

Article

Effect of Fluoroalcohol Chain Extension Modified HTPB Binder on the Combustion Performance of Aluminized Propellants

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Abstract: To enhance both the mechanical properties of hydroxyl-terminated polybutadiene (HTPB) binder and the combustion efficiency of aluminized propellants, 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol (OFHD) was employed as a chain extender to impart mechanical regulation to the HTPB binder. Mechanical testing showed that the mechanical properties of fluoride-modified HTPB polyurethane (FPU) were significantly improved: the peak tensile strength of the optimized samples reached 1.99 MPa, and the elongation at break attained 486%. The structural characterization of the FPUs was conducted using Fourier transform infrared (FTIR) spectroscopy. Thermogravimetry-mass spectrometer (TG-MS) analysis revealed that the initial thermal decomposition temperature of the FPU shifted from 170 °C to 162 °C, accompanied by the release of fluorine-containing fragments during decomposition. Analysis of the combustion residue indicated that the addition of OFHD can reduce the agglomeration of aluminum (Al) powder in aluminized propellants. Dynamic pressure characteristics results showed an augmented pressurization rate under argon and oxygen atmospheres, increased by 18.67% and 37.29%, respectively. Heat release tests indicated that the aluminized propellants with the addition of OFHD had a higher combustion heat, being increased by 6.57%. The binder system is expected to be applied in aluminized propellants to improve the mechanical properties and combustion efficiency of Al powder.

Keywords: fluoroalcohol chain extender; HTPB binder; mechanical property; thermal decomposition; aluminized propellants; combustion performance



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1. Introduction

Hydroxyl-terminated polybutadiene (HTPB) has been widely utilized as a binder in composite solid propellants [1,2]. HTPB exhibits a transparent appearance and demonstrates fluidity at room temperature, which is attributed to the numerous unsaturated double bonds within its macromolecular chain that confer unique physical chemical properties. Its low glass transition temperature enables propellants to maintain elasticity even at low temperatures [3–5]. When used as propellant matrixes, especially for propellants that need to be loaded under extreme conditions, HTPB binders are expected to possess excellent mechanical properties. The tailoring of mechanical properties can be accomplished by employing bonding agents to modulate the interfacial bonding between fillers and binders [6] and by adjusting the binder's network structure via the use of curing agents, crosslinking agents, and chain extenders [7,8]; of these, chain extension stands out as a straightforward and efficient method. Commonly used chain extenders include small-molecule diol or diamine chain extenders [9] such as 1,4-butanediol, ethylene glycol, and 2,4-diamino-3,5-dimethylthiotoluene.

Aluminum (Al) powder is widely used in the propellant industry due to its advantages of high combustion calorific value, high energy density, good stability, and cost-effectiveness [10,11]. However, Al powder tends to form a large condensed phase with the molten alumina (Al₂O₃) generated during combustion, resulting in incomplete combustion

of the Al and causing decreased combustion performance of solid rocket propellant. Moreover, these condensed phases will cause serious erosion of the insulation layer within the propellant combustion chamber and the nozzle components [12,13].

Research has demonstrated that the incorporation of fluorinated compounds can effectively mitigate the issue of condensed phase agglomeration [14–16]. A pre-ignition reaction (PIR) occurs between fluorine from a fluorine-containing polymer and the Al_2O_3 monolayer shell surrounding the Al particles, and the resulting aluminum fluoride (AlF_3) can sublime at a lower temperature, so that the newly exposed Al can react directly with the oxidizing agent. With the increase in the contact area, the reaction rate is improved and the energy release of the system is expanded. Sippel and colleagues [17] used tailored Al/PTFE composite particles for ignition, resulting in a smaller aggregate than the initial composite particles, thereby altering the combustion behavior of the solid propellants, resulting in a potential reduction in two-phase flow losses in rocket motors. Zhou et al. [18] added homemade organic fluoride into the propellant to replace part of AP, and the gaseous fluoride molecules released in the combustion process assisted in hindering the agglomeration and improving the combustion efficiency of the propellant. However, all of the above methods use solid fluorides, which, in HTPB propellants, leads to a decrease in the oxidizing agent and Al powder content, ultimately reducing the overall energy output. To address this challenge, fluoridation of the binders is expected to solve this problem. The application of liquid fluorinated binders can safeguard the original solid content while improving the combustion efficiency of the Al powder. Shen et al. [8,19] prepared hydroxyl-terminated polyether polyurethane elastomers grafted with fluoroalcohols and added this preparation to aluminized propellant, which also effectively alleviated the Al powder agglomeration and promoted energy release.

Aiming to enhance the mechanical properties of HTPB and simultaneously utilize organic fluorine to improve the combustion performance of Al powder, fluoroalcohols were selected as chain extenders for the experiment. Among numerous fluoroalcohols available, 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol (OFHD) stands out as the most suitable choice due to its relatively low melting point and high fluorine content of 58%.

In this study, varying contents of OFHD chain extender were incorporated into an HTPB binder to facilitate the curing process and yield polyurethane elastomer. Mechanical tests, Fourier transform infrared (FTIR) spectroscopy, and thermogravimetry-mass spectrometer (TG-MS) analysis were used to study the effects on structure, mechanical properties, and thermal decomposition properties. Aluminized propellant specimens based on this binder system were prepared, and their combustion behavior was assessed by comparing it against that of a control sample. Furthermore, morphological assessments, particle size distribution analysis of the combustion residue, combustion reaction rate evaluation, and combustion heat evaluation were carried out to gain comprehensive insights into the performance of the modified propellant.

2. Materials and Methods

2.1. Materials

The hydroxyl-terminated polybutadiene (HTPB) was provided by the Liming Research Institute of Chemical Industry (Luoyang, China), having an average molecular weight of 3000 and hydroxyl value of 0.74 mmol/g. The 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol (OFHD; purity, 98%) was purchased from Bide Pharmatech Co., Ltd. (Shanghai, China) for use as the chain extender. Toluene-2,4-diisocyanate (TDI; purity, 98%) and Triphenylbismuth (TPB; purity, 98%) were provided by Aladdin Biochemical Technology Co., Ltd. (Shanghai, China) for use as the curing agent and catalyst, respectively. Dioctyl adipate (DOA; analytical reagent) was purchased from Yingkou Tianyuan Chemical Research Institute Co., Ltd. (Yingkou, China) for use as the plasticizer. Spherical Al powder was bought from the Angang Group Aluminum Powder Co., Ltd. (Anshan, China) and is a commonly used metal fuel in propellant systems. Its nominal purity is 99%, with the impurities being mainly Si and Fe. The median diameter (D_{50}) of the Al powder is 18.8 μm . Ammonium

perchlorate (AP; industrial grade, $D_{50} = 120 \mu\text{m}$) was obtained from Jiangyang Chemical Industry Co., Ltd. (Taiyuan, China) for use as the oxidizing agent.

2.2. Preparation of FPU

The formulation of different FPU is detailed in Table 1. The molar ratio of OH to NCO was maintained at a 1:1 ratio for the combination of (HTPB + OFHD) and TDI. The DOA was mixed with the HTPB in a 1:1 mass ratio. In the reaction procedure, both ends of HTPB and OFHD contain -OH functional groups, which chemically react with the -NCO functional groups contained in the curing agent TDI to form the network structure to complete the curing process. The reaction mechanism is shown in Figure 1.

Table 1. The raw material ratios for FPU.

Samples	Ratio *	HTPB/g	OFHD/g	TDI/g	DOA/g	TPB
FPU0	1/0/1	4.50	0	0.29	4.50	
FPU1	3/1/4	4.50	0.15	0.39	4.50	
FPU2	2/1/3	4.50	0.22	0.44	4.50	
FPU3	1/1/2	4.50	0.44	0.58	4.50	0.05%
FPU4	1/2/3	4.50	0.87	0.87	4.50	
FPU5	1/3/4	4.50	1.31	1.16	4.50	
FUP6	1/4/5	4.50	1.75	1.45	4.50	

* -OH (or -NCO) ratio of HTPB/OFHD/TDI.

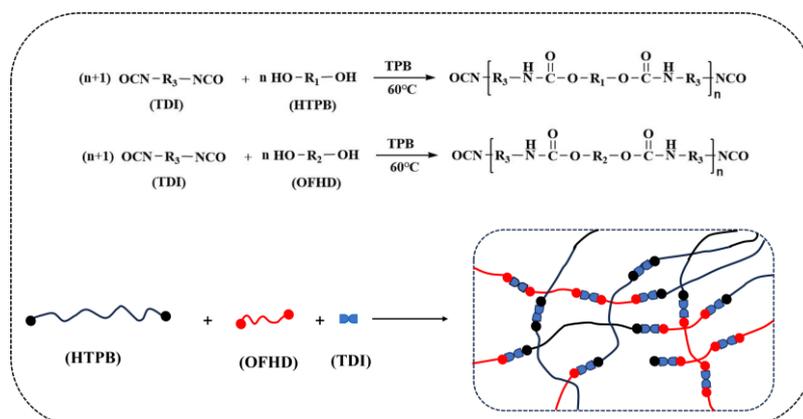


Figure 1. The reaction mechanism among OFHD, HTPB, and TDI.

Due to the fact that the melting point of the OFHD chain extender exceeded the processing temperature, it was firstly mixed with the weighed DOA and stirred continuously in a 60 °C water bath until completely dissolved. Subsequently, the HTPB, TDI and TPB were added and stirred well in a 60 °C water bath for 0.5 h, after which the blend was poured into PTFE molds. The mixture was then subjected to vacuum treatment to remove air bubbles before being cured in an oven at 60 °C for a duration of 6 days. The preparation process is shown in Figure 2.

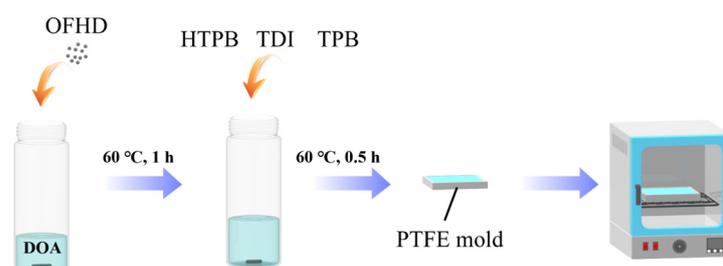


Figure 2. FPU preparation procedure schematic diagram.

2.3. Preparation of FPU0/Al/AP and FPU5/Al/AP Propellants

The FPU5 polyurethane, with its excellent mechanical properties, was chosen as the propellant binder, and the FPU0 polyurethane, being without fluorine, served as the control group. Guo et al. [20] prepared HTPB propellants with Al contents of 16–24 wt% and added a kind of organic fluoride. The effects of Al and fluorine contents on the combustion performance of HTPB propellants have been investigated. Considering the fluorine content of the FPU5, we chose a propellant formulation containing 14 wt% of FPU binder, 26 wt% of Al, and 60 wt% of AP.

The procedure for preparing the propellants is shown in Figure 3. Firstly, the beaker was filled with a weighed amount of the binder system without TDI, and then the weighed amounts of Al powder and AP were added to the beaker sequentially, being stirred well after each addition. Finally, the TDI was added and stirred well. All the above steps were carried out under the condition of a 60 °C water bath. The slurry was thoroughly stirred and poured quickly into quartz tubes (dimensions: $\Phi 7 \times 15$ mm), degassed under vacuum in a 60 °C oven to remove air bubbles, and left for 6 days to finish curing.

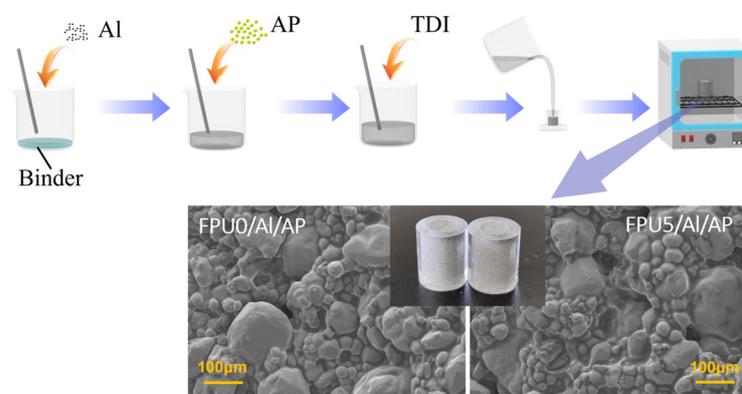


Figure 3. Schematic diagram of FPU0/Al/AP and FPU5/Al/AP propellants.

2.4. Characterization

The mechanical properties of the FPUs were measured using an INSTRON 3343 universal testing machine (Instron Corporation, Norwood, MA, USA). The FPUs were cut into dumbbell shapes, and each sample was tested at least 5 times to obtain the average value at a constant tensile rate of 200 mm/min. FTIR spectroscopy was recorded via a VERTEX70 spectrometer (Bruker, Werder Bremen, Germany) set at a resolution of 4 cm^{-1} over a wavelength range of $4000\text{--}600 \text{ cm}^{-1}$ using KBr plates. Thermal decomposition was performed using a thermo plus EV2/thermo mass photo (Rigaku Corporation, Tokyo, Japan). The samples were heated from 25 °C to 800 °C at a heating rate of 10 °C/min under air condition.

The propellants were ignited using a CO₂ laser (Mianyang Aurora Science and Technology Co., Ltd., Mianyang, China) under ambient conditions. The ignition and combustion processes were recorded using a high-speed camera (Revealer X113, HF Agile Device Co., Ltd., Hefei, China) at a frame rate of 10,000 frames per second. The surface morphologies of the propellant samples and combustion products were observed via scanning electron microscopy (SEM, S4800, Hitachi, Tokyo, Japan). The particle size distribution test was performed via a laser particle sizer (Mastersizer 3000, Malvern Instruments Ltd., Worcestershire, UK) using dispersing solvent of ethanol and ultrasonic dispersion for 5 min.

The reaction rate of the propellant samples was examined by using a custom-designed hermetically sealed combustion chamber having a volume of approximately 20 cm³. The aluminized propellant samples were placed in the central groove of the combustion canister. Ignition was initiated by applying a 24 V voltage across the nickel-chromium alloy wire that was in direct contact with the samples, thereby triggering the combustion process. A

microcomputer automatic calorimeter (TRHW-7000C, Hebi Tianrun Electronic Technology Co., Ltd., Hebi, China) was employed to measure the combustion heat data.

3. Results and Discussion

3.1. Mechanical Properties of FPU

In polyurethane elastomers, the existence of hard and soft segments induces microphase separation, which significantly influences the mechanical properties of the elastomer material. The terminal hydroxyl group on the chain extender molecules reacts with the diisocyanate of the curing agent to generate a hard segment phase that is instrumental in enhancing tensile strength. Conversely, the soft segment component, namely HTPB, contributes to increasing the elongation. The mechanical properties of the FPU with various contents of the OFHD chain extender are shown in Figure 4. It can be clearly seen that the incorporation of the OFHD has a pronounced effect in terms of improving the mechanical properties of the FPU. With the increase in OFHD content, both the tensile strength and elongation at break initially rise but then decline. The FPU5 polyurethane exhibits a peak tensile strength of 1.99 MPa, while the maximum elongation at break is achieved by the FPU4 polyurethane, reaching 486%.

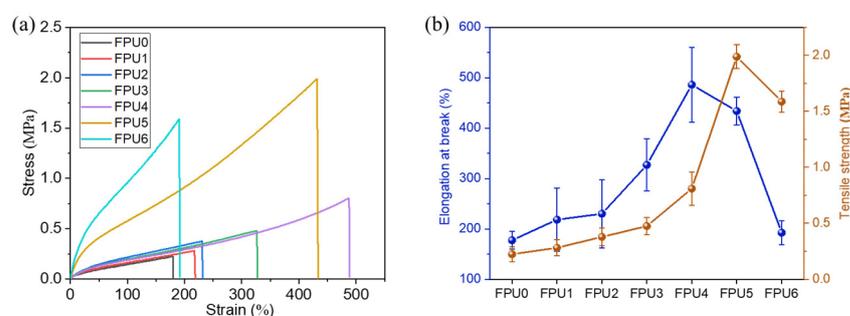


Figure 4. Mechanical properties of FPU with different OFHD contents: (a) tensile stress–strain curves; (b) summary of the tensile properties for the various FPU.

During the reaction, the -NHCOO- group generated by the reaction between alcohol hydroxyl group and diisocyanate introduced a polar group that contained an active hydrogen group. This led to the formation of hydrogen bonds within the added chain segments and secondary cross-linking events, and secondary cross-linking occurred, thereby strengthening the intermolecular forces and creating a cross-linked network structure, which boosted tensile strength. With the increase in hard segment content in the HTPB binder system, the aggregation ability between the hard segments was enhanced, promoting the development of a microphase separation morphology [21–23]. This resulted in significant improvement in the mechanical properties of the FPU. However, it is worth noting that excessively hard segments can also have detrimental effects on the mechanical properties. Based on these results, the mechanical properties of the FPU5 polyurethane were generally superior, and all subsequent studies were conducted using the FPU0 and FPU5 polyurethanes.

3.2. FTIR Spectra Analyses

The FTIR spectroscopy was employed to analyze the functional groups of the raw materials and the cured polyurethane products FPU0 and FPU5, and the results are shown in Figure 5. The characteristic peaks at 729 and 968 cm^{-1} in the HTPB, FPU0, and FPU5 spectra correspond to cis-RCH=CHR and trans-RHC=CHR configurations, respectively. The characteristic peaks at 1163 cm^{-1} and 1228 cm^{-1} are attributed to the symmetric and asymmetric stretching vibrations of -CF_2 groups, respectively. The peak at 2264 cm^{-1} corresponds to the stretching vibration peak of -NCO , and the broad peak at 3425 cm^{-1} is attributed to the -OH stretching vibration peak [24–26]. After reaction with the TDI, as seen in the FTIR spectra of both the FPU0 and FPU5, a new peak appears at 3325 cm^{-1} ,

which represents the N-H stretching vibration in a carbamate structure. Additionally, the peak at 1541 cm^{-1} is indicative of the N-H bending vibration in the same carbamate structure [24,27]. Notably, the characteristic peaks corresponding to -OH and -NCO functionalities exhibit diminished intensity and eventually disappear, which indicates that the curing reaction occurred and reached completion.

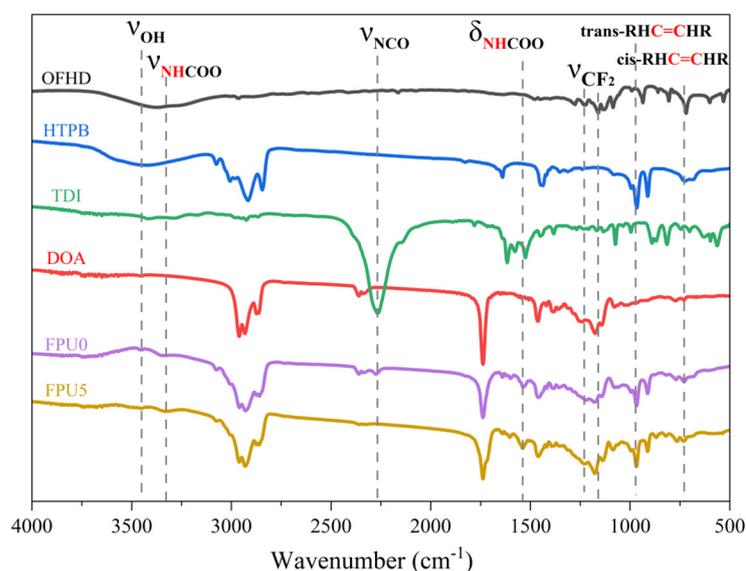


Figure 5. FTIR spectra of each raw material and polyurethane after the curing reaction.

3.3. Thermal Decomposition of FPU_s

To investigate the influence of the OFHD chain extender on the thermal decomposition behavior of the HTPB binders, TG-MS tests were conducted on the FPU₀ and FPU₅, and the results are shown in Figure 6. In the TG-MS curves, the change curves of the percentage of weight loss and the rate of weight loss with temperature and the change curve of ion flow of some gas products in the decomposition process with temperature were drawn. More variations of the ion peak intensities of the decomposition product fragments with temperature are shown in the 3D diagrams. Table 2 lists the partial ionic fragments produced by the decomposition of the FPU₀ and FPU₅. Both FPU_s demonstrated a comparable change pattern, but the introduction of the OFHD chain extender caused an advancement of the initial decomposition temperature. Specifically, this temperature decreased from $170\text{ }^{\circ}\text{C}$ to $162\text{ }^{\circ}\text{C}$ upon the introduction of the OFHD component. According to the evolution of the TG-MS curve, the thermal decomposition process of the FPU_s can be broadly categorized into three stages (as detailed in Table 3). The first stage is the urethane bond cleavage, exothermic cyclization, and cross-linking of the remaining HTPB, accompanied by partial decomposition of the cyclized products into low molecular weight species [24,28,29], and the decomposition of the DOA also begins. At this stage, the FPU₅ polyurethane exhibited a weight loss percentage that was 6.8% higher than that of the FPU₀, which could have been caused by the breakage of the $-\text{CF}_2$ bonds present in the OFHD chain extender. Consistently, a large amount of F^- signal ($m/z = 19$) was also observed in the FPU₅ polyurethane during thermal decomposition, but no F^- signal was observed in the FPU₀ polyurethane during thermal decomposition. Therefore, the weight loss of the FPU₀ was higher than that of the FPU₅ in the second stage. The latter two stages primarily consist of the thermal decomposition of the residues formed in the previous temperature range. This progression is also evident from the 3D diagram depicting the intensity of decomposition product ion peaks for both FPU_s. It shows the corresponding changes in signal intensity across these three distinct temperature ranges, which align with the temperature intervals observed in the TG data.

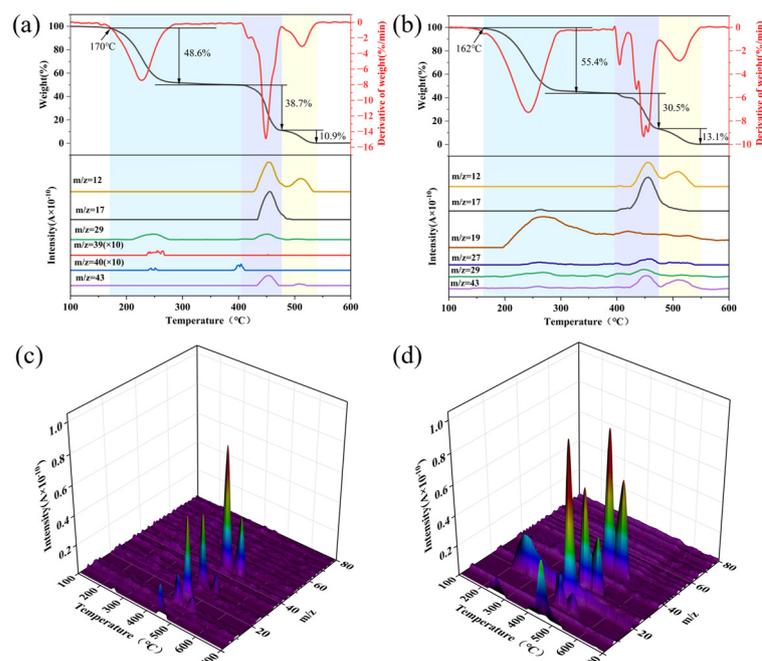


Figure 6. (a) TG-MS curves of the FPU0 under air atmosphere; (b) TG-MS curves of the FPU5 under air atmosphere; (c) 3D diagram of the current intensity of FPU0 decomposition products; (d) 3D diagram of the current intensity of FPU5 decomposition products.

Table 2. Partial ion fragments produced by FPU0 and FPU5 decomposition.

m/z	Fragment Ions	m/z	Fragment Ions
12	C	29	C ₂ H ₅ , CHO
14	CH ₂	30	CH ₂ NH ₂ , C ₂ H ₆ , CHO
15	CH ₃	31	CF, CH ₃ NH ₂
16	O, CH ₄	39	C ₃ H ₃
17	OH, NH ₃	42	NCO, C ₃ H ₆
18	H ₂ O	43	C ₃ H ₇ , HNCO
19	F ⁻	44	CO ₂ , C ₂ H ₄ NH ₂
26	C ₂ H ₂	68	C ₅ H ₈
27	C ₂ H ₃	72	C ₄ H ₈ O

Table 3. FPU0 and FPU5 thermal decomposition stages.

Samples	The First Stage/°C	The Second Stage/°C	The Third Stage/°C
FPU0	170~405	405~477	477~540
FPU5	162~396	396~475	475~550

3.4. Comparison of Combustion Properties

To examine the combustion characteristics, a high-speed camera was used to record the combustion state of the samples at various times after ignition. The combustion products from the two aluminized propellant samples were collected under atmospheric pressure. The corresponding combustion flame images are shown in Figure 7. As the surface begins to burn, Al particles on the burning surface are progressively exposed and melted. This process will break through the oxide layer, allowing the Al particles trapped at the burning surface to come into direct contact with one another. While the Al particles tend to aggregate and form larger aggregates, they maintain an irregular structure composed of both solid and liquid phases rather than fully liquefying. As these aggregates continue to melt, the skeletal structure of the Al clusters gradually collapses, transforming into more regular

spherical Al droplets [30,31]. Such scattered agglomerates can be clearly seen in the yellow circles in Figure 7a.

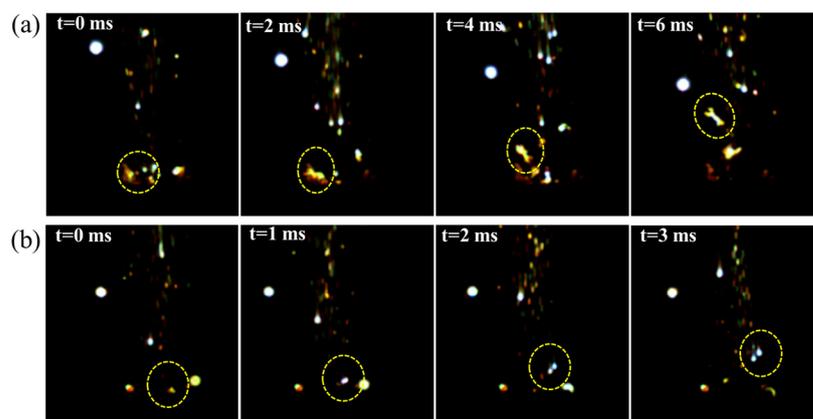


Figure 7. Combustion process of energetic composite samples under atmospheric pressure environment: (a) FPU0/Al/AP; (b) FPU5/Al/AP.

When the OFHD chain extender was incorporated, the fluoride accelerated the reaction between the Al core and the oxidizing agent surrounding the Al particles by destroying the Al_2O_3 shell layer. Moreover, the sublimation of AlF_3 along with gases evolved from the thermal decomposition of fluoride played a role in fragmenting the agglomerates of the Al powders during combustion, thereby abbreviating the ignition process of the Al particles. Consequently, the duration of the Al particles' presence on the burning surface was diminished, which led to a reduced extent of agglomerations of Al particles in the burning surface, as evidenced by the yellow circles in Figure 7b [17,18].

Figure 8 presents the SEM morphology depicting the post-combustion residue morphology for both aluminized propellants. The residues are predominantly spherical in shape, with the size of the combustion residue from the FPU5/Al/AP propellant samples being smaller than that of the residue from the FPU0/Al/AP samples, indicating less agglomeration. To provide a more direct visualization of the particle size distribution of these combustion residues, the particle size distribution test was carried out using a laser particle sizer. The results of the particle size distribution test are shown in the insert maps in Figure 8, revealing that the D_{50} value of the residue generated by the FPU0/Al/AP propellant samples was $41.1 \mu\text{m}$, whereas the D_{50} value for the residue from the FPU5/Al/AP propellant samples was $18.2 \mu\text{m}$. This phenomenon is consistent with the research results of Zhou [18,32], which introduced solid fluoride into the propellant formulation instead of part of the oxidizing agent. This finding signifies that the addition of the OFHD chain extender effectively diminished the rate of the Al powder agglomeration.

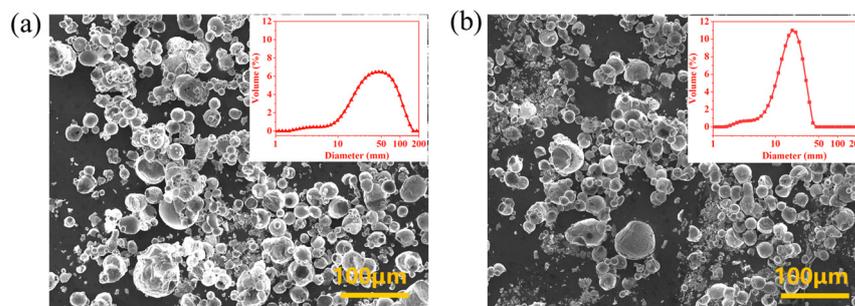


Figure 8. SEM images and particle size distributions of condensed combustion products for the two aluminized propellants: (a) FPU0/Al/AP; (b) FPU5/Al/AP.

3.5. Dynamic Pressure Characteristics and Heat Release

The reaction rate of energetic material is characterized by the combustion rate of the energetic material or the pressurization rate in a closed container [33–35]. The pressure–time curves of the samples during combustion in different atmospheres were measured by means of a closed combustion tank device to obtain the peak pressure of combustion and the rate of pressurization Figure 9. The point at which the pressure began to increase was defined as the starting point, and the ratio of the pressure difference between the peak point and the starting point to the time difference was defined as the boost rate [33]. As shown in Figure 9, the peak pressure and boost rate of combustion were increased under argon or oxygen conditions. The pressurization rate of the FPU5/Al/AP propellants increased by 18.67% under an argon atmosphere, and the pressurization rate of the FPU5/Al/AP propellants increased by 37.33% under an oxygen atmosphere. The pressurization rate of the fluorinated propellants after ignition was clearly higher under both argon and oxygen atmospheres, which indicates that the introduction of OFHD chain extender can improve the burning rate and increase the rate of energy release of aluminized propellants. The combustion heat of the propellant samples was measured using a microcomputer automatic calorimeter under a condition of 3 MPa argon. The combustion heat value of the FPU5/Al/AP propellant formulation reached 9427 J/g, and the combustion heat value of the FPU0/Al/AP propellant formulation reached 8846 J/g. The aluminized propellants with the addition of OFHD had a higher combustion heat, being increased by 6.57%. Compared with the introduction of solid fluorides by physical methods [18], we improved the energy performance of the propellant without reducing the oxidizing agent and Al powder content.

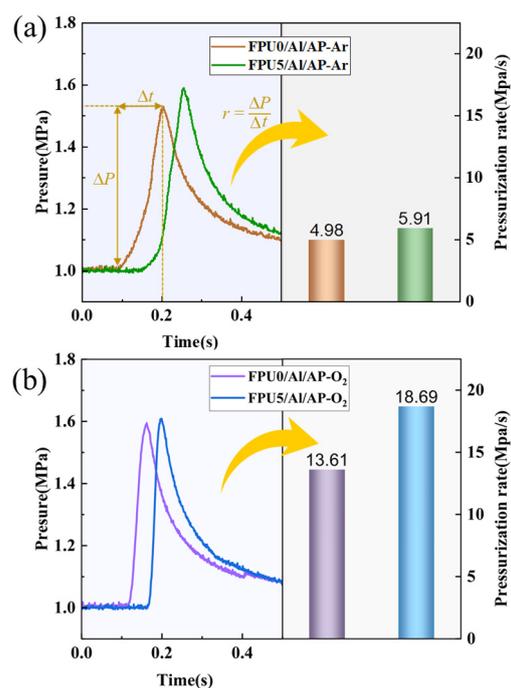


Figure 9. Dynamic pressure characteristics of the two aluminized propellants: (a) dynamic pressure characteristics under argon conditions; (b) dynamic pressure characteristics under oxygen conditions.

4. Conclusions

In this study, an OFHD chain extender was employed to enhance the mechanical attributes of an HTPB binder, and its application within aluminized propellants was also explored. The mechanical properties of HTPB polyurethane using an OFHD chain extender have been greatly improved. Compared with the FPU0 polyurethane elastomers, the tensile strength of the FPU5 significantly improved, from 0.22 MPa to 1.99 MPa, and the elongation at break increased from 177% to 433%. The TG-MS analysis revealed that the fluorinated

polyurethanes exhibited an earlier decomposition onset compared to their non-fluorinated counterparts. The introduction of the OFHD chain extender accelerated the initial decomposition of the polyurethane elastomers, releasing ionic fragments. The combustion test of the aluminized propellants demonstrated that FPU can effectively alleviate the agglomeration problem of Al particles, the combustion residue D_{50} of propellant demonstrated a reduction from 41.1 μm to 18.2 μm , and the combustion efficiency of the propellant was enhanced. Additionally, in dynamic pressure characteristics and heat release tests, the fluorinated propellants led to an improvement in energy release rate and energy performance. Consequently, the use of an OFHD chain extender shows promising potential for practical applications within the realm of aluminized propellant technology.

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Conflicts of Interest: There are no conflicts to declare.

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