Effect of carbon black powder content on thermal, physical, and mechanical properties of carbon fabric reinforced phenolic composite

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ABSTRACT

Using heat-resistant fiber-reinforced phenolic composite materials (carbon fiber, glass fiber, etc.) to protect the rocket motor from high temperature has confirmed its superiority thanks to its thermal insulation and high-temperature resistance. The improvement of thermal protection properties of materials to diversify the thermal protection material family is a growing trend. Accordingly, this paper focuses on determining the influence of the percentage of carbon nano powder (0-14%) on the thermal, physical and mechanical properties of carbon fiber/phenolic matrix composite (CPC) in order to find out the extent of reasonable proportion of carbon powder to improve thermal protection. The results indicated that the addition of carbon powder with a content of about 6–10% significantly improved the thermal protection efficiency of CPC materials. The determined thermophysical parameters are the basis for calculating and designing of solid rocket motor heat insulation layer.

Keywords: Thermal protection material; Ablative composites; Phenolic resin; Carbon black.

1. INTRODUCTION

For the solid rocket motor (SRM), the propellant grain produces gas products with high temperatures (2000 - 3500 K), pressures of 6 - 30 MPa, and speeds of about 200 - 250 m/s, greatly affecting the structural strength and reducing the engine efficiency if it is not thermally protected.

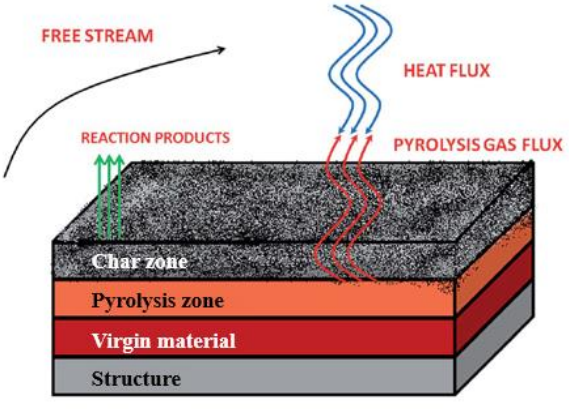


Figure 1. *Thermal protection according to the ablation mechanism [1].*

Analysis of thermal protection materials and methods, found that carbon fiber/phenolic composite (CPC) has good thermal protection thanks to the high temperature resistance of carbon cloth and high char yeild char rate of phenolic resins compared with other polymers, as well as the ability of phenolic resins to maintain charring layer profiles for heat resistance and insulation.

This material belongs to the group of thermal protection materials according to the ablation mechanism (figure 1). The solid carbonaceous residue, called char, which is composed mainly of carbon, the sublimation temperature of about 4000 K, acts as an insulating layer and barrier to deep penetration of heat into the inner material layer [2]. However, CPC materials still have the disadvantage that the char yield is not high (about 60–70%) due to the molecular structure containing methylene bridges with low binding energy and the oxidation caused by the atomic oxygen in the hydroxyl group (-OH). In addition, shrinkage when hot pressed in the mold is also a limitation of phenolic resin. Due to such a disadvantage, there are two main methods to improve the thermal protection of phenolic composite materials: 1 – modification of phenolic resin by organic compounds containing elements Si, Bo, P, etc.; 2: Adding high-temperature-resistant fillers such as carbon nano powder, carbon nanotubes, silicon carbide, etc. [3, 4].

Continuing the research direction on CPC materials used as thermal protection materials for SRM has been reported in the article [5], in this study, the authors focus on determining the influence of carbon black powder content on the thermal-physical and mechanical properties of CPC materials in order to find a reasonable range of carbon black (CB) powder content to improve thermal protection for this material. The limit of the carbon powder content was investigated to 14 wt% of phenolic resin, because when the carbon powder content is too large (over 15 wt%), it limits the filling ability of the material when hot pressed in the mold [6]. The thermal physical and mechanical properties that were determined include: Thermal conductivity K, heat capacity C_p, và density ρ , flexural strength σ_u , and Oxy-acetylene torch test.

2. EXPERIMENTAL

2.1. Experimental process

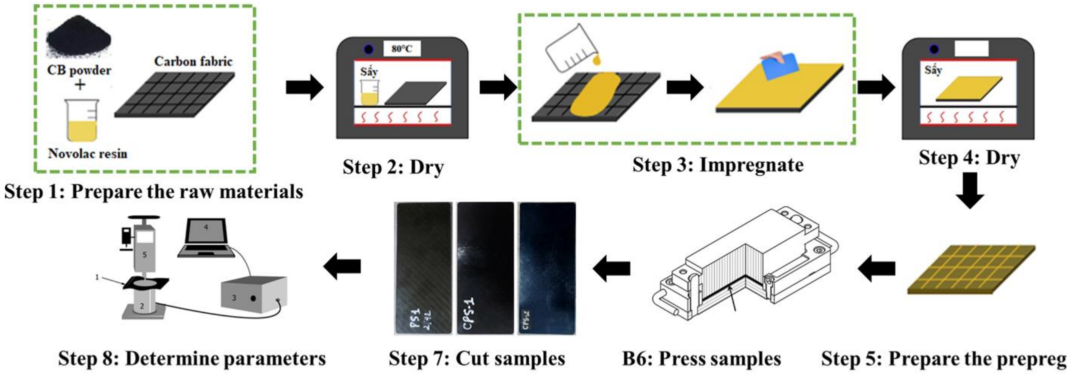


Figure 2. *Experimental process.*

The experimental procedure was carried out according to the steps shown in the diagram in Fig. 2.

2.2. Materials

- ***Raw materials:*** A Novolac (NPF) – type phenolic resin was provided by Institute of Chemistry and Materials, Academy of Military Science and Technology. The curing behavior of a novolac resin (NPF) is cured with hexamethylenetetramine (HMTA), and the amount of curing agent (HMTA) is about 10-15 wt% of phenolic resin. In this study, the amount of HTMA was fixed at 14 wt%. The cure agent HMTA (kindly supplied by GHTECH-China), Ethanol absolute $\geq$ 99,7% (supplied by GHTECH-China), carbon fabric type 3K (YC-3101), carbon black nanopowder N330 (China), see table 1, were used.

- ***Preparation of resin:*** The mixture of novolac resin, absolute ethanol, and curing agent is weighed in a ratio of 1:1:0.14 into a beaker and stirred on a JJ-1 stirrer to form a liquid solution.

Table 1. *Characteristics of carbon black nanopowder N330.*

Type	Density at 20°C (g/cm^3)	Particle size (nm)	Boiling point (°C)	Thermal Conductivity (W/mK)
ASTM N330	1.7 – 1.9	28-36	3500	0,320

- ***Preparation of carbon black powder (CB):*** Carbon black nanopowder was dried in an oven at 80 ^oC for 3 hours, then stirred with resin for 5 hours.

- ***Preparation of prepreg:*** The carbon fabric is cut as required, then soaked in industrial alcohol to remove impurities, then the fabric was dried and impregnated with novolac resin with a resin/fabric ratio of about 1.8-2:1. The process of impregnating the resin on the fabric needs to ensure that the fabric is evenly absorbed by the resin and the surface density is even. Semi-finished fabric after impregnating resin (called prepreg) was dried at 50 ^oC for 15 hours before pressing.

2.3. Pressing cycle selection

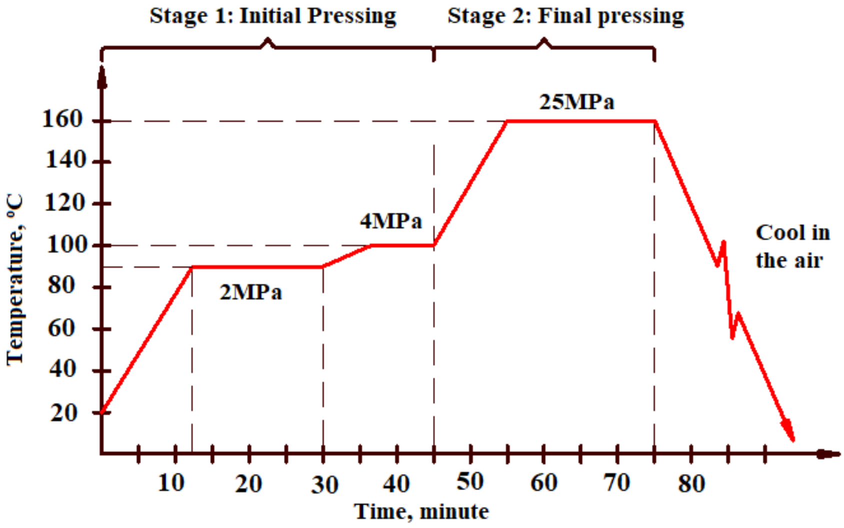


Figure 3. *Schematic representation of Pressing Cycle for Composite Carbon Fiber/NPF.*

Refer to the relevant documents and research results in the work [5]. The schematic representation of Pressing Cycle for carbon powder-reinforced CPC material is presented in Fig. 3, including two stages:

Stage 1 -The initial pressing stage comprises initial heat-up and one (or more) temperature dwells. The primary goals during cure are to enable full saturation of the fiber bed by resin during low viscosity conditions; transition of resin from a solid state to a gel state; facilitate mold filling, and prepare for the final pressing stage. Therefore, this stage is the critical period for product quality.

Stage 2 - The final pressing stage at 160 ^oC with pressures of 25 MPa for 30 minutes to ensure complete curing of the resin.

Table 2. *Testing samples.*

Sample	Compositon
PS-1	Composite CPC (0 wt% CB).
CPS-1	Composite CPC (+ 7 wt% CB).
CPS-2	Composite CPC (+ 14 wt% CB).

The pressing process was carried out on a direct thermocompression machine (symbol: Starmark – Fig. 4b), with a pressure of up to 30 tons and a temperature of up to 230 °C. The prepregs were cut into rectangular sheets, 60 mm in width and 150 mm in length, and were pressed in the mold according to the diagram as shown in figure 3 (the number of prepregs for one sample is 7 sheets). There are 3 groups of samples surveyed; symbols and sample composition are given in table 2. The mold and the samples after pressing are indicated in Fig. 4a and Fig. 5a.


(a) (b)

Figure 4. *Structure of mold (a) and the thermocompression machine (Starmark) (b).*

2.4. Testing and method procedures

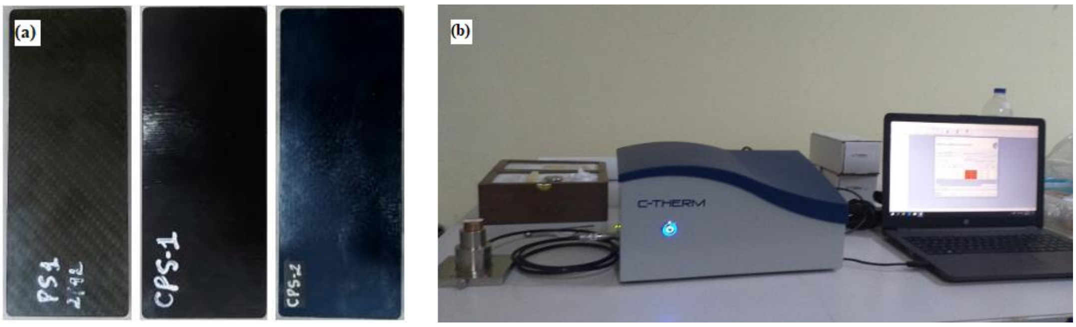
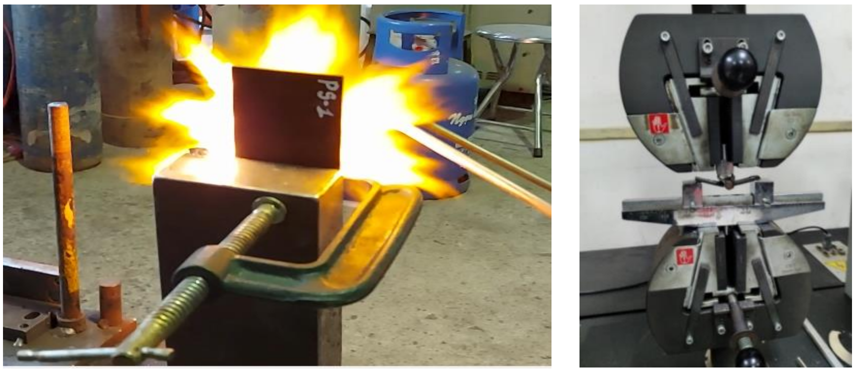


Figure 5. *Testing samples (a) and thermal conductivity analyzer (C-Therm) (b).*

Based on the evaluation criteria of fiber-reinforced polymer materials used as thermal protection materials, in this study, some property parameters were investigated, including:

- Density (ρ_V), g/cm^3: Volumetric density is determined by the ratio of mass/volume of the sample.

- Thermal properties: ASTM D7984-16 was used to determine thermal properties such as thermal conductivity (k), W/(m.K), and specific heat (Cp), J/(kg.K). The size of the samples test was 60 mm in length by 60 mm in width. The experimental set-up is shown in Fig. 5b on a thermal conductivity analyzer (C-Therm or TCi) at the Metrology Center, Institute of Technology/General Department of Defense Industry.



(a) (b)

Figure 6. *Oxy-acetylene torch test (a) and compression equipment FU/R50KN-CKS (b)*

- Mechanical property: The flexural strength is determined according to the standard TCVN 10592-2014-913192. The size of the samples test was 80 mm in length by 15 mm in width. This test was measured on a compression equipment FU/R50KN-CKS (Fig. 6b) at the Metrology Center, Institute of Technology/General Department of Defense Industry.

- Ablation testing: The ablation rate was evaluated by the oxyacetylene torch test according to the ASTM E285-80 standard. The standard describes the testing of flat ablative panels in an environment of a steady flow of hot gas provided by an oxyacetylene burner. The size of the samples test with oxy-acetylene torch was 60 mm in length by 60 mm in width, the distance between nozzle and samples was 20 mm. This test is shown in Fig. 6a and was measured at the Technology Center/Military Technical Academy.

3. RESULTS AND DISCUSSION

3.1. Effect of carbon black powder content

Table 3. *The thermal-physical-mechanical parameters of the sample were investigated.*

Sample	**Thermal properties**			**ρ (g/cm^3)**	**σ_u (Mpa)**
	u (mm/s)	**k, (W/(m.K))**	**c_p (J/(kg.K))**		
PS-1	0.192	0,504±0,002	**776,60**	1,53	754
CPS-1	**0.154**	0,48±0,002		1,39	466
CPS-2	0.189	0,45±0,002		1,34	542
Với: k, c_p, u, ρ, σ_u – The coefficients of thermal conductivity and specific heat, the ablation rate, the density, and the flexural strength of the sample are, respectively.					

The investigated thermal-physical-mechanical parameters are presented in table 3 and graphed in Fig. 7 and Fig. 8. The results show that:

- Specific heat: The specific heat capacity of the investigated samples remained constant and reached a value of approximately 776.60 J/kg.K, which is approximately 1.7 times that of ordinary steel (460 J/(kg)..K), indicating that the thermal energy required to raise the unit temperature of a unit mass of CPC samples is greater, indicating that the insulation efficiency of this group of materials is good.

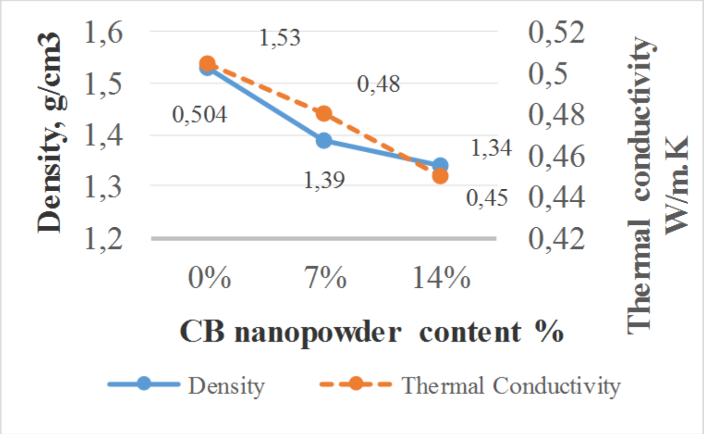


Figure 7. *Effect of CB powder content on CPC material density and thermal conductivity.*

- Thermal conductivity and density: Compared with the CPC material, when increasing the carbon powder content, the thermal conductivity and density both decrease (Fig. 7). This can be explained by the fact that the properties of the composite material are greatly influenced by the properties of the component materials. The carbon black nanopowder has a lower thermal conductivity coefficient than the thermal conductivity of CPC materials, so adding carbon powder will reduce the thermal conductivity of CPC materials, which will increase the thermal protection effect of the material. When compared to ordinary steel, the thermal conductivity of composite materials is very low, only about 1% of that of ordinary steel (50 W/m.K), demonstrating the material has good insulation performance. Meanwhile, the density is 6 times smaller than steel (density of steel = 7.85 g/cm^3).

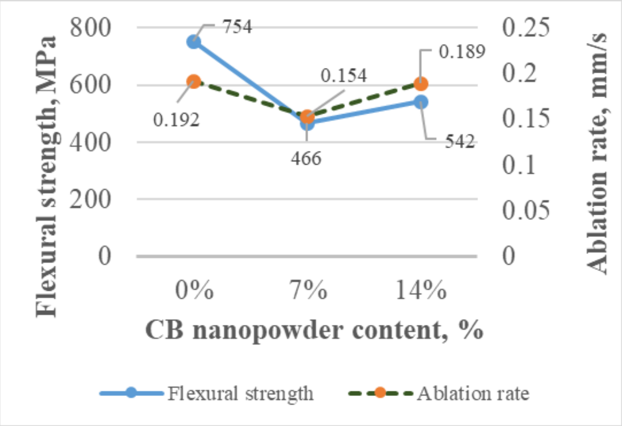


Figure 8. *Effect of CB powder content on CPC material flexural strength and ablation rate.*

- Ablation rate and flexural strength: The transformation laws of ablation rate and flexural strength under the influence of carbon powder content are similar (Fig. 8). The flexural strength and ablation rate decreased significantly when the carbon black powder content was increased to 7%, then slightly increased to 14%. The change in the ablation rate may be due to the fact that in Novolac resin there is always a hydroxyl group (-OH), which means that when exposed to high heat flow, the oxygen in this group will combine with the carbon in the charring layer to produce gases such as CO and CO_2, which lead to rapid wear of the top surface char. Carbon powder is not only a material that can withstand high temperatures, but also when added to CPC material, it will reduce the ratio of OH groups due to the reduction of the resin ratio. Obviously, the addition of CB powder will reduce the ablation rate of CPC materials. The ability to protect heat under the influence of high-temperature and high-velocity combustion products will be more effective.

3.2. Product testing

On the basis of achieved results and practical requirements, two types of thermal protection bottoms for FMV-T2 weapon motors have been made and actual field tests have been conducted: Type 1-is made from materials pure CPC (0% carbon powder) - symbol: BVN1 (Fig 9a); Type 2-is made from CPC material with 10% CB powder added - symbol: BVN2 (Fig. 9b).

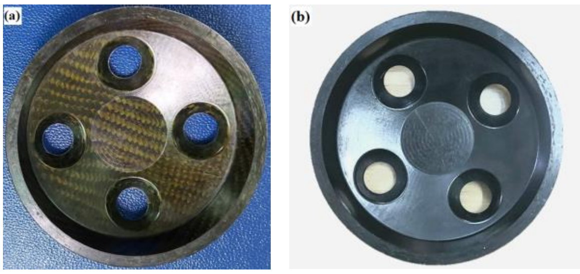


Figure 9. *Thermal protection BVN1 (a) and BVN2 (b).*

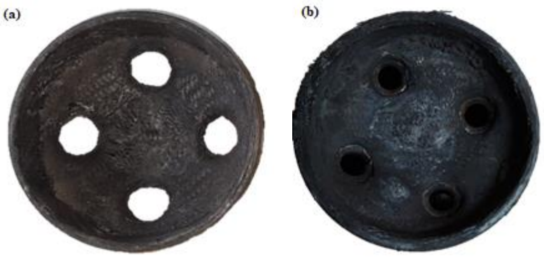


Figure 10. *Thermal protection BVN1 (a) and BVN2 (b) after actual testing on the motor of the FMV-T2 weapon.*

The results show that the thermal protection bottoms all ensure the thermal protection function without causing damage due to the influence of heat on the motors. Thermal protection bottom shape after engine operation remains as configured (Fig. 10), confirming both thermal protection bottoms are satisfactory. However, the addition of CB powder provided improvement in the thermal protection of CPC material, as evaluated by the ability of erosion resistance of the surface layer at the nozzle inlet.

4. CONCLUSIONS

The effect of carbon powder content on the thermophysical and mechanical properties of CPC materials has been studied, showing a significant thermal protection effect when the CPC material is reinforced with CB powder. The results indicated that with an amount of CB powder equivalent to 6–10 wt% of novolac resin, the CB powder-reinforced CPC material has a low thermal conductivity and a low ablation rate, i.e., a good thermal protection effect. The research results are the basis for the design problem of the thermal protection layer of the SRM shell from CPC material.

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REFERENCES

[1]. Colonel Vijay Kumar† and Balasubramanian Kandasubramanian, *“Advances in Ablative Composites of Carbon Based Materials: A Review”,* American Chemical Society, (2019), DOI: 10.1021/acs.iecr.9b04625.

[2]. Maurizio Natali, Jose Maria Kenny, Luigi Torre (2016), “*Science and technology of polymeric ablative materials for thermal protection systems and propulsion devices: A review*”, Elsiver, Volume 84, (2016).

[3]. Maurizio Natali, Marco Monti, Debora Puglia, José Maria Kenny 1, Luigi Torre*, “Ablative properties of carbon black and MWNT/phenolic composites: A comparative study”, Elsiver,* Composite: Part A, (2012).

[4]. Kaihong Tang, Ailing Zhang, Tiejun Ge, Xiaofeng Liu, Xiaojun Tang , and Yongjiang Li, *“Research progress on modification of phenolic resin”,* Materials Today Communications, Elsevier, (2020), DOI: 10.1016/j.mtcomm.2020.101879.

[5]. Đinh Văn Hiến, Trần Ngọc Thanh, Hồ Ngọc Minh, Nguyễn Tuấn Anh, Trần Xuân Tiến, *“Nghiên cứu ép đáy bảo vệ nhiệt động cơ vũ khí FMV-T2 từ vật liệu composite cốt vải cacbon/nền phenolic”,* Tạp chí nghiên cứu KHCNQS, số đặc san 10/2021, ISSN 1859-1043.

[6]. William B. Hall, *“Standardization of the Carbon-Phenolic Materials and Processes”,* NASA Grant No. NAG8-545 - Mississippi State University Mississippi State, (1988).

TÓM TẮT

Ảnh hưởng của bột nano cacbon đến tính chất cơ-nhiệt-lý của vật liệu composite cốt vải cacbon/nền phenolic

Sử dụng vật liệu composite nền phenolic/cốt sợi chịu nhiệt (sợi cacbon, thủy tinh,...) để bảo vệ nhiệt cho động cơ tên lửa đã khẳng định được tính ưu việt nhờ khả năng cách nhiệt và chịu nhiệt độ cao. Việc nâng cao tính năng bảo vệ nhiệt của vật liệu nhằm đa dạng hóa họ vật liệu bảo vệ nhiệt là một xu thế phát triển. Theo đó, bài báo trọng tâm xác định ảnh hưởng của tỉ lệ bột nano cacbon (0 - 14%) đến tính chất nhiệt – lý và cơ học của vật liệu composite cốt vải cacbon/ nền phenolic (CPC) nhằm tìm ra phạm vi tỉ phần bột cacbon hợp lý để nâng cao khả năng bảo vệ nhiệt. Kết quả chỉ ra rằng việc bổ sung bột cacbon với hàm lượng khoảng 6-10% cải thiện đáng kể khả năng bảo vệ nhiệt của vật liệu CPC. Các tham số nhiệt lý vật liệu đã xác định là cơ sở tính toán thiết kế lớp bảo vệ nhiệt động cơ tên lửa nhiên liệu rắn.

Từ khóa: Vật liệu bảo vệ nhiệt; Composite tan mòn; Nhựa Phenolic; Bột cacbon.