

Research Article

Effect of Carbon Nanotubes on the Microstructure and Thermal Property of Phenolic/Graphite Composite

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Received 10 May 2018; Revised 19 July 2018; Accepted 26 July 2018; Published 2 September 2018

Academic Editor: Maurizio Volpe

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In this work, composites based on phenolic resin (P), graphite powder (G), carbon fibers (CFs), and carbon nanotubes (CNTs) were prepared by using hot compression molding. The effect of CNTs on the microstructure and thermal property of these composites was investigated. FESEM analysis indicated that the surface structure of phenolic/graphite composites became more dense and homogeneous with the presence of CNTs. The carbonization behavior of composites was characterized by using thermal gravimetric analyses (TGAs). TGA data showed that the presence of CNTs in phenolic/graphite composites enhanced their thermal stability, by increasing the temperature of maximum weight loss rate (T_m) during pyrolysis and decreasing the weight loss after pyrolysis. In addition, incorporation of CNTs into phenolic/graphite composites reduced significantly their open porosity.

1. Introduction

Phenolic resins are the oldest synthetic plastics commercially applied in a broad range of applications such as paints, adhesives, and composites. There are two types of phenolic resin, the resole type (self-curing, one-step resin) and the novolac type (two-stage resin). It was reported that phenolic resin can provide the intermolecular hydrogen bonding, which acts as the domain driving force that interacts with hydroxyl, carbonyl, amide, ester, and other hydrogen-bonding functional groups [1]. Therefore, phenolic resins have been widely used as a matrix for composites.

Recently, carbon nanotubes (CNTs) have been used as reinforcements in polymer matrices to improve their mechanical and electrical properties [2–4]. Although some experimental data indicated the strength enhancement by the presence of CNTs in the polymer matrix [1, 5, 6], no strength enhancement or limited enhancement was observed in other works [7–9]. There are two important factors that might limit the applications of this reinforcement. The first one is the homogeneous dispersion of CNTs in the polymer matrix. The

second one is the effective translation of CNT strengths (interaction between the CNTs and polymer matrix). For the effective translation of strength, the strong CNT-matrix bonds are required; thus, surface properties of CNTs became very important. Various methods have been used to enhance the dispersion of CNTs, such as the covalent modification, using surfactants, and polymers wrapping [10].

It was reported that carbon-carbon (C-C) composites combined both high strength and high stiffness with high thermal resistance ($\sim 2000^\circ\text{C}$) and lightweight. The microconstituents of these C-C composites include carbon fibers, pyrolytic carbon matrix, and pores [11]. Adding the CNT component into C-C composites is the new approach for improving the property of C-C composites. CNTs could have played important roles in C-C composites, such as an interlock with higher heat friction [12], an antioxidizing agent and a thermal protective barrier [13], and a heat dissipator throughout the phenolic matrix [14]. Saeed et al. [15] successfully fabricated the carbon fiber-reinforced CNT-phenolic nanocomposites by melt mixing. They reported that the addition of CNTs improved thermal stability and ablation

properties of the carbon fiber-reinforced composites. Adding 0.05% CNTs into their composites increased the char yield from 47% to 49% (at 900°C). The authors signaled that the CNT-phenolic interface could have an important role in thermal resistance of the composite. Saghar et al. [16] recently also reported that addition of 0.1 wt.% CNTs into carbon fiber-phenolic matrix composites reduced their ablation from 0.042 mm/s to 0.038 mm/s.

On the contrary, Newling and Walker [17] reported that addition of graphite powder decreased the shrinkage tendency of the phenolic matrix during carbonization and also enhanced the carbon yield. Fitzer et al. [18] reported that the strength translation of the carbon fiber-reinforced composite increased from 40% to 60% by adding 50% graphite powders into the resin matrix prior to its carbonization. Besides, during the pyrolysis (carbonization), the resin matrix was converted to carbon, thus increasing the porosity and decreasing the density. The typical densification process was thereafter carried out by using either resin impregnation or chemical vapor infiltration (CVI) and then by the high-temperature heat treatment (graphitization). It was reported in the literature that the main factors influencing the physical properties of the C-C composite are (i) its components (composition, property, and interaction), (ii) carbonization, (iii) deposition of pyrocarbon, and (iv) graphitization, with the composition of constituent parts being the most important factor [19–22].

In this work, CNTs were added into the phenolic resin/graphite composite fabricated by the hot compression molding. The effects of CNTs on the morphology and properties of phenolic/graphite composites were investigated.

2. Experimental

2.1. Materials. The phenolic resin powder was synthesized by the reaction of phenol and formalin. The specific gravity of the as-synthesized powder was 0.337 and its melting point was 84°C. To provide the mechanical strength of composites, the carbon fibers (T-650/35 PAN-based plain weave) of diameter $\sim 7 \mu\text{m}$ were used in this study. The density of carbon fibers (CF) is 1.77 g/cm^3 , and their thermal conductivity is $\sim 14 \text{ W/mK}$. Before using for fabrication of composites, these fibers were thermally treated in air (at 400°C for 2 hours).

The custom-made carbon nanotubes (CNTs) were produced by the CVD method as supplied by the Institute for Materials Science (Vietnam). The as-prepared CNTs have the outer diameter of 10–30 nm, inner diameter of 5–15 nm, and length of 5–30 μm . Thermal conductivity and density of these CNTs are $\sim 1950 \text{ W/mK}$ and $\sim 1.6 \text{ cm}^3$, respectively. Before using for fabrication of composites, carboxylic groups have been grafted on the surface of these CNTs under chemical treatment using the $\text{H}_2\text{SO}_4/\text{HNO}_3$ mixture [23, 24].

Flake-shaped graphite powder (particle size of 30–50 μm and density of $\sim 2.2 \text{ g/cm}^3$) was purchased from Sigma-Aldrich.

2.2. Fabrication of Composite. To fabricate the phenolic sample and its composites, a mixture (P solution) with the phenolic resin : hexamethylenetetramine : ethanol ratio by

weight of 50:6:44 was prepared by using a mechanical mixer.

Graphite powder (G), chopped carbon fiber (CF), and CNTs were then added into the P solution to form the composites. For each composite sample, the ratio of P : G : CF : CNT by weight was 1 : 3 : 0.2 : 0.05.

These as-prepared 6 samples, such as P, G/P, G-CF/P, CNT/P, CNT-CF/P, and CNT-CF-G/P, were then heated up to 80°C for 3 hours (for removing the residual solvents) and subsequently hot-pressed. The hot-pressed process took place at 120°C (for 30 minutes) and then at 165°C (for 30 minutes) under a pressure of 150 kg/cm^2 . After cooling to room temperature, all samples have been machined in the dimensions of 10 mm \times 10 mm \times 10 mm.

Table 1 shows the mix design for the 6 types of samples: P, G/P, G-CF/P, CNT/P, CNT-CF/P, and CNT-CF-G/P composites.

2.3. Composite Characterization. The morphological investigation of the prepared composites was carried out by using the field-emission scanning electron microscope (FESEM S4800, Hitachi, Japan). The carbonization behavior of composites was characterized by using thermal gravimetric analyses (TGAs). TGA was conducted by using the STA 409PC Netzsch equipment. These composites were heated from room temperature to 1000°C at a rate of $20^\circ\text{C}\cdot\text{min}^{-1}$ under nitrogen atmosphere with a flow rate of $50 \text{ cm}^3\cdot\text{min}^{-1}$.

The density of composites was determined by dividing their mass by the volume of cubic sample. The open porosity of composites was measured by using the Archimedes method with water as the immersing agent (water impregnation method [11]).

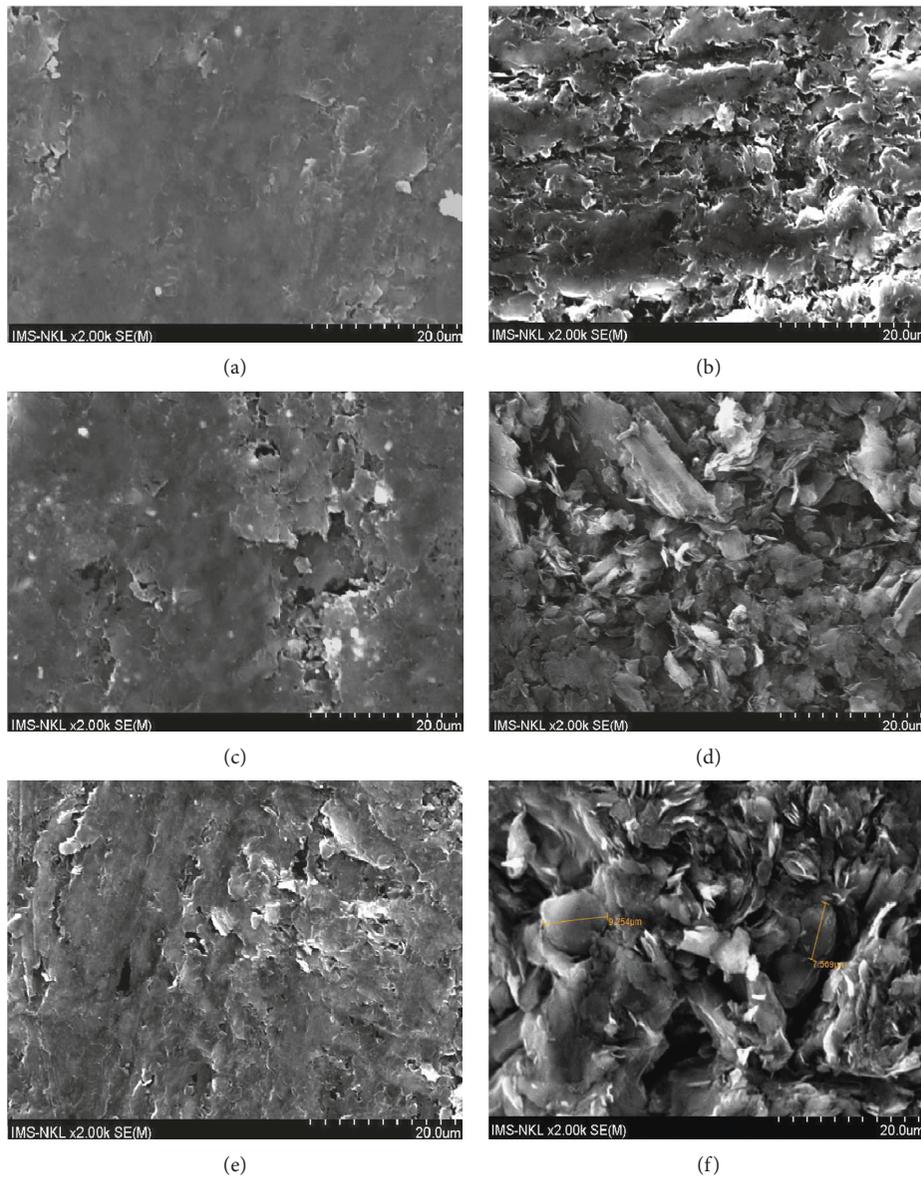
3. Results and Discussion

3.1. Microstructure Study. For the comparative studies, we divide these 6 samples into two groups, such as P, G/P, and G-CF/P samples and CNT/P, CNT-CF/P, and CNT-CF-G/P samples.

Figure 1 presents the SEM images of P, G/P, and G-CF/P samples before and after carbonization. As can be seen in Figure 1(a), before pyrolysis, the SEM images indicate the relatively homogeneous microstructure without the appearance of large pores on the surface of resin P. However, the surface of these pyrolyzed composites was porous and heterogeneous (Figure 1(b)). These results indicated that P resin was strongly decomposed by pyrolysis, especially in its external surface. It should be noted that the deep pores appearing inside the microstructure indicated poor and fast pyrolysis behavior of G/P and G-CF/P composites (Figures 1(d) and 1(f)). In addition, after pyrolysis, the presence of G in the P matrix increased its porosity (Figures 1(b) and 1(d)). Higher porosity was also observed for G-CF/P composites (Figure 1(e)). This high porosity could be explained by the low P resin content in these composites that made the graphite powder incompletely wet, leading to the weak binding and increasing porosity. In carbonization, carbon from phenolic resins contained high content of closed pores [25]. However, to obtain the high-strength C-C

TABLE 1: Mix design of P, G/P, G-CF/P, CNT/P, CNT-CF/P, and CNT-CF-G/P composites.

Composite samples	Phenolic resin	Graphite powder	Carbon fiber	Carbon nanotubes
P	x			
G/P	x	x		
G-CF/P	x	x	x	
CNT/P	x			x
CNT-CF/P	x		x	x
CNT-CF-G/P	x	x	x	x

FIGURE 1: SEM images of composites before (left) and after (right) pyrolysis ($\times 2,000$): P (a, b), G/P (c, d), and G-CF/P (e, f).

composites, resin content should be limited below 15 wt.%, due to the pyrolysis shrinkage of phenolic resins [6, 7]. Therefore, it was not recommended to increase the resin content for reducing the porosity of composites. Incorporation of nanofillers (CNTs) into the P matrix is expected to reduce its porosity.

Figures 2 and 3 present the SEM images at high magnifications of CNTs (before and after acid treatment) and

CNT/P nanocomposites (before and after pyrolysis), respectively. Regarding CNT component, before acid treatment, CNT bundles and aggregates have been observed in Figures 2(a) and 2(c). To fabricate the CNT/resin composite, these bundles and aggregates could reduce highly the mechanical property of nanocomposites. As can be seen in Figures 2(b) and 2(d), by surface modification, these

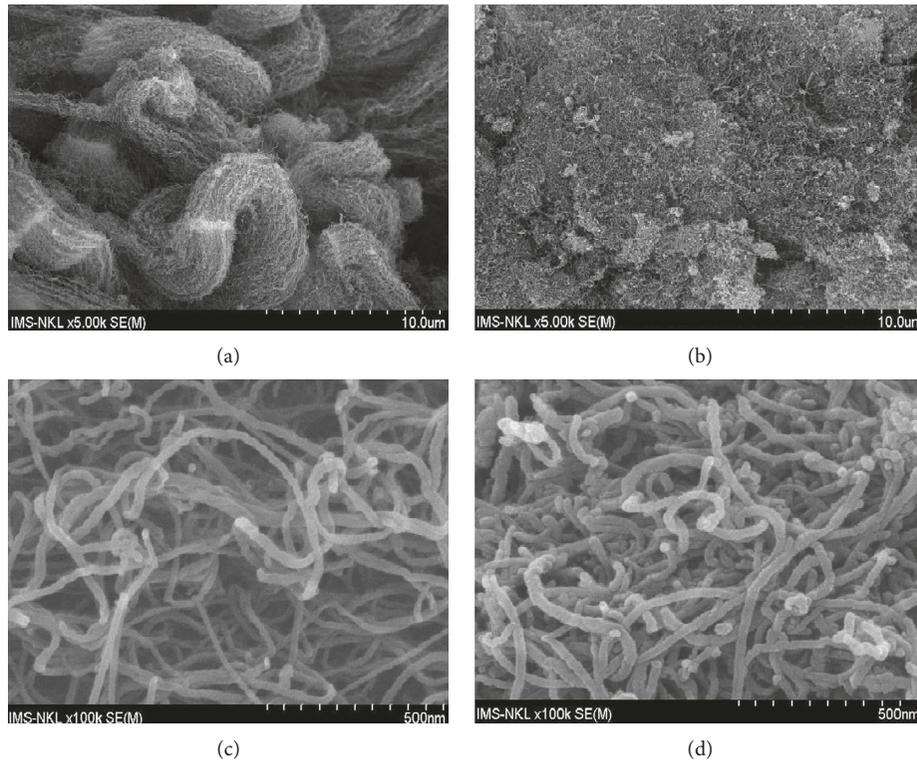


FIGURE 2: SEM images at low ($\times 5,000$) and high ($\times 100,000$) magnifications of CNTs: before (left) and after (right) acidic modification.

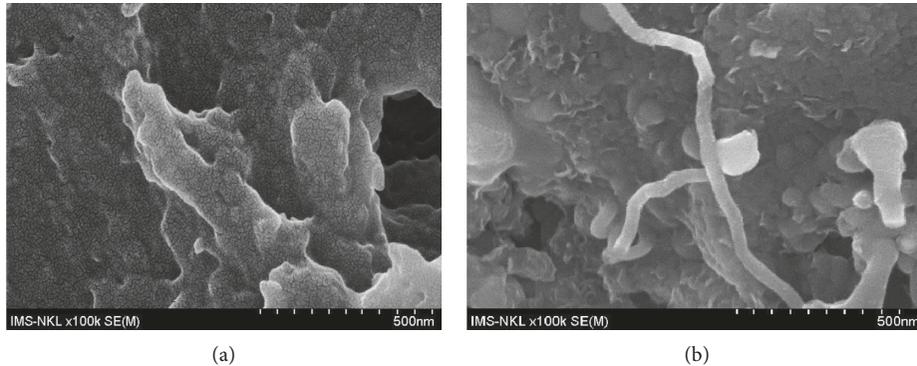


FIGURE 3: SEM images at high magnifications ($\times 100,000$) of CNT/P nanocomposites: before (a) and after (b) pyrolysis.

aggregations of CNTs were significantly reduced, leading to the homogeneous dispersion of CNTs in the resin matrix. The SEM images of CNT/P nanocomposite samples (Figure 3) indicated that the surface of CNTs was coated by thick coatings. The outer diameter of coated CNTs (after pyrolysis) was ~ 50 nm (Figure 3(b)), which was much larger than that of untreated CNTs (e.g., ~ 30 nm). These coatings were still strongly adherent on the surface of CNTs after pyrolysis, indicating the strong interaction between modified CNTs and resin matrices (via the carboxylic groups on the surface of CNTs [24]). Thus, acid modification of CNTs might enhance the load transfer at the CNT-resin interface.

Regarding 3 other composites of CNT/P, CNT-CF/P, and CNT-CF-G/P (Figure 4), the effect of CNT on the

microstructure of these composites was very impressive, especially for the CNT-CF-G/P sample. As shown in Figures 4(a) and 4(b), for both before and after pyrolysis, the incorporation of CNT into the P matrix reduced significantly its porosity and made its surface more compact. However, the small pores were still observed substantially after pyrolysis, at high magnification for CNT/P composites (Figure 3(b)). To improve the microstructure of CNT/P composites, other fillers, such as G and CF, were used simultaneously with CNTs for the P matrix. As can be seen in Figures 4(c)–4(f), the addition of both G and CF into CNT/P improved significantly its surface morphology, not only before pyrolysis but also after pyrolysis. This finding indicated the slow pyrolysis behavior of G-CF-CNT/P, which did not decompose the composite structure.

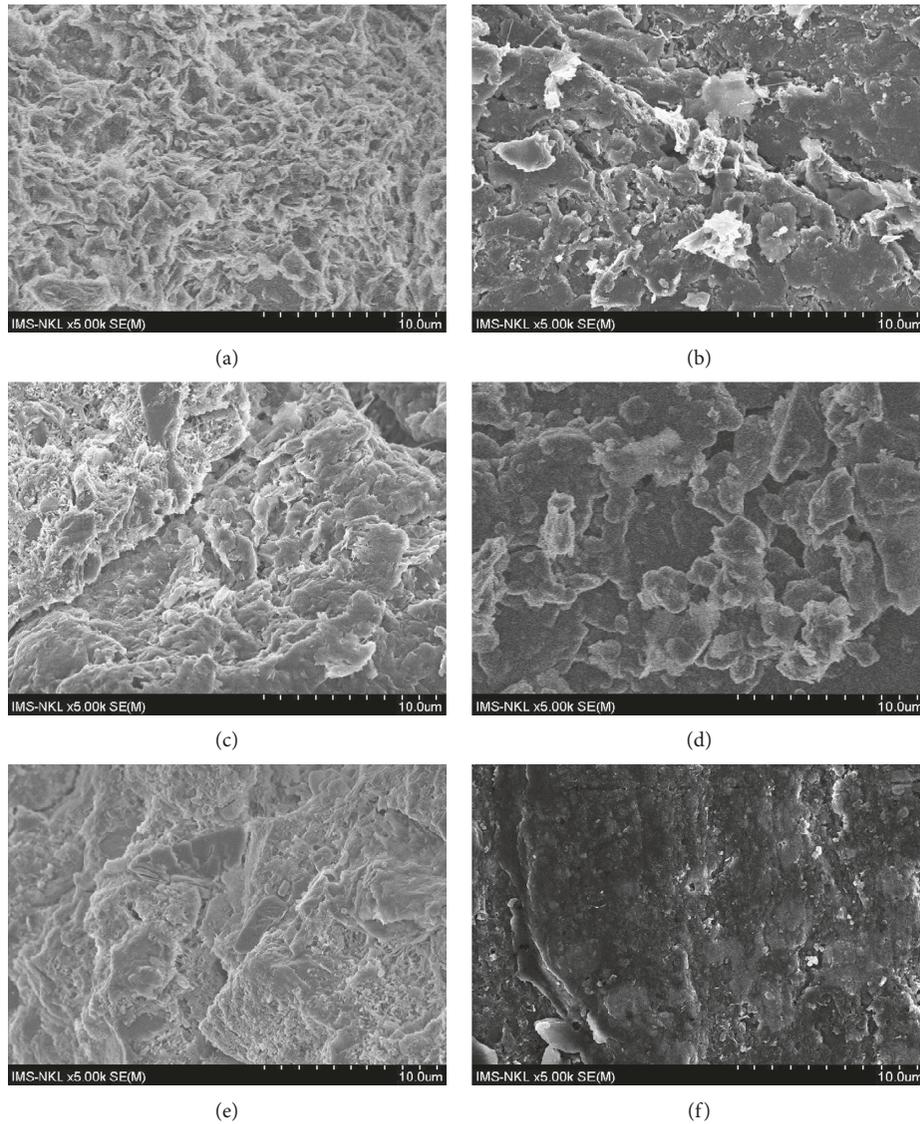


FIGURE 4: SEM images of composites before (left) and after (right) pyrolysis ($\times 5,000$): CNT/P (a, b), CNT-CF/P (c, d), and CNT-CF-G/P (e, f).

3.2. Thermal Property. The effect of CNTs on the thermal stability of phenolic resin was studied using thermogravimetric analysis (TGA). The composite samples were heated from room temperature to 1000°C . This heating process converts gradually the phenolic resin matrix to a carbon matrix.

The TGA curves for phenolic resin (P), G/P, and G-CF/P composites are presented in Figure 5. Figure 6 presents the TGA and DTG curves of CNT/P, CNT-CF/P, and CNT-CF-G/P composites.

As can be seen in Figure 5(a), the pyrolysis (thermal degradation) of phenolic resin exhibits three thermolytic regions. The first region below 400°C was the thermal decomposition of free cross-linked molecules, such as water, unreacted phenol, and formaldehyde [15]. Thus, in this region, the weight loss should be caused by the evolution of unreacted monomers. In this region, the mass loss rate maximum (DTG diagram) was obtained at 107.2°C (T_{m1}).

The T_{m1} represented the temperature at which the maximum weight loss rate occurred in region 1.

The second and third regions were located at $400\text{--}600^{\circ}\text{C}$ and $600\text{--}1000^{\circ}\text{C}$, respectively. These two regions could be attributed to the decomposition of the cross-linked molecules with the evolution of carbon monoxide, carbon dioxide, methane, phenols, and cresols [5]. In region 2, the mass loss rate maximum was obtained at 512.1°C (T_{m2}).

For better comparison of TGA data, we assume the temperature at 5% loss in mass (T_{initial}) as the initial thermal degradation temperature. It was found that the T_{initial} of the neat phenolic resin was 109°C . Table 2 presents the values of T_m , T_{initial} , and % weight remaining at 600°C and 1000°C for phenolic resin and its composites, respectively.

Regarding the contribution of graphite reinforcement, as seen in Table 2, it was found that the presence of graphite in phenolic resin (Figure 6) increased the T_{m1} , T_{m2} , and

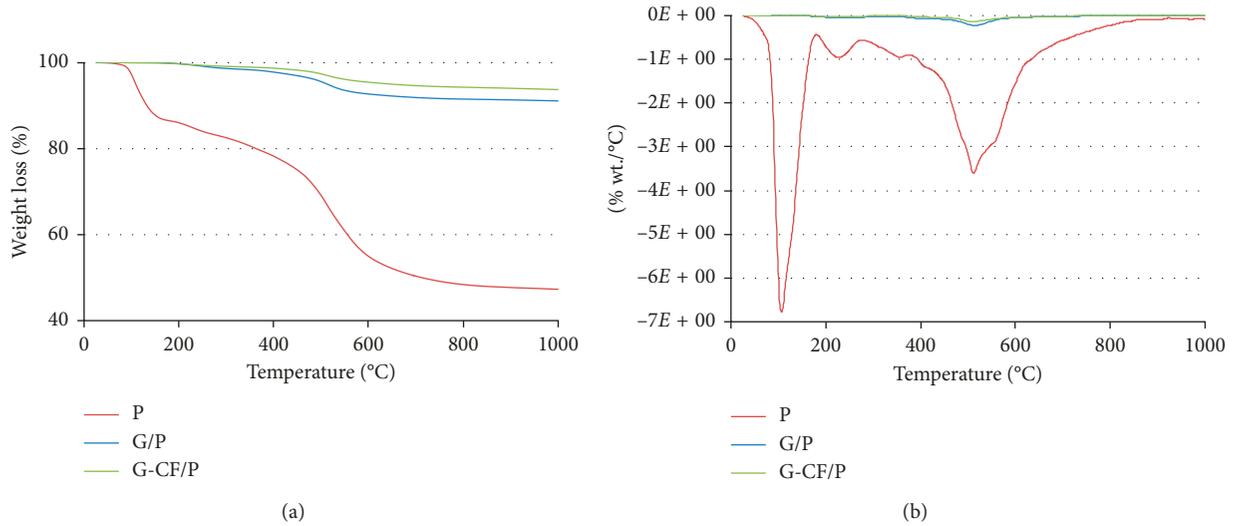


FIGURE 5: Thermal analysis of P, G/P, and G-CF/P composites: (a) TGA diagram and (b) DTG diagram.

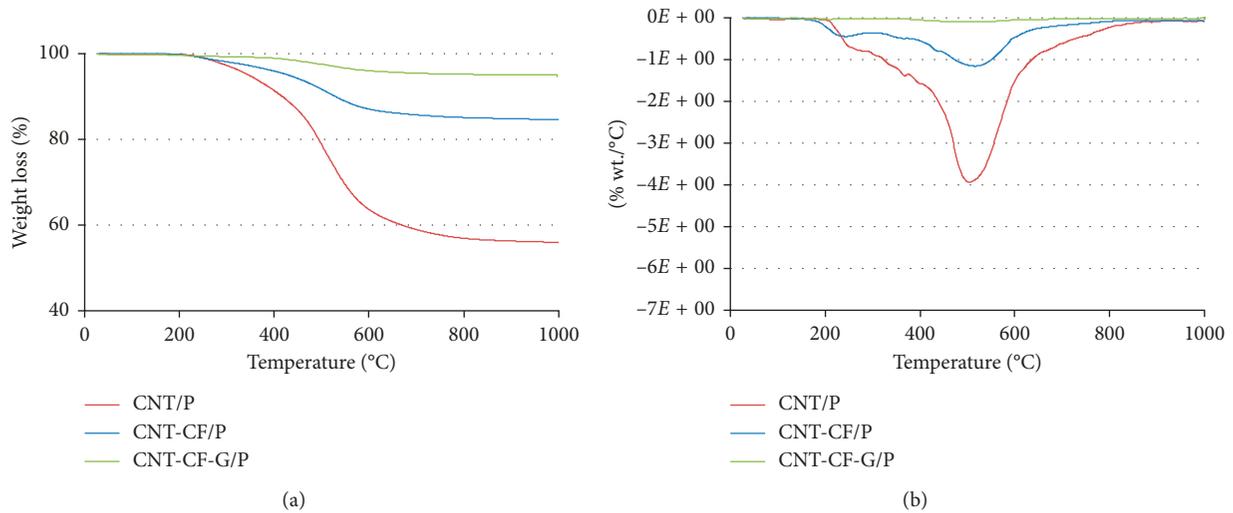


FIGURE 6: Thermal analysis of CNT/P, CNT-CF/P, and CNT-CF-G/P composites: (a) TGA diagram and (b) DTG diagram.

T_{initial} values. Adding the graphite into phenolic resin also significantly reduced the mass loss of resin during the pyrolysis. At 1000°C, the char yields of the neat phenolic resin and G/P composite were found to be 47% and 91%, respectively. Compared to CNT (sample CNT/P), adding the graphite into phenolic resin has a superior enhancement in thermal stability.

For CF reinforcement, adding CF into the G/P composite (G-CF/P) increased its char yield, from 92.7% to 95.4% (at 600°C) and from 91% to 93.7% (at 1000°C). Similar results are observed when adding CF into the CNT/P composite (CNT-CF/P), but its enhancement in thermal stability was lower than that of the G/P composite.

An interesting finding is that adding CNTs into the G-CF/P composite has maximum enhancement in thermal stability, among these 6 samples. As can be seen in Table 2, the presence of CNTs in the G-CF/P composite enhanced its thermal stability, by increasing T_{m2} (from 511°C to 522°C),

T_{initial} (from 635°C to 1000°C), and char yield (from to 93.7% to 95%, at 1000°C). This suggests that CNTs increase the bonding between CF and G with the phenolic matrix, resulting in dense carbon-carbon composites.

3.3. Density and Open Porosity of Composites. By converting the phenolic resin matrix to a carbon matrix, the pyrolysis process could enhance the shear modulus due to the high stiffness of the carbon matrix. However, the shrinkage and mass loss during pyrolysis created the porous microstructure that reduced the strength of the composite [26]. It was reported that carbon from phenolic resins contained a high content of closed pores [25], whereas the open porosity could affect the thermal expansion and oxidative stability of the C-C composite.

In this study, before and after the pyrolysis process, the apparent density and open porosity of all composite samples

TABLE 2: Values of T_m , $T_{initial}$, and % weight remaining at 900°C and 1000°C, for P resin and its nanocomposites.

Composite samples	T_m (°C)		$T_{initial}$ (°C; 5% loss in mass)	% remains at 600°C	% remains at 1000°C
	T_{m1}	T_{m2}			
P	107.2	512.1	109	55	47.3
G/P	257.3	515.6	510	92.7	91
G-CF/P	227	510.8	634.6	95.4	93.7
CNT/P		505	347	63.7	55.9
CNT-CF/P	244	517	432	87.1	84.6
CNT-CF-G/P	206.5	522.3	1000	96.1	95

TABLE 3: Apparent density and open porosity values of composites before and after pyrolysis.

Number	Composite	Apparent density (g/cm ³ ; ±0.01)	Open porosity (%; ±1)
1	G/P	Before pyrolysis	1.94
		After pyrolysis	1.82
2	G-CF/P	Before pyrolysis	1.86
		After pyrolysis	1.74
3	CNT-CF-G/P	Before pyrolysis	1.85
		After pyrolysis	1.71

were determined and compared. Table 3 summarizes the values of their apparent density and open porosity.

As can be seen in Table 3, the presence of CNTs (as nanofillers) in the composite reduced significantly its open porosity after pyrolysis. In addition, the apparent density of unpyrolyzed and pyrolyzed composites has the lowest value for G-CF-CNT/P samples, followed by G-CF/P and G/P composites. This small reduction could be attributed to the reduction of graphite powder content in the composites (graphite has a higher value of density, as compared to both CF and CNTs). These values of density and open porosity are strongly coherent with their morphological investigation represented in Figures 1 and 2.

High-performance carbon-carbon composites required a high value of density (e.g., >1.8 g/cm³). However, there are significant differences between the coefficient of thermal expansion of the carbon fibers and resin matrix; thus, during the cooling process, they could generate the internal stresses and stress cracks inside the composite [27]. In addition, the shrinkage during pyrolysis created pores and cracks, thus reducing the density (Table 3). To obtain the desired value of density (>1.9 g/cm³), this carbonized CNT-CF-G/P composite should be then infiltrated with carbon (via its open pores) by using CVI (chemical vapor infiltration).

4. Conclusions

The main findings of this research were as follows:

- (i) The homogeneous and dense G/P, G-CF/P, and G-CF-CNT/P composites were successfully fabricated by using hot compression molding.
- (ii) The TGA data indicated that the presence of CNTs in the phenolic/graphite composite enhanced its thermal stability, by increasing T_{m2} (from 511°C to 522°C), $T_{initial}$ (from 635°C to 1000°C), and char yield (from 93.7% to 95%, at 1000°C). This suggests

that CNTs increase the bonding between CF and G with the phenolic matrix, resulting in dense carbon-carbon composites.

- (iii) The incorporation of CNTs into the phenolic/graphite composite reduced significantly its open porosity (from 15% to 10%).

The CVI process for densification of this carbonized CNT-CF-G/P composite is now under investigation. After the CVI process (CH₄-Ar gases, at 1100°C during 4 hours), the final CNT-CF-G/P composite could have a higher value of density (~1.9 g/cm³) and lower open porosity (<3%), as compared to its values before CVI.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

This work was financially supported by the Vietnam Academy of Science and Technology (Project no. VAST.TĐ. AN-QP.01/17-19).

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