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*Research paper*

## Studies on the Effect of Nitrate Esters on the Properties of Advanced Energetic Propellants

Amit Kumar<sup>1,2\*</sup>, Prakash V. Chavan<sup>3</sup>, Vaibhav S. Sadavarte<sup>2</sup>,  
Debdas Bhowmik<sup>2</sup>, S.S.N.M. Santosh Mada<sup>2</sup>,  
Shrikant M. Pande<sup>2</sup>

<sup>1</sup> *Bharati Vidyapeeth Deemed University, College of Engineering, Ph.D. research scholar, Pune, 411043, India*

<sup>2</sup> *High Energy Materials Research Laboratory, Pune, 411021, India*

<sup>3</sup> *Bharati Vidyapeeth Deemed University, College of Engineering, Pune, 411043, India*

\* *E-mail: kumaraa007@rediffmail.com*

**Abstract:** Propulsion designers all over the world are exploring the possibility of achieving higher performance by enhancing the energy of solid propellants. This can be achieved by replacing non-energetic ingredients with energetic ones or by replacing low density ingredients, particularly binders, with higher density ones, without affecting the processibility and ageing characteristics. The same has been attempted by using nitroglycerine (NG) and butanetriol trinitrate (BTTN) as plasticizers in propellant compositions. In the present study, NG and BTTN have been used in different plasticizer to polymer ratios (PI/Po) and various parameters of each composition have been theoretically predicted. Three propellant compositions plasticized with NG, BTTN and a 1:1 combination of NG and BTTN, have been processed and analyzed for targeted properties. From the theoretical data, it was observed that there is a negligible increase in density impulse beyond a PI/Po ratio of 2, apart from the higher density and calorimetric values of the NG-plasticized propellant; these plasticizers have a significant effect on the ballistic and mechanical properties. Another observation was that the elongation of BTTN and NG/BTTN (1:1) plasticized propellants is significantly higher at a low crosshead

rate than NG-plasticized propellant, implying that the two former propellants have higher strain capabilities at low temperatures and can be used for missiles having long term low temperature storage requirements. Thermal decomposition studies have been carried out by DSC, and for each composition 5 distinct peaks were observed.

**Keywords:** nitroglycerine, NG, butanetriol trinitrate, BTTN, strain capability, thermal decomposition

## 1 Introduction

Solid rocket propellants, designed to deliver propulsive energy, are broadly classified as homogeneous (double base propellants; DBP) or heterogeneous (composite propellants; CP) with specific impulses ( $I_{sp}$ ) ranging from 210-220 s for DBPs to 240-243 s for CPs [1]. Composite modified double base (CMDB) propellants based on energetic nitroglycerine (NG) plasticized nitrocellulose (NC) binder, filled with ammonium perchlorate (AP) and aluminum (Al), and composite propellants based on non-energetic hydroxyl terminated polybutadiene (HTPB) binder filled with AP-Al exhibit a delivered  $I_{sp}$  of 240-245 s at 7 MPa. CMDB propellants possess a low density (1.66 g/cm<sup>3</sup>), low solid loading capability and inferior low temperature strain capability, and therefore have limitations for case-bonded motor applications. On the other hand, a CP based on the polymer HTPB and the non-energetic plasticizer dioctyl adipate (DOA) has relatively better energetics, allows high solid loading (86-88%), possesses better low temperature strain capability (down to -25 °C) and is suitable for both case bonded and cartridge loaded applications [2]. The option of using energetic plasticizers with this type of binder is not possible due to its immiscibility with energetic plasticizers like nitrate esters.

Since DBPs, CMDBs and CPs have reached a plateau in terms of energy ( $I_{sp}$ ) using conventional ingredients in the compositions (NC-NG-AP-Al or HTPB-AP-Al), there are continuing research efforts to improve the performance of solid propellants to meet advanced requirements (*e.g.* higher payloads, longer range, quick reaction, reduced smoke, *etc.*) for civil and defense applications.

Attempts are being made to develop high performance advanced energetic propellants with enhanced density and specific impulse, by increasing the total solid loading, making use of energetic binders, energetic plasticizers and incorporating a higher percentage of energetic solid ingredients like nitramines. To achieve enhanced performance, it is desirable that all of the ingredients that are proposed to be used in solid propellants should be energetic in nature.

Therefore propellant developers are exploring the use of dense binder systems with polymers:

- polyethers,
- polyesters,
- nitrile/butadiene rubbers, *etc.*,

or energetic polymers:

- glycidyl azide polymer (GAP),
- poly(3,3'-bis(azidomethyl)oxetane) (poly-BAMO),
- poly(3-nitratomethyl-3-methyloxetane) (poly-NIMMO), *etc.*,

which are miscible with energetic plasticizers:

- butanetriol trinitrate (BTTN),
- trimethylolethane trinitrate (TMETN), *etc.*,

to increase the energy and density. The performance of such propellants is further enhanced by the incorporation of advanced oxidizers *viz.* nitramines, *e.g.*:

- hexogen (RDX),
- octogen (HMX),
- hexanitrohexaazaisowurtzitane (CL-20),

due to their positive heats of formation [2].

Consequently an attempt has been made to develop advanced energetic propellants with improved density and energy as compared to conventional HTPB-AP-Al based propellants, using a nitrate ester plasticized polyester polyol binder system, which possesses an excellent low temperature strain capability. SPB-255, a polyester polyol, was chosen as the pre-polymer, to develop a CP with NG and/or BTTN as plasticizer, AP and HMX as oxidizers and Al as fuel, because of its excellent miscibility with energetic nitrate ester plasticizers, as reported by Pande *et al.* [3]. Bhowmik *et al.* [4] have reported that a plasticizer to polymer ratio (PI/Po) of 70:30 is the optimum for achieving good mechanical properties in the case of an energetic binder based on 'hydroxyl terminated polyester polyol' plasticized with BTTN, and it has potential use in solid rocket propellants. Theoretical analysis of an advanced energetic propellant with the reported binder plasticized with NG, BTTN and a 1:1 combination of NG/BTTN has been carried out to determine the thermodynamic parameters with respect to changes in the PI/Po ratio and these results are discussed in Section 3.1. Pande *et al.* [3] have also studied the mechanical properties of an NG-plasticized polyester polyol pre-polymer based solid propellant and recommended its suitability for case-bonded rocket motor applications.

The present study focuses mainly on the characteristics of NG and/or BTTN plasticized polyester polyol pre-polymer based advanced energetic propellants. The objectives of this study were to determine:

- theoretical rocket performance parameters,
- physical properties,
- sensitivity of formulation,
- thermal properties,
- ballistic properties, and
- mechanical properties.

The reason for the selection of NG and BTTN as the energetic plasticizers was their high density, high oxygen balance and high calorific-value, among the various available energetic plasticizers *viz.* NG, BTTN, TMETN and TEGDN as listed in Table 1. The theoretical performance predictions for high energy propellants with NG, BTTN and NG/BTTN (1:1) plasticized formulations have been made with varying PI/Po ratios (0.50 to 3.00), keeping all other ingredients and their percentages the same as detailed in Section 3.1. Based on this theoretical analysis, a negligible benefit is observed in the density impulse of propellants having a PI/Po ratio above 2. However, the propellant becomes more sensitive to friction/impact stimuli as this ratio is increased. Hence, advanced energetic propellants based on a polyester polyol pre-polymer, plasticized with NG, BTTN or a 1:1 combination of NG and BTTN having a PI/Po ratio of 2 have been developed and their various properties that have been analyzed, are reported in this paper.

**Table 1.** Physico-chemical properties of some energetic plasticizers

S. no.	Energetic plasticizer	Density [g/cm <sup>3</sup> ]	Oxygen balance [%]	Cal-Val [cal/g]
1	NG	1.59	+3.50	+1750
2	BTTN	1.52	-16.00	+1570
3	TMETN	1.46	-34.00	+1220
4	TEGDN	1.33	-66.60	+616

## 2 Materials and Methods

### 2.1 Formulation and raw materials

The polyester polyol, a hydroxyl terminated polycaprolactone pre-polymer having a hydroxyl value of 38-40 mg of KOH/g, hydroxyl functionality of 3.70-3.90, number average molecular weight  $M_n$  (by Vapor Pressure Osmometry, VPO) of 5700-6200 and density 1.15 g/cm<sup>3</sup>, was used as the binder. It is white soft waxy solid and is miscible with all types of nitrate ester plasticizers. Energetic plasticizers NG (18.20%N) and BTTN (17.43%N); ammonium

perchlorate (purity >99%); aluminum powder (mean particle size 15  $\mu$ );  $\beta$ -HMX (purity >99% and acidity <0.02%), sourced from Indian origin companies, were used. All other ingredients were purchased from M/s Sigma Aldrich Chemical Pvt. Ltd. and used without purification.

Three propellant compositions with a PI/Po ratio of 2 were selected from the theoretical analysis (ref. Section 3.1 and Table 2) and were formulated using the polyester polyol polymer, plasticized with NG, BTTN and NG/BTTN (1:1) and were coded as P-10, P-11 and P-12, respectively. The detailed propellant compositions, with the exact percentages of chemical ingredients, are listed in Table 2 and note (#) below it.

## 2.2 Propellant processing

The propellants were processed in batch sizes of 3.50 kg in a 5 L vertical planetary mixer (VPM) by the standard procedure for composite propellant processing. After the establishment of the process parameters for the initial studies, the batch size was scaled up to 70 kg in an IKA (Germany Make 100 liter) VPM. The important process parameters to be maintained during the propellant processing were mixer blade rotations per minute (RPM), mixing time, vacuum level (20-30 torr), temperature during processing ( $50 \pm 2$  °C), curing agent addition temperature ( $50 \pm 2$  °C), curing temperature ( $50 \pm 2$  °C), curing time (144 h) *etc.* Mixer parameters, like mixer blade RPM and mixing time, depend on the type of mixer employed with the limitation that the final propellant slurry must be homogeneous with respect to its chemical ingredients and the end of mix viscosity (EoMV) should be such that it can be cast flawlessly. The energetic binder (polyester polyol + NG/BTTN + TMP + nBD + 2-nitrodiphenylamine (2-NDPA)) was de-aerated in a mixer bowl for about 3 h at  $50 \pm 2$  °C until the moisture level had been reduced to less than 0.08%, followed by sequential and incremental addition of the oven dried solid ingredients and subsequent mixing. Once homogeneity of the propellant slurry was ensured, the curing agent isophorone di-isocyanate (IPDI) was added and mixing continued for 30 min. The casting of the slurry, in 150×150×150 mm cartons for the physical and mechanical property specimens, was carried out by the slurry cast technique [5, 6]. These cartons were then cured at  $50 \pm 2$  °C for 144 h in a water-jacketed oven, followed by X-ray radiography for detection of flaws, such as voids, cracks, and porosity.

## 2.3 Characterization methods

The propellant samples were evaluated for their physical properties (EoMV, density), thermal properties (auto-ignition temperature, calorimetric value),

**Table 2.** Theoretical performance predictions

Sample No. #	Polyol [%]	NG [%]	BTTN [%]	PI/Po ratio	Flame temperature [K]	C* [m/s]	Density [g/cm <sup>3</sup> ]	Specific impulse [s]	Mol. Wt(M <sub>w</sub> )	C <sub>p</sub> /C <sub>v</sub>
P-1	16.27	8.14	–	0.50	3457.39	1622.30	1.78	260.80	25.04	1.14
P-2	16.27	–	8.14	0.50	3452.29	1628.30	1.77	268.90	24.83	1.14
P-3	16.27	4.07	4.07	0.50	3390.35	1618.50	1.78	267.50	24.67	1.14
P-4	12.21	12.20	–	1.00	3631.76	1618.70	1.81	267.80	26.37	1.13
P-5	12.21	–	12.20	1.00	3623.22	1628.20	1.80	269.30	26.02	1.13
P-6	12.21	6.10	6.10	1.00	3581.60	1620.40	1.80	267.80	25.96	1.13
P-7	9.76	14.65	–	1.50	3719.40	1611.90	1.83	267.40	27.20	1.13
P-8	9.76	–	14.65	1.50	3709.15	1623.70	1.82	269.20	26.77	1.13
P-9	9.76	7.32	7.32	1.50	3677.09	1616.10	1.82	267.70	26.76	1.13
P-10	<b>8.14</b>	<b>16.27</b>	–	<b>2.00</b>	<b>3770.50</b>	<b>1605.70</b>	<b>1.84</b>	<b>266.80</b>	<b>27.77</b>	<b>1.17</b>
P-11	<b>8.14</b>	–	<b>16.27</b>	<b>2.00</b>	<b>3759.63</b>	<b>1619.10</b>	<b>1.83</b>	<b>268.90</b>	<b>27.27</b>	<b>1.13</b>
P-12	<b>8.14</b>	<b>8.14</b>	<b>8.14</b>	<b>2.00</b>	<b>3765.36</b>	<b>1612.40</b>	<b>1.84</b>	<b>267.80</b>	<b>27.69</b>	<b>1.13</b>
P-13	6.97	17.44	–	2.50	3803.23	1600.40	1.85	266.20	28.18	1.17
P-14	6.97	–	17.44	2.50	3792.30	1615.10	1.84	268.50	27.64	1.17
P-15	6.97	8.72	8.72	2.50	3777.41	1605.50	1.85	266.80	27.84	1.17
P-16	6.10	18.31	–	3.00	3825.36	1596.00	1.86	265.70	28.48	1.17
P-17	6.10	–	18.31	3.00	3814.65	1611.60	1.84	268.20	27.91	1.17
P-18	6.10	9.15	9.15	3.00	3802.41	1601.90	1.85	266.40	28.14	1.17

# The propellant compositions consisted of Al: 18%, HMX: 21%, AP: 35%, IPDI: 0.8%, TMP and nBD 0.15%, 2-NDPA: 0.34% apart from the polyester polyol, NG and BTTN.

mechanical properties (tensile strength, elongation and E-modulus) and ballistic properties (burn rate, pressure index and temperature sensitivity).

Solid strand burning rates (SSBR) were determined in the pressure range 3.50-11 MPa by the acoustic emission technique [7-9]. The technique involves combustion of propellant strands (150×6×6 mm) submerged in water, by means of Nichrome wire in a nitrogen pressurized bomb. The acoustic signals, generated due to perturbations caused by propellant deflagration, in the ultrasonic range are uni-directionally transmitted through the water medium and sensed by an acoustic piezo-electric transducer. These signals are then passed through a pre-amplifier, post-amplifier and displayed on an oscilloscope *vs.* time. The burn rate is taken as the average of five readings and the standard deviation of the measurement was less than 0.20 mm/s. The pressure index (n-value) was calculated from the SSBR data using Vielle's law:

$$r = a(P_c)^n \quad (1)$$

where  $r$  is burn rate,  $a$  is temperature sensitivity,  $P_c$  is chamber pressure,  $n$  is pressure index.

The calorimetric values were determined in a Parr adiabatic bomb calorimeter at 0.0029 g/cm<sup>3</sup> loading density, by burning ~1 g samples in an argon atmosphere and measuring the heat released during combustion under adiabatic conditions.

The end of mix viscosity (EoMV) and viscosity buildup was measured using a Brookfield Viscometer (model: HBT dial type), by inserting a T-C spindle at a rotating speed of 2.50 RPM at a predetermined temperature. The density of the cured propellant samples was measured using helium gas pycnometry.

The sensitivity to impact stimuli was determined by the fall hammer method with a 2 kg drop weight in a Bruceton staircase apparatus [10] and the results are given in terms of the height of the statistically obtained 50% probability of explosion ( $H_{50}$ ). The friction sensitivity was measured on a Julius Peter apparatus [11] by incrementally increasing the load from 0.20 to 36 kg, until there was no ignition or explosion in five consecutive test samples. The sensitivity tests were carried out at ambient temperature (30 ±2 °C) and RH of 55-60%.

The mechanical properties were determined with a uniaxial testing machine (Make: Instron; Model TIC-1185, UK) using dumbbell shaped specimens according to ASTM D-638 Type-IV standard [12], at three crosshead rates.

### 3 Results and Discussion

#### 3.1 Theoretical performance predictions [13]

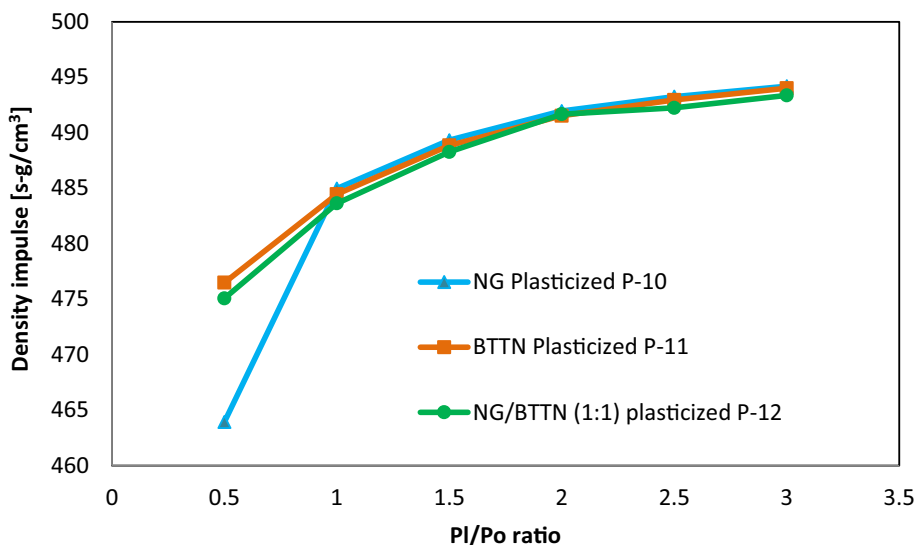
The thermodynamically calculated performance parameters of the high energy propellant (Ps) formulations based on an energetic binder (26%) loaded with a solid filler: aluminium (18%), AP (35%) and HMX (21%), were analyzed. The energetic binder consisted of a polyester polyol polymer plasticized with NG and/or BTTN, an antioxidant, a chain extender, a cross linker and a curing agent. A total of 18 formulations, having three different nitrate ester plasticizers *viz.* NG, BTTN and a 1:1 combination of NG and BTTN, with different PI/Po ratios, ranging from 0.50 to 3, were investigated for further theoretical predictions. The thermochemical properties were predicted under equilibrium chamber conditions, with an expansion ratio from 7 to 0.10 MPa, using minimization of the Gibb's free energy. The combustion and nozzle efficiencies were presumed to be 100%. The results for the 18 formulations are listed in Table 2.

The theoretical mean density of the NG-based formulations was higher than that for the other combinations due to NG's higher constituent density contribution. The formulations plasticized with BTTN exhibited higher values of specific impulse and characteristic velocity compared to those of the NG and NG/BTTN (1:1) formulations, for a given PI/Po ratio because:

- BTTN has a higher heat of combustion value (9071 J/g) than NG (6061 J/g) and the NG/BTTN (1:1) combination,
- BTTN produces low average molecular weight combustion products,
- $\sqrt{(T_f/M_w)}$  is high for BTTN-plasticized formulations compared to the remaining plasticizer systems.

As the PI/Po ratio was increased for each plasticizer, the flame temperature and density increased, however this increase became less significant beyond a PI/Po ratio of 2. The variation of density impulse *vs.* PI/Po ratio is plotted in Figure 1. The density impulse of the formulations increases with an increase in PI/Po ratio, but the increase becomes marginal beyond a ratio of 2. In order to benefit from both of these effects, a PI/Po ratio of 2 was considered for further evaluation. Moreover, an increase in the PI/Po ratio in the propellant beyond a certain limit could result in increased sensitivity of the propellant to friction and impact stimuli. Therefore, 3 formulations, with PI/Po ratios of 2, out of the 18, were selected for further propellant processing and evaluation.



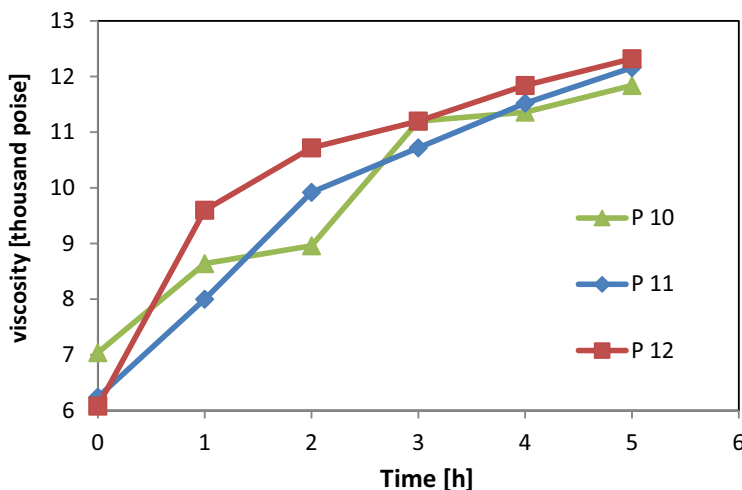


**Figure 1.** Density Impulse vs. PI/Po ratio

## 3.2 Physical properties

### 3.2.1 End of mix viscosity (*EoMV*)

The *EoMV* of the NG-plasticized P-10 formulation was higher (7040 P) than the BTTN-plasticized P-11 (6240 P) and NG/BTTN (1:1) plasticized P-12 (6080 P) formulations. Viscosity buildup data for these 3 formulations at 30 °C, generated up to 5 h from end of mixing, are shown in Figure 2. It may be observed that the reaction rate of the pre-polymer and IPDI was faster in the P-12 formulation than the others. Reaction kinetics studies of these formulations are in progress for future work.



**Figure 2.** Propellant slurry viscosity vs. time

### 3.2.2 Density

The measured density of the cured propellants are listed in Table 3 and closely agrees with the theoretical calculated density. As predicted, the formulations having NG ( $\rho = 1.60 \text{ g/cm}^3$ ) exhibited higher density than BTTN ( $\rho = 1.52 \text{ g/cm}^3$ ) based propellants because of the higher constituent density of NG.

**Table 3.** Physical, thermal and sensitivity properties

Composition	Theoretical density [g/cm <sup>3</sup> ]	Measured density [g/cm <sup>3</sup> ]	Cal-Val [cal/g]	Temp. sensitivity (5-55 °C) [%/°C]	H <sub>50</sub> (2 kg weight) [cm]	Friction sensitivity (insensitive upto) [kg]	Auto ignition temperature [°C]
P-10	1.84	1.83	1678	0.19	26.00	8.90	178.40
P-11	1.83	1.81	1580	0.11	42.50	9.50	181.30
P-12	1.84	1.82	1629	0.12	27.50	9.10	182.00
$\beta$ -HMX	–	–	–	–	27.00	18.00	–

### 3.3 Sensitivity data

#### 3.3.1 Impact sensitivity

The 3 propellants under study and  $\beta$ -HMX as a standard explosive were subjected to impact and friction sensitivity tests. The results are listed in Table 3. It may be seen that the impact sensitivity for P-10 is high (26 cm), due to the higher impact sensitivity of NG (15 cm) compared with BTTN (58 cm). The impact sensitivity showed a decreasing trend for P-10, P-12 and P-11, respectively.

#### 3.3.2 Friction sensitivity

A similar trend was also observed for friction sensitivity, as listed in Table 3. The threshold energy for initiation of a propellant by friction appears to be reduced with the incorporation of NG in the formulation. A high friction sensitivity of NG-based formulations is due to the greater sensitivity of NG to heat, due to which, during the friction test, hot zones are created resulting in activation of the propellant.

### 3.4 Thermal properties

#### 3.4.1 Calorimetric value

The calorimetric value of NG-plasticized P-10 is higher (1678 cal/g) than the NG/BTTN (1:1) plasticized P-12 (1629 cal/g) or the BTTN only plasticized P-11 (1580 cal/g). NG is oxygen rich (oxygen balance (*OB*): +3.50%) as compared to BTTN which is oxygen deficient (*OB*: -16%). The calculated oxygen balance of P-10 (*OB*: -19.30%) is higher than that of P-11 (*OB*: -22.50%) and P-12 (*OB*: -20.90%), which results in better combustion for P-10 than the others during the calorimetric test, leading to an enhanced calorimetric value. As the percentage of oxygen available for combustion is increased in the formulation, the heat of combustion increases. The observed calorimetric values are in agreement with the proportion of oxygen in the formulations.

#### 3.4.2 Auto ignition temperature

The autoignition temperature of the propellants increases from P-10 to P-12, in proportion to the NG content; however, the increment is not significant.

### 3.5 Ballistic properties

#### 3.5.1 Burn rate

The solid strand burn rate was measured in the pressure range 3.50 to 11 MPa, at intervals of 2 MPa, and the results are listed in Table 4. Since it is well established that the burn rate and pressure exponent are highly influenced by solid loading, percentage of oxidizer (AP) and its particle size, these have been kept the same in all 3 compositions. This ensures that there is no change in burn rate and pressure exponent due to variations in solid content. In other words, it can be stated that the change in burn rate and pressure exponent is only due to variations in the type of plasticizer used.

**Table 4.** Variation in Strand burn rate with change in plasticizer

Composition	Average burn rate [mm/s] at pressure [MPa]					Pr exponent ( $\eta$ ) over Pr range [MPa]			
	3.50	5.00	7.00	9.00	11.00	$\eta_{3.5-7}$	$\eta_{5-9}$	$\eta_{7-11}$	$\eta_{3.5-11}$
P-10	8.10	9.51	11.56	13.22	14.97	0.51	0.56	0.57	0.54
P-11	7.81	9.05	10.45	11.91	13.03	0.42	0.47	0.49	0.45
P-12	7.90	9.43	11.20	12.76	14.24	0.50	0.51	0.53	0.51

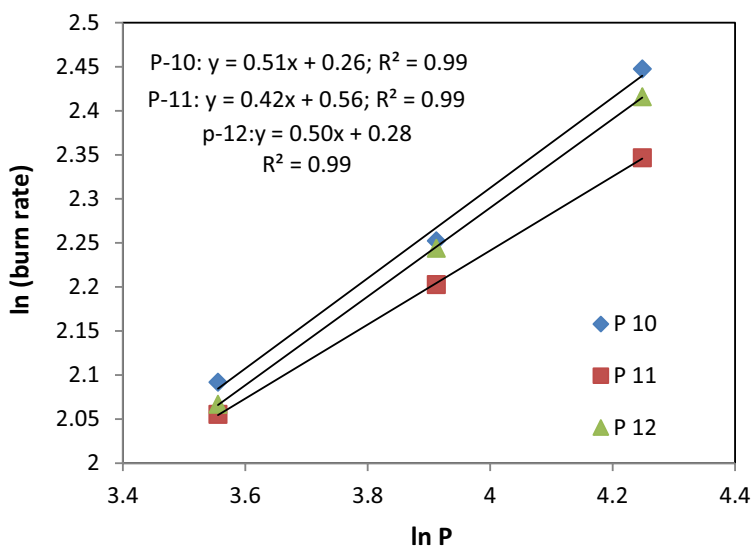
It was observed that the BTTN-plasticized P-11 composition has a relatively lower burn rate (7.81 to 13.03 mm/s for 3.50 to 11 MPa) at all pressures compared to the NG/BTTN (1:1) plasticized P-12 (7.90 to 14.24 mm/s), whereas NG-plasticized P-10 shows a higher burn rate (8.10 to 14.97 mm/s) when compared with the other compositions at the corresponding pressures. The P-10 and P-12 samples exhibited 4-15% and 1-9% higher burn rates than P-11, respectively. The high burn rate of P-10 may be due to its higher oxygen balance compared to the other two, as discussed in Section 3.4.1 and a lower value of its autoignition temperature. The high burn rate of P-10 may also be due to the lower decomposition temperature of the nitrate ester (192 °C) in this formulation than for the other two, as confirmed by the DSC studies and discussed in Section 3.6. The burn rates of all three compositions increased with pressure as per Vielle's law, and the effect of the nitrate ester type on the burn rate becomes more significant at higher pressures.

Klohn *et al.* [14] in their study of nitrate ester (NG and TMETN) plasticized nitramine solid propellants reported that up to 10% AP loading, replacement of 25% TMETN by 25% NG produces little change in burn rate, however at a higher AP concentration the difference in burn rate due to NG and TMETN can no longer be neglected. The advanced energetic propellants reported in the present paper

consisted of a constant but high (35%) AP concentration and it was observed that the use of a specific energetic plasticizer influences the burn rate at both low and high pressures, as reported by Klohn *et al.* [14].

### 3.5.2 Pressure exponent

As the pressure exponent is an important parameter for stable motor operation, it was estimated from the strand burn rate in four different pressure ranges by plotting  $\ln(\text{burn rate})$  vs.  $\ln(\text{pressure})$  as presented in Figures 3-6. The slopes of these plots are taken as the pressure exponent in Vielle's law. It may be observed that there is a marked difference in the pressure exponent value for propellant formulations having different plasticizers at all pressure ranges. In particular, the BTTN-plasticized formulation exhibits a lower pressure index value ( $\sim 0.42$ - $0.49$ ) than the NG plasticized formulation ( $\sim 0.51$ - $0.57$ ). It was observed that the NG-plasticized propellant is relatively more susceptible to burn rate enhancement due to an increase in pressure. Also, the NG/BTTN (1:1) plasticized P-12 has a relatively increased pressure index compared to the BTTN only plasticized P-11, due to the presence of NG.



**Figure 3.**  $\ln(\text{burn rate})$  vs.  $\ln(\text{pressure})$  (3.5-7 MPa)

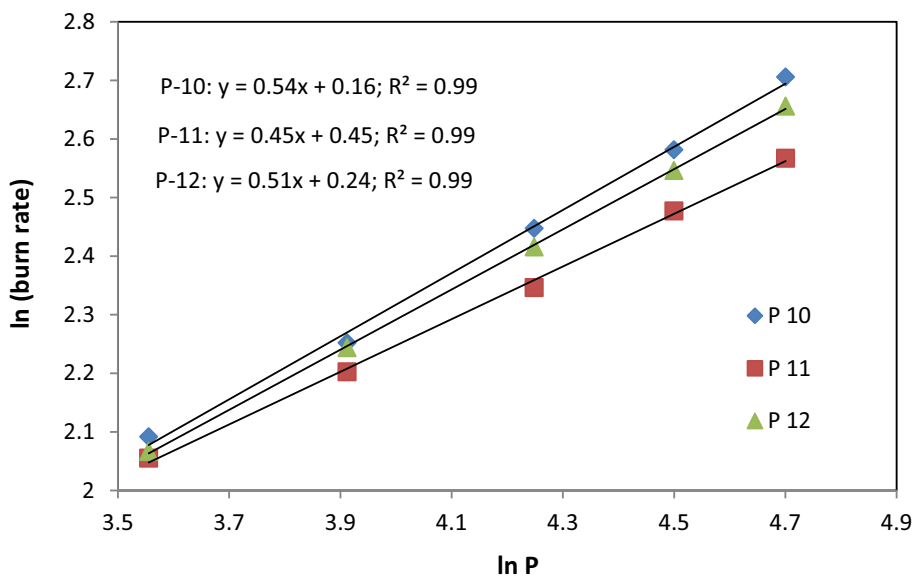


Figure 4.  $\ln(\text{burn rate})$  vs.  $\ln(\text{pressure})$  (3.5-11 MPa)

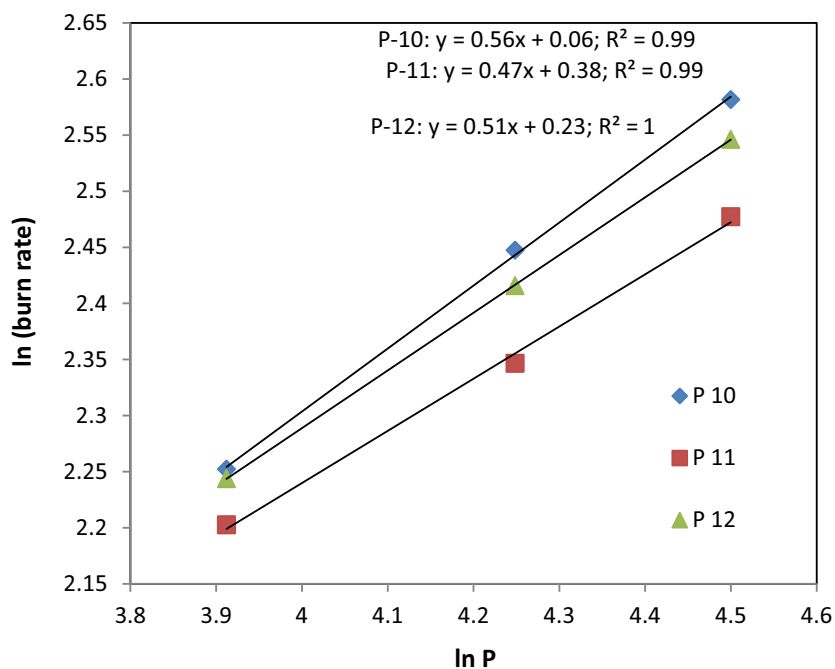
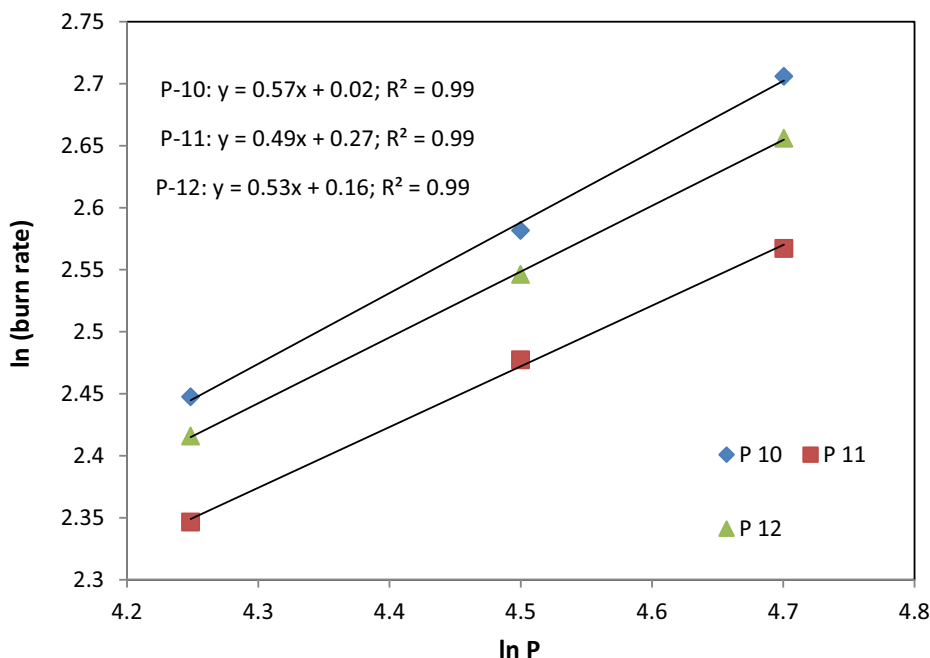


Figure 5.  $\ln(\text{burn rate})$  vs.  $\ln(\text{pressure})$  (5-9 MPa)



**Figure 6.**  $\ln(\text{burn rate})$  vs.  $\ln(\text{pressure})$  (7-11 MPa)

For all 3 compositions, with an increase in pressure, the pressure exponent value increases, *viz.* for P-10 the pressure exponent value increases from 0.51 to 0.57 when the pressure range is changed from 3.50-7 to 7-11 MPa, and this increase in the pressure index value makes the composition more susceptible to burn rate enhancement with pressure.

The reason for the enhancement of the pressure index due to NG is not exactly understood, but a possible explanation could be due to the content of  $\text{NO}_2$  released during combustion. The molar concentration of  $\text{NO}_2$  produced by the combustion of NG will be much higher than that from BTTN. As observed in the combustion of double base propellants, when the  $\text{NO}_2$  content is increased, on increasing the pressure, an increased burn rate is observed due to the enhanced heat feedback to the condensed phase. When the  $\text{NO}_2$  concentration increases during combustion, the dark zone thickness is reduced. This is followed by the approach of the luminous flame closer to the regression surface, resulting in enhanced heat feedback at high pressure and hence high burn rate. However, at low pressures, the luminous flame is away from the burning surface, leading to a reduced burn rate. The overall consequence of a high  $\text{NO}_2$  concentration is lower burning rates at low pressure and higher burning rates at high pressure, *i.e.* higher pressure index value.

### 3.5.3 Temperature sensitivity

The temperature sensitivity of the burn rate in a temperature range of +5 to +55 °C has been determined from the strand burn rate, and is listed in Table 3. It was found to be higher for the NG-plasticized formulation P-10 (0.19 %/°C) than P-11 (0.11 %/°C) and P-12 (0.12 %/°C).

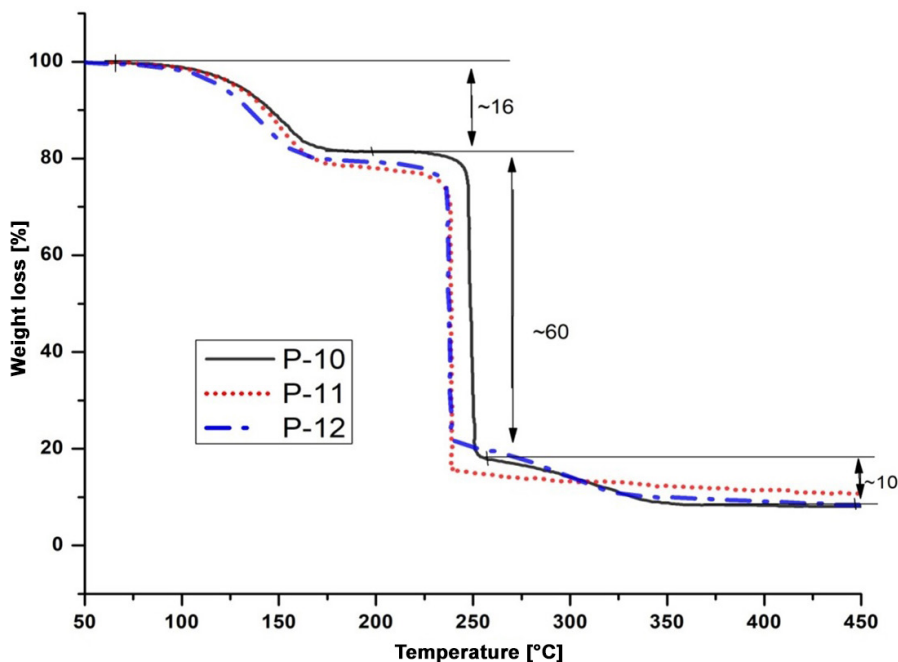
### 3.6 Thermal studies

The formulations under study were subjected to thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) to understand the thermal decomposition pattern. The TGA-DSC experiments were carried out with an SDT Q600 (Make: TA instruments) at a heating rate of 10 °C/min from room temperature to 500 °C, under a purge gas (nitrogen, flow rate 100 ml/min). The sample pans were of Al<sub>2</sub>O<sub>3</sub>. The empty pans were initially tared in the instrument by placing them in the sample and reference beams. An empty alumina pan was used as reference. The sample was placed in the tared alumina pan and weighed. A sample mass of 1 ±0.20 mg was prepared as thin disks. The pan is then brought to equilibrium at the starting temperature of 50 °C. The sample was then temperature-programmed through to the completion of the exothermic/endothemic transition at the preselected heating rate. For this study the experiments were performed at least in duplicates. The thermal decomposition of all three compositions exhibited a three stage pattern in TGA, as shown in Figure 7:

- volatilization followed by thermal decomposition of the energetic nitrate ester,
- decomposition of the nitramine (HMX), and
- decomposition of AP.

The weight loss in the first stage was around 16%, in the second stage around 60% and 10% in the final stage. The char yield was observed to be around 14% for all three compositions.



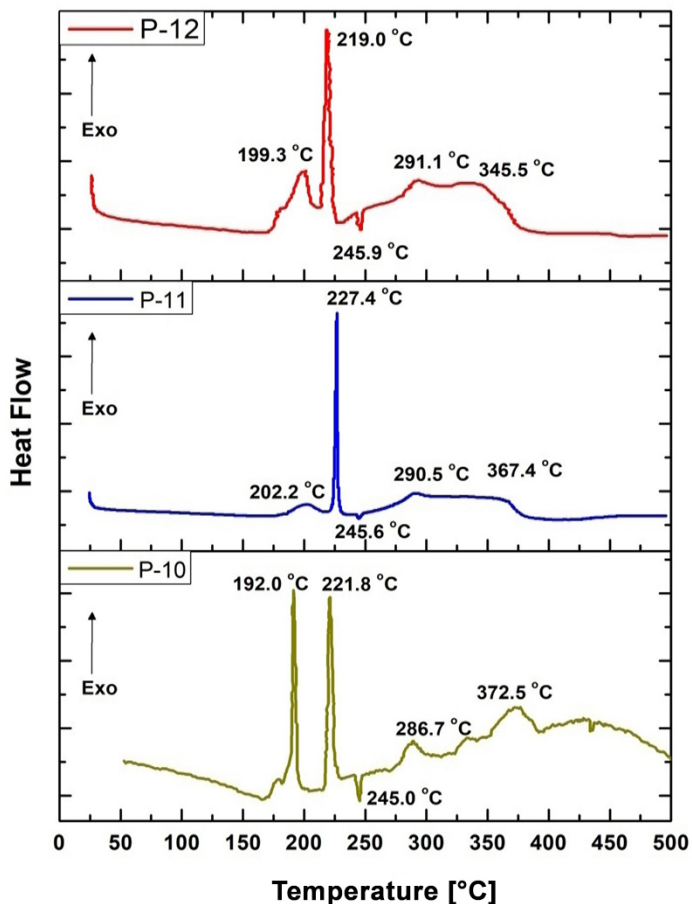


**Figure 7.** TGA curves

To further understand the exact pattern and enthalpy change at each stage, a DSC study was performed, as shown in Figure 8. A summary of the results is given in Table 5. The DSC curves of all three compositions showed a similar pattern, with slight shifts in the peak temperatures. For the NG-based composition (P-10), the first exothermic peak was observed at 192 °C with an enthalpy change of 307.40 J/g, which is due to volatilization and decomposition of NG [15, 16]. An exothermic peak at 221.80 °C is due to decomposition of HMX. Thermal decomposition of the propellants under study shows similar results with respect to the HMX decomposition temperature as reported by Fifer *et al.* [17], wherein the decomposition temperature of HMX is reduced from 280 to 219–227.40 °C when heated in the presence of AP. The reduction in the decomposition temperature of HMX may be due to the presence of AP, which has a melting point significantly less than HMX, and since it is reported in the literature that compounds with melting points less than the nitramine decomposition onset tend to lower the temperature of the nitramine thermolysis [17, 18]. The presence of an NH<sub>3</sub> environment instead of gases like H<sub>2</sub>, CO, O<sub>2</sub> or NO may also be the reason for the reduction in

the HMX decomposition temperature from ~280 to 221 °C, as reported by Palopoli *et al.* [19]. The small endothermic peak at 245 °C is the phase transition of AP from orthorhombic to cubic. The exothermic peaks at 286.70 and 372.50 °C are the low temperature decomposition and complete decomposition of AP respectively, as against 300 and 450 °C respectively for pure AP [20]. Similar behaviour for the reduction of the decomposition peak of AP in the presence of HMX has also been reported by Pivkina *et al.* [20], where they have studied the thermal decomposition of binary mixtures of HMX and AP and reported a synergistic effect of AP on HMX decomposition, which effectively reduces the onset temperature of HMX decomposition by approximately 60 °C, and at the same time the AP decomposition is catalyzed by HMX's gaseous products. A study by Saito *et al.* [21] also confirmed a marked reduction in the ignition time of AP-based composite propellants on addition of HMX, due to lowering of the onset of the HMX exothermic reaction.

Similarly, P-11 and P-12 were also subjected to DSC studies. The peak due to volatilization and decomposition of the nitrate ester was slightly shifted to higher temperature (202.20 °C for P-11 and 199.30 °C for P-12) compared to P-10. The lower peak temperature for the decomposition of the nitrate ester (NG) for P-10 (192 °C), compared to P-11 (202.20 °C) and P-12 (199.30 °C), could be the reason for its higher burn rate, as reported in Section 3.5.1. It is very interesting to note here that the peaks responsible for the complete decomposition of AP for BTTN (367.40 °C) and NG/BTTN (1:1) (345.50 °C) plasticized compositions were shifted to a lower temperature than for the NG-plasticized composition (372.50 °C). The shift to a lower temperature of the complete decomposition temperature peak of AP may be attributed to the variation in the burning rates for these compositions.



**Figure 8.** DSC thermograms

**Table 5.** Thermal decomposition temperature and enthalpy data by DSC

Composition	Step									
	1 <sup>st</sup>		2 <sup>nd</sup>		3 <sup>rd</sup>		4 <sup>th</sup>		5 <sup>th</sup>	
	Temperature [°C]	$\Delta H$ [J/g]	Temperature [°C]	$\Delta H$ [J/g]	Temperature [°C]	$\Delta H$ [J/g]	Temperature [°C]	$\Delta H$ [J/g]	Temperature [°C]	$\Delta H$ [J/g]
P-10	192.00	-307.40	221.80	-231.70	245.00	24.70	286.70	-127.40	372.50	-175.60
P-11	202.20	-95.35	227.40	-255.50	245.60	9.70	290.50	-83.10	367.40	-30.99
P-12	199.30	-208.40	219.00	-248.70	245.90	14.10	291.10	-61.00	345.50	-183.10

### 3.7 Mechanical properties

This study reports similar effects on the strain capability (embrittlement) of propellants with plasticizers NG, BTTN and their combination, as reported by Zimmerman *et al.* [22] for TMETN/diethylene glycol dinitrate (DEGDN) and BTTN. They reported severe embrittlement of propellants containing TMETN and DEGDN after 30 days of storage at  $-54\text{ }^{\circ}\text{C}$ , however the same was not true for BTTN-plasticized propellant. They also showed that BTTN combined with either DEGDN or TMETN did not cause embrittlement after long storage at  $-40\text{ }^{\circ}\text{C}$ .

Adel *et al.* [23] reported that, for solid propellant grains similar to the ones under study here (viscoelastic materials), the mechanical properties determined at a slow crosshead rate simulates the load experienced under long term storage at low temperature, and that at a high crosshead rate simulates the load experienced due to a quick stimulus, like ignition, vibration, acceleration *etc.* The actual mechanical property requirements for any propellant depends on the type of grain geometry, temperature and loads it is expected to experience during long term storage. Hence the tensile properties of the present propellants have been determined at three different crosshead rates (0.50, 50 and 1000 mm/min) at ambient temperature, in order to simulate the loads experienced during long term storage at low temperature, ambient conditions and quick stimulus requirements, respectively, and are listed in Table 6. It may be seen that NG-plasticized P-10 has a high modulus and low elongation at break at 50 mm/min crosshead rate, as compared to both the P-11 and P-12 propellant systems. It may also be observed from these data that at the low crosshead rate (0.50 mm/min), elongation at break values for P-10 are significantly lower, with higher modulus, than the other two propellants. The tensile strengths of these compositions had similar values at each strain rate, *viz.* at 50 mm/min it varied from 0.48 to 0.51 MPa and at 0.50 mm/min it varied from 0.42 to 0.50 MPa. These values of elongation at break and E-modulus at different strain rates indicate the superior tensile properties of BTTN and NG/BTTN (1:1) plasticized propellants compared to the NG-plasticized one, especially for case bonded applications with very low temperature requirements.

**Table 6.** Tensile properties of propellants at three different cross head rates

Composition	Cross head rate [mm/min]*											
	0.5				50				1000			
	<i>TS</i> [MPa]	<i>E</i> [MPa]	$\epsilon_m$ [%]	$\epsilon_b$ [%]	<i>TS</i> [MPa]	<i>E</i> [MPa]	$\epsilon_m$ [%]	$\epsilon_b$ [%]	<i>TS</i> [MPa]	<i>E</i> [MPa]	$\epsilon_m$ [%]	$\epsilon_b$ [%]
P-10	0.50	9.70	14.60	78.00	0.48	7.60	16.20	25.60	0.52	8.50	18.40	32.10
P-11	0.42	4.20	17.60	206.00	0.51	4.70	18.80	94.80	0.63	5.00	21.00	108.80
P-12	0.42	4.60	17.20	141.00	0.49	4.80	18.10	51.90	0.61	4.70	22.50	66.90

\* *TS* – Tensile Strength; *E* – Tensile Modulus;  $\epsilon_m$  – elongation at maximum stress;  $\epsilon_b$  – elongation at break

It is very interesting to note that for all three propellants, at a low crosshead rate (0.50 mm/min), the elongation at break values are significantly higher than the values at 50 mm/min. This distinct characteristic of these propellants is the opposite to that of HTPB-based propellants, in which elongation at break values at low strain rates are less than the values at high strain rates. Kolonko *et al.* [24] made similar observations during their work on the high molecular weight PE-PCP pre-polymer. Two possible reasons for high elongation at a low crosshead rate could be:

- the presence of a highly plasticized binder, and
- the presence of a coil-type structure of the cured binder, which at low temperature becomes unwound slowly during stretching, leading to a higher elongation.

## 4 Conclusions

The PI/Po ratio plays an important role for energetic nitrate ester plasticized polyol-based advanced energetic propellants, however beyond a PI/Po ratio of 2 there is no significant gain in density impulse. NG-plasticized propellants have a higher density and calorimetric value, however, the specific impulse of BTTN-plasticized propellants is greater at all PI/Po ratios. Plasticizers affect the burn rate and pressure exponent of a propellant. NG-plasticized propellants have 4-15% higher burn rate than BTTN-plasticized propellants, and the changes in burn rate and pressure exponent are more significant at higher pressure than at lower pressure. The thermal decomposition study by DSC showed five distinct peaks for all three compositions, with a reduction in the thermal decomposition temperature of HMX (221.80 °C for P-10, 227.40 °C for P-11 and 219 °C for P-12), and AP, due to the synergistic effect of AP on HMX decomposition,

which effectively reduces the onset temperature of HMX decomposition by approximately 60 °C, whilst at the same time AP decomposition is catalyzed by HMX's gaseous products. It was observed that elongation at break values of BTTN and NG/BTTN (1:1) plasticized propellants are significantly higher at a low crosshead rate than NG-plasticized propellant, which corresponds to long term storage at low temperature, implying that BTTN and NG/BTTN (1:1) plasticized propellants can be used for missiles having the requirement of very low storage temperatures.

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