Experimental Studies on Advanced Sheet Explosive Formulations Based on 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) and Hydroxyl Terminated Polybutadiene (HTPB), and Comparison with a RDX-based System

Suresh Kumar JANGID *, Mahadev B. TALAWAR, Mrityunjay Kumar SINGH, Tribhuvan NATH, Rabindra Kumar SINHA

High Energy Materials Research Laboratory, Defence Research and Development Organization (DRDO), Ministry of Defence, Sutarwadi, Pune-411 021, India
*E-mail: jangidskumar@yahoo.co.in

Abstract: The present investigation reports the use of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) in sheet explosive formulations. In this study, hydroxyl terminated polybutadiene (HTPB) based sheet explosives were prepared incorporating the powerful explosive CL-20 as a partial replacement for hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). The effects of incorporating CL-20 on the performance, sensitivity, thermal and mechanical properties of the sheet explosive compositions are reported. Sheet explosive formulation containing 80% of RDX and 20% of HTPB-binder was studied as control sample. HTPB-binder consisted of 12% HTPB, 2.9% dioctyl adipate (DOA) and 5.1% dioctyl phthalate (DOP). HTPB was cured with 4,4’-methylene diphenyl di-isocyanate (MDI) to form urethane linkages. The incorporation of 20% of CL-20 in place of RDX led to a remarkable increase in the velocity of detonation (VOD), of the order of 7680 m/s, and to better mechanical properties in terms of tensile strength (1.14 MPa) compared to the control formulation [RDX /HTPB-binder (80/20)]. The 20% CL-20 incorporated sheet explosive formulation also showed remarkable increases in impact and shock sensitivity. Thermal analysis of the sheet explosive compositions has also been carried out using differential scanning calorimetry (DSC).

Keywords: hazardous materials, sheet explosive, explosive reactive armour (ERA), CL-20, RDX
1 Introduction

A sheet explosive is a polymer bonded explosive (PBX) [1] in sheet form, that is comprised of energetic materials/explosives, such as 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) provide the power/energy to accomplish the objectives of the system. Polymers provide a continuum for the dispersion of the HEMs and play a vital role in deciding the structural integrity and flexibility, as well as the sensitivity of sheet explosive compositions.

Conventional explosives have some major drawbacks, such as poor mechanical properties and rather high sensitivity. Improvement of these properties can be achieved by the application of plastic binder systems. Natural rubber/crepe rubber is generally used as a binder for sheet explosive formulations. However, this sheet explosive has a limited shelf-life because the natural rubber tends to undergo deterioration due to oxidation of the isoprene units during storage [2]. Thus, polymers like thermoplastic elastomers (TPEs), such as copolymers of ethylene and vinyl acetate [ethylene vinyl acetate (EVA) copolymers] and Estane have found application as binders in sheet explosive formulations [3, 4]. Among the polymers, low molecular weight liquid poly-butadienes with terminal functional groups, like hydroxyl terminated polybutadiene (HTPB), have found wide application in the area of propellants and PBXs [5, 6]. HTPB is a preferred choice due to its clean curing reactions, stable urethane linkages formed by isocyanate curing, and superior fuel content. The application of HTPB can be extended to sheet explosives [7].

Sheet explosives are one of the most versatile explosives, having dual use, viz. military and civil. Sheet explosives find wide application in the fields of welding [8], cladding and demolition devices. Sheet explosives have also gained tremendous importance as components of Explosive Reactive Armour (ERA) [9-12]. The concept of ERA for the protection of armoured vehicles such as tanks has given further impetus to research in the area of sheet explosives. RDX based sheet explosive compositions are available to defeat different types of shaped charge warheads. However, there is also a need to introduce additional capability into modern ERA systems to defeat kinetic energy projectiles. For this purpose, optimized sensitivity and higher VOD sheet explosives are required.

2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane [13, 14] (HNIW or CL-20) is one of the most widely studied energetic cage compounds for explosive and propellant applications due to its high performance in comparison to conventional energetic materials such as RDX. Four stable polymorphic
forms (α, β, γ and ε) of CL-20 have been reported at ambient temperature and atmospheric pressure. However, ε-CL-20 has been found to have the largest density and best thermal stability [15].

CL-20 based plastic bonded explosive formulations have been reported by many researchers [16-18]. Roux et al. [18] reported CL-20 based cast cure PBXs. Compositions containing CL-20 and HTPB in 91:9 ratio delivered a VOD of the order of 8850 m/s. Friction/impact/shock sensitivity and overall vulnerability of the composition were reported to be comparable to the HMX-Estane based pressed explosive LX-14, having a VOD of the order of 8840 m/s.

In view of the above and our continued research and development work in the area of sheet explosives [3, 4, 7], we report here studies on the incorporation of CL-20 in sheet explosive formulations. The sensitivity, performance and thermolysis data obtained for the CL-20 based sheet explosive formulations are compared with RDX based sheet explosive under similar experimental conditions. To the best of our knowledge there have been no reports in the literature on the use of CL-20 in the sheet explosive formulations. The results reported in this work will be a valuable addition to researchers, scientists and technologists working in the explosives field.

2 Materials and Methods

Caution!!!: The materials used in the current study fall under the sensitive category. Therefore the materials must be handled with care by persons with the appropriate skills and knowledge. The materials fall under the category of 1.1 HD in accordance with the United Nations classification of high energy materials. All of the safety rules and guidelines must be followed by a person skilled in this field when working with these materials.

ε-CL-20 (particle size: 22 µm) and RDX (particle size: 5-6 µm) were used as the major energetic components in the development of the sheet explosive formulations. CL-20 and RDX were obtained from authorized in-house developed resources. The purity of the RDX and CL-20 was ascertained prior to their use in the explosive formulations. Basic experiments such as thin layer chromatography (TLC) were carried out for both RDX and CL-20. The spectroscopic data generated for CL-20 also matched reported data from our laboratory [13, 19, 20]. CL-20 and RDX were coated with 6% dioctyl phthalate (DOP) to enhance their safety aspects during the processing of the explosive formulations.
The binder HTPB was obtained from Anabond, India. Dioctyl adipate (DOA), procured from a local source, was added as a plasticizer. Dioctyl phthalate (DOP) from procured from a local source. 4,4’-Methylene diphenyl di-isocyanate (MDI) (make: Merck, density 1240 kg/m$^3$, isocyanate value: 3.3 meq./g) was added as the curing agent. The formulations were processed by a solventless technique.

The mechanical properties of these formulations in sheet form were determined using a Hounsfied 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 the standard method using Archimedes principle. The sensitivity of the explosive formulations to impact stimuli was determined by applying the fall hammer method (2 kg drop weight) as per the Bruceton staircase approach and the results are given in terms of the statistically obtained 50% probability of explosion ($h_{50}$). The friction sensitivity was measured on a Julius Peter’s apparatus by standard methodology, subjecting the sample to incrementally increased loads from 0.2 to 36 kg until no detonation was observed in five consecutive tests [21]. The shock sensitivity was measured by the aluminum block gap test by determining the minimum shock wave pressure that would initiate detonation of the sheet explosive sample (diameter 62 mm, thickness 5 mm). A cylindrical pressed RDX/Wax (95:5) donor charge, of diameter 30 mm and height 100 mm having a density of 1.64 g/cm$^3$ and VOD of 8100 m/s, was used to generate the shock wave. The wave was allowed to pass through an aluminum block of 63 mm diameter and 2.7 g/cm$^3$ density of height varying from 10 to 30 mm. The critical pressure ($P$) in kbar across the aluminum block by which the sheet explosive can be detonated with 50% probability was determined from the relation [22, 23].

$$P = 502.8 \cdot e^{-0.06038x}$$

where: $P$ – critical pressure in kbar, $x$ – thickness of the Al block in mm.
The velocity of detonation (VOD) was measured by the ionization probe technique. Pin type ionization probes (twisted enamel copper wire) located at predetermined points were used as sensors for detecting the arrival time of the detonation wave. An oscilloscope (YOKOGAWA DL9140, 1 GHz) was used for data acquisition.

Thermal analysis was carried out using a differential scanning calorimeter (Perkin Elmer DSC-7). A sample weight of about 0.5 mg was heated at various heating rate (5, 10 and 20 °C/min) in the temperature range 50-350 °C for the determination of the decomposition temperature. The energy of activation of the selected compositions was calculated using the Kissinger equation [24, 25]. The morphology of some of the selected sheet explosive compositions was assessed using a scanning electron microscope (SEM Philip ICON Model SEM-XL30).

3 Processing of the Sheet Explosive Formulations

The binder 12% HTPB, along with 2.9% dioctyl adipate (DOA) and lecithin (0.3% of batch size, additional), as well as ferric acetyl acetone (FeAA) (0.01% of HTPB, additional), was transferred to a steam jacketed horizontal kneader system equipped with sigma-type blades, and the ingredients were mixed under vacuum (10 Torr) at 30-40 °C for about 15 min. 85.1% DOP coated RDX and CL-20 were added to the polymeric matrix in three portions. The contents were mixed for about 1-1.5 h under vacuum (10 Torr) at 40-45 °C. Subsequently, the temperature was reduced to ~25 °C and MDI was added in a stoichiometric ratio of NCO:OH. The mixing was continued for a further 30-40 min. The dough was stored for partial curing under controlled relative humidity. When the shore hardness had reached 10-20 Shore-A Nos., the dough was ready for rolling. The sheet forming equipment was a rolling machine system containing two rollers. The dough was rolled between the two rollers at ambient temperature to obtain sheets of the desired thickness. Curing of the sheet explosive was carried out at room temperature (25 ± 2 °C) for 24 h under controlled relative humidity (RH 50 ± 5%).

CL-20/HTPB-binder (80/20) could not be prepared properly in sheet form. The obtained formulation was of fluffy in nature. Therefore scanty study was done on CL-20/HTPB-binder (80/20) formulation. Further study could not be carried out due to poor mechanical properties.
4 Results and Discussion

In order to handle the materials in a safe manner, energetic materials, i.e. RDX and CL-20 were coated with 6% of DOP.

The processing was carried out under controlled relative humidity to avoid air pocket formation due to reaction between the isocyanate and water molecules [26].

\[
2 \text{R-N=C=O} + \text{H}_2\text{O} \xrightarrow{} \text{R-N-C-N-R} + \text{CO}_2
\]

Isocyanate Water Substituted urea

During processing, one of the hydroxyl groups of the HTPB molecule reacts with MDI to form a long linear chain due to the creation of urethane linkages [26].

\[
\text{R}_1\text{OH} + \text{O=C=N-R}_2 \xrightarrow{} \text{R} - \text{O-C-N-R}
\]

Hydroxyl Isocyanate Urethane

Thus, MDI was used in a stoichiometric ratio because an excess of isocyanate leads to an increase in the possibility of allophanate formation, due to cross-links between the urethane and isocyanate, resulting in an increase in the hardness of the materials [26].

\[
\text{O=C=N-R}_2 + \text{R}_1\text{-O-C-N-R}_2 \xrightarrow{} \text{R}_1\text{-O-C-N-R}_2
\]

Isocyanate Urethane Allophanate

FeAA was used as the cure catalyst. The high surface tension of the liquid binder can hinder the wetting of the explosive particles. Thus, a surface active agent, lecithin, was incorporated as a processing aid, to reduce the surface tension and promote good mixing.
The results for the density and tensile strength of the formulations are listed in Table 1. It is very clear from Table 1 that formulations containing 20 and 40% CL-20 exhibited higher densities (1507 and 1460 kg/m$^3$, respectively), as well as higher tensile strength (only in the case of 20% CL-20) compared to the control formulation (RDX/HTPB-binder). It was also observed that incorporation of CL-20 above 20% gave sheet explosives with poor tensile strength properties. When RDX (80%) was completely replaced by CL-20, then the tensile strength (0.28 MPa) was further drastically reduced. This may be attributed to the fluffy nature of the explosive formulations. This trend may be also due to various factors such as packing patterns, shape, size and morphology of the CL-20 particles in the formulations. The SEM images obtained for the RDX/HTPB-binder (80/20) and CL-20/HTPB-binder (80/20) compositions, shown in Figure 1, revealed the effective coating of coating of RDX in the RDX based composition. However the morphology of the CL-20 based sheet explosive composition revealed a break in the structural integrity of the CL-20 particles. This may be one of the reasons for the poor mechanical properties obtained for the CL-20/HTPB-binder (80/20) formulation.

<table>
<thead>
<tr>
<th>Composition RDX/CL-20/HTPB-binder</th>
<th>Density [kg/m$^3$]</th>
<th>TS [MPa]</th>
<th>Elongation [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>80/0/20</td>
<td>1430</td>
<td>1.00</td>
<td>11</td>
</tr>
<tr>
<td>60/20/20</td>
<td>1507</td>
<td>1.14</td>
<td>11</td>
</tr>
<tr>
<td>40/40/20</td>
<td>1460</td>
<td>0.57</td>
<td>10</td>
</tr>
</tbody>
</table>

Figure 1. SEM images for RDX/HTPB-binder (80/20) and CL-20/HTPB-binder (80/20).
Table 2. VOD and sensitivity characteristics of the formulations

<table>
<thead>
<tr>
<th>Composition RDX/CL-20/HTPB-binder</th>
<th>Sensitivity parameters</th>
<th>VOD [m/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Impact $(h_{50})$ [m]</td>
<td>Friction [N]</td>
</tr>
<tr>
<td>80/0/20</td>
<td>0.75</td>
<td>353</td>
</tr>
<tr>
<td>60/20/20</td>
<td>0.40</td>
<td>314</td>
</tr>
<tr>
<td>40/40/20</td>
<td>0.25</td>
<td>235</td>
</tr>
</tbody>
</table>

The sensitivity characteristics of the RDX/CL-20/HTPB-binder sheet explosives are listed in Table 2. The formulations incorporating 20-40% CL-20 gave higher impact sensitivities $(h_{50})$ of 0.25-0.40 m compared to the RDX based formulation. The friction sensitivity of the compositions also increased with an increase in the percentage of CL-20 in the formulation. This may be due to the inherent higher friction sensitivity of the individual ingredient CL-20 (94 N). In the shock sensitivity tests, the 50% probability of detonation of the RDX/CL-20/HTPB-binder (60/20/20) formulation was found to be 11.1 GPa, which is more sensitive compared to 18.0 GPa for the RDX based formulation. The VOD of the formulation containing 20% CL-20 as partial replacement for RDX, was found to be 7680 m/s, which is superior to the RDX based control formulation, as listed in Table 2. Addition of 40% of CL-20 led to an intermediate value of VOD. This may be the result of optimized packing of the solid particles for 20% CL-20 composition, which is also reflected in the density difference of the 20 and 40% CL-20 based compositions.

The reference formulation RDX/HTPB-binder (80/20) showed non-defeatable kinetic energy (KE) projectile behaviour due to its insensitivity. The KE projectile was made from a metallic penetrator to create a lower shock pressure on the target than a chemical energy projectile (explosive warhead), i.e. a more shock-sensitive sheet explosive is required for initiation by a kinetic energy projectile. The shock sensitivity data obtained should be in the range of 4.0-14.1 GPa for safe handling and processing, as well as for initiation by a KE projectile. The sheet explosive formulation containing 20% CL-20 was found to be more sensitive in terms of impact as well as shock stimuli, and had a higher VOD compared to the reference RDX/HTPB-binder formulation. Hence, this formulation may find application in explosive reactive armour for defeating KE projectiles.

It was also observed that a further increase in CL-20 content to 40% caused the impact and friction sensitivities to increase. Thus, these compositions are not safe for handling and processing. Further work is in progress in this laboratory in order to use CL-20 with different binder systems in order to develop safe sheet explosive compositions.
Figure 2. DSC thermograms of individual ingredients and selected compositions: RDX/HTPB-binder (80/20), RDX/CL-20/HTPB-binder (60/20/20) and RDX/CL-20/HTPB-binder (40/40/20).

The DSC curves at the heating rate of 10 °C/min, for RDX, CL-20, RDX/HTPB-binder (80/20), RDX/CL-20/HTPB-binder (60/20/20) and RDX/CL-20/
HTPB-binder (40/40/20) are shown in Figure 2. It was observed that the DSC curves for RDX and RDX/HTPB-binder (80/20) showed RDX melting endotherms at ~205 °C, followed immediately by decomposition exotherms at 237 and 231 °C, respectively. However, on incorporating 20% CL-20 in this formulation, the RDX melting endotherm was not observed because decomposition commenced before 200 °C. The decomposition exotherms for compositions RDX/CL-20/HTPB-binder (60/20/20) and RDX/CL-20/HTPB-binder (40/40/20) occurred at 229 °C and 216 °C respectively, as broad peaks which represent decomposition of both RDX and CL-20. The decomposition temperature for composition RDX/CL-20/HTPB-binder (60/20/20) was found to be closer to the decomposition temperature of RDX at about 237 °C, which indicates greater compatibility with the binder than RDX/CL-20/HTPB-binder (40/40/20). The heat output increased with increases in CL-20 content in the formulation because of the higher heat of formation of CL-20.

The compatibility study of the compositions can also be done by determining of the kinetics of the decomposition. Thermal analysis of selected formulations, such as RDX/HTPB-binder (80/20), RDX/CL-20/HTPB-binder (60/20/20) and RDX/CL-20/HTPB-binder (40/40/20), were obtained by DSC at various heating rate (5, 10 and 20 °C/min).

Table 3. Kinetics parameters for the sheet explosive compositions

<table>
<thead>
<tr>
<th>Composition</th>
<th>β  [°C/min]</th>
<th>T_p [°C]</th>
<th>T_p [K]</th>
<th>1/T_p</th>
<th>-ln(β/T_p²)</th>
<th>E_a [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RDX/CL-20/HTPB-binder (80/0/20)</td>
<td>5</td>
<td>220.17</td>
<td>493.32</td>
<td>0.00203</td>
<td>10.79</td>
<td>144.04</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>231.33</td>
<td>504.48</td>
<td>0.00198</td>
<td>10.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>239.00</td>
<td>512.15</td>
<td>0.00195</td>
<td>9.48</td>
<td></td>
</tr>
<tr>
<td>RDX/CL-20/HTPB-binder (60/20/20)</td>
<td>5</td>
<td>219.70</td>
<td>492.85</td>
<td>0.00203</td>
<td>10.79</td>
<td>144.93</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>228.67</td>
<td>501.82</td>
<td>0.00199</td>
<td>10.13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>238.64</td>
<td>511.79</td>
<td>0.00195</td>
<td>9.48</td>
<td></td>
</tr>
<tr>
<td>RDX/CL-20/HTPB-binder (40/40/20)</td>
<td>5</td>
<td>203.62</td>
<td>476.77</td>
<td>0.00210</td>
<td>10.72</td>
<td>127.15</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>215.83</td>
<td>488.98</td>
<td>0.00205</td>
<td>10.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>223.34</td>
<td>496.49</td>
<td>0.00201</td>
<td>9.42</td>
<td></td>
</tr>
</tbody>
</table>

The decomposition peaks of the sheet explosive compositions RDX/HTPB-binder (80/20) and RDX/CL-20/HTPB-binder (60/20/20) were observed in the range 219-239 °C at different heating rates (5, 10 and 20 °C/min) and are listed in Table 3. It was also observed that the decomposition peak shifted towards higher temperatures with increasing heating rate. This is due to the activation
energy involved in such transitions, and the data were analyzed by the Kissinger equation to estimate the activation energies for the exothermic decomposition peak. The different variables used for the determination of the activation energies are given in Table 3. The activation energy of both compositions were observed to be about 145 kJ/mol, which is similar to that of RDX itself (158 kJ/mol [27]). This suggested that explosives of both compositions RDX/HTPB-binder (80/20) and RDX/CL-20/HTPB-binder (60/20/20) are compatible with the binder system. However, in the case of RDX/CL-20/HTPB-binder (40/40/20), the activation energy was observed to be about 127 kJ/mol. Therefore, the energy of activation data obtained may indicate a less compatible nature of RDX/CL-20/HTPB-binder (40/40/20) in comparison to RDX/HTPB-binder (80/20) and RDX/CL-20/HTPB-binder (60/20/20).

5 Conclusions

The experimentally obtained sheet explosive containing 20% CL-20 was found to be more sensitive in terms of shock stimuli compared to the reference RDX/HTPB-binder formulation. Hence, the formulation may find application in explosive reactive armour for defeating kinetic energy projectiles. The VOD of the sheet explosive formulation RDX/CL-20/HTPB-binder (60/20/20) was found to be superior to the RDX based control formulation. However, further addition of CL-20 (40%) to the formulation led to a decrease in VOD. This may be due to several physicochemical properties (size, shape and morphology) of CL-20 and fluffy nature of sheet explosive. The lowering of the performance of the CL-20 (40%) based explosive formulation needs further detailed investigation. It can be inferred that the results obtained in the present investigation indicate that the formulation containing 60/20 weight percent RDX/CL-20 formulation with HTPB binder are the most promising for ERA applications.

Acknowledgements

The authors are grateful to Director, HEMRL for his constant encouragement and permission to publish this work.

References


