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Formulation Tailoring for Ballistic Properties of Composite Propellants

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Abstract: An aluminized AP/HTPB propellant formulation was experimentally studied, and the effect of formulation parameters i. e. particle size of AP, catalysts on burning rate and pressure exponent were discussed. The results show that the burning rate of propellant decreases with increasing the average AP particle diameter but with large diameters the dependence of burning rate becomes weak. Liquid ferrocene catalyst is more effective to increase the burning rate as compared to solid iron oxide. A 50% rise in burning rate with liquid ferrocene catalyst is observed while 22% rise with solid catalyst. The experimental results of burning rate and pressure exponents were compared with the calculated results of the combustion model. Model predictions and the experimental data are in good agreement.

Key words: physical chemistry; composite propellants; burning rate; pressure exponent; catalyst; formulation

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1 Introduction

The combustion phenomena of solid propellants involve complex physicochemical changes from solid to liquid and gas. One of the greatest challenges to the propellant formulators is to understand the process of solid propellant combustion and to determine the burning rate of a given formulation. Burning rate of AP/HTPB propellants is highly dependent on particle size, shape and distribution of AP. These variables also have a significant effect on the mechanical and processing properties of propellants.

In spite of enormous current knowledge in the field of solid propellant combustion for the theoretical and experimental concerns, the assessment of the new propellant burning rate for a target application is still empirical as well as the follow-up of the experience and the previous production and test data. This is due to the fact that most of the models are of qualitative nature and do not accurately predict the combustion properties of real propellant formulations[1,2]. To bridge this gap between the theoretical models and the practical propellant formulations, more results oriented modeling efforts and reliable experimental data are required.

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Therefore, several experiments were conducted by mixing a number of propellant formulations to study the correlations between formulation parameters and propellant properties in this paper. The experimental results of burning rate and pressure exponent were discussed and compared with the theoretical predictions of a simplified combustion model developed by the authors.

2 Analysis and Experiments

2.1 Performance Estimations

Thermochemical calculations were performed using the computer code PPC97 to optimize a propellant formulation for the maximum energy. A preliminary propellant formulation for an optimized performance is given in Table 1 and its theoretical energy performance of this formulation is given in Table 2.

Table 1 Proposed propellant formulations

ingredient	mass fraction / %
HTPB (hydroxyl terminated polybutadiene) TDI (toluene diisocyanate) MAPO (trimethylaziridinyl phosphine oxide) antioxidizing agent	11
AP (ammonium perchlorate) trimodal	67.5
Al (aluminium)	18.0
plasticizer	3.0 - 3.5
burning rate catalyst	0.5 - 0.0
total	100.0

Table 2 Theoretical energy performance of the proposed propellant formulation

performance parameter	value
combustion temperature T_c/ K	3400
nozzle exit temperature T_e/ K	2157
average specific heats ratio in nozzle, k	1.138
isobaric combustion heat, Q / kJ · kg^{-1}	5633
characteristic velocity, C^* / m · s^{-1}	1600
thrust coefficient, C_F	1.593
specific impulse, I_s/ m · s^{-1}	2547

Note: $*p_c$ = 6.0 MPa, standard expansion ratio.

Considering a 92% overall energy conversion efficiency of the actual rocket motor, the delivered specific impulse is expected to reach at 2343 m · s^{-1}.

The density of the proposed propellant formulation can be estimated from the densities of its ingredients:

$$\rho_p = \frac{1}{\sum_{i=1}^{8} \frac{A_i}{\rho_i}} \approx 1.760 \text{ g} \cdot \text{cm}^{-3} \quad (1)$$

Where A_i is the mass fraction of the ingredient i in the formulation and ρ_i is the respective density. The calculated density is in close agreement with the experimental results.

2.2 Experimental Work

An experimental program was designed to establish a correlation between various formulation parameters and the propellant properties. State of the propellant ingredients were selected as given in Table 1. AP particle sizes and their distributions, amount and type of catalyst and binder curative ratio were varied to study the effect on the propellant properties.

A sufficient quantity of raw materials was prepared and homogenized to ensure a uniform batch. A small-scale vertical mixer was used for mixing the propellant slurry and later the scale was enhanced to a larger mixer to observe the effect. Several mixes of propellant slurry were prepared to tailor the formulation. Propellant slurry was casted in rectangular cartons under vacuum and cured at 70 ℃ in oven for 3 days. Samples were prepared from the cured propellant and were tested for burning rate, pressure exponent, temperature sensitivity of burning rate and various mechanical properties (stress, strain, and modulus). Rheological tests were also performed for propellant slurry after mixing and during casting operation. Burning rate was measured using acoustic strand burning technique and the mechanical properties were tested on a standard Instron testing machine. The results obtained (statistical mean value of five test samples) from these tests have been summarized and discussed below.

3 Results and Discussion

3.1 Burning Rate and Pressure Exponent

Burning rate of the propellant was generally adjusted by two methods, i) by varying the mixing ratio of coarse to fine AP and ii) by adding the catalyst. So in the experment the tri-modal AP compositions were firstly varied while the total contents of AP remained unchanged. The proportions of various AP fractions with the measured burning rate (r) at 6.0 MPa and pressure exponent are given in Table 3.

Table 3 Various proportions of coarse and fine AP with burning rate and pressure exponent

formulation code	AP(%)				r /mm · s^{-1} (6.0 MPa)	pressure exponent n
	fine 10 μm	type Ⅲ 135 μm	type Ⅱ 250 μm	type Ⅰ 340 μm		
AH-101	3.5	24.0	–	40.0	5.81	0.420
AH-104	11.5	28.0	–	28.0	6.02	0.398
AH-105	11.5	28.0	28.0	–	6.44	0.387
AH-106	5.0	31.5	31.0	–	6.49	–
AH-107	15.0	26.5	26.0	–	6.39	0.400
AH-108	25.0	21.5	21.0	–	6.93	0.430
AH-110	25.0	21.5	21.0	–	6.88	0.430
AH-112	30.0	19.0	18.5	–	7.48	–
AH-113	35.0	16.5	16.0	–	8.74	0.530

Three types of spherical and one type of non-spherical AP were used, referred to as type Ⅰ, Ⅱ, Ⅲ, and 'fine' respectively. In formulations AH-101 and 104, type Ⅰ, Ⅲ, and fine AP were used. Formulation AH-105 was reproduced with the same compositions as that of No. 104 but replacing type Ⅰ AP with type Ⅱ. This change results in increasing the burning rate and reducing the pressure exponent of propellant which is according to the expected trend. The rest of the propellant formulations were prepared by using type Ⅱ AP as coarse fraction and type Ⅰ was not used in later mixes. Formulations AH-106 ~ 108 were charged with varying proportion of fine and coarse where fine AP proportion was increased from 5% – 25% which was further increased up to 35% in formulation leading to No. AH-113. Formulation AH-110 was just the repetition

of No. 108 to verify the results. A good reproducibility of the results was observed from Nos. 108 and 110.

The results of the experimental burning rate versus fine AP contents are plotted and shown in Fig. 1. It can be seen from the figure, the burning rate rises with the increase in fine AP contents. The rise becomes more quick when fine AP contents are increased from approximately 20% onward. This effect is more clearly visible from Fig. 2, where mass average diameter d_{43} of the three AP fractions is plotted against the burning rate at 5.5 and 6.0 MPa.

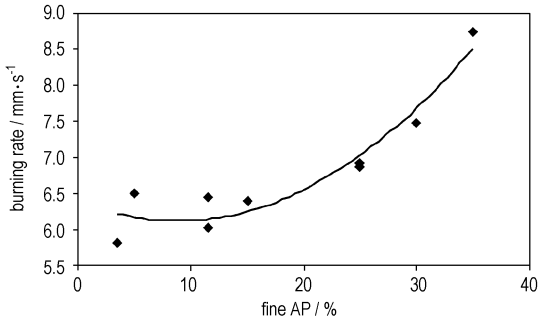

Fig. 1　Effect of fine AP on burning rate of propellant

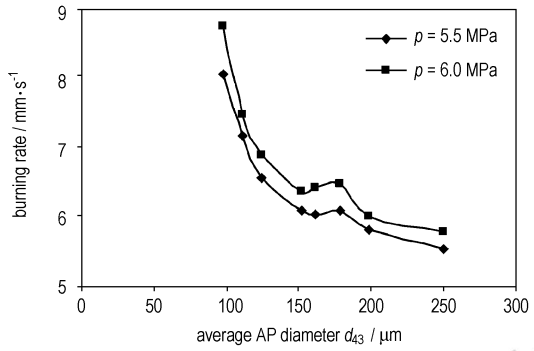

Fig. 2　Change in burning rate with AP mean diameter

The burning rate 999decreases noticeably with d_{43} increasing, but, when d_{43} increasing, such behavior has also been observed in previous studies with bi-modal oxidizer at stoichiometric oxidizer/fuel ratios[3,4]. Our base formulation is also near stoichiometric (slightly fuel rich) composition.

This trend of burning rate dependence can be explained if we consider the structure of the combustion zone. With multi-modal packing compositions there is a lattice of large crystals, and the interstices are filled with a mixture of fuel and fine oxidizer. If burning rate of this mixture is high enough, flame propagates between crystals of coarse oxidizer and burning rate is roughly equal to fine oxidizer burning rates. On the other hand, if the mixture in the interstices burns very slowly the value of burning rate is nearly equal to coarse value, resulting in lower rates.

Then the effect of solid and liquid catalysts on burning rate was also studied while the other conditions were kept constant. The experimental results of burning rate with 0.5% solid iron oxide catalyst and 0.5% liquid ferrocene catalyst are reported in Table 4 along with neutral formulation (no catalyst) for comparison. Tertiarybutyl ferrocene (TBFe) is more effective to increase the burning rate as compared to solid iron oxide. A 50% rise in burning rate is observed as compared to 22% rise with solid catalyst. Further experiments were carried out by using only liquid ferrocene catalyst.

Table 4　Effects of solid and liquid catalysts on burning rate

formulation code	catalyst	r/mm · s^{-1} (5.5 MPa)	r/mm · s^{-1} (6.0 MPa)	percent of r increase
AH-101	no catalyst	5.55	5.81	0
AH-109	0.5% Fe_2O_3	6.77	7.14	22%
AH-103	0.5% TBFe	8.34	8.69	50%

The burning rate and pressure exponent with the addition of various amount of ferrocene catalyst are given in Table 5. Formulations AH-117, 115, along with AH-103 and 102 show on the whole the increase in burning rate as increasing the percentage of TBFe catalyst in the propellant formulation and a lower burning rate pressure exponent when the fine AP contents are not changed. It is observed that the burning rate in the range of 8 – 9 mm · s^{-1} could be achieved with a slight addition of a TBFe catalyst (formulations AH-117&115) and even without a catalyst (formulation AH-113, Table 3). The final selection between the both options may depend on designer's choice based on other performance properties like mechanical behavior, processability, storage and safety. Liquid catalysts have a disadvantage of migration towards the interface at propellant surface and thus decrease the storage life of propellant. New prepolymers are developed in which ferrocene is grafted and linked to the HTPB prepolymer chain and cannot migrate. High burning rate aluminized propellants containing ferrocene derivatives have been the origin of many accidents in the industry due to their increased sensitivity level[5]. This

greater sensitivity associated with violent effects, demands special precautions to be observed for their handling and production.

Table 5 Effect of catalyst amount on burning rate

formulation code	TBFe / %	fine AP / %	r/mm · s^{-1} (6.0 MPa)	n
AH-117	0.1	15.0	8.23	0.36
AH-115	0.2	15.0	8.83	0.33
AH-103	0.5	3.5	8.69	0.38
AH-102	1.0	3.5	9.17	–

3.2 Combustion Modeling

A simplified model for the combustion of AP-HTPB propellants was developed within the framework of well-known BDP (Beckstead-Derr-Price) multiple flame model[6]. The model is one-dimensional and steady state in nature and incorporates single oxidizer particle size. A picture of the multiple flame model is shown in Fig. 3. Three flames as postulated by the BDP model are the AP monopropellant flame, primary flame and final diffusion flame. AP flame is followed by a diffusion flame where the oxidizer rich products of the flame (~30% Oxygen) react with the fuel rich binder pyrolysis products. The height of the diffusion flame is related to the AP particle size. The smaller the particle size is, the closer the flame and higher the heat flux to the surface and therefore the burning rate of the propellant. The pyrolysis of the inert binder (HTPB) is purely endothermic. The heat flux from the final flame serves primarily to keep the binder regressing. Complete description of the combustion model, computational descriptions and the model input parameters are given in Ref. [7].

Formulation given in Table 1 was used to calculate the burning rates for a representative propellant. No additives were considered for these calculations. Final flame temperature used as an input parameter in the model was calculated using the propellant performance code PPC97. The model accounts for only single oxidizer particle size. Multimodal oxidizer burning rates were computed using statistical mass average diameter of various oxidizer modals. The results of burning rates for the given formulation were calculated at various pressures and plotted in Fig. 4 for 5 μm, 20 μm and 200 μm oxidizer sizes. The effect of oxidizer particle size on calculated burning rates is obvious for the three oxidizer modals up to 10 MPa pressure. As a quantitative comparison with the experimental values the pressure exponent for a 200 μm AP propellant is computed as 0.390 (T_0 = 300 K, p_c = 5 – 10 MPa, R = 0.992) which is in a good agreement with the measured exponent for formulation AH-104 in Table 3 under the similar conditions. A slight inflection in the slope of caculated burning rates for a 20 μm AP propellant is attributed to the fraction of oxidizing reactants (β_F) shift (from 1 to 0), that means diffusion control region is dominant. Calculations show that β_F effect occurs at lower pressures as particle size increases. For 5 μm, it occurs at about 12 MPa, for 20 μm at about 3.5 MPa and for 200 μm β_F shift occurs below 1 MPa.

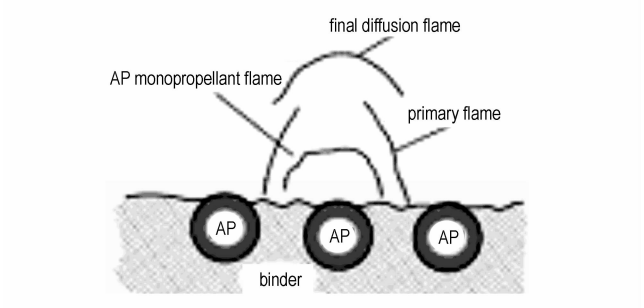

Fig. 3 A sketch of the multiple flames model

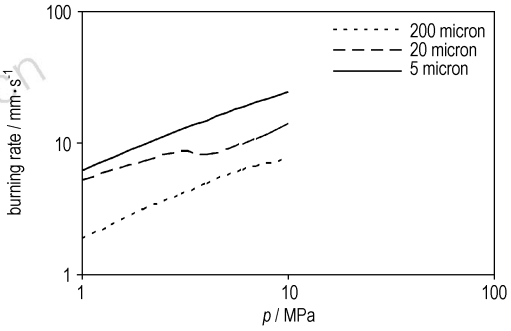

Fig. 4 Effect of pressure and oxidizer particle size on caculated burning rates

Figure 5 shows the decrease in burning rate with increase in oxidizer particle size at 6.0 MPa pressure for the sake of comparison with the experimental measured burning rates. A reasonable agreement is found between model predictions and experimental rates for relatively large oxidizer particle size. The model cannot follow the trend at lower sizes (~100 μm). This deviation is due

to shifting transition from diffusion flame to the AP flame control at this particular pressure.

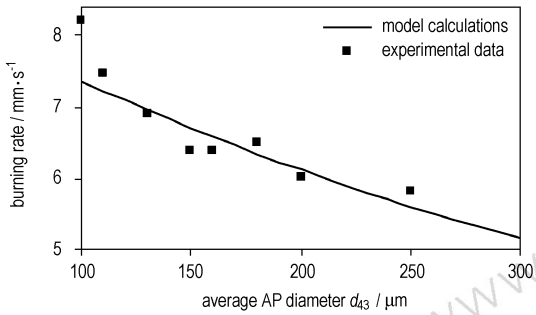

Fig. 5　Experimental and calculated burning rates with change in oxidizer particle size

The good agreement of model calculations with the experimental data does not prove the generalized applicability of the model to any propellant formulation because of the incorporation of many empirical factors for the calculations. However, it is believed that the model can be used for a reasonable initial assessment of burning rates and pressure exponent prior to any formulation development. In this way much saving in time and cost can be made by reducing the formulation processing trials.

4　Conclusions

Experimental work and laboratory tests were performed on the proposed propellant formulation. The formulation was tailored for burning rate and pressure exponent. Effect of various fine AP proportions on these parameters is discussed. The propellant burning rate decreases with increase in average particle diameter of AP fractions, but with large diameters the dependence of burning rate becomes weak. A 50% increase in burning rate is achieved with ferrocene catalyst as compared to 22% rise with equivalent amount of iron oxide. The experimental results of propellant burning rate have been compared with the theoretically calculated results from a simplified combustion model. The model predictions are in good agreement with the experimental results. The experimental data and the combustion model could be useful for propellant developments in saving time and cost for future works.

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复合推进剂弹道特性的配方调节研究

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摘要: 实验研究了含铝 AP/HTPB 推进剂的配方,讨论了燃速及压力指数与配方参数的关系。结果表明,推进剂燃速随平均 AP 粒子直径的增大而降低,但在大直径范围,这种趋势减缓。液体二茂铁催化剂可提高 50% 的推进剂燃速,而固体氧化铁可提高 22%。液体二茂铁催化剂能比固体氧化铁更有效地提高燃速。燃速与压力指数的实验结果同燃烧模型的理论计算结果进行了比较,预估结果与实验数据符合较好。

关键词: 物理化学; 复合推进剂; 燃速; 压力指数; 催化剂; 配方设计

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