Defence Science Journal, Vol. 66, No. 2, March 2016, pp.100-106, DOI : 10.14429/dsj.66.9250

Effect of Nano Cr_2O_3 in HTPB/AP/Al Based Composite Propellant Formulations

Dhirendra Kshirsagar, Ramesh Kurva, Kashinath Dhabbe, Lalita Jawale, Sudhir, Vrushali Khire, and Mehilal*

High Energy Materials Research Laboratory, Pune- 411 021, India
**E-mail: drmehilal@yahoo.co.in*

ABSTRACT

Different compositions have been prepared by incorporating nano sized chromium oxide from 0.25 % to 1 % in HTPB/AP/Al based composite propellant formulation having 86% of solid loading and studied its effect on viscosity build-up, thermal, mechanical and ballistic properties. The findings reveal that on increasing the percentage of nano Cr_2O_3 in the composition, there is an increase in end of mix viscosity, elastic modulus and tensile strength while elongation decreases accordingly. The data on thermal properties envisage the reduction in thermal decomposition temperature of ammonium perchlorate as well as formulations based on HTPB/AP/Al. The data on ballistic properties reveal that there is an enhancement in burning rate from 6.11 mm/s to 7.88 mm/s at 6.86 MPa, however, marginal increase in pressure exponent ('n' values) from 0.35 to 0.53 with 1 wt % of nano Cr_2O_3 was observed in comparison to reference composition without chromium oxide.

Keywords: Composite propellant, nano chromium oxide, pressure exponent, burning rate

NOMENCLATURE

AP	Ammonium perchlorate
HTPB	Hydroxyl terminated polybutadiene
HRTEM	High resolution transmission electron microscopy
SEM	Scanning electron microscopy
DSC	Differential scanning calorimeter
n	Pressure exponent

1. INTRODUCTION

Composite solid propellant is composed of an elastomeric polymeric binder, in which solid particles, such as oxidiser, fuel, and additives are incorporated. Rockets and missiles propelled by composite propellant basically contains an oxidiser mainly ammonium perchlorate (AP), a binder such as hydroxyl terminated polybutadiene (HTPB) and a metallic fuel like aluminium powder along with certain process aids as well as ballistic modifiers[1]. The burning rate of composite propellant is considered to be one of the most important properties governing the ballistic performance of solid rocket motors which in turn depends mostly on particle characteristics of oxidizers, burning rate of the catalysts and metallic fuel[2]. To achieve the desired burning rate of composite propellant formulations, the amount of oxidiser, particle size of oxidiser and burning rate modifiers are added as variables. Ammonium perchlorate is used as an oxidiser in composite propellant formulation as the major ingredient[3] in different size fractions to enhance the burning rate. However, fine and superfine particle fractions of AP increases the burning rate concurrently, also viscosity of propellant slurry, thus, casting of slurry becomes difficult[4].

Therefore, to cope with such problems, burning rate modifiers are preferred. The burning rate modifiers are transition metal oxides (TMOs) or their complexes. The burning rate modifiers are added in small quantities affect the burning rate by lowering the thermal decomposition temperature of AP and binder[5]. The effect of transition metal oxides on thermal decomposition of ammonium perchlorate was studied and reviewed by various workers[5, 6]. Rastogi[7], *et al.* has studied the combustion behaviour of polystyrene-ammonium perchlorate composite solid propellants using $(NH_4)_2Cr_2O_7$, $Cr_2(CO_3)_3$, Cr_2O_3, CuO, and $CuHCO_3$, found that the rate of decomposition of NH_4ClO_4, polymer and propellant composition degradation were enhanced. Yim[8], *et al.* has studied the effect of Cr_2O_3 along with Fe_2O_3 in non-aluminised NH_4ClO_4-HTPB based propellant and found that Cr_2O_3 is a better burning rate modifier to achieve higher burning rate with low pressure exponent value compared to Fe_2O_3. However, in aluminised composition, the burning rate efficacy for the above burning rate modifier and pressure exponent decreases with increasing aluminium content. Carvalheira[9], *et al.* has investigated the effect of Fe_2O_3 and Cr_2O_3 as burning rate modifiers in non- aluminised Phase Stabilised Ammonium Nitrate /HTPB composite propellant. They observed that Cr_2O_3 significantly increases both the burning rate and pressure exponent value. Carvalheira[10], *et al.* also studied Fe_2O_3 and Cr_2O_3 as burning rate modifiers in simple ammonium nitrate-hydroxyl terminated polybutadiene-IPDI propellant formulation for gas generators and found that Cr_2O_3 is a effective in increasing the burning rate while reduces it pressure exponent value.

Further, there is a great interest in application of

Received 16 September 2015, revised 03 March 2016, online published 22 March 2016

nanometer-sized metal oxides as burning rate modifiers in a solid propellant formulation. Consequently, Singh[11], *et al.* has studied the effect of nanometer form of chromium oxide on thermal decomposition of ammonium perchlorate and found that nano-chromium oxide is effective in reduction of thermal decomposition temperature.

Due to advantages of reduction in thermal decomposition temperature of ammonium perchlorate on incorporation of nano Cr_2O_3, an exhaustive literature survey was carried out to find out its application in composite propellant formulation based on HTPB/AP/Al. However, literature search reveals that a detailed study has not been carried out using nano- Cr_2O_3 in composite propellant formulations. Therefore, a systematic study has been carried out by incorporating nano- Cr_2O_3 in composite propellant formulation having 86 per cent solid loading.

2. EXPERIMENTAL

2.1 Materials

Both nano and micron sized chromium oxides, AR grade, were purchased from Sigma-Aldrich. Ammonium perchlorate, procured from M/s Pandian Chemicals Ltd., Cuddalore was used in bimodal distribution having average particle sizes 300 µm and 50 µm in the ratio of 3.5:1, respectively. Hydroxyl terminated polybutadiene manufactured by free radical solution polymerisation, having average molecular weight ($\bar{M}_n$) of 2560 g/mol with hydroxyl number of 43 mg KOH/g, was procured from M/s Anabond Ltd, Chennai. Aluminium powder having average particle size 15 ± 3 µm, was procured from M/s The Metal Powder Company, Madurai (India) and used as such. Dioctyl adipate (DOA), toluene diisocyanate (TDI), N-phenyl-2-naphthylamine (Nonox-D), trimethylolpronane (TMP) and 1, 4-butanediol (n-BD) were also procured from trade and used as such.

2.2 Characterisation

The particle size of nano- Cr_2O_3 was determined by NANOPHOX particle size analyzer (NX0084), Germany, based on dynamic light scattering technique in an aqueous medium after sonicating for 5 min. The particle size of micron sized Cr_2O_3 was determined by laser based particle size analyser CILAS, model 1064L, France, in an aqueous medium. The crystal phase and crystallite size of nano sized Cr_2O_3 was determined by Phillips PANalytical X'pert pro powder X-ray defractometer using Cu-K_α radiation in the range 20° to 90°. The purity of nano- Cr_2O_3 was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) Model: JY Ultima – 2000, France. The particle size of nano-Cr_2O_3 was determined on high resolution transmission electron microscopy (HRTEM) of FEI Technai TF 30 with FEG having resolution of 0.14 nm. The specific surface area (SSA) of nano- Cr_2O_3/micron- Cr_2O_3 was determined by BET surface area analyser, Gemini VII 2390t, Micromeritics, USA, based on nitrogen adsorption technique after degassing the sample at 250 °C for 6 h followed by determination of surface area at liquid nitrogen temperature (77 K).

The Brookfield dial type viscometer, model HBT was used for the measurement of end of mix viscosity of propellant slurry by inserting a T-C spindle at a rotating speed of 2.5 rpm at a predetermined temperature. A thermal study on decomposition of ammonium perchlorate/propellant was carried out on a Perkin Elmer, Pyris DSC-7. The DSC experiments were carried out in ultra pure nitrogen atmosphere at a heating rate of 10 °C/min. The mechanical properties like tensile strength, E-modulus and percentage elongation were determined on Hounsfield universal testing machine (UTM) using dumbbells conforming to ASTM-D-638 type IV at a cross head speed of 50 mm/min at ambient temperature. The calorimetric value and density of propellant formulations were determined by parr isoperibol bomb calorimeter 6200 and helium gas pycnometer, respectively.

The burning rate of cured propellant samples was determined by acoustic emission technique in an inert environment (N_2) at 5.88 MPa, 6.86 MPa, 7.84 MPa using a 750 cc stainless steel bomb. The bomb was equipped with a piezoelectric transducer and a lid with a panel for holding the propellant strands. An acoustic signal was generated by rapid release accompanying the propellant combustion.

The propellant samples were cut in the form of strands having dimensions of 150 mm × 6 mm × 6 mm and ignited from one end using nichrome wire. When the propellant strand burned, an acoustic pulse was generated and measured using an oscilloscope. The burning rate of the propellant strand was calculated by dividing the length of the strand by the duration of acoustic pulse. An error in the measured burning rate in the range of ±0.2 mm/s may be due to a dimensional variation of propellant strand and length measurement error.

2.3 Incorporation of Nano and Micron Sized Cr_2O_3 in Composite Propellant Formulation

To a vertical planetary mixer (15 litre), 504 g of prepolymer resin, i.e., hydroxyl terminated polybutadiene (HTPB), 150 g of dioctyl adipate (DOA) as a plasticizer along with 5 g of antioxidant, i.e., 2-phenyl naphthylamine (Nonox-D) and 6 g of bonding agent (a mixture of 1,1,1-trimethylol propane and 1,4-butanediol) except curative were charged and the whole mixture was mixed well for half an hour followed by mixing under vacuum for another half an hour to drive out entrapped air. After this, 25 g of nano- Cr_2O_3 /micron- Cr_2O_3 was added and mixed thoroughly for 10 min. Further, 900 g of Al powder (~15 µm) was added to the mix. After complete addition of Al, it was again mixed for another 20 min. After this, 3375 g of ammonium perchlorate (bimodal having particle sizes 300 µm and 50 µm) was added and mixed in such way that homogenous mixing could take place. The overall mixing temperature was maintained at 40±2 °C. After addition of complete solid ingredients, the mixing of composition was further carried out under vacuum for half an hour. At this stage, 35.0 g of toluene di-isocyanate (TDI) was added and mixed for another 40 min. The composition was cast into 100 mm inner diameter (ID) mould by vacuum casting technique and cured at 50 °C for 5 days[12].

The percentage of nano- Cr_2O_3 /micron- Cr_2O_3 used for this study was varied from 0.25% to 1.0% in place of coarse ammonium perchlorate.

3. RESULTS AND DISCUSSION

Initially both nano and micron sized Cr_2O_3 were fully characterised and studied for the catalytic effect on AP followed by their evaluation in composite propellant formulations.

3.1 Characterisation of Nano and Micron Sized Chromium Oxide

3.1.1 Determination of Particle Size by NANOPHOX

The particle size of nano- Cr_2O_3 by NANOPHOX particle size analyser reveals that surface mean diameter of the product was found to be 41 nm whereas distribution of nano particle varies from 29 nm to 60 nm (Fig. 1).The particle size of micron sized Cr_2O_3 is found to be 1.13 micrometer. Although the data obtained from NANOPHOX are qualitative in nature, it provides a reasonable evaluation of the size distribution.

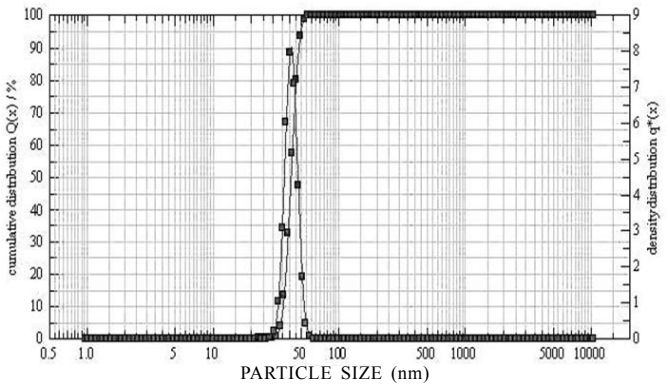

Figure 1. Particle size distribution of nano- Cr_2O_3.

3.1.2 Determination of Specific Surface Area by BET Surface Area Analyser

Specific surface area of nano- Cr_2O_3 and micron- Cr_2O_3 using BET surface area analyser at liquid nitrogen temperature reveal that specific surface area of nano- Cr_2O_3 is 15.41 m^2/g whereas specific surface area of micron- Cr_2O_3 is 2.86 m^2/g. It is clear from above data that the nano Cr_2O_3 is finer than the micron Cr_2O_3, therefore, better catalysing effect envisaged.

3.1.3 Powder X-ray Diffraction

The nano- Cr_2O_3 /micron- Cr_2O_3 was characterised for its crystallite size using powder XRD technique and the obtained XRD patterns are presented in Figs. 2 and 3, respectively. It is clear from the XRD patterns that nano- Cr_2O_3/micron- Cr_2O_3 is crystalline in nature. The XRD patterns have clear six distinguishable peaks which correspond at 2θ value of 24.77, 33.80, 36.28, 41.54,50.26, 54.86, 63.58 and 65.38, respectively, are due to nano- Cr_2O_3 /micron- Cr_2O_3 phase which is in agreement with the standard data file (JCPDS Card No 38-1479)[13]. The Fig. 2 also clearly reveals the broadened peaks at base in case of nano Cr_2O_3 confirming the smaller crystallite size.

3.1.4 Determination of Purity

The purity of nano- Cr_2O_3 /micron- Cr_2O_3 was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) using high temperature argon plasma. The percentage of chromium content in nano and micron chromium

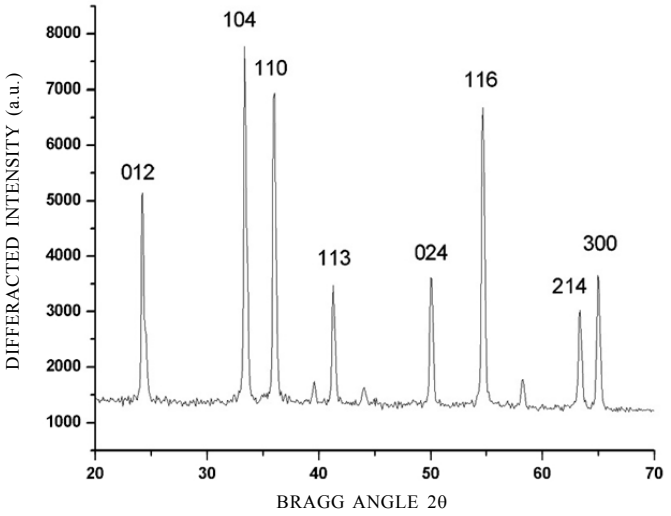

Figure 2. X-ray diffraction pattern of nano-Cr_2O_3.

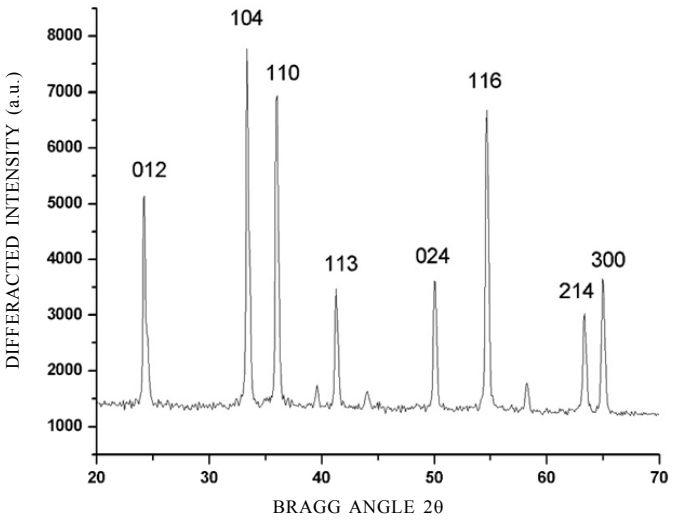

Figure 3. X-ray diffraction pattern of micron Cr_2O_3.

oxide was found to be 68.11 % and 68.09, respectively (68.42 % theoretical). Based on the chromium content, the purity of nano- Cr_2O_3 /micron- Cr_2O_3 was found to be greater than 99.5%.

3.1.5 Determination of Particle Size and Surface Morphology

The particle size of nano- Cr_2O_3 was determined by HRTEM and the image obtained is presented in Fig. 4. It is clear from Fig. 4 that particles of nano- Cr_2O_3 are nearly spherical in nature and average particle size is in the range of 40 nm. In the same way, the surface morphology of micron sized chromium oxide was determined by SEM and presented in Fig. 5. It is clear from figure that the particles are spherical in nature.

3.2 Catalytic Effect of Nano and Micron Sized Cr_2O_3 on Ammonium Perchlorate

Prior to evaluation of ballistic properties in composite propellant formulations, the catalytic effect of nano- Cr_2O_3 /

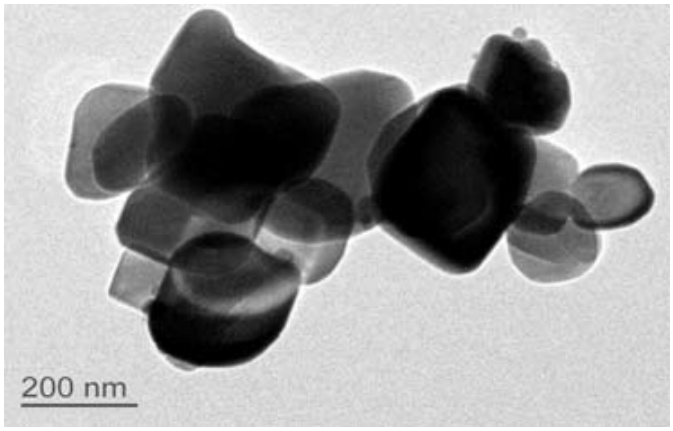

Figure 4. Image of nano- Cr_2O_3 by high resolution transmission electron microscopy.

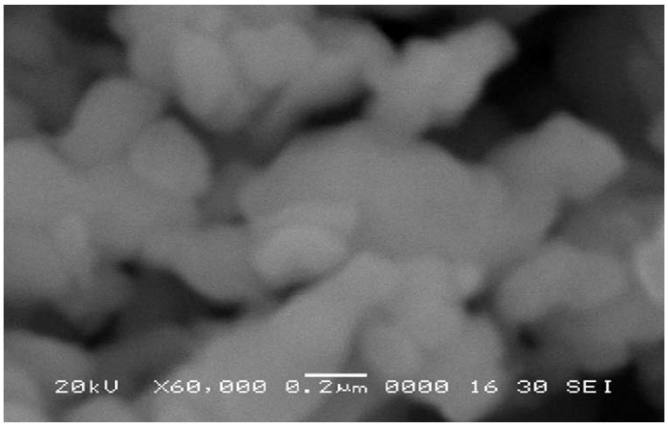

Figure 5. Image of micron Cr_2O_3 by scanning electron microscopy.

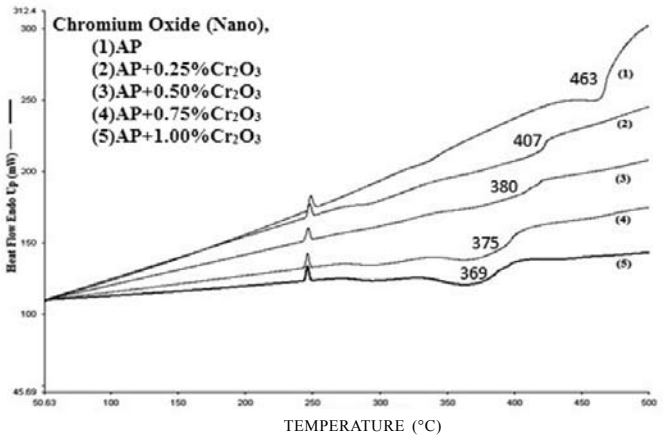

Figure 6. DSC thermogram of ammonium perchlorate having different % of nano-Cr_2O_3.

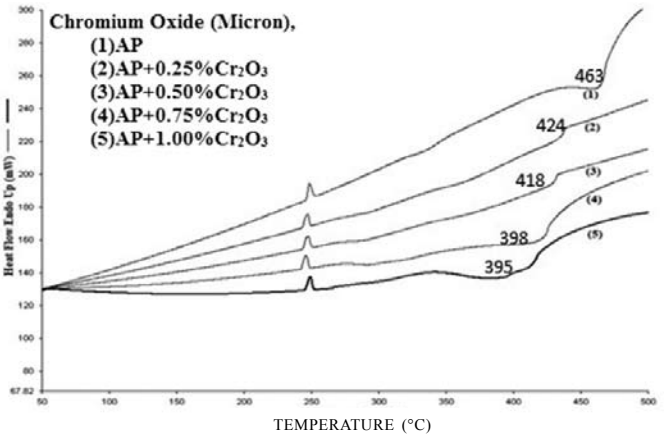

Figure 7. DSC thermogram of ammonium perchlorate having different % of micron-Cr_2O_3 .

micron- Cr_2O_3 were studied for thermal decomposition of ammonium perchlorate by incorporating 0.25 to 1% with the help of DSC. The DSC samples were prepared by blending ammonium perchlorate and Cr_2O_3 in a mortar using a pestle. The DSC thermograms obtained for nano Cr_2O_3 and micron sized Cr_2O_3 are presented in Figs. 6 and 7, respectively. The thermograms clearly indicate that on addition of nano-Cr_2O_3 /micron- Cr_2O_3, the thermal decomposition temperature of ammonium perchlorate decreases. The lowering of thermal decomposition temperature of ammonium perchlorate with nano- Cr_2O_3 is found to be more effective up to 0.5% concentration. Thus, it is clear from Fig. 6 that the thermal decomposition temperature of AP without any ballistic modifier is 463°C whereas on addition of nano Cr_2O_3 at 0.25, 0.50, 0.75 and 1wt % level the thermal decomposition temperature became 407,380,375 and 369°C, respectively. This effect was found less prominent in case of micron Cr_2O_3 as presented in Fig. 7, where thermal decomposition temperature of AP with 0.25, 0.50, 0.75 and1 wt % level became 424,418,398 and 395°C, respectively. This finding further infers that nano- Cr_2O_3 has a very good catalytic effect on thermal decomposition of ammonium perchlorate due to higher specific surface area in comparison to micron sized Cr_2O_3.

3.3 Evaluation of Nano and Micron Sized Cr_2O_3 in Composite Propellant Formulation

The propellant formulations were processed by incorporation of nano Cr_2O_3 /micron Cr_2O_3 from 0.25 to1 wt % level by replacing coarse AP and studied their effect on viscosity built up, thermal, mechanical and ballistic properties. The composition details are presented in Table 1.

Table 1. Formulation details of propellant compositions in percentage

Ingredients	Reference composition	Developed compositions			
		Comp. 1	Comp. 2	Comp. 3	Comp. 4
Binder (HTPB+TDI+DOA)	14.00	14.00	14.00	14.00	14.00
AP Coarse (300 µm)	52.50	52.25	52.00	51.75	51.50
AP Fine (50 µm)	15.50	15.50	15.50	15.50	15.50
Al(P)	18.00	18.00	18.00	18.00	18.00
Nano Cr_2O_3/micron Cr_2O_3	0.00	0.25	0.50	0.75	1.00

Table 2. Effect of nano and micron sized Cr_2O_3 on viscosity and mechanical properties

Composition (per cent)	Viscosity @ 40 °C (Pa.s)	TS (MPa)	E-Mod (MPa)	Elongation (per cent)
Reference	670	0.62	3.43	45.00
Nano Cr_2O_3 (0.25)	712	0.78	4.03	40.20
Nano Cr_2O_3 (0.50)	740	0.84	4.24	35.27
Nano Cr_2O_3 (0.75)	765	0.90	4.63	30.24
Nano Cr_2O_3 (1.00)	797	0.93	5.07	27.71
Micron Cr_2O_3 (0.25)	704	0.76	3.73	42.11
Micron Cr_2O_3 (0.50)	722	0.83	4.13	37.42
Micron Cr_2O_3 (0.75)	745	0.87	4.49	33.69
Micron Cr_2O_3 (1.00)	757	0.91	4.81	30.03

3.3.1 Effect of Nano and Micron Sized Cr_2O_3 on Viscosity

The different composite propellant compositions were prepared to study the end of mix (EOM) viscosity by varying the content of nano Cr_2O_3 and micron Cr_2O_3 from 0.25 wt % to 1.0 wt % using Brookfield viscometer and results obtained are presented in Table 2. The data presented in table clearly indicate that as content of nano chromium oxide in composition increases the EOM viscosity of propellant slurry also increases from 712 Pa.s to 797 Pa.s in comparison to viscosity of reference composition to that of 670 Pa.s. The enhancement in viscosity built up may be due to finer particle size and higher specific surface area of nano Cr_2O_3.

3.3.2 Effect of Nano and Micron Sized Cr_2O_3 on Mechanical Properties

The data on effect of nano and micron sized Cr_2O_3 on mechanical properties such as tensile strength (TS), % elongation and elastic modulus (E-mod) of the cured propellant sample as well as reference composition maintaining 86% solid loading are presented in Table 2.It is clear from the table that as the percentage of nano Cr_2O_3 increases in the composition, TS and E-mod also increases marginally while percentage elongation decreases. This may be attributed to high surface area of fillers. Thus, the value of TS and E-mod for nano Cr_2O_3 enhances from 0.78 MPa and 4.03 MPa to 0.93 MPa and 5.07 MPa in comparison to 0.62 MPa and 3.43 MPa that of reference composition. However, reverse trend was observed in the case of % elongation for the studied compositions.

3.3.3 Effect of Nano and Micron Sized Cr_2O_3 on Thermal Properties

Thermal properties of studied compositions containing nano and micron sized Cr_2O_3 along with reference composition were carried out using DSC technique and thermograms obtained are presented in Figs. 8 and 9, respectively. It is clear from Figs. 8 and 9 that reference composition shows an endotherm at 246.67 °C due to phase change of ammonium perchlorate from orthorhombic to cubic. After that, a small decomposition peak was observed around 304°C followed by a sharp decomposition peak at 403 °C which on incorporation of nano Cr_2O_3 , the final decomposition peak shifts from 403 °C to 387 °C as concentration of nano Cr_2O_3 increases from 0.25 to 1 wt % level. These findings reveal that nano Cr_2O_3 is very effective in catalysing the decomposition of composite propellant formulation. The same trend has also been observed with micron sized Cr_2O_3 to a lesser extent on thermal decomposition temperature in comparison to nano Cr_2O_3.

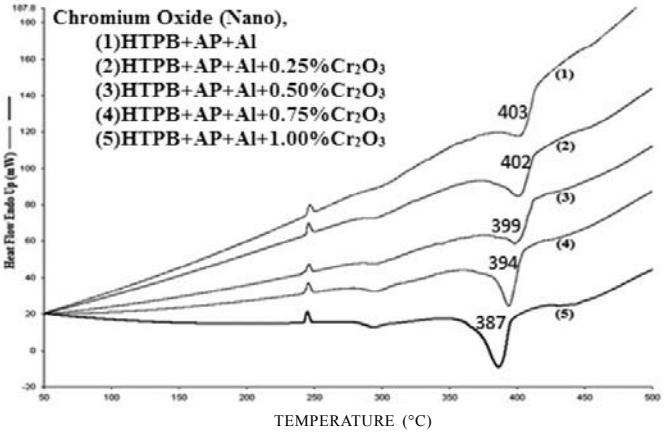

Figure 8. Effect of nano sized Cr_2O_3 on thermal decomposition of composite propellant formulation.

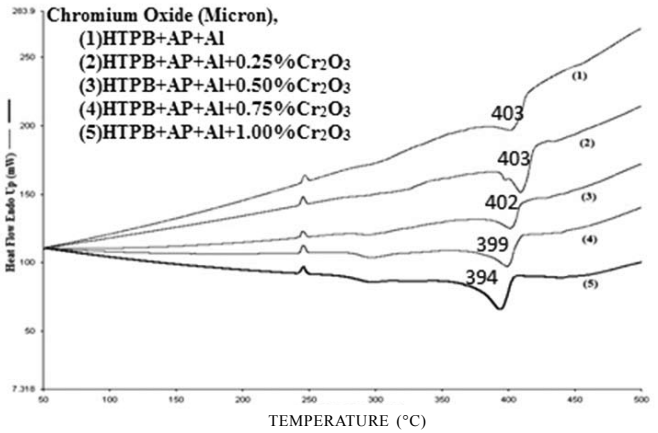

Figure 9. Effect of micron sized Cr_2O_3 on thermal decomposition of composite propellant formulation.

3.3.4 Effect of Nano and Micron Sized Cr_2O_3 on Ballistic Properties

The effect of nano and micron sized Cr_2O_3 on ballistic properties of the studied compositions such as density; cal-val, burning rate and pressure exponent were evaluated as-

3.3.4.1 Effect of Nano and Micron Sized Cr_2O_3 on Density

The density of cured propellant formulations was determined on gas pycnometer and data obtained are presented in Table 3. It is clear from Table 3 that the density of reference composition as well as studied formulations were found in the range of 1765 to 1777 kg/m^3 clearly envisage that no variation in density.

Table 3. Effect of nano and micron sized Cr_2O_3 on ballistic properties

Composition (per cent)	Solid strand burning rate at MPa (mm/s)			Density (kg/m^3)	Pressure Exponent (n)	Cal-Val (kJ /kg)
	5.88	6.86	7.84			
Reference	6.00	6.11	6.55	1777	0.35	6489.54
Nano Cr_2O_3 (0.25)	7.16	7.55	8.00	1777	0.38	6451.86
Nano Cr_2O_3 (0.50)	7.19	7.59	8.11	1778	0.42	6430.92
Nano Cr_2O_3 (0.75)	7.20	7.72	8.30	1782	0.49	6384.87
Nano Cr_2O_3 (1.00)	7.22	7.88	8.40	1783	0.53	6368.12
Micron Cr_2O_3 (0.25)	7.13	7.46	7.94	1777	0.37	6447.67
Micron Cr_2O_3 (0.50)	7.15	7.48	8.00	1779	0.39	6418.36
Micron Cr_2O_3 (0.75)	7.19	7.61	8.20	1780	0.45	6380.68
Micron Cr_2O_3 (1.00)	7.20	7.66	8.26	1781	0.48	6359.75

3.3.4.2 Effect of Nano and Micron Sized Cr_2O_3 on Calorimetric Value

The data on calorimetric value (Cal-Val) of the studied propellant formulations are presented in Table 3. It is clear from the table that the vcal-val of reference composition was found to be 6489.54 kJ /kg whereas on incorporation of nano Cr_2O_3 and micron Cr_2O_3 it decreases slightly. The decrease in cal-val is attributed to inertness of nano Cr_2O_3 and micron Cr_2O_3 that replaced ammonium perchlorate in propellant formulations.

3.3.4.3 Effect of Nano and Micron Sized Cr_2O_3 on Burning Rate

The data on solid strand burning rate (SSBR) of samples (6 X 6 X 150 mm) determined by acoustic emission technique are given in Table 3. It is clear from the table that as the percentage of nano chromium oxide increases in the composition burning rate also increases accordingly. The Table 3 also reveals that 3% increase in burning rate was observed with nano Cr_2O_3 in comparison to micron sized Cr_2O_3 at 1.0% level. The burning rate enhancement using nano and micron sized Cr_2O_3 in the composition clearly infers that as concentration of catalyst touches the concentration level of 1 wt %, the enhancement in burning rate ceases, indicating that the optimum concentration level of catalyst is around 1wt% for the formulation and so no higher concentration level was studied. The increase in burning rate may be due to high specific surface area of nano Cr_2O_3 in comparison to micron Cr_2O_3.

3.3.4.4 Effect of Nano and Micron Sized Cr_2O_3 on Pressure Exponent (n)

The pressure exponent (n) was determined using SSBR data at different pressures by plotting a curve of $\ln r_b$ vs. $\ln p$ and calculated the pressure exponent from the slope of the curve[15] and data obtained are presented in Table 3. It is clear from the table that pressure exponent of the reference composition was found to be 0.35 whereas on addition of nano Cr_2O_3 and micron sized Cr_2O_3 , the pressure exponent value marginally increases from 0.35 to 0.53 and 0.35 to 0.48, respectively at 1 wt % level.

4. CONCLUSION

A successful attempt has been made to incorporate nano Cr_2O_3 in composite propellant formulation from 0.25 to 1% by replacing coarse ammonium perchlorate but maintaining 86% solid loading and studied its effect on end of mix viscosity, mechanical, thermal and ballistic properties. The data reveals that there is an increase in end of mix viscosity from 712 Pa.s to 797 Pa.s on incorporation of nano Cr_2O_3 from 0.25 to 1% level, whereas EOM viscosity of reference composition is 670 Pa.s at the same temperature and marginal improvement in mechanical properties was also observed. Further, nano Cr_2O_3 is found to be very effective in lowering the thermal decomposition temperature of the studied compositions in comparison to micron sized Cr_2O_3. The data also reveals that there is an enhancement of 3% in burning rate with nano Cr_2O_3 in comparison to micron sized Cr_2O_3 at 1% concentration level. Further, improvement in pressure exponent value was observed on addition of nano and micron sized Cr_2O_3 in studied composite propellant formulations.

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ACKNOWLEDGMENT

Authors would like to thank Mr Sumit Bhandarkar for raw material characterisation and Mr Manoj Vemuri for rendering lab facility during this study.

CONTRIBUTORS

Dr Dhirendra Kshirsagar received his MSc (Analytical Chemistry) from Shivaji University, Kolhapur, in 2001 and PhD in Chemistry from Savitribai Phule Pune University, in 2014. He is actively involved in evaluation of nano-sized burning rate catalyst for composite propellant.
In the present manuscript he is responsible for the full characterisation of nano /micron Cr_2O_3.

Mr Ramesh Kurva obtained his MTech in Chemical Engineering from IIT Delhi in 2000. Presently working as a Deputy Director at High Energy Materials research Laboratory, Pune.
His role in the present manuscript is processing of composite formulation by incorporating nano/micron Cr_2O_3.

Mr Kashinath Dhabbe received his MSc (Organic Chemistry) from Shivaji University, in 1998. His area of specialisation is analysis of raw materials of composite propellant ingredients and finished products.
His main role in the present manuscript is chemical and instrumental analysis of the ingredients and finished products.

Mrs Lalita Jawale received her MSc (Organic Chemistry) from University of Pune, in 1995. She is actively involved in determination of calorific and calorimetric values of propellants and explosives samples as well as burning rate of composite propellants.
Her main role in the present manuscript is evaluation of ballistic properties of the studied compositions.

Mr Sudhir obtained his MSc (Physical Chemistry) from C.C.S. University, Meerut, in 2003. Presently working as a Scientist at High Energy Materials research Laboratory, Pune. His area of specialisation is processing of composite propellant.
His main role in the present manuscript is propellant processing based on nano and Micron sized Cr_2O_3.

Dr (Mrs) Vrushali Khire obtained her PhD in Chemistry from University of Pune, in 2009. Presently she is working as Deputy Director at High Energy Materials research Laboratory, Pune. Her area of specialisation is processing of gun propellant and solid rocket propellant.
Her main contribution in the present manuscript is coordination of processing activities and testing.

Dr Mehilal received his PhD in Chemistry from Allahabad University, in 1985. Presently he is working as Joint Director at High Energy Materials research Laboratory, Pune.
His main role in the present manuscript is conceiving of idea, its implementation and monitoring as well as drafting of the article.