Central European Journal of Energetic Materials, **2012**, *9*(1), 49-58
ISSN 1733-7178

Development of a Composite Propellant Formulation with a High Performance Index Using a Pressure Casting Technique

Kurva RAMESH, Shekhar N. JAWALKAR, Swati SACHDEVA, MEHILAL* and Bikash BHATTACHARYA

High Energy Materials Research Laboratory,
Pune-411021, India
**E-mail: drmehilal@yahoo.co.in*

Abstract: There is a continuous demand for high performance composite propellant formulations to meet future requirements. The performance of composite propellant formulations can be enhanced by the addition of energetic oxidizers, like ADN/HNF as well as an energetic binder & a plasticizer. However, on incorporation of energetic ingredients, the composition becomes sensitive, and thus processing, handling and transportation pose a greater threat. Therefore, a moderately high burn rate composition having a burn rate ~ 13-14 $mm \cdot s^{-1}$ at 7000 kPa was tailored by increasing the solid loading of the propellant from 85.15% to 87.27% with the help of ammonium perchlorate and process aids without affecting the burn rate and mechanical properties. The tailored composition was studied for different properties such as end of mix viscosity, density, mechanical & ballistic properties. The evaluated data reveal that the end of mix viscosity of the tailored composition is higher than the base composition, i.e., 672 $Pa \cdot s$ and 2340 $Pa \cdot s$ at the same temperature; however, this viscosity was castable using a pressure casting technique. The properties of the cured propellant reveal that there is an enhancement of density from 1.74 $g \cdot cm^{-3}$ to 1.79 $g \cdot cm^{-3}$ with no other changes in mechanical properties. The performance index of the tailored composition has been increased from 416 to 437, well supported by results of ballistic evaluation motors of 2 kg.

Keywords: composite propellant, high density, high performance index, pressure casting, solid loading

Introduction

Composite solid propellants are being used in various missile applications, basically containing ammonium perchlorate (65-70%), a metallic fuel like aluminum powder (15-20%) and a liquid binder such as hydroxyl terminated polybutadiene (10-15%), along with certain process aids and diisocyanate based curatives [1]. Composite propellant formulations based on AP/HTPB/Al have achieved their optimized performance. Therefore, there is a continuous effort to enhance the performance of composite propellant formulations. The performance of composite propellant formulations can be enhanced by the addition of an energetic oxidizer, like ammonium dinitramide (ADN), hydrazinium nitroformate (HNF), along with azide based polymers [2-5] such as glycidyl azide polymer (GAP), bisazidomethyloxetane (BAMO), and polyglycidyl nitrate (PLN). However, the major drawbacks of such compositions are difficulty in their processing and instability of azide polymers as high temperature curing causes degassing due to breakage of the $-N_3$ linkage of the binder.

In further continuation of this work, certain nitramine based high explosives like 1,3,5-trinitro-1,3,5,-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7,-tetraazacyclooctane (HMX) [6] and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) [7] have also been used extensively in composite propellants and their behavior has been studied in detail. The findings of these studies indicate that these compounds are capable of producing higher energy output compared to standard compositions as well as a higher performance index. The only drawback of nitramine based compositions is low burn rate and higher pressure index (n) value, and also the composition becomes sensitive, thus processing, handling and transportation possess a greater threat.

Further to this, different researchers have also studied in detail the effect of RDX and HMX on the performance index or the volumetric specific impulse, using only nitramine based compositions such as cross linked double base (XLDB), composite modified cast double base (CMCDB), nitrate ester plasticized polyether (NEPE) propellants [8], and claimed performance index increases on addition of AP and Al, respectively. However, the study referred to does not reveal any control on mechanical properties.

In view of the advantage of the performance index and keeping the same mechanical properties of the enhanced performance index composition, a systematic study was carried out by taking a moderately high burn rate composition having a burn rate 13-14 $mm \cdot s^{-1}$ at 7000 kPa with solid loading 85.15%, and incorporating coarse ammonium perchlorate and certain process aids to increase the performance index without affecting the burn rate and the mechanical properties. The tailored composition was studied for different properties such as end of mix viscosity, density, mechanical & ballistic properties.

In the following section, we report the development of high performance index propellant formulations using a pressure casting technique and comparison of the performance data of a 2 kg motor of the developed composition with that of the standard composition.

Experimental

Materials

Ammonium perchlorate (AP), supplied from M/s Pandian Chemicals Ltd., Cuddalore, was used in triamodal distribution having average particle sizes 300, 50 and 6 μm. Hydroxyl terminated polybutadiene (HTPB), manufactured by free radical solution polymerization, having a molecular weight (M_n) of 2560 with hydroxyl value of 43 mg KOH/g, was procured from M/s Anabond Ltd., Chennai. Aluminium powder, having average particle size 15 ± μm, was procured from M/s Metal Powder Company, Madurai (India) and used as such. Dioctyl adipate (DOA), toluene di-isocyanate (TDI), N-phenyl-2-naphthylamine (Nonox-D), trimethylolpropane (TMP), 1,4-butanediol (n-BD), copper chromite and iron oxide were also procured from trade and used as such.

Characterization

The particle sizes of the solid ingredients was determined by a Laser based CILAS Particle Size Analyzer, model 1064, France, in non-aqueous medium. The viscosity build-up was determined by a Brookfield viscometer, model HBT dial type. The mechanical properties like tensile strength, % of elongation and *E*-modulus of the cured propellant samples were also evaluated using dumb-bells on a tensile testing machine, Hounsfield, conforming to ASTM D638 at a cross head speed of 50 $mm\cdot min^{-1}$ at ambient temperature. The burning rate was determined by the acoustic emission technique [9]. The performance of the motor was evaluated using a motor of 2 kg grain having 115 mm outer diameter with 60 mm inner diameter and 200 mm length.

Method

All of the experimental mixing of the composite propellant was carried out at 5 kg batch level in a vertical planetary mixer. A general procedure for the preparation of the composition is described in detail.

To a planetary mixer (cap. 15 L) 504.0 g of prepolymer resin i.e. hydroxyl terminated polybutadiene (HTPB), 195.0 g of dioctyl adipate (DOA) as a plasticizer along with 2.5 g of antioxidant, i.e., N-phenyl-2-naphthylamine (Nonox-D) and 6.0 g of bonding agent, a mixture of 1,1,1-trimethylolpropane and 1,4-butanediol, except curative, were charged and the whole system was mixed well for 0.5 h followed by mixing under vacuum for another 0.5 h to drive out entrapped air. After this, 850.0 g Al powder (particle size ~15 µm) was added. After complete addition of Al, it was again mixed for another 0.33 h. Subsequently, 1.506 kg of ammonium perchlorate (avg. particle size 300 µm), 1.15 kg of ammonium perchlorate (avg. particle size 50 µm) and 0.85 kg of ammonium perchlorate (avg. particle size 6 µm) were added and mixed in such a way that homogenous mixing could take place. The overall mixing temperature was maintained at 50 ±2 °C. After addition of all the solid ingredients, the mixing of the composition was further carried out under vacuum for 0.5 h. In the mean time, the temperature of the mix was reduced to 40 ±2 °C. At this stage, 33.5 g of toluenedi-isocyanate (TDI) was added and further mixed for another 0.67 h.

The composite slurry, thus prepared, was cast using a pressure casting technique. In this technique, pressure on the propellant is exerted mechanically by using an hydraulic piston.

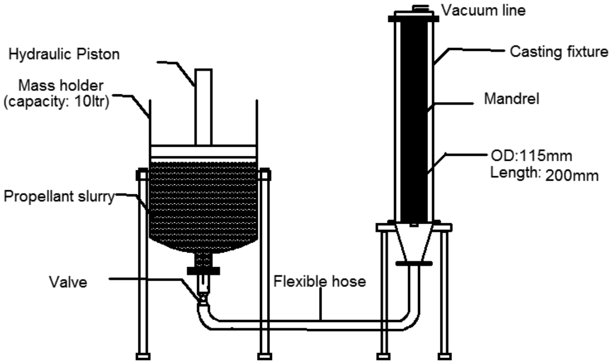


Figure 1. Schematic diagram of pressure casting using a hydraulic piston.

Pressure casting

During pressure casting, the initial propellant slurry was cast in a mass holder (capacity 10 L) under vacuum to remove any entrapped air bubbles. After this, the mass holder was taken out and kept under an hydraulic press aligned to an hydraulic piston. The pressure (up to 1 MPa) was applied on the propellant slurry. The propellant slurry was fed into a mould from the bottom through a flexible hose as depicted in Figure 1. After completion of casting, the mould was detached from the assembly and kept in a water jacketed oven for curing at 50 ±2 °C for 5 days. The mandrel was de-cored from the mould and its mechanical and ballistic properties evaluated.

Results and Discussion

To achieve a high performance index from the developed composite propellant formulations without affecting the mechanical and ballistic properties, the solid loading was increased from an initial 85.15% to 87.27%, and compositions thus prepared are presented in Table 1. Initially, based on Table 1, all the prepared compositions were at the 5 kg level for the evaluation of mechanical and ballistic properties. However, for the determination of the performance index, the same composition was cast using a pressure casting technique into a 2 kg motor for static testing. Further, the effect of a higher solid loading to achieve a higher performance index on viscosity build up, mechanical and ballistic properties are discussed here in detail.

Table 1. Formulation details of developed compositions

Ingredients	Standard composition (wt %)	Composition (I) (wt %)	Composition (II) (wt %)	Composition (III) (wt %)
HTPB+TDI	10.78	11.6	11.6	11.6
DOA	3.9	1.0	1.0	1.0
Adduct	0.12	0.12	0.1	0.09
n-BD	--	--	0.02	0.04
AP	67.7	70.0	70.0	70.0
Al	17.0	17.0	17.0	17.0
Ballistic modifiers and others	0.5	0.28	0.28	0.27

Effect of solid loading on viscosity build-up

The effect of solid loading on viscosity build-up is presented in Table 2. It is clear from the table that value of the end of mix (EOM) viscosity of the developed composition is very high in comparison to the standard composition. Thus, the end of mix viscosity of the developed composition is 2176 Pa·s at 38 °C while the value for the standard composition is 608 Pa·s at the same temperature. The viscosity build up is very fast in the case of the developed composition in comparison to that of the standard, where it reaches 4640 Pa·s after 3.5 h, whilst in the case of the standard this value is only 1064 Pa·s. The increase in the end of mix viscosity as well as the build-up may be attributed to the incorporation of a higher percentage of fine ammonium perchlorate as well as a lower percentage of dioctyl adipate (1%). The higher percentage of fine AP requires more liquid ingredients for wetting. As the percentage of DOA is less, it is not possible to wet it completely. Reduced wetting means low blanketing, which triggers a fast reaction between the –OH groups of HTPB and the –NCO groups of TDI, giving a faster build-up. However, the higher viscosity of the developed composition was cast successfully using a pressure casting technique which produced flawless grains.

Table 2. Data on viscosity build up for standard and developed compositions

Time (h)	Standard Composition Viscosity (Pa·s)	Developed Composition Viscosity (Pa·s)
End of mix	608	2176
0.5	640	2340
1	672	2400
1.5	690	2528
2	786	2784
2.5	914	2880
3	978	4000
3.5	1064	4640

Effect of solid loading on mechanical and ballistic properties

The mechanical properties of the cured propellant were determined at ambient temperature using a tensile testing machine, Hounsfield, at 50 mm·min^{-1} speed and the data obtained are presented in Table 3. It is clear from the table that the mechanical properties, such as tensile strength, Young's modulus and % elongation of the studied compositions number 1 and 2 are not close to the standard composition, whereas in the case of composition number 3, it is almost identical to the standard composition. The high increase in tensile strength of composition 1 and 2 is mainly due to reduction in DOA content (percentage was reduced from 3% to 1%).

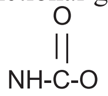
Moreover, to have values of the mechanical properties close to those of the standard composition, compositions numbers 1 and 2 were further modified with the help of certain process aids, mainly butanediol (n-BD), and the final values of the mechanical properties were brought into the same range, that is, tensile strength 0.9 to 1.01 MPa, *E*-modulus 3.5 to 4.0 MPa with % elongation 35 to 40%, meeting the values of the standard composition. In the presently studied composition with higher solid loading and reduced content of DOA, incorporation of a small percentage of 1,4-butanediol was found to be very effective in achieving mechanical properties as per the standard due to the presence of telechelic hydroxyl functional groups. These, after reaction with TDI, produce urethane linkages  $(\text{—}\,NH\text{-}\overset{\overset{O}{||}}{C}\text{-}O\,\text{—})$ which add extra elongation and reduce the modulus of the cured composition.

Table 3. Data on the mechanical and ballistic properties for the standard and the developed compositions

Composition	Tensile strength (MPa)	E – Modulus (MPa)	Elongation (%)	SSBR $mm \cdot s^{-1}$ at 7000 kPa	Density $(g \cdot cm^{-3})$
Standard composition	0.91	3.55	39.6	13.7	1.74
Composition (I)	1.69	10.15	23.6	13.7	1.79
Composition (II)	1.19	5.68	31.2	13.7	1.79
Composition (III)	0.9	3.72	40.1	13.7	1.79

The ballistic properties, such as the burning rate of the developed composition, was also studied using an acoustic emission technique at 7000 kPa, and the data obtained are presented in Table 3. It is clear from the table that the burning rate of all the studied compositions are in the range of 13.5 ±0.2 $mm \cdot s^{-1}$ at the specified pressure, meeting the objective of the present study. Furthermore, the density of the cured sample was determined following Archimedes principle and the data obtained are also presented in Table 3. The data reveal that there is a marked increase in density in comparison to the standard composition, that is, from 1.74 $g \cdot cm^{-3}$ to 1.79 $g \cdot cm^{-3}$ for the newly developed composition. The increase in density may be attributed to the higher loading of solid ingredients. This increase in density is one of the important factors in achieving a high performance index.

Performance of the ballistic evaluation motor

After achieving high density for the developed composition, whilst keeping the same mechanical properties, a 2 kg ballistic evaluation motor (BEM) was cast, cured and static tested. The *p-t* and *F-t* profile curves obtained are presented in Figure 2 and 3, respectively. It is clear from the figures that the *p-t* profile curve as well as the *F-t* profile curve are almost the same as those of the standard composition. The basic difference in both the curves is in their performance values which are presented in Table 4. The values of $\int P_c dt$, $\int F dt$, c^* and Isp are 257.11, 9192.78, 1575.99 and 239.08 for the standard composition, whereas the values for the developed composition are 268.99, 9799.22, 1610.34 and 244.13, respectively. The new composition has thus an edge over the standard composition. The performance index value of the developed composition, obtained by multiplying density and Isp, is 437 in comparison to 416 for the standard composition.

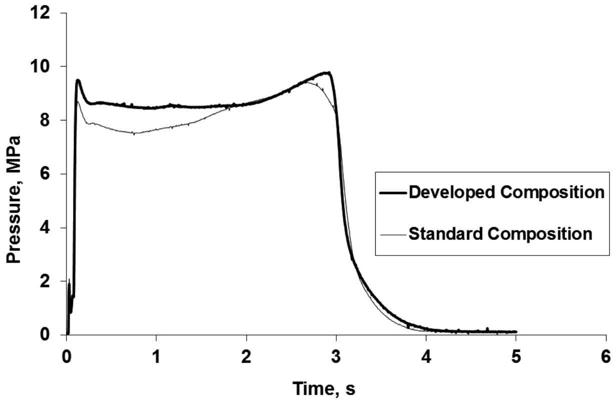


Figure 2. *p-t* profile curves of the developed and the standard compositions.

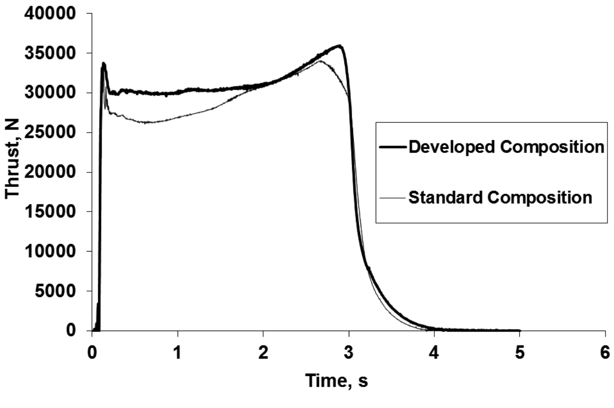


Figure 3. *F-t* profile curves of the developed and the standard compositions.

Table 4. Data on density, *Isp* and performance index for the standard and the developed compositions

	Density (g cm^{-3})	$\int P_c dt$	$\int F\, dt$	c^* ($m\ s^{-1}$)	*Isp* (*s*)	Performance index
Standard composition	1.74	257.11	9192.78	1575.99	239.08	416
Developed composition	1.79	268.99	9799.22	1610.34	244.13	437

Conclusion

A new composition with a high performance index having 87.27% solid loading, meeting the mechanical and ballistic properties of a composition with 85.15% solid loading, has been successfully developed. The performance index of the developed composition is 437 in comparison to 416 for the base composition. The developed high performance index composition may find application where such characteristics are needed to meet the ballistic requirement.

References

[1] *Propellants, Manufacturing, Hazards and Testing, American Chemical Society*, (Boyars C., Klager K., Eds), Washington D.C, **1969**, p. 88.

[2] Langlet A. , Wingborg N., Ostmark H., ADN: A New High Performance Oxidizer for Solid Propellants, *International Journal of Energetic Materials and Chemical Propulsion*, **1997**, *4*, 1-6.

[3] Gadiot G.M.H.J.L., Mul J.M., Meulenbrugge J.J., Korting P.A.O.G., Schnorkh A.J., Schoyer H.F.R., New Solid Propellants Based on Energetic Binders and HNF, *Acta Astronautica*, **1993**, *29,* 771-779.

[4] Gadiot G.M.H.J.L, Hoffmans D.W., Korting P.A.O.G., Leenders A.P.M., Clean Propellants for Commercial Applications, *International Journal of Energetic Materials and Chemical Propulsion,* **1997**, *4*, 1-6.

[5] Schoyer H.F.R., Schnorkh A.J., Korting P.A.O.G., van Lit P.J., First Experimental Results of an HNF/Al/GAP Solid Propellant, *AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit*, T.L. 33rd, Seattle, WA, July 6-9, **1997**.

[6] Muthiah R.M., Varghese, Rao S.S., Ninan K.N., Krishnamurthy V.N. Realization of an Eco-friendly Solid Propellant Based on HTPB-HMX-AP System for Launch Vehicle Applications, *International Journal of Energetic Materials and Chemical Propulsion*, **1997**, *4*, 1-6.

[7] Yang R., An H., Tan H., Combustion and Thermal Decomposition of HNIW and

HTPB/HNIW Propellants with Additives*, Combustion and Flame*, **2003**, *135*, 463-473.

[8] Couturier R., Advanced Energetic Binder Propellants, in: *Solid Rocket Propulsion Technology,* (A. Davenas, Ed.), Pergamon Press, Oxford, **1993**, pp. 510-511.

[9] Caveny L.H., Pokrocos L. M., Lelshain G.R., *High Pressure Burning Rates of Multibase Propellants*, Department of Aerospace and Mechanical Sciences, Princeton University, New Jersey, AMS-1377, **1977**, 75.