IMPACTS OF GRAPHENE ON THE COMBUSTION AND INFRARED EMISSION CHARACTERISTICS OF THE PYROTECHNIC COMPOSITION BASED ON MAGNESIUM-TEFLON-VITON

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Abstract

Graphene has been studied and developed for application in many civil and military fields. In particular, the application of increasing the performance of high-energy materials in the military has received much attention in recent years. This article presents studies on the influence of graphene additives on some combustion characteristics and infrared emission of the pyrotechnic composition based on Magnesium-Teflon-Viton (MTV). EDX analysis and SEM images are used to evaluate the distribution of graphene in the pyrotechnic mixture. Graphene additives added to the MTV pyrotechnic mixture did not significantly affect the burning rate, but significantly changed the combustion temperature and infrared emission of the pyrotechnic compositions.

Keywords*: *Graphene; burning rate; infrared emission; Magnesium-Teflon-Viton.

1. Introduction

Pyrotechnic compositions based on Magnesium-Teflon-Viton (MTV) are an important energy material that has been studied for application in infrared decoys used on aircraft to counter infrared missiles. Currently, research to improve the infrared emission efficiency of the MTV composition is an important issue that scientists are very interested in. The burning rate and infrared emission efficiency of MTV pyrotechnic composition are adjusted by additives, including nano additives [1]-[3]. The added nano additives have the advantage of increasing the heat, efficiency and reaction rate of the mixture [1]. These additives can be nano metals (Ni, Cu, Al), nano metal oxides (Fe_2O_3, CuO, Co_2O_3) and some carbon materials such as graphene (G), graphene oxide (GO), deoxygenated graphene oxide (RGO), carbon nanotubes (CNTs) [1], [3], [4].

Carbon nanomaterials such as G, GO, RGO, CNTs are synthesized from graphite - a natural form of carbon. Graphite has special physical and mechanical properties thanks to its layered honeycomb atomic structure. Carbon atoms are bonded together

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with sp^2 hybridization, on a layer plane (graphene), creating highly mobile π electrons. As a result, carbon atoms in the same plane are covalently bonded to each other, while between layers are bonded together by Van der Waals forces, allowing them to slide over each other. They are used as heat-resistant materials, batteries, lubricants, etc. [5]. Carbon nanomaterials all have large surface areas, they release carbon soot that has the ability to emit like a black body when burned (according to the Stefan-Boltzmann law), thus increasing the infrared emission ability (in the appropriate wavelength bands) of the MTV pyrotechnic composition [1], [3], [6].

This article presents research results on the impacts of graphene on the burning and infrared emission characteristics of the MTV pyrotechnic composition.

2. Experiment

2.1. Materials and sample preparation

The binder solution was equiped by soaking viton rubber (with 66% fluorine content, BS Chemical Co., Ltd., China) in acetone (at a ratio of 0.05 g/mL) for about 8 hours before adding graphene (tacked layers with a thickness of 10-50 nm and a length of 200-2000 nm, produced by Suzhou Tanfeng Graphene Technology Co., Ltd., China) using a sample homogenizer. The Mg (particle size ≤ 63 µm, supplied by E. B. Alloy Casting & Forging, Co., Ltd., China) and Teflon (particle size ≤ 10 µm, supplied by BS Chemical Co., Ltd., China) were dry-mixed before affixing them to this binder solution. The pyrotechnic samples were granulated on a 0.8 mm sieve and dried for 1 hour before being dried for 2 hours at 60°C. Many studies have shown that the MTV sample with an Mg content of 60-65% (with Viton content fixed at 5%) by mass exhibits reliable ignition ability, a high burning rate, and high infrared emission efficiency [7]-[9]. Therefore, the authors select the MTV sample with Mg/PTFE/Viton content % = 65/30/5 for investigation. The pyrotechnic samples based on Mg/Teflon/Viton/Graphene were introduced in Tab. 1.

Tab. 1. The sample of MTV/graphene compositions

Material	**Particle size (µm)**	**Content (% wt)**						
		M0	**M1**	**M2**	**M3**	**M4**	**M5**	**M6**
Mg	≤ 63	65	65	65	65	65	65	65
Teflon (PTFE)	≤ 10	30	30	30	30	30	30	30
Viton A		5	5	5	5	5	5	5
Graphene (external content)	0.01-0.05 (thickness)	0	2	4	6	8	10	12

2.2. Experimental techniques

The SEM imaging (FESEM S-4800, Hitachi, Japan) and EDX technique (Horiba-7593H, Japan) was used to specify the distribution of graphene in the pyrotechnic compositions. The high-speed camcoder (Handycam FDR-AXP55, Sony, Japan) was used to confirm the linear burning rate of the pyrotechnic samples that were squeezed into cylindrical acrylic tubes (25 mm height and 12 mm diameter) (Fig. 1a) [10]. The burning rate, u (mm/s), is calculated using the following formula: $u = \frac{L}{t}$ (mm/s). The relative burning rate, Z, is defined as the ratio of the burning rate of the MTV pyrotechnic composition containing additives to that of the MTV pyrotechnic composition without additives. The combustion temperature was determined using a Wre (5%) - Wre (20%) thermocouple, which can measure temperatures up to 2500°C [11] (Fig. 1b) [12]. The Spectroradiometer (SR-5000N, CI Sytem, Israel) was used to determine spectral radiance of the pyrotechnic composition (Fig. 1c) [10]. Each sample was tested at least 3 times, taking the average result for each measurement.

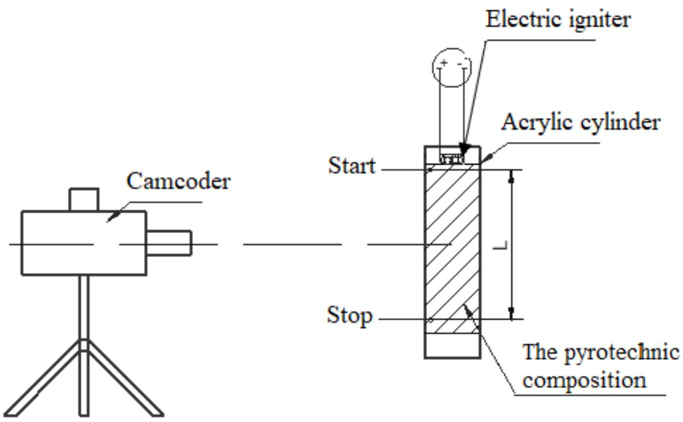

Fig. 1a. Experimental determination of burning rate.

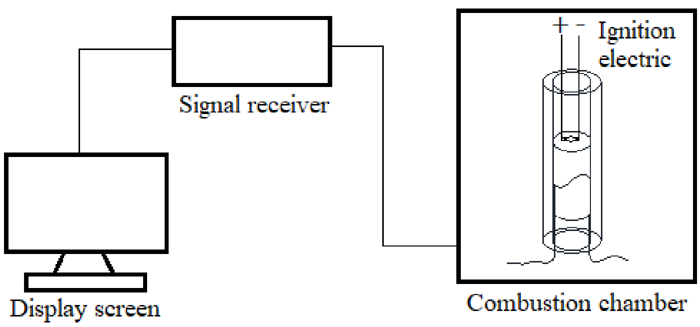

Fig. 1b. Experimental determination of combustion temperature.

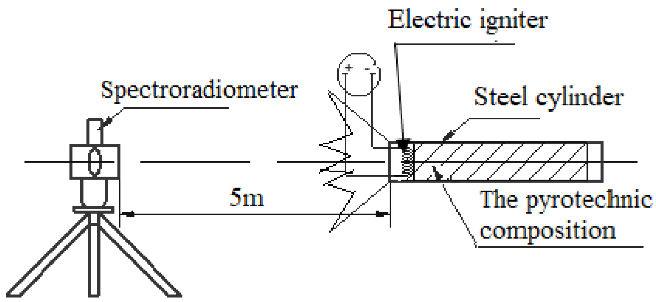

Fig. 1c. Experimental determination of spectral radiance.

3. Results and discussions

3.1. The dispersion of graphene in the MTV composition

The even dispersion of graphene in the pyrotechnic mixture is an important requirement for the stable combustion and infrared emission process. Therefore, after preparing the pyrotechnic composition, it is necessary to evaluate the distribution of nano additives in the mixture by SEM and EDX techniques.

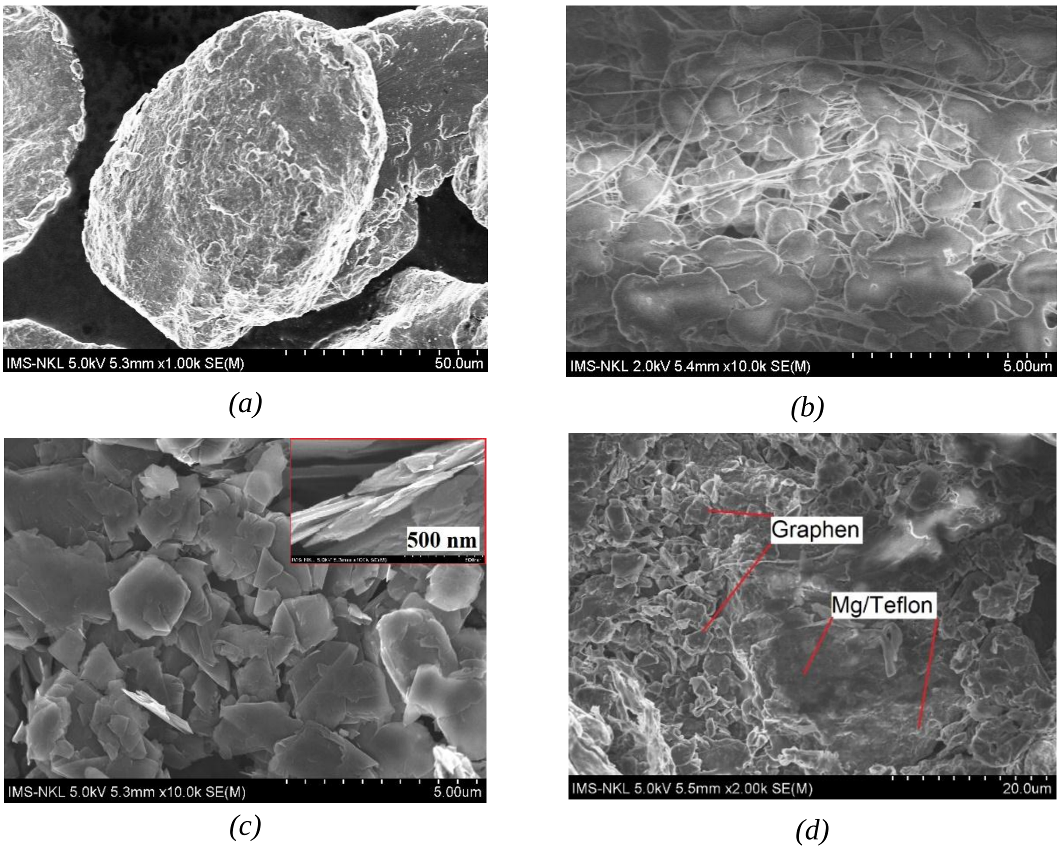

Fig 2. (a) SEM image of Mg particles, (b) SEM image of Teflon, (c) SEM image of Graphene, and (d) SEM image of Graphene/Viton rubber on Mg/PTFE particles.

The SEM images in Figs. 2a, b, c allow us to evaluate the physical sate, morphology and particle size of the raw material before making the MTV composition. SEM imaging results show that graphene were surrounded by Viton binder and evenly adhered to the surface of Mg/Teflon particles (Fig. 2d).

EDX analysis results of the M0 (average) and M4 samples at three different points on the surface of the pyrotechnic sheet (M4_1, M4_2, M4_3) showed the presence of graphene in the pyrotechnic mixture (Tab. 2, Fig. 3). M4_a and M4_t in Tab. 2 are the average mass at 3 positions and the theoretically calculated mass (according to the manufactured component ratio), respectively.

From Tab. 2, the amount of graphene added is determined by the increase in the mass % C content in the MTV-graphene samples compared to the M0 sample (no graphene added): 33.68% in the M4_t sample compared to 17.19% in the M0 sample (average value). The results of EDX analysis at 3 points and SEM images show the presence of graphene distributed alternately on the surface of Mg/PTFE micro particles. This can be seen that the dispersion of graphene is relatively uniform. Additionally, because the EDX mapping area is only 20 μm × 20 μm in size and the magnesium particles are covered by a layer of viton (containing PTFE and graphene), the determined magnesium content is lower than the nominal value.

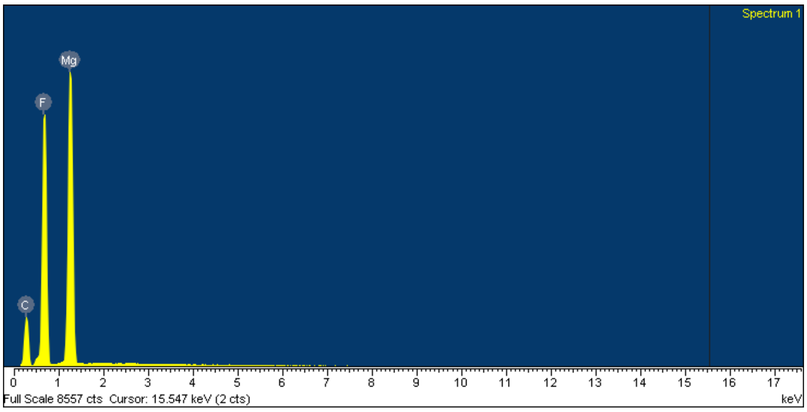

Fig. 3. EDX analysis results of M4_1 sample.

Tab. 2. EDX analysis results of graphene distribution

Elements	**M0 (average)**	**M4_1**	**M4_2**	**M4_3**	**M4_a (average)**	**M4_t (theory)**
	Weight%	**Weight%**	**Weight%**	**Weight%**	**Weight%**	**Weight%**
C	17.19	30.81	36.65	33.57	33.68	15.56
F	32.16	46.24	32.75	12.13	30.37	24.16
Mg	32.12	22.95	30.59	54.30	35.95	60.19

3.2. Impact of graphene admixture on the linear burning rate of the MTV composition

The linear burning rate of the MTV pyrotechnic samples were specified with different graphene content. The results were introduced in Tab. 3 and Fig. 4. The relative burning rate Z was the ratio of the burning rate of the mixture with graphene to the mixture without graphene.

Tab. 3. The burning rate of the MTV pyrotechnic samples

Sample	**% Graphene (external content)**	**Density (g/cm^3)**	**Burning rate, *u* (mm/s)**	**Relative burning rate, Z**
M0	0	1.60	5.3	1
M1	2	1.59	5.8	1.1
M2	4	1.61	5.7	1.1
M3	6	1.60	5.6	1.1
M4	8	1.62	5.5	1
M5	10	1.63	5.4	1
M6	12	1.62	5.7	1.1

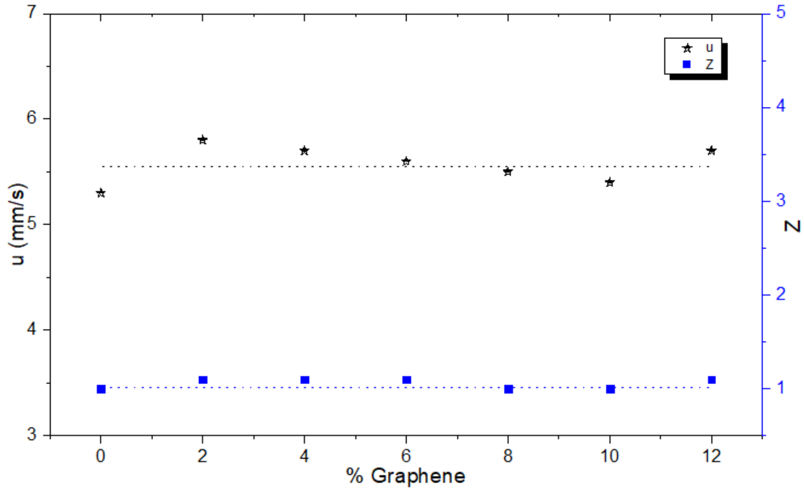

Fig. 4. Impact of graphene on the burning rate of the MTV pyrotechnic composition.

For the combustion process of MTV composition when graphene is added, the burning rate of the MTV pyrotechnic mixture is almost unchanged compared to the M0 sample (Fig. 4). When continuing to increase the graphene content, the burning rate of the mixture also does not change much. This shows that the added graphene does not affect the burning rate of MTV composition much. The reason is that in the pyrotechnic combustion process, graphene is an inert substance that does not participate in the reaction (can reduce the burning rate by absorbing heat, reducing the amount of heat transferred to the combustion surface), but it itself has excellent heat transfer ability (facilitating the heat transfer process of the mixture). These two factors compensate for each other, so the combustion spread of the system takes place normally, the burning rate is almost unchanged.

3.3. Combustion temperature and infrared emission characteristics of the MTV pyrotechnic compositions with graphene

Experimental process to measure combustion temperature and infrared emission ability, the MTV composition is burned in air environment, with the participation of air oxygen reaction. In which, the air content participating in the reaction to reach the experimental combustion temperature is calculated using MATLAB [13]. Impact of graphene additivies on the combustion temperature and infrared emission (characterized by spectral radiance value L_λ) of the MTV mixture are presented in Tab. 4.

From Tab. 4, we can see that when the amount of air participating in the reaction accounts for about 53-66% of the total mass of the reactants, the combustion temperature calculation results will be consistent with the experiment. When the oxygen content of the air participating in the reaction increases, Mg, carbon soot (produced in the primary reaction area) and nano-structured graphene easily react with oxygen in the air to form MgO, CO (secondary reaction area).

Tab. 4. Impact of graphene-additives on the combustion temperature and the spectral radiances of MTV composition

Sample	**Content of ingredients (theoretical), %**		**Combustion temperature, *K***		**$L_{\lambda1\text{-}\lambda2}$ ($W \cdot sr^{-1} \cdot cm^{-2} \cdot \mu m^{-1}$)**			
	MTV-graphene	**Air**	**Theoretical**	**Practical**	**2.5-3 µm**	**3-5 µm**	**2.5-5 µm**	**8-10 µm**
M0	47	53	2376	2380	0.7508	2.4316	3.1823	0.1566
M1	45	55	2226	2260	1.0263	2.5307	3.5569	0.1691
M2	42	58	2227	2283	1.1524	2.4053	3.5577	0.1668
M3	39	61	2275	2282	1.2965	2.7567	4.0532	0.1746
M4	37	63	2237	2276	1.2429	2.9142	4.1570	0.1869
M5	36	64	2108	2140	1.2198	2.8851	4.1048	0.1891
M6	34	66	2106	2170	1.1590	2.6165	3.7755	0.1657

The proportion of oxygen participating in the combustion reaction increases with the graphene content. However, the amount of oxygen participating is not enough to oxidize CO to CO_2, leading to a decrease in the heat release. As a result, the combustion temperature tends to decrease. Thus, the role of graphene is mainly in providing carbon "sheets" with large surface areas, helping to enhance the process of converting thermal energy into infrared radiation. They have almost no impact on catalyzing combustion or increasing the heat release.

When the MTV compositions are supplemented with graphene additives, the spectral radiance increases significantly compares to the M0 sample and peaks with the sample containing 8% graphene, although the burning rate remains almost unchange, while the combustion temperature tends to decrease. When the graphene content is higher than 8%, the infrared emission ability begin to decrease. The emission energy value of the M4 sample (8% graphene) according to the spectral radiance is: $L_{2.5\text{-}3}$ = 1.2429, $L_{3\text{-}5}$ = 2.9142, $L_{2.5\text{-}5}$ = 4.1570; $L_{8\text{-}10}$ = 0.1869 ($W \cdot sr^{-1} \cdot cm^{-2} \cdot \mu m^{-1}$). The increased spectral radiance of the MTV system is due to the emission efficiency of the graphene carbon "sheets" and the increase of the combustion products MgO, CO (products of the reaction between Mg, C with oxygen in the air).

When the graphene content continues to increase beyond 8%, the spectral radiance of the MTV mixture tends to decrease. This is because, although increasing the graphene content increases the source of the emissive carbon "sheet" for the system, when the graphene content is > 8%, the heat of the system still does not increase, leading to the heat source not being enough to supply the emission of graphene.

4. Conclusion

With its large surface area and blackbody-like emission, graphene has increased the infrared emission of MTV-based pyrotechnic mixtures. The spectral radiance of MTV sample containing 8% graphene has increased 1.3 times (in the 2.5-5 μm wavelength band) compared with sample without additives. During the reaction content of air oxygen depending on the burning rate, the combustion temperature of the system tended to decreased from about 2400 K to 2150 K when adding graphene. Although graphene is an inert substance (which can reduce the burning rate), but it has good heat transfer ability (which can increase the burning rate), which leads to the combustion rate of MTV mixture when graphene is added not changing much, approximately 5.5 mm/s.

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ẢNH HƯỞNG CỦA GRAPHEN ĐẾN ĐẶC TÍNH CHÁY VÀ PHÁT XẠ HỒNG NGOẠI CỦA THUỐC HỎA THUẬT TRÊN CƠ SỞ MAGIE-TEFLON-VITON

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Tóm tắt: Graphen đã được nghiên cứu và phát triển ứng dụng trong nhiều lĩnh vực dân sự và quân sự. Trong đó, ứng dụng làm tăng hiệu quả hoạt động của các vật liệu năng lượng cao trong quân sự nhận được nhiều quan tâm trong những năm gần đây. Bài báo trình bày các nghiên cứu về sự ảnh hưởng của phụ gia graphen lên một số đặc trưng cháy và khả năng phát xạ hồng ngoại của thuốc hỏa thuật trên cơ sở Magie-Teflon-Viton (MTV). Phương pháp phân tích EDX và ảnh SEM được sử dụng để đánh giá sự phân bố của graphen trong hỗn hợp thuốc hỏa thuật. Phụ gia graphen được bổ sung vào hỗn hợp thuốc hỏa thuật MTV không ảnh hưởng nhiều đến tốc độ cháy, nhưng lại làm thay đổi đáng kể nhiệt độ cháy và khả năng phát xạ hồng ngoại của thuốc hỏa thuật.

Từ khóa: *Graphen; tốc độ cháy; phát xạ hồng ngoại; Magie-Teflon-Viton.*

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