**INSTITUTO LATINO-AMERICANO DE CIÊNCIAS DA VIDA E DA NATUREZA (ILACVN)**

**ENGENHARIA FÍSICA**

# EFEITO DO GRAFITE EXPANDIDO NA COMBUSTÃO E TAXA DE QUEIMA DE COMBUSTÍVEIS E PROPELENTES SÓLIDO E HÍBRIDO

**GABRIELE THAMIRES MULLER**

Foz do Iguaçu
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Trabalho de Conclusão de Curso apresentado ao Instituto Latino-Americano de Ciências da Vida e da Natureza da Universidade Federal da Integração Latino-Americana, como requisito parcial à obtenção do título de Bacharel em Engenharia Física

Orientador: Prof. Dra. Priscila Lemes
Coorientador: Prof. Dr. Alon Gany

Foz do Iguaçu
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Trabalho de Conclusão de Curso apresentado ao Instituto Latino-Americano de Ciências da Vida e da Natureza da Universidade Federal da Integração Latino-Americana, como requisito parcial à obtenção do título de Bacharel em Engenharia Física.

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# SUMÁRIO

# 1 INTRODUÇÃO

O desenvolvimento de sistemas de propulsão mais seguros, eficientes e controláveis tem motivado intensa pesquisa em propelentes sólidos e motores híbridos. Nesse contexto, a propulsão híbrida combina combustível sólido e oxidante líquido, oferecendo vantagens como maior segurança, motivo de ser amplamente considerada para o setor de turismo aeroespacial, além de possibilidade de controle de empuxo e de queima. Um dos principais desafios desta tecnologia é a baixa taxa de regressão típica de combustíveis poliméricos, que limita o empuxo. Ao mesmo tempo, propelentes sólidos convencionais exigem controle preciso da taxa de regressão para atender melhor desempenho. Dentro desse cenário, este Trabalho de Conclusão de Curso reúne três artigos científicos que investigam o uso de grafite expandido (EG) como aditivo inovador para manipular e aumentar a taxa de queima de combustíveis sólidos e propelentes, buscando conciliar maior empuxo com boas propriedades mecânicas e de segurança.

O primeiro artigo, intitulado “Expandable graphite effect on solid fuel and propellant combustion", apresenta o estudo inicial do efeito do grafite expandido sobre a queima de combustíveis sólidos para motores híbridos e do propelente sólido à base de perclorato de amônio (AP) e poliéster. Neste trabalho, o EG é caracterizado como uma forma intercalada de grafite com moléculas de enxofre que, ao ser aquecida, incha e se alonga formando fibras muito maiores que as partículas originais. O estudo foi conduzido por meio de ensaios experimentais em um motor híbrido de laboratório, utilizando um bloco cilíndrico de poliéster com e sem a adição de 5% em massa de grafite expandido, para determinar a taxa de regressão do combustível em função do fluxo mássico de oxigênio. Além disso, foram realizados ensaios de amostras de propelente sólido compostas por 75% de AP e 25% de poliéster, contendo diferentes frações em massa de EG (0,5% a 5%), onde avaliou-se a influência do aditivo na taxa de queima e na estabilidade da chama em condições atmosféricas. Resultados obtidos evidenciaram que a adição de cerca de 5% em massa de EG a um combustível polimérico de poliéster pode duplicar a taxa de regressão. Imagens de alta velocidade da superfície de queima mostraram fibras de EG penetrando e se projetando no escoamento gasoso quente, reforçando a hipótese de aumento de transferência de calor por condução através das fibras. Ensaios com o propelente composto por 75% AP e 25% poliéster com EG mostraram que o aditivo reduz a taxa de queima e, acima de 3%, pode até extinguir a chama. Assim, o EG se destaca como aditivo para aumentar a regressão em combustíveis poliméricos de motores híbridos e ramjets (tipo de motor a jato sem compressor ou turbina). Em contraste, a aplicação de EG em propelentes sólidos ainda depende de novas formulações e condições específicas a serem estudadas.

O segundo artigo, “Increasing Burning Rate and Motor Thrust By Expandable Graphite Additives”, aprofunda essa investigação ao analisar diferentes tipos comerciais de grafite expansível, variando tamanho de floco e temperatura de início de expansão, em uma gama mais ampla de combustíveis e propelentes. O trabalho combina a visualização da superfície de queima de combustíveis, poliéster, polibutadieno com terminação hidroxila (HTPB) e parafina, contendo EG com ensaios de combustão de propelente AP-polímero em pressão atmosférica. Neste trabalho, a metodologia foi organizada em duas etapas principais. Na primeira, investigaram-se os fenômenos de superfície de combustíveis sólidos poliméricos (HTPB, poliéster e parafina) contendo 3% em massa de diferentes tipos de grafite expansível, moldados em placas e submetidos à chama de um maçarico de propano, com registro por filmagem em alta velocidade para acompanhar em detalhe a expansão das partículas de EG, a formação das “fibras” na superfície e sua interação com a camada de material fundido. Na segunda etapa, foram preparados e ensaiados amostras de propelentes compósitos à base de 75% de perclorato de amônio (AP) em massa e 25% de ligante polimérico HTPB ou poliéster, nos quais o EG substituiu parte do ligante em frações entre 0,5 e 5%; foram então queimados em condições atmosféricas, medindo-se o tempo de regressão e registrando-se novamente a superfície por vídeo de alta velocidade, de modo a quantificar a taxa de queima em função do tipo e da fração mássica de EG. Nos combustíveis para propulsão híbrida, confirma-se o aumento de até duas vezes na taxa de regressão, enquanto o efeito em HTPB é mais moderado e praticamente inexistente em parafina. Já nos propelentes sólidos, o estudo evidencia um resultado fundamental: em formulações AP-HTPB, a adição de EG pode elevar a taxa de queima em 60% ou mais. Em contrapartida, nos propelentes AP-poliéster, o EG praticamente não aumenta a taxa de queima e, para determinados tipos, chega a extinguir a combustão em teores mais altos. O artigo conclui que o grafite expandido pode atuar como importante intensificador de taxa de queima em motores híbridos e sólidos, desde que o tipo de EG e sua fração em massa sejam cuidadosamente ajustados à matriz combustível específica.

O terceiro artigo, “Thermal characteristics of expandable graphite as a burning rate enhancer in hybrid propulsion”, foca nos aspectos termoquímicos e físicos que sustentam os efeitos observados nos trabalhos anteriores. Por meio de microscopia eletrônica de varredura, análise termogravimétrica combinada com fluxo de calor (TGA/DSC) em atmosfera inerte e oxidante, além de filmagens de alta velocidade de partículas individuais de EG durante aquecimento controlado. O estudo caracteriza diferentes tipos de grafite expansível quanto à composição, temperatura de início de expansão, entre cerca de 150 a 240 graus Celsius, e comportamento de perda de massa. Resultados importantes evidenciam que partículas de EG podem se alongar em até uma ordem de grandeza em relação ao tamanho original, formando fibras milimétricas a partir de flocos de 100 a 350 $\mu$m. Além disso, quando incorporado a um combustível de poliéster (5% em massa), o EG desloca a decomposição térmica e a ignição em atmosfera oxidante para temperaturas cerca de 100 graus Celsius mais baixas em comparação com o polímero puro, com uma etapa de decomposição mais rápida e seguida por reação violenta. Esses achados indicam que o EG não somente aumenta a condução de calor para o interior do combustível por meio das fibras, mas também favorece a ignição e a gaseificação do polímero, oferecendo uma explicação termoquímica mais completa para a elevação da taxa de regressão em motores híbridos.

De forma integrada, os três artigos têm como objetivo geral compreender e demonstrar o potencial do grafite expandido como aditivo de controle e aumento da taxa de queima em sistemas de propulsão híbrida e de propelente sólido. O primeiro trabalho estabelece a prova de conceito em poliéster para motores híbridos e revela limitações em um propelente AP-poliéster; o segundo amplia o escopo para diferentes matrizes e tipos de EG, identificando condições em que se obtém ganho significativo de taxa de queima e empuxo, especialmente em AP-HTPB; e o terceiro aprofunda a interpretação física e térmica dos fenômenos que sustentam esses resultados. Em conjunto, esses estudos fornecem uma base experimental e conceitual para o uso do EG como intensificador de taxa de queima, contribuindo para o desenvolvimento de motores híbridos mais competitivos e de propelentes sólidos com desempenho ajustável sem comprometer as propriedades mecânicas dos materiais envolvidos.

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# Expandable graphite effect on solid fuel and propellant combustion

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## ARTICLE INFO

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## ABSTRACT

This paper presents an investigation on a novel method for manipulating and enhancing the burning of solid fuels and propellants by expandable graphite additive. Expandable graphite (EG) is a form of intercalated graphite. At elevated temperature it undergoes an increase in volume, forming elongated strings/fibers many folds longer than the original particles/flakes. It was found experimentally that the addition of 1-5% of expandable graphite (original particle size 100-150 micrometer, onset of expansion at 200-230°C) to a polymeric fuel matrix (polyester) in hybrid combustion, increased the fuel regression rate by 2 fold and more. It was hypothesized that the EG strings forming near the burning surface protrude into the hot gas environment increasing heat transfer into the fuel via conduction. Furthermore, the swelling effect at the surface layer might increase the effective surface area, hence further increasing the burning rate. High-speed photography of a surface subjected to flame in oxidizing atmosphere showed EG fibers protruding and growing on the surface, supporting the increased heat transfer hypothesis. On the other hand, the addition of the same EG to an ammonium perchlorate-based propellant showed a tendency to reduce burning rate and even extinguish the flame at EG fractions higher than about 3-5%. It is concluded that in the case of hybrid or solid fuel ramjet combustion, EG can serve as a novel and effective burning rate enhancer while employing polymeric fuels of good mechanical properties in contrast to paraffin fuels which have inferior mechanical properties. The influence of EG on the combustion of solid propellants needs further investigation, looking for combinations of EG and propellant types that may exhibit a similar effect.

## 1. Introduction

The objective of this research was to investigate the effect of expandable graphite (EG) additive on the burning rate of solid fuels (with relation to hybrid combustion or solid fuel ramjets) and solid propellants.

Expandable graphite is a form of intercalated graphite, where guest ingredients (typically, small molecular fractions of sulphur or nitrogen-based compounds) are introduced among its crystalline layers. It appears as particles/flakes of a typical size of 100-500 micrometer. At elevated temperatures (typically between 140 and 300°C, depending on the preparation method), it starts to swell and elongate, forming worm-like fibers or strings several folds longer than the size of the original particles [1].

Expandable graphite is a heat transfer promoter [2] used in phase change materials (PCMs) to increase their thermal conductivity. Other specific properties of expandable graphite besides high thermal conductivity are corrosion resistance, softness, and compression resilience. Studies [3–5] revealed properties of mixtures of paraffin or polymers with expandable graphite such as flammability, thermal conductivity, and stability. It was noted that occasionally EG may act as a flame retardant, possibly due to swelling or accumulation over the burning surface.

Nevertheless, combustion rate enhancement has been reported as well: Elanjickal and Gany [6] investigated the influence of small mass fractions (1%-5%) of EG particles in the solid fuels of hybrid motors, demonstrating some 2-fold increase in burning rate for polymeric materials (particularly polyester) and up to 50% increase for paraffin wax. Their theoretical model (in good agreement with the experiments) assumed an increase in heat transfer into the bulk fuel due to conduction through EG fibers forming at the surface layer and protruding into the hot gas environment. Muller and Gany [7] conducted high-speed photography of a polymeric fuel (polyester) subjected to flame in oxidizing atmosphere (air) at atmospheric pressure. They showed the penetration and growth of expandable graphite fibers during combustion within a characteristic time of a few tens of milliseconds, supporting the hypothesis of enhanced heat transfer to the fuel via conduction. Hahma [8] showed substatial burning rate enhancement in firing tests of energetic charges consisting of pressed pyrotechnic powders containing 1% EG (and occasionally a higher percentage). He assumed that the reason was mainly crumbling of the burning surface layer due to swelling and enlargement of the EG flakes near the surface.

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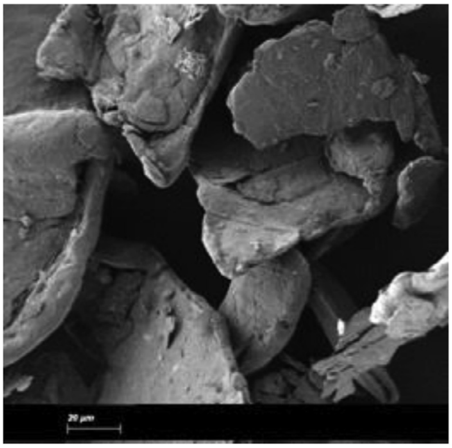


**Fig. 1.** SEM photograph of original expandable graphite flakes, Type ES 100 C10, nominal size 100-150 micrometer, of Graphit Kropfmühl GmbH, Germany [1]. Picture size 150 × 150 micrometer.

The effect of EG on the combustion of solid fuels and propellants received only little attention in the literature, while according to our research it may be very promising. This article presents further experimental investigation on this subject.

## 2. Material and methods

The research has been mainly experimental, consisting of several setups and procedures. The first set of experiments showed the effect of EG additive on the fuel regression rate in hybrid propulsion. It was derived from static firing tests of a lab-scale hybrid motor employing polyester fuel in the form of a hollow cylinder, 190 mm length, 20 mm initial port diameter, with gaseous oxygen (oxidizer) flowing through the port. Firing tests at a range of oxygen mass flux from about 10 to 80 kg/(s m$^2$) were conducted without and with 5% of expandable graphite additive. Test chamber pressure was within a typical range of 8-12 bar, but no effect of the pressure on the fuel regression rate was observed. The EG flakes used were Type ES 100 C10, nominal size 100-150 micrometer, of Graphit Kropfmühl GmbH, Germany [1], characterized by temperature of onset of expansion of 200-230°C. See SEM photograph in Fig. 1. The polyester elemental composition, as determined by a ThermoScientific$^{TM}$ Flash 2000 CHNS analyzer, was $C_{42}H_{41}O_{10}$ (approximately $CHO_{0.25}$).

The second test procedure was exposure of a slab of polyester fuel containing different mass fractions of EG (up to 5% of the overall fuel amount) to a burner flame in atmospheric environment and observing the behavior of the EG fibers growing on the surface. The aim was mainly qualitative. Some quantitative data such as characteristic length and time of the growing fibers, were presented in a previous publication by these authors [7].

The third set of tests comprised the burning of strands of solid propellants at atmospheric pressure. The propellants used consisted of 75% ammonium perchlorate (AP) oxidizer of 200 micrometer mean particle size and 25% polyester as the fuel binder with different mass fractions (from 0.5% to 5%) of expandable graphite, added in place of part of the polyester.

## 3. Results and discussion

### 3.1. Solid fuels in hybrid motors

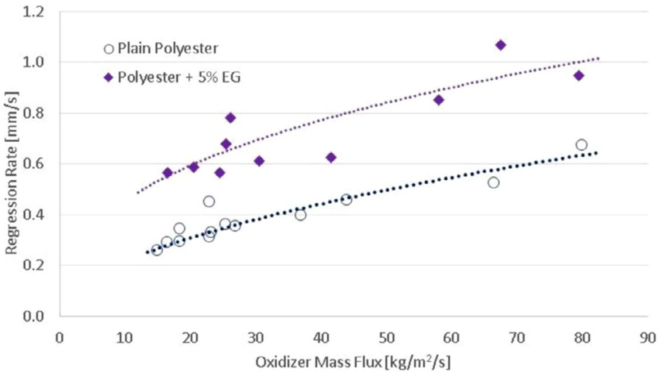


**Fig. 2.** Comparison between the fuel regression rate in a polyester / oxygen hybrid motor vs oxygen mass flux without and with 5% EG additive.

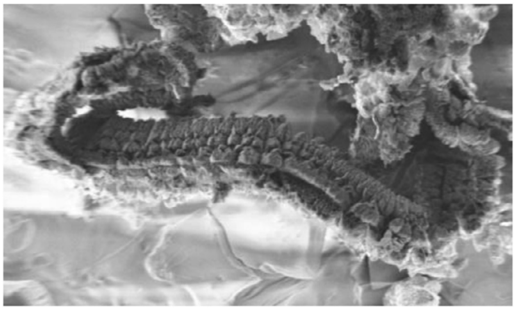


**Fig. 3.** SEM image of an expanded EG fiber (1-1.2 mm long) as observed on the fuel surface after combustion (after [6]).

Figure 2 presents a comparison of data of firing test results of fuel regression rate in a hybrid motor for plain polyester and for polyester with 5% of expandable graphite. The accuracy of the experimental points is ±5%. The Enhancement of regression rate due to the EG additive is substantial, some 2-fold and more, over a range of oxidizer (oxygen) mass fluxes. Similar results were obtained in earlier research in our group [6]. Elaboration on the energetic performance (also included in [6]) showed practically no theoretical or experimental effect of the EG inclusion on the specific impulse or characteristic velocity. That research analyzed paraffin wax fuel as well, revealing a similar, but less pronounced, regression rate enhancement effect. It also developed a model attributing the EG effect to additional heat transfer mechanism due to conduction through the EG fibers, exhibiting good agreement with the experimental results. A picture of an expanded EG fiber observed on the fuel surface after combustion is presented in Fig. 3 (after [6]).

### 3.2. High-speed photography of the burning fuel surface

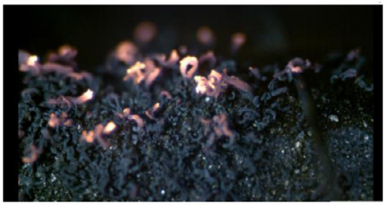
High-speed (1000 frames per second) video movies of the burning surface of polyester fuel slabs subjected to a burner flame in open air surrounding, revealed very interesting details about the behavior of EG strings. One could observe the strings penetrating through the surface layer into the surrounding hot gas environment, glowing due to the flame, and growing to a final length (typically about 1 mm) within 20-60 ms. Measurement and distribution of the characteristic time and length of the expanded fibers were reported by these authors [7]. Figure 4 presents a series of snapshots taken from a high-speed video movie of a fuel containing 3% EG. The aim of the figure is to demonstrate the dynamics of processes occurring on the burning surface, implied by the variation of the EG strings position, shape, and glowing.

### 3.3. Solid propellants

Figure 5 presents a series of pictures taken during atmospheric pressure combustion of solid propellant strands consisting of 75% AP / 25% polyester with different mass fractions of expandable graphite additive.


(a) 0 (Ignition)

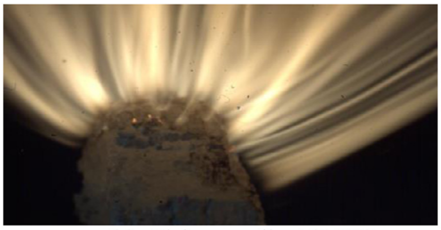

(b) 0.5 s

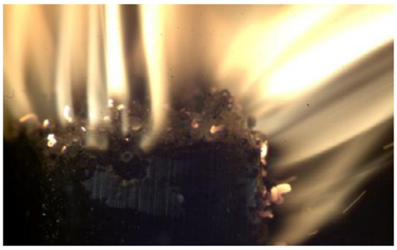

(c) 1 s


(d) 1.5 s

**Fig. 4.** Processes occuring on the surface of a polyester fuel containing 3% EG, during flame. Field of view width about 12 mm. Time from ignition is indicated.

*One can see that this type of EG (ES 100 C10 of Graphit Kropfmühl GmbH) in combination with the AP / polyester propellant had somewhat retarding effect on the propellant combustion. The flame was the largest and the most luminous for the plain propellant, getting less extensive with the increase in EG mass fraction. The difference was not large up to about 2% EG. However, at 3% EG the flame became unstable, and when ignited it would occasionally extinguish after a short burn time. At 5% EG it was almost impossible to sustain the flame after ignition. Figure 6 summarizes quantitatively the propellant burning rate at atmospheric pressure vs the EG mass fraction, showing the decrease in burning rate with increasing EG mass fraction, as indicated by the flame behavior in Fig. 5. The burning rate data revealed spread and possible error within* ±10%. *Apparently, the accumulation of EG fibers on the burning surface disturbed the diffusive interactions of the reactants as well as the heat feedback from the flame to the gasifying surface. This effect should be studied further. Possibly, with different types of expandable graphite (different size, expansion characteristics, and temperature of onset of expansion), different propellant compositions, and higher pressures, the influence would be different, and combustion enhancement might be observed. One should refer to Hahma [8], who reported substantial increase in regression rate when adding EG to energetic charges made of pressed pyrotechnic ingredients.*


(a) Plain propellant (0 EG)


(b) 1% EG


(c) 2% EG

**Fig. 5.** Qualitative pictures from high-speed (1000 frames per second) video movies of atmospheric pressure burning of 75% AP / 25% polyester propellant strands containing different fractions of EG type ES 100 C10. Strand width 8 mm. The pictures are not to exact scale.

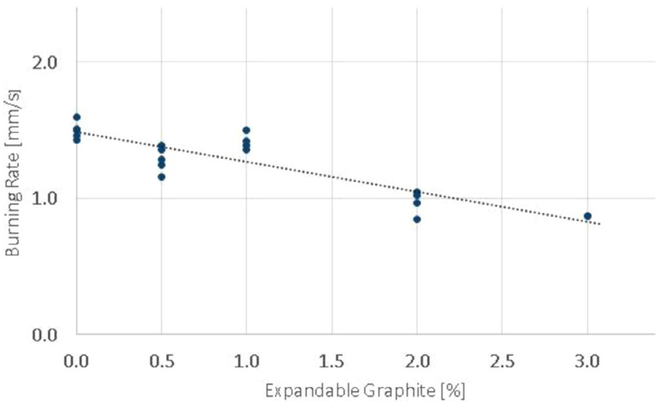


**Fig. 6.** Burning rate at atmospheric pressure vs mass fraction of expandable graphite for a 75% AP / 25% polyester solid propellant.

## Conclusions

Expandable graphite (EG) was studied for its effect on combustion of solid fuels and solid propellants. The peculiar property of expandable graphite is its swelling and elongation at elevated temperatures, e.g., from 100-150 micrometer particles to a millimeter and more string. Combustion experiments with the addition of 5% EG to a solid polyester fuel in a hybrid motor resulted in a 2-fold enhancement of the fuel regression rate. Furthermore, high-speed video pictures showed penetration and growing of EG fibers on the burning surface. On the other hand, combustion experiments of solid propellant strands consisting of 75% AP and 25% polyester, revealed a decrease of burning rate when adding 0.5%-3% of EG, and difficulty to sustain combustion for larger EG fractions. The main practical conclusion is, that in the case of hybrid combustion of polymeric fuels, expandable graphite additive can be used as an effective regression rate enhancer. Further conclusion is that the increase in regression rate is likely to be due to conductive heat transfer to the fuel through the EG fibers. As regards solid propellants, further research is required to find out the effect of different types of EG on various propellants, looking for combinations of EG and propellant types that may lead to enhancement of the burning rate.

## Declaration of Competing Interest

There are no conflicts to declare.

## Acknowledgments

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# Increasing Burning Rate and Motor Thrust by Expandable Graphite Additives

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**Controlling rocket thrust may be done via propellant burning rate catalysts and enhancers. This paper presents an experimental investigation on increasing the thrust of hybrid and solid motors by adding a small fraction of expandable graphite (EG) within the binder matrix to enhance burning rate. EG is a form of intercalated graphite flakes that upon heating change their appearance to elongated fibers/strings of substantially larger length and volume. The elongated EG strings at the burning surface are hypothesized to conduct heat from the hot surroundings to the bulk, thereby increasing the burning rate. High-speed photography of the surface phenomena of fuel slabs containing EG additive subjected to flame supports the greater effect on burning rate enhancement (up to twofold) for polyester versus hydroxyl-terminated polybutadiene or paraffin wax fuels in hybrid motors. Similar investigation on the burning of ammonium perchlorate–polymer solid propellant strands revealed different surface phenomena and substantial burning rate increase (60% and more) for hydroxyl-terminated polybutadiene versus polyester binder with 5% EG additive. It can be concluded that EG can serve as a novel burning rate and thrust enhancer without deterioration of the mechanical properties of the polymeric fuel/binder for hybrid (including solid fuel ramjet) and solid propellant motors.**

## I. Introduction

THIS paper summarizes a research on the effect of different types of expandable graphite (EG) on the surface phenomena of various solid polymeric/paraffin fuels (related to hybrid propulsion) and on the burning rate of solid propellants consisting of various polymeric binders and ammonium perchlorate (AP) as an oxidizer. The research reveals a way for increasing hybrid and solid motor thrust via enhancement of the fuel/propellant burning rate.

Graphite crystal consists of carbon layers (Fig. 1). It is possible to insert guest materials among the layers, forming an intercalated structure. EG, appearing as flakes of a typical size of 100–500 $\mu$m (and even more), is a sort of such structure, where often the guest materials may be sulfuric acid or nitric acid. Its main property is that when heating to a high temperature, starting at about 140–300°C, the flakes elongate and swell due to evolution of volatile ingredients, forming worm-like strings longer by an order of magnitude than the original flake size.

Muller et al. [1] presented measured mass loss of certain types of EG flakes under controlled heating, as well as original shapes of the flakes. Elanjickal and Gany [2] showed a scanning electron microscope (SEM) image of an expanded, elongated EG string after heating (firing test in a hybrid combustor). Because of the substantially higher heat conductivity of graphite compared to polymeric and organic materials, EG is used as a heat transfer promoter in phase-change materials (PCMs) [3]. For a similar reason, Elanjickal and Gany [2] hypothesized that the inclusion of a small fraction of EG particles/flakes within the solid matrix of a fuel in a hybrid combustor would increase the fuel regression rate. They assumed that during the regression of the burning/gasifying fuel surface, the embedded EG flakes would be exposed to the hot surface zone, elongate, and protrude to the hot environment above the surface—hence, conducting heat via the EG strings into the bulk material, increasing the overall heat transfer, thereby enhancing burning rate. Indeed, their static firing tests of hybrid motors backed by theoretical prediction demonstrated a twofold regression rate increase and more when adding 5% EG, particularly in the case of polyester fuel. Furthermore, computations by Elanjickal and Gany [2] using the thermochemical code CEA [4] revealed that the theoretical energetic performance (specific impulse, characteristic velocity) remains practically the same when adding EG to the fuel binder. Muller and Gany [5,6] studied surface phenomena of slabs of polyester fuel containing 1–5% of EG subjected to a flame at atmospheric conditions. They focused on one fuel (polyester) and one type of EG, ES 100 C10, nominal size 100 $\mu$m, of Graphit Kropfmühl GmbH, Germany [7], characterized by temperature of onset of expansion of 200–230°C. By tracking individual EG particles/strings emerging from the solid fuel bulk to the surface, using high-speed video photography, they were able to follow the growing of the particles with time, revealing the size (length) distribution of the strings (average size for that specific EG type about 1.1 mm) and growing time (average of about 28 ms). In addition, some preliminary experiments detected the burning rate at atmospheric pressure of AP-polyester propellants with the same type of EG particles at a range of mass fractions, revealing no apparent burning rate enhancement and even some retarding, as well as a difficulty to sustain combustion for EG additive fraction higher than 3% [6].

The main purpose of the present study was to explore how different types of EG (different initial size and different temperature of onset of expansion) affect the combustion of fuels and propellants of various compositions. Besides the investigation in our research group, we could hardly find a reference in the literature to a similar investigation. Nevertheless, one should note the publication by Hahma [8], who investigated the effect of EG additives on pyrotechnic pressed formulations, with the main aim to increase the light and radiation emission.

## II. Materials and Methods

The investigation had two main experimental efforts: the first part focused on surface phenomena of solid fuels with and without 3% of EG additive, subjected to flame. These experiments are relevant to the combustion of solid fuels in hybrid or airbreathing (ramjet) motors. The fuels analyzed were hydroxyl-terminated polybutadiene (HTPB), polyester, and paraffin wax. Fuel slabs with 50 mm × 30 mm surface were subjected to an external propane torch flame (the field of view was much smaller than the slab, about 6 mm long). Each fuel was casted with five different EG types. During flame application, the surface was video photographed at a rate of 700 pictures per second (pps) and a field of view 6 mm long using a Phantom V310 camera. The purpose of this investigation was to identify common and different characteristics of the different fuels and different EG flakes. The HTPB

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slabs were prepared by mixing prepolymer of polybutadiene with about 9% curing agent isophorone diisocyanate (IPDI) and 1% of dibutyltin dilaurate (DBTDL) catalyst and casting in a mold. Curing was done at room temperature (about 23°C) within a few days. The polyester slabs were of cured erco® E-7 unsaturated orthophthalic polyester prepared from commercial polyester resin and methyl ethyl keton peroxide hardener. The polyester elemental composition, as determined by Thermo Scientific™ Flash 2000 CHNS analyser, was $C_{42}H_{41}O_{10}$ (approximately $CHO_{0.25}$). Curing time at room temperature was a few hours. The paraffin wax fuel slabs were prepared by melting blocks of paraffin PW 624 (melting temperature 62–66°C, density $0.834\ \mathrm{g/cm^3}$) obtained from HBO Bazan group, Israel, casting and solidifying in a mold. The general formula of paraffin wax is $C_nH_{2n+2}$, where $n = 20\text{–}40$.

The second effort of this research aimed at determining the burning rate at atmospheric pressure of two AP-polymer solid propellant formulations, each containing several EG-type additives of mass fraction ranging from 0.5 to 5%. Combustion visualization using high-speed (2600 pps) video photography of the burning surface as well as low-speed video recording of the flame were carried out. Propellant strands 7 mm × 7 mm cross section and 20 (±0.2) mm length were prepared. The polymer binder types were either HTPB or polyester. All propellant samples contained 75% (by mass) of AP (0.67 fraction of 400 $\mu$m and 0.33 fraction of 200 $\mu$m particles). The addition of EG was in place of the binder; hence, the mass fraction of binder + EG together was always 25%. Weighing and mixing of the propellant ingredients were done manually, hence introducing errors estimated at ±5%.

EG flakes of various manufacturers and characteristics (denoted as EG types) for this research were selected to cover a range of average original sizes (from 100 to 350 $\mu$m) and temperatures of onset of expansion ($T_{\mathrm{exp}}$, nominally from 150 to 240°C) to figure out the influential property. Table 1 presents the EG types used. The EG flakes were obtained from two manufacturers: Graphit Kropfmühl GmbH, Germany (denoted as GK), and NGS Trading and Consulting GmbH, Germany (denoted as NGS). Figure 2 presents SEM images of the specific original EG flakes under consideration. Element analysis [1] revealed that the atomic % composing the EG types analyzed was relatively similar, having about 91–94% of carbon (C), 4–7.5% oxygen (O), and 1–1.5% sulfur (S), indicating that the EG types under consideration were apparently intercalated by sulfuric acid.

As shown in Table 1 and Fig. 2, the various EG types exhibit variations both in size and in temperature of onset of expansion $T_{\mathrm{exp}}$. Nevertheless, one could learn about the influence of the original flake size by comparing the effect of EG types 1 and 2, having the same $T_{\mathrm{exp}}$ (200–230°C) but substantially different nominal sizes (100 vs 350 $\mu$m, respectively). As well, EG types 3 and 4 have the same size (300 $\mu$m), but very different $T_{\mathrm{exp}}$ (150 vs 240°C, respectively), allowing to compare the effect of temperature of onset of expansion.

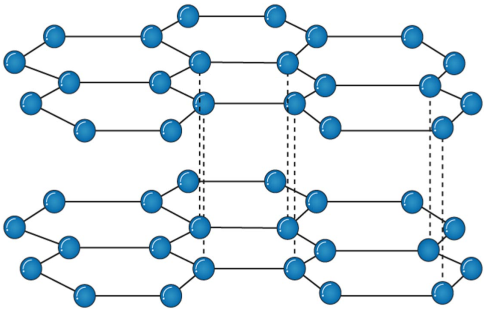
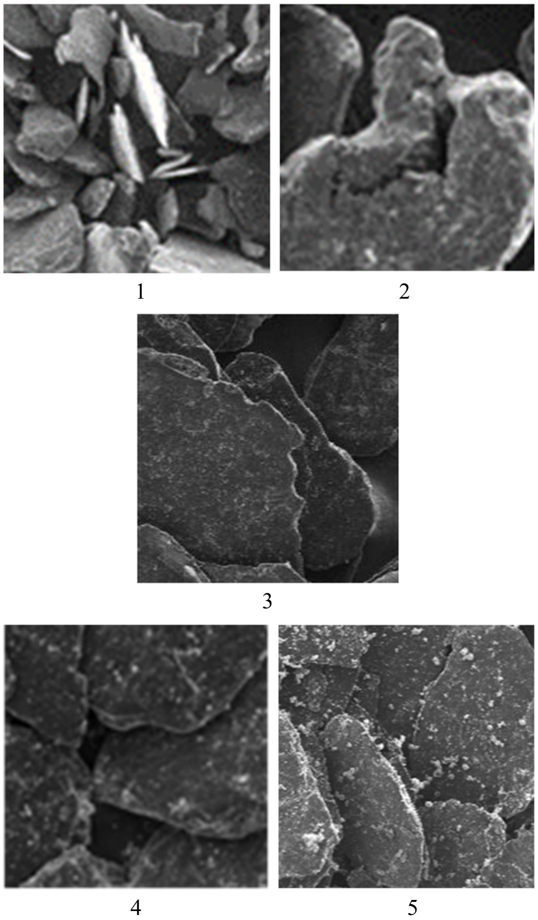


Fig. 1 Graphite crystal structured layers.

Table 1 Specifications of the EG flake types used

| No. | Type (manufacturer) | Size, $\mu$m | $T_{\mathrm{exp}}$, °C |
|---|---|---|---|
| 1 | ES 100 C10 (GK) | 100 | 200–230 |
| 2 | ES 350 F5 (GK) | 350 | 200–230 |
| 3 | Ex 95 50 250 RZ (NGS) | 300 | 150 |
| 4 | Ex 50 95 200 YO (NGS) | 300 | 240 |
| 5 | Ex 80 92 200 YO (NGS) | 177 | 240 |



1 2 3 4 5

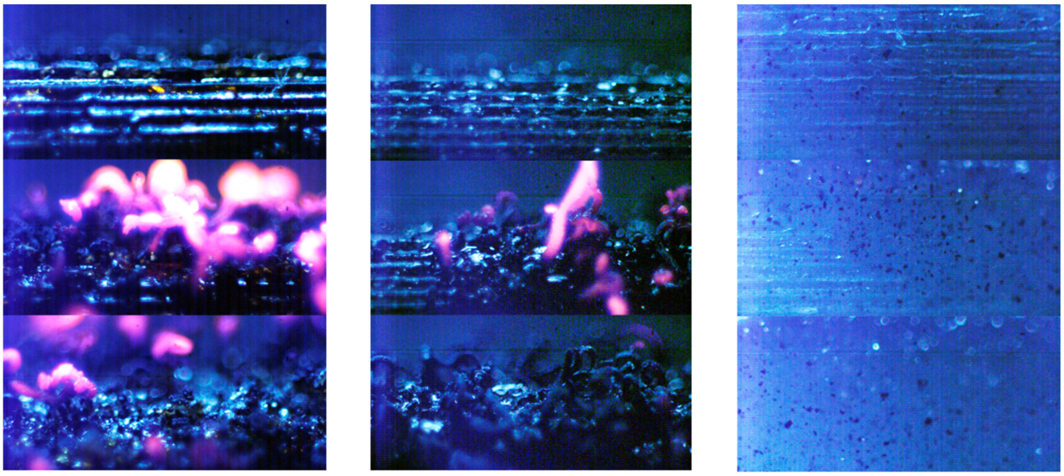
Fig. 2 SEM images of the five types of EG flakes under consideration (as detailed in Table 1). The actual dimensions of each image are 500 $\mu$m × 500 $\mu$m.

## III. Results and Discussion

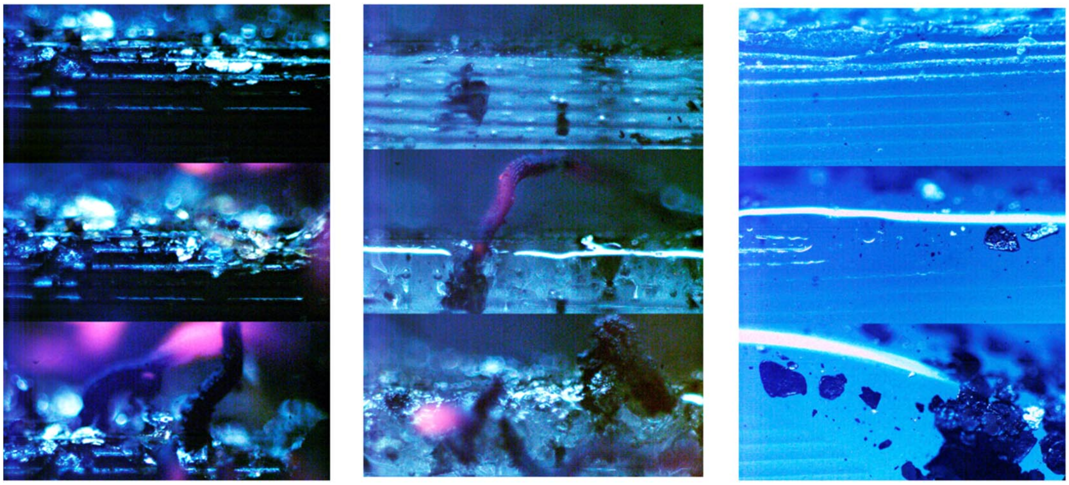
### A. Solid Fuels Subjected to Flame

Figure 3 presents short sequences from high-speed (700 pps) video movies, showing the dynamic surface phenomena of the three fuels under consideration (polyester, HTPB, and paraffin wax). Each of the fuels was tested with 3% of five different EG additives as listed in Table 1 and shown in Fig. 2. The objective of these experiments was to reveal the behavior of the different samples. For clarification, explanation on the features observed in Fig. 3 follows: each frame consists of a sequence of three images at increasing time order. The lines on the surface resulted from the casting mold surface; in a way, they helped noticing fuel consumption and melt generation. The colors are somewhat artificial; nevertheless the glowing objects (pink with internal white colors) are the EG strings (burning or very hot) protruding above the surface. Occasional darker long strings can be observed. White shining lines indicate reflection from a molten material. In the case of the polyester fuel, EG strings protruding and growing at the surface and glowing from the flame could be observed. The pictures reveal penetration of the EG strings from the bulk to the surface while expanding; occasionally it implied breaking and dispersion of small pieces of the polymer. The edge of the sample remained solid.

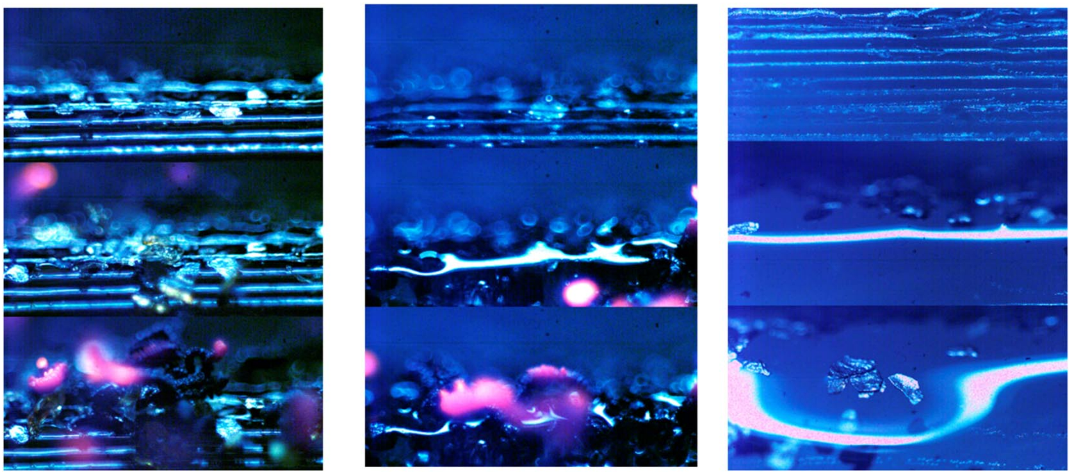
The HTPB samples showed somewhat other behavior. EG strings could be observed like in the case of the polyester. However, with time progressing (particularly for EG2-EG5), one can notice some waviness/distortion of the fuel surface as well as slight reflection



Polyester fuel + EG1 HTPB fuel + EG1 Wax fuel + EG1



Polyester fuel + EG2 HTPB fuel + EG2 Wax fuel + EG2



Polyester fuel + EG3 HTPB fuel + EG3 Wax fuel + EG3

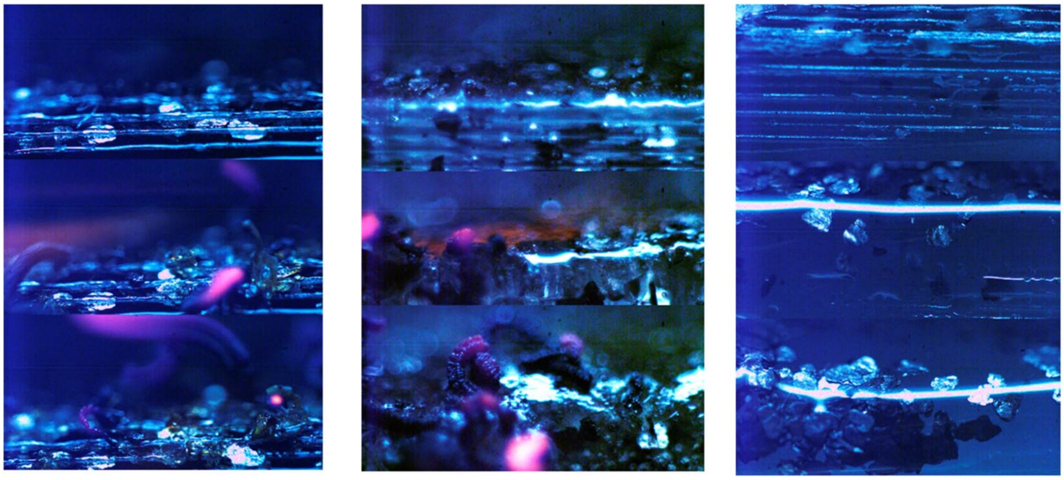
**Fig. 3 Sequences from high-speed (700 pps) video movies of the dynamic surface phenomena of polyester, HTPB, and paraffin wax fuels containing 3% of different EG types, subjected to flame. The frame of each fuel and EG type combination is composed of three consecutive images demonstrating the progression of the surface processes. Images' actual size is 6 mm.**

(light lines), indicating local zones of surface softening and melting. The EG string protrusion and expansion caused some deformation of the surface.

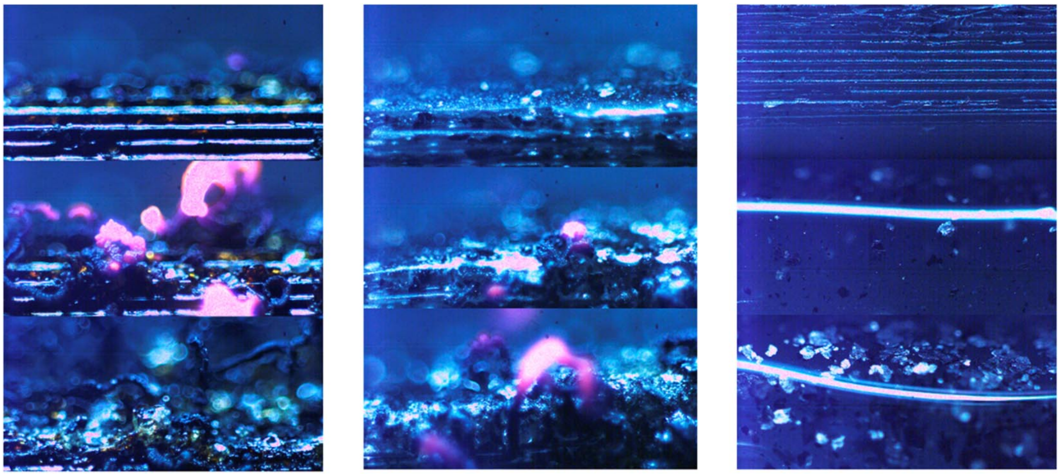
The wax samples demonstrated extensive surface melt layer formation, showing lines of light reflection. The embedded EG flakes remained within the melt layer. No expansion, elongation, ignition, or glowing of the EG particles took place during the flame application on the surface, since the melting temperature (62–66°C) is well below the temperature of onset of expansion of EG (150–240°C, for the EG types employed in this research).

### B. Burning and Surface Phenomena of Solid Propellants

The burning rate at atmospheric pressure of the propellant formulations and EG types and mass fractions under consideration was determined by measuring the time for the flame propagation from the top of a strand along its 20 mm length. Ignition was accomplished by



Polyester fuel + EG4 HTPB fuel + EG4 Wax fuel + EG4



Polyester fuel + EG5 HTPB fuel + EG5 Wax fuel + EG5

**Fig. 3 (Continued).**

a small propane torch igniter. Errors due to time measurement could be within ±0.5 s (±5–10%). As stated before, AP-HTPB and AP-polyester propellants were tested. Propellant strands without EG additive were first tested for reference, followed by testing of each of the propellants with the various types and mass fractions of EG.

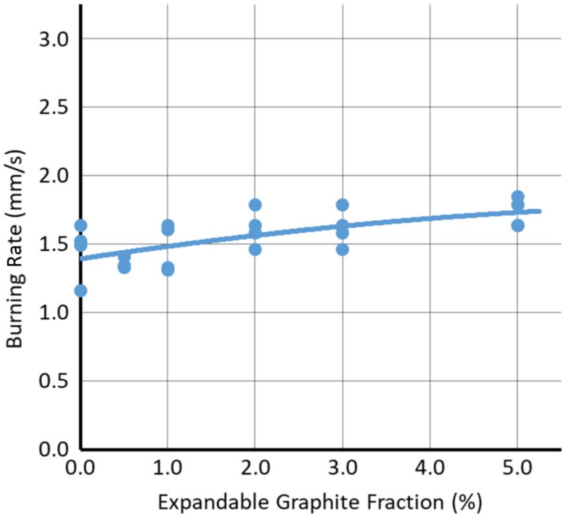


**Fig. 4 Burning rate vs EG mass fraction for an AP-HTPB propellant with an EG type 1 additive.**

### 1. *AP-HTPB Propellants*

Figures 4–8 show the burning rate of AP-HTPB propellants containing a number of EG types over a range of EG mass fractions up to 5%. Interestingly, although the effect of EG additive on the HTPB fuel regression rate in hybrid combustion was smaller than that for polyester fuel, in the propellant case a substantial effect on increasing the burning rate with increasing EG fraction was noticeable for the HTPB binder. In general, the higher the EG mass fraction, the higher was the burning rate. To determine the effect of original flake size, isolating it from the influence of temperature of onset of expansion, the pair of EG flakes type 1 and type 2 was analyzed. Each EG type within the pair had a similar temperature of onset of expansion of 200–230°C but a large difference of original flake size (100 vs 350 $\mu$m, respectively). One can learn from Figs. 4 and 5 that the flake size effect is dominant. The propellant with EG type 2 exhibited substantially higher burning rate, revealing up to about 60% increase in burning rate for 5% EG, whereas EG type 1 caused a burning rate increase of 20–25% at the most. In EG type 4 (and to some extent in EG type 5) we noticed a significant deviation from the regular trend of monotonically increasing burning rate with increasing EG mass fraction. A high peak of burning rate at mass fraction of 1% was demonstrated (Figs. 7 and 8). This phenomenon is promising; however, because of the irregular behavior, we repeated the experiments of EG type 4 (Fig. 7). It broadened the spread of results around the average, but the trend was not changed. Yet, in our opinion, further investigation is needed before concluding that there is an optimum for high burning rate at some relatively low EG mass fraction.

The second aspect, the temperature of onset of expansion, could be isolated by comparing propellants containing EG flakes of a similar

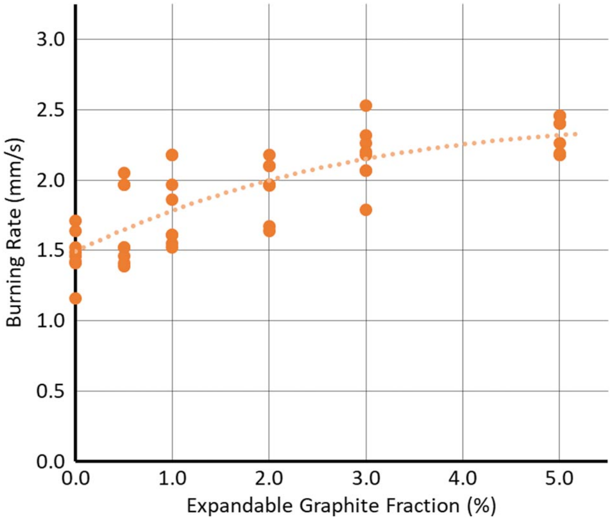


**Fig. 5 Burning rate vs EG mass fraction for an AP-HTPB propellant with an EG type 2 additive.**

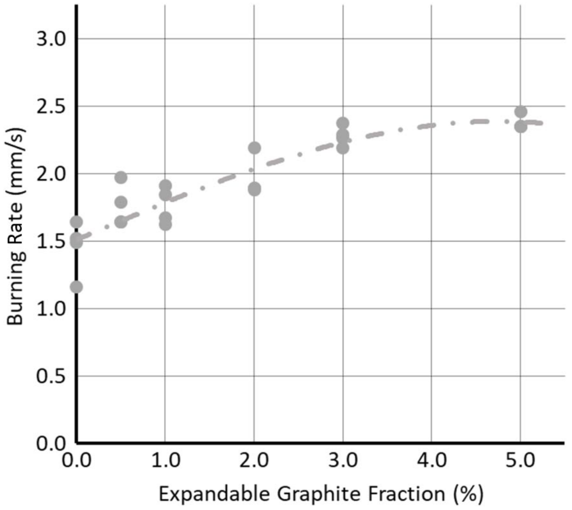


**Fig. 6 Burning rate vs EG mass fraction for an AP-HTPB propellant with an EG type 3 additive.**

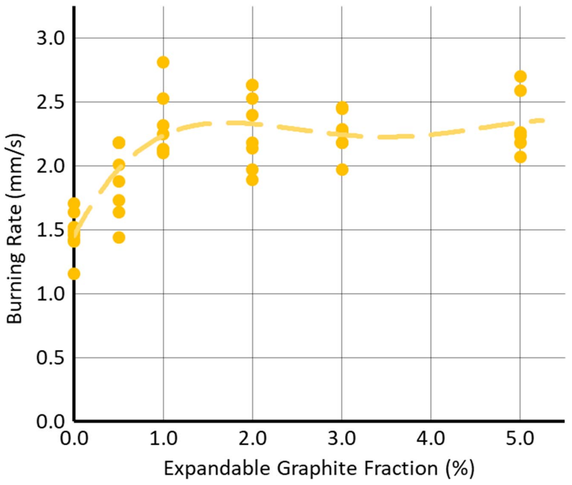


**Fig. 7 Burning rate vs EG mass fraction for an AP-HTPB propellant with an EG type 4 additive.**

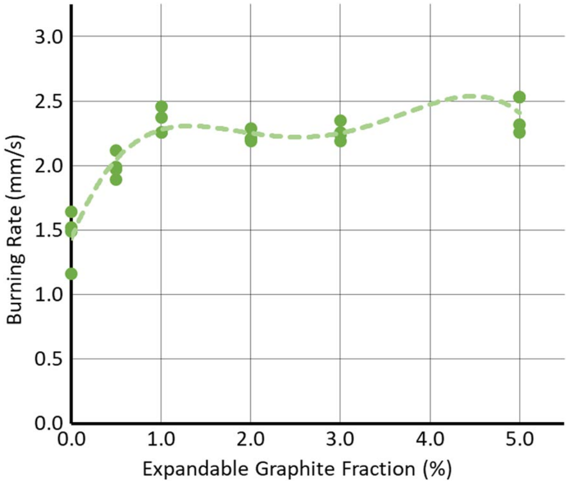


**Fig. 8 Burning rate vs EG mass fraction for an AP-HTPB propellant with an EG type 5 additive.**

size but different temperature of onset of expansion. The best comparison can be between two propellants, both containing EG flakes of 300 $\mu$m size (types 3 and 4), where the former has a temperature of onset of expansion of 150°C and the latter 240°C. The experiments (Figs. 6 and 7, respectively) revealed that both EG types 3 and 4 demonstrated a similar, high increase in burning rate (as high as 60% at 5% EG mass fraction compared to the plain HTPB fuel). However, EG type 3 of the lower temperature of onset of expansion showed a gradual increase of burning rate when increasing its mass fraction, whereas EG type 4 showed a noticeable increase in burning rate already at low EG mass fraction. One may conclude that the EG size effect is more dominant than the influence of the temperature of onset of expansion for the propellant formulations tested.

Figure 9 summarizes the burning rate experiments of all AP-HTPB tests with the five types of EG. One can readily observe that the least effect on the burning rate was due to the EG of the smallest particle size (EG type 1, nominal size 100 $\mu$m). The EG types of the larger particle sizes exhibited substantially greater enhancement of burning rate. By selecting the appropriate EG type and mass fraction, one can have a good new means for burning rate enhancement.

### 2. *AP-Polyester Propellants*

Figures 10–14 exhibit the burning rate of AP-polyester propellants containing a number of EG types over a range of EG mass fractions up to 5%.

Figure 15 summarizes all burning rate tests conducted with AP-polyester propellants over a range of EG mass fractions up to 5%, comparing the influence of the five types of EG. One can see that in contrast to the AP-HTPB propellants, where a noticeable influence of

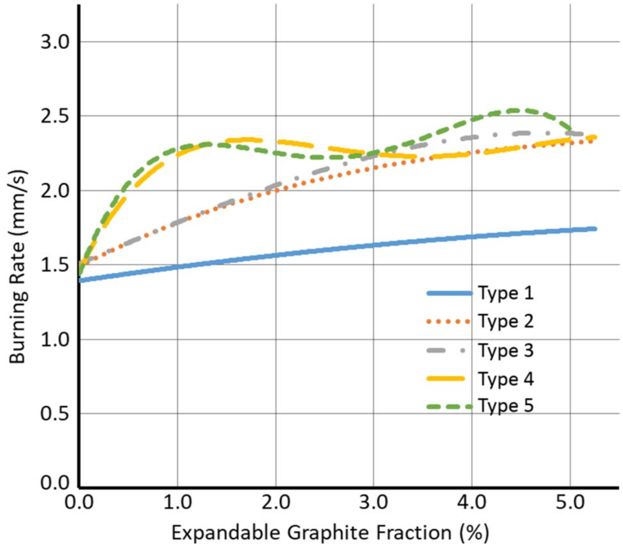


**Fig. 9 Summary of burning rate vs EG mass fraction for AP-HTPB propellants with all types of EG additives.**

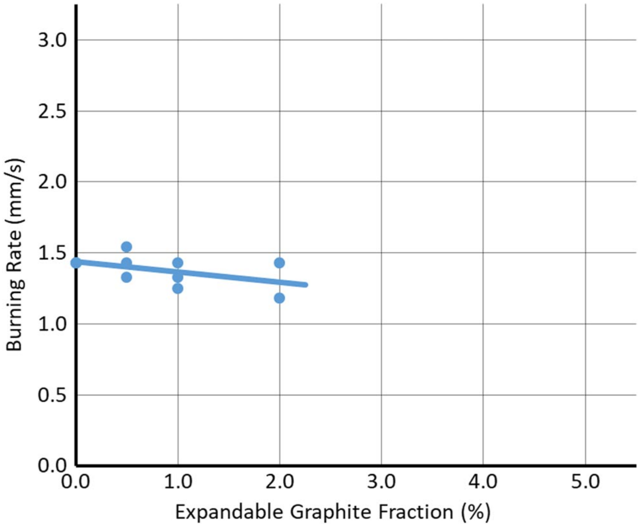


**Fig. 10 Burning rate vs EG mass fraction for an AP-polyester propellant with an EG type 1 additive.**

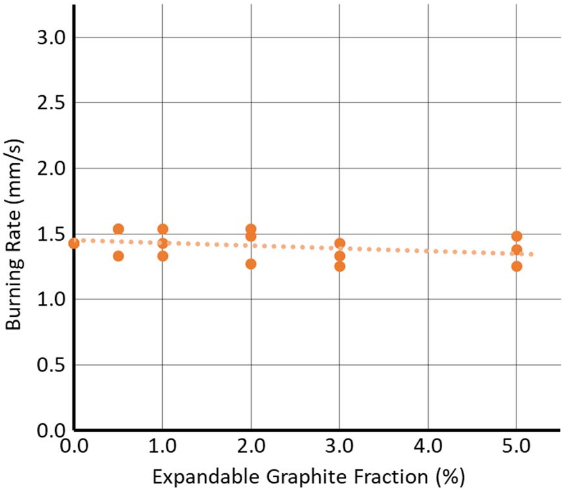


**Fig. 11 Burning rate vs EG mass fraction for an AP-polyester propellant with an EG type 2 additive.**

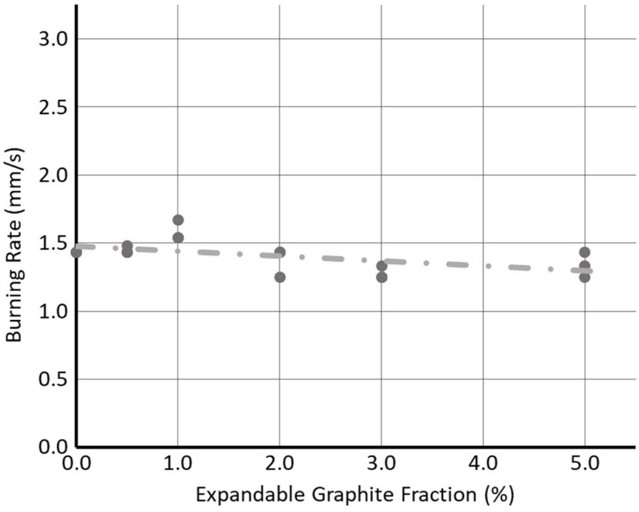


**Fig. 12 Burning rate vs EG mass fraction for an AP-polyester propellant with an EG type 3 additive.**

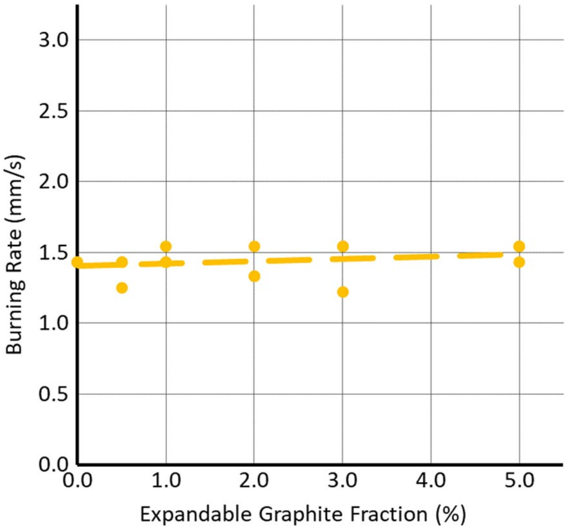


**Fig. 13 Burning rate vs EG mass fraction for an AP-polyester propellant with an EG type 4 additive.**

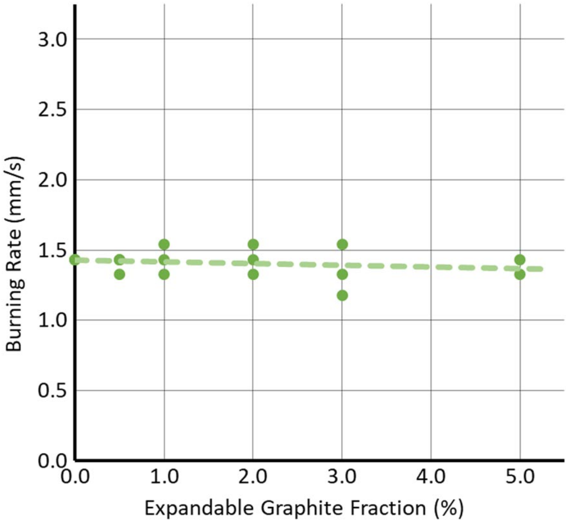


**Fig. 14 Burning rate vs EG mass fraction for an AP-polyester with an EG type 5 additive.**

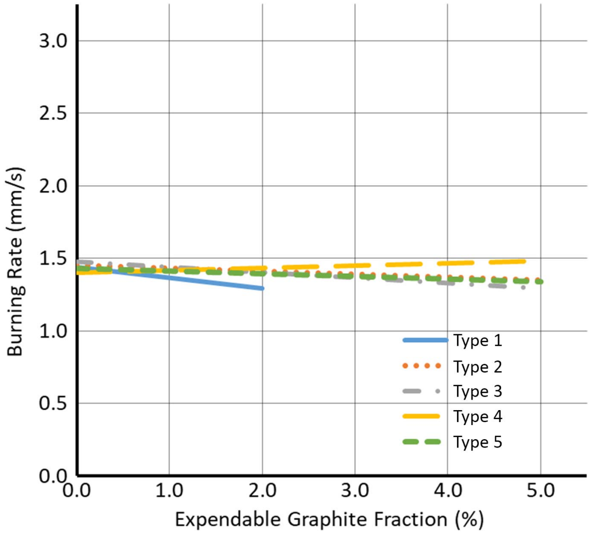
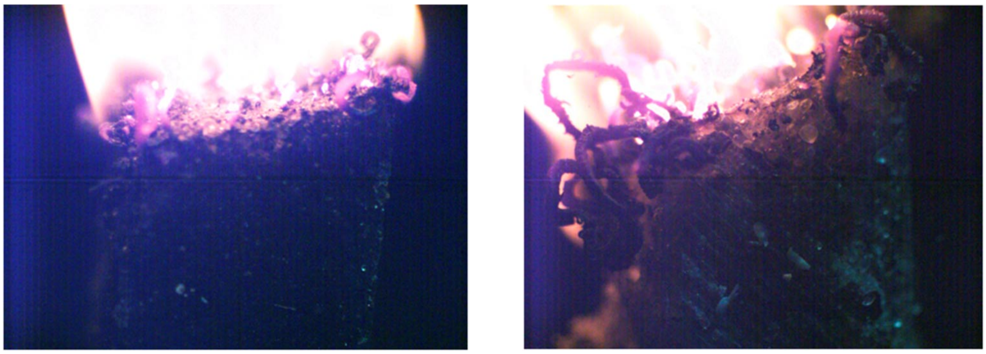


**Fig. 15 Summary of burning rate vs EG mass fraction for AP-polyester propellants with all types of EG additives.**

**Fig. 16 Quenching process of AP-polyester propellant containing 3% EG type 1 (smallest flakes, 100 $\mu$m). Actual picture width is 12.5 mm.**

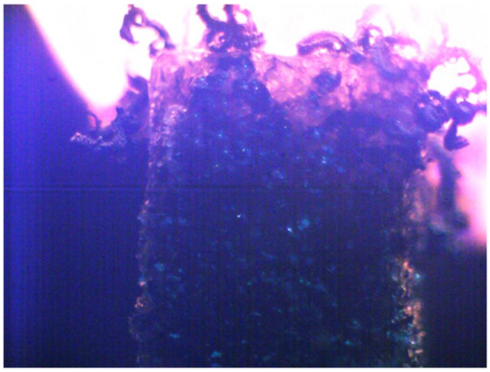
the EG additives was observed, the EG additives had only little effect on the burning rate of AP-polyester propellants. The behavior was very similar for all EG types, and the burning rate remained almost identical to that of the plain propellant (and sometimes even somewhat lower). Furthermore, the effect of EG type 1 (the smallest flake size) was negative and retarding (see also [5]). In EG mass fractions of 3% and above, the propellant ignited but could not sustain combustion for more than few seconds. See the quenching process of the propellant with 3% of EG type 1 in Fig. 16. The other EG types did enable combustion also with 5% EG. Apparently, the main factor was the flake size.

Taking high-speed (2600 pps) video movies of the burning propellant surface at atmospheric pressure, we noticed that larger original EG flakes produced larger and longer final strings. This phenomenon was common for both the AP-HTPB and the AP-polyester propellants. However, the EG strings' presence and activity on the surface was less intense for the AP-polyester than for the AP-HTPB propellants. For demonstration, Fig. 17 presents images from the high-speed movies of the burning surface of AP-HTPB propellants, and Fig. 18 shows similar images for AP-polyester propellants, both containing 2% of all five EG types under consideration.



AP-HTPB + EG1

AP-HTPB + EG2

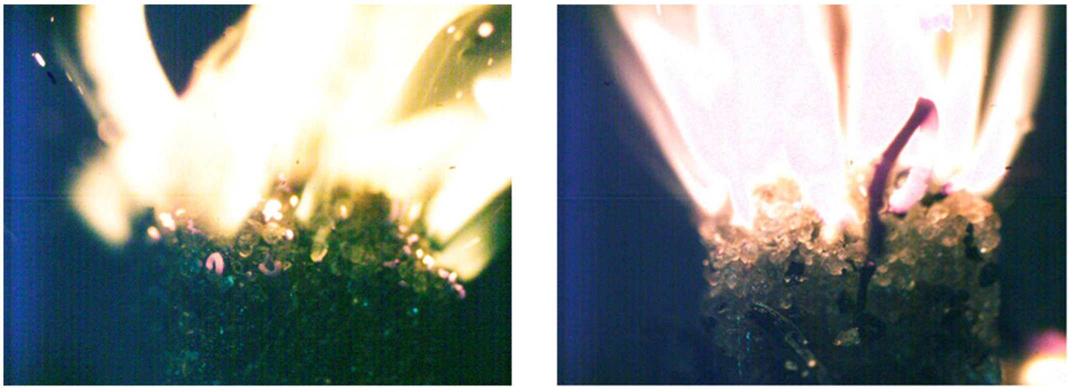


AP-HTPB + EG3

AP-HTPB + EG4

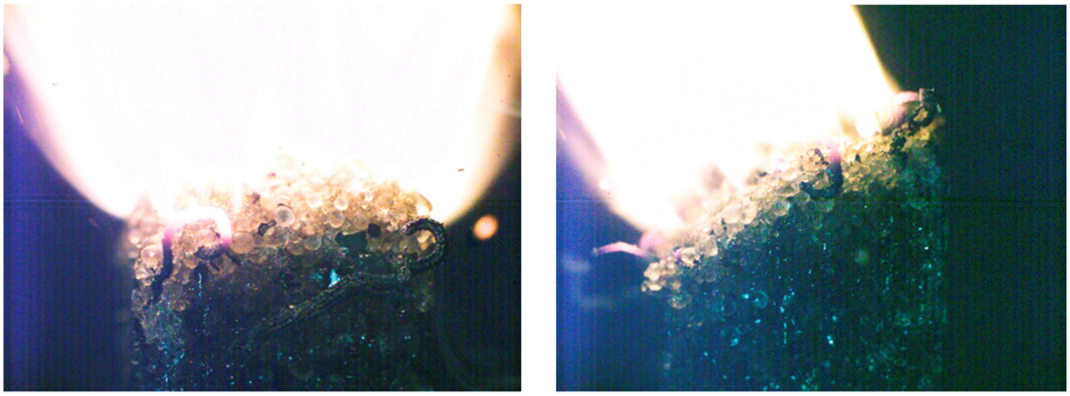
AP-HTPB + EG5

**Fig. 17 Images of the burning surface of AP-HTPB propellants containing 2% of different EG types taken from high-speed (2600 pps) video movies. The actual width of the field of view is 12.5 mm. The photographs reveal that larger initial EG flakes form larger elongated EG strings.**



AP-Polyester + EG1 AP-Polyester + EG2

AP-Polyester + EG3



AP-Polyester + EG4 AP-Polyester + EG5

**Fig. 18 Images of the burning surface of AP-polyester propellants containing 2% of different EG types taken from high-speed (2600 pps) video movies. The actual width of the field of view is 12.5 mm. Like in the case of AP-HTPB propellants, larger initial EG flakes resulted in longer strings. However, the EG strings' presence and activity on the surface was less intense than for AP-HTPB propellants shown in Fig. 17.**

## IV. Conclusions

In previous publications, we studied various aspects related to the effect of EG additives. Among them were the effect of EG on the burning rate of the fuels in hybrid propulsion, the surface phenomena of EG-containing polyester fuel subjected to flame, and the thermal properties of EG flakes and polymeric fuels containing EG. This research broadens the investigation on the surface phenomena of fuels subjected to flame at atmospheric conditions, with relation to the effect of EG on the burning rate of the fuels in hybrid propulsion. Three fuels (HTPB, polyester, and paraffin wax) containing five types of EG flakes were studied. The research consisted of high-speed video movies (700 pps) of the surface. The main conclusions are as follows: in the case of HTPB and polyester fuels, EG strings form from the embedded flakes, protrude, and grow above the surface. Their apparent size is larger for larger original EG flake types. Polyester fuels occasionally show what seems to be break of small fuel pieces at the site of EG string protrusion. While such phenomenon may increase the burning rate, it may not be the main reason for doubling the burning rate in hybrid combustion as was observed previously and attributed to increased heat transfer via conduction through the EG strings. HTPB exhibited indication for occasional local surface melting. Such phenomenon, together with the more flexible surface behavior, may reduce the EG heat transfer effect, supporting the smaller effect in hybrid combustion compared to the case of polyester. Paraffin wax exhibited very different surface behavior. It formed a relatively thick melt layer containing many original EG flakes. The flakes did not expand and did not protrude from the surface; hence, their effectiveness in conducting heat from the hot surrounding to the bulk was limited, supporting the small effect on regression rate enhancement in hybrid firing tests.

The study on the influence of various types and fractions of EG additives on two composite propellant formulations, AP-HTPB and AP-polyester, resulted in original and very significant findings.

Regarding the AP-polyester composite propellants, it was demonstrated that the addition of any type and fraction of EG did not increase burning rate. Practically, the burning rate with EG additive was more or less the same as that of the plain propellant. Furthermore, the EG type 1 additive with the smallest original flakes (nominally, 100 μm) exhibited a retarding effect, slightly decreasing the burning rate at small EG mass fractions, and avoiding sustained combustion for EG fraction of 3% and above.

On the other hand, the AP-HTPB propellants exhibited a noticeable effect on the burning rate due to EG additives. Basically, all EG types showed a similar trend of increasing the propellant burning rate with increasing the EG mass fraction. Nevertheless, we could notice clear differences. The larger EG flakes demonstrated more prominent enhancement of the burning rate (up to 60% and more for 5% EG). The effect of the EG type 1 with the smallest particle size (100 $\mu$m) was substantially smaller (up to 20–25% increase in burning rate). There was no clear effect of the onset of the temperature of expansion of EG in the case of the propellants tested. Practically, in our experiments the effect of EG flake size was more dominant than that of the temperature of onset of expansion.

To summarize, this research concludes that expandable graphite can be a significant burning rate enhancer in both hybrid and solid motors, thus enabling a substantial increase of motor thrust when matching the appropriate EG type to the specific fuels and propellants.

## Acknowledgment

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Propellants, Explosives, Pyrotechnics

RESEARCH ARTICLE

# Thermal characteristics of expandable graphite as a burning rate enhancer in hybrid propulsion

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**Abstract**

Hybrid propulsion, consisting of solid fuel and liquid oxidizer, exhibits major advantage regarding safety, development costs, energetic performance, and controllability. Hence, it has been considered for space and other propulsion programs. One of the characteristic features of hybrid motors, that may be of major disadvantage, is their relatively low thrust due to the characteristic low regression rate of the typical polymeric solid fuels. This research group had revealed that a small fraction of an expandable graphite (EG) additive could double the burning rate and thrust of hybrid motors. EG is an intercalated form of graphite, elongating and swelling, getting a worm-like string shape at elevated temperatures. In an earlier work it was hypothesized that enhanced heat transfer via conduction through the EG strings protruding from the hot surface, is a significant parameter increasing the burning rate. In the present investigation, thermal analysis revealed that the ignition temperature of polyester fuel containing 5 wt% of EG, is substantially lower than that of the pure polymer, which may promote higher burning rate as well. High-speed photography of the surface of EG-containing solid fuels as well as that of individual EG particles during controlled heating, demonstrated the dynamic behavior resulting in the formation of EG strings longer by an order of magnitude compared to the original particles. The different phenomena were related to the observation of enhanced burning rate.

**KEYWORDS**
burning rate, burning rate enhancer, expandable graphite, hybrid propulsion

## 1 | INTRODUCTION

Hybrid propulsion has been considered for in-space and space-launch propulsion, as well as for other missions because of special advantages compared to liquid and solid propulsion. One of the main advantages is safety, resulting from the separation between the solid fuel and liquid (or gaseous) oxidizer, leading as well to lower development times and costs. Other advantages are higher energetic performance (specific impulse), thrust control, shutdown, and re-ignition capabilities (in contrast to solid motors); and a simpler control system because of the use of a single liquid system as well as the insulation of the wall by the internal-burning solid fuel (compared to liquid engines) [1]. For those reasons hybrid propulsion has been considered for future space tourism vehicles (see, for instance, the launching of SpaceShipOne in 2004 as the first manned private space flight [2]). One of the characteristic features of hybrid motors, that may be of major disadvantage, is their relatively low thrust due to the low regression (burning) rate of the common polymeric solid fuels (typically, an order of magnitude lower than that of solid propellants). Karabeyoglu et al. [3], Karabeyoglu and Cantwell [4], and collaborators proposed and investigated the use of paraffin wax as a liquefying, high regression rate fuel for overcoming the low thrust feature of hybrid motors. Investigation and modeling of paraffin wax combustion with different oxidizers have been conducted at our lab in the Technion as well (Weinstein and Gany [5], Sisi and Gany [6], and Ben-Basat and Gany [7]).

Paraffin fuel exhibits a negative feature concerning its strength and low softening/melting temperature. In contrast to polymeric fuel grains, which demonstrate good mechanical properties, resistance to thermal and pressure shocks, and minor effect by external temperature, paraffin wax has relatively poor mechanical properties, may soften when exposed to high external temperature, and can be subjected to creep due to temperature and acceleration. It is thus of great significance to find ways for increasing regression rate (and hence, thrust) in hybrid propulsion without deteriorating the mechanical properties of the fuel. In general, the common catalysts used in solid propellants for increasing burning rate, are of only minor effect in hybrid combustion. The reason is that in hybrid combustion, forced convection heat transfer from the flame to the condensed fuel dominates the regression rate.

Elanjical and Gany [8] hypothesized that expandable graphite (EG) additive may serve as a burning rate enhancer in hybrid propulsion. Expandable graphite is an intercalated form of graphite, where a small fraction of guest molecules (typically sulfur or nitrogen compounds) is inserted between the layers of the graphite crystal. EG appears in the form of small particles/flakes (characteristic size 100–500 μm). At elevated temperatures (typically, between 140 and 300 °C, depending on the preparation method), these particles elongate and swell, forming worm-like strings/fibers many folds longer than the original particles. Because of the substantially greater heat conductivity of graphite compared to polymeric materials, EG is a heat transfer promoter [9]. It is used in phase change materials (PCMs) to increase their thermal conductivity. Different properties of EG mixed within a plastic or wax matrix including flammability, conductivity, and occasionally flame retarding, have been investigated in [10–12]. In an earlier investigation, our research group interpreted the increase in regression rate in hybrid combustion as resulting from heat conduction through the EG strings from the hot gases to the fuel bulk, when protruding over the burning surface [8]. To the best of our knowledge, besides our research group there has not been application of EG for enhancement of fuel or propellant burning rate in propulsion system. Nevertheless, Hahma [13] investigated the addition of EG to pressed pyrotechnic compositions, with the main goal to increase light emission. He argued that the reason for increased burning and light emission rates was crumbling of the burning surface due to EG swelling.

Muller and Gany [14–15] exposed polyester slabs containing expandable graphite (original nominal particle/flake size about 100 μm) to a burner flame at ambient conditions. They used high-speed photography (1000 pictures per second), revealing the penetration of elongated EG strings from the fuel bulk to the flowing hot gases. The films showed the particles growing process over the surface attaining an average length of 1–1.2 mm within a typical time of a few tens of ms.

The objective of this work was to investigate the thermal characteristics of expandable graphite particles/flakes and to relate them to the effect of burning rate enhancement observed in hybrid combustion.

## 2 | EXPERIMENTAL PROCEDURE AND INSTRUMENTATION

Investigation of the thermal characteristics included several efforts: first, scanning electron microscope (SEM) imaging of several original EG flake types having different activation (onset of expansion) temperatures (between 150 and 240 °C) and different initial sizes (nominally from 100 to 350 μm) according to the supplier data; in certain cases, atomic composition analysis was conducted as well. Second, combined thermogravimetric and heat flow analysis (TGA/Heat Flow) to study the behaviour of EG powders in both inert and oxidizing atmospheres under controlled, slow heating. Then, a similar analysis of polymeric fuels with and without EG additives. Further, high-speed photography of EG powders and individual particles subjected to gradual temperature elevation, revealing the process of expansion and elongation during the increase of temperature.

### 2.1 | Expandable graphite types

The EG flakes/particles were obtained from two commercial suppliers: Graphit Kropfmühl (GK) GmbH, Germany, hereafter indicated as GK; and NGS Trading and Consulting GmbH (Germany), hereafter indicated as NGS. The EG types analyzed, as specified by the provider, were:

1. ES 100 C10 of Graphit Kropfmühl (GK) GmbH, Germany, nominal flake size 100 μm, onset of expansion 200–230 °C (considered normal temperature range).
2. ES 350 F5 of Graphit Kropfmühl (GK) GmbH, Germany, nominal flake size 350 μm, onset of expansion 200–230 °C (normal range).
3. Ex 95 50 250 RZ of NGS Trading and Consulting GmbH (Germany), nominal flake size 300 μm, onset of expansion 150 °C (low range).
4. Ex 50 95 200 YO of NGS Trading and Consulting GmbH (Germany), nominal flake size 300 μm, onset of expansion 240 °C (high range).
5. Ex 80 92 200 YO of NGS Trading and Consulting GmbH (Germany), nominal flake size 177 μm, onset of expansion 240 °C (high range).

## 3 | EXPERIMENTAL RESULTS

### 3.1 | SEM Imaging and elemental composition

Scanning electron microscope images were obtained using Quanta 200 FEI E-SEM instrument. This device could also provide the chemical composition, detecting the elements via energy dispersive spectroscopy (EDS), as shown below. Figure 1 presents a SEM image of EG type ES 100 C10 of GK (nominal size 100 μm). One can observe particles/flakes whose surface dimensions are larger than the nominal size. It is assumed that the size is determined by the mesh intervals that the particles can pass through, hence, particles with uneven dimensions can pass according to their narrower dimension.

Figure 2 shows atom analysis data of this composition. The major elements detected (in atomic %): carbon (C) 91.7, oxygen (O) 7.3, sulphur (S) 0.9. It complies with the fact that one of the major guest materials in the preparation of EG is sulphuric acid.

Figure 3 presents a SEM image of EG type ES 350 F5 of GK (nominal size 350 μm). It is noted that the flake thickness of this sample is typically in the range of 40–70 μm.

Figure 4 presents a SEM image of EG type Ex 95 50 250 RZ of NGS (nominal size 300 μm and specifically low activation temperature of 150 °C).

Figure 5 presents a SEM image of EG type Ex 50 95 200 YO of NGS (nominal size 300 μm). In this case, an element analysis was conducted as well, displaying the results in Figure 6. The analysis revealed the atomic % of 3 major elements: carbon (C) 93.7, oxygen (O) 5.3, and sulphur (S) 1.0. These results are similar to those of EG

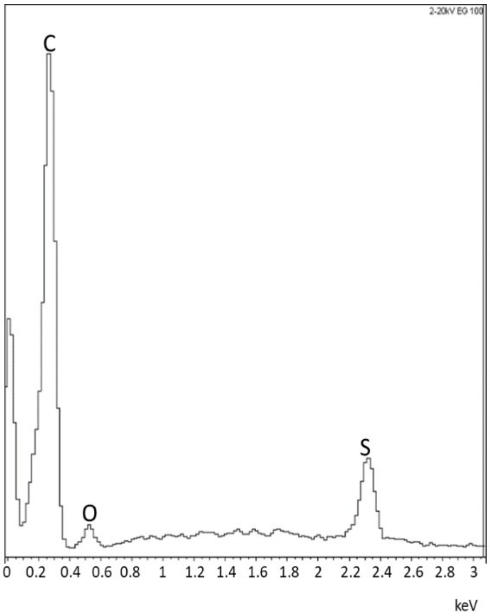

FIGURE 2 Composition of EG type ES 100 C10 of GK, (relative atomic % of the major elements).

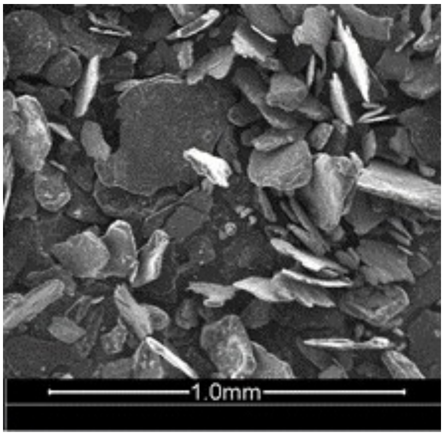

FIGURE 1 EG type ES 100 C10 of GK, nominal size 100 μm.

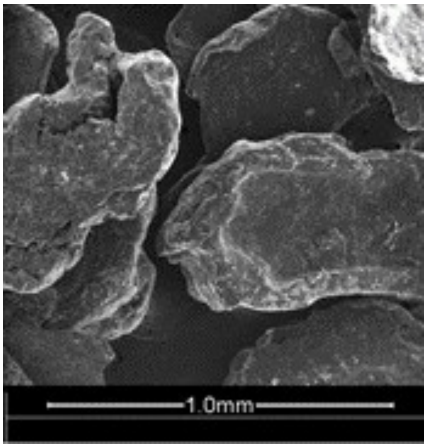

FIGURE 3 EG type ES 350 F5 of GK, nominal size 350 μm.

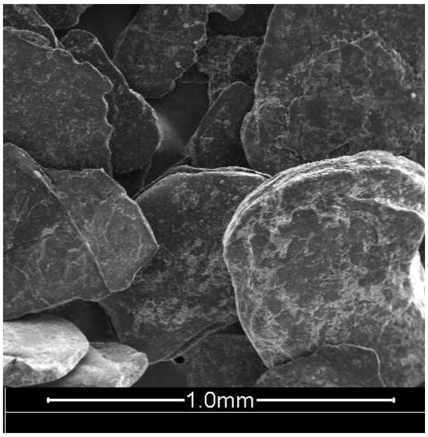

**FIGURE 4** EG type Ex 95 50 250 RZ of NGS, nominal size 300 μm.

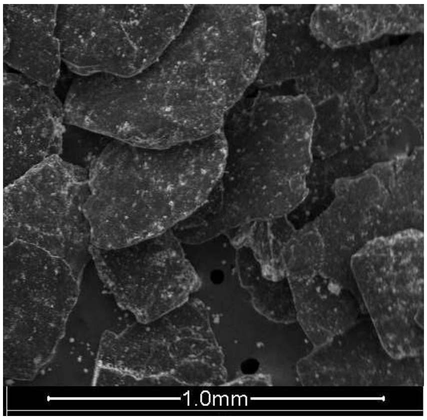

**FIGURE 5** EG type Ex 50 95 200 YO of NGS, nominal size 300 μm.

sample ES 100 C10 of GK (shown in Figure 2) and are representative of a common EG composition.

Figure 7 presents a SEM image of EG type Ex 80 92 200 YO of NGS. It has the same high activation temperature (240 °C) as Ex 50 95 200 YO (Figure 5), however type Ex 80 92 200 YO has a smaller nominal particle size (177 μm) than that of Ex 50 95 200 YO (300 μm).

Figure 8 shows the atomic % of the major elements in the sample: carbon (C) 94.4, oxygen (O) 4.3, and sulphur (S) 1.3. Here, as well, the composition is generally like that of the previous cases shown in Figures 2 and 6 (approximately ± 2% with regard to the carbon (C)).

## 3.2 | Thermogravimetric (TGA) analysis of EG powders

Thermogravimetric (TGA) analysis with temperature elevation at a rate of 10 °C/min in inert (nitrogen) atmosphere was conducted using a TGA/DSC3 + Star System, Mettler Toledo device for selected EG types, to determine the temperature of onset of mass loss indicating the initial EG swelling and elongation, as well as the EG mass loss at further temperature increase. Heat flow (DTA analysis) is not shown, because in this case, its energy effect on pyrolysis or combustion system is minor.

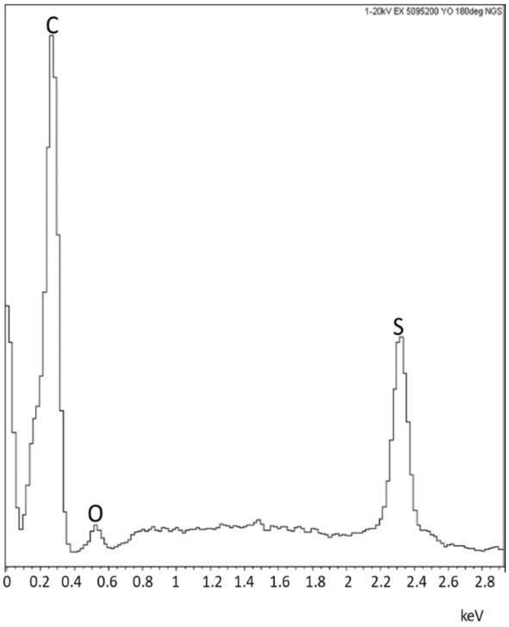

**FIGURE 6** Composition of EG type Ex 50 95 200 YO of NGS, (relative atomic % of the major elements).

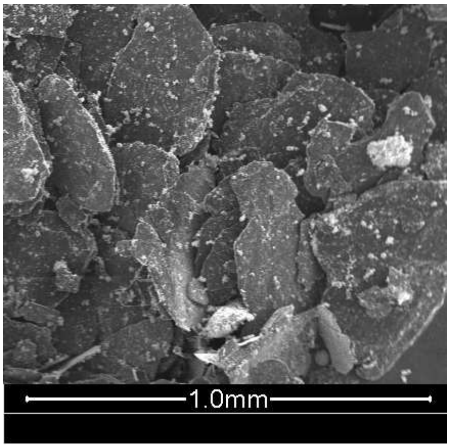

**FIGURE 7** EG type Ex 80 92 200 YO of NGS, nominal size 177 μm.

Figure 9 presents the TGA plot determined for EG type ES 100 C10 of GK. One can see that mass loss at a low rate starts before 200 °C and accelerates at about 250 °C (in correspondence with the provider data of 200–230 °C). An inflection point is observed at about 270 °C. The overall mass loss up to 400 °C is about 10 %. This is a result of gas generation which causes the EG to expand and swell.

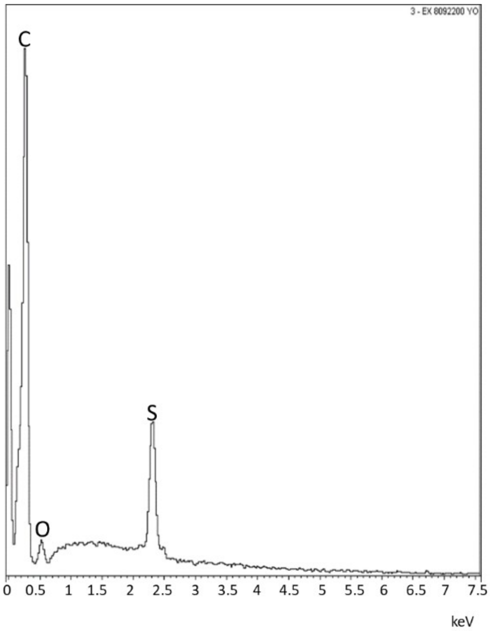

**FIGURE 8** Composition of EG type Ex 80 92 200 YO of NGS, (relative atomic % of the major elements).

Figure 10 presents the TGA plot for EG type Ex 95 50 250 RZ of NGS. This EG type is characterized by the provider as one with a low activation temperature (150 °C). According to the TGA data, some mass loss can be observed at temperatures even lower than 100 °C. However, an accelerated mass loss occurs in the range of 160–170 °C.

## 3.3 | Thermal effect on polyester fuel decomposition and ignition

Thermogravimetric / Heat Flow analysis was conducted on polyester fuel for plain material and for material with an EG additive, using Setaram Instrumentation Temperature Analyzer LABSYS evo STA (simultaneous TGA/DTA thermal analysis). Tests were done both in inert atmosphere (argon) and in oxygen, showing different behavior of the polymeric fuel and revealing the specific effect of EG additives.

Figure 11 presents the mass loss and heat flow during heating of polyester in argon at a rate of 10 °C/min. One

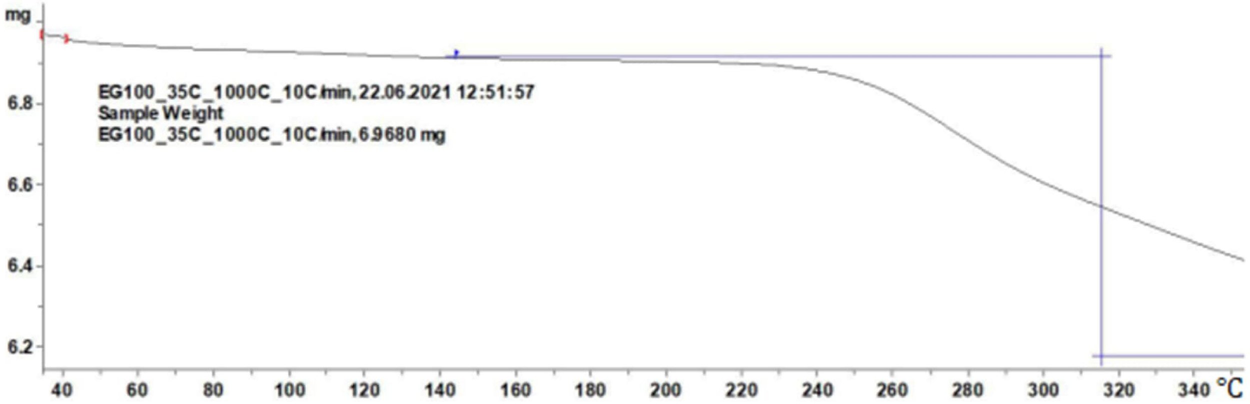

**FIGURE 9** Mass loss during heating at 10 °C/min in nitrogen atmosphere of an EG type ES 100 C10 of GK using Mettler TGA device.

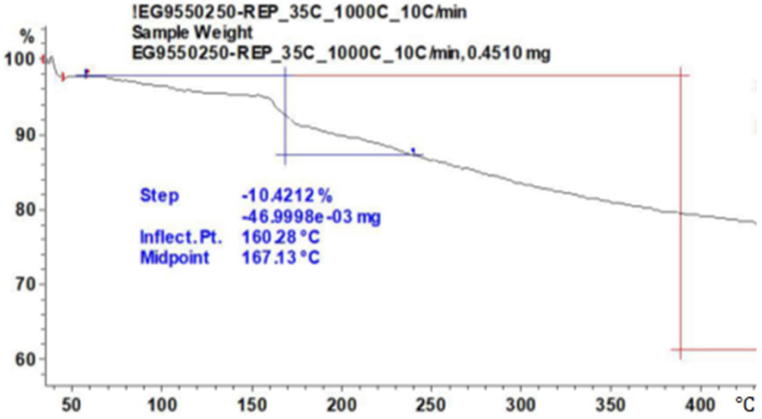

**FIGURE 10** Mass loss during heating at 10 °C/min in nitrogen atmosphere of an EG type Ex 95 50 250 RZ of NGS using Mettler TGA device.

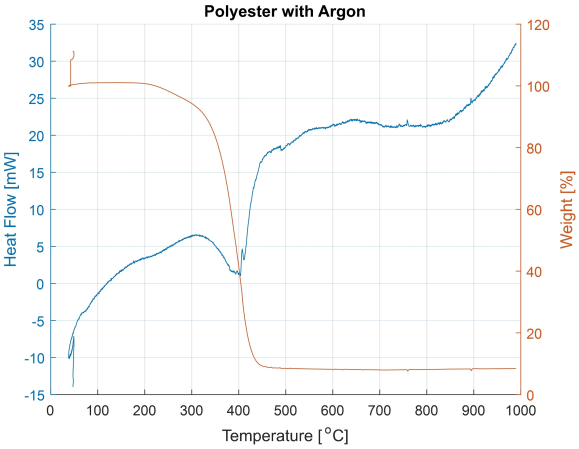

**FIGURE 11** Mass loss and heat flow during controlled heating at 10 °C/min of plain polyester in argon, showing the endothermic gasification between approximately 300 and 400 °C.

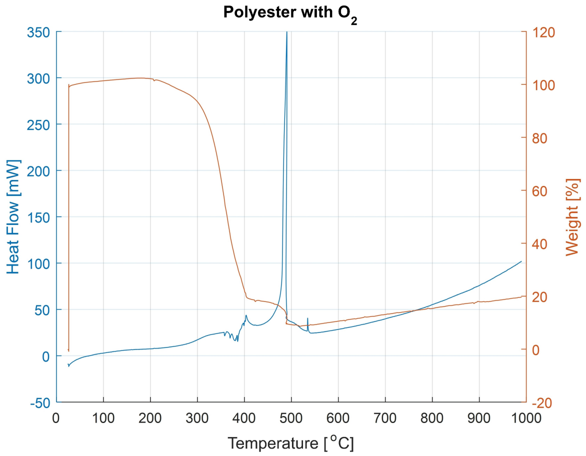

**FIGURE 12** Mass loss and heat flow during controlled heating at 10 °C/min of plain polyester in oxygen, showing the endothermic gasification similarly to the behaviour in argon, and an extensive reaction (ignition) approximately at a 100 °C higher temperature.

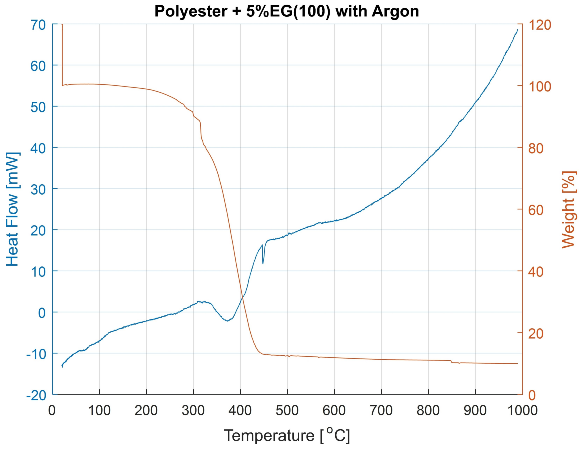

**FIGURE 13** Mass loss and heat flow during controlled heating at 10 °C/min of polyester containing 5 wt% EG in argon, revealing the same behavior as plain polyester.

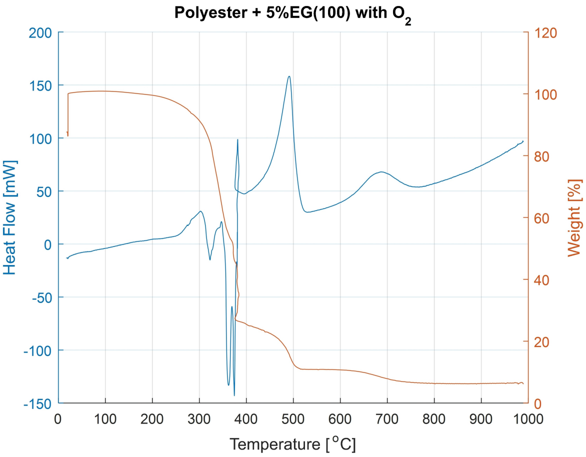

**FIGURE 14** Mass loss and heat flow during controlled heating at 10 °C/min of polyester containing 5 wt% EG in oxygen, revealing a steep mass loss and endothermic decomposition process at a lower temperature followed by an immediate violent exothermic reaction (ignition).

can observe the beginning of mass loss around 300 °C with a sharp slope having a midpoint at about 380 °C. The mass loss process results from endothermic gasification of the polyester, as indicated by the heat flow curve. This analysis was repeated for polyester in oxygen atmosphere (Figure 12). The mass loss curve looks similar. However, about 100 degrees above the mid mass loss process, a very sharp peak of heat release occurs, indicating ignition of the decomposition gases. Conducting the same test for polyester containing 5 wt% of EG type ES 100 C10 of GK in argon (Figure 13), we have seen practically no difference compared to the case with no EG in inert atmosphere (Figure 11). However, when conducting the test in oxygen (Figure 14), the mass loss curve was shifted to a lower temperature (mid-point at about 350°C) and became very steep, as is reflected by a strong endothermic peak; then a violent reaction started immediately after, at about 100 degrees lower than in the case of no EG. This fact may be one of the factors promoting a higher regression rate in hybrid combustion when adding EG to a polyester fuel.

## 3.4 | High-Speed photography of EG particles/flakes during heating

Visualization and measurement of individual EG particles response to heating has been conducted using a special device. A 2-mm wide, 60 mm long tape made of Kanthal (a high-temperature iron / chromium /

aluminium alloy) was placed between two supporting blocks connected to an electric power source. Passing controlled current through the metal tape would cause an increase in temperature and could also be planned for a predetermined final temperature. Expandable graphite particles placed on the tape would heat-up to the tape temperature. Temperature recording by a Chromel-Alumel thermocouple (TC) attached to the tape at the vicinity of the particles could give a rough estimate because of the relatively slow response of the TC compared to the rate of temperature increase. Simultaneous high-speed motion pictures (700 pictures per second) using Phantom V310 camera, were taken during the heating process, revealing the increase in particle size with increasing the temperature from room-temperature to approximately 400 °C. A general photo of the test arrangement is presented in Figure 15. Close-up of the Kanthal tape installation can be seen in Figure 16.

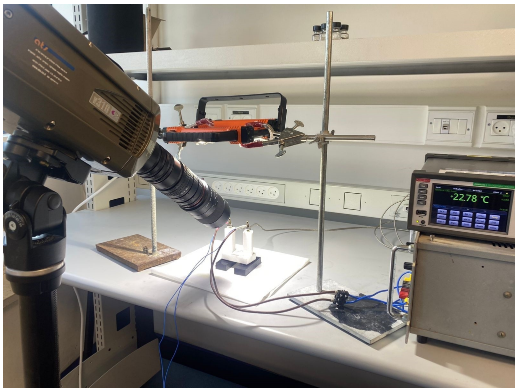

**FIGURE 15** Test arrangement for controlled heating of individual EG particles with simultaneous high-speed photography.

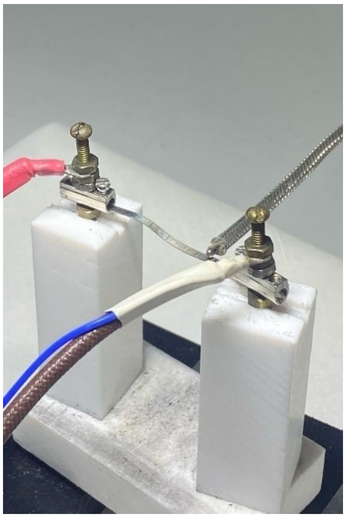

**FIGURE 16** Close-Up of the Kanthal Tape Installation.

Figure 17 presents a series of pictures from a high-speed movie of EG particles type ES 100 C10 of GK, nominal original size 100 μm, during stages of heating. These particles are the smallest ones used, reaching a maximum size of about 1 mm when expanding. Their expansion is moderate compared to that of larger particles. Figure 18 shows a similar series of pictures like Figure 17, but for of EG type EX 50 95 200 YO of NGS. These are particles of much larger original size (nominally 300 μm). Accordingly, they exhibit substantially greater expansion, attaining a length of about 2–3 mm and noticeable swelling.

## 4 | DISCUSSION

The research revealed certain thermal and physical characteristics of expandable graphite. Some of them may be related to previous findings showing that the addition of a small fraction of expandable graphite particles/flakes to polyester fuel in hybrid combustion substantially enhances the regression (burning) rate of the fuel. In an earlier work the elongation of the original EG particles during heating had been hypothesized to add a channel of extensive heat transfer from the hot gases to the fuel bulk via conduction through the EG strings protruding from the surface. This research investigated the changes occurring to the EG particles during heating using several techniques. Thermogravimetric analysis revealed the mass loss vs temperature. High-speed photography of individual particles during heating showed the change in size. One can assume that mass loss is due to gasification of volatile components of the EG, and that the evolving gas causes expansion of the particle. An interesting finding from the themogravimetric analysis was that polyester fuel containing 5 wt% of EG particles, demonstrated accelerated decomposition and a lower ignition temperature by about 100 °C when heated in oxygen atmosphere compared to the case of plain polyester. This may be one of the factors promoting enhanced burning rate when adding EG. One can also see that various types of EG particles exhibit different expansion characteristics and final size, which may affect the burning rate of the fuel. In general, elongated strings formed were longer by an order of magnitude than the original particles/flakes.

Expandable graphite additive was found to be an effective regression rate enhancer for polymeric fuels (mainly polyester) in hybrid motors. This research investigated the thermal behavior of expandable graphite particles/flakes. It revealed that different types of EG have different temperatures of onset of expansion. Most interestingly, mass loss and ignition of polyester during

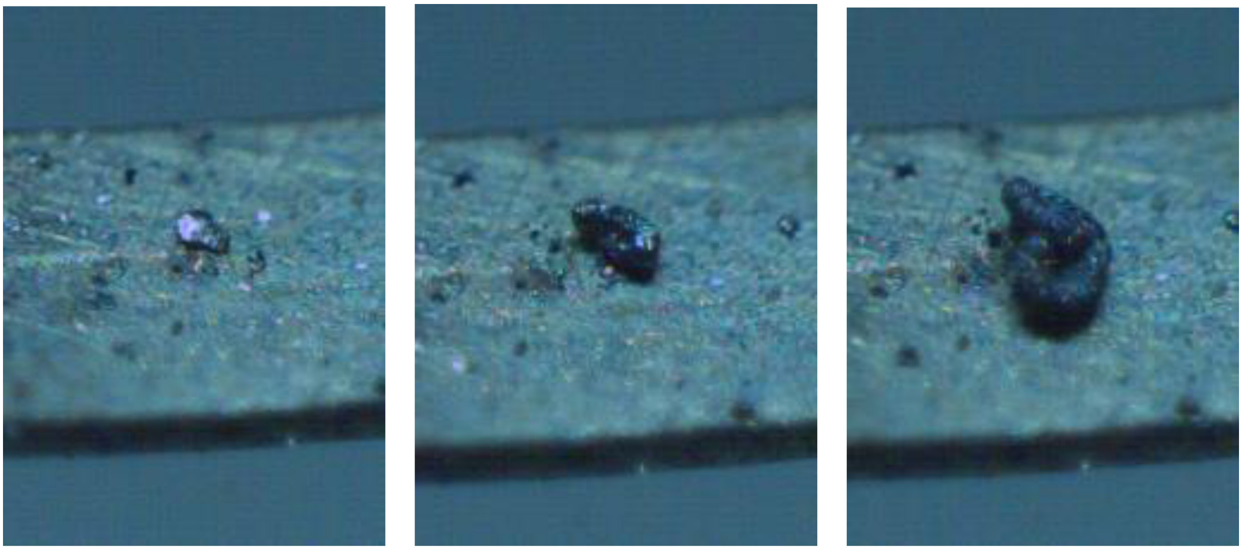

**FIGURE 17** Stages in expansion of EG particles Type ES 100 C10 of GK, nominal size 100 μm from room temperature to approximately 400 °C. The particles are placed on a Kanthal tape, 2 mm wide.

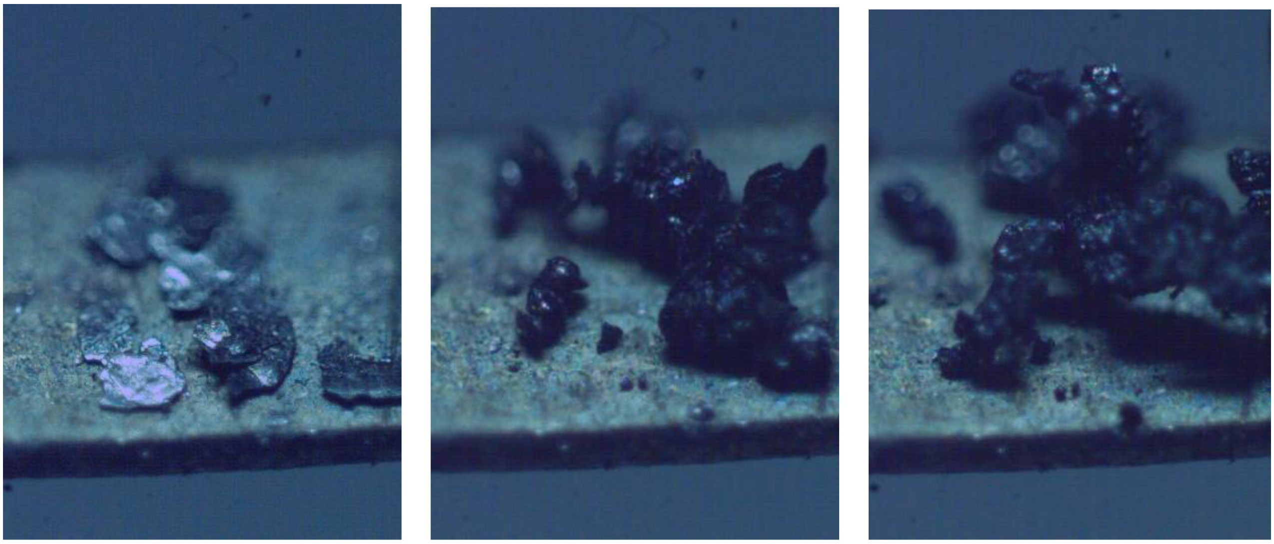

**FIGURE 18** Stages in expansion of EG particles type EX 50 95 200 YO of NGS, nominal size 300 μm, from room temperature to approximately 400 °C. The particles are placed on a Kanthal tape, 2 mm wide.

TGA analysis in oxygen seems to be noticeably promoted by the inclusion of 5 wt% EG within the polymeric matrix. This phenomenon adds an aspect correlating with the overall effect of EG additive on enhancement of regression rate of polyester in hybrid propulsion.

## ACKNOWLEDGMENTS

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## DATA AVAILABILITY STATEMENT

Data are mostly specified in the manuscript. Any additional data are available on request by the author, whereas certain data are available in the open literature.

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## 3 CONSIDERAÇÕES FINAIS

Os estudos realizados permitem concluir, de forma integrada, que o grafite expandido se consolida como um aditivo promissor para controle e aumento da taxa de queima em sistemas de propulsão híbrida e em propelentes sólidos, desde que respeitadas as particularidades de cada matriz combustível. Em combustíveis poliméricos para motores híbridos, especialmente poliéster, pequenas frações mássicas de EG, de 1 a 5%, levam ao aumento de até duas vezes na taxa de regressão, sem prejuízo significativo no desempenho termodinâmico e preservando boas propriedades mecânicas do combustível. Já em propelentes sólidos AP-HTPB, o EG mostra potencial de elevar a taxa de queima em 60% ou mais, ao passo que em propulsores AP-poliéster o aditivo pode atuar de forma neutra ou até prejudicial à combustão em certas condições. Esses resultados reforçam a ideia central de que a eficácia do grafite expandido depende da combinação específica entre tipo de EG e formulação do combustível ou propelente.

O primeiro estudo, focado no efeito do grafite expandido sobre combustíveis sólidos para propulsão híbrida e em propelente AP-poliéster, teve o papel de demonstrar experimentalmente que a inclusão de 5% em massa de EG em combustível poliéster pode duplicar a taxa de regressão. Com visualização clara de fibras milimétricas de EG, foi possível observar a projeção no escoamento gasoso e evidenciar o aumento da transferência de calor por condução para o interior do combustível. Em contraste, o mesmo aditivo na mesma faixa de concentração levou à redução da taxa de queima e até à extinção da chama em tiras de propelente 75% AP e 25% poliéster em pressão atmosférica. Isso indica que o acúmulo de fibras na superfície pode interferir negativamente no fluxo de calor e na difusão dos reagentes. Esse trabalho estabelece, portanto, a prova de conceito do uso de EG como intensificador de regressão em combustíveis de motores híbridos e, ao mesmo tempo, evidencia limites importantes para sua aplicação direta em determinados propelentes sólidos.

O segundo estudo amplia o escopo ao investigar diferentes tipos comerciais de EG, variando tamanho de floco e faixa de temperatura de expansão, em diversas matrizes poliméricas e em propelentes AP-polímero. Na propulsão híbrida, confirma-se o ganho mais expressivo em combustíveis poliéster, um efeito moderado em HTPB e praticamente nulo em parafina, reforçando a influência do estado físico da camada superficial (sólida ou líquida) sobre a capacidade das fibras de EG se expandirem e se projetarem no escoamento. Em propelentes AP-HTPB, o estudo evidencia um aumento sistemático da taxa de queima com a fração mássica de EG, com destaque para flocos maiores de aproximadamente 350 μm, que levam a incrementos da ordem de 60% ou mais em 5% de aditivo, enquanto flocos de aproximadamente 100 μm apresentam ganho bem inferior. Já em AP-poliéster, o EG não aumenta a taxa de queima e pode até dificultar a sustentação da chama em teores mais altos. Em conjunto, esses resultados sustentam a conclusão de que o tamanho de partícula de EG é um parâmetro dominante, mais relevante que a temperatura de início de expansão, e que o aditivo pode ser explorado como ferramenta de ajuste fino de empuxo em motores híbridos e sólidos, desde que cuidadosamente agregado à matriz adequada.

O terceiro estudo estuda em detalhe as características térmicas e físicas de diferentes tipos de grafite expandido e sua interação com o combustível poliéster. As análises TGA/DSc em atmosferas inerte e oxidante, combinadas com microscopia eletrônica de varredura e filmagens de alta velocidade de partículas individuais durante o aquecimento, mostram que os diferentes EGs apresentam faixas distintas de temperatura de início de expansão (aproximadamente 150 a 240 graus Celsius) e diferentes graus de elongação, atingindo comprimentos até uma ordem de grandeza ao floco original. Um resultado particularmente relevante é que o poliéster contendo 5% em massa de EG apresenta decomposição acelerada e ignição em atmosfera oxidante em temperaturas cerca de 100 graus Celsius mais baixas do que o polímero puro que oferece uma explicação adicional para a elevação da taxa de regressão observada nos motores híbridos. Esse estudo, portanto, fundamenta fisicamente o mecanismo proposto nos trabalhos anteriores, combinando o papel da condução de calor através das fibras de EG com o efeito de antecipação da decomposição e ignição do polímero.

Para trabalhos futuros, recomenda-se uma investigação sistemática do efeito da pressão e da escala do motor sobre o desempenho de combustíveis e propelentes contendo EG, pois grande parte dos testes foi realizada em condições de pressão atmosférica, no entanto, a resposta em faixas de pressão mais elevadas, típicas de motores operacionais, pode alterar o balanço entre condução, convecção e difusão. É importante também explorar um espaço paramétrico mais amplo de combinação entre tipo de EG (tamanho de floco, composição, temperatura de expansão) e matriz combustível/binder, incluindo outros sistemas além de poliéster, HTPB e parafina, e outros oxidantes além de AP, de modo a identificar formulações que reproduzam os ganhos de taxa de queima observados em combustíveis híbridos. Adicionalmente, mostra-se relevante estudar o efeito da adição de grafite expandido em combustíveis e propelentes sob condições de ensaio que reproduzam a queima em motores de foguete reais, com perfis de pressão, tempo de queima, resfriamento e regime de escoamento similares aos de operação em voo ou em bancos de teste em escala representativa.