Combustion Study of Composite Solid Propellants Containing Metal Phthalocyanines

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Abstract Transition metal Phthalocyanines have been used as burn rate modifiers for AP-HTPB composite solid propellants. An effort has been made to investigate the effect of Cu-Co-and Fe Phthalocyanines on the burn rate of composite propellants, as also on the combustion characteristics of such propellants. The burn rate has been determined in Crawford Strand Burner at 56 kg/cm^2 pressure as also in low pressure burner setup at vacuum of 0.5 kg/cm^2. Thermal analysis was performed using Thermo Gravimetric Analyzer (TGA), Differential Scanning Calorimeter (DSC) and heat of reaction has been measured by conventional Bomb Calorimeter. Scanning Electron Microscope (SEM) and Elemental Analyzer have been used for material characterization and possible composition of composite solid propellants. Metal Phthalocyanines have been found to influence the decomposition and to enhance the burn rate of the composite solid propellants.

Keywords Composite Solid Propellant, Burn Rate, Combustion Characteristics, Metal Catalysts, Fuel-Binder

1. Introduction

The design and operation of a rocket motor depends upon the burn rate of the propellant and the grain geometry of the propellant grain. The knowledge of burn rate thus becomes an important condition for a successful design of a solid rocket motor. The combustion chamber pressure has been found to be one of the most important design parameter, as the burn rate is exponentially dependent on the pressure. All the same, at a selected combustion chamber pressure, the designed burn rate of the propellant is feasible with the selected propellant not always available. The right selection of oxidizer particle size and oxidizer percentage does modify the burn rate; however the designed mechanical strength and other characteristics also get affected by these. Embedding metal wires or staples in the propellant also allows modification of burn rate; however the logistics and other complexities have desisted selection of this method as an attractive method of modification. The burn rate of a composite propellant can also be modified by incorporating burn rate modifier catalysts. In fact, this method has been found to be the best and most effective method. Extensive research has been advanced in search of an effective catalyst, and metal Phthalocyanines happen to be one of such catalysts.

The MPcs are candidate materials in high technology applications like molecular electronics, liquid crystal displays, gas sensors and organic laser materials. Their useful properties are attributed to their efficient electron transfer abilities. The central cavity of MPc is known to be capable of accommodating 63 different elemental ions. The functions of MPc are almost universally based on electron transfer reactions because of the 18 π electron conjugated ring system found in their molecular structure [1]. They have excellent stability against heat, light and air- moisture, and found to be effective in many especially designed catalytic reactions [2]. Bill, et al. [3] have suggested their uses as radiation absorbers. Henry [4] has reported their activeness for catalyzing oxidation reactions. According to Hronec, et al. [5] metal Phthalocyanines act towards electrode reduction of oxygen. Wheatley et al. [6] reported improvement of thermal stability and enhancement of burn rate with decreased pressure exponent by adding copper Phthalocyanines (CuPc). Lundstrom et al. [7] used CuPc as a low pressure combustion chamber. Fong, et al. [8] studied the effect of CuPc in AP-HTPB based propellant and reported increase of the pressure range of combustion and enhancement of burn rate of DDI cured HTPB. Bain and Rudy [9] reported the tendency towards combustion instability by addition of CuPC. Kandaz, et al. [10] as well as Bolker and Salker [11] conducted studies with Cobalt Phthalocyanine (CoPc). Zheng and Zhang [12] found that Iron Phthalocyanine (FePc) has large ionization potential and better di-oxygen binding capability making them a worthy catalyst. Eileen, et al. [13] showed high oxygen reduction activity by using FePc. In the light of this, the background investigation has been carried out using CuPc, CoPc and FePc as catalysts in AP-HTPB

composite solid propellants. Combustion study of solid propellants containing various contents of MPcs have been investigated and an effort has been made to obtain detailed experimental data on the burning characteristics of AP-HTPB based solid propellants to understand the role of MPcs as burn rate modifier.

2. Experimental

2.1. Materials

Cobalt (II) Phthalocyanines (CoPc), 97%, Iron (II) Phthalocyanines (FePc), 90% and Copper (II) Phthalocyanines (CuPc), 95% were purchased from Alfa Aesar India Ltd. HTPB of R45M grade was supplied by kind request from Vikram Sarabhai Space Center (VSSC), India. Ammonium Perchlorate (AP) was purchased from Tamilnadu Chlorate, India Ltd. Bis(2-ethylhexyl) adipate (BEHA) of 99%, and Tolylene-2,4-diisocyanate (TDI) of 95% pure were procured from Sigma-Aldrich. **Glycerol of analytical grade from CDH India Ltd. was used for propellant formulation.**

2.2. Processing of Solid Propellants

The composite solid propellants (CSPs) were formulated by using HTPB fuel binder and AP as a solid oxidizer. AP composition was taking uniform, 70 percent, in all such propellants samples. The average particle sizes of AP were 44μ and 250μ in the ratio of 3:1 in the propellant samples. BEHA was used as a plasticizer. The products made with it have good softness and excellent viscoelastic property. It was dehumidified before the usage. Toluene Di-Isocyanate (TDI) was used as a curing agent because it reacts with hydroxyl groups in HTPB to form poly urethane linkages. Besides this, Glycerol was used as a cross-linking agent to provide necessary branching for the fuel binder. The CuPc, CoPc and FePc have been used as burn rate modifier catalysts. The composition is given below (Table 1) in weight percentages, catalysts are added extra. The requisite quantity of ingredients was weighed properly, thoroughly mixed, casted and cured for 6 days at 60 ±1 ℃ in a hot air oven and cut into strands for the experimentation.

Table 1. Composition of solid Propellant samples by weight percents

AP	70	70	70	70
HTPB	21.60	21.60	21.60	21.60
DOA	6.60	6.60	6.60	6.60
TDI	1.68	1.68	1.68	1.68
Gly	0.12	0.12	0.12	0.12
CuPc	-	2.00	-	-
CoPc	-	-	2.00	-
FePc	-	-	-	2.00

2.3. Instrumentals

Thermal decomposition process of the propellants was carried out with the help of Shimadzu DTG-60 Thermo Gravimetric Analyzer (TGA) and differential thermal analysis (DTA) techniques whereas, TA Instrument USA-Q10 differential scanning calorimeter (DSC) was used to characterize the propellant samples at heating rate of 10 ℃/min, in the temperature range between 30 to 300 ℃. The surface examination of propellant samples were performed with the help of scanning electron microscopy (SEM) (Model: Jeol-JSM 6390 LV, Japan) with the following specification; accelerating voltage (10 KeV), secondary electron image mode, and with 20 mm working distance. The test samples were mounted on aluminum stub and coated with gold metal to avoid electrical charging during analysis. Heat of reactions of prepared propellant samples was determined with the help of Digital Bomb Calorimeter (ARICO, India) at atmospheric pressure and inert atmosphere. Linear burn rates of solid propellants were measured by using standard Crawford Strand Burner and Low Vacuum combustion setup respectively.

3. Results and Discussion

3.1. Thermal Properties

Thermal decomposition characteristics of solid propellants (as shown Figure 1) with and without catalysts (MPcs) are investigated by thermo gravimetric analysis (TGA). The percentage weight loss and residual mass percent of each sample between 30 to 500 ℃ have been evaluated and properly presented in Table 2. The decomposition of Virgin AP-HTPB sample was found to be three staged, but on addition of 2% of CuPc, CoPc and FePc. The thermal decomposition has become a two staged decomposition with a sudden mass loss, thus increasing the decomposition rate. The decomposition patterns indicated that primarily depolymerization and partial decomposition of crosslinked HTPB matrixes. Certain products made by self-cyclization at given temperature which may decompose comparatively at higher temperature range.
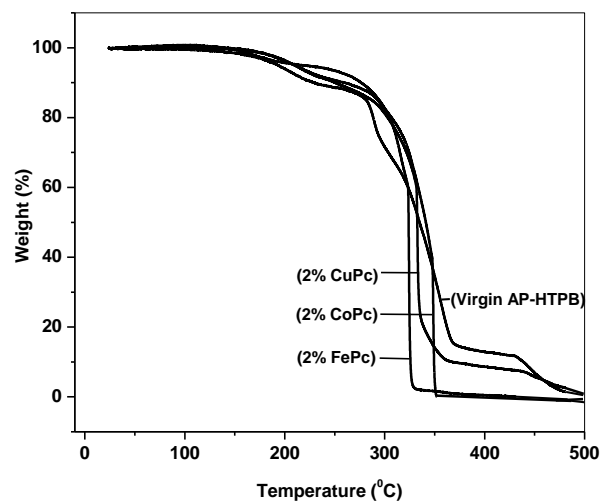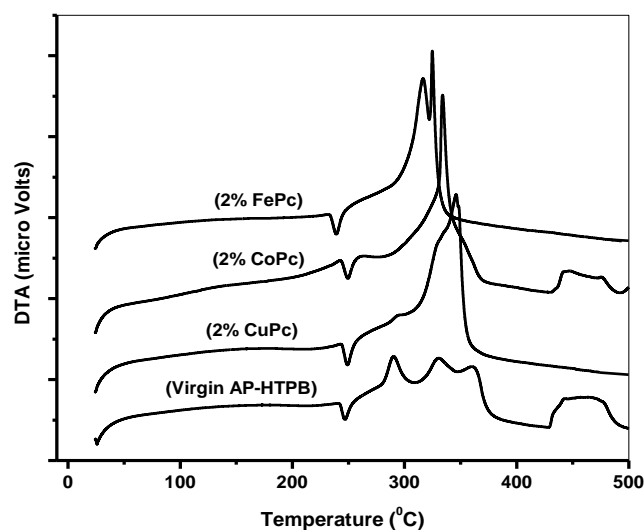

Figure 1. TGA curves for propellant samples

Table 2. Thermal decomposition (TGA) data of propellant samples

Sample	Start T (℃)	End T (℃)	Weight Loss (%)	Residual Mass (%)
Virgin AP-HTPB	30	260	11.72	
	260	400	75.17	1.47
	400	500	11.64	
CuPc	30	260	6.45	
	260	400	84.30	0
	400	500	9.25	
CoPc	30	260	11.58	
	260	400	86.12	0
	400	500	2.30	
FePc	30	260	10.20	
	260	400	83.76	0
	400	500	6.04	

Figure 2. DTA thermograms of propellant samples

The DTA thermograms (as shown in Figure 2) of solid propellant sample with and without catalysts (MPcs) showed that the AP molecules are subjected to phase transformation nearly 250 ℃ in all such propellants. There is no remarkable difference between first endothermic peaks, however, the variation in exothermic peak due to oxidation of AP molecule within the fuel-binder matrix was observed by the incorporation of MPcs catalysts. FePc was found to influence larger compared to other MPcs as clearly presented in Table 3. Based on the literature, it has been found that the thermal decomposition of AP under isothermal conditions is started even at 150 ℃. The complex decomposition mechanisms of AP facilitate several unusual characteristics in wide temperature range.

The observation made in this study is suggested that the AP molecule undergoes autocatalytic reaction at 245 ℃, which stops after the decomposition of approximately 30%, leaving ammonium perchlorate as the residual itself as also investigated [14, 15]. At temperatures above 250 ℃, the decomposition of AP occurs which is not autocatalytic but it
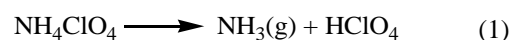
shows partial loss in mass with the function of temperature. The first endothermic peak in DSC analysis as presented in Table 4 corresponds to the transition from orthorhombic to cubic phase as there is no significance mass loss observed. Just after the endothermic peak, an exothermic peak has also been observed, which refers to decomposition of AP relatively at temperature. This finding is in accordance with the reports of Rajic and Suceska [16].

Table 3. Differential thermal analysis (DTA) data

Sample	Sample (mg)	Endo Peak (℃)	Exo Peak (℃)
Virgin AP-HTPB	3.46	249	428
CuPc	3.60	248	336
CoPc	3.62	246	346
FePc	3.76	244	334

The decomposition mechanism of AP-HTPB based propellants can be illustrated through following steps;

The dissociation-sublimation of AP takes place in low temperature (300 ℃) region,

$$NH_4ClO_4 \longrightarrow NH_3(g) + HClO_4 \qquad (1)$$

In the second step, HTPB reacts with $HClO_4$ and extracts the hydrogen content and forms HCl and H_2O. Then the carbonaceous residue reacts with O_2 to form CO and CO_2. The addition of MPc increases the rate of extraction of O_2 from $HClO_4$ due to the metal Phthalocyanine redox couple, thus increasing the overall rate of reaction [17].

$$MPc^{II} + \bar{O}_2 \longrightarrow MPc^{III}O_2 \qquad (2)$$

$$MPc^{III}O_2^- + e^- \xrightarrow{\bar{H}} Product + MPc^{III} \qquad (3)$$

$$MPc^{III} + e^- \longrightarrow MPc^{II} \qquad (4)$$

Measurement of heat of reaction experiments were performed in a digital bomb calorimeter under a closed hood. The experiments were carried out in the presence of 2L of distilled water at ambient condition. Approximately 1g samples were placed on a stainless steel crucible, and combustion was initiated with an ignition unit via electrical discharge through a Ni-Cr alloy fuse wire (length of 10 cm) in contact with the sample. Temperature increases were determined from PT-sensor embedded in the system. The accuracy of the system was determined by measuring the standard energy of combustion of benzoic acid, having a quoted energy of combustion of 6318 cal/g. Using the standard calibration method, total 3 calibrations were done, the experimental heat capacity for the unit was 2476cal/℃. As shown in Table 5 it can be observed that the calorific value of the catalyzed AP-HTPB propellants have increased substantially in comparison with the non-catalyzed AP-HTPB propellants. The higher the percentage of catalyst, the higher is the calorific value. It can be inferred that sample with Iron Phthalocyanine as catalyst has highest heat of reaction followed by Cobalt Phthalocyanine and then Copper Phthalocyanine. This inferred that the MPcs certainly

enhanced the enthalpies on the incorporation in solid propellants.

Table 4.   Differential scanning calorimeter data

Sample	Sample Mass (mg)	Onset T (℃)	Endo Peak T (℃)	End set T (℃)
Virgin AP-HTPB	3.35	245	245	253
CuPc	3.47	244	246	252
CoPc	3.44	245	247	255
FePc	3.30	244	246	253

Table 5.   Results of heat of reaction

Sample	Heat of reaction at ambient condition (cal/gm)
Virgin AP-HTPB	1094.74
CuPc	1165.55
CoPc	1239.41
FePc	1266.10

3.2. Surface Characterization

SEM image of virgin-AP HTPB propellant (Figure 3) showed that AP and HTPB have blended well with each other and have formed a uniform composite matrix. On the addition of 2% CuPc, the texture of propellants become irregular but dispersion of MPcs molecules was found to uniform throughout the surfaces. AP particles were also seen encapsulating with HTPB which leads to development of cubic crystal rather than spherical shape. SEM images evidence the morphology of the material and the absence of micro-voids and dewetting phenomena. We notice that on the addition of 2% CoPc, the mixture is not homogeneous as compared to the virgin AP-HTPB mixture but the consistency is better than the sample of 2% CuPc. Small amounts of AP-HTPB chunks coated with CoPc can be seen in SEM image.

3.3. Elemental Analysis

In this analysis, each sample was combusted at high temperatures in oxygen rich environment and all the combustion products were swept out of the combustion chamber by an inert carrier gas (helium). These products were passed over a heated high purity copper which removes unconsumed oxygen and converts nitrogen oxides into nitrogen gas. These gases were passed through a thermal conductivity detector which detects the amount of Carbon, Hydrogen, Nitrogen and Sulfur present in the compound. Table 6 gives the results of the CHNS Analysis. It can be observed that the C/N Ratio has increased on the addition of Metal Phthalocyanines. This phenomenon has to be studied further to get an insight into the actual combustion process that is taking place.
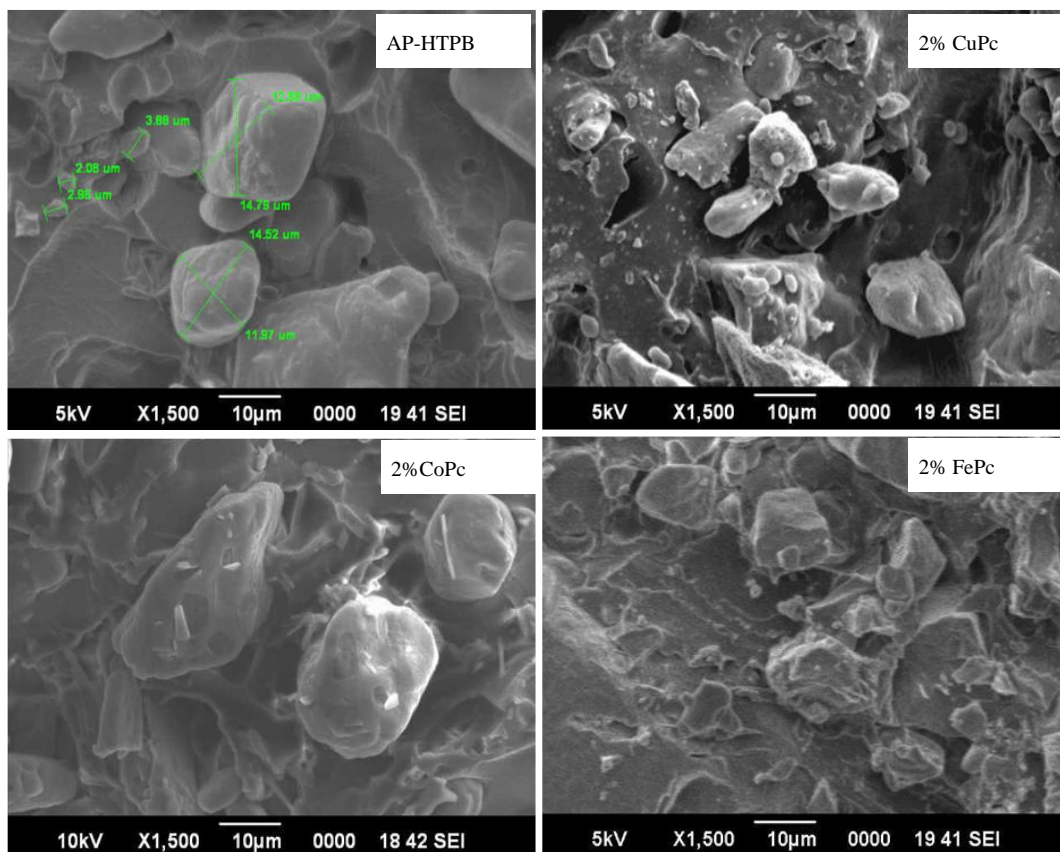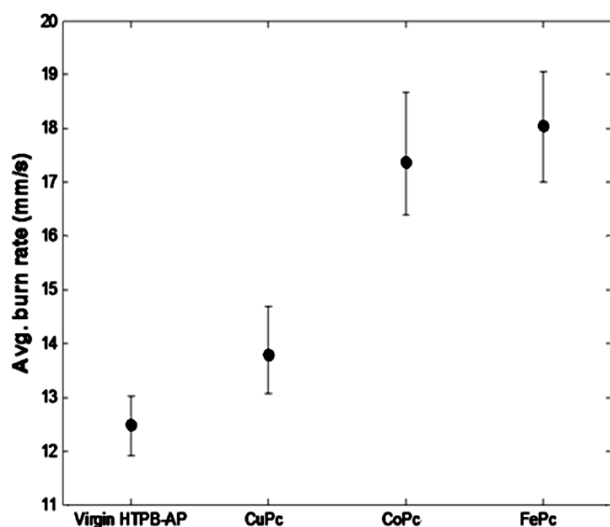

Figure 3.   Surface morphologies of solid propellant samples

Table 6. Results of CHNS elemental analysis

Sample	Sample Weight (mg)	C/N Ratio	N%	C%	H%
Virgin AP-HTPB	5.52	2.97	8.40	24.96	6.28
CuPc	5.50	3.25	8.56	27.80	6.10
CoPc	5.56	3.25	8.40	27.32	6.51
FePc	6.54	3.00	8.74	26.15	6.44

3.4. Burning Characteristics

The burn rate studies at high operating pressures were investigated using a Crawford Strand Burner. The propellant strands were electrically ignited and the time taken for 4 cm length of the strand to combust was recorded and then burn rate was calculated. The firing vessel was filled with nitrogen gas at 56 kg/cm^2 to simulate the operating chamber pressure conditions. From Figure 4 we notice that there is an increase in the burn rate of the propellants on the addition of metal phthalocyanines. Of all the propellant samples, with FePc as catalyst have the highest burning rate in comparison with others at high pressure. Similar effect with FePc was also observed by Fong et al. [8]. This increase in burn rate could be because of the MPc addition. The addition of MPc increases the O$_2$ reduction activity which is controlled by the MPc^{II}/MPc^{III} redox couple as quoted in the mechanism in the earlier section.
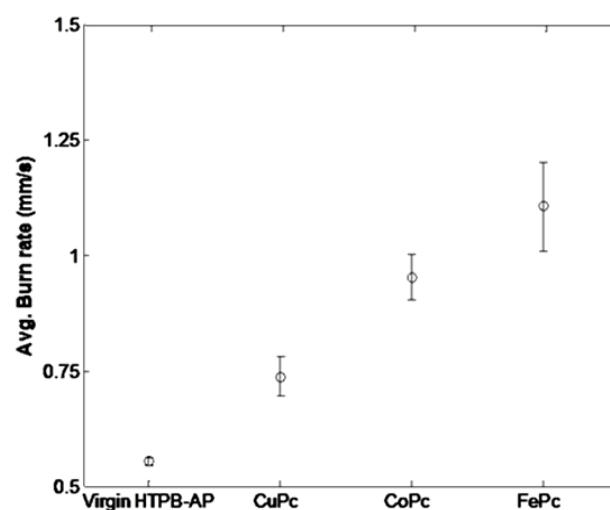

Figure 4. Plot of burn rate of propellants at high Pressure

The burn rate studies at low vacuum operating pressures were investigated using a Low Vacuum Strand Burner. The propellant strands were electrically ignited and the time taken for 3 cm length of the strand to combust was recorded and then burn rate was calculated. The firing vessel was filled with vacuum up to 0.5 kg/cm^2 in order to simulate the operating chamber pressure conditions. From the Figure 5, we notice that there is an increase in the burn rate of the propellants on the addition of metal Phthalocyanines. Of all the propellant samples, samples with Iron Phthalocyanines

as catalyst have the highest burn rate in comparison with others at low vacuum conditions.

As the pressure increases, the speed of the elementary reactions in the decomposition of AP-HTPB rises which may lead to the flame being closer to the material. This could be the reason for the increase in burn rate with pressure.

The burn rate studies at high pressure were carried out in a Crawford Burner and the burning rate was obtained by sequential breaking of two fused wires, which were embedded in the propellant strands. For few cases, there was difficulty to get burning signal and sometime even there was no signal. The experiments on those cases had been repeated by several times until the burn rate data was reproducible in an average sense. While performing the experiments, it has been observed that the propellant strands of CoPc are getting damp by absorbing moisture. Thus, the special care for storing the propellant strands is necessary.

Figure 5. Plot of burn rate of propellants at low pressure

4. Conclusions

The following conclusions can be drawn from the present investigations on the combustion characteristics of AP-HTPB composite solid rocket propellants with and without metal Phthalocyanines as burn rate modifiers.

All the samples except the one with 2% CuPc blendedwell with the AP-HTPB slurry. This is because CuPc coats the slurry as soon as it comes in contact with the slurry and does not mix thoroughly to get a consistent mixture as compared to the other metal phthalocyanines used.

On addition of 2% of CuPc, CoPc and FePc, the thermal decomposition of virgin AP-HTPB which was found to be a three staged decomposition has become a two staged decomposition with a sudden mass loss, thus increasing the decomposition rate.

Addition of metal phthalocyanines does not show appreciable reduction in onset, endset and endothermic peak temperatures; however, a significant reduction in the exothermic peak temperature has been observed.

The presence of metal phthalocyanines in the AP-HTPB sample has increased the heat of reaction of the composite solid rocket propellant which means the catalysts can lead to more completeness of the combustion of AP-HTPB propellant.

The addition of metal phthalocyanines has been found to increase the burning rate of the propellants in both high pressure and low vacuum conditions. This is beneficial because the enhanced burning rate can attribute to better performance of the rocket.

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