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Effect of Curing Parameter on the Mechanical Properties and Bond Strength at Propellant-Liner Interfaces in Rocket Motors

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This study investigates the effect of curing parameters (Rt) on the mechanical properties and bond strength of propellants and liners in rocket motors compared to the design values. The optimal curing parameters for the propellant and liner in interface bonding were identified. Hydroxyl-terminated polybutadiene (HTPB) was used as the binder, while toluene diisocyanate (TDI) was employed as the curing agent. Various curing parameters were tested, with Rt values for the propellant (0.75 to 1.55) and liner (0.90 to 1.70). The results showed that the best mechanical properties for the liner and propellant were achieved at Rt values of 0.90 and 1.11, respectively. Subsequent interface bonding tests and analyses determined the optimal curing parameters to be 0.90 for the liner and 1.15 for the propellant. These optimal parameters resulted in a bond strength of 0.75 MPa, with the mechanical properties of the propellant and liner exceeding the required design values. The findings from this study can be utilized to enhance the manufacturing process of rocket motors and ensure their reliable performance.

1. Introduction

Solid rocket motors consist of several components, including the motor tube, insulation, liner, propellant and other elements (Sureshkumar et al., 2013). The bond strength at the propellant-liner interface affects the burning surface area of the propellant. If separation occurs between the propellant and the liner, the burning surface area will deviate from the designed specifications. This deviation can impact the pressure and thrust generated during combustion, potentially causing the rocket's performance to fail to meet the specified requirements (Thirapat et al., 2021). Additionally, it may lead to safety issues during rocket operation due to irregular ignition. Separation at the propellant-liner interface can arise due to various factors, such as changes in material properties or long-term storage. During production, the propellant and liner are subjected to different types of stress, including thermal stress caused by environmental temperature fluctuations in storage areas and mechanical stress from vibrations during transportation, ignition, and rocket movement. Therefore, both the propellant and liner must have sufficient tensile strength and elongation to withstand these stresses.

This research utilizes hydroxyl-terminated polybutadiene (HTPB), which exhibits excellent aging resistance, long shelf life, and low viscosity, allowing for solid particles to enhance the rocket's combustion energy and act as a binder. Toluene diisocyanate (TDI) is used as the curing agent. The study of the aging behavior of composite solid propellants, with HTPB as the primary material, focuses on the cross-link density, generally determined by the curing parameter or the molar ratio of isocyanate groups to hydroxyl groups (Götz, 2002). Key factors influencing bond properties include the type and proportion of liner and propellant, as well as the manufacturing process (Pang and Zheng, 2004). Therefore, the materials chosen for the liner must be compatible with the propellant. Adhesion between the liner and the propellant occurs through polymerization, involving the reaction between isocyanate groups and hydroxyl groups (Liao and Lee, 2015). In the formulation of the liner, beyond selecting a curing agent with suitable mechanical properties, it is crucial to ensure an adequate amount of isocyanate groups from TDI in the liner to react with the hydroxyl groups from HTPB in the propellant.

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Additionally, atmospheric moisture must be considered to achieve the designed bond strength between the materials (Huang et al., 2012).Accordingly, this study investigates how the curing parameter (Rt) influences both the mechanical properties and interfacial bond strength of HTPB-based propellants and liners. While previous research has typically focused on either mechanical or bonding aspects in isolation, this work simultaneously correlates Rt with tensile strength, elongation, density, and adhesion. Such an integrated approach offers novel insights for optimizing formulation and manufacturing strategies in solid rocket motor design.

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

Hydroxyl-terminated polybutadiene (HTPB) is a versatile prepolymer characterized by reactive hydroxyl end groups that facilitate further chemical modification, particularly through cross-linking reactions with isocyanates to form polyurethane networks. Owing to its inherent flexibility, low viscosity, and high energy content, HTPB has been extensively utilized as a binder in composite rocket propellants. Wu et al. (2023) demonstrated that HTPB-based binders provide a mechanically robust yet flexible matrix capable of incorporating substantial amounts of energetic additives, including metallic fuels and oxidizers, without compromising mechanical performance. In addition, Long et al. (2021) reported that HTPB-based propellants exhibit excellent tensile strength and elongation characteristics, rendering them suitable for solid rocket motor applications. In this study, HTPB with a hydroxyl value of 0.51 mmol/g was sourced from Zibo Qilong Chemical Industry Co., Ltd. Toluene diisocyanate (TDI) serves as a primary curing agent in the synthesis of polyurethane materials due to its ability to react with hydroxyl groups to form highly cross-linked urethane structures. This cross-linking enhances both the mechanical strength and density of the resulting polymer. Oertel (1994) highlighted the role of TDI in increasing polyurethane rigidity, noting its higher specific gravity compared to HTPB, which contributes to the overall density of the cured propellant. In the present study, TDI with an isocyanate content of 46 % was procured from Sigma Aldrich Co., Ltd.

2.2 Methods

This section comprises three parts: (i) preparation of liner specimens for mechanical property testing, (ii) preparation of propellant specimens for mechanical property testing, and (iii) preparation of rectangular specimens for bond strength testing between the liner and propellant.

2.2.1 Preparation of Liner Specimens for Mechanical Property Testing

The preparation of liner specimens for mechanical property testing began by stirring HTPB in a vacuum mixer at 80 °C under vacuum pressure for 2 hours, ensuring moisture removal. Zinc oxide and silicon dioxide were dried in a hot air oven at 120 °C in atmospheric pressure for 48 hours to eliminate any residual moisture. The dried materials were mixed with HTPB and other ingredients, except TDI, according to the proportions specified in Table 1. This mixing process was performed at room temperature under vacuum pressure for 2 hours to produce a uniform mixture. TDI was subsequently introduced to the blend and mixed for an additional 5 minutes under atmospheric pressure to achieve homogeneity. The mixed liner was then cast into molds based on calculated weights to obtain the desired specimen thickness, as shown in Figure 1A. To remove air bubbles, the molds were placed in a vacuum chamber at room temperature under vacuum pressure for 15 minutes. Afterward, the molds were left to cure at room temperature at atmospheric pressure for 24 hours. Once fully cured, the specimens were removed from the molds and subjected to standardized mechanical property testing. This entire process was repeated with different Rt values for the liner, as indicated in Table 1, to investigate the effects of varying the curing parameters.

Table 1: Materials used to produce liners at different Rt values.

Constituent of Liner Specimens	Weight percentage, %				
	Rt 0.90	Rt 1.10	Rt 1.30	Rt 1.50	Rt 1.70
Hydroxyl terminated polybutadiene (HTPB)	64.12	62.75	61.40	60.08	58.77
Toluene diisocyanate (TDI)	6.48	7.85	9.20	10.52	11.83
Zinc oxide	19.50	19.50	19.50	19.50	19.50
Other	9.90	9.90	9.90	9.90	9.90

Note: “Other” refers to a combination of plasticizer, processing aid, cure catalyst, thixotropic agent, and chain extender. The exact composition is consistent across all formulations and maintained at 9.90 % by weight.

2.2.2 Preparation of Propellant Specimens for Mechanical Property Testing

In the preparation of propellant specimens for mechanical property testing, HTPB was stirred in a vacuum mixer at 80 °C under vacuum pressure for 2 hours to remove moisture. Aluminum powder (Al) and ammonium perchlorate (AP) were dried separately in a hot air oven at 80 °C under vacuum pressure for 6 hours. The primary mixture, excluding Al, AP, and TDI, was combined at 80 °C under vacuum pressure for 2 hours in a vertical planetary batch mixer, as shown in Figure 1B. Subsequently, Al, AP, and TDI were gradually added to the mixture and stirred at 40 °C under vacuum pressure for an additional 2 hours to achieve homogeneity. The propellant mixture was then cast into molds, as shown in Figure 1C. Air bubbles were removed by placing the molds in a vacuum chamber under vacuum pressure for 20 minutes at 50 °C. The specimens were then cured in an explosion-proof hot air oven at 50 °C at atmospheric pressure for 120 hours. After curing, the specimens were carefully removed from the molds and subjected to standardized mechanical property testing. The entire process was repeated with different Rt values for the propellant, as per the experimental design in Table 2.

Table 2: Materials used to produce propellant at different Rt values.

Constituent of Propellant Specimens	Weight percentage, %				
	Rt 0.75	Rt 0.95	Rt 1.11	Rt 1.15	Rt 1.55
Hydroxyl terminated polybutadiene (HTPB)	9.344	9.263	9.200	9.184	9.029
Toluene diisocyanate (TDI)	0.316	0.397	0.460	0.476	0.631
Aluminum powder (Al)	18.50	18.50	18.50	18.50	18.50
Ammonium perchlorate (AP)	67.50	67.50	67.50	67.50	67.50
Other	4.34	4.34	4.34	4.34	4.34

Note: “Other” refers to a combination of plasticizer, bonding agent, processing aid, antioxidant, and burning rate catalyst. The exact composition is consistent across all formulations and maintained at 4.34 % by weight.

2.2.3 Preparation of Rectangular Specimens for Bond Strength Testing between Liner and Propellant

For preparing rectangular specimens to test the bond strength between the liner and propellant, the rectangular mold was initially cleaned, and sandblasting was performed to prepare the surface, followed by a coating of chemlok 213 adhesive, which was left to dry for 1 hour. The liner material was prepared as previously described and poured into the mold coated with chemlok 213, as shown in Figure 1D. After allowing the liner to cure for at least 24 hours, the mold, now containing the cured liner, was assembled in the mold for rectangular specimens, as shown in Figure 1E. The propellant was prepared as previously described and cast in the mold, and the propellant was cured for at least 120 hours before demolding, as shown in Figure 1F. This procedure was repeated for various Rt values of both the liner and the propellant as per Table 3.

Table 3: Experimental design for determining the bond strength between the propellant and the liner.

Repeat of Rt values	1	2	3	4	5	6	7	8	9	10	11	12
Rt Liner	0.90	0.90	0.90	0.90	1.50	1.50	1.50	1.50	1.70	1.70	1.70	1.70
Rt Propellant	0.75	0.95	1.15	1.55	0.75	0.95	1.15	1.55	0.75	0.95	1.15	1.55

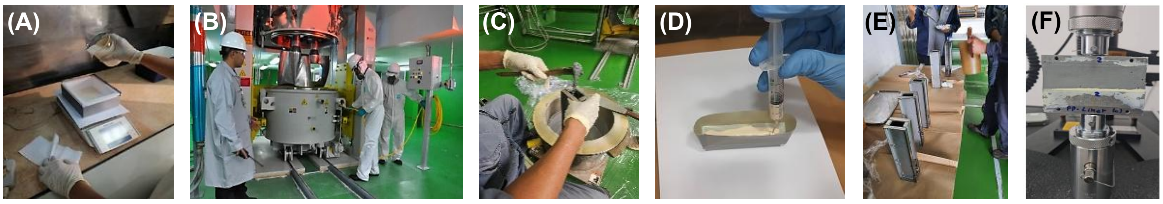

Figure 1: Preparation of liner, propellant and rectangular specimens.

2.3 Measurements

This section consists of two parts that are mechanical properties testing and interface bond properties testing.

2.3.1 Mechanical Properties Testing

The density of the liner and propellant was determined using a Density Analyzer (Mettler Toledo XP 105). Tensile strength and elongation for the liner and propellant were subsequently measured via a Universal Testing Machine (Instron 5965), with specimens prepared following ASTM D638 Type IV.

2.3.2 Interface Bond Properties Testing

The bond strength at the interface between the liner and propellant was evaluated using a Universal Testing Machine (Instron 5966) under ambient temperature. This test is crucial for determining the adhesion efficacy between the two materials, directly impacting the durability and performance reliability of the composite solid propellant in practical applications.

3. Results and Discussion

The test results in this research are divided into three sections. These results are compared with the design values for quality control in the production of solid rocket motors, as shown in Table 4. This comparison aims to determine which curing parameters are suitable for practical use.

Table 4: Design values for quality control in the production of liner and propellant.

	Design value of liner	Design value of propellant	Test conditions
Tensile Strength (MPa)	≥1.20	≥0.60	25 °C, 100mm/min
Elongation (%)	≥150.0	≥35.0	25 °C, 100mm/min
Density (kg/m^3)	≤1,200	≥1,750	25 °C

3.1 Mechanical Properties of Liner

Tensile strength tests indicated that as the curing parameter increased, the tensile strength also increased, as shown in Figure 2. This is because the increase in curing agent enhances the cross-linking between the isocyanate groups (NCO) and hydroxyl groups (OH), resulting in a harder liner. The acceptable range for the Rt value, according to Table 4, is between 0.90 and 1.70, with an Rt value of 1.70 providing the highest tensile strength for the liner at 6.90 MPa.Elongation tests revealed that as the curing parameter increased, the elongation decreased, as shown in Figure 2. This is because increased cross-linking results in a harder liner, which reduces its elasticity. The acceptable range for the Rt value, according to Table 4, is between 0.90 and 1.70, with an Rt value of 0.90 providing the highest elongation at 643.66 %.Density tests showed that as the curing parameter increased, the density also increased, as shown in Figure 4. This is because TDI (toluene diisocyanate) has a specific gravity of 1,220 kg/m^3, which is higher than HTPB (hydroxyl-terminated polybutadiene) with a specific gravity of 900 kg/m^3, following the mixing rules. The acceptable range for the Rt value, according to Table 4, is between 0.90 and 1.70, with an Rt value of 0.90 resulting in the lowest density at 1,153.20 kg/m^3.

3.2 Mechanical Properties of Propellant

Figures 3 and 4 illustrate the effects of increasing the curing parameter on the mechanical properties of the propellant. Figures 3 - 4 do not show the propellant at Rt 0.75 because the decrease in curing agent content resulted in insufficient cross-linking between the NCO groups and OH groups, as shown in Figure 6A.

Tensile strength testing showed that as the curing parameter increased, the tensile strength also increased, as shown in Figure 3. This is because increasing the curing agent leads to more cross-linking between isocyanate groups and hydroxyl groups. The acceptable range for the Rt value, according to Table 4, is between 0.95 and 1.55, with an Rt value of 1.55 giving the highest tensile strength of the propellant at 1.21 MPa.

Elongation testing showed that as the curing parameter increased, the elongation decreased, as depicted in Figure 3. This is because increased cross-linking in the material leads to greater stiffness, reducing flexibility. For an Rt value within the range of 0.95 - 1.11, according to Table 4, an Rt value of 0.95 resulted in the highest elongation of 111.51 %.Density testing showed that as the curing parameter increased, the density also increased, as illustrated in Figure 4. This is because TDI has a specific gravity of 1,220 kg/m^3, which is higher than HTPB with a specific gravity of 900 kg/m^3, following the mixing rules. The acceptable range for the Rt value, according to Table 4, is between 0.95 and 1.55, with an Rt value of 1.55 resulting in the highest density at 1,762.20 kg/m^3.

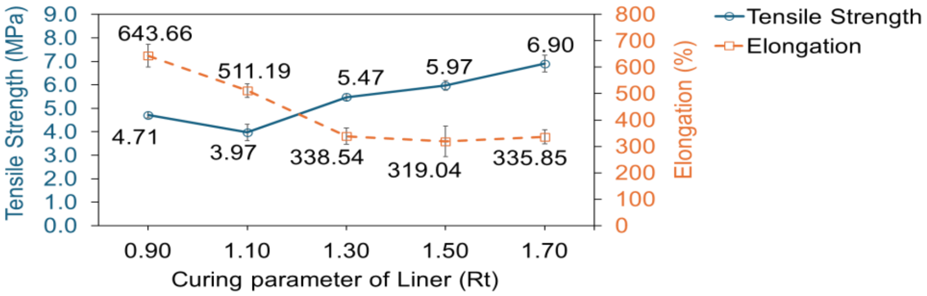

Figure 2: Tensile strength and elongation of liner. Error bars represent S.D. from five replicates (n = 5).

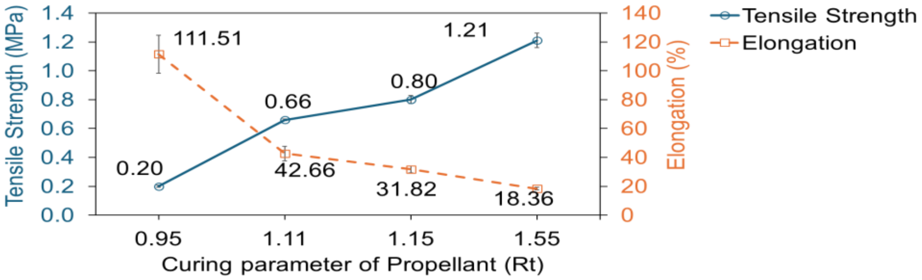

Figure 3: Tensile strength and elongation of propellant. Error bars represent S.D. from five replicates (n = 5).

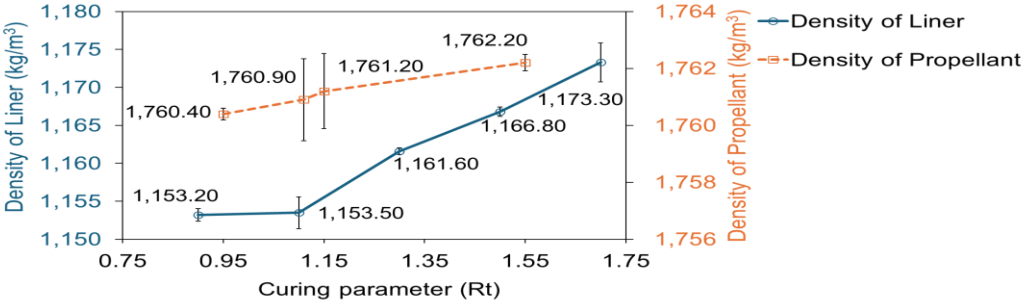

Figure 4: Density of liner and propellant. Error bars represent S.D. from three replicates (n = 3).

3.3 Bond Strength of Propellant - Liner

Figure 5 illustrates the results from testing, showing that the maximum bond strength between the liner and propellant is 0.79 MPa, which occurs at a curing parameter of 0.90 and 1.55.

When considering various other properties of the propellant, it was determined that the propellant with an Rt value of 1.15 exhibited superior elongation properties at 25 °C compared to the propellant with an Rt value of 1.55. Therefore, the optimal curing parameters for the liner and propellant are 0.90 and 1.15, respectively, resulting in a bond strength of 0.75 MPa.

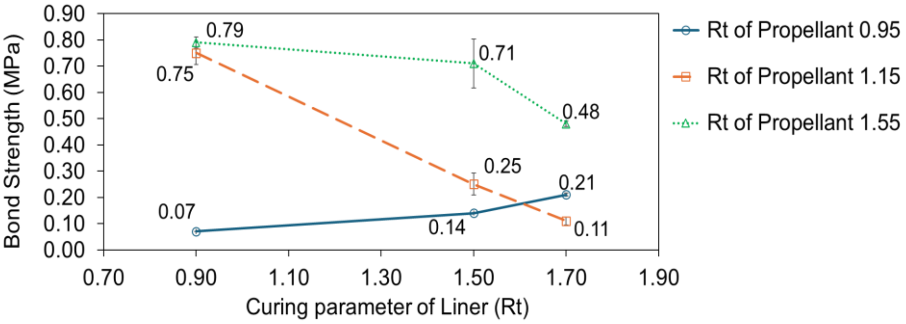

Figure 5: Bond strength at propellant-liner interfaces. Error bars represent S.D. from three replicates (n = 3).

From the graph, it is evident that when both materials have a curing parameter greater than 1.0, their combination tends to decrease bond strength. This is because the curing parameter represents the molar ratio of isocyanate groups to hydroxyl groups (NCO/OH ratio), influencing the formation of a cross-linked network between the rubber matrix of the liner and the hydroxyl groups of the propellant, as shown in Figure 6B.

When the liner has an Rt value either less or more than 1.0 and is bonded with a propellant that has an Rt value less than 1.0, the bond strength decreases. This is due to the propellant having a higher quantity of hydroxyl groups compared to isocyanate groups, resulting in lower mechanical properties for the propellant, as shown in Figures 6C-D.Therefore, when the liner has an Rt value less than 1.0 and is bonded with a propellant that has an Rt value greater than 1.0, it results in increased bond strength. This is due to the formation of a cross-linked network between the hydroxyl groups of the liner and the isocyanate groups of the propellant, as shown in Figure 6E.The maximum bond strength obtained in this study was 0.79 MPa at an Rt of 0.90 for the liner and 1.55 for the propellant. When compared to the findings of Wu et al. (2023), who reported bond strengths in the range of 0.5 – 0.9 MPa for HTPB-based systems under similar loading conditions, the results here fall within a comparable range, thereby validating the experimental design and formulation. Additionally, Liao and Lee (2015) demonstrated that a well-balanced NCO/OH ratio between liner and propellant could result in bond strengths exceeding 0.70 MPa, particularly when isocyanate-rich systems are bonded with hydroxyl-rich substrates—an outcome consistent with the improved adhesion observed in the 0.90/1.15 Rt combination in this study. Similarly, the mechanical properties of both liner and propellant in the present study exceed the design criteria shown in Table 4 and are also consistent with the reported range from Wu et al. (2023), who highlighted tensile strengths of 1.1–1.3 MPa and elongation above 100 % for optimized formulations. This confirms the compatibility and effectiveness of the curing strategy implemented here, especially for mission-critical solid rocket motor applications where interfacial integrity and flexibility must be balanced.

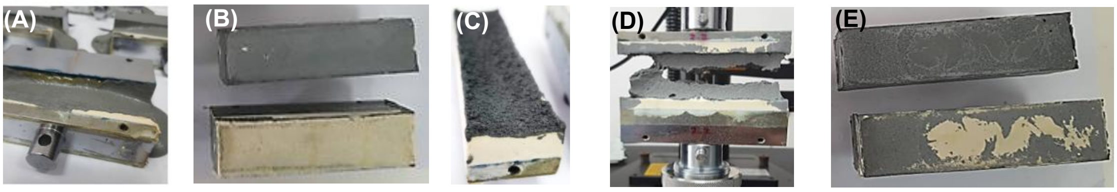

Figure 6: Rectangular specimens for bond strength testing between liner and propellant at various Rt. (A) The propellant at Rt 0.75; (B) Rt of liner 1.7 and propellant 1.55; (C) Rt of liner 0.90 and propellant 0.95; (D) Rt of liner 1.7 and propellant 0.95; (E) Rt of liner 0.90 and propellant 1.15.

4. Conclusions

Modulation of the curing parameter (Rt) involves augmenting the concentration of isocyanate groups (NCO) through increased curing agent (TDI) addition, while concomitantly reducing hydroxyl group (OH) density via decreased binder (HTPB) content. This alteration in stoichiometry significantly impacts the mechanical properties and interfacial bond strength between the rocket propellant and liner. Specifically, tensile strength exhibits a positive correlation with Rt, attributed to enhanced cross-linking between NCO and OH moieties. Conversely, elongation demonstrates an inverse relationship due to the increased network rigidity imparted by heightened cross-link density. Density also increases as a function of Rt, stemming from the higher specific gravity of TDI (1,220 kg/m^3) compared to HTPB (900 kg/m^3). Experimental results, evaluated against design criteria for mechanical properties of both liner and propellant, indicate optimal Rt values of 0.90 and 1.15. These parameters not only exceed design specifications but also yield a composite bond strength of 0.75 MPa when used in conjunction.

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