Compatibility Investigations on Novel Energetic Formulations of Nitrogen Rich Azole [Bistetrazolylamine(BTA)]

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Outline

- Background
- Objective
- Bistetrazolylamine and Binders: Synthesis and characterization
- STANAG 4147: Test procedure, criterion.
- Compatibility studies: Results and Discussion
- Activation energy: Comparison with various systems
- Conclusion
# High Nitrogen Tetrazole Derivatives as Insensitive High Energy-Density Materials

![Chemical structures of HyAmNTz, TNMTz, BTA, and TKX-50](image)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Tetrazole derivatives</th>
<th>Conventional explosives</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HyAmNTz</td>
<td>TNMTz</td>
</tr>
<tr>
<td>Density, g/cc</td>
<td>1.969</td>
<td>1.918</td>
</tr>
<tr>
<td>Thermal stability, T_{dec.} (^{\circ})C</td>
<td>150</td>
<td>100</td>
</tr>
<tr>
<td>VOD, m/s</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P_{cj}, GPa</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Friction sensitivity, N</td>
<td>144</td>
<td>9</td>
</tr>
<tr>
<td>Impact sensitivity, J</td>
<td>5.5</td>
<td>9</td>
</tr>
<tr>
<td>Spark sensitivity, J</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Objective

- To investigate the compatibility of binders with Bistetrazolylamine (BTA), in an effort to assess the applicability of the molecule in explosive and propellant formulations.

- BTA represents one of the attractive energetic candidates with high-energy density and insensitivity, a rare combination.

- Although synthesis and characterization of novel high energy-insensitive molecules are reported, very few have been tested for their compatibility with known binders.

- Lack of information on the compatibility and stability of high nitrogen molecules hinders their further development as a formulation.

- The mixtures chosen for our study:
  - Bistetrazolylamine-Glycydyl azide Polymer (BTA-GAP)
  - Bistetrazolylamine-Poly nitratomethyl methyl oxetane (BTA-PNIMMO)
  - Bistetrazolylamine-Ethyl cellulose (BTA-EC)
Bistetrazolylamine (BTA)

- High density CHN molecule. (1.86 g/cc)
- Symmetrical tetrazolyl groups on the central nitrogen-high energy system not local minima.
- Presence of substitution and salt formation changes the structure to most stable low energy form.
BTA shows excellent thermal stability up to 240°C.

DSC curve shows maximum heat release within a short temperature range.

P-t curve was measured to understand the ignitability and pressure response of BTA.
### Energetic binders: GAP & PNIMMO

<table>
<thead>
<tr>
<th>Binder</th>
<th>Mol. Weight, $M_n$, gmol$^{-1}$</th>
<th>Density, gcc$^{-1}$</th>
<th>Glass transition, $T_g$, °C</th>
<th>Decomposition temperature, $T_p$, °C</th>
<th>Heat of decomposition, Jg$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAP</td>
<td>2835</td>
<td>1.35</td>
<td>-51.2</td>
<td>241.5</td>
<td>1917</td>
</tr>
<tr>
<td>PNIMMO</td>
<td>1295</td>
<td>1.28</td>
<td>-55.5</td>
<td>204.6</td>
<td>1123</td>
</tr>
</tbody>
</table>

EC with 48% ethoxy content was procured from Sigma Aldrich and used as received.
Importance of Compatibility studies

- Compatibility of novel energetic materials with components of formulations/composites are crucial for their safety and functioning. Ideally compatible materials should not have any chemical interaction with each other over a prolonged period.

- STANAG 4147, MIL-STD-268B and MIL-STD-650 explains the various test procedures and compatibility criteria for energetic materials. VST, IST, TG and DSC analysis includes the various test for determining the compatibility.

Compatibility using micro-calorimetry as per STANAG 4147

- High degree of accuracy in temperature profile and high sensitivity (nW) of micro-calorimeter is advantageous to measure heat flow over a long period. 6 channel TAM III from TA was used.

- Test measurements:
  
  1:1 mixture by weight of:
  Energetic material (BTA) + sample(binder)

- Degree of compatibility:

  \[ D = \frac{2M}{(E+S)} \]

  - M = Heat generation for the mixture (J g\(^{-1}\))
  - E = Heat generation for energetic material (BTA) (J g\(^{-1}\))
  - S = Heat generation for the sample (binder) (J g\(^{-1}\))

- Acceptance criteria:

  Criteria:
  
  - D > 3 : Incompatible
  - 2 < D < 3 : Another method should be used
Thermal decomposition of BTA, GAP and PNIMMO occurs within a closer range of temperature.

PNIMMO showed a faster heat accumulation rate at 85°C when compared to the other components.
Compatibility: BTA-GAP

- Compared with the individual components, mixture showed increase in heat accumulation after 60 h.
- No appreciable heat release rate over 168 h.
- BTA: -18.9 J/g; GAP -22.6; BTA-GAP: -14.05 J/g
- D<2
Compatibility : BTA-PNIMMO

- Notably the mixture has lower heat release rate when compared to PNIMMO
- BTA: -18.9 J/g; PNIMMO: 95.6; BTA-PNIMMO: -19.3 J/g
- D<2

- BTA dilutes the heat release of the mixture by acting as a thermally stable heat sink.
- Exponential increase in heat release rate for PNIMMO after 40 h.

Compatible mixture
Compatibility : BTA-EC

- The mixture has higher heat release rate when compared to components
- BTA: $-18.9 \text{ J/g}$; EC: $-10.95$; BTA-EC: $-1.4 \text{ J/g}$
- $D < 2$

- EC showed an increase in heat release after 80 h.
- Presence of BTA has accelerated the heat release of EC.
- Lewis acid nature of BTA aiding possible hydrolysis of ether linkages.

Compatible mixture
Compatibility: BTA-TDI

- BTA showed a greater degree of incompatibility with curing agent TDI, indicative of the reaction between the imino hydrogens and iso cyanate group.

- On comparison with the heat release rate of curing reaction with PNIMMO, reaction of BTA with TDI seems to take place at a slower rate.

- The terminal primary hydroxyl groups of PNIMMO will have a preferential reaction with isocyanate compared to that of imino groups in BTA.
Comparison of DSC

DSC profiles of BTA/binder mixtures before and after HFC study

- Decomposition characteristics of the formulations are preserved after the compatibility tests with binders.

Representative DSC profile of BTA-GAP
Activation energy calculations

- Activation energy of decomposition of the energetic mixtures; BTA-GAP & BTA-PNIMMO was calculated.
- Kissinger and Ozawa equations were used for evaluation.
- BTA-GAP $E_a = 240 \pm 5$ kJ/mol
- BTA-PNIMMO $E_a = 130 \pm 3$ kJ/mol
- BTA-GAP mixture showed a higher activation energy required for decomposition.
- Results indicative of ease of initiation/decomposition for BTA-PNIMMO.

DSC profiles of BTA-PNIMMO
Conclusions

- Compatibility of BTA with common energetic binders (GAP & PNIMMO) as well as with a non energetic binder (EC) were studied as per STANAG 4147.

- Binders showed good compatibility with BTA paving the way to visualize use of BTA as energetic ingredient/fuel.

- DSC analysis on the post experiment samples showed no considerable dilution of energy or change in heat flow profile.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Normalized Heat, Jg(^{-1})</th>
<th>Degree of compatibility, D</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTA-GAP</td>
<td>-14.05</td>
<td>0.67</td>
<td>Compatible</td>
</tr>
<tr>
<td>BTA-PNIMMO</td>
<td>-19.28</td>
<td>0.50</td>
<td>Compatible</td>
</tr>
<tr>
<td>BTA-EC</td>
<td>-1.4</td>
<td>0.09</td>
<td>Compatible</td>
</tr>
</tbody>
</table>
Thank You