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SHORT COMMUNICATION

Glycidyl Azide Polymer-based Enhanced Energy LOVA Gun Propellant

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ABSTRACT

In this study, cyclotrimethylene trinitramine propellants with triacetin (TA)-plasticised cellulose acetate (CA) and nitrocellulose (NC) combination as binders were evaluated for low vulnerable ammunition (LOVA). Triacetin was replaced by energetic plasticiser; glycidyl azide polymer (GAP) in increments to enhance the performance in terms of force constant . In addition to ballistics, parameters like vulnerability, mechanical and thermal properties of GAP-based propellants in comparison to those of TA-based propellants, were also determined. The study brings out that the incorporation of 2-6 per cent GAP in place of TA resulted in the enhancement of force constant by 22-70 J/g and improved overall combustion characteristics. DSC revealed that thermal decomposition of GAP-LOVA propellants evolved more energy than TA-LOVA propellants. GAP-based LOVA propellant similar to TA-plasticised LOVA propellant, was found superior to NQ propellant in vulnerability tests as well as in hot fragment conductive ignition (HFCI) studies. As regards mechanical properties, incorporation of GAP resulted in improved compression strength.

Keywords: Low vulnerable ammunition, LOVA, glycidyl azide polymer, GAP, gun propellent, triacetin, cellulose acetate, energetic plasticiser, force constant, combustion characteristics, HFCI, hot fragment conductive ignition

1. INTRODUCTION

Weapon designers are faced with the twin task of defeating ever more challenging armoured targets as well as developing less prone low vulnerable ammunition (LOVA) systems. These tasks are highly challenging as contradictory requirements of high performance and reduced vulnerability have to be satisfied. Consequently, programmes aimed at developing enhanced energy LOVA propellants are pursued all over the globe.

Glycidyl azide polymer (GAP), an energetic hydroxyl-terminated polyether with pendant alkyl azide groups[1] polymer is emerging as the high potential binder[2] (high molecular weight) as well as energetic plasticiser[3] (low molecular weight) for advanced solid gun propellants. Its positive heat of formation (+ 28 kcal/mol) coupled with exothermic cleavage of azide bond[4] during combustion with the release of 170 kcal/mol enhance the performance of the system. At the same time, it is non-vulnerable to mechanical stimuli. Moreover, it produces higher proportion of low molecular weight combustion products like CO, H_2, and N_2 rather than CO_2 and H_2O. Although, findings on effect of incorporation of low molecular weight GAP in

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cellulose acetate butyrate-based LOVA formulations have been reported[5], the literature indicates that no work has been reported on GAP-plasticised cellulose acetate-based LOVA.The authors[6] have carried out limited studies in the past on low molecular GAP-incorporated propellant formulations comprising 78 per cent RDX, 12 per cent CA, 4 per cent NC (12.2 % *N*) and 6 per cent GAP. The composition delivered force constant of 1150 J/g and had compression strength of 290 kg/cm^2. In the present study, the work has been extended to realise higher force constant and improved compression strength. Cellulose acetate was retained as a binder as its thermoplastic nature assists in processing while its endothermic decomposition behaviour improves vulnerability properties of the compositions. Effect of replacement of TA by GAP as an energy enhancer as well as other ballistic properties, vulnerability and mechanical properties have been assessed during this study.

2. MATERIALS & METHODS

LOVA compositions based on inert binder CA (weight average molecular weight Mw 67000 and acetyl content 34.5 % as acetic acid) in combination with NC (12.6 % nitrogen content and ether alcohol solubility 98 % and RDX (5 μm) were formulated. Low molecular weight GAP was incorporated in varying percentage as replacement of inert plasticiser TA. GAP (Mn 387) used in this study was synthesised by one-step method, ie, simultaneous polymerisation of epichlorohydrin and replacement of *Cl* by the N_3 group[4].The replacement of *Cl* by N_3 was confirmed on the basis of the disappearance of the band at 740–660 cm^{-1} and appearance of a sharp peak at 2100 cm^{-1} in the IR spectra.

The propellant formulations were processed on the laboratory scale (1.25 kg batch) by solvent process using ~20 per cent solvent (by weight) comprising a mixture of acetone and alcohol in 70 : 30 ratio. All the components were incorporated in a sigma blade mixer for 6 h to obtain homogeneous propellant dough while maintaining temperature in the range 35–40 °C by circulating hot water through the external jacket.The dough was subsequently extruded in a heptatubular geometry by applying 5 MPa pressure using a vertical hydraulic press of 60 ton capacity.Extruded strands were cut to 16.5 mm length and dried in a hot air oven at 40 °C till the volatile matter was brought to the level of < 0.5 per cent. The dried propellant samples were tested for physical measurements like web size, length, diameter and density.

Thermochemical properties of formulations were theoretically computed by applying HEMRL's Therm Program[7]. Ballistic parameters were also determined by statically evaluating the propellant at 0.18 g/cm^3 loading density in a closed vessel of 700 cm^3 capacity. Compression strength and percentage compression were determined on a Hounsfield H25KS material testing machine. Thermal decomposition studies were undertaken to understand the energy release and decomposition behaviour by applying DSC technique. Vulnerability of the propellants was assessed by determining impact and friction sensitivity as well as ignition temperature. Impact sensitivity was determined by Bruceton Staircase method using 2 kg fall weight, and friction sensitivity was determined on Julius Peter's apparatus by subjecting sample to incremently increasing load from 0.2 kg to 36.0 kg.

The impact sensitivity results have been reported in terms of height of fall of weight corresponding to 50 per cent probability of initiation of sample (h_{50}) and friction sensitivity has been reported in terms of load in kg up to which the sample did not get initiated in 5 consecutive tests. Ignition temperature was determined at 5 °C/min in Julius Peters setup. The hot fragment conductive ignition (HFCI) test was conducted to get insight of the survivability of weapon systems (such as tanks, ships) containing stowed ammunition by simulating hot fragments generated from the penetration of armour plates by shaped charge jets or kinetic energy penetrators[8,9]. The details of the test are described[10]. The response of the propellant to the hot steel fragments was determined by

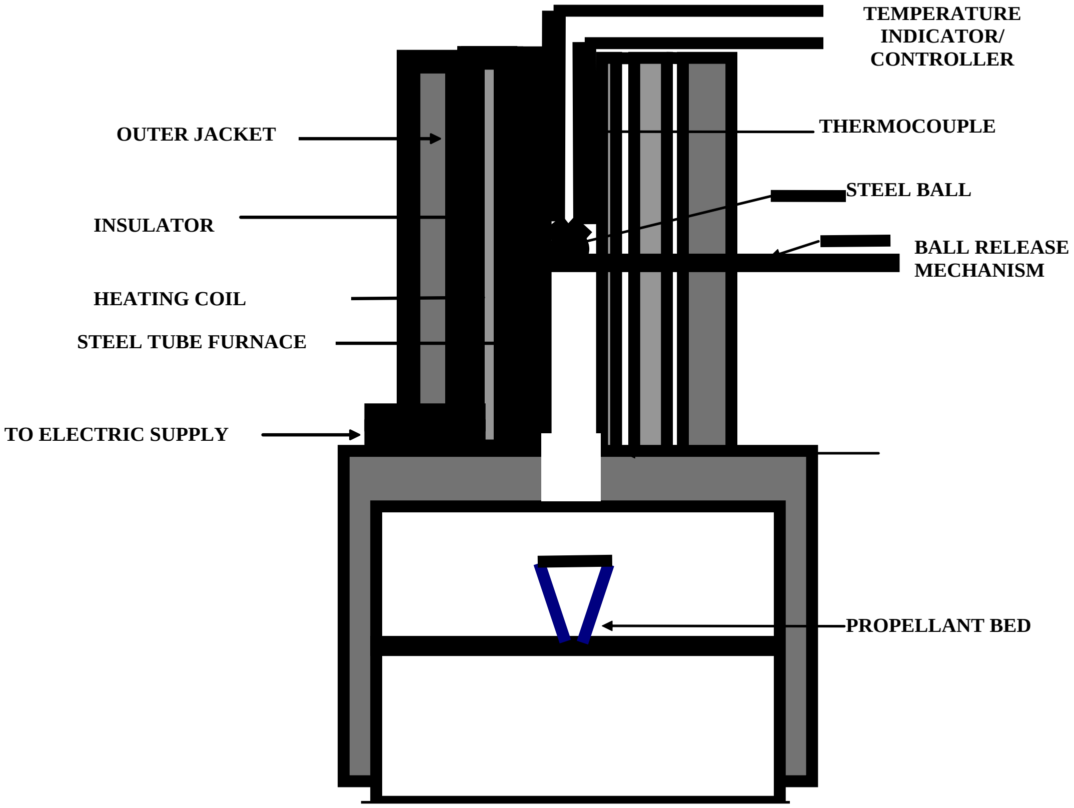


Figure 1. Schematic diagram of hot fragment conductive ignition test apparatus

observing whether or not ignition occurred. The temperature was either raised or lowered based upon the response of the propellant and the test was repeated. The schematic diagram of HFCI test apparatus assembled in the laboratory is shown in Fig.1.

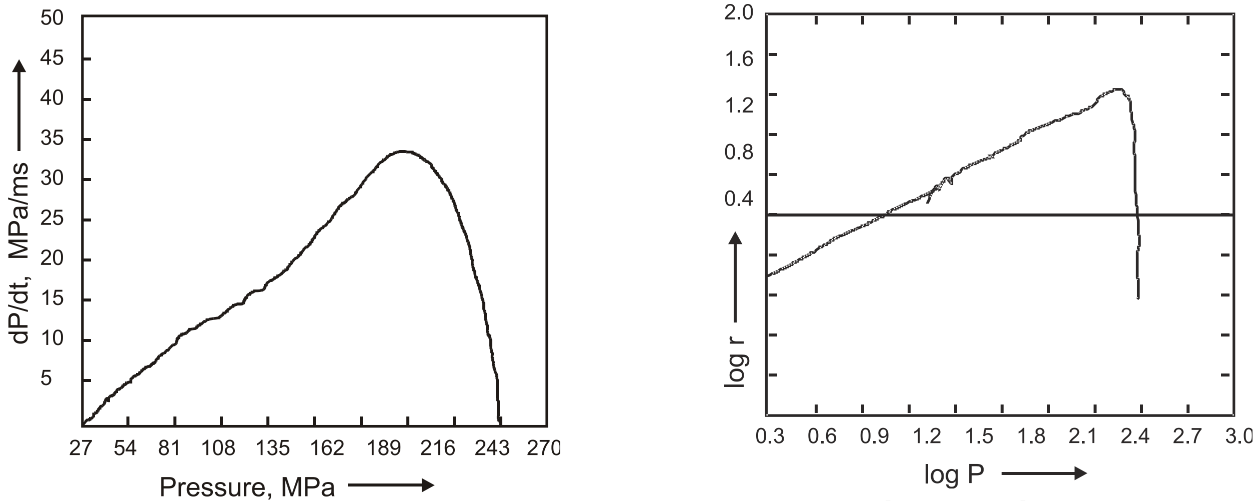
3. RESULTS & DISCUSSION

The theoretical predictions of thermochemical characteristics of different compositions (Table 1) indicate that the force constant increased to the level of 1152 – 1211 J/g from 1130 J/g on replacement

Table 1. Chemical formulations and theoretical thermochemical data

	Composition No.			
	1	2	3	4
RDX	75	75	75	75
NC (N_2 12.6 %)	10	10	10	10
Cellulose acetate	9	9	9	9
Triacetin	6	4	2	-
Glycidyl azide polymer	-	2	4	6
Theoretical thermochemical data at 0.18 g/cc				
Flame temperature (K)	3061	3125	3183	3225
Force constant (J/g)	1146	1168	1189	1211
P_{max} (MPa)	252	256	261	266
Co-volume (cm^3/g)	1.00	1.00	1.00	0.998
n value (moles/g)	0.045	0.045	0.045	0.045
Gamma	1.2579	1.2583	1.2587	1.2591

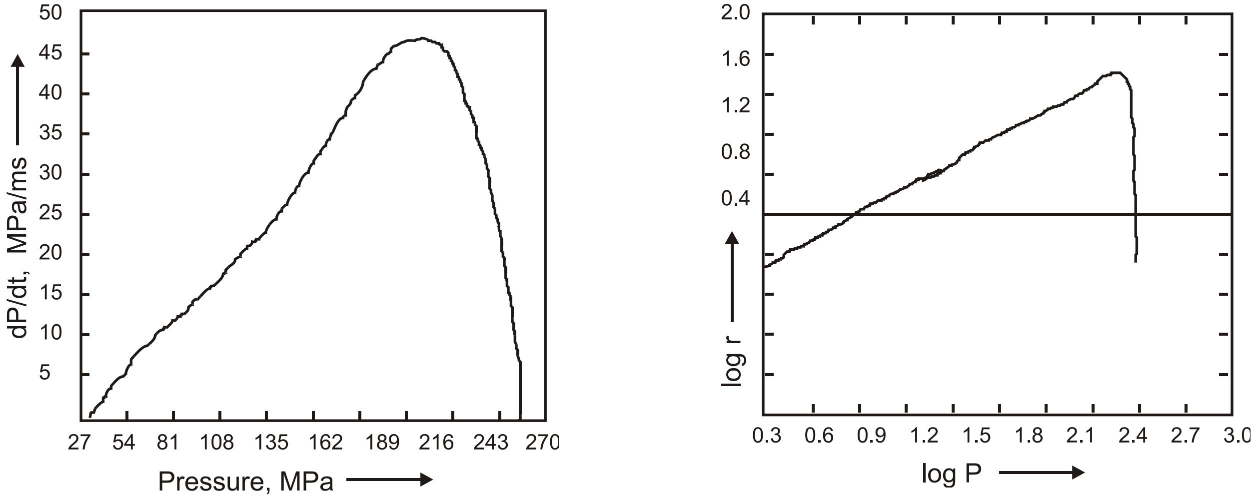
of 2-6 per cent TA by GAP amounting to improvement up to the extent of 65 J/g with a corresponding rise in flame temperature from 3061 K to 3225 K. These trends can be explained on the basis of positive heat of formation of GAP and exothermic cleavage of azide bond structure $-CH_2-N = N_2$ to $-CN + N_2 + H_2$ coupled with low molecular weight of combustion products of GAP. Force constants experimentally determined in closed vessel evaluation are in close agreement with the theoretically computed values. Increase in GAP content also led to a significant increase in linear burning rate coefficient, β_1 from 0.099 cm/s/MPa to 0.119 cm/s/MPa, probably due to the high energy released at the burning surface on decomposition of GAP. Another interesting observation for GAP-based propellants was lower value of pressure exponent, α(0.85 to 0.80) than in the case of TA-plasticised composition. It may be due to the higher stand-off distance between the luminous flame and the burning surface of GAP-based propellants, despite increase in the reaction rate in the dark zone on addition of GAP.[2,6,12,13] The *dP/dt* versus *P* and log *r* versus log *P* profiles obtained from the closed vessel evaluation of GAP-incorporated propellants established that GAP contributes towards efficient combustion of LOVA gun propellant in contrast to irregular combustion observed for TA-containing gun propellant (Figs 2 and 3). These trends are highly advantageous from application point of view. Another significant observation was the improvement



***dP/dt* versus pressure**

log *r* versus log *P*

Figure 2. Closed-vessel curves for 6 per cent TA-based composition



***dP/dt* versus pressure**

log *r* versus log *P*

Figure 3. Closed-vessel curves for 6 per cent GAP-based composition

Table 2. Results of closed-vessel evaluation (at 0.18 g/cc loading density) and mechanical properties

Composition	1	2	3	4
Force constant (J/g)	1130	1152	1178	1200
Linear burning rate coefficient (β_1 cm/s/MPa)	0.099	0.106	0.114	0.119
P_{max} (MPa)	244	250	256	261
Pressure exponent (α)	0.85	0.83	0.82	0.80
Mechanical properties				
Compression strength (kg/cm^2)	435	466	470	502
Compression (%)	9.0	9.2	9.4	9.5

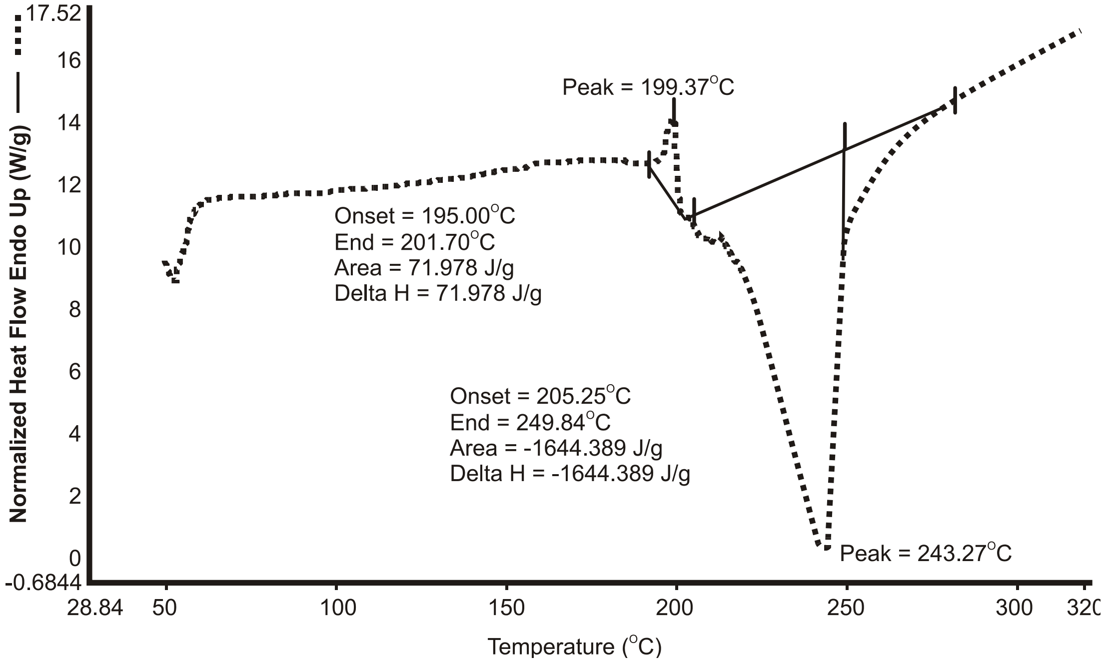
of compression strength (435 kg/cm^2 to 502 kg/cm^2) without adverse effect on per cent compression (Table 2) which may be due to involvement of pendant polar azide in intra- and inter-chain interaction.

Thermal decomposition studies in DSC (Fig. 4) revealed that both TA and GAP-plasticised compositions (Table 3) exhibit an endotherm with T at 199 °C followed by an exotherm with T of ~ 244 °C. However, GAP-based gun propellants evolved higher ΔH (–1879 to 2366 J/g) than TA-based gun propellant (–1644 J/g). These results establish high energy potential as well as compatibility of GAP as component of LOVA system.

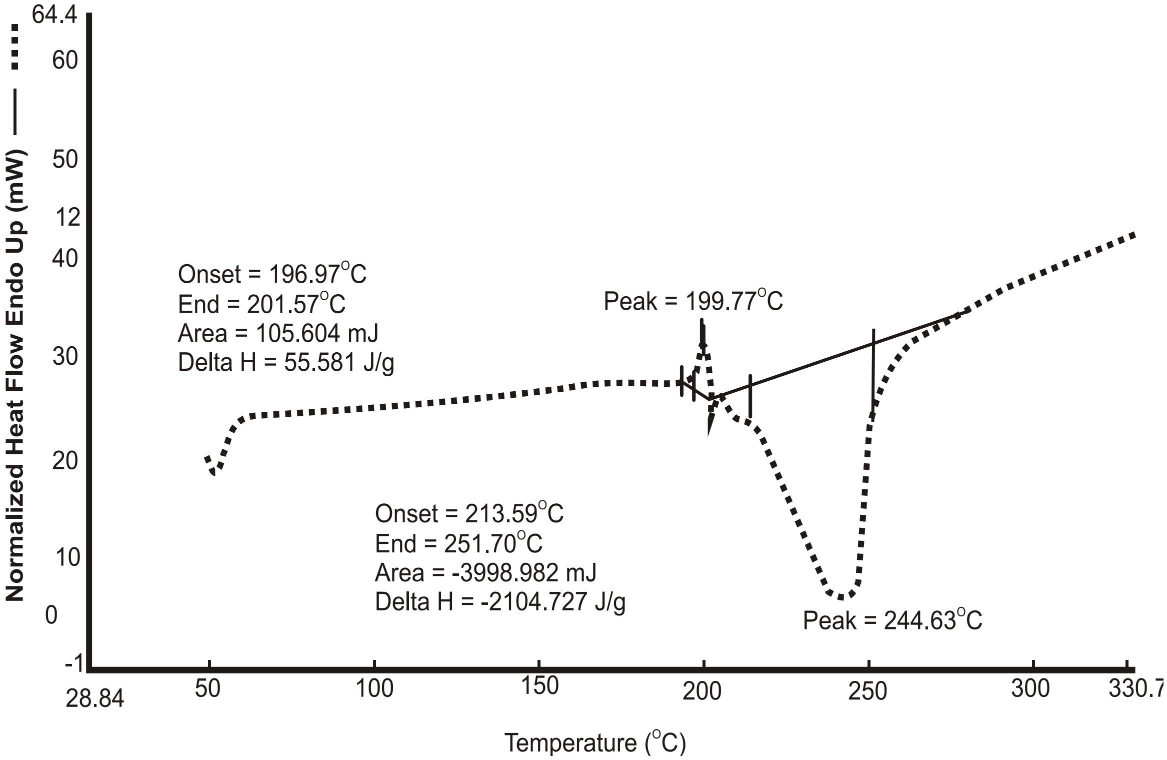
Table 3. Result of thermal behaviour by DSC

	Composition No.			
	1	2	3	4
Endotherm (°C)	199	199	199	199
ΔH (J/g)	72	56	89	68
Exotherm (°C)	243	245	238	244
ΔH (J/g)	-1644	-1879	-2105	-2366

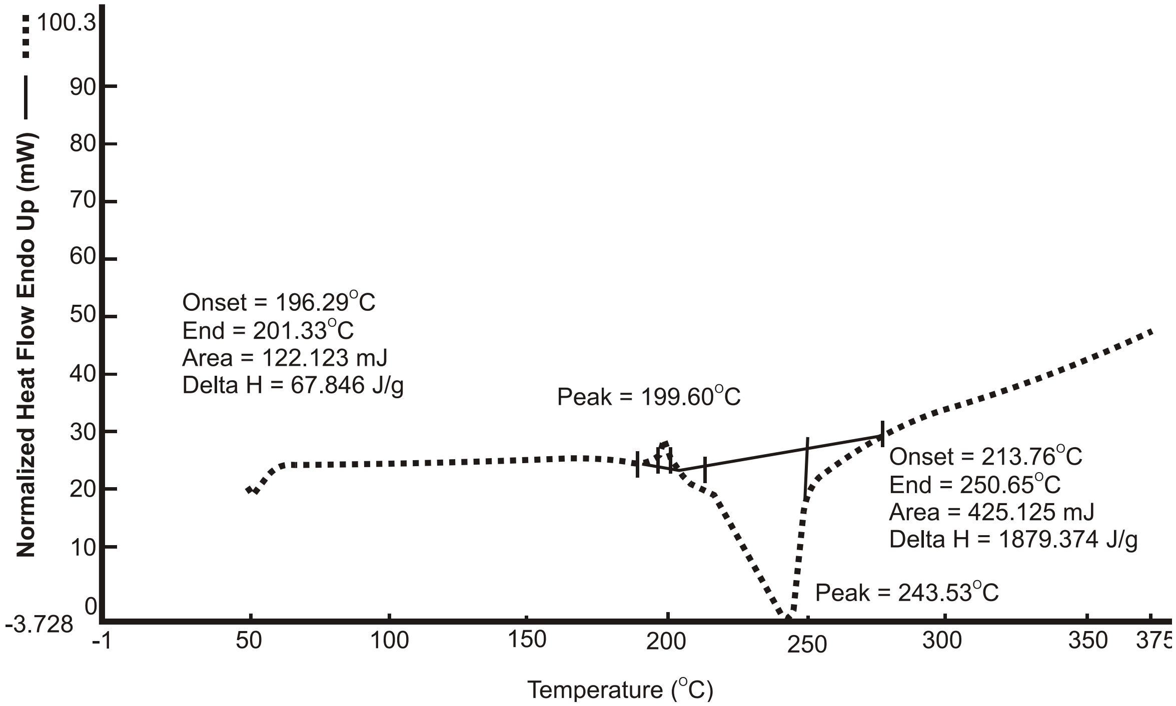
Vulnerability of the compositions, viz., ignition temperature and friction sensitivity (Table 4) remained almost unaltered on replacement of TA by GAP.However, there was a marginal decrease in height of 50 per cent explosion (h_{50}) which is in line with the observation of Schedlbauer[2] and can be attributed to the polar nature of pendant azido group. HFCI criteria is of great importance from the operational point of view



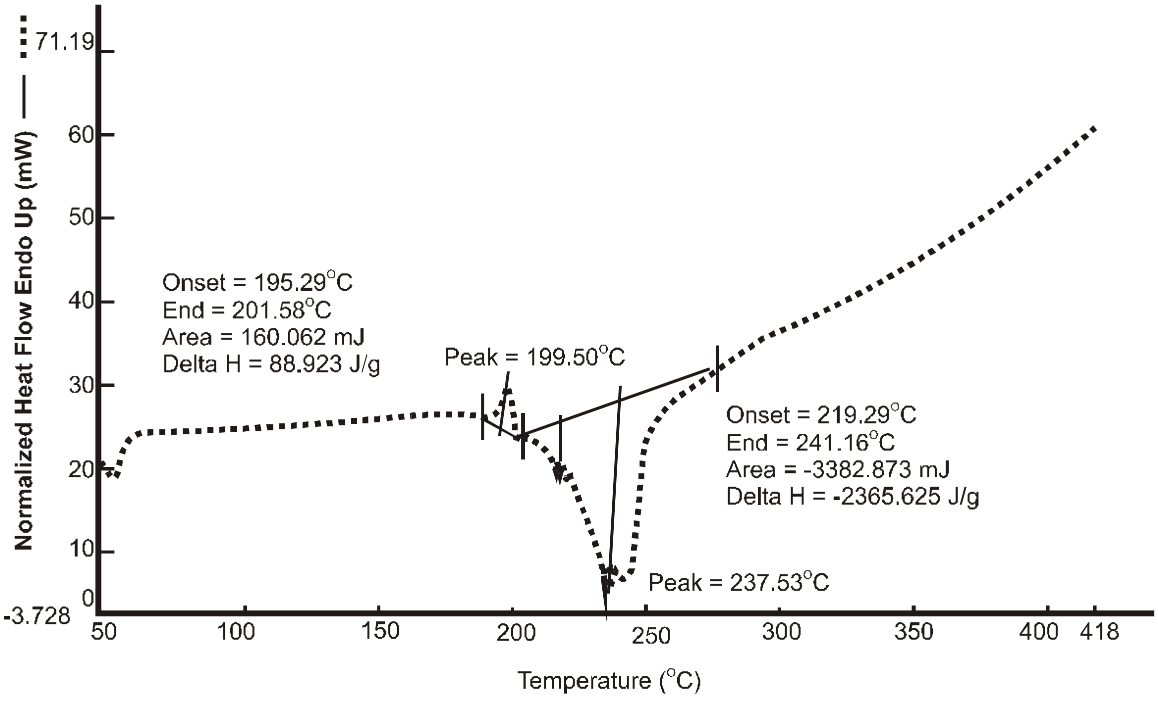
(a)


Normalized Heat Flow Endo Up (mW)
64.4
60
50
12
40
30
20
10
0
-1
28.84
50
100
150
200
250
300
330.7
Temperature (°C)
Onset = 196.97°C
End = 201.57°C
Area = 105.604 mJ
Delta H = 55.581 J/g
Peak = 199.77°C
Onset = 213.59°C
End = 251.70°C
Area = -3998.982 mJ
Delta H = -2104.727 J/g
Peak = 244.63°C

(b)


Normalized Heat Flow Endo Up (mW)
100.3
90
80
70
60
50
40
30
20
10
0
-3.728
-1
50
100
150
200
250
300
350
375
Temperature (°C)
Onset = 196.29°C
End = 201.33°C
Area = 122.123 mJ
Delta H = 67.846 J/g
Peak = 199.60°C
Onset = 213.76°C
End = 250.65°C
Area = 425.125 mJ
Delta H = 1879.374 J/g
Peak = 243.53°C

(c)



(d)

Figure 4. DSC profile of LOVA propellant compositions: (a) composition 1 contains 6 per cent TA (b) composition 2 contains 4 per cent TA + 2 per cent GAP (c) composition 3 contains 2 per cent TA + 4 per cent GAP, and (d) composition 4 contains 6 per cent GAP.

as it reflects vulnerability to ignition due to hot spall fragment penetration. Both TA- and GAP-based LOVA compositions (1 and 2) did not respond up to 1050 °C and underwent sustained burning with flame on fall of steel ball preheated to 1065 - 1150 °C, whereas conventional NQ propellant underwent sustained burning in contact with ball preheated to merely 330 °C (Table 5). These results establish that LOVA propellants studied are less prone to thermal ignition by spall of fragments than the current gun propellants. It is envisaged that the flexible binder acts as a heat sink in the conductive ignition process, dissipating heat from the hot fragment as well as that generated by the exothermic decomposition of nitramine,[14] and thereby interrupting the heat feedback required for self-sustained decomposition of the propellant[15]. Incorporation of GAP in place of TA has not affected the stability properties of propellant as seen from Table 6. These results indicate that there is no change in the values of methyl violet test (No brown fumes at 120 °C up to 150 min)

Table 4. Results of vulnerability tests

	Composition No.			
	1	2	3	4
Ht. for 50% explosion, h_{50}	49	48	45	43
(cm)	28.8	28.8	28.8	28.8
Friction insensitive up to (kg)	>350	>350	>350	>350
Ignition temperature (°C)				

Table 5. Results of HFCI test

Composition	Temperature (°C)	Observations
NQ	330	Long duration smoke, sustained ignition and hissing sound.
1 (6 % TA)	1150	Long duration smoke, sustained ignition, hissing sound followed by a flame.
2 (3 %TA and 3 % GAP)	1110	- do -
3 (6 % GAP)	1065	- do -

Table 6. Stability test

Parameters	Composition No.			
	1	2	3	4
Heat test at 71°C (min)	8	17	16	16
Methyl violet test at 120 °C NBF (min)	150	150	150	150
B & J test at 120 °C (cc/5 g)	0.2	0.2	0.2	0.2

and B and J test (0.2 cc/5g at 120 °C), whereas there was only marginal change in heat test value (16 min at 71 °C).Thus, low vulnerability of LOVA propellants can be attributed to not only the high decomposition temperature of RDX (> 200 °C) compared to that of nitrate esters but also flexible nature of CA unlike relatively rigid polymeric structure of NC due to the presence of highly polar $O\text{-}NO_2$ groups.

4. CONCLUSION

GAP-based LOVA gun propellants developed during this study were found superior to TA-based LOVA propellants in terms of enhanced energy, improved combustion characteristics, and reduced pressure exponent as well as mechanical properties while retaining desirable vulnerability characteristics.

The data brings out that enhanced energy LOVA gun propellants with a force constant of around 1200 J/g and flame temperature 3200 K can be formulated by incorporating GAP as an energetic plasticiser for binder comprising NC and CA.

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