Research paper

Studies on rheological properties and process parameters of TNT based castable high explosive compositions

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Abstract

High explosive compositions are formulated and used depending on their properties like performance parameters, processabilty, sensitivity, storage life, etc. TNT, RDX and HMX are commonly used high explosives. Although, the performance of TNT is inferior compared to RDX and HMX, but it is widely used as an energetic binder/ casting medium in compositions due to its low melting point, insensitivity and its stability in molten condition. Energetic materials like RDX/HMX are incorporated into TNT filling to increase the efficiency of the composition. Rheological behavior is one of the most important factors in determining the ease of processing of castable materials. The mixing parameters and physical characteristics of ingredients in the composition influence the rheological behavior of the composition and quality of high explosive filling. To achieve free flowing castable and processable compositions, a systematic study on the parameters such as proportion of HMX, particle size of HMX, temperature of melt, mixing duration and stirring rate/speed on viscosity of the composition was carried out. In addition to this, the sensitivity and performance parameters of the formulations were also evaluated.

Keywords: HMX, TNT, viscosity, performance, temperature of melt

1. Introduction

High explosives are used to achieve the desired terminal effect, i.e., destruction of tactical and strategic targets. The effectiveness of an explosive depends on two factors namely, the amount of energy available in the explosive and the rate of release of available energy when the explosion occurs. These functional properties can be optimized by adopting an appropriate processing method to achieve the desired quality of filling. Processing of high explosives[1] is the method of working/operations required, during the manufacture of various types of charges. The operations include establishing process parameters and defect free filling/loading technique for various explosive formulations taking into account the sensitivity and stability of the explosive compounds/composition and rheological properties of the composition.

The prime methods for loading of high explosives are casting and pressing method. Castable compositions[2] are flowable (relatively viscous) fluids at ambient or elevated temperatures. These compositions are melt-cast in TNT based explosive compositions or cast-cured as in the case of castable PBXs[3]−[5] whereas pressable compositions[6] are free flowing moulding powders compressible to desired shape and dimensions.

TNT is widely used as filling as well as a molten medium for most high explosive melt-cast fillings due to its conveniently low melting temperature (80.6 °C), its stability in molten condition for relatively long periods, high decomposition temperature (240 °C) well separated from its melting point and stable over the normally encountered environmental temperature range[1]. The major demerit with TNT is shrinkage of 10.8% by volume

giving rise to wide range of defects like voids, air pockets, Cracks, piping, etc. It is also relatively less powerful, thus, energetic compounds like RDX/HMX are incorporated into TNT filling to increase the efficiency of the composition. RDX/HMX remains suspended in the liquid TNT during the process and molten TNT on solidification acts as an energetic binder for RDX/HMX crystals, which are uniformly distributed in the filling.

Rheological behavior[7] of a material depends on time and space scales of observation/experiment. The former is important as a measure of the ratio of the rate of inherent processes in a material to the time of experiment or observation. The latter determines the necessity to treat a material as homogeneous or heterogeneous. What makes high explosive materials interesting in this context is the fact that their time constants for flow are not of the same order of magnitude as their processing times for casting. Under the ambient temperature these are solids, while in very short processing times, they may behave as a fluid/viscous material. This dual nature (fluid-solid) is referred to as visco-elastic behavior. Hence studies of viscosity/rheological testing of composition used as filling in casing becomes very vital.

The rheology of composition-B and a dependency of viscosity upon the particle shape, size and distribution of RDX were studied[8]. The authors concluded that high explosive compositions are dilatants, thixotropic, pseudoplastic and non-Newtonian. The flow behaviour of pure and commercial molten TNT when subjected to very high rates of shear in a rotational viscometer over the temperature range of 82.0 to 95.4 °C was studied[9] and investigated the effect of stirrer speed and its design on change in particle size and viscosity. A shear-thinning viscosity model was developed[10] for molten composition-B at elevated temperature using falling ball viscometer data.

The particle size and its shape have been widely accepted as the vital factors affecting the viscosity of melts. These factors can also be correlated with a single parameter namely the specific surface area of the solid particles affecting the viscosity of the melt. Hence, a systematic study on the parameters such as proportion of HMX, particle size of HMX, temperature of melt, mixing duration, stirring rate/speed, and viscosity of the composition was carried out to correlate the effect of each parameter on viscosity of the compositions along with sensitivity and performance parameters.

2. Experimental
2.1 Materials

HMX powder prepared in-situ having bimodal (125–250 µm and 125 µm) and trimodal (500–800 µm, 250–500 µm and 250 µm) combinations with varying proportions of particle sizes were used to study bulk density, average particle size and specific surface area. TNT was obtained from High Explosives Factory, Pune and used as such without further purification. Castable compositions were prepared by varying the proportion of HMX/TNT. The details of the compositions and proportion of HMX particle sizes are given in Table 1.

Table 1   Details of HMX/TNT based compositions.

Sl. No.	Composition HMX/TNT	Proportion of HMX Particles [µm]
I	0/100	—
		Bimodal 125–250/125
II	10/90	60/40
III	20/80	60/40
IV	30/70	60/40
V	40/60	60/40
VI	50/50	60/40
		Trimodal 500–800/250–500/250
VII	60/40	25/40/35
VIII	70/30	25/40/35

2.2 Characterization

Particle size and specific surface area of HMX combinations were determined using particle size analyzer (CILAS, Model 1064L). Brookfield Digital Viscometer, Model DV-I was used for measurement of viscosity of the melts. The bulk density on various particle sizes of HMX combinations was determined using densitometer. The velocity of detonation (VOD) was determined by ionization probe technique. The pin type ionization probes (twisted enamelled copper wire) placed at a predetermined points used as sensors for detecting the arrival time of detonation wave and recorded by oscilloscope (YOKOGAWA DL9140, 1 GHz). The impact sensitivity of composition was determined by using fall hammer test apparatus applying Bruceton Staircase Method[11]. Friction sensitivity was determined on Julius Peters apparatus operating up to 360 N using standard methodology[12].

3. Results and Discussion
3.1 Effect of particle size of HMX combination on specific surface area and bulk density

The different ratio of bimodal and trimodal HMX particle size combinations and their characteristics, i.e., mean diameter, surface area and bulk density are presented in Table 2. It is clear from the table that bimodal combinations corresponding to mean diameter of 120–125 µm realized bulk density to 1213 kg m^{-3}. The table also infers that the specific surface area increases with decrease in mean diameter. Further, bulk density versus different ratios of bimodal and trimodal particle size of HMX combinations were also plotted (Figure 1 and Figure 2) and these figures are parabolic in nature. The Figure 1 reveals that bulk density of bimodal HMX increases steeply from 10/90 to 40/60 combinations and found constant for combinations of 50/50 and 60/40 followed by decrease in higher ratios. In the same way, Figure 2 infers that bulk density of particle size of HMX combinations also increases from 10/40/50 to 25/40/35 ratios and the maximum value lies between 25/40/35 and 40/40/20 ratio.

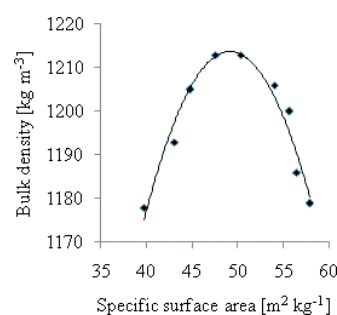Further, specific surface area of bimodal particle size of

Table 2   Bimodal and trimodal particle size combination of HMX.

Sr. No.	Different particle size [μm] ratios of HMX					Mean diameter [μm]	Specific surface area [m² kg⁻¹]	Bulk density [kg m⁻³]
	125–250	125	500–800	250–500	250			
1	90	10	—	—	—	140.46	39.755	1178
2	80	20	—	—	—	136.31	43.081	1193
3	70	30	—	—	—	131.86	44.769	1205
4	60	40	—	—	—	125.85	47.551	1213
5	50	50	—	—	—	119.71	50.320	1213
6	40	60	—	—	—	114.58	54.008	1206
7	30	70	—	—	—	108.34	55.663	1200
8	20	80	—	—	—	104.70	56.452	1186
9	10	90	—	—	—	100.02	57.894	1179
10	—	—	10	40	50	166.12	38.333	1246
11	—	—	25	40	35	171.54	39.919	1311
12	—	—	40	40	20	179.75	40.161	1280
13	—	—	50	40	10	199.25	38.391	1238
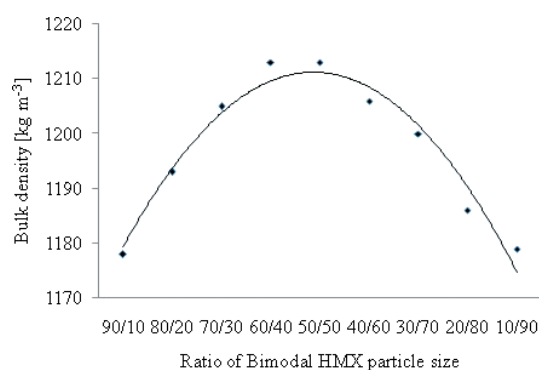
Figure 1   Effect of bimodal ratio of HMX particle sizes on bulk density.
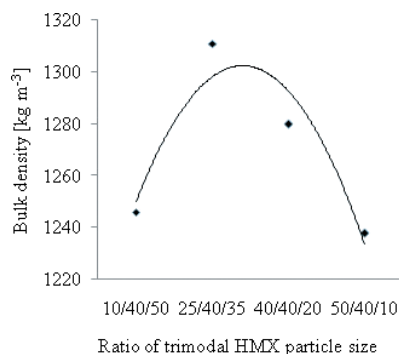
Figure 2   Effect of trimodal ratio of HMX particle sizes on bulk density.

HMX combinations versus bulk density was also plotted (Figure 3), is parabolic in nature, and similar trend was observed as a Figure 1.

The above study infers that bulk density of powders depends upon the shape and ratio of volume to surface area of the particles, which are function of the mean diameter of particles. The specific surface area of finer particles is large while the volume is small as they vary with the square and cube of the diameter, respectively. On the other hand, the packing of exclusively medium and coarse particles is not optimum due to interstitial voids between the particles. Thus, optimum packing density can

Figure 3   A plot of specific surface area of bimodal HMX combinations and bulk density.

be achieved by taking an appropriate combination of different particle sizes to minimize the voids. The maximum bulk density achieved for bimodal HMX is about 1213 kg m⁻³, while for the trimodal it is about 1311 kg m⁻³. This could be attributed to the mean diameters of the different particles that govern the specific surface area of each combinations and filling the voids between the particles. Hence, in the present study, bimodal and trimodal HMX having particle size combinations of 60/40 and 25/40/35, respectively, were chosen.

3.2 Effect of HMX content on viscosity

Viscosity of various HMX/TNT compositions (as shown in Table 1) was measured at 90 °C temperature and data obtained are shown in Figure 4. The figure infers that on increasing content of HMX in TNT melt viscosity increases accordingly. It is observed that there is a gradual increase in viscosity up to 40% content of HMX whereas drastic increase in viscosity was observed beyond 40% content of HMX in TNT melt. This may be due to simultaneous increase of solid suspension and decrease of liquid TNT content in the composition. However, it was observed that HMX content beyond 70% resulted in non-flowable and semi-solid nature of composition hence, viscosity of such compositions could not be measured.
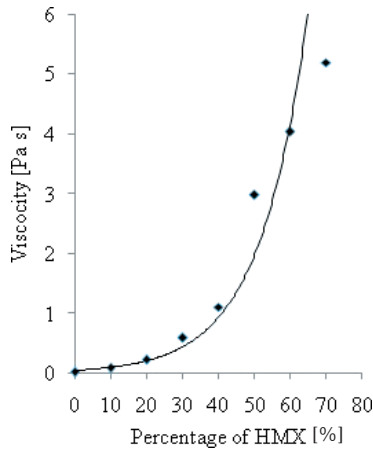
Figure 4   Effect of HMX proportion on viscosity of molten HMX/TNT compositions.

Table 3   Effect of temperature on viscosity.

Composition	Viscosity [Pa s]			
	82 °C	85 °C	90 °C	95 °C
I	0.100	0.050	0.032	0.030
II	0.360	0.130	0.092	0.080
III	0.825	0.660	0.230	0.190
IV	1.300	1.020	0.600	0.540
V	5.450	3.950	1.120	0.970
VI	9.600	6.950	2.990	2.400
VII	10.600	7.385	4.050	3.580
VIII	12.650	8.025	5.200	4.740
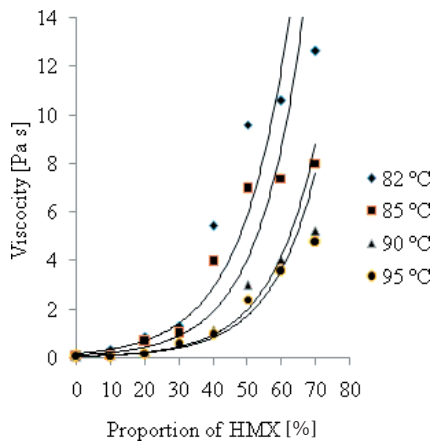
Figure 5   Effect of temperature on viscosity of molten HMX/TNT compositions.

3.3 Effect of temperature on viscosity

Viscosity of various HMX/TNT formulations was measured at four different temperatures (82, 85, 90, 95 °C) and data obtained are shown in Table 3 and Figure 5. It is clear from both Table 3 and Figure 5 that as content of HMX increases in TNT melt, viscosity increases accordingly. Further, a substantial decrease in viscosities was observed on increase of temperature from 85 to 95 °C. The trend of differential decrease of viscosity with increase in temperature can be attributed to the behavior of the molten TNT component at experimental temperatures. The heat capacity of TNT varies in the temperature range of 83–120 °C can be explained by the following equation[13]

$$\Delta H = 0.045 - 0.246\,T + 4.205 \times 10^{-4}\,T^2$$

where, ΔH is heat capacity (J/mol), and T is temperature.

The above equation implies that viscosity decreases at high temperatures due to high heat capacity and molecular freedom of motion therefore, proportion of TNT in various HMX/TNT compositions and particle sizes of HMX govern the viscosity and flow property of the composition.

3.4 Effect of mixing duration on viscosity

Prior to determination of viscosity, the composition was stirred at 100 rpm for 2.5 hr at 90 °C in a kettle. The homogenous composition obtained was transferred to a preheated vessel and viscosity was measured at a interval of 0.5 hr by maintaining the same temperature. The effect of mixing duration on viscosity of HMX/TNT compositions is given in Table 4. It can be seen from the Table 4 that there is no substantial increase in viscosity was observed for the compositions having bimodal HMX loading up to 50% but an increasing trend was observed for 60/40 and 70/30 HMX/TNT compositions based on trimodal HMX up to 1.5 h and beyond that no significant change in viscosity. The marginal increase in viscosity of compositions up to 50% HMX loading may be due to streamlining of particles without any formation of major aggregates. The initial build up of viscosity with increase in mixing duration for higher loading of HMX may be attributed to the formation of aggregates/agglomerates of HMX and dissolving process of HMX in molten TNT.

Table 4   Data on viscosity for HMX/TNT combinations at different mixing duration.

Composition	Viscosity [Pa s]					
	Duration of Mixing [h]					
	0.0	0.5	1.0	1.5	2.0	2.5
I	0.030	0.032	0.032	0.032	0.032	0.032
II	0.097	0.105	0.110	0.117	0.122	0.122
III	0.240	0.270	0.300	0.350	0.360	0.360
IV	0.610	0.650	0.660	0.680	0.720	0.730
V	1.160	1.170	1.210	1.240	1.270	1.280
VI	3.150	3.180	3.220	3.310	3.360	3.360
VII	4.050	4.500	4.800	4.950	5.050	5.100
VIII	5.200	5.420	5.500	5.580	5.590	5.600
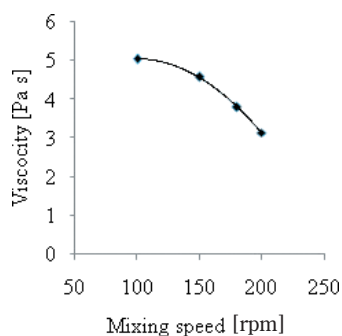
Figure 6   Effect of stirring rate on viscosity of HMX/TNT (60 /40) composition.

Further, the increase in viscosity of molten TNT is due to dissolution of HMX in TNT proportional to the quantity of HMX content in the composition. As there is a simultaneous increase of solid HMX content and decrease of molten TNT in the compositions, the effect of dissolution is more prominent in compositions with higher loading of HMX. The duration of mixing beyond which viscosity remains constant is called as optimum mixing time. The figure reveals that the optimum mixing time is about 1.5 h for HMX/TNT 60/40 and 70/30 compositions. Thus the mixing time for these compositions was limited to 2.5 h assuming that no further increase in viscosity.

3.5 Effect of stirring rate on viscosity

The effect of stirring rates of 100, 150, 180 and 200 rpm for 2 h on viscosity of HMX/TNT (60/40) composition (particle size of HMX : 500−800μm/250−500μm/250μm, 25 /40/35) was measured at 90°C temperature and data obtained are presented (Figure 6). It is clear from Figure 6 that viscosity of the composition decreases in a nearly linear fashion with increase in stirring speed. The decrease in viscosity may be attributed to high rate of shearing of molten TNT. The high shear rate breaks the aggregates formed during the prolonged stirring of the solid ingredients at constant string rate and other electro viscous bonds.

3.6 Effect of mean diameter of HMX on viscosity

The effect of mean diameter of bimodal HMX particles on viscosity of HMX/TNT compositions having loading of HMX from 10 to 50% were carried out (Table 5). It is clear from Table 5 that there is a marginal decrease in viscosity was observed on increase of mean diameter of HMX particles which may be due to decrease of specific surface area and better packing.

3.7 Performance and sensitivity properties of HMX/TNT compositions

The performance of HMX/TNT as well as sensitivities to impact and friction were determined by using standard methods (Table 6). The data in Table clearly reveal that density and velocity of detonation (VOD) increases linearly with the proportion of HMX. The figure of insensitiveness (FoI) decreases on incorporation of HMX in TNT melt from 94 to 47 compared to TNT (FoI 130). It may be due to substitution of impact sensitive ingredient HMX (FoI 60) in

Table 5   Effect of mean diameter on viscosity (bimodal HMX) (at $t = 0$ mixing time).

Composition	Viscosity [Pa s]				
	Mean Diameter [μm]				
	100	104	108	115	120
II	0.107	0.107	0.105	0.097	0.092
III	0.320	0.290	0.250	0.240	0.230
IV	0.740	0.710	0.680	0.610	0.600
V	1.230	1.200	1.200	1.160	1.120
VI	3.520	3.220	3.180	3.150	2.990

Table 6   Performance and sensitivity properties of HMX/ TNT formulations.

Composition	Density [kg m^{-3}]	VOD [m s^{-1}]	Sensitivity	
			FoI	Friction [N]
I	1580	6837	130	360
II	1610	6973	94	360
III	1630	7095	87	360
IV	1660	7288	72	324
V	1690	7543	70	324
VI	1720	7855	66	324
VII	1770	7990	48	324
VIII	1800	8100	47	288

place of less sensitive TNT (FoI 130). The low FoI value for 60/40 and 70/30 HMX/TNT compositions is due to the coarser particles in trimodal HMX. The coarser particles are more prone to kinetic energy (impact) reaction thereby releases the energy leading to explosion. Further, all the studied compositions were found insensitive towards friction. This may be due to uniform coating of TNT over HMX particles which absorb rubbing energy generated from friction because of heat sink nature of TNT.

4. Concluson

A successful study has been carried out by taking bimodal and trimodal HMX in different ratios and determined their physical characteristics followed by incorporation in TNT melt. The effect of stirring rate, mixing duration and temperature on viscosity on incorporation of bimodal and trimodal HMX in TNT melt was studied. The data reveal that optimum bulk density of bimodal and trimodal was found to be 1213 kg m^{-3} and 1311 kg m^{-3}, respectively. Further, there is a decrease in viscosity was observed as increasing in temperature and stirring rate, however, a marginal increase in viscosity was observed with increasing duration of mixing. The performance and sensitivity of the studied compositions were increased on increase of HMX content in the TNT melt.

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