PhD THESIS ABSTRACT

"POLYMERIC COMPOSITE FORMULATIONS FOR NEW GENERATIONS OF ROCKET PROPELLANTS"

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Polymeric composite materialsrepresent the fundament of modern rocket and space propulsion technology. Rockets have been around for hundreds of years; the Chinese were the first to develop rockets with solid propellants more than 800 years ago. Composite rocket propulsion research has experienced significant developmentsduring the last 75 years and the rate of innovation has beensteadily progressing. Although numerous studies on new propellant components are currently undertaken, no significant changes have been made to the solid composite propellants used in rocket propulsion in the previous 30 years. The new modified/enhanced propulsion systemsstill contain elements that are harmful to the environment. Due to its exceptional chemical and physical characteristics (high thermal stability, low shock sensitivity, good compatibility, and extended shelf-life), current composite propellant formulations use ammonium perchlorate (AP) as an oxidizer. But it has significant drawbacks as well, like hazardous combustion products (residues of chlorinated compounds and perchlorates), that are a significant threattothe ecosystems. For instance, the solid boosters from the European launch vehicle Ariane 5 trigger a volumetric discharge of hydrochloric acid into the atmosphere of about 270 metric tons. The first objectiveto improve the environmental impact should address the elimination of the acidsproduced during AP decomposition. Most of the dangerous substancesare spread in the atmosphere, leading to the ozone layer's reduction as well as the pollution of water with perchlorate ions, a phenomenon that has an adverse impact on human health by obstructing the thyroid gland's ability to absorb iodine. Children represent the most sensitive group because in their case thyroid interference can lead to neurodevelopmentalproblems.

Compounds in the field of composite rocket propellants must be evaluatedto find the best *"candidate"* to replace ammonium perchlorate while still meeting the three criteria of performance, cost, and safety. The next step in the development of energetic materials is the design of a solid propellant that can function beingboth *"eco-friendly"* and *"low-vulnerability".*Consequently, the idea of *"composite ecological propellant"*draws the attention of experts in both the field of energetic materials and the field of environmentalprotection.

The objectiveof the doctoral thesis *"Polymeric composite formulations for new generations of rocket propellants"* was to develop an *"environmentally friendly"* solid composite propellantwhich exhibit a lower environmental impact and can be used in the equipment of both military and civilian missile launchsystem but possessing both performance and safety characteristics at least comparable to current systems. In this study, theory, synthesis, and design are balanced with the topics of the composite polymer mixture and the employed propulsion mechanism. The emphasis is therefore on current data on the components employed in the composite mixture and the relationship between the design of the propulsion system and its application.

To achieve this objective, the work was divided into four parts. The first part, Chapter I, reviews the types of existing propellants, thesubstances currently employed in the production process, qualitatively and quantitatively highlighting their advantages and disadvantages, describing the approach followed during the original theoretical and experimental research. The energetic characteristics of the propulsion systems, particularly important in the design process, as well as their determination methods and techniques, are

also highlighted here. The second part of the thesis, respectively *Chapters II and III*, present the design, development and characterization of components and composite mixtures, such as: thermal analyzes (differential scanning calorimetry, differential thermal analysis, thermogravimetric analysis, thermal cycles (freeze- thawing)), compositional (Fourier transform infrared spectroscopy, X-ray diffraction, proton nuclear magnetic resonance), morphology (scanning electron microscopy and micro CT), mechanical properties (compression and tensile tests, dynamic mechanical analysis) and determinations of safety and performance characteristics (charge density, heat of combustion, specific volume, combustion rate at ambient pressure, sensitivity to friction, sensitivity to impact, thermal stability in vacuum).

The third part, *Chapter IV*, presents the analytical techniques, and methods for determining ballistic characteristics(burning speed, gas co-volume, propellant force, burning time, maximum pressure, burning rate coefficient, exponential burning rate coefficient, the fraction of burnt propellant and the progressiveness coefficient) for the developed fuel formulations. Combustion wave and heat processes from the gas phase to the condensed phase are also discussed to highlight the relevant combustion mechanisms. The experimental and analytical data were obtained from tests using the manometric bomb and the subscale rocket motor test stand.

The final section, *Chapter V*, summarizes general findings and innovative contributions. The most significant of these are the following prospective composite fuels research and developmentareas:

- The development of new "eco-friendly" oxidizers, based on phase-stabilized ammonium nitrate by using potassium salts;
- Obtaining a nanometric burning rate moderator based on iron oxide;
- New polyester-polyols from polyethylene terephthalate capable of partially or totally replacing the commercial polyols as binders for solid rocket propellants, to reduce costs and facilitate the concept of "circular economy" at the national level;
- Development and demonstration the applicability of new types of flexible polyurethanes from synthesized polyester-polyols, mixed with an energetic plasticizer (triethylene glycol dinitrate, TEGDN), a commercial polyol and an aromatic polyisocyanate, as binders in composite solid propellants;
- Fabrication of polymer composite materials and validation of their applicability as propellants through experimental firings in a pressure bomb and on the rocket motor test stand.