EXPLORING ALKALINE PERIODATE SALTS AS ECO-FRIENDLY OXIDIZERS FOR SOLID ROCKET PROPELLANTS

Hristofor Skandaliev[1,2], Vesislava Toteva[1]

[1]University of Chemical Technology and Metallurgy
8 Kliment Ohridski Blvd., Sofia 1797, Bulgaria, vesislava@uctm.edu (V.T.)
[2]Club for aerospace technology "Zodiac"
100 „Tzar Osvoboditel"St., Kyustendil 2500, Bulgaria, fori2ivanov@yahoo.com (H.S.)

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ABSTRACT

The development and experimental characterization of composite solid rocket propellants utilizing alkaline metaperiodates (KIO_4 and $NaIO_4$) as alternative oxidizing agents are presented. The physicochemical, mechanical, and sensitivity properties of these formulations were systematically evaluated. Differential thermal analysis was conducted to investigate high-temperature decomposition behaviour and to identify the dominant reaction mechanisms. Limited ballistic testing, including laboratory-scale ground tests and experimental rocket flights, was conducted to assess the practical feasibility of these systems. Comparative analysis with conventional composite propellant formulations demonstrates that periodate-based systems can achieve functional energetic and ballistic performance within specific application domains, while potentially offering environmental benefits. These findings indicate that alkaline metaperiodates constitute a promising class of oxidizers for environmentally focused energetic material systems.

Keywords: alkaline periodates, "green" rocket propellants, pyrotechnic compositions, thermokinetics, ballistic research.

INTRODUCTION

The growing emphasis on environmental sustainability has driven significant demand for alternative, eco-friendly materials across high-tech sectors, including aerospace, military, and civilian industries. Efforts to replace perchlorates, which are widely used as oxidizers and can account for up to 90 % of the mass in composite propellant formulations, have led to the development of numerous new energy-rich materials over the past two decades [1]. These materials are synthesized using advanced technologies and are often highly sensitive, explosive, and, in some cases, toxic chemical compounds [2 - 4].

In the insistent search for alternative oxidizers, one logical step is to use halogen compounds like perchlorates. Fluorine and its compounds are the strongest known oxidants, but their use is limited due to their high toxicity [5]. Research on the applications of organic and inorganic iodates and periodates remains limited, with relatively few studies published in this area.

Ammonium periodate (NH_4IO_4) contains its own fuel component and is capable of spontaneous combustion, releasing a large amount of energy and gaseous products, but is extremely thermally unstable, decomposing explosively at around 200°C. The reasons for the high sensitivity to mechanical influences and the low threshold of high-temperature decomposition of NH_4IO_4 have been thoroughly investigated by de Rezende et al. [6]. In addition, NH_4IO_4 is classified as a substance harmful to human health. Given these considerations, the commercial application, as well as its incorporation into solid rocket fuels and pyrotechnic compositions, is not recommended [4, 7].

KIO_4 and $NaIO_4$ are both stable alkaline metaperiodate salts; however, in contrast to ammonium periodate, they do not contain an intrinsic fuel component within their molecular structure. These oxysalts of periodic acid are

weakly hygroscopic, with high density and relatively high content of free oxygen. Despite their high molecular weight, they are now being reconsidered for solid rocket propellants due to their lower environmental impact.

A comparative characteristic of the properties of these periodates and other widely used inorganic oxidizers are given in Table 1 [5].

As shown in Table 1, KIO_4 and $NaIO_4$ exhibit significantly higher densities than conventional oxidizers such as ammonium perchlorate and potassium perchlorate. The relatively high molecular mass of iodine-containing decomposition products generally limits the achievable specific impulse, which explains why alkaline periodates cannot directly compete with state-of-the-art oxidizers in high-performance solid rocket propellants.

Nevertheless, when maximum specific impulse is not the dominant design criterion, and factors such as burning rate, density-related performance, or environmental impact prevail, the limitations of alkaline periodates become less restrictive. Accordingly, they may serve as functional oxidizers in environmentally oriented energetic systems.

The literature review shows that at the beginning of the 21st century, there was an increased interest in research into the use of the alkaline metaperiodates KIO_4 and $NaIO_4$ as oxidizers in various pyrotechnic compositions [8]. Most of the developments are aimed at replacing potassium perchlorate and barium nitrate with alkaline periodates as "green" oxidizers in illumination, incendiary [9], and delaying [10] compositions, gas generators [11], nanothermites, etc. [8]. Some solid, energetic composites can also serve as potential biocides [12]. However, published data on the use of alkaline metaperiodates as oxidizers for solid rocket propellants is limited, prompting research to obtain and characterize these environmentally friendly energetic compositions.

The aim of this study is to develop composite solid rocket propellants utilizing alkaline metaperiodate oxidizers, specifically KIO_4 and $NaIO_4$. The research focuses on evaluating these propellants by investigating their primary performance characteristics and assessing their suitability as environmentally friendly alternatives in energetic compositions.

EXPERIMENTAL

Materials and methods

Materials

Eight composite solid propellant formulations, denoted PI-1 to PI-8, were prepared using alkaline metaperiodates as oxidizing agents.

Potassium and sodium metaperiodates (KIO_4 and $NaIO_4$, Sigma - Aldrich, Merck) with a particle size in the range of 50 - 60 μm were used (determined by sieving / optical microscopy). Spherical aluminium powder (< 45 μm, Reade Advanced Materials) was deliberately selected for its favourable rheological behaviour in low-binder formulations, together with its predictable behaviour and reproducible performance. Sulphur was added in selected formulations as a thermal decomposition initiator, while isomalt (ISOMALT ST-PF, BENEO) served both as an auxiliary organic fuel component and as a processing aid. A low-viscosity epoxy resin (EPOLAM 2040) and hardener (EPOLAM 2042) were selected to ensure effective dispersion of solid components and reproducibility of the prepared

Table 1. Basic properties of some inorganic oxidizers.

Oxidizer	Solubility in water, g/100 g H_2O	Density, g cm^{-3}	Oxygen balance, %
KIO_4	0.51	3.618	+ 27.8
$NaIO_4$	14.4	3.865	+ 29.9
$KClO_4$	2.08	2.150	+ 46.2
NH_4ClO_4	20.0	1.950	+ 34.0
KNO_3	31.6	2.109	+ 40.0
$NaNO_3$	91.2	2.257	+ 47.0
NH_4NO_3	212.0	1.725	+ 20.0

propellant samples [13, 14]. In one formulation, a commercially available one-component polyurethane (PU) binder (Technicoll® 8344 1-K PUR) was included for comparative evaluation. Red iron(III) oxide (Fe_2O_3) was used as a combustion catalyst, while activated carbon powder served as a phlegmatizer to reduce sensitivity (Table 2).

The samples are prepared by manually mixing the components, initially homogenizing the epoxy resin and hardener, then adding the powder components (first the metal, then the additives and finally the oxidant). The resulting paste enables straightforward molding into forms of various geometries and dimensions. Curing is completed at 50°C over a period of approximately 6 h. The resulting specimens are cylindrical in shape.

Methods

Density determination

The theoretical density of the investigated propellant compositions was calculated using the PROPEP 3 software, applied for the simulation of thermochemical transformations. The experimental (bulk) density was determined by the conventional mass-to-volume ratio method, in accordance with standard procedures, where the sample mass and geometrical volume were used. The relative density was calculated as the ratio of the experimental to the theoretical density and expressed as a percentage.

The deviation between theoretical and experimental densities indicates residual porosity, while the relative density reflects the degree of compaction and structural uniformity of the samples, in agreement with typical composite solid propellant behaviour [1, 2].

Thermal analysis

To evaluate the propellant formulations, thermal behaviour was assessed using thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) on a Netzsch STA 449-F5 Jupiter. For these analyses, the samples were ground to a fine powder to ensure uniform thermal response. Representative portions of the powder were placed into standard ceramic crucibles and analysed in air, at atmospheric pressure from 20 to 1000°C, with a heating rate of 10°C min^{-1}.

Static firing methodology

To determine chamber pressure under various geometric configurations of the propellant charge and to calculate the corresponding burning rate, a series of static tests was conducted using small rocket motors. Chamber pressure was measured using a WIKA mechanical pressure gauge, EN 837-1 - compliant, accuracy class CL 2.5, with a nominal measuring range of 0 - 100 bar (0 - 10 MPa). A pressure gauge was connected to the combustion chamber through a flexible pressure line. The analogue pressure readings were documented by video recording of the experiments, enabling frame-by-frame extraction of pressure data, accurate determination of the motor operating time, and subsequent secondary data processing.

Test motor configuration and preliminary ballistic estimation

The test motors were loaded with three BATES propellant grains each. Prior to the experimental campaign, a preliminary simulation of the internal ballistic process and an initial estimation of the

Table 2. Composition of the investigated composite propellants (wt.%).

Sample	KIO_4	$NaIO_4$	Al	S	C	Isomalt	Fe_2O_3	Epoxy	Polyurethane
PI-1	70	-	7	5	-	-	-	18	-
PI-2	-	75	6	4	-	-	-	15	-
FPI-3	70	-	-	-	-	15	+ 0.1	15	-
PI-4	-	70	-	-	-	10	+ 0.1	20	-
PI-5	35	38	7	5	+ 2	-	-	15	-
PI-6	35	38	7	5	-	-	-	15	-
PI-7	75	-	10	-	-	-	+ 0.1	-	15
PI-8	-	75	10	-	-	-	+ 0.1	15	-

expected operating parameters were performed using the widely available MS Excel spreadsheet SRM.xls developed by Richard A. Nakka [15]. Impact and friction sensitivities were evaluated using BAM (Bundesanstalt für Materialforschung und -prüfung) standard methods.

RESULTS AND DISCUSSION

Physicomechanical properties of the obtained samples

The cured propellant grains exhibited visibly high hardness. Visual inspection revealed no significant structural defects such as pores, cracks, or other macroscopic imperfections. After complete curing, the prepared samples exhibited bulk densities in the range of 2.25 - 2.65 g cm^{-3}, as summarized in Table 3.

The composite propellant formulations were chosen to encompass a variety of binder, fuel, and oxidizer ratios, allowing an investigation into differences in energetic performance and thermokinetic characteristics. Formulations showing high relative density, a favourable burning rate at atmospheric pressure, and distinctive thermal decomposition profiles were considered most promising. Samples PI-7 and PI-8, which lack sulphur, exhibited uneven burning processes. Based on these criteria, four formulations (PI-1, PI-2, PI-5, and PI-6) were selected for thorough experimental and ballistic evaluation, while the other four showed comparatively lower performance.

Detailed values for the selected formulations are presented in Tables 4 and 5. Theoretical density values were used in PROPEP 3 simulations to calculate thermochemical performance parameters, as they represent the idealized, fully dense propellant compositions, allowing consistent comparison between formulations independent of porosity or processing-induced voids.

Prismatic specimens were subjected to mechanical testing to determine tensile and flexural strength as well as Young's modulus. In addition, the hygroscopic behaviour of the samples was evaluated using standard assessment methods (Table 4).

Modelling of combustion processes

Thermochemical modelling of the combustion behaviour of the experimental solid fuel formulations was carried out using the open-access Propellant Evaluation Program PROPEP 3 (version 1.0.3.0) [16]. The program enables equilibrium-based calculations of propulsion-relevant parameters, including the specific impulse (Isp) at a defined operating pressure, the propellant formulation density, and the characteristic temperatures in the combustion chamber (Tch) and at the nozzle exit (Tex). Additionally, PROPEP 3 provides detailed information on the composition of the combustion products, including their phase distribution and overall molar mass (Table 5). All thermochemical calculations were performed under identical conditions for consistency.

The predicted values of the specific impulse are moderate and fall within the range typically reported for conventional sugar-based (rocket candy) propellants [17]. Nevertheless, the calculated composition of the gaseous and condensed combustion products indicates

Table 3. Comparison of theoretical and experimental densities, and burn rate at open air, of propellant samples PI-1 to PI-8.

Composition/ parameter	Teorethical density, g cm^{-3}	Measured density, g cm^{-3}	Relative density	Burn rate at open air, mm s^{-1}
PI-1	2.6108	2.5664	98.3	2.2
PI-2	2.7041	2.6473	97.9	3.1
PI-3	2.7041	2.2525	95.7	0.76
PI-4	2.3543	2.2695	96.4	0.72
PI-5	2.6035	2.5410	97.6	1.32
PI-6	2.6325	2.5746	97.8	3.85
PI-7	2.5829	2.4847	96.2	1.46
PI-8	2.7389	2.6430	96.5	2.2

Table 4. Physicomechanical and sensitivity properties of propellant formulations PI-1, PI-2, PI-5, and PI-6.

Specimen / Parameter	Tensile strength σ , MPa	Flexural strength σ , MPa	Elastic modulus E, GPa	Hygroscopicity (%), mass change, 7 days at 75 % RH	Impact / friction sensitivity
PI-1	11.8	8.6	3.81	0.6	No reaction
PI-2	10.9	7.9	3.54	1.9	No reaction
PI-5	11.6	8.2	4.33	1.4	No reaction
PI-6	11.5	8.35	4.51	1.5	No reaction

RH - relative humidity

Table 5. Measured ballistic parameters from four static firing tests of the PI-6 propellant.

Composition	Specific Impulse I_{sp}, s	Density, g cm^{-3}	Chamber temperature T_{ch}, K	Exhaust Temperature T_{ex}, K	Molecular Weight of the exh. mixture	Main exhaust products
PI-1	159.5	2.6108	2584	1471	52.00	CO, H_2, KI, Al_2O_3
PI-2	161.0	2.7041	2732	1837	49.26	CO, H_2, NaI, H_2O, CO_2, Al_2O_3
PI-5	161.1	2.6035	2542	1556	47.30	CO, H_2, KI, NaI, H_2O, CO_2, Al_2O_3
PI-6	161.6	2.6325	2643	1699	49.84	CO, H_2, KI, NaI, H_2O, CO_2, Al_2O_3

that further formulation optimization is feasible. An important advantage of the studied propellants is the absence of chlorine-containing combustion products, which classifies them as environmentally preferable rocket propellants [18].

Thermal decomposition behavior of the investigated propellants

The thermal decomposition behaviour of three of the most promising formulations investigated was examined using thermogravimetric analysis coupled with differential scanning calorimetry (TG - DSC). The thermal decomposition of alkaline metaperiodates as individual substances has been studied in various publications [5, 19 - 21]. Still, there are no articles on propellant compositions or on the shapes obtained in this study.

Specific results for the mass loss (TG) and heat flow (DSC) during the thermal decomposition of the fuel sample PI-1 are presented in the curves shown in Fig. 1.

The TG curve of the PI-1 sample indicates the onset of thermal decomposition at 149°C, which is facilitated by the melting of sulphur in the composition at 105 - 110°C. This phase transition enhances diffusion among components and initiates the decomposition of the oxidizer, which partially converts to potassium iodate (KIO_3) and the simultaneous release of oxygen (O_2). The first exothermic DSC peak appears at 280°C, corresponding to a mass loss of 16 %. A second exothermic peak at 336°C (mass loss ~3 %) reflects the oxidation of fuel components by the released oxygen, primarily occurring in the condensed phase. Between 350°C and 450°C, gas-phase reactions dominate, leading to rapid mass loss (33 %) and a pronounced exothermic peak at 430°C, indicative of intense thermal decomposition.

Up to 600°C, oxidation of condensed products continues alongside endothermic decomposition of KIO_3 via parallel pathways to KI (with O_2 release) and K_2O (with O_2 and molecular iodine evolution), resulting in minor mass changes. Aluminium melts at 642°C, producing a small endothermic DSC signal, while γ-Al_2O_3 formation exposes the metallic core to oxidizing gases [22]. This triggers exothermic oxidation of aluminium, peaking at 656°C, with a slight TG mass increase due to Al_2O_3 formation.

Above ~650 - 700°C, the major exothermic reactions

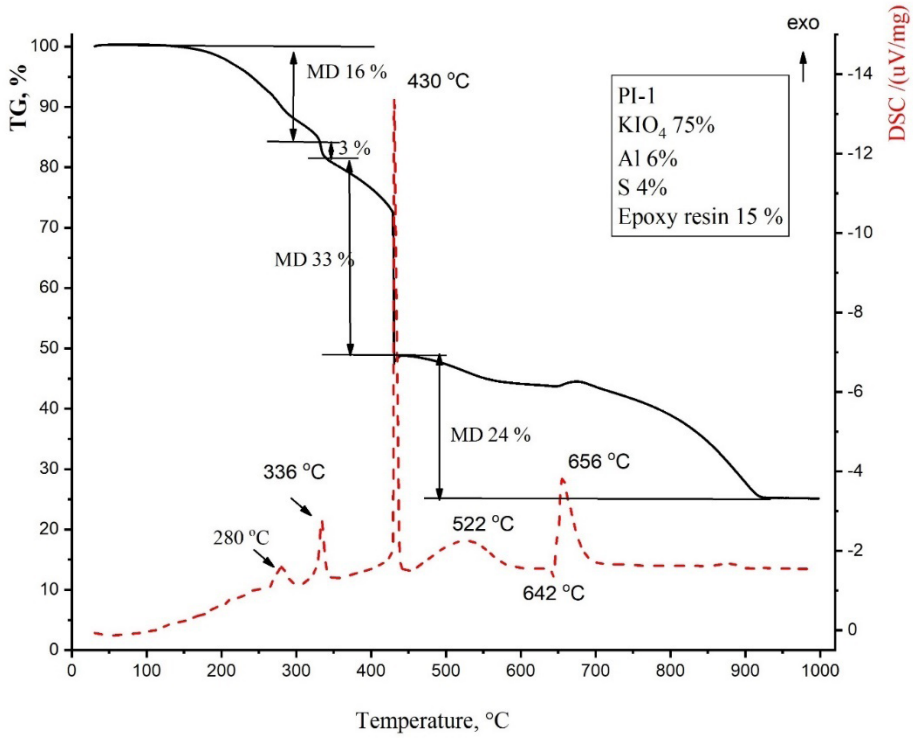

Fig. 1. TG - DSC curves of propellant composition PI-1.

conclude, and the metallic phase is fully converted to thermodynamically stable Al_2O_3, forming an inert matrix that encapsulates residual potassium, sulphur, and iodine species. The release of volatile products (K, I, HI, S_2–S_4, SO, SO_2, H_2S) becomes diffusion-limited and proceeds gradually. Subsequent dissociation, recombination, and equilibrium processes among residual compounds (e.g., KI/K_2I_2 ↔ K/I/HI, sulphur allotropes S_2–S_4, SO ↔ SO_2, $CO/CO_2/H_2/CS_2$ formation) generate a quasi-stationary state.

The overlapping endothermic and exothermic events lead to a nearly smooth DSC curve up to 1000°C, while TG distinctly registers the cumulative mass loss of ~20 % in the final decomposition stage.

The thermal decomposition of the PI-2 propellant composition proceeds through the same three-stage mechanism as observed for composition PI-1, which is clearly evidenced by the TG curve (Fig. 2). The principal differences between the two systems lie in the distribution and release of energy during decomposition.

The DSC curve of PI-2 exhibits a well-defined and intense exothermic peak at 287°C. This thermal effect is attributed to the initial solid-state decomposition of sodium periodate ($NaIO_4$) to sodium iodate ($NaIO_3$), occurring before melting. The process is exothermic and is accompanied by the vigorous release of reactive oxygen species, which initiate a self-sustaining reaction with the organic fuel, sulphur, and, to a lesser extent, aluminium present in the fuel matrix.

A second exothermic effect is observed at 419°C. At this temperature, the previously formed $NaIO_3$ undergoes melting, which significantly enhances mass transport, facilitates diffusion processes, and increases the overall reactivity of the system components. Within the temperature interval up to 500°C, the molten $NaIO_3$ further decomposes via two parallel pathways to form either NaI or Na_2O, accompanied by additional release of reactive oxygen.

A key distinguishing feature of the thermal decomposition behaviour of this composition is that aluminium oxidation occurs prior to reaching its melting temperature. This conclusion is supported by the absence of a characteristic exothermic effect near 660°C, commonly associated with molten aluminium oxidation,

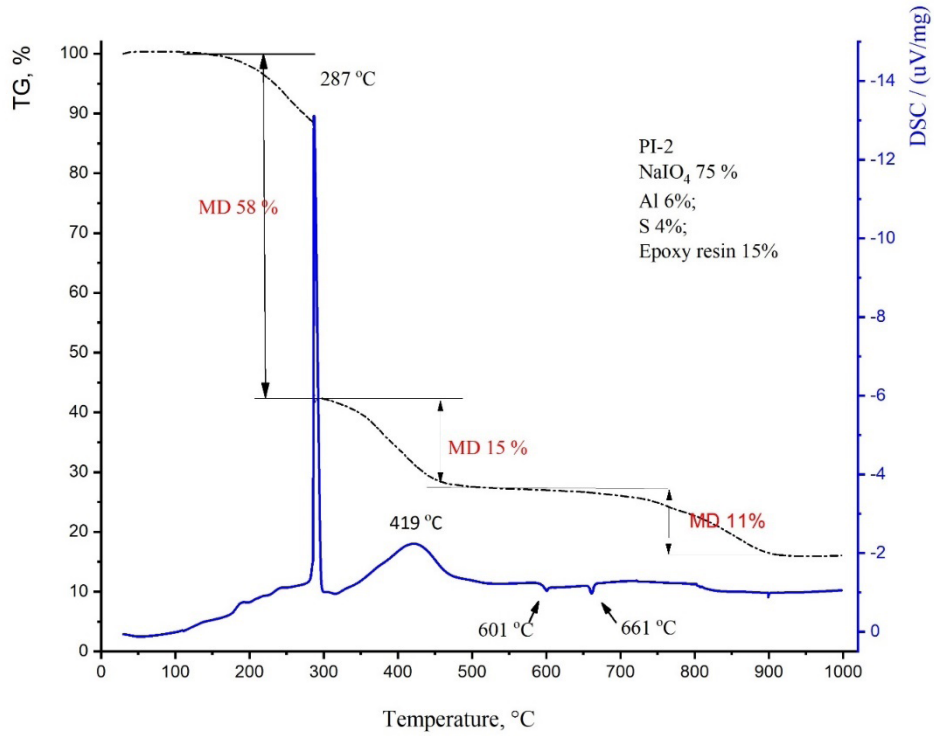

Fig. 2. TG - DSC curves of propellant composition PI-2.

which is otherwise observed in composition PI-1 containing potassium periodate (KIO_4) as the oxidizer.

In the fuel composition PI-6, where both alkali metaperiodates act as co-oxidizers, the mechanism and pattern of thermal decomposition differ significantly from those observed in other studied systems (Fig. 3). The thermogravimetric (TG) curve does not display the clearly defined three-stage mass loss seen in other compositions. Instead, the individual decomposition steps, previously identified separately in PI-1 and PI-2, overlap. This behaviour is also reflected in the corresponding thermal effects recorded in the DSC curve.

Decomposition begins in the temperature range of 180 - 200°C. The first distinct exothermic peak appears at 269°C and corresponds to the primary exothermic decomposition of sodium metaperiodate ($NaIO_4$) into sodium iodate ($NaIO_3$). The second exothermic effect (331°C) is associated with the analogous primary decomposition of potassium metaperiodate (KIO_4) into potassium iodate (KIO_3), which is also exothermic.

The oxygen released in both processes actively reacts with the fuel components, forming gaseous combustion products. This interaction appears as a continuous mass loss in the TG curve. Additional exothermic peaks observed at approximately 400°C and 523°C are caused by the decomposition of $NaIO_3$ and KIO_3, respectively, into their iodides and oxides. During this stage, the released oxygen continues to oxidize the non-metallic components of the fuel composition.

At around 640°C, an oxidation reaction with molten aluminium occurs, seen as a well-defined exothermic effect in the DSC curve. Evolution of volatile combustion products continues up to approximately 850°C. This process does not significantly affect the system's energetic balance and manifests only as a residual mass loss of about 9 %.

Oxygen balance of the investigated compositions

The oxygen balance (OB) was calculated according to the classical solid-propellant methodology, considering only the non-metallic combustible elements (C, H, and S) with complete oxidation to CO_2, H_2O, and SO_2, normalized to 100 g of composition.

The resulting OB values for the four formulations

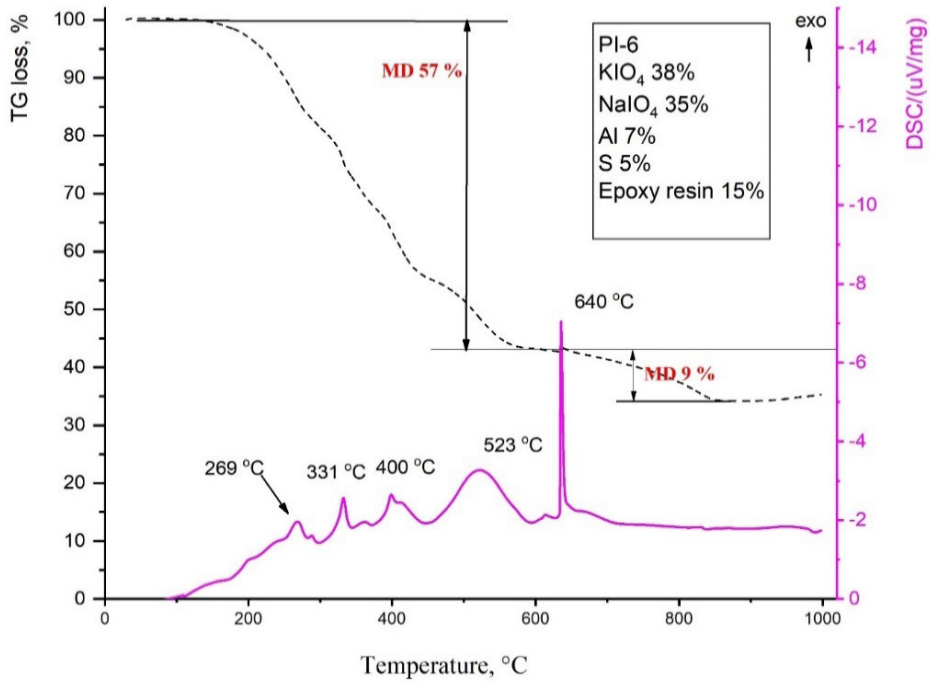

Fig. 3. TG - DSC curves of propellant composition PI-6.

are PI-1 = -17.4 %, PI-2 = -15.8 %, PI-5 = -23.5 %, and PI-6 = -18.2 %, respectively, classifying all compositions as fuel-rich.

Internal ballistic behaviour during static firings

The PI-6 propellant composition was chosen for both internal ballistic and experimental flight testing. This selection was based on a thorough evaluation of energetic performance indicators and thermokinetic behaviour, as observed among the various formulations investigated. Of particular note, PI-6 demonstrated the highest burning rate at atmospheric pressure, along with a unique thermal decomposition profile that set it apart from the other compositions, as outlined above (Table 3, Fig. 3).

In total, four ground static firings were carried out utilising the PI-6 propellant composition. These tests provided valuable insights into the operational characteristics and performance of the propellant under controlled conditions.

The principal operating parameters and derived ballistic characteristics obtained from these tests are summarized in Table 5.

The experimental data obtained at the present stage are not sufficient for a precise determination of the pressure exponent ”n“ in Vieille’s burning rate law, $r = ap^n$, nor for a comprehensive characterization of the combustion process parameters. The conducted static firings provide a first-order insight into the internal ballistic behaviour of the investigated composite propellant.

Test flights of experimental rockets

For the flight testing, a family of experimental rockets designated BIO, was used. These rockets were designed and manufactured using biodegradable elements and composite materials derived from readily available natural raw materials.

The BIO-3 rocket (lift-off mass 2.7 kg) was the first vehicle successfully launched and recovered using the PI-6 propellant. The rocket reached an apogee of 1388 m with a total flight time of 16 s, demonstrating the practical feasibility of alkaline periodate-based composite propellants in real flight conditions. Subsequent test launches were conducted using the BIO-4 rocket (launch mass 3.8 kg), the ZODIAC rocket (4.6 kg), and the BIO-5

Table 5. Measured parameters from 4 static tests of PI-6 solid propellant.

Test No.	Propellant mass, kg	Kn = A_b /A_t	t burn, s	P, MPa	Burn rate, mm s^{-1}
#1	0.63	140 - 178	2.5	3.4	5.8
#2	0.65	191 - 220	2.1	4.15	6.9
#3	0.64	215 - 281	1.95	5.9	7.6
#4	0.65	234 - 301	1.82	6.7	8.1

rocket (6.5 kg). Both predicted and measured flight velocities for all rocket models remained below Mach 1. The flight test results showed good agreement with the preliminary ballistic simulations.

CONCLUSIONS

The conducted experimental investigations demonstrate the feasibility of using alkaline periodates (KIO_4 and $NaIO_4$) as oxidizers in solid rocket propellant formulations. Even when combined with relatively conventional components such as epoxy resin, aluminium, and sulphur, the resulting composite propellants exhibit stable combustion behaviour.

The developed periodate-based composites are characterized by high density, good mechanical strength, low hygroscopicity, and favourable processing properties, allowing easy molding into charges of various geometries and dimensions. Metallized formulations burn stably at atmospheric pressure, with measured burning rates in the range of 1.32-3.85 mm s^{-1}.

The high density of periodate propellants partially compensates for inherent limitations such as relatively low specific impulse and the formation of high-molecular-weight combustion products. A key benefit of the propellants examined is that they do not produce chlorine-containing combustion products, thereby categorising them as environmentally preferable ("green") rocket propellants.

Internal ballistic studies indicate stable and uniform combustion of the PI-6 composition at pressures between approximately 3.4 MPa and 6.7 MPa. Experimental flight tests conducted with rocket models having lift-off masses from 2.7 kg to 6.5 kg demonstrated consistent flight performance and good agreement with preliminary ballistic predictions.

The results obtained thus far provide a solid foundation for further development of solid rocket propellants based on alkali metal periodates. Of particular interest for future work is a detailed analytical characterization of the combustion products to assess both the environmental impact and the practical advantages of these formulations.

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