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EFFECT OF LOW-CONCENTRATION GADOLINIUM DOPING ON THE THERMAL PROPERTIES OF MWCNT COMPOSITES

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In this study, the thermal properties of multiwalled carbon nanotubes doped with 5 wt% gadolinium were analyzed. Thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) and transmission electron microscopy were successfully employed for material characterization. Transformations in the TGA profiles of the synthesized carbon-based nanocomposite were investigated. The specific heat capacity value of that nanocomposite was attributed to the influence of Gd doping. For gadolinium-doped MWCNTs, a C_p value of 826.4 J/(kg·K) was observed at 630.4 K. These findings highlight the potential of rare-earth-doped carbon nanomaterials for use in thermal interface materials and other heat management applications in advanced electronics and energy systems.

Keywords: carbon nanotubes, gadolinium, TEM, TGA, specific heat capacity

1. Introduction

The development of next-generation materials and electronic devices is a major focus of contemporary research, with carbon nanomaterials doped with various metals receiving a particular attention. Among these, multiwalled carbon nanotubes (MWCNTs) have attracted a significant interest owing to their remarkable physicochemical properties, unique structure and nanoscale dimensions. These features make MWCNTs promising candidates for applications in low-dimensional phonon physics and thermal management. Importantly, the structural characteristics of MWCNTs directly influence their thermal behaviour, particularly their specific heat capacity and thermal conductivity. Despite extensive studies, empirical approaches are still often employed to predict the thermal behaviour of MWCNTs as comprehensive thermodynamic data remain limited. This lack of reliable information is especially critical since specific heat capacity is a key thermodynamic parameter for evaluating internal energy, free energy and chemical reactivity in MWCNT-based systems [1].

Functionalization of carbon nanotube surfaces is also a challenging task but provides new opportunities for tailoring the properties of nanomaterials [2]. In Ref. [3], the effect of functionalization on the properties of nanocomposite sheets made of high-density polyethylene and MWCNTs was investigated using oxidized MWCNTs and amine-functionalized MWCNTs. Another important factor is the synthesis method. In Ref. [4], MWCNTs were synthesized by both arc discharge and chemical vapour deposition methods for comparative investigation. Transmission electron microscopy (TEM) results demonstrated the advantages of the arc discharge method as the resulting nanotubes were well graphitized. Acid treatment can also introduce various functional groups, which in turn can alter the physicochemical properties of carbon nanotubes and enhance their potential in chemical sensing applications.

Depending on their structure and wall thickness, carbon nanotubes exhibit different thermal conductivities [5, 6]. The main factors affecting thermal conductivity include the MWCNTs density, the number of structural defects, the nanotube arrangement within arrays, the measurement direction relative to the tube alignment, temperature and MWCNTs type.

The diverse properties of carbon nanomaterials enable a wide range of applications. Carbon nanomaterial coatings, for instance, have shown promise in biomedical applications, particularly for implants used in implantology, cardiology and neurology [7]. The unique one-dimensional (1D) nanostructure of carbon nanotubes also facilitates their integration into macroscopic architectures such as 1D fibres, 2D films and 3D sponges or aerogels. Due to their excellent mechanical and electrical properties, MWCNTs and MWCNTs-based hybrid materials are ideal building blocks for flexible batteries [8]. Such batteries, which retain their function under various mechanical deformations, are attracting increasing interest for use in emerging portable and wearable electronic devices.

Optimizing the performance of these materials requires a thorough understanding of the decomposition mechanisms of MWCNTs over time, particularly under thermal stress [9, 10]. The isothermal oxidation of MWCNTs has been investigated by thermogravimetric analysis (TGA) over a temperature range of 573–823 K [9]. Oxidation was found to be controlled by both chemical and diffusion processes, depending on the temperature range. According to Ref. [11], thermogravimetry-differential thermogravimetry (TG–DTG) data indicate that the high-temperature treatment in an inert atmosphere effectively improves the thermal stability of CNTs under ambient conditions.

The doping of nanocomposites, including carbon-based materials, with various metals can significantly alter their optical, electronic, magnetic and thermal properties [12–15]. Carboxyl-functionalized MWCNTs serve as efficient nanoplatforms for immobilizing multiple molecules through covalent bonding, hydrogen bonding, or π–π stacking interactions [16–18].

In our previous works [19–26], we investigated the functionalization, doping, morphology, structural and photoelectrical characteristics of carbon nanotubes, as well as their potential applications. The aim of the present study is to perform an investigation of the thermogravimetric behaviour and specific heat capacity for MWCNTs doped with 5% gadolinium.

2. Experimental details

2.1. Sample preparation

The initial carbon nanotubes were synthesized via the arc discharge method and subsequently functionalized [23, 24] for further doping. In previous studies [19–22], Gd-doped MWCNTs were synthesized via a hydrothermal method. The same approach was used to synthesize MWCNTs doped with 5% Gd. All reagents for synthesis were obtained from Sigma-Aldrich, USA, and used without further purification.

Transmission electron microscopy imaging was made with a *Hitachi* (Japan) HT 7700 TEM microscope at room temperature. An accelerating voltage of 110–120 kV and magnifications of x60-100 were selected.

TGA was performed on a *NETZSCH* simultaneous thermal analyzer STA 409 PC/PGTGA in the air atmosphere.

2.2. TEM microscopy

The morphologies and structures of different carbon nanomaterials, such as pristine multiwalled carbon nanotubes, carboxyl-functionalized multiwalled carbon nanotubes (F-MWCNTs) and 5% Gd-doped MWCNTs (5%Gd-MWCNTs), were analyzed by transmission electron microscopy (TEM), focusing primarily on their size, shape and distribution. The findings are presented in Fig. 1, which includes a 100 nm scale bar (in yellow).

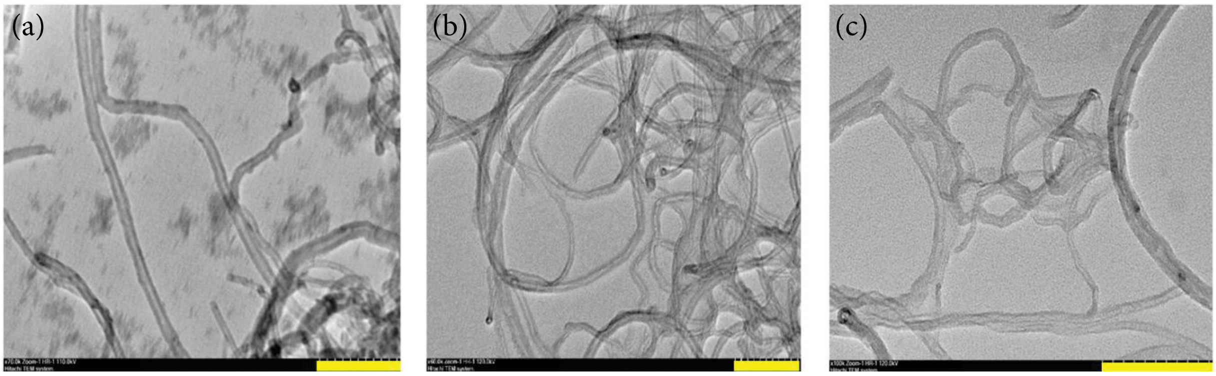

Fig. 1. TEM images of synthesized MWCNT (a), F-MWCNT (b) and MWCNT with 5% Gd dopant (c).

The structural features and transformations of F-MWCNTs are presented in Refs. [23–24]. The tubular morphology of all MWCNTs, along with surface textures ranging from smooth to mildly heterogeneous ones, was confirmed as reported in Refs. [8, 21–24]. Acid treatment notably enhanced the solubility of multiwalled carbon nanotubes by introducing carboxylic functional groups (–COOH) at their sidewalls and tips. Furthermore, the properties of gadolinium-doped MWCNTs were also investigated in Ref. [24].

2.3. TGA/DSC analysis

Thermogravimetric analysis is an effective technique for evaluating thermal stability and the degree of functionalization of carbon nanotube materials [28]. To investigate the thermal behaviour of carbon-based nanomaterial, the thermal degradation experiment was conducted in air. The TGA curve of 5% Gd-doped MWCNTs is presented in Fig. 2.

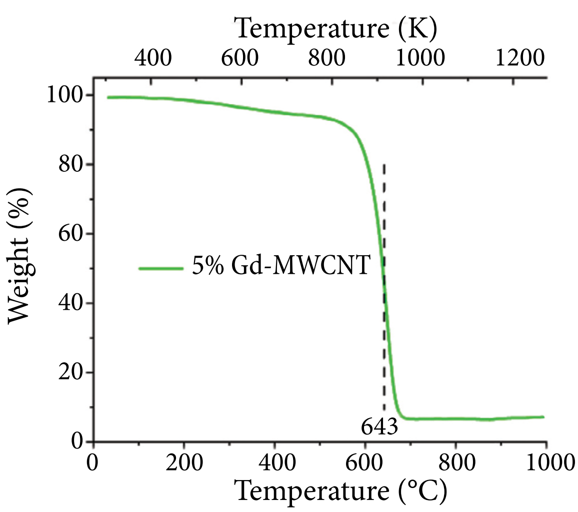

Fig. 2. TGA curve of 5% Gd-MWCNTs.

The TGA results from Fig. 2 represent the features of mass loss for the carbon nanocomposite with increasing temperature.

As we reported earlier in Refs. [21, 24], pristine MWCNTs were not thermally stable at temperatures above 500°C, exhibiting a single-step degradation process between 500 and 700°C with approximately 10% residual ash. In the case of the 5% Gd–MWCNT nanocomposite, a similar major degradation step was observed within the same temperature range. However, an additional weight-loss step appeared at a lower temperature, corresponding to a mass loss of about 7%. A comparable trend was also reported in Refs. [21, 24] for our carboxyl-functionalized MWCNTs, which was attributed to intermolecular reactions between carboxylic groups and the evaporation of physically adsorbed water molecules from the MWCNT structure. In the present study, this low-temperature mass loss can be associated with the presence of hydroxyl groups that reacted with gadolinium. The pronounced weight loss observed between 500 and 700°C indicates the complete decomposition of MWCNTs, leaving less than 10% residual ash, a value consistent with that of undoped MWCNT [21, 24]. For the 5% Gd–MWCNT nanocomposite, the DTG peak observed at 643°C is shifted toward higher temperatures compared to the carboxyl-functionalized MWCNTs (DTG peak ~625°C) and is close to the value obtained for pristine MWCNTs [24]. This shift may be attributed to the presence of Gd_2O_3 or Gd^{3+} ions, which can act as thermostabilizing agents, enhancing the oxidation resistance of the CNTs.

The specific heat capacities of carbon nanomaterials were determined from differential scanning calorimetry data through computational processing [24, 27–28]. The specific heat capacity C_p for the 5% Gd–MWCNT composite exhibits a non-monotonic temperature dependence which is characterized by two distinct maxima, each followed by a local minimum (Fig. 3). This behaviour suggests the occurrence of multiple, sequential thermally activated processes within the composite. The first, minor maximum and its subsequent minimum occur at lower temperatures and correlate with the initial, low-temperature mass loss observed in the TGA data (Fig. 2). These features are attributed to surface-related phenomena, such as the desorption or reorganization of functional groups. The second, sharp maximum coincides precisely with the onset of the primary decomposition step in the TGA curve, marking the initiation of the composite's major thermal degradation. This C_p peak corresponds to the energy absorption required for the initial breakdown of the nanocomposite structure. Following this peak, the C_p value decreases rapidly to a local minimum at 826.4 K. This minimum can be associated with the transition to the heat capacity of the residual material. As the MWCNT matrix combusts, the carbon scaffold is consumed, leaving a stable Gd_2O_3 residue, consistent with the 5–8% residual mass in the TGA. In this case, the sharp drop in C_p reflects the transition from a high-surface-area carbon-based nanocomposite to a non-nanostructured, low-mass metal oxide. The subsequent gradual increase in C_p represents the intrinsic heat capacity of the newly formed Gd_2O_3 residue at elevated temperatures.

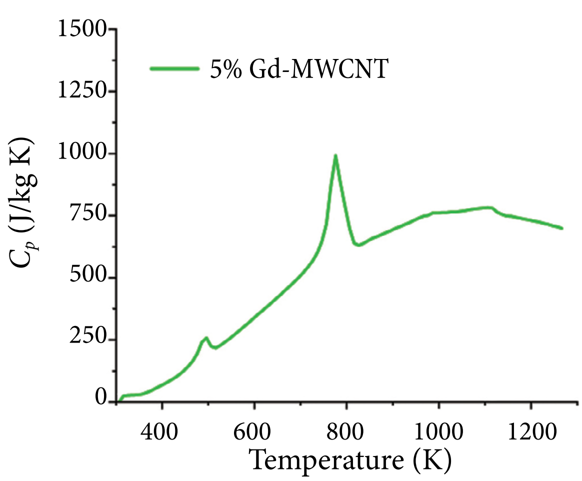

Fig. 3. Temperature dependences of specific heat capacity for 5% Gd-MWCNT.

Table 1 presents the minimum specific heat capacity values of CNT doped with 5% gadolinium.

Table 1. Data of specific heat capacity minimum for 5% Gd–MWCNT nanocomposite.

Sample	*T*, K	C_p, J/kg K
5% Gd–MWCNT	826.4	630.4

The low specific heat capacity of 5 wt% Gd-doped multi-walled carbon nanotubes (Table 1) can be attributed to several factors:

– Low Gd doping can introduce isolated defects that modify the phonon density of states, thereby suppressing low-frequency acoustic phonons and reducing C_p. Defect-induced phonon scattering broadens the vibrational modes, particularly at low doping levels where Gd clustering is negligible.

– The 4f electrons of Gd can enhance electron–phonon coupling, leading to damping of phonon modes at elevated temperatures and limiting the increase in C_p at low doping compared to higher concentrations.

– Paramagnetic Gd may promote spin–phonon interactions above its Curie temperature, diverting energy into magnetic excitations and further lowering C_p. Local lattice distortions arising from diluted Gd moments can also contribute to phonon damping.

– At high temperatures, isolated Gd atoms exhibit minimal Schottky contributions; however, short-range magnetic correlations or Kondo-like effects can suppress C_p by channelling energy away from lattice vibrations.

3. Conclusions

Carbon nanocomposite materials, such as MWCNTs doped with 5% gadolinium, were produced. Accordingly, the microstructures of the samples were investigated using electron microscopy methods. The morphology of the nanotubes was characterized by smooth and homogeneous surfaces. The chemical transformations and thermal properties of the synthesized samples were confirmed by TGA measurements, which showed that carbon nanotubes are not thermally stable at temperatures above 500°C and undergo two-step degradation. The specific heat capacity of MWCNTs doped with

5% gadolinium was determined to be 630.4 J/kg·K at 826.4 K, and the potential mechanism for this low value was also discussed.

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NEDIDELĖS KONCENTRACIJOS GADOLINIO PRIEMAIŠŲ ĮTAKA DAUGIASIENIŲ ANGLIES NANOVAMZDELIŲ KOMPOZITŲ TERMINĖMS SAVYBĖMS

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