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Study of Aging Characteristics for Metalized HTPB Based Composite Solid Propellants Stored in Ambient Conditions

Prakhar Jain, Vineet Kumar Rathi and Shelly Biswas*

Department of Space Engineering and Rocketry, Birla Institute of Technology, Mesra, Ranchi - 835 215, India

**E-mail: shellybiswas@bitmesra.ac.in*

ABSTRACT

The aging of any propellant is defined as the change in the physical, chemical, and performance parameters of solid rocket propellants. The propellant's service life and aging properties are important parameters of the study, especially for missiles and other defense applications. Hydroxyl-terminated polybutadiene (HTPB) based composite solid propellants with ammonium perchlorate (AP) are the most prominently used propellants in the operations of solid rocket motors in the defense and space sectors. Thus, studying this composite solid propellant is of essential when determining ambient service life. Performance parameters studied in this research are burn rate under high-pressure conditions in Crawford bomb setup, Thermogravimetric Analysis, and Fourier Transform Infrared Spectroscopy (FTIR). SEM and X-ray Diffraction (XRD) analysis of the aged sample were also conducted to ascertain the chemical composition and morphological changes in the samples. Naturally aged propellant strands manufactured in different years have been compared with freshly prepared ones to establish a trend for deriving conclusions. The results from different analysis techniques, FTIR, XRD, and FESEM, depicted that oxidation of metals happens while aging of propellant due to atmospheric moisture, and the metal oxides prominently affect the propellant chemical composition and decomposition process of the propellant samples. The ballistic properties of the aluminium added samples showed an increment in burn rate. In contrast, the bimetal addition of aluminium and magnesium combined as an additive decreased the ballistic burn rate.

Keywords: Composite solid propellants; Aging; Service life; Metalized composite solid propellants; Burn rate; Thermogravimetric analysis

NOMENCLATURE

t_E	: Time in years at temperature T_E
t_T	: Time in days at test temperature T_T
F	: Reaction rate change factor, here 2.5
T_E	: In-service temperature
T_T	: Test temperature
ΔT_F	: Temperature interval for F, here 10 K
Y	: Year
D	: Day
K	: Kelvin
$_E$	: In-service scenario
$_T$	: Test scenario
$_F$	: Scaling factor

1. INTRODUCTION

Since the beginning of missile and rocket development, solid propellants have been of utmost importance. The application of solid propellants can be traced back to the Chinese and Mongols, who started to use simple forms of gunpowder or potassium nitrate to create fireworks or to launch projectiles[1].

With research and development, solid propellants were distinguished into two categories based on the type of mixture and multiple differentiations based on properties, performance, and safety[2]. Propellants with a homogenous mixture are double-base propellants, whereas heterogeneous mixture propellants are known as Composite Solid Propellants (CSP). CSP consists of fuel, oxidizer, binder, and other additives such as curing agents, energetic particles, etc. The binder is one of the most important parts of CSP composition as it holds all other ingredients together. The most significantly used CSP consists of a Hydroxyl-Terminated Polybutadiene (HTPB) binder with Ammonium Perchlorate (AP) and other additives, are found to be applicable in defense and space sectors. The CSPs have simple designs, and transportation is much easier. Another significant advantage of using solid propellants is the storability factor. Numerous composite propellants were prepared using various propellant ingredients, and their burning properties were examined[2-4]. Solid propellants also have a good shelf life. As for the properties mentioned above, solid rocket propellants have a prominent application in solid rocket boosters and ready-to-launch missiles.

1.1 Aging

Aging refers to the slow and complex process of deterioration in the chemical, physical, and ballistic properties

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of the propellant sample. These changes are usually driven by the interaction of the sample with physical and ambient conditions over a long time. This deterioration of properties over time degrades the performance of propellant in extended periods and thus determines the service life of a propellant sample. Solid rocket propellant grains are usually manufactured in bulk and stored for use as per requirements. Also, grain transfer takes place to rough and harsh launch site locations. Due to all these processes, the properties of the propellant grain get affected over time, and the grain might not deliver the required performance. These degradations are majorly due to thermal shocks, mechanical loads, and the effect of moisture on the grain[1].

The available literature and research have shown that aging is complicated, specifically complex, and slow in solid propellants. This is due to numerous extrapolating factors. All these may lead to the deterioration of mechanical properties, such as the formation of cracks, migration, etc. Changes may also happen in their chemical properties, such as decomposition temperature, adiabatic flame temperature, burn rate, etc. Thus, understanding the chemical phenomenon and aging mechanisms helps in determining the shelf life of a propellant[1].

1.2 Aging of Composite Solid Propellants

In composite solid propellants, the prominent phenomena responsible for physical and chemical degradation are oxidation, hydrolysis, humidification, decomposition, crosslinking, etc. The outer surface layer is the most affected part of the propellant sample. This is because it is directly in contact with the air and moisture. Aging in composite solid propellants is also affected by the composition of the propellant[5].

1.3 Types of Aging Studies

Aging is generally characterised by two methods:

1.3.1 Accelerated Aging Studies

In accelerated aging, propellants age faster by curing them at elevated temperatures, which reduces the time needed for the aging of the propellant and reduces research time.

1.3.2 Natural Aging Studies

In the natural aging process, propellants are stored in an appropriate environment to age naturally over time. The surrounding temperature conditions depend upon the weather conditionsof the place, and so do all other ambient properties.

Accelerated aging usually covers only thermal loads. Using a scaling factor of F = 2.5 per 10 K temperature with the deployment of generalized van't Hoff rule (GvH)[6], the time periods of 2.5-year natural aging is shortened to 2.5, 6, and 15 days when the accelerated aging is conducted at temperatures of 363 K, 353 K, and 343 K respectively. Similarly, 10 years of natural aging is shortened to 10, 24, and 60 days at an accelerated aging temperature of 363 K, 353 K, and 343 K, respectively.

As the aging process is generally caused by chemical reactions, an empirical formula basedon GvH is prominently used for setting up a relation between naturally aged time and accelerated aged time at different temperature conditions[7]. GvH rule uses precisely two different mechanisms of the temperature dependence of HTPB along with its oxidation behavior[8] and is based on the below-mentioned equation[7]:

$$t_E = \frac{t_T F\left(\dfrac{T_T - T_E}{\Delta T_F}\right)}{365.25} \tag{1}$$

Naseem[1], *et al.* conducted a comprehensive study on the aging characteristics of AP/HTPB-based composite solid rocket propellant. The study shows significant changes in the physical characteristics when stored at low temperatures due to the migration of plasticizers leading to degraded propellant performance.

Thomas[5], *et al.* studied the accelerated aging of composite solid propellants with nano- additives. In the study, the authors observed a decreasing trend in the burn rate, which was more significant at higher pressures. These drops in the burn rate were small (<10 %). The authors also clearly show the difference between the impacts created by natural aging and accelerated aging through fluorescent imaging experiments. The research clearly exhibits that extrapolating and fast-tracked tests have not always delivered accurate results and do not naturally match deterioration in properties and performance. This conclusion was derived using the fluorescent imaging experiment[6].

Adel[7], *et al.* worked on the shelf life of AP/Al/HTPB composite solid rocket propellant, which is serviceable. They also gave a comparison between the natural and accelerated aging of the mentioned propellant. While the different types of aging exhibit similar trends in the change of properties, the discrepancies in results obtained are a matter of study. The research also describes the hydrolysis effect as the primary aging mechanism of the aluminized HTPB/AP- based propellant samples.

The change in the mechanical properties with time of aging for three Aluminised HTPB- based rocket propellant formulations was studied by using Dynamic Mechanical Analysis (DMA)[9]. The propellant samples containing AP and Al particles with different Al content and particle size were used for the analysis in accelerated aging conditions of 60 °C and 90 °C and fitted to an exponentially modified Gaussian (EMG) function to predict the aging phenomenon. The mechanical properties of aluminized solid rocket propellants with tensile strength, impact, and friction sensitivity were investigated to ascertain the effect of aging on the propellant[10]. The mechanical properties at the time of break were used to study the aging behavior of HTPB/AP propellant. Relaxation was preferred as one of the guides of aging, and a finite element computerprogram was used to simulate these relaxation tests[11]. Accelerated-aging tests at 40, 60, and 80 °C for 5000 h were performed on HTPB propellant with viscoelastic measurements to study the effect of aging on energetic materials[12]. The role of crosslinking agent density on the aging behavior of HTPB/AP-based composite solid propellants was studied by Hocaoglu[13], *et al.* The aging effect was characterized by the molar ratio of di-isocyanate to the total hydroxyl (NCO/OHratio) content and the molar ratio of triol to diol (triol/diol ratio) content.

The effect of nano titania additives on HTPB/AP propellant was studied using accelerated aging, and it was found that

85 % solid loading and nano additive added sample led to an increase in the burn rate by about 12 % with morphological changes. The 80 % solid loaded sample should have a 7 % decrease in burn rate[14]. The thermal decomposition kinetics for naturally aged AP/HTPB-based bleed propellants samples were carried out, and the activation energy and pre-exponential factor were estimated using Ozawa and Kissinger methods[15].

The microstructure damage of solid propellants under multi-axial loading[16] and uniaxial stress[17] was studied to understand how axial stress affects the life of the propellant. The accelerated aging of composite solid propellants was studied using the cyclic-thermal method as a function of temperature[18], under vacuum conditions[19], using non-destructive indentation technique[20], by using Dynamic Mechanical Analysis (DMA), Sol-Gel-Analysis (SGA) and Gel Permeation Chromatography (GPC)[21], the effect of antioxidants, burn rate enhancers, and plasticizers[22], on the degree of crosslinking[23], softening behaviour[24], the effect of humid condition[25-26], alternating temperature[27], cyclic and isothermal aging[28] and effect of copper chromite additive on combustion of AP[29]. Aging kinetics and its mechanism under elevated temperatures were studied by using the Arrhenius model, and it was concluded that ambient humidity has an adverse effect on mechanical properties, but this effect was reversible[30].

Himanshu[31], *et al.* used the Arrhenius equations and Berthelot equations to draw a comparison between the prediction of the shelf life of composite solid propellants and concluded that the Arrhenius equation varies the shelf life exponentially whereas the Berthelot equation has power-law variation. To establish a relation between these two equations, accelerated aging was conducted, and the activation energy used to estimate the shelf life was in line with the reported values.

The above-mentioned literature clearly indicates that the shelf life of solid propellants is of utmost importance for the optimum performance of the CSP. The comparative ballistic performance and chemical degradation and morphological analysis of the aged CSP under both accelerated, and natural conditions are required to understand the actual phenomenon of aging ofthe CSP. Past research work concentrates mainly on accelerated aging, but natural aging is essential for the study of actual storage life. Although changes in burn rate and mechanical properties of a propellant have been studied earlier, no investigation has been carried out on the actual chemical change or compositional change in the propellant. Thus, the present study describes the ballistic performance altercations, morphology, and chemical structure or compositional altercations in the long-term natural storage of these propellants, which is essential for understanding the aging phenomenon and, thus, the life of a propellant.

2. METHODOLOGY

In this research, we have dealt with samples of HTPB/AP with different compositions manufactured in 2018. The samples were aged naturally for four years in ambient/natural conditions[32]. The samples were stored in a well-maintained desiccator using calcium chloride as a desiccant in the naturally occurring atmospheric conditions of Mesra, Ranchi, Jharkhand. The average maximum temperature reported during the period was 303 K, the average minimum temperature reported was 291 K, and the average mean temperature was 297 K. The region experienced an annual average total precipitation of 1400 mm and an annual average humidity level of 63 %[33]. The samples were evaluated for burn rate, and Thermal Gravimetric Analysis (TGA) was used to study the changes in physical and chemical properties over increasing order of temperatures. Table 1 represents the list of naturally aged samples that have been taken for testing and analysis.

Table 1. Samples manufactured originally, aged naturally

Propellants	Additive	Additive %	Year of Mfg.
HTPB/AP	Al	5 %	2018
HTPB/AP	Al	10 %	2018
HTPB/AP	Al-Mg	5 % - 5 %	2018
HTPB/AP	Al	5 %	2022
HTPB/AP	A1	10 %	2022
HTPB/AP	Al-Mg	5 % - 5 %	2022

2.1 Processing of HTPB-Based Composite Solid Propellant Strands

Table 2 depicts the composition of the solid propellant used in the present study. The processing starts with the dehumidification of HTPB and Dioctyl Adipate (DOA) to remove moisture. HTPB is then mixed with DOA and glycerol (0.6 %) in an adequate ratio. AP coarse and AP fine in the ratio of 2:1 are mixed in the same order of addition, batch-wise, for proper mixing. Further, additives are added as per requirements. Toluene Di-Isocyanate (TDI) is added at the last to prevent pre-mature curing. The propellant slurry is made using the hand mixing method. The total time for mixing is 150 min. Later, the propellant slurry is poured into the mold and kept on the vacuum casting unit for 2 hrs to remove air bubbles. Finally, the sample is cured under appropriate conditions.

Table 2. Composition of HTPB-Based propellant samples

Sample No.	Oxidizer (AP)%	Binder (HTPB) %	Aluminium %	Magnesium %	DOA %
1	65	23.48	5	-	6.52
2	65	18.48	10	-	6.52
3	65	18.48	5	5	6.52

2.2 Experimental Studies

2.2.1 Burn Rate Studies

The burn rate tests of CSP have been conducted using a high-pressure Crawford setup. The instrument uses nitrogen gas to create an inert and pressurized environment. Various other equipment has been used in the instrument setup for data collection. The instrument uses a dial- type pressure gauge to track and record the pressurization of the bomb pressurised from a High-Pressure Nitrogen Cylinder (HPNC). The setup also consists of a surge tank, which is responsible for the strict maintenance of pressure inside the bomb during the test. As the combustion takes place, exhaust gases are released, which

Table 3. Burn rates of HTPB-based CSP samples for years 2022 and 2018[32]

Sample	Pressure (MPa)	Burn rate (mm/sec) Y – 2018[32]	Burn rate (mm/sec) Y - 2022	Change in burn rate (%)
	1.4	7.7±0.13	7.75±0.14	+ 0.65
HTPB/AP + 5 % Al	2.8	9.6±0.17	9.75±0.17	+1.56
	4.2	10±0.18	10.12±0.18	+1.2
	1.4	7.9±0.14	8.53±0.15	+7.97
HTPB/AP + 10 % Al	2.8	9.9±0.18	10.03±0.18	+1.31
	4.2	11.9±0.22	12.22±0.22	+2.69
	1.4	7.7±0.14	6.6±0.12	-14.29
HTPB/AP + 5 % Al + 5 % Mg	2.8	10.9±0.21	9.73±0.17	-10.73
	4.2	13.1±0.23	10.48±0.19	-20

may lead to an increase in pressure during the test. The burn rate test before and after aging was carried out using propellant strands of 100 mm in length and fuse wires placed at 50 mm in length. The timer starts as soon as the first fuse wire gets cut off and stops as soon as the second fuse wire cuts off. The test was conducted at three different pressure conditions (1.4 MPa, 2.8 MPa, and 4.2 MPa). Three experiments were conducted on each sample at each pressure, and the average value of the results was considered. The results were used to compare with the results of the test performed previously when the samples were freshly prepared 4 years ago, and hence, a trend line was established.

2.2.2 *Thermal Decomposition Study*

A thermal decomposition study has been carried out to understand the decomposition reactions taking place for propellant samples. It was completed using the TGA technique in the Simultaneous Thermogravimetric Analyzer (STA) PG LUXX 409. The decomposition process was analyzed to study the change in the decomposition mechanism over a 4-year time period, and the results were compared with the results of the same test performed 4 years ago.

2.2.3 *Fourier Transform Infrared (FTIR) Spectroscopy Analysis*

FTIR offers a wide range of operations, such as identifying the chemical composition of a propellant sample. It also has the capability to provide data to perform quantitative analysis on unknown particle additives or contaminants of any type. FTIR was performed on HTPB-based propellant samples to study the change in composition that could have taken over time in the propellant samples and predict the behavior of the samples in terms of their performance.

2.2.4 *Surface Morphology And Crystalline Structure Analysis*

The surface morphology of the aged samples was analyzed using a Field Emission Scanning Electron Microscope (Model: Sigma300) Carl Zeiss, Germany. The instrument has a magnification range of 25 X to 1200 KX and a resolution of ≥3 nm. The EDX analysis was also carried out using the same instrument. The detectors used are secondary electron detectors for surface morphology and topology analysis, whereas silicon drift detectors are used for energy dispersive x-ray spectroscopy or EDX analysis. The samples were coated with gold to make them conductive so that when electron beams were passed on the samples, they could emit a variety of signals, which were captured by the detector to provide the surface image.

The phase detection and crystal structure of the fresh and aged propellant samples were conducted using Powder X-ray diffraction, Rigaku, Japan, Smart lab 9 KW, 2Θ angle range: 3°- 120°, 3 KW power, Hypix 3000 & SC-70 used as detectors.

3. RESULTS AND DISCUSSION

Several tests were conducted to study the performance parameters of aged propellants to establish a comparative study to understand the effects of aging.

3.1 Burn Rate Tests

The burn rate tests of HTPB-based naturally aged CSP samples with metal additives have been conducted from low to high pressures. The test was conducted using a Crawford bombsetup at pressures of 1.4 MPa, 2.8 MPa, and 4.2 MPa. The length of the strand test was 50 mm. Table 3 shows the

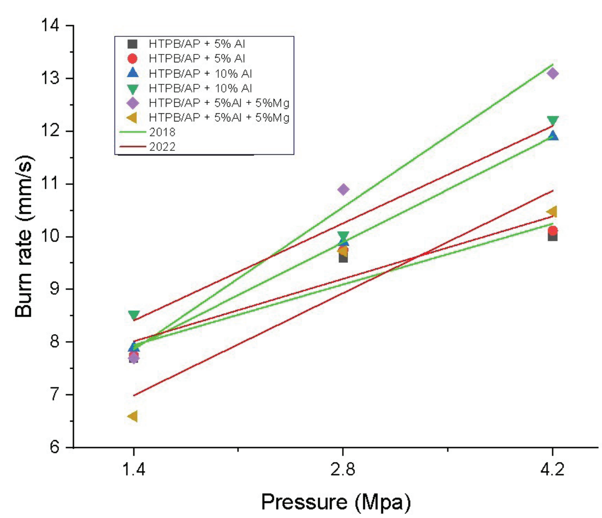


Figure 1. Burn rate vs. pressure trends for reported samples.

results of the burn rate test performed on aged samples and data that was collected 4 years ago when samples were freshly prepared. Figure 1 depicts the trend of burn rate for original and aged samples.

From Table 3 and Fig. 1, it is clear that the HTPB-based composite solid propellant with only aluminium as an added energetic particle shows a rise in burn rate after aging. Adel[7], *et al.* supported this rise in burn rate for aluminium mixed propellant samples. This can be explained by discussing the combustion model of heterogeneous solid propellants. The burning in CSP is dominantly controlled by the primary diffusion flame. The primary diffusion flame is responsible for heat transfer from the flame to the propellant surface. Due to natural aging, aluminium forms aluminium oxides due to a reaction with moisture in the atmosphere. The formation of aluminium oxides leads to a rise in the adiabatic flame temperature, which leads to higher heat transfer to the propellant surface and thus increases the burn rate. The same phenomenon is not observed in the composite solid propellant sample with magnesium and aluminium both combined as added energetic particles. This is due to the difference in the melting and boiling points of the components. The melting point of aluminium oxide is 2320K[34], and the boiling point of aluminium is 2750K[34]. As the melting point of aluminium oxide is less than the boiling point of aluminium, during the combustion process, as the melting temperature of the oxide is reached, the melting oxide retracts from the surface, thus giving higher heat transfer to themolten metal and thus faster combustion. The retraction of metal oxide is mainly due to the non- soluble nature of aluminium oxide. Aluminium oxides and aluminium are characterized by very low solubility with each other, and oxides of aluminium also have very high surface tension but possess low interfacial surface tension between the oxide and the metal. For these reasons, metal oxide has a tendency to accumulate and retract from the surface of the metal exposing it to higher temperatures.

In the case of magnesium, the melting point of oxide (3080K[35]) is much higher than the boiling point of metal (1385K[35]). When the temperature rises and finally reaches the boiling point of the metal, the metal oxide skin ruptures and finally breaks down. This initiates burning and is followed by the formation of a flame envelope around the molten metal droplet, leading to the vaporization of oxides. As the thermal conductivity of magnesium (156 W m^{-1} K^{-1})[35] is very low, the

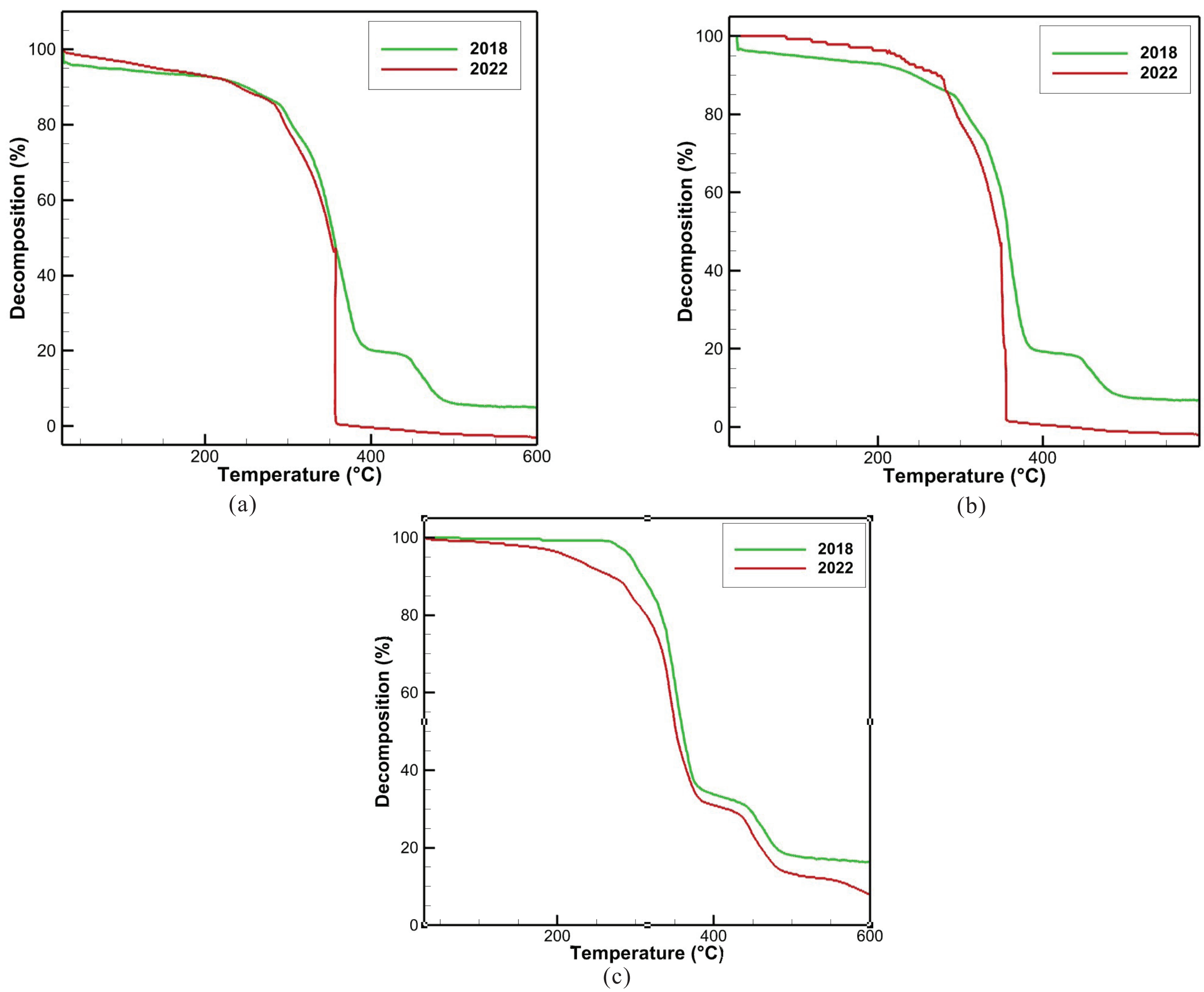


Figure 2. TGA curves for CSP samples of (a) HTPB/AP + 5% Al, (b) HTPB/AP + 10% Al, and (c) HTPB/AP + 5% Al+5% Mg.

heat conduction is also low, which causes a delay in raising the temperature of metal inside the oxide skin, which takes time. The two interplaying factors of the high melting point of oxide and lower thermal conductivity of magnesium lead to the requirement of higher time to rupture the oxide layer for exposure of the metal and thus, the burning rate of the propellant decreases[36].

3.2 Thermogravimetric Analysis

The Thermogravimetric Analysis (TGA) has been performed on the aged sample to study the decomposition process of the propellant samples. The results have shown a significant change in the reaction kinetics of the heterogeneous propellant sample. Figures 2(A), 2(B), and 2(C) show the thermal decomposition of HTPB/AP + 5 % Aluminium, HTPB/AP + 10 % Aluminium, and HTPB/AP + 5 % Aluminium + 5 % Magnesium, respectively, compared with their corresponding curve of freshly prepared samples.

The TGA curves for the aged sample HTPB-AP with Al 5 % (2022) and its original sample (2018) have been presented in Fig. 2 (A). It can be clearly observed from the figure that the step-like structure in the decomposition curve of the original sample (2018) corresponds to the decomposition of AP, HTPB, and then the decomposition of the partially decomposed products of AP and HTPB. In the aged sample (2022), it is clearly observed that there is a sudden decrease in the mass of the sample at a temperature of about 370 ^{o}C. This clearly indicates the effect of Al_2O_3, which fastens the decomposition reaction, as already mentioned in section 3.1. Thus, the effect of aging is clearly observed in the case of a 5 % Al added sample. The TGA curves for the original (2018) and aged sample (2022) for HTPB-AP-10 % Al (Fig. 2(B)) indicate the change in slopes as compared to the original sample. This clearly indicates that the decomposition mechanism in the sample is altered due to the presence of Al -10 %. As the amount of aluminium is more than that of the 5 % Al added sample, its oxide formation would also have a pronounced effect. The change in the slope of the curve also indicates the change in decomposition reactions taking place during the process, which alters the reaction mechanism as well.

Thus, the formation of aluminium oxide in the aged propellant is expected to affect these changes. These results are in accordance with the burn rate results, where an enhancement in the burn rate is observed dueto the formation of aluminium oxide during the aging process. The TGA curves for the original (2018) and aged sample (2022) for HTPB-

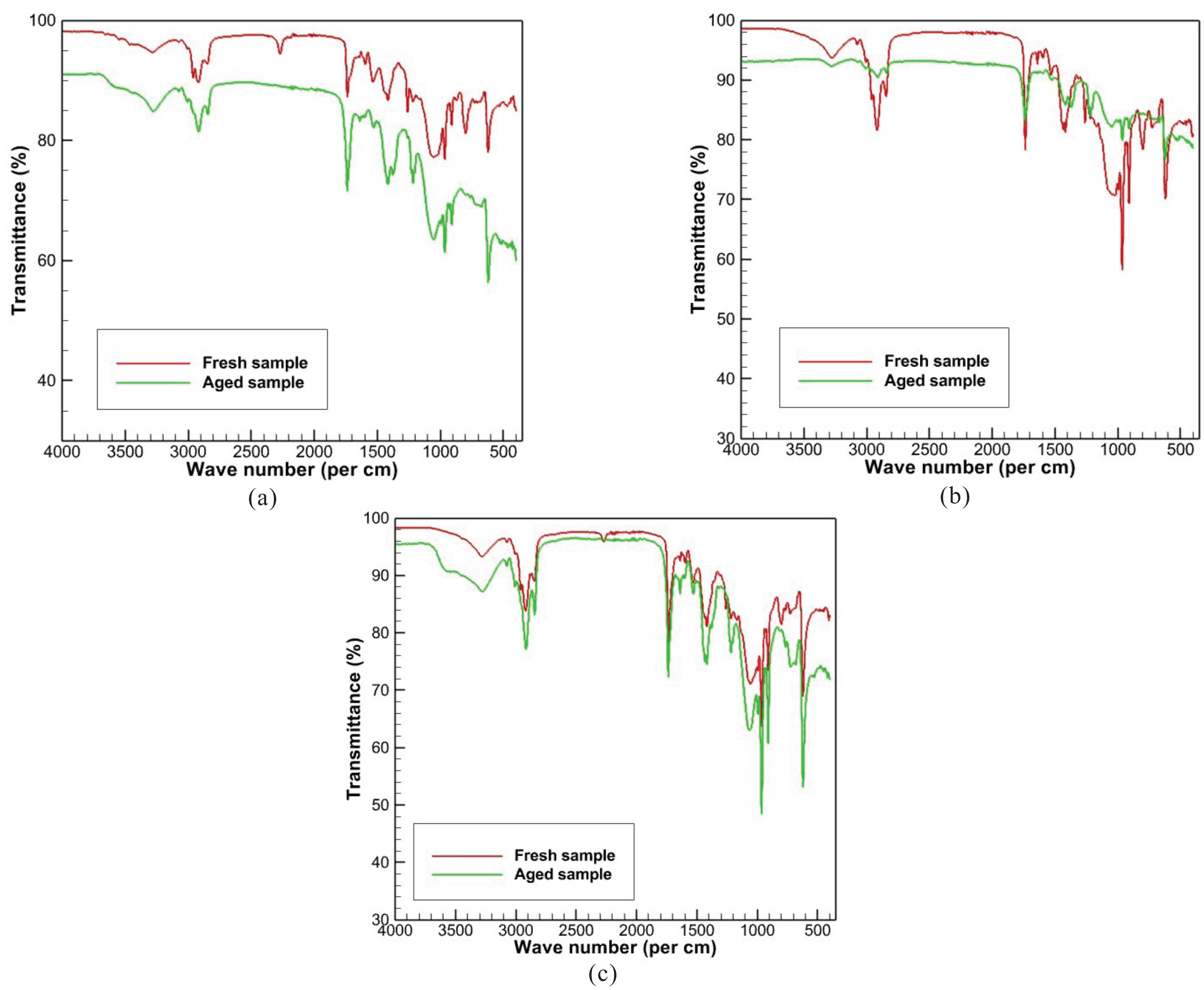
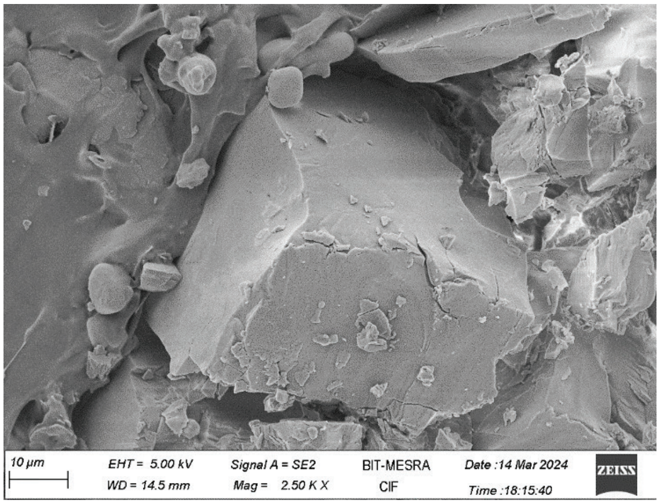
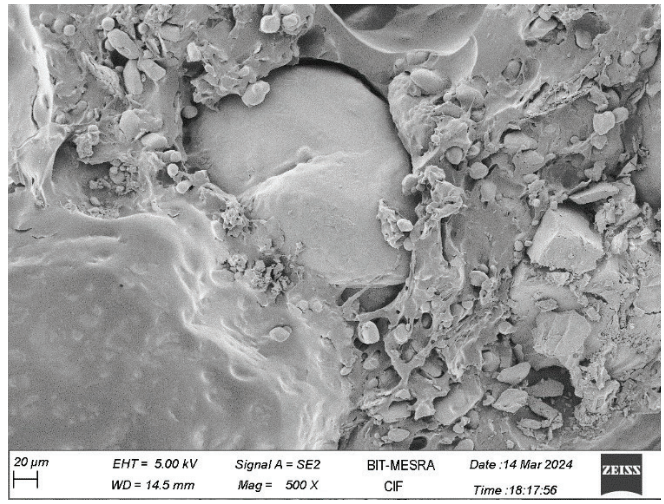


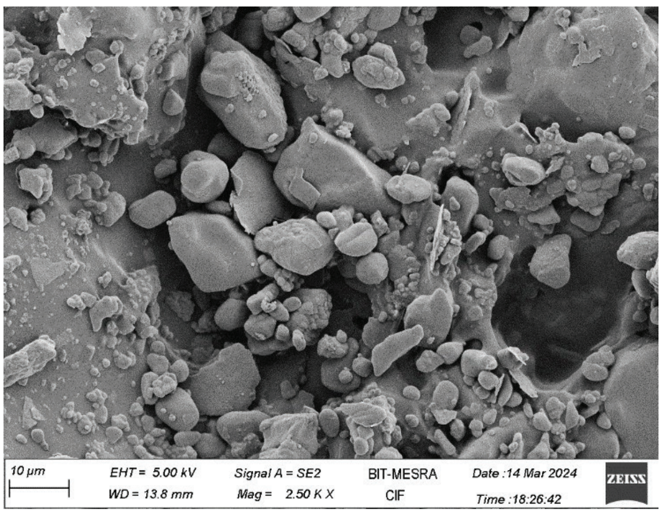
Figure 3. FTIR peak comparisons of fresh and 4-yr aged CSP samples: (a) HTPB/AP + 5% Al, (b) HTPB/AP + 10 % Al, and (c) PVC/DBP/AP + 5 % Al.



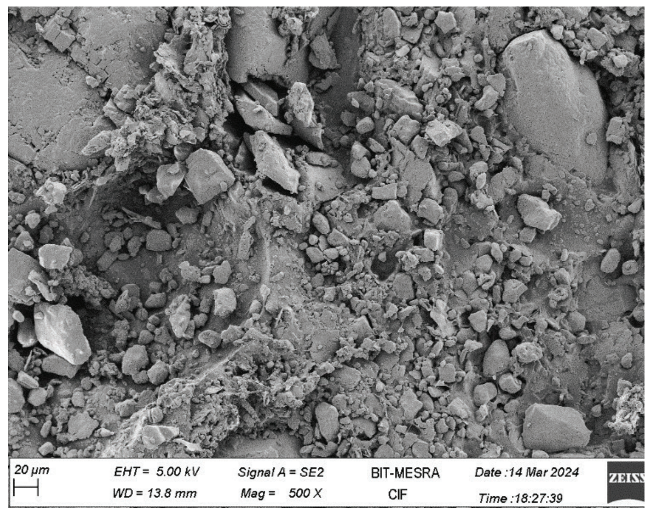
SEM image of AP/HTPB/Al(5 %)(X2500)



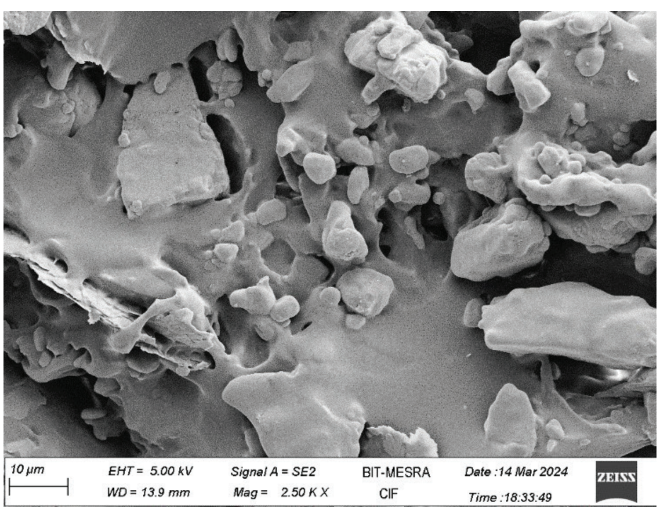
SEM image of AP/HTPB/Al(5 %)(X500)



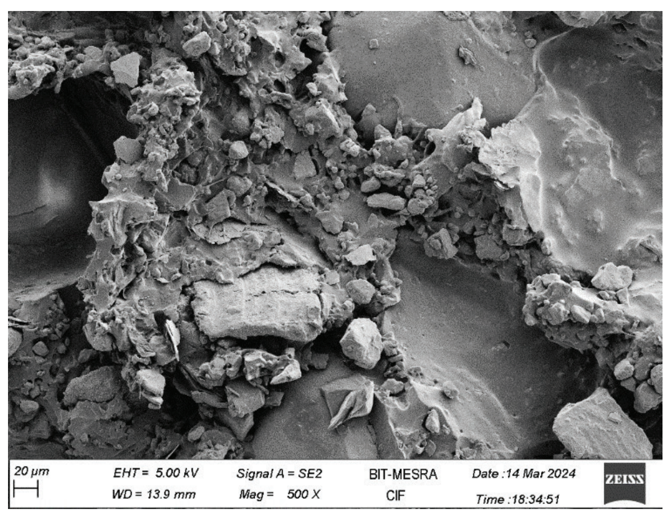
SEM image of AP/HTPB/Al(10 %) (X2500)



SEM image of AP/HTPB/Al(10 %) (X500)



SEM image of AP/HTPB/Al-Mg (10 %) (X2500)



SEM image of AP/HTPB/Al-Mg (10%) (X500)

Figure 4. SEM morphology of the aged CSP samples of: (a) HTPB/AP + 5 % Al, (b) HTPB/AP+ 10 % Al & HTPB/AP + 5% Al+ 5 % Mg, (d) HTPB/AP + 10 % Mg.

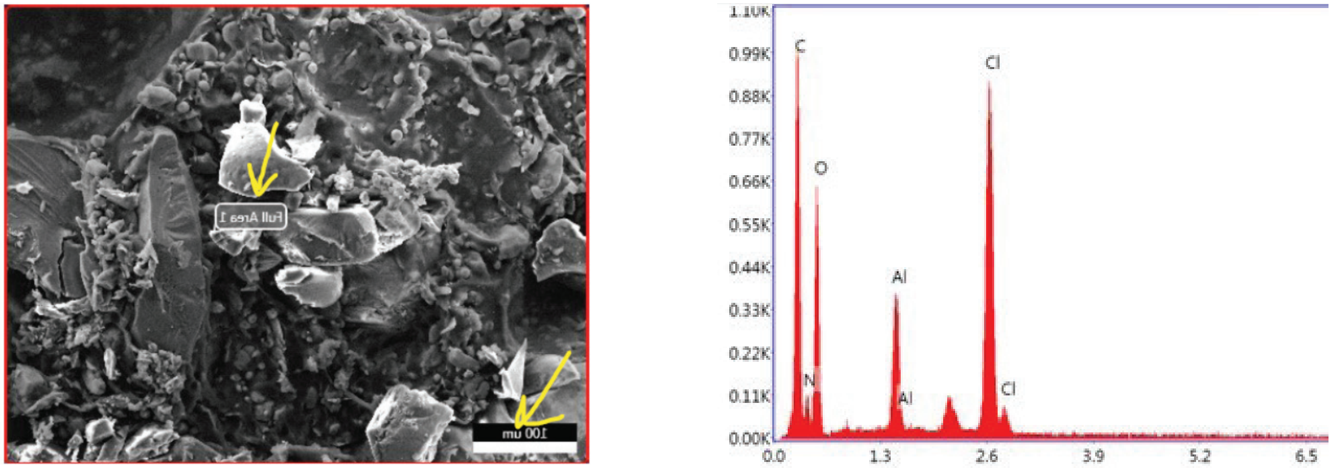
AP-10 % Al-Mg (Fig. 2(C)) indicate that there is a marked difference between the original and aged samples. This sample has the effect of the aluminium oxide and magnesium oxide, which form during the process of aging, and this leads to a decrease in the temperature at which decomposition takes place[37]. There is also a decrease in the mass of the sample at around 100 ^{o}C which is due to the presence of vaporization of water.

This mass loss is observed in all the aged samples. These results are in accordance with those of the burn rate results.

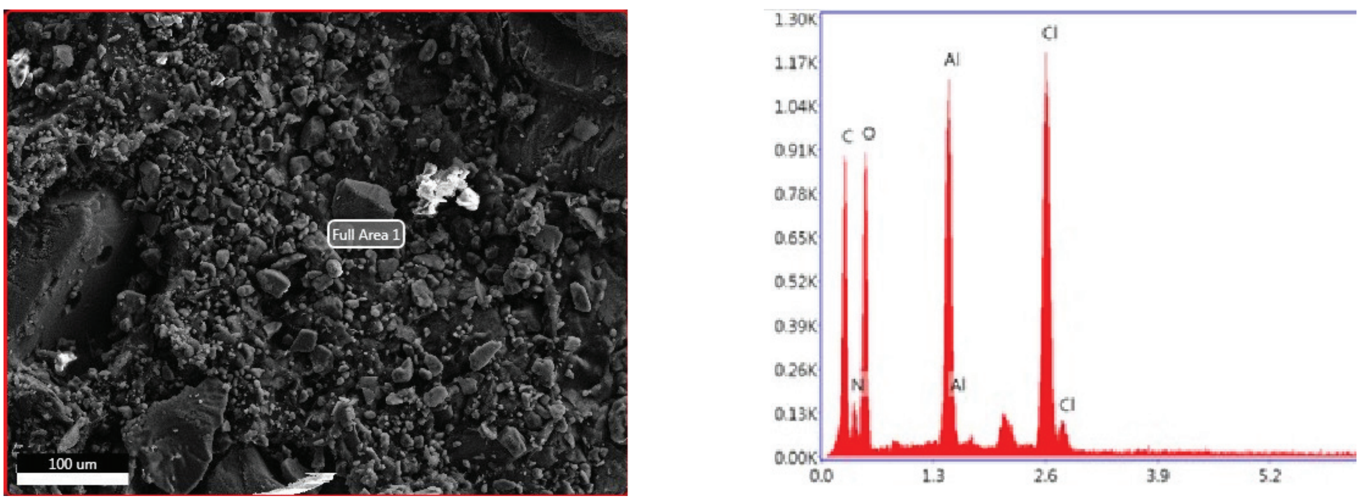
3.3 Fourier Transform Infrared Spectroscopy

Figure 3 depicts the infrared spectroscopy curve of both aged and freshly prepared samples of HTPB/AP with aluminium and magnesium metal additives.

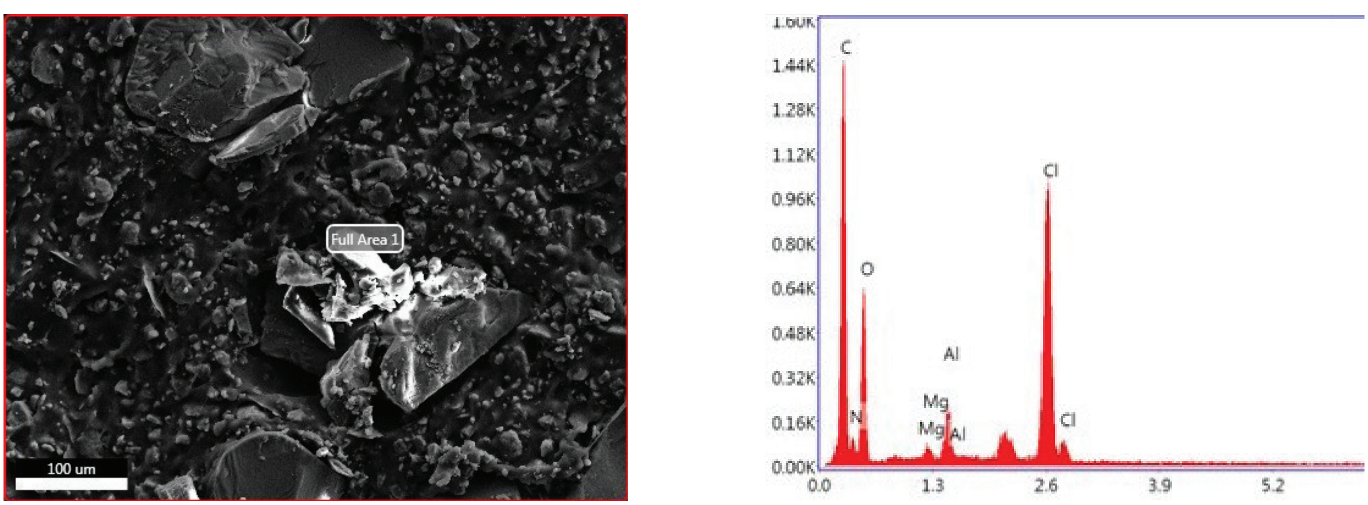
The plots of FTIR for metalized HTPB-AP depicted in Fig. 3 (A), (B), and (C) clearly indicate that the original and aged samples have different peaks, which correspond to the presence of a different phase in which Al is present. In the original sample (2018), the significant peaks correspond to the peaks of pure Al at 1062, 1256, 1404, 1586, and 2930. There are small peaks of low intensity for Al_2O_3 at 617, 759,



AP/HTPB/Al(5%)



AP/HTPB/Al(10%)



AP/HTPB/Al-Mg-10

Figure 5. EDX of the aged CSP samples: (a) HTPB/AP + 5 % Al, (b) HTPB/AP + 10 % Al & HTPB/AP + 5 % Al+5 % Mg.

1370, and 1397 as well. The peak for Al-C is also visible in the original sample. Although the aged sample (2022) contains pure Al peaks at 1062, 1256, 1404, and 2930; these are small peaks with low intensity, clearly indicating that the Al metal had undergone oxidation during the aging process. The peaks of Al_2O_3 are very dominant in the aged sample (465, 554, 617, 630, 652, 759, 1370, 1397, 1630), these peaks are sharp and have very high intensity, clearly indicating that the Al metal of the solid propellant is converted to aluminium oxide. Apart from this, the peaks due to the presence of HTPB, DOA, and TDI were also obtained. The typical peaks for C=C (1724), C-H (2845), =C-H (723 to 1030, 2912), C-O (1246), and C-O-C (1134) are obtained in the FTIR curve. These peaks correspond to the signature peaks for HTPB[38]. The Al-C peak at 790 is very sharp in the aged sample, clearly indicating an interaction between the hydrocarbon parts of the propellant and that of Al metal. A broad peak in the range of 3200-3550 for O-H stretching was obtained in the aged sample and was absent in the original sample. This clearly indicates moisture absorption by the aged sample. From the above observations, it can be concluded that FTIR is a very effective method for studying the aging of propellants as it clearly indicates the oxidation of the metals and absorptionof moisture in the propellant.

3.4 Scanning Electron Microscopic (SEM) and Energy Dispersive X-ray (EDX) Analysis

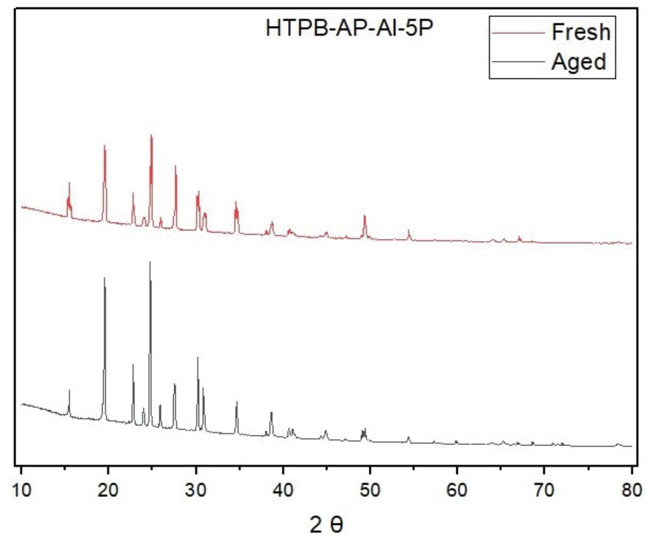
The FESEM analysis of the aged samples was carried out, and Fig. 4 presents the surface morphology of the aged samples for a magnification of 2500 and 500. It can be clearly inferred from the SEM image that the aged samples had development of cracks, and also, there were gaps or pores in the structure for 5 % and 10 % Al metal added samples; thus, it would decrease the packing density of the samples, this may be the reason for the increase in the burning rate for these two propellant samples.

In the Al-Mg added sample, the structure was more uniform than in the other samples, but an agglomeration of the AP fine particles was observed; this could be due to the moisture absorption by the samples. This type of agglomeration and moisture absorption may be the reason for the lower burning rate for the bi-metal added samples.

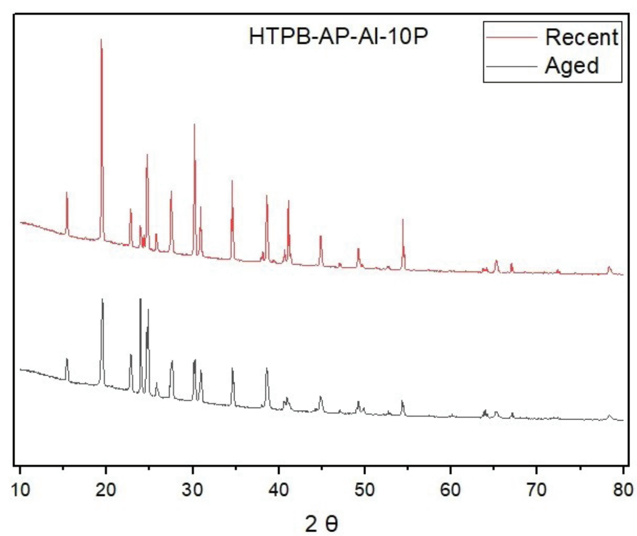
The EDX analysis of the aged propellant samples is presented in Fig. 5. It can be clearly observed from the figure that the aged samples contained carbon, nitrogen, oxygen, chlorine, andAl for the Al added samples, and in the Al-Mg sample, the presence of both metals was detected.It is inferred that oxygen is one major component containing 26 to 33 present for the propellant samples. The oxygen content would affect the burning characteristics of the propellant samples.

3.5 X-ray Diffraction (XRD) Analysis

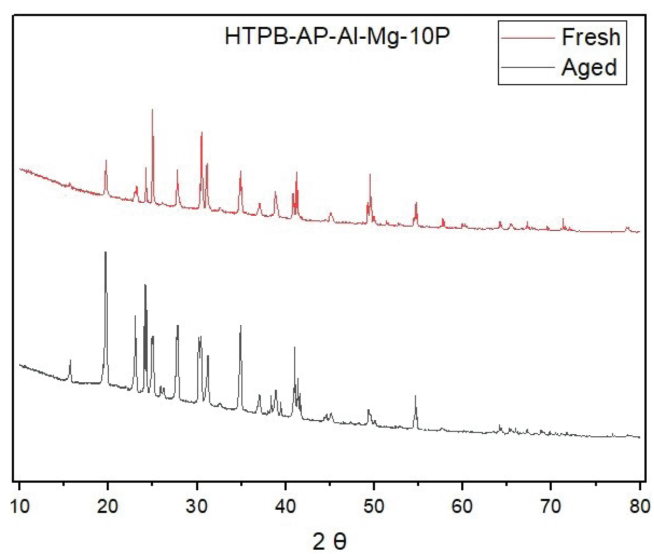
Figure 6 represents the XRD analysis of both aged and freshly prepared samples of HTPB/AP with aluminium and magnesium metal additives. It can clearly be observed from the comparison peaks of XRD for the fresh and aged samples that the peak points are different forthe fresh and aged samples, and even the intensity of the peaks has also altered due to the aging effect. The peaks at 2Θ (Theta) of 38.03, 44.95, 65.2, and



(a) HTPB-AP-Al-5P-fresh and aged



(b) HTPB-AP-Al-10P-fresh and aged



(c) HTPB-AP-Mg-10P-fresh and aged

Figure 6. XRD peaks of fresh and 4-yr aged CSP samples: (a) HTPB/AP + 5 % Al, (b) HTPB/AP + 10 % Al & HTPB/AP + 5% Al+5% Mg.

78.4 for pure Al are obtained for all three fresh samples. The peaks for AP at 2Θ of around 15.3, 19.4, 24.6, 30.1, and 40.7 is present in all the propellant samples.

The aged samples contained the typical X-ray diffraction peak of Al_2O_3 at 2θ = 25.8, 34.95°, 44.3°, 52.65°, 57.59°, 68.54° and 78.2° in all the aged propellant samples. The 2θ = 36.9,41.61, 62.91, and 78.44 are the typical peaks obtained for MgO in the aged sample of HTPB/AP+5% Al+5% Mg. These XRD peaks clearly indicate the oxidation of Al and Mg in the aged samples, and these would contribute to the variation in the burning rate and the thermal decomposition of the aged samples.

Thus, it could be concluded from the present study that natural aging of the HTPB-based CSP with 5 % and 10 % aluminium for 4 years in ambient conditions shows a rise in burn rate dominantly due to oxidation of aluminium and aluminium oxides. The burn rate tests performed on the Crawford bomb setup prominently reflected that the addition of aluminium as an energetic particle, in fact, affects the performance of the propellant sample aging. The rise in burn rate is small and does not have much potential to affect the ballistic performance of the rocket motor.

On the contrary, the HTPB samples containing both aluminium and magnesium as energetic particles in a 5 % - 5 % combination show a significant reduction in burn rate as the effect of magnesium oxides overpowers the effect of aluminium oxides resulting in degradation of performance after aging. The presence of Al in the HTPB sample affected its decomposition, which takes place at a lower temperature in the aged samples. This is due to the formation of Al_2O_3, which helps the decomposition process. The FTIR plots and XRD graphs of different aged samples of HTPB/AP-based propellants have indicated a confirmed formation of aluminium oxide in the aged sample, which would clearly affect its decomposition process. The SEM images also indicate cracks formed in the aged samples. Thus, it can be inferred that the ballistic performance in the rocket motor would be affected by aging as it would lead to a higher burning rate and, thus higher generation of combustion gases, thereby changing the motordynamics altogether.

4. CONCLUSIONS

The present study aims to ascertain the effect of the natural aging of metalized propellant samples stored under ambient temperature for a period of 4 years. The change in the structural and compositional degradation of the propellant would lead to a change in its ballistic properties as well as its thermal decomposition. The FTIR and XRD analysis further confirmed that the oxidation of metals and absorption of moisture in the sample take place under natural aging conditions. The following conclusions are obtained:

- Burn rate increment was observed in the HTPB/AP/Al samples due to the formation of Al_2O_3 as compared to the fresh samples when tested in the Crawford bomb setup.
- Burn rate decrement in the bi-metal added propellant HTPB/AP/Al-Mg samples due to the formation of magnesium oxides.
- The speculation of oxidation of aluminium to form aluminium oxides was confirmed from the FTIR and XRD analysis of the aged propellant samples.
- Step-wise thermal decomposition of HTPB/AP + 5 % Al and HTPB/AP + 10 % Al was seen in fresh samples, where a sudden decrease in the mass was observed at 643 K due to the effects of aluminium oxides formation in the aged samples.
- The surface morphology and EDX analysis further confirm the changes due to degradation and moisture absorption of the aged samples.

Thus, it can be concluded that the presence of metal additives in propellant samples directly affects the performance after aging. Aluminium increases the burn rate after aging due to aluminium oxide formation, whereas magnesium decreases the burn rate after aging due to MgO formation. Oxidation of metals happens during the aging of propellant due to atmospheric moisture, and the metal oxides prominently affect the propellant chemical composition and decomposition process of the propellant samples.

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CONTRIBUTORS

Mr Prakhar Jain is pursuing his Master of Technology in Rocket Propulsion from the Department of Space Engineering and Rocketry, Birla Institute of Technology, Mesra, Ranchi. He is also the founder of a space tech startup incorporated as Synodic Space Labs Private Limited and is working on various space technologies of the future.
In the present work, he carried out the experimental work related to burn rates, FTIR characterization, TGA studies and prepared the first draft and corrections for the present manuscript.

Mr Vineet Kumar Rathi is pursuing his Master of Technology in Rocket Propulsion from the Department of Space Engineering and Rocketry, Birla Institute of Technology, Mesra, Ranchi. His areas of interest include: Solid rocket propulsion systems. In the present work, he carried out the experimental work related to burn rates, FTIR characterization, TGA studies and helped in the editing of the first draft of the present manuscript.

Dr Shelly Biswas obtained PhD degree from the Centre for Energy Studies, IIT Delhi in 2014. Currently, She is working as an Assistant Professor in the Department of Space Engineering and Rocketry. She works on Fuels and combustion, green propellants, and micro thrusters. Her areas of interest include: Green solid and liquid propellants-based micro thrusters, propellant formulation and its characterization for green solid propulsion applications, HCl reduction in thruster exhaust, and aging studies of solid propellants.
In the present study, she has contributed to the conceptualisation of the work, supervision, reviewing, editing, and drafting of the manuscript and carried out the revision versions of the manuscript.