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Modern Binders for Solid Propellants: Mechanical and Technological Aspects of Performance Formation

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Abstract. *Modern solid propellants are widely used in various propulsion systems, where their performance is determined not only by energetic characteristics but also by the properties of binder systems that ensure structural integrity and stability of the propellant grain. The aim of this study is to analyze modern binders for solid propellants and to develop an approach to selecting effective compositions based on both physicochemical and mechanical characteristics.*

The study is based on the analysis and generalization of current binder systems used in solid propellants, including thermosetting and thermoplastic binders, with consideration of their influence on mechanical behavior, structural integrity, and operational performance. It is shown that binder properties significantly affect not only the energetic performance but also the mechanical strength, deformation resistance, and reliability of propellant grains under operational conditions. An integrated approach to the selection of binder systems is proposed, which combines energy-based and mechanical criteria.

The proposed approach allows for a more comprehensive evaluation of solid propellant efficiency and can be used in the design and development of advanced propulsion systems with improved performance and reliability.

Keywords: *solid rocket propellant; binder, thermoplastic elastomer; thermosetting polymer; additive manufacturing; 3D printing; recycling; specific impulse; thermodynamic modeling.*

1. Introduction

Solid-propellant rocket engines (SPREs) hold a key place in modern aerospace and defense systems due to their constant readiness, high reliability, relative simplicity of design, and long shelf life. In recent years, their strategic importance has increased many times in the context of their active usage as launch boosters [1], [2]. The ability of SPREs to provide rapid launch and acceleration from mobile or size-limited platforms in the context of modern highly maneuverable combat makes them an indispensable element of rapid deployment systems, as clearly proved by trends in the equipment of advanced world armies. Under these conditions, requirements for manufacturability, cost, and production efficiency of engines come to the fore, relevating the search for new solutions for their key component – the binder.

Binding materials serve as the structural framework of the propellant charge, combining energetic fillers (oxidizers and metallic fuel) into a monolithic, mechanically strong, and stable structure. The physicochemical properties of the binder directly affect not only the rheological properties of the propellant composition during manufacture but also the final energy characteristics, combustion stability, service life, and overall engine operational safety. Historically, the dominant position in this area has been occupied by thermosetting polymers, such as carboxyl- and hydroxyl-terminated polybutadienes (CTPB, HTPB) [3], polyurethanes, and epoxy resins. These materials, forming irreversible three-dimensional cross-linked networks during vulcanization, provide high thermal stability, resistance to creep, and good mechanical properties at elevated temperatures. It is noteworthy that some linear polymers, formally classified as thermoplastics, due to their high melting point exceeding the thermal decomposition temperature, behave in practice like thermosetting materials, which excludes their processing by melting.

However, modern demands, caused as well by the need of quick reaction – increasing efficiency, safety, and reducing lifecycle costs – bring fundamentally new require-

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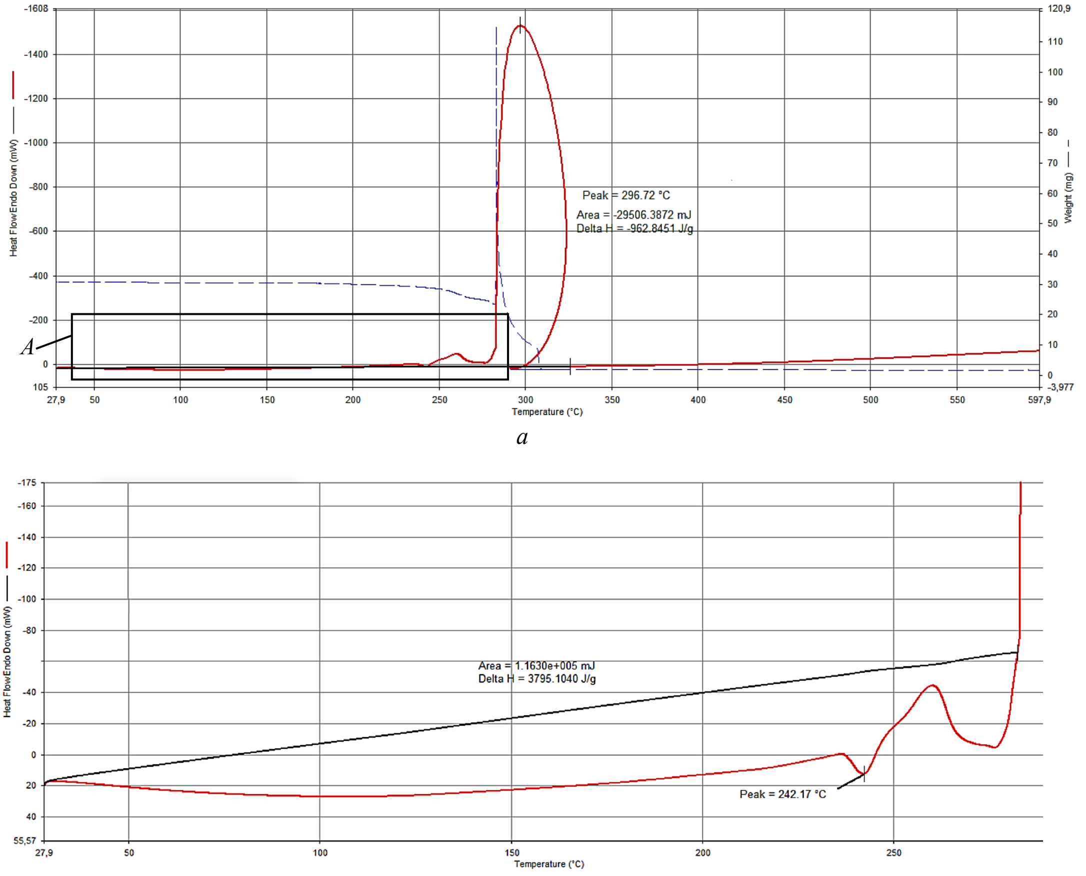
rements for binders to the forefront. Classical thermosetting systems, despite their advantages, have fundamental limitations: their processing is irreversible, which eliminates the possibility of recycling defective or decommissioned charges, and the manufacture of engines with complex geometry requires expensive mechanical equipment and tooling. It is these limitations that stimulate the active search for alternatives, among which thermoplastic elastomers (e.g., ethylene-vinyl acetate (EVA) and polyolefins) with low melting points hold a special place. Parallel to polymer systems, non-polymeric binders can also be used. These include crystalline materials (e.g., trinitrotoluene, urea), which act as a matrix when melted and form a strong composition upon solidification, and low-melting-point metals and their alloys (such as indium, gallium), serving simultaneously as high-energy fuel and a binding phase. Their ability for reversible melting paves the way for revolutionary approaches in rocket propellant production, including efficient recovery of valuable components and the use of additive technologies (3D printing) [4], which can drastically reduce the time and cost of producing specialized SPREs, including for mass-produced unmanned aerial vehicles.

In addition to their chemical function, binders should be considered as structural elements that determine the mechanical behavior of the propellant grain. From a mechanical engineering perspective, the binder significantly affects stress distribution, deformation resistance, crack formation, and overall structural integrity under thermo-mechanical loading. Therefore, the selection of binder systems must account not only for energetic performance but also for mechanical reliability during operation.

2. Limitations

To determine the required operating range of melting temperatures for promising binders, a thermogravimetric analysis was carried out on a fuel composition with 20 % polyurethane, 15 % aluminium, 65 % AP. Other binders will have slightly different parameters for the ignition temperature, but the difference will be insignificant.

The graph (Fig. 1 *a*) shows that ignition occurs at a temperature close to the onset temperature of thermal decomposition of ammonium perchlorate (~300 °C). At the same time, it is also visible (Fig. 1 *b*) that there is a peak at 242 °C, which corresponds to a second-order phase transition of ammonium perchlorate (Fig. 2) from the orthrohombic to the cubic modification [5], causing an abrupt change in its volume, which can lead to the formation of microcracks.



a

b

Fig. 1. Thermogravimetric analysis of fuel with 20 % polyurethane, 15 % aluminum, 65 % AP: *a* – thermogravimetric analysis; *b* – enlarged area *A* (27.9 °C–292 °C)

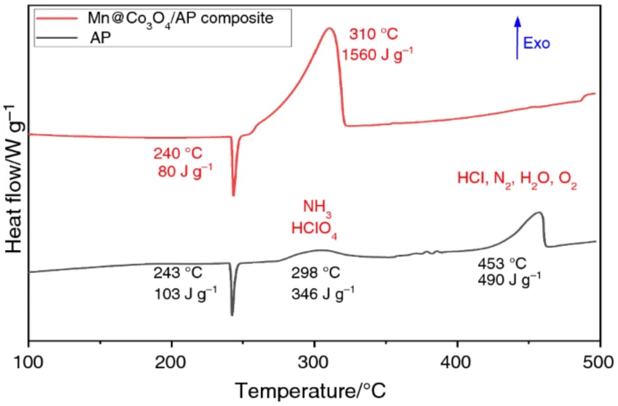


Fig. 2. DTA diagram of ammonium perchlorate [6]

Also, in Fig. 1, it can be seen that the sample mass begins to decrease starting from 60 °C, and this process intensifies at 240–250 °C, which can be explained by phenomena such as solvent evaporation from the binder, evaporation of residual moisture and impurities from AP, and the onset of AP decomposition itself.

Based on all of the above, let us assume that the melting point of a potential binder should not exceed 150 °C (423 K). On the other hand, based on operational characteristics, let us set the lower melting point limit at 50 °C (323 K).

3. Research methods

3.1. Thermosetting Binders

Historically, the basis of solid rocket propellant production has been thermosetting polymers. The most common representative is hydroxyl-terminated polybutadiene (HTPB). According to fundamental research presented in the journal *Propellants, Explosives, Pyrotechnics*, HTPB demonstrates superior wetting of ammonium perchlorate and aluminum surfaces, ensuring a high filling degree and composition stability [7].

Polyurethane binders occupy a special niche due to their exceptional strength. Research published in the *Journal of Polymer Science* details the mechanism of three-dimensional network formation and the resistance of polyurethanes to various aggressive environments [8]. At the same time, as noted in a review in *Progress in Aerospace Sciences*, some linear polymers, including certain types of polyurethanes, due to their high melting/decomposition temperature, functionally behave as thermosetting materials [9].

Epoxy resins find application in special areas. Work in *Composite Materials* provides a detailed analysis of their highest strength characteristics and adhesion, as well as modification methods to reduce brittleness [10].

3.2. New Generation Thermoplastic Binders

The development of thermoplastic elastomers opens up possibilities for additive manufacturing. Ethylene-vinyl acetate (EVA) with a vinyl acetate content of 25–40 % demonstrates an optimal balance between flexibility and melting point. Research in *Additive Manufacturing* confirms that EVA compositions maintain stability at high solid filler content and are suitable for 3D printing by fused deposition modeling (FDM) [11]. EVA is also suitable for manufacturing flexible parts, which is important for producing case-bonded solid propellant grains [12].

A promising direction is the development of polyolefin binders. A review in *Polymer Reviews* systematizes data on the use of polypropylene and polyethylene as binders, noting their improved thermal characteristics and chemical resistance compared to EVA [13], although they have a higher melting point.

3.3. High-Energy Crystalline Substances

A special category consists of crystalline binders. Trinitrotoluene (TNT) is traditionally used in cast explosive compositions. The classic monograph *High Energy Materials: Propellants, Explosives and Pyrotechnics* describes its properties, advantages, and disadvantages, such as a tendency to migrate [14].

Other crystalline high-energy substances, for example, urea, can also be used as binders.

3.4. Low-Melting Metallic Alloys

An innovative direction is the use of metallic binders based on indium, gallium, and their eutectic alloys. An article in *Advanced Engineering Materials* experimentally investigates the properties of a gallium-indium alloy, its wetting ability, and application for creating functional composite materials [15]. It is worth noting that there is a risk of chemical reaction between the alloy components and the oxidizer; this issue requires separate research.

4. Analysis of the results

The following presents the results of thermodynamic modeling for fuels based on various binders. Calculations were performed for a combustion chamber pressure of 69 bar (1000 psi), nozzle exit pressure of 1 bar (14.5 psi), and initial component temperature of 298 K (25 °C).

It should be emphasized that the simulation results reflect general trends under ideal conditions. Actual engine performance will be lower than calculated for several reasons:

1. Process Non-Ideality: Incomplete chemical reactions, dissociation of combustion products in the chamber, and heat losses.

2. Design Factors: Erosion of the nozzle thermal protection coating, which absorbs part of the heat, and two-phase losses associated with the condensation of refractory particles, primarily metal oxides such as Al_2O_3 and Fe_2O_3.

3. Technological Deviations: Inability to ensure absolute homogeneity of the fuel matrix and the presence of

passive impurities. A key example is the oxide film (Al_2O_3) on the surface of aluminum powder, which reduces the total energy release.

4. Composition Variation: The chemical composition of raw materials, especially polymeric binders (e.g., epoxy resins), may vary slightly between different manufacturers and even between batches, affecting the rheological and energy properties of the fuel.

The calculation was performed in the ProPep program (Martin Marietta). Screenshots of the fuel performance calculation results are presented. Data are provided for two nozzle flow models:

FROZEN (Frozen equilibrium in the first row): Assumes that the composition of combustion products is fixed after the combustion chamber and does not change in the nozzle.

SHIFTING (Shifting equilibrium in the second): Assumes that the composition of combustion products continuously adjusts, maintaining chemical equilibrium at the current pressure and temperature at each point in the nozzle.

The real value of specific impulse usually lies between these two approximations. For comparative analysis, the higher value corresponding to the SHIFTING model is typically used.

5. **Key parameters of the section**

IMPULSE: Specific impulse under ideal nozzle expansion conditions in seconds.

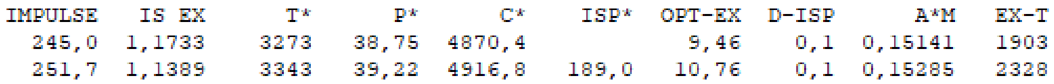
T: Temperature in the combustion chamber in Kelvin.

ISP: Specific impulse for an engine without a nozzle (“with a hole”) in seconds.

OPT-EX: Optimal expansion (ratio of nozzle exit area to throat area).

EX-T: Temperature at the nozzle exit in Kelvin [16].

Below are the results of calculations for polymeric binders (Fig. 3–12) were performed considering 20 % binder (except for polybutadiene) based on existing experience with various compositions and the rheology during solid fuel grain forming.



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IMPULSE   IS EX     T*     P*      C*     ISP*  OPT-EX  D-ISP      A*M    EX-T
  245,0  1,1733   3273  38,75  4870,4           9,46    0,1  0,15141   1903
  251,7  1,1389   3343  39,22  4916,8   189,0  10,76    0,1  0,15285   2328
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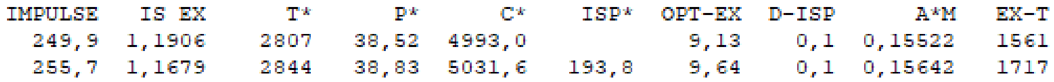
Fig. 3. Fuel performance calculation results for Space Shuttle fuel, 16 % aluminum, 69.8 % AP, 0.2 % iron oxide, 12 % Polybutadiene acrylic acid acrylonite, 2 % Epoxy curing agent [17]



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IMPULSE   IS EX     T*     P*      C*     ISP*  OPT-EX  D-ISP      A*M    EX-T
  249,9  1,1906   2807  38,52  4993,0           9,13    0,1  0,15522   1561
  255,7  1,1679   2844  38,83  5031,6   193,8   9,64    0,1  0,15642   1717
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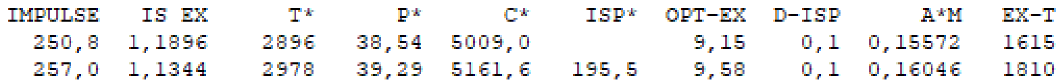
Fig. 4. Fuel performance calculation results 15 % aluminum, 65 % AP, 20 % polyurethane



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IMPULSE   IS EX     T*     P*      C*     ISP*  OPT-EX  D-ISP      A*M    EX-T
  250,8  1,1896   2896  38,54  5009,0           9,15    0,1  0,15572   1615
  257,0  1,1344   2978  39,29  5161,6   195,5   9,58    0,1  0,16046   1810
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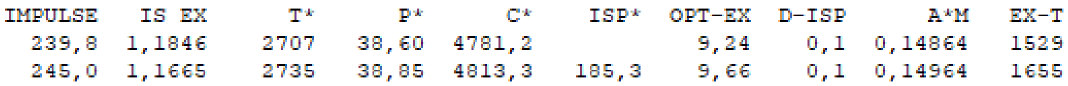
Fig. 5. Fuel performance calculation results 15 % aluminum, 65 % AP, 20% epoxy



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IMPULSE   IS EX     T*     P*      C*     ISP*  OPT-EX  D-ISP      A*M    EX-T
  239,8  1,1846   2707  38,60  4781,2           9,24    0,1  0,14864   1529
  245,0  1,1665   2735  38,85  4813,3   185,3   9,66    0,1  0,14964   1655
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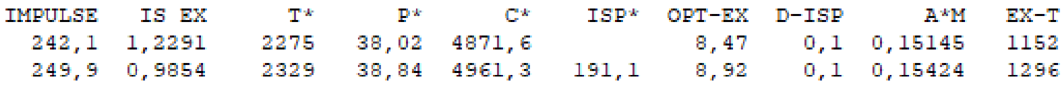
Fig. 6. Fuel performance calculation results 15 % aluminum, 65 % AP, 20 % EVA



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IMPULSE   IS EX     T*     P*      C*     ISP*  OPT-EX  D-ISP      A*M    EX-T
  242,1  1,2291   2275  38,02  4871,6           8,47    0,1  0,15145   1152
  249,9  0,9854   2329  38,84  4961,3   191,1   8,92    0,1  0,15424   1296
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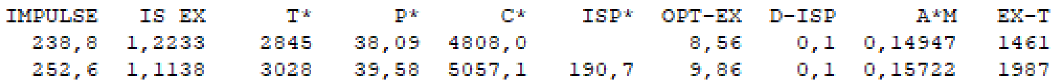
Fig. 7. Fuel performance calculation results 15 % aluminum, 65 % AP, 20 % polyethylene



```
IMPULSE   IS EX     T*     P*      C*     ISP*  OPT-EX  D-ISP      A*M    EX-T
  238,8  1,2233   2845  38,09  4808,0           8,56    0,1  0,14947   1461
  252,6  1,1138   3028  39,58  5057,1   190,7   9,86    0,1  0,15722   1987
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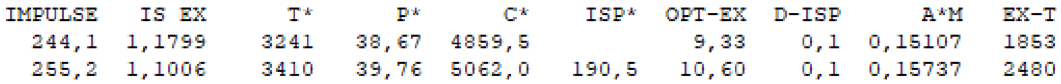
Fig. 8. Fuel performance calculation results 30 % TNT, 70 % AP



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IMPULSE   IS EX     T*     P*      C*     ISP*  OPT-EX  D-ISP      A*M    EX-T
  244,1  1,1799   3241  38,67  4859,5           9,33    0,1  0,15107   1853
  255,2  1,1006   3410  39,76  5062,0   190,5  10,60    0,1  0,15737   2480
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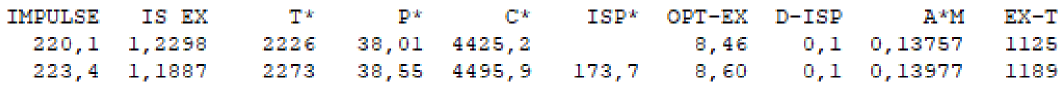
Fig. 9. Fuel performance calculation results 20 % TNT, 10 % aluminum, 70 % AP



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IMPULSE   IS EX      T*      P*      C*     ISP*  OPT-EX  D-ISP      A*M    EX-T
  220,1  1,2298    2226   38,01  4425,2            8,46    0,1  0,13757    1125
  223,4  1,1887    2273   38,55  4495,9    173,7   8,60    0,1  0,13977    1189
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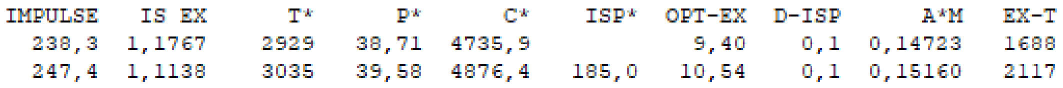
Fig. 10. Fuel performance calculation results 30 % urea, 70 % AP



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IMPULSE   IS EX      T*      P*      C*     ISP*  OPT-EX  D-ISP      A*M    EX-T
  238,3  1,1767    2929   38,71  4735,9            9,40    0,1  0,14723    1688
  247,4  1,1138    3035   39,58  4876,4    185,0  10,54    0,1  0,15160    2117
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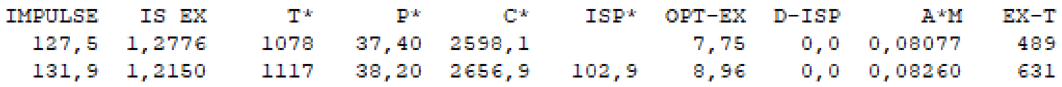
Fig. 11. Fuel performance calculation results 20 % urea, 10 % aluminum, 70 % AP



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IMPULSE   IS EX      T*      P*      C*     ISP*  OPT-EX  D-ISP      A*M    EX-T
  127,5  1,2776    1078   37,40  2598,1            7,75    0,0  0,08077     489
  131,9  1,2150    1117   38,20  2656,9    102,9   8,96    0,0  0,08260     631
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Fig. 12. Fuel performance calculation results 12.5 % Indium, 12.5 % Gallium, 75 % AP

Analyzing the calculation results, it is easy to see that for polymeric binders, the specific impulse differs little (240–257 s, maximum about 7 % deviation).

Compositions with TNT also show a close specific impulse (238–255 s).

Compositions with urea showed a somewhat lower result (220–223 s), but when using aluminum as a high-energy additive, urea proves to be a quite workable component-replacement for thermosetting binders (237–247 s). There are concerns about the corrosive activity of urea towards aluminum, but they are unfounded [18].

The composition with the In-Ga alloy raises the most questions because these are relatively active metals but yield low specific impulse. This may be due to incorrect thermodynamic modeling, or it may be related to the small amount of gas in the combustion products, as, for example, in a thermite mixture (Fe_2O_3 + Al), which releases a lot of heat but cannot create thrust because all reaction products are refractory compounds. As is known, work is performed by hot gases. In any case, additional research is needed.

All calculation results with comparative characteristics of binders are given in the table 1.

Table 1. Comparative Characteristics of Binder Materials

Property / Material	HTPB	Polyurethane	Epoxy Resins	EVA	Polyethylene	TNT	Urea	In-Ga Alloys
Material Type	Thermo-setting *	Thermo-setting *	Thermo-setting	Thermoplastic Elastomer	Thermoplastic Polymer	Crystalline Explosive	Crystalline Substance	Low-Melting Metal Alloy
Processing Temp.**, °C	60–80	60–100	20–150	80–120	160–180	80–85	132	15–200
Mechanical Properties	High elasticity, good strength	High strength and wear resistance	High strength, brittleness	Flexibility, impact viscosity	Stiffness, strength	Brittleness	Brittleness, high hardness	Plasticity, low strength
Specific Impulse, s ***	252	256	257	245	250	252–255	223–247	132
Recyclability	No	No	No	Yes	Yes	Additional research needed	Additional research needed	Yes
Suitability for 3D Printing	Very Low	Very Low	Low (DIW)	High (FDM, DIW)	Medium (FDM)	Low (hazard)	Low (hazard)	High (special methods)
Key Advantages	Proven technology, reliability	Strength, oil resistance	High strength, adhesion, low shrinkage	Ease of processing, flexibility	Thermal stability, chemical resistance	High energy, simplicity of use	Availability, high energy content	Electrical conductivity, fuel function
Main Disadvantages	Irreversible process, long curing	Sensitivity to moisture	Brittleness, need for precise dosing	Limited temperature range	High processing temperature	Low stability, migration	Relatively high melting point	High density, cost, corrosion

A fundamental transformation of the approach to creation of solid rocket propellants is associated with two interrelated trends: the introduction of additive technologies and the transition to a circular economy. Traditional methods, such as casting and vacuum pressing, face fundamental limitations, including long production cycle times (up to several weeks), high defect rates, geometric limitations, and the impossibility of correcting defects. Additive technologies (3D printing) offer a paradigm shift, allowing the creation of propellant grains with programmable internal architecture, which was previously unattainable [19].

Among the key methods of fuel 3D printing, fused deposition modeling (FDM) stands out, ideally compatible with thermoplastic binders such as ethylene-vinyl acetate (EVA). This process assures precise control over the distribution of the propellant composition within the grain volume, creating complex combustion channels that control the engine's thrust profile [20]. An alternative is direct ink writing (DIW), a method of extruding highly filled pastes, which is suitable for temperature-sensitive materials, including compositions with ammonium perchlorate. Research shows that using DIW, it is possible to introduce solid energetic components without loss of rheological properties [20]. For photopolymerizing systems, including modified polybutadienes, stereolithography (SLA) is promising, providing high printing resolution [21]. By combining these methods, engineers can create fuels with a programmed combustion law, where the concentration of energetic components and geometry vary throughout the volume for precise control of engine characteristics.

In parallel to the technological revolution, a rethinking of the material lifecycle is taking place. The reversibility of the melting-curing processes of thermoplastic and metallic binders (EVA, In-Ga alloys) lays the foundation for recycling [7]. Defective or decommissioned charges can be remelted with subsequent extraction and reuse of valuable components–oxidizer, metallic fuel, and the binder itself. Reports from pioneer companies in this area (e.g., Firehawk Aerospace) show, that the transition to additive technologies using thermoplastics can reduce charge production time from 15–60 days to 3–6 hours, indicating a significant economic effect [22], [23]. Furthermore, the robotic 3D printing process minimizes manual labor and personnel contact with hazardous materials, radically increasing safety and reducing the volume of hazardous waste generated during the mechanical processing of traditional charges.

6. Prospects and Key Research Directions

The conducted comparative study of classical and prospective binders for solid rocket propellants allows for a number of key conclusions. Thermodynamic analysis showed that for standard compositions based on ammonium perchlorate and aluminum with a polymeric binder, the stability of energy characteristics is observed. The specific impulse for such systems, regardless of the type of polymer (HTPB, polyurethane, epoxy resins, or thermoplastics like EVA and polyolefins), varies within a narrow range of 240–257 s. This result indicates that the choice of a specific polymeric binder from the point of view of pure energy is not critical and should be determined primarily by technological and operational parameters–such as rheology during production, processability, cost, and suitability for recycling.

The study of crystalline binders revealed varying prospects for their application. Trinitrotoluene (TNT) demonstrated energy comparable to polymeric systems; however, its use as a binding matrix is still constrained by its inherent disadvantages–high hardness and, accordingly, a tendency to form microcracks. In its turn, urea showed somewhat lower energy performance in its pure form, but its combination with aluminum allowed achieving a specific impulse in the range of 237–247 s, bringing it closer to traditional solutions, but it is also prone to cracking risk. The combination of this acceptable energy intensity with low cost and low melting point opens up potential for urea as an object for further applied research.

The most ambiguous results were obtained for metallic binders based on an indium-gallium alloy. Despite the theoretically high heat of combustion, the calculated specific impulse was low. The most likely explanation for this is the predominance of condensed phases in the combustion products, incapable of performing effective expansion work in the nozzle, by analogy with thermite compositions. This indicates the need for a fundamental revision of formulations involving such alloys, possibly through the introduction of gas-generating additives, and mandatory subsequent experimental verification.

7. Conclusions

The conducted analysis shows that modern trends in the development of binders for solid rocket propellants are characterized by a transition from classical thermosetting systems to materials with fundamentally new functional properties. If traditional polybutadiene and polyurethane binders remain the optimal solution for serial products due to proven technology and reliability, then the future lies with materials that provide increased functionality.

A key trend is the development of binders capable for reversible phase transitions. This ability opens up opportunities not only for additive technologies but also for a wider class of innovative solutions. The ability to repeatedly melt thermoplastic elastomers and metal alloys lays the foundation for recycling technologies, enabling the creation of economically efficient and environmentally sustainable production cycles.

Thus, the evolution of binding materials is moving towards the creation of multicomponent functional systems, where the binder not only plays the role of a structural framework but also contributes to the energy of the composition, provides specified rheological properties, and allows for multiple uses. Further progress in this area will be determined by successes in interdisciplinary research at the intersection of polymer chemistry, materials science, and composite technology.

The scientific novelty of this work lies in the development of an integrated approach to the selection of binder systems for solid propellants, which simultaneously considers physicochemical characteristics and mechanical behavior of the propellant grain. In contrast to conventional approaches focused mainly on energetic parameters, the proposed approach incorporates strength and structural integrity criteria, enabling a more comprehensive assessment of propellant performance.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, including financial, personal, authorship, or any other nature that could affect the research and its results presented in this article.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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Сучасні зв’язуючі речовини для твердих палив: механічні та технологічні аспекти формування характеристик

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Анотація. *Активний розвиток систем озброєння, зокрема безпілотних літальних апаратів, посилює вимоги до технологічності, економічної ефективності та безпеки виробництва твердих ракетних палив, ключовим компонентом яких є зв’язуюче. Провести комплексну оцінку енергетичних, експлуатаційних та технологічних характеристик різних класів зв’язуючих матеріалів для визначення найперспективніших напрямів їх подальшого застосування та розвитку. Дослідження базувалося на термодинамічному моделюванні в програмному комплексі ProPep для розрахунку ключових енергетичних параметрів (питомий імпульс, температура в камері згоряння). Додатково виконано термогравіметричний аналіз для встановлення термічних обмежень щодо температури плавлення зв’язуючих. Моделювання показало, що енергетичні характеристики палив на основі різних полімерних зв’язуючих є близькими (питомий імпульс 240–257 с). Кристалічні зв’язуючі (тринітротолуол, сечовина) демонструють компромісну енергетику, але схильні до утворення тріщин. Металічні сплави (In-Ga) показали низький питомий імпульс (132 с) через значну частку конденсованих продуктів згоряння. Констатовано зміну парадигми у виборі зв’язуючого: ключовими критеріями стали не енергетичні показники, а технологічна універсальність, придатність до адитивних технологій (3D-друк) та можливість рециклінгу. Найбільш перспективними є термопластичні еластомери (наприклад, EVA), що відкривають шлях до створення паливних зарядів складної геометрії та впровадження циклічної економіки.*

Ключові слова: *тверде ракетне паливо; зв’язуюче; термопластичний еластомер; термореактивний полімер; адитивні технології; 3D-друк; рециклінг; питомий імпульс; термодинамічне моделювання.*