon nanomaterials (carbon nanodots, carbon nanotubes, and graphene nanosheets) integrated into a sodium metasilicate + gypsum matrix. these 3D carbon coatings exhibit impressive fireproofing on wooden substrates, withstanding fire injections at temperatures up to 1050°C. They play a critical role in suppressing flame propagation and charring, reducing carbonization areas. Thermogravimetric analysis confirms that the 3D carbon coating produces significant char residue at 800°C, indicating enhanced thermal insulation due to its robust 3D carbon structure. Additionally, This improved performance in flame retardancy and EMI shielding is attributed to the strategic inclusion of carbon nanomaterials in the composite, which fine-tunes resistance and dielectric loss, allowing efficient electromagnetic absorption.

Keywords: Three-dimensional Carbon; Fire retardancy; Electromagnetic interference shielding; Construction coating; Carbon nanocomposites

1. Introduction

In contemporary times, wood has emerged as a predominant material of choice, particularly within the realm of construction. These compounds play a pivotal role in augmenting wood's resistance to fire, achieved through a multifaceted approach that involves mitigating the heat liberated during the initial phases of combustion, curbing the emission of smoke and volatile substances, and retarding the propagation of flames across the surface of the material [1].

In line with this, the present study employs an advanced homogenization technique to introduce an innovative category of environmentally benign, halogen-free, and minimally toxic 3D carbon composite-infused flame retardant and EMI shielding coating onto wooden substrates. The insights garnered from this work shed light on the potential of 3D carbon composites as promising contenders for multifunctional construction coatings, boasting exceptional attributes in terms of fire resistance and EMI shielding capabilities.

2. Experimental

2.1 Synthesis of carbon composites

The 0D (CNs), 1D (CNTs), and 2D (GNs) carbon nanomaterials employed in this study were synthesized as described in the proceeding section. First, the CN products were synthesized by thermal pyrolysis of citric acid and urea at 250 °C under microwave. The weight ratio of citric acid/urea was set at 2:1, and the microwave power was used at 720 W for 10 min. The CNT products were grown by catalytic chemical vapor deposition at 900 °C, where NiO and acetylene ($Ar:H_2:C_2H_2$ = 94:1:5 in v/v/v) served as catalyst and carbon precursor, respectively [2]. The GN samples were exfoliated from natural graphite powders by the modified Hummers' method, as previously described [3].

These carbon nanomaterials were homogeneously dispersed in ethanol solution through an ultrasonic bathing technique. Herein four combinations of carbon nanomaterials including 0D + 1D, 0D + 2D, 0D + 1D + 2D, and 1D + 2D, were prepared, designated to C-01, C-02, C-012, and C-12, respectively. The as-prepared carbon composites were then mixed via the equal weight ratio, and the liquid mixture (solvent: ethylene glycol) was placed into a high-performance homogenizer (IKA, Model T25, Germany). The homogenizing dispersion process was carried out at ambient temperature for 0.5 h, After that, the carbon composites were separated from filtering apparatus and then dried at 105 °C in an oven overnight.

2.2 Fireproof performance of carbon composite coatings

To examine the fire-retardant performance, the fireproof coating (including sodium metasilicate + gypsum) mixed with four types of carbon composites (i.e., C-01, C-02, C-012, and C-12 samples) were prepared to coat over wooden plate. Herein each fireproof coating consisted of 20 mL of sodium metasilicate, 0.408 g of gypsum, and 1.8 g of carbon composite. The wooden plates (i.e., three plywood) were carefully cut into a rectangle shape (ca. 3 × 4 cm^2) with the average thickness of ~0.8 cm. The fireproof slurries were then well dispersed and then stirred by a magnetic bar at 160 rpm overnight. The as-prepared slurries were pasted on the wooden substrates with a doctor blade and then dried at 60 °C in an oven overnight. The thickness of each carbon composite coating was well controlled within 0.3 mm. To facilitate a comparative analysis, we also prepared the base fireproof coating, consisting of sodium metasilicate and gypsum.

The flame retardancy of the construction coatings on wooden plates was evaluated by using a high-performance flamethrower. The distance between the coating and the top of flame was set at 2 cm, where the surface temperature on the wooden plates was kept at 1050 °C. In the fireproof test system, three thermocouples (K type) were adopted to measure the surface temperatures of the plates. The burnt areal ratio was calculated by dividing its plank area (i.e., 12 cm^2).

2.3 EMI shielding performance of carbon composite coatings

To assess the effectiveness of EMI shielding, uniform layers of the carbon composite were applied evenly onto wallpaper substrates. The thickness of each carbon composite coating was meticulously controlled to be within a range of 0.12 mm. In order to establish a baseline, an electrical appliance (utility frequency: 60 Hz) emitting an electric field of 350 V/m and a magnetic field of 43 × 10^{-6} T was activated, serving as a reference background. The methodology employed for measuring anti-electromagnetic wave performance involved the use of a specific electrical appliance, which was entirely enveloped by the carbon-coated wallpaper.

2.4 Materials characterization

The morphology and structure of carbon composites was characterized by high-resolution transmission electron microscope (HR-TEM, JEOL, JEM-2100). thermos-gravimetric analyzer (TGA, Perkin Elmer TA7) was adopted to inspect the thermal stability and calorimetric change of carbon coatings. The TGA analysis was conducted under the air atmosphere with a heating rate of 5 °C/min, ramping from 50°C to 800°C.

3. Results and discussion

TEM micrographs of the as-prepared CNs, CNTs, CNT/GN composite, and

CN/CNT/GN composite are thoughtfully presented in Figure 1. Upon close examination, it is evident that the CN sample assumes a spherical morphology with an average diameter measuring 3.5 nm. In contrast, the CNT sample exhibits a tubular structure characterized by a remarkably high aspect ratio exceeding 100. The CNT/GN composite reveals an intricate configuration where coiled CNTs are interwoven within the 2D graphene sheets, collectively forming a 3D carbon network.

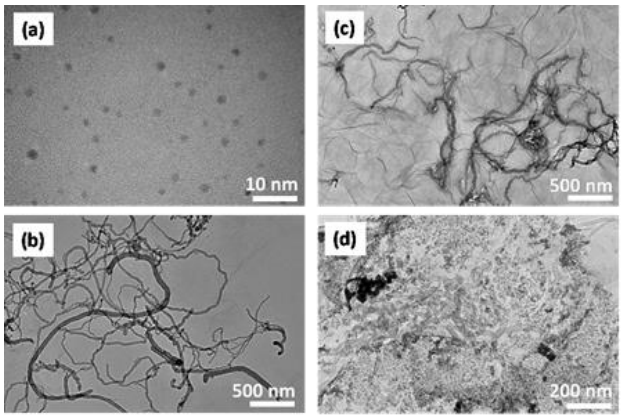

Figure 1. TEM micrographs of (a) CNs, (b) CNTs, (c) CNT + GN, and (d) CN + CNT+ GN composites.

To inspect the flame retardancy, as depicted in Figure 2. The TGA curves for all the samples consistently exhibited three distinct weight-loss stages: (i) dehydration (100–200 °C): this stage primarily involves the release of water vapor from the mixture of gypsum and sodium metasilicate, (ii) ignition and decomposition (200–350 °C): during this phase, the materials undergo ignition and subsequent decomposition, and (iii) pyrolysis and degradation (550–700 °C): this stage involves further pyrolysis and degradation of the materials. Across all the samples, it is noteworthy that the primary weight loss occurs during the dehydration stage (i), as water vapor is liberated from the gypsum + sodium metasilicate mixture. Importantly, the presence of CN + CNT + GN composites notably delays the onset of maximal decomposition. The order of maximal derivative weight can be outlined as C-012 (~175°C) > C-01 and C-02 (~120°C) > C-12 (~100°C).

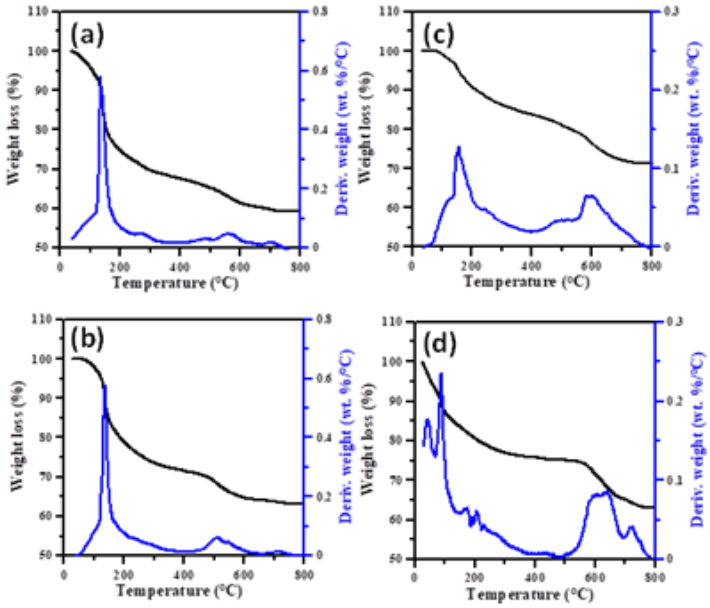

Figure 2. TGA curves and their derivatives weight as a function of temperature: (a) C-01, (b) C-02, (c) C-012, and (d) C-12 coating.

The EMI shielding performance also showed a similar sequence with the reduction in magnetic field, as depicted in Figure 3(a). Notably, this outcome underscores the significant enhancement in the EMI shielding capacity of the construction coating attributed to the incorporation of the 3D carbon composite coating.

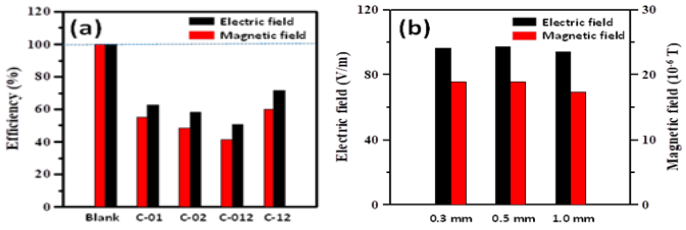

Figure 3. (a) The shielding efficiency of magnetic and electric field by different carbon coatings and (b) magnetic and electric field shielded by C-012 coating with different thicknesses.

The enhanced EMI shielding performance achieved through the utilization of the 3D carbon coating can be attributed to a synergistic effect that involves both reflection-loss phenomena within the 3D carbon composites. This effect can be categorized into two main types: the first type is a result of resonant behaviors arising from the presence of the CN + CNT + GN interface, On the flip side, functionalized CNs can be considered optical semiconductors capable of emitting highly intense blue light (~430 nm) when exposed to ultraviolet illumination (~360 nm). In general, achieving an optimal

resistance and dielectric loss is beneficial for enhancing the electromagnetic wave absorption capacity of a material [4]. Hence, the inclusion of CN fillers within CNTs (C-01), GNs (C-02), and CNT + GN (C-012) composites plays a pivotal role in tuning the resistance and dielectric loss, thereby facilitating electromagnetic absorption by carbon composites. This explains why C-01, C-02, and C-012 coatings outperform the C-12 coating, as illustrated in Figure 3(b) showcases the influence of layer thickness on the EMI shielding performance of the C-012 coating.

4. Conclusions

This work demonstrated the feasibility of 3D carbon coating, consisted of CNs (0D), CNTs (1D), GNs (2D nanomaterials), and sodium metasilicate + gypsum matrix, for flame retardancy and EMI shielding applications. The resulting 3D carbon coatings on wooden plates displayed superior fireproof performance based on the experimental results of fire injection at 1050°C. TGA analysis of the 3D carbon coating revealed that high mass of char residue can be obtained at 800 °C, indicating the enhanced thermal insulating performance through the robust design of 3D carbon architectures. The 3D carbon coatings showing a satisfactory EMI shielding effect. This improved EMI shielding performance could be attributed to the inclusion of CN fillers within CNT + GN composites plays a pivotal role in tuning the resistance and dielectric loss, thereby facilitating electromagnetic absorption by carbon composites. Accordingly, the carbonaceous composites could be engineered as not only fire-retardant fillers but also EMI absorbers through the robust design of 3D carbon coating.

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