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Effects of Accelerated Aging and Primer on the Mechanical Properties and Bond Strength at Propellant–Liner Interfaces

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This study explores the influence of accelerated aging and primer composition on the bond strength at the solid propellant–liner interface. Tris(methyl-aziridinyl) phosphine oxide (MAPO) was employed as the primary bonding agent, formulated with two curing agents—toluene diisocyanate (TDI) and isophorone diisocyanate (IPDI)—in varying ratios. Propellant samples were subjected to accelerated aging at 70 °C for 0, 8, 16, and 24 days, corresponding to simulated storage durations of 0, 3, 6, and 9 years under ambient conditions. Mechanical testing revealed that increasing aging time resulted in higher tensile strength and hardness, accompanied by a gradual reduction in elongation, indicative of increased crosslink density and polymer matrix stiffening. Bond strength at the propellant–liner interface was evaluated using tensile tests on rectangular specimens coated with primers of different compositions. Among all formulations tested, the MAPO:IPDI ratio of 1:9 demonstrated superior adhesion performance, maintaining the highest bond strength across all aging intervals. Compared to unprimed controls, this formulation improved bond strength by 18 – 55 %, depending on aging duration. These results provide valuable insights for optimizing primer design and aging protocols in the production of solid rocket motors, thereby enhancing the long-term reliability and structural integrity of propulsion systems.

1. Introduction

Rocket propulsion technology plays a critical role in modern defense, space exploration, and aerospace industries. The reliability of solid rocket motors depends largely on the performance of solid propellants, particularly on the integrity of the bond between the propellant and the liner. The liner not only serves as insulation but also facilitates adhesion, and the interfacial bond strength directly affects mechanical durability, safety, and service life of propulsion systems (Sureshkumar et al., 2013).

Accelerated aging is a key method for evaluating long-term reliability, since thermal and environmental stresses can progressively degrade both bulk properties and interfacial adhesion (Cerri and Bohn, 2009). To improve bonding at the propellant–liner interface, primers are widely applied as interfacial coupling agents. Among them, isophorone diisocyanate (IPDI) and toluene diisocyanate (TDI) are the most common, with distinct chemical reactivity and curing kinetics that strongly influence adhesion strength (Park et al., 2020). Selecting an appropriate primer formulation is therefore essential for reducing debonding risk and maintaining stability during storage.Previous studies have highlighted that interfacial degradation is a critical determinant of rocket motor shelf life (Lei et al., 2022), while oxidative crosslinking of hydroxyl-terminated polybutadiene (HTPB) binders reduces ductility during aging (Michael, 2003; Li et al., 2021). Work on MAPO-containing primers further showed enhanced bonding when combined with diisocyanates (Guo et al., 2014; Park et al., 2020). More recently, molecular simulations confirmed the role of interface-driven crosslinking in governing mechanical response (Ling et al., 2025). However, the combined effects of primer composition and accelerated aging remain insufficiently explored in HTPB-based systems.

This study builds on previous work on curing parameters at the propellant–liner interface (Kitinirunkul et al., 2025) and extends the scope to primer formulation and accelerated aging. The objectives are: (i) to evaluate

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the influence of thermal aging on the mechanical properties of the propellant, (ii) to determine the adhesion performance of different primer formulations under fresh and aged conditions, and (iii) to establish correlations between degradation behavior and underlying chemical mechanisms. These findings aim to provide practical guidelines for optimizing primer selection and predicting long-term interfacial reliability in solid rocket motors.

2. Methodology

This section comprises three parts: (i) materials, (ii) methods, and (iii) measurements, all of which are described in detail below.

2.1 Materials

The propellant formulation was based on hydroxyl-terminated polybutadiene (HTPB) with a hydroxyl value of 0.523 mmol/g (Zibo Qilong Chemical Industry Co., Ltd.) and cured with toluene diisocyanate (TDI) containing 47.4 % isocyanate groups (Sigma-Aldrich Co., Ltd.). Table 1 summarizes the compositions used in both the propellant and liner formulations.

Table 1: Compositions of propellant and liner formulations.

	Propellant (wt. %)	Liner (wt. %)
Hydroxyl terminated polybutadiene (HTPB)	9.18	60.20
Toluene diisocyanate (TDI)	0.48	10.40
Aluminum powder (Al)	18.50	-
Ammonium perchlorate (AP)	67.50	-
Zinc oxide	-	19.50
plasticizer, processing aid, antioxidant, burning rate, etc.	4.34	9.90

2.2 Methods

The experimental procedure consisted of two main parts: (i) preparation of propellant specimens for accelerated aging and mechanical testing, and (ii) preparation of rectangular specimens for evaluating interfacial bond strength. The detailed procedures for specimen preparation, mixing, casting, curing, and testing were described in our previous publication (Kitinirunkul et al., 2025). In the present work, the same methods were applied, with the addition of primer application steps prior to propellant casting. Primer formulations shown in Table 2 were coated on cured liner surfaces before propellant casting. The specimens were subjected to accelerated aging at 70 °C for 8, 16, and 24 days.

2.2.1 Preparation of Propellant Specimens for Accelerated Aging and Mechanical Testing

Propellant specimens were cast using the formulation shown in Table 1 and prepared according to the experimental procedure illustrated in Figure 1. The samples were then subjected to accelerated aging at 70 °C for specified durations before mechanical testing.

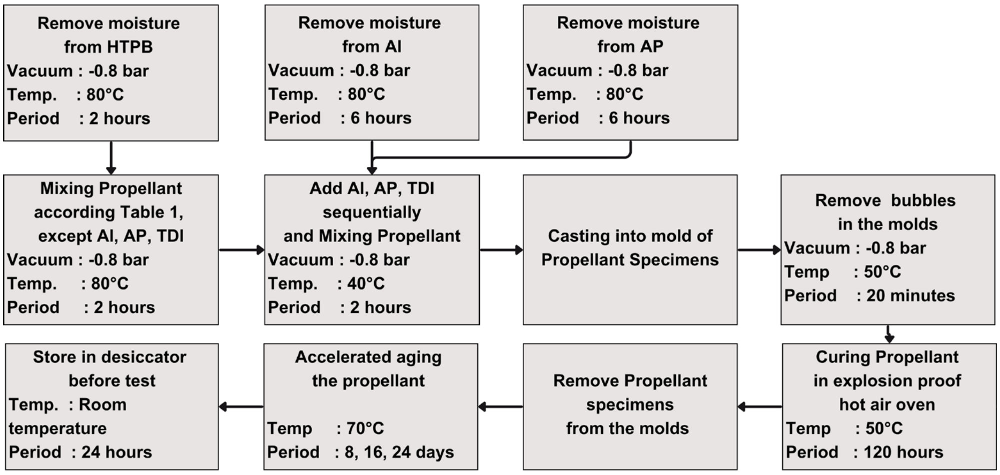


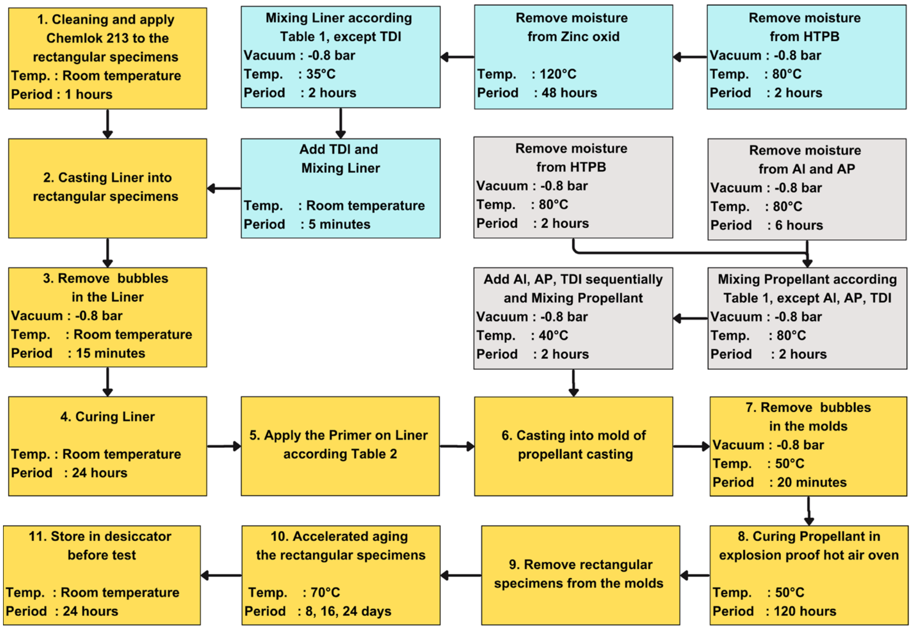
Figure 1: Flowchart of propellant specimen preparation.

2.2.2 Preparation of Rectangular Specimens for Interfacial Bond Strength Testing

Rectangular specimens were prepared using the same propellant and liner compositions as shown in Table 1. The preparation procedure is detailed in Figure 2, including primer application prior to curing.

Table 2: Primer formulations and mixing ratios.

	Primer 1	Primer 2	Primer 3	Primer 4	Primer 5	Primer 6	No Primer
Type	*IPDI : MAPO*			*TDI : MAPO*			-
Ratio	1 : 9	5 : 5	9 : 1	1 : 9	5 : 5	9 : 1	-



2.3 Measurements

The properties of the aged and unaged specimens were evaluated through both mechanical and adhesion testing.

2.3.1 Mechanical Properties Testing

Tensile strength and elongation were measured using a Universal Testing Machine (UTM, Instron 5965) according to ASTM D638 (Type IV) at 25 °C and 100 mm/min crosshead speed.
Hardness (Shore A) was measured using a Bareiss BS61/HPE II durometer.

2.3.2 Interface Bond Properties Testing

Bond strength between the propellant and liner was assessed using a UTM at ambient temperature, with a crosshead speed of 20 mm/min. Adhesion failure surfaces were also observed to determine failure modes.

3. Results and Discussion

The experimental results are categorized into two sections: (i) mechanical properties of the solid propellant, and (ii) interfacial bond strength between the propellant and liner. All results were compared against the design criteria for quality control in solid rocket motor production, as summarized in Table 3.

Table 3: Design values for quality control in solid rocket motor production.

Property	Unit	Design value	Test conditions
Tensile Strength	MPa	≥0.50	25 °C, 100 mm/min
Elongation	%	≥25	25 °C, 100 mm/min
		≥20	70 °C, 20 mm/min
Hardness	Shore A	≥45	25 °C
Interfacial Bond Strength	MPa	≥0.55	25 °C, 20 mm/min

Equivalent natural aging durations of 3, 6, and 9 years were estimated from accelerated aging at 70 °C for 8, 16, and 24 days using Van't Hoff's rule with a rate factor (F) of 3 and ΔT of 10 °C, as summarized in Table 4. Cerri and Bohn (2009) reported F values of approximately 3 for aging processes with activation energies of 80–120 kJ/mol. Similarly, Michael (2003) confirmed the applicability of this assumption in HTPB-based systems. These findings validate the use of thermal acceleration to simulate long-term storage effects.

Table 4: Accelerated aging durations and corresponding natural aging equivalence.

Accelerated Aging, Days	0	8	16	24
Natural Aging, Years	0	3	6	9

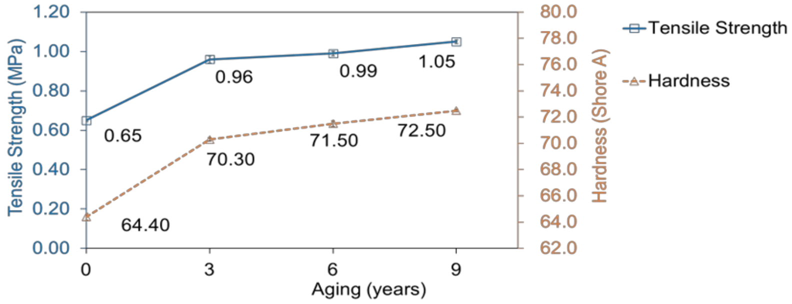


Figure 3: Tensile strength and hardness of propellant over aging duration.

3.1 Mechanical Properties of the Propellant

Figures 3–4 illustrate the changes in tensile strength, hardness, and elongation of the propellant over equivalent aging durations of 0–9 years. The error bars denote standard deviations from five replicates (n = 5). Both tensile strength and hardness showed a gradual increase with aging, consistent with prior findings in HTPB-based systems. This trend is attributed to oxidative crosslinking, which enhances stiffness and limits molecular mobility (Michael, 2003; Li et al., 2021). In addition, the fundamental curing reaction between hydroxyl (–OH) groups in HTPB and isocyanate (–NCO) groups in TDI/IPDI forms urethane linkages, thereby increasing crosslink density (Ramos et al., 2005). Wang et al. (2022) also noted that increased crosslinking raises shear modulus, thereby reinforcing tensile properties. Throughout all aging intervals, the tensile strength remained above 0.50 MPa and hardness exceeded 45 Shore A, meeting the design requirements summarized in Table 3.

Conversely, elongation declined over time due to restricted polymer chain movement resulting from denser crosslinking (Wang et al., 2022; Li et al., 2021). Nevertheless, elongation remained above 25 % at 25 °C and 20 % at 70 °C, meeting the minimum ductility criteria. These trends align with the findings of Cerri and Bohn (2009), supporting the long-term mechanical reliability of the formulation under accelerated aging conditions. It should also be noted that the slight deviation in elongation at 70 °C occurred at the initial condition (0 year). This anomaly is likely due to specimen variability, such as small air bubbles trapped during casting, and falls within the standard deviation of repeated tests.

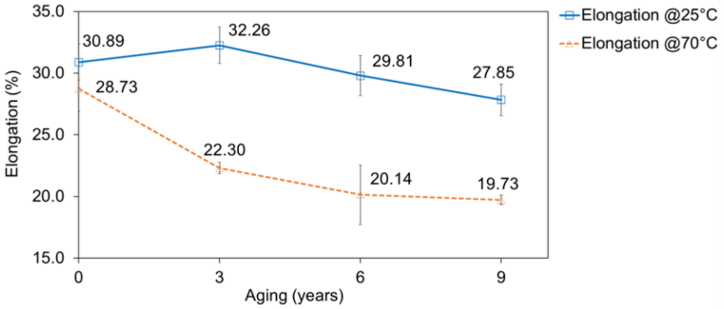
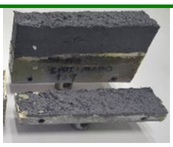
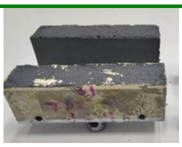
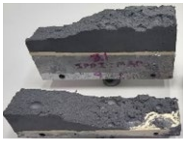
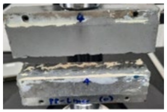


Figure 4: Elongation of propellant over aging duration.

3.2 Interfacial Bond Strength at the Propellant–Liner Interface

Six primer formulations and an unprimed control were evaluated against the design threshold of 0.55 MPa (Table 5). The control reached 0.71 MPa with propellant residue on the liner, indicating cohesive failure and adequate baseline adhesion. Primer 3 (IPDI:MAPO = 9:1) gave the highest and most consistent bond (0.84 MPa, cohesive failure). Primer 4 (TDI:MAPO = 1:9) marginally exceeded the threshold (0.56 MPa). By contrast, Primer 1 (IPDI:MAPO = 1:9) showed the lowest strength (0.16 MPa); visual inspection revealed undercured propellant at the interface, likely due to IPDI’s slower curing kinetics. Primer 1 was nevertheless retained for further study because of possible long-term benefits.These results are consistent with previous experimental reports that MAPO enhances interfacial bonding when combined with diisocyanates (Guo et al., 2014; Park et al., 2020). Recent molecular simulations also support a mechanistic interpretation: Ling et al. (2025) demonstrated interface-driven crosslinked network formation and its influence on the mechanical response of composite propellants. Together, experimental and computational evidence indicate that primer composition and curing kinetics control both initial adhesion and long-term interfacial durability under thermal aging.

Table 5: Interfacial bond strength and fracture surface morphology at the propellant–liner interface with different primer formulations (0-year aging).

	IPDI : MAPO		TDI : MAPO	
Ratio	Bond Strength (MPa, n=3)	Fracture Surface	Bond Strength (MPa, n=3)	Fracture Surface
1 : 9	(Primer 1) 0.16±0.03		(Primer 4) 0.56±0.04	
5 : 5	(Primer 2) 0.38±0.16		(Primer 5) 0.41±0.01	
9 : 1	(Primer 3) 0.84±0.06		(Primer 6) 0.15±0.08	
No Primer	0.71±0.09			

Following initial evaluation, selected primer formulations were subjected to accelerated aging at 70 °C for 8, 16, and 24 days, simulating 3, 6, and 9 years of storage. Bond strength results, shown in Figure 5, revealed a consistent increase over time for all specimens. This enhancement is attributed to ongoing NCO–OH reactions that promote interfacial crosslinking during storage. This trend aligns with oxidative crosslinking behavior previously observed in the bulk matrix (Section 3.1), contributing to enhanced interfacial properties during aging. Primer 3 (IPDI:MAPO = 9:1) consistently outperformed other formulations, increasing bond strength by up to 55 % relative to the control and maintaining values above the 0.55 MPa threshold across all aging periods. Primer 4 (TDI:MAPO = 1:9) showed moderate improvement until 6 years but plateaued thereafter, suggesting limited long-term efficiency.Although Primer 1 (IPDI:MAPO = 1:9) demonstrated significant gains at later stages, it failed to meet the design criterion at early periods, indicating unsuitability for immediate use despite potential in long-term storage scenarios. These trends align with earlier curing observations, reinforcing the role of isocyanate content in bond development. Primer 3 is therefore recommended for applications requiring durable adhesion under aging-sensitive conditions.

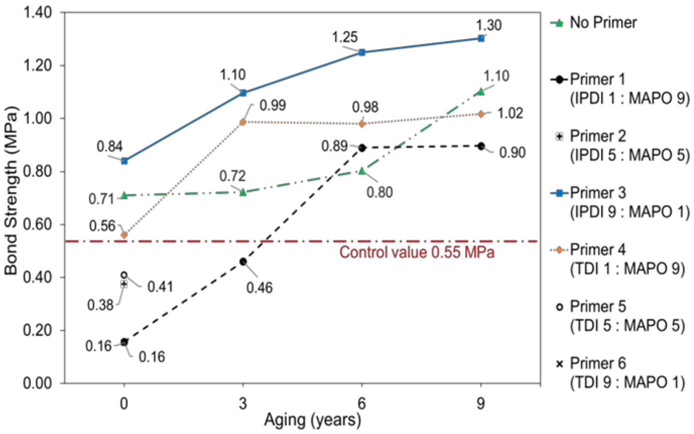


Figure 5: Bond strength at the propellant–liner interface with different primer formulations over aging durations.

These findings align with Guo et al. (2014), who reported that increasing MAPO concentration enhances interfacial bonding, particularly when combined with diisocyanates, and with Park et al. (2020), who showed that MAPO-based primers improve adhesion with both IPDI and TDI systems. The present study extends these results by highlighting that primer composition not only governs initial adhesion but also determines long-term durability under thermal aging. In particular, the superior performance of IPDI:MAPO (9:1) underscores the role of slower curing kinetics in sustaining interfacial crosslinking and ensuring reliable adhesion during storage.

4. Conclusions

Accelerated aging results confirmed that the propellant maintained mechanical integrity over an equivalent service life of 0–9 years, with all properties remaining above the quality control thresholds. Among the primer formulations, IPDI:MAPO at a 9:1 ratio (Primer 3) consistently provided the highest and most durable bond strength under thermal aging. These findings demonstrate that primer composition is a critical factor for ensuring long-term interfacial reliability, offering a practical guideline for solid rocket motor applications requiring extended storage stability.

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