1. INTRODUCTION

Sheet explosive\(^1\) is a flexible polymer bonded explosive (PBX) comprises energetic materials like hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)/octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) uniformly dispersed in a polymeric matrix. High energy materials (HEMs) such as RDX, HMX, etc., in explosive formulations provide the power/energy to achieve desired performance for the system. Polymeric materials such as hydroxyl terminated polybutadiene (HTPB), ethyl vinyl acetate (EVA), natural rubber provide continuum for dispersion of energetic materials and play vital role in deciding structural integrity and flexibility as well as safety during handling and transportation of sheet explosives. In addition to metal cutting, demolition and metal welding, sheet explosive is an important component of explosive reactive armour (ERA)\(^2-4\). ERA consists of sandwiched sheet explosive which provide additional protection to armoured vehicles including tanks against attack by projectiles and shaped charge warheads. Conventional explosives such as RDX/TNT and HMX/TNT have drawbacks such as poor mechanical properties and a rather high sensitivity. Improvement in these parameters can be achieved by the use of polymeric binder systems.

RDX-based sheet explosive formulations with various binders like natural rubber and thermoplastic elastomers (TPEs) such as copolymers of ethylene and vinyl acetate [ethylene vinyl acetate (EVA) copolymers] and Estane have been studied\(^5-6\). These formulations were prepared by rolling process. The pentaerythritol tetranitrate (PETN)-based high energy sheet explosive formulation (DXD-19) was prepared by extrusion process and average value of the velocity of detonation was reported to be 7200 m/s\(^7\). Among low molecular weight polymers like hydroxyl terminated polybutadiene have been found wide application in the area of propellants and PBXs\(^8\) due to the presence of higher fuel content, clean curing reaction and stable urethane linkage formed by isocyanate curatives. HMX-based PBXs with various polymer matrices have been formulated and investigated\(^9,10\). The velocity of detonation and impact sensitivity for castable HMX-based formulation with 20 per cent HTPB-IPDI binder system was reported to 8020 m/s and 8.44 J, respectively\(^11\). The velocity of detonation of RDX and HMX-based formulations with 18 per cent HTPB-HMDI binder system was also reported to 7526 m/s and 7812 m/s, respectively\(^12\). HTPB-based sheet explosive formulations have also been reported\(^13,14\).

Thermal characterisation and analysis of energetic materials and their formulations are important not only for understanding the kinetics of their thermal decomposition, but also for assessing the effect of their exothermic decomposition on the potential hazards in their handling, processing, and storage\(^15,16\). Thermal characterisation of PBX containing RDX or HMX with HTPB-binder has been reported by different authors\(^17-21\).

The performance, sensitivity and thermal analysis data obtained from HMX-based sheet explosive formulation have been compared in this paper with the existing conventional RDX-based sheet explosive formulation\(^13,14\).
2. EXPERIMENTAL

2.1 Materials

HMX (particle size: 10 µm) and RDX (particle size: 5 µm - 6 µm) were used as energetic materials in sheet explosive formulations. HMX and RDX were obtained from in-house developed resources. HMX and RDX were coated with 6 per cent dioctyl phthalate (DOP) to enhance the safety aspects during the processing of explosive formulations.

HTPB was obtained from Anabond, India and dioctyl adipate (DOA) procured from local source was added as plasticizer. 4,4’-Methylene diphenyl diisocyanate (MDI) was procured from trade and added as curative. The formulations were processed by solventless technique.

2.2 Characterisation Methods

The mechanical properties of formulations were determined using Hounsfield Universal Testing Machine (capacity 25 kN) at a strain rate of 50 mm/min. The samples were prepared according to ASTM D638 type IV. The density was measured by standard method using Archimedes principle. The impact sensitivity of the sheet explosive formulations were determined by using the fall hammer method (2 kg drop weight) as per the Bruceton staircase approach and results are given in terms of statistically obtained 50 per cent probability of explosion (h50). A set of 25 experiments was conducted at various height intervals for each formulation. The friction sensitivity was determined on a Julius Peters apparatus operating up to 360 N using standard methodology. The shock sensitivity was measured by aluminium block gap test to determine the minimum pressure of a shock wave that can initiate detonation of the sheet explosive sample (diameter 63 mm, thickness 7 mm). A cylindrical pressed RDX:Wax (95:5) of diameter 30 mm and height 100 mm was used as a donor charge to generate the shock wave. The wave was allowed to pass through an aluminium block of 63 mm diameter with a height varying from 10 mm to 30 mm. The critical pressure (P) in GPa across the aluminium block by which the sheet explosive can be detonated with 50 per cent probability was determined from the following relation.

\[ P = 50.28 \times 10^{0.0003x} \]

where \( x \) = thickness of the Al block in mm

The velocity of detonation (VOD) was determined by the ionisation probe technique in which the pin type ionisation probes (twisted enamel copper wire) placed at predetermined points used as sensors for detecting the arrival time of detonation wave and recorded by the oscilloscope (YOKOGAWA DL9140, 1GHz).

Thermal analysis was carried out by a differential scanning calorimeter (Perkin Elmer DSC-7). Approximately 0.5 mg of sample was taken at various heating rates at 5 °C/min - 20 °C/min in the temperature range of 50 °C - 350 °C for the determination of the exothermic decomposition temperature. The activation energy and thermokinetic parameters of formulations were determined by applying the Kissinger kinetic equation,

\[ \ln \left( \frac{\beta}{T_p^2} \right) = \ln \left( \frac{A R}{E_a} \right) - \frac{E_a}{RT_p} \]

where \( \beta \) is the heating rate (°C/min), \( T_p \) is the exothermic decomposition (peak) temperature (K), \( A \) is the pre-exponential factor (frequency factor), \( E_a \) is the activation energy (kJ/mol) and \( R \) is the gas constant (8.314 J/K mol).

Prior to processing the sheet explosive formulations, the theoretical performance prediction of HMX based sheet explosive formulations using BKW code which is based on FORTRAN executable program was carried out. The value of \( a \), \( b \), \( \theta \) and \( \kappa \) were taken as 0.5, 0.16, 400, and 10.91, respectively, to determine the theoretical VOD, where \( a \), \( b \), \( \theta \) and \( \kappa \) are BKW equation constants. The theoretical maximum density (TMD) was calculated by using formula as \[ \text{TMD} = \frac{\Sigma W_i/\Sigma W_i/\rho_i}{} \] where, \( W_i \) is weight percentage of \( i \) component, \( \rho_i \) is density of \( i \) component. The theoretical data for sheet explosive formulation RDX/HTPB-binder (80/20), HMX/HTPB-binder (80/20) and HMX/HTPB-binder (78/12) are given in Table 1. The VOD of explosives and formulations was calculated at TMD. The formula weight of sheet explosive formulations was taken as 100 g. The oxygen balance for RDX, HMX and sheet explosive formulations is determined using standard formula.

2.3 Theoretical Performance Prediction

The binder HTPB alongwith dioctyl adipate (DOA), lecithin and ferric acetyl acetonate (FeAA) were added into sigma blade mixer (speed: 35 RPM) and the ingredients were mixed under controlled vacuum condition at 40 °C - 50 °C for about 15 min. The DOP coated RDX or HMX was added to the polymeric matrix and mixed for about 2 h under vacuum at 40 °C - 50 °C. Subsequently, the temperature was brought down to ~25 °C and MDI was added. The mixing was continued for another 30 min - 40 min. The dough was kept for partial curing under controlled relative humidity at room temperature. The

<table>
<thead>
<tr>
<th>Explosives and formulations</th>
<th>Formula</th>
<th>TMD (kg/m³)</th>
<th>Calculated VOD (m/s)</th>
<th>Detonation pressure (GPa)</th>
<th>Oxygen balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RDX</td>
<td>C₃H₄N₂O₇</td>
<td>1816</td>
<td>8819</td>
<td>35.4</td>
<td>-21.61</td>
</tr>
<tr>
<td>RDX/HTPB-binder (80/20)</td>
<td>C₂₀H₂₆N₂₂O₁₉</td>
<td>1522</td>
<td>7389</td>
<td>20.9</td>
<td>-78.56</td>
</tr>
<tr>
<td>HMX</td>
<td>C₃H₄N₂O₇</td>
<td>1900</td>
<td>9161</td>
<td>39.6</td>
<td>-21.61</td>
</tr>
<tr>
<td>HMX/HTPB-binder (80/20)</td>
<td>C₂₀H₂₆N₂₂O₁₉</td>
<td>1567</td>
<td>7568</td>
<td>22.5</td>
<td>-78.56</td>
</tr>
<tr>
<td>HMX/HTPB-binder (78/22)</td>
<td>C₂₀H₂₆N₂₂O₁₉</td>
<td>1540</td>
<td>7464</td>
<td>21.4</td>
<td>-84.14</td>
</tr>
</tbody>
</table>
semi-cured dough was rolled between two rollers at ambient temperature to obtain sheets of desired thickness. Curing of sheet explosive was carried out at room temperature for 24 h in a controlled relative humidity.

3. RESULTS AND DISCUSSION

In order to handle materials in safe manner, energetic materials such as RDX and HMX were coated with 6 per cent dioctyl phthalate. The high surface tension of the liquid binder can hamper the wetting of the explosive particles. Therefore, a surface active agent lecithin was incorporated as processing aid to reduce the surface tension for better mixing.

The practically, maximum 78 per cent loading of HMX in HTPB-binder was achieved. It may be due to various factors such as packing patterns, shape and morphology of the HMX particles.

The results on density and tensile strength, percentage elongation of the formulations are given in Table 2. It is clear from the Table 2 that formulations containing HMX exhibited higher density and marginally lower tensile strength compared to reference formulation (RDX/HTPB, 80/20). The SEM images for RDX, HMX and sheet explosive formulations (Fig. 1) were revealed that solid particles uniformly distributed in the polymeric matrix and mostly particles are coated with

![Figure 1. SEM Images for (a) RDX, (b) RDX/HTPB (80/20), (c) HMX, and (d) HMX/HTPB (78/22).](image)

<table>
<thead>
<tr>
<th>Formulations</th>
<th>Density (kg/m³)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation (per cent)</th>
<th>Sensitivity parameters</th>
<th>Experimental VOD (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMX/HTPB-binder (78/22)</td>
<td>1470</td>
<td>0.9</td>
<td>12</td>
<td>Impact, h₅₀ (J): 10.8, Friction (N): &gt; 360, Shock (GPa): 12.5</td>
<td>7300</td>
</tr>
</tbody>
</table>
The sensitivity characteristics of the RDX/HMX-HPB sheet explosives are given in Table 2.

HMX-based sheet explosive gave higher impact sensitivity ($h_{50}$) of 10.8 J compared to RDX-based formulation (14.7 J). In shock sensitivity test, the 50 per cent probability of detonation of HMX/HPB formulation was found at 12.5 GPa which is more sensitive compared to 16.0 GPa for RDX-based formulation. The VOD of formulation containing HMX was found to be 7300 m/s which is relatively higher to RDX based reference formulation as shown in Table 2. It may be an outcome of optimised packing of solid particles for HMX in formulation which is also reflected in density difference of both formulations. The trends in experimental VOD of sheet explosive formulations in this study were confirmed by calculated VOD based on BKW code (Table 1).

Higher sensitivity of sheet explosive formulation to shock stimuli is required for initiation by kinetic energy projectile because KE projectile is made from metallic penetrator to create low shock pressure on target than chemical energy projectile (explosive warhead). The sheet explosive formulation containing HMX was found to be more sensitive in terms of shock stimuli and higher VOD compared to the reference RDX/HPB formulation.

The thermal analysis for both the sheet explosive formulations was studied using differential scanning calorimetric (DSC) technique at various heating rates, $\beta$ (5 °C/min, 10 °C/min, 15 °C/min, and 20 °C/min). The decomposition exothermic peaks for RDX/HPB (80/20) and HMX/HPB (78/22) were observed in the range 220 °C - 239 °C and 260 °C- 279 °C, respectively at different heating rates (5 °C/min, 10 °C/min, 15 °C/min, and 20 °C/min) and shown in Table 3 and Figs. 2 and 3. It was also observed that decomposition peak shifts toward higher temperatures with increasing heating rate.

The activation energies were calculated from the peak temperature ($T_p$) for maximum reaction rate for decomposition of sheet explosive formulations using Kissinger kinetic equation. Kissinger plots of these formulations are shown in Fig. 4 and the calculated data are given in Table 3. The activation energies of RDX/HPB (80/20) and HMX/HPB (78/22) formulations were observed about 146.90 kJ/mol and 170.08 kJ/mol, respectively. The results also indicate that HMX based formulation is more thermally stable than reference formulation. The activation energy for RDX/HPB (80/20) and HMX/HPB (80/20) formulations has been reported as 157 kJ/mol - 159 kJ/mol and 182 kJ/mol - 187 kJ/mol, respectively\textsuperscript{18,21}. The reason for difference in activation energies between results for studied formulations and the references might be the purity.

### Table 3. Kinetic parameters for sheet explosive formulations

<table>
<thead>
<tr>
<th>Formulations</th>
<th>$\beta$ (°C/min)</th>
<th>$T_p$ (°C)</th>
<th>$T_p$ (K)</th>
<th>$\ln(\beta/T_p)$</th>
<th>$\lnA$ (min$^{-1}$)</th>
<th>$E_a$ (kJ/mol)</th>
<th>$\lnA$ (min$^{-1}$)</th>
<th>linear correlation co-efficient ($r^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RDX/HPB (80/20)</td>
<td>5</td>
<td>220.17</td>
<td>493.32</td>
<td>2.03</td>
<td>10.79</td>
<td>146.90</td>
<td>34.87</td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>228.50</td>
<td>501.65</td>
<td>1.99</td>
<td>10.13</td>
<td></td>
<td></td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>234.26</td>
<td>507.41</td>
<td>1.97</td>
<td>9.75</td>
<td></td>
<td></td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>239.00</td>
<td>512.15</td>
<td>1.95</td>
<td>9.48</td>
<td></td>
<td></td>
<td>0.996</td>
</tr>
<tr>
<td>HMX/HPB (78/22)</td>
<td>5</td>
<td>259.72</td>
<td>532.87</td>
<td>1.88</td>
<td>10.95</td>
<td></td>
<td></td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>267.77</td>
<td>540.92</td>
<td>1.85</td>
<td>10.28</td>
<td>170.08</td>
<td>37.44</td>
<td>0.994</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>273.96</td>
<td>547.11</td>
<td>1.83</td>
<td>9.90</td>
<td></td>
<td></td>
<td>0.994</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>278.60</td>
<td>551.75</td>
<td>1.81</td>
<td>9.63</td>
<td></td>
<td></td>
<td>0.994</td>
</tr>
</tbody>
</table>
and crystal defects of the explosives, the effect of the particle size used\textsuperscript{28} and differences in the composition of the polymeric binders\textsuperscript{29}.

4. CONCLUSIONS

The VOD of formulation containing HMX was found marginally superior to RDX-based reference formulation. The sheet explosive containing HMX was found to be more sensitive in term of shock stimuli compared to the reference RDX/HTPB formulation. HMX-based sheet explosive formulation is found more thermally stable compared with RDX sheet explosive formulation. It can be inferred that, the results obtained in the present investigation indicate that the formulation containing HMX with HTPB binder could be promising for ERA application to defeat lower caliber KE projectiles and high explosive anti-tank ammunition.

REFERENCES


CONTRIBUTORS

Mr S.K. Jangid received his MSc (Chemistry) from University of Rajasthan, Jaipur. Presently, he is working as Scientist ‘D’ at HEMRL, Pune. He is actively involved in processing of polymer based explosive formulations. His area of research interest include high explosive processing, polymer based explosives, theoretical calculation and thermal study of HEMs. In current study, he has contributed in the preparation and characterisation of sheet explosive formulations, theoretical prediction, data interpretation and preparation of the manuscript.

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