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Effect of cross-linking bonding agent on the ballistic characteristics of composite solid rocket propellant at high operating pressure

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Effect of cross-linking bonding agent on the ballistic characteristics of composite solid rocket propellant at high operating pressure

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Abstract. The novel cross-linking bonding agent, designated as MSC, was meticulously synthesized and subsequently incorporated into the existing bonding agent matrix with the primary objective of significantly enhancing the mechanical properties of composite propellant. This enhancement is achieved by improving the interfacial interactions between the bonding agent and the solid particles, which are crucial for withstanding the various stresses that are produced as a result of combustion loading conditions, as well as fluctuations in environmental conditions, transportation, and handling, all without adversely affecting the ballistic performance of the propellant. In the course of this research endeavour, the substitution of the cross-linking MSC bonding agent for the widely recognized reference bonding agent MAPO has resulted in a notable improvement in the mechanical properties, particularly concerning the strain values that correlate with the stress values. This substitution has effectively doubled the maximum strain value while still maintaining an acceptable maximum stress value, along with a commendable value for Young's modulus within the various propellant formulations being considered. A range of different compositions of composite propellant was systematically investigated in order to accurately measure the linear burning rate and to thoroughly study the effects brought about by the replacement of the MSC bonding agent in lieu of the traditional bonding agent MAPO. The presence of the bonding agent is expected to facilitate a more regular and stable burning process of the composite propellant, particularly under conditions of high dynamic pressure, thereby contributing to more predictable combustion characteristics. Furthermore, various nozzle diameters were employed, each providing distinct burning rates and pressures, thereby enabling the determination of the pressure exponent and the burning rate constant through systematic experimentation and analysis.

Keywords: MAPO, MSC, Burning rate, Bonding agent, and Dynamic pressure.

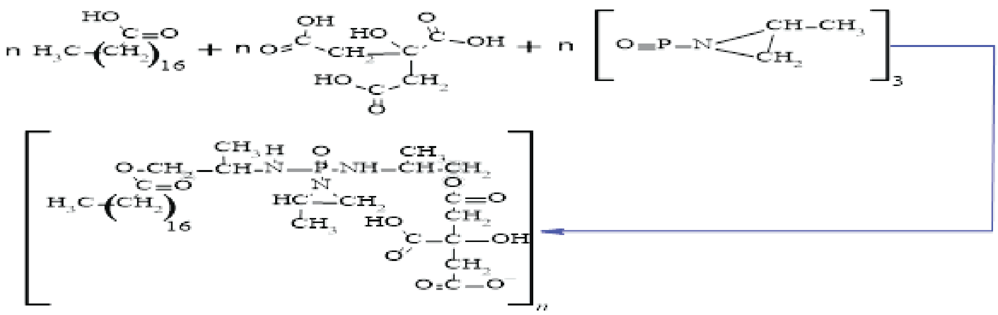
1.Introduction

Composite energetic materials, such as composite propellants, are predominantly formulated with a hydroxyl-terminated polybutadiene (HTPB)-derived polyurethane binder, ammonium perchlorate (AP) as the oxidizer, aluminium (Al) powder as the metallic fuel, and supplementary processing and ballistic additives[1]. The mechanical and adhesive properties of the elastomeric binder are critical design parameters, as structural failures in these composites often originate from interfacial separation between the oxidizer and binder matrix[2]. To mitigate this, bonding agents like methyl aziridinyl phosphine oxide (MAPO) and MT-4—a product of reacting 2 moles of MAPO with 0.7 moles adipic acid and 0.3 moles tartaric acid—are employed[3]. Another notable agent, MSC, synthesized via the reaction of 2 moles MAPO with 0.7 moles stearic acid and

0.3 moles citric acid, forms a copolymer (poly (isopropylamine N-(2-methyl-1-aziridinyl) phosphine oxide octadecenoate)-co-(2-hydroxypropane-1,2,3-tricarboxylate)) (see Equation.1)[4]. While MSC enhances strain and stress tolerance in aluminized propellants, its application in neutralized propellants yields improved strain but suboptimal stress and yield values[5].

Aziridine-functionalized compounds, such as MAPO and MSC, are integral to propellant composites, augmenting adhesion within the matrix to elevate mechanical performance[6]. These agents, typically incorporated at low concentrations (0.3–0.5% of the formulation), act as interfacial mediators by chemically bonding with the polymeric binder during curing and physically interacting with solid oxidizer particles[7]. This dual functionality creates an "elastic bridge," which doubles stress resistance, triples strain capacity, and stabilizes modulus values, thereby producing a tougher, more elastic composite[8]. MSC, for instance, enhances cross-linking density via its three functional groups, improving stress-strain behaviour while maintaining Young's modulus[9]. However, such additives are effective exclusively in AP-based systems and do not interfere with the curing kinetics of AP/HTPB formulations[10].

This study investigates the dual objectives of optimizing mechanical properties without compromising burning rates in composite propellants[11]. Mechanical performance was experimentally evaluated for formulations A and B, incorporating MAPO and MSC bonding agents, alongside variants to assess MSC's cross-linking efficacy[12]. Ballistic properties were concurrently analysed to quantify MSC's impact on combustion behaviour[13].



Equation.1: formation of MSC bonding agent

In the binder matrix, MSC operates bifunctionally: (1) its aziridine rings homopolymerize on oxidizer surfaces, forming a robust interfacial layer that chemically links particles to the HTPB matrix via hydrogen bonding with AP and HTPB, and (2) it compensates for the matrix's inherent elasticity deficit, enhancing stress and yield characteristics[5]. This dual mechanism underscores MSC's role in balancing mechanical integrity and ballistic performance in advanced propellant systems[14].

2.Experemental

2.1 Materials and preparation of bonding agent MSC

2.1.1 Materials

The (MSC) adhesive agent is synthesized using several key chemical constituents. Methyl aziridinyl phosphine oxide (MAPO), a yellow viscous liquid, serves as a primary component, exhibiting a boiling point between 118 and 125 °C, a density of 1.079 g/cm^3, and limited water solubility under standard conditions. Citric acid, a white crystalline powder under ambient conditions, has a melting point spanning 156 to 162 °C. Similarly, stearic acid exists as a white powdered solid at room temperature, with a narrower melting range of 69.3–69.9 °C. Copper chloride, a dark tan powdered compound, demonstrates a significantly higher melting point of 498 °C and solubility in methanol. The latter solvent, methanol, is employed in the process at a high purity level of 99.8%. Each material's distinct physicochemical properties, including phase behaviour, thermal stability, and solubility, are critical to their functional roles in the composite adhesive formulation.

2.1.2 Preparation

The synthesis of the MSC bonding agent involves reacting a specified molar ratio of MAPO with monocarboxylic fatty acid (octadecanoic acid) and tricarboxylic acid (2-hydroxypropane-1,2,3-tricarboxylic acid, commonly termed citric acid). Initially, a designated molar proportion of MAPO is dissolved in 150 mL of methanol as the reaction solvent. The solution is subsequently transferred to a three-necked flask fitted with a reflux condenser and containing the initiator $CuCl_2$. The mixture is continuously stirred and maintained at 58°C in a thermostatically controlled water bath for 3 hours. Concurrently, a methanol solution (300 mL) containing stoichiometrically calculated quantities of octadecanoic acid and citric acid is introduced into the reaction system via a continuous dropping funnel. The acidic components are administered in four equal aliquots at 20-minute intervals to ensure gradual incorporation. Post-reaction, the solvent is removed through vacuum distillation, and the resultant MSC product is isolated via vacuum drying at 70°C. Subsequent to synthesis, the bonding agent undergoes comprehensive characterization, including quantification of density (g cm^{-3}), equivalent weight, aziridine content (%), dynamic viscosity (cp), moisture content (%), and refractive index, to evaluate its physicochemical properties.

2.2 Composite solid rocket propellant (CSRP) materials and preparation

2.2.1 Materials

The chemicals employed in this study comprised hydroxyl-terminated polybutadiene (HTPB), a viscous liquid exhibiting a viscosity of 50–70 poise, a density of 0.91 g/cm^3, and a number-average molecular weight (Mn) between 2000 and 3000. The hydroxyl group content of HTPB ranged from 0.8 to 0.9 mg.eq. OH/g of HTPB. Additional components included ammonium perchlorate (AP) with particle sizes of 400, 200, and 7–11 µm, alongside aluminium (Al) particles sized 35–45 µm. The bonding agents, methyl salicylate-based compound (MSC) and tris (1-(2-methyl aziridinyl)) phosphine oxide (MAPO), were utilized to enhance adhesion. Toluene diisocyanate (TDI) served as the curing agent, while dioctyl azelate (DOZ) functioned as the plasticizer. All materials demonstrated high purity, ensuring consistency in experimental conditions and minimizing potential contamination during synthesis and analysis.

2.2.2 Preparation

A casting methodology was employed in the development of two distinct composite propellant formulations. The adhesive utilized in this investigation was HTPB prepolymer, possessing an equivalent OH/g HTPB of 0.85 mg, in conjunction with DOZ as a plasticizer and MSC, alongside MAPO functioning as a bonding agent. The prepolymer, bonding agent, and plasticizer were amalgamated at temperatures ranging from 43 to 50 °C, subsequent to which solid constituents (comprising AP at 72%, Al at 15%, and binder at 13%) were incrementally introduced and meticulously mixed for a period of 30 minutes. Following the mixing phase, a curing agent (TDI) was incorporated in a precise quantity to sustain an NCO/OH ratio of 0.75, and mixing was executed for a comparatively brief duration. The degasification procedure is designed to eradicate air bubbles from the slurry to accomplish a non-porous propellant amalgamation. This operation entailed positioning the cast specimens within an evacuated chamber for 30 minutes, succeeded by neutralization utilizing compressed nitrogen. The propellant slurry was subsequently cast into a bespoke mold to yield cured propellant specimens in block form, characterized by dimensions of 200.0 mm in height, 150.0 mm in length, and 150.0 mm in width, as illustrated in Figure (3).

Subsequent to the degassing procedure of the cast propellant slurry, the curing protocol was executed within an electric oven calibrated to a temperature of 60 °C for a span of (7–8) days. Thereafter, the electric oven was deactivated, and following a 24-hour interval that allowed the propellant temperature to descend to approximately 25 °C, the careful extraction of the propellant from the mold was conducted. The resulting sheets were then meticulously finalized and encased in polyethylene packaging accompanied by a silica-gel dehydrator to mitigate any potential detrimental effects resulting from humidity. The primary constituents of the composite propellant formulations prepared are delineated in Table (1), presented in terms of weight percentage.

Table.1: The primary components of the composite propellant formulations prepared.

Formulation	Binder %	AP %	Al %	MSC %	MAPO %	TDI NCO/OH%
A	13	72	15	0	0.3	0.75
B	13	72	15	0.3	0	0.75

2.3 physical properties result of MSC

The MSC bonding agent presents as a viscous blue liquid at ambient conditions, characterized by hydrophobic behaviour and an absence of detectable odour. To empirically characterize its physical properties, a series of standardized laboratory analyses were systematically conducted. Table.2 summarizes the quantitative outcomes of these evaluations, which include critical parameters such as density (g/cm^3), equivalent weight, aziridine content (%), dynamic viscosity (centipoise), moisture content (%), and refractive index. These metrics collectively provide a comprehensive profile of the material's physicochemical attributes, essential for assessing its compatibility and performance in composite propellant applications.

Table.2: the physical properties of MSC bonding agent.

Property	Equivalent weight	Density (g/cm^3)	Aziridine content (%)	Refractive index	Viscosity (cp)	Water content (%)
Results	174.4	1.1028	32.74	1.4631	424000	0.002

2.4 Mechanical properties measurements

The stress-strain behaviour and elastic modulus of each fabricated specimen were experimentally measured. Tensile testing was performed using a ZWICK model 1487 materials testing machine at 25°C, with a minimum of five samples tested per composite formulation. Average values from these tests were computed and documented. The investigation centered on a composite propellant containing 72% ammonium perchlorate (AP) as a solid oxidizer, 15% aluminium (Al) powder as a metallic fuel, and 13% HTPB polymeric binder. These components were homogenized under controlled time and temperature conditions before being cast into molds measuring 200×150×150 mm. The molds were cured in an oven at 60°C for 168 hours, after which they were sectioned into individual sheets.

Test specimens were precision-cut using a JANNAF-compliant hydraulic press. Notably, due to equipment constraints, the final specimen thickness was 11.04 mm below the standard specification. To ensure data reliability, quality checks involved X-ray inspection to detect defects like voids or cracks. Approved specimens were then stored in desiccators at 25°C and 30% relative humidity prior to testing.

3.Resultes

3.1 Mechanical properties of propellant samples

Evaluating the mechanical properties of the two propellant formulations (A and B), each incorporating distinct bonding agents (MAPO and MSC), was critical to verifying their ability to endure anticipated pressure, thermal, and mechanical stresses during storage and combustion. Mechanical testing of the propellant samples was conducted at 25°C, with key parameters summarized in Table 3. Measuring Shore A_0 hardness served as a critical quality control step to confirm complete curing, ensuring the specimens were suitable for mechanical evaluation.

As shown in Table.3, Formulation A demonstrated inferior mechanical performance compared to Formulation B. This disparity is attributed to the bonding agent type: while MSC enhanced yield strength and stress resistance in Formulation B, its use in Formulation A resulted in significantly lower maximum strain values, compromising overall mechanical integrity. These findings underscore the pivotal role of bonding agent selection in optimizing propellant durability under operational conditions.

Table.3: Stress-strain characteristics of different propellant formulations at 25°C.

Formulations	Max. Stress σ (kg_f/cm^2)	Max. Strain ε (%)	Young's Modulus E_0 (kg_f/cm^2)
A	10.4	27.8	44.5
B	8.71	47.9	25.9

Incorporating the MSC bonding agent at a fixed concentration of 0.3% (by total formulation weight) markedly improved the mechanical performance of Formulation B. This additive increased the propellant's ultimate strength (σ) and strain capacity compared to Formulation A, while maintaining a lower—yet functionally adequate—Young's modulus (E_0) for long-term shelf stability and aging resistance. The results highlight how MSC optimizes strength and deformability without compromising durability over time.

3.2Measurement of propellant combustion properties

The ballistic performance of the propellant formulations was evaluated using a standardized 2-inch motor test apparatus. In this method, the propellant was cast into cylindrical molds (2-inch diameter), cured, and subsequently integrated into the motor assembly. Combustion tests were conducted with 6mm nozzles to generate high pressures and burning rates, enabling the determination of pressure exponent (n) and burning rate constant (a) through empirical analysis. The burning rate (r) was calculated by measuring the web thickness of the cylindrical propellant grain, while Figure 1and 2 details the finalized 2-inch rocket motor assembly used for ballistic testing.

Figure 1. The grains of CSRP before assembly

Figure 2. The 2 inch motors after assembly

Two consecutive firings per formulation were performed to ensure reproducibility. The linear burning rate data, plotted against pressure for distinct nozzle diameters, were analyzed using the Vieille equation ($r = a \cdot P^n$), where r represents burning rate (mm/s), a is the pre-exponential factor, P is combustion pressure (Pa), and n is the pressure exponent. A computational least-squares regression method was applied to derive a and n, parameters that are formulation-specific and empirically determined rather than theoretically predicted. These values are conventionally ascertained via methods such as Strand Burner tests or Ballistic Evaluation Motors (BEMs). Crucially, a and n are valid only within defined pressure ranges, necessitating multiple parameter sets to model broader pressure regimes.

When plotted on logarithmic axes, the Vieille equation produces a linear relationship, with the slope (n) directly influencing combustion stability. Elevated n values (e.g., $n > 0.6$) induce steep burn rate-pressure dependencies, risking uncontrollable pressure spikes and catastrophic motor failure. Conversely, low n values (e.g., $n \approx 0$) result in pressure-insensitive combustion, complicating ignition and steady-state operation. For practical applications, optimal pressure exponents lie between 0.2 and 0.6, balancing ignition reliability and combustion stability. For instance, a pressure exponent of $n = 0.2$ ensures rapid burn rate escalation at low pressures, facilitating reliable motor start-up. Strand Burner testing of Formulations A and B yielded distinct pressure exponents ($n_A = 0.43$ and $n_B = 0.27$) and exponential factors ($a_A=2.653$ and $a_B=3.461$), both within the acceptable operational range, underscoring their suitability for controlled combustion under steady-state conditions. These results highlight the critical role of bonding agents and formulation chemistry in tailoring ballistic performance for propulsion systems.

3.3 Burning rate resulted

The linear burning rate data, derived from experimental ballistic evaluations conducted using two rocket motors equipped with 6 mm nozzles, were calculated using established methodologies. These results, referenced at 180 bar and 20.0°C, are summarized in Table.4 to facilitate comparative analysis of propellant performance.

Table.4: represent the value of burning rate of each formula at 180 bars.

Formulations	r (mm/s) at P 180 (1.013×10^5 Pa)	Pressure exponent(n)	Sensitivity factor(a)
A	24.745	0.43	2.653
B	14.065	0.27	3.461

The findings highlight the significant influence of bonding agents on the physicochemical and combustion characteristics of solid propellants. Specifically, the incorporation of the mesoporous silica composite (MSC) bonding agent was observed to enhance mechanical integrity and aging resistance in composite propellants. However, its impact on ballistic performance necessitates rigorous investigation, particularly due to its role in forming a hardened interfacial layer on ammonium perchlorate (AP) oxidizer particles. This layer delays flame penetration by increasing AP degradation time, thereby retarding the overall burning rate.

The MSC bonding agent reduced the pressure dependency of the burning rate (pressure exponent, n = 0.27), promoting combustion stability at elevated pressures. In contrast, propellant formulation A, utilizing MAPO as the bonding agent, exhibited a higher-pressure exponent (n = 0.43), correlating with unstable combustion under high-pressure conditions. Comparative analysis revealed a marked reduction in burning rate from 24.745 mm/s (Formulation A) to 14.065 mm/s (Formulation B) upon substituting MAPO with MSC. This decrease is attributed to improved adhesion between the polymeric binder and oxidizer, which mitigates flame propagation at the binder-oxidizer interface, resulting in a more controlled and uniform combustion process.

Furthermore, Figure.3 and Figure.4 MSC's cross-linking properties enhanced thermal stability and interfacial bonding, contributing to a plateau-burning behaviour. These outcomes underscore the critical role of bonding agent selection in tailoring combustion dynamics, particularly in balancing pressure sensitivity and operational stability. The findings advocate for the strategic use of MSC in formulations requiring reduced pressure exponents and enhanced combustion predictability, especially in high-pressure propulsion systems.

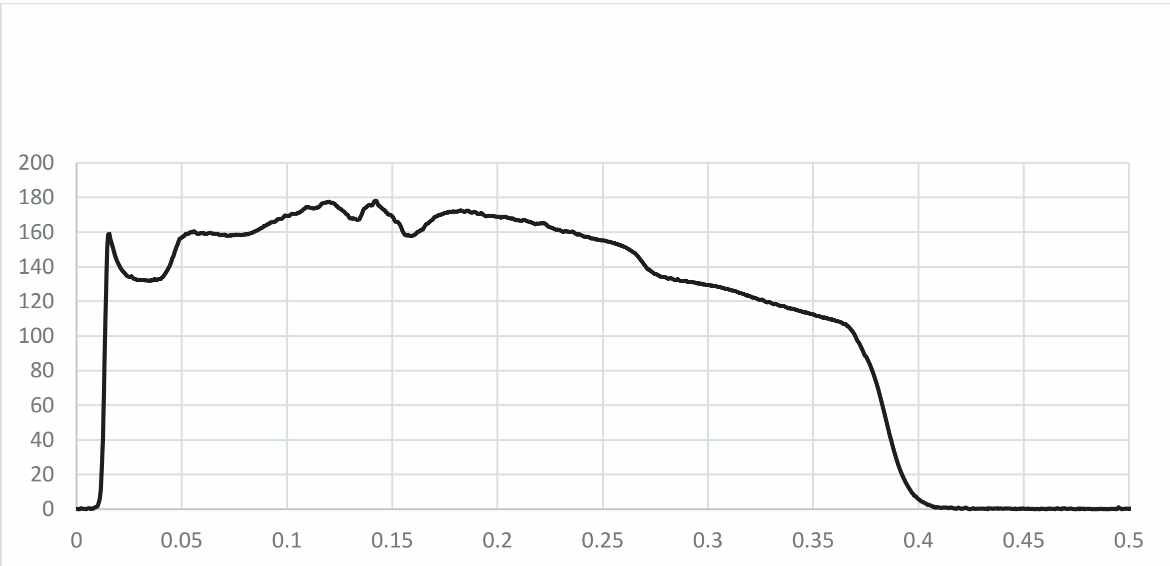


Figure.3:PT curve of formula A represent on irregular burning at high dynamic pressure (y axis represents on pressure in bar, x axis represents on time in second).

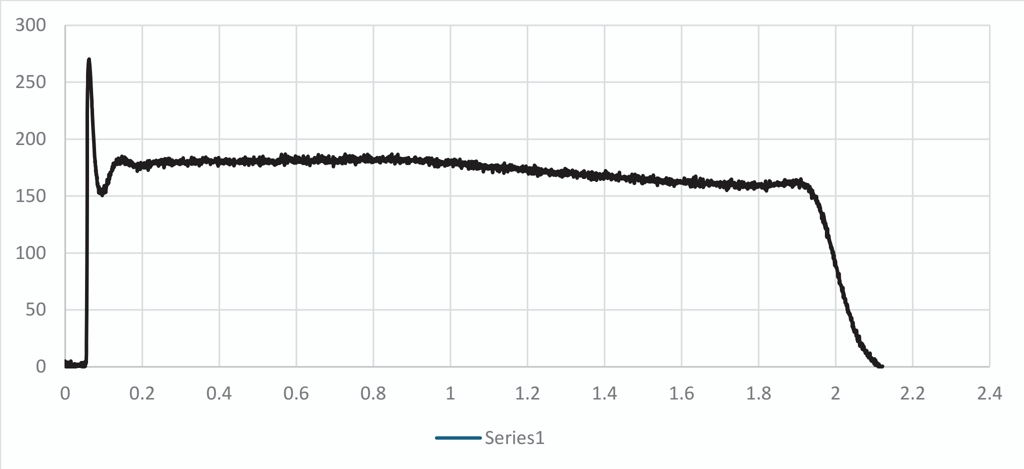


Figure.4:PT curve of formula A represent on regular burning at high dynamic pressure (y axis represents on pressure in bar, x axis represents on time in second).

4.Conclusion

This study demonstrates the critical role of bonding agents, specifically MSC and MAPO, in optimizing the mechanical and ballistic properties of composite propellants. The introduction of MSC significantly enhanced the mechanical strength, strain capacity, and stress resistance of the propellant, particularly in Formulation B, compared to MAPO. These improvements in mechanical properties are linked to MSC's dual functionality, enhancing adhesion at the binder-oxidizer interface and compensating for the elasticity deficit in the matrix. Moreover, the ballistic tests revealed that MSC reduced the pressure exponent of the propellant, promoting more stable combustion performance at elevated pressures. While the burning rate was lower for Formulation B, this trade-off in burning rate was beneficial for improved combustion stability and predictable performance. The findings emphasize the importance of carefully selecting bonding agents to tailor propellant behaviour for specific propulsion system requirements, balancing mechanical durability with controlled burning rates and stable combustion.

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