Formulation and characterizations of nanoenergetic compositions with improved safety

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Abstract 16152
Context of the study

- Quest for safe matter for propulsion and explosives

- The properties of energetic material compounds are strongly affected by the microstructural properties of the main material (crystal size, shape, morphology, purity, defects, and the microstructure of intercrystalline voids)

Two ways to achieve less sensitive energetic materials

- Optimize conventional crystallization conditions (RDX, HMX)
- Significantly reduce the crystal size

Development of nanosized energetic materials
Context of the study - Concept

- **Key point:**

  nanostructuring matrix \((M)\)

  \( \sim 100\text{nm} \)

  Explosive:

  \((M) \leq 10\text{wt}\% \)

  + explosive particles \((E) \geq 90\text{wt}\% \)

  \[ \begin{array}{c}
  \text{MEMEME} \\
  \text{EMEMEM} \\
  \text{MEMEME} \\
  \text{EMEMEM}
  \end{array} \]

  \[ \text{E} = \begin{array}{c}
  \text{N} \\
  \text{O}_2\text{N} \\
  \text{N} \\
  \text{N} \\
  \text{NO}_2 \\
  \end{array} \]

  Propellant:

  \((M) = \text{reductant} \)

  + oxidizer particles \((O)\)

  \[ \begin{array}{c}
  \text{MOMOMO} \\
  \text{OMOMOM} \\
  \text{MOMOMO} \\
  \text{OMOMOM}
  \end{array} \]

  Ex.: \(O = \text{AP}\)

  Objective: reduction of RDX particles size

  Improve safety without degradation of performances

  Objective: increase of the oxidizer/reductant atoms interface

  Improve combustion behavior without degradation of safety

- **Ex.:** \(O = \text{AP}\)

- **Propellant:**

  - Three dimensional polymer
  - Low-density mesoporous polymer
  - Nanosized pores (open pores)

- **Objective:**

  Increase of the oxidizer/reductant atoms interface

  Improve combustion behavior without degradation of safety
Prepared and tested materials

✓ Synthesis and formulation
✓ Physical characterizations
✓ Energetic results

Conclusions and prospects
Synthesis of the nanostructuring matrix:

\[
\begin{align*}
\text{Phloroglucinol (0.7)} + \text{Nitrophloroglucinol (0.3)} + \text{Formaldehyde (2)} &\xrightarrow{\text{Ca(OH)}_2} \\
\text{Water/EtOH 45/55} &\rightarrow \text{Synthesis solvent} \\
\text{50°C} &\rightarrow \text{Pores containing synthesis solvent} \\
\text{to +1h to +1day} &\rightarrow \text{(P/NP7/3)F gels} \\
\text{Gel cut into pieces} &\rightarrow \text{Gel washed with ethanol} \\
\end{align*}
\]

Formulation of AP and RDX nanodispersions.
Impregnation of the nanostructuring matrix with AP or RDX:

Case 1:
- EtOH
- AP (Water)
- 63°C

Case 2:
- GBL
- RDX (GBL)
- 93°C
Synthesis and formulation

Charge crystallization and drying process:

Case 1: AP

1. Cryotransfer (liquid nitrogen)
2. Freeze drying +
3. Dry crushing (vibratory ball mill)

- AP saturated solution
- AP nuclei
- Cryogel (P/NP7/3F)/AP

Case 2: RDX

1. Cryotransfer (liquid nitrogen)
2. Exchange GBL → EtOH (-20 °C)
3. Exchange EtOH → Water ambient T

- RDX saturated solution
- RDX nuclei
- Cryogel (P/NP7/3F)/RDX

Case 1: AP

1. Cryotransfer (liquid nitrogen)
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- RDX saturated solution
- RDX nuclei
- Cryogel (P/NP7/3F)/RDX
Physical characterizations

X-ray diffraction measurement:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P/NP7/3F)/PA 20/80</td>
<td>100-130nm</td>
</tr>
<tr>
<td>(P/NP7/3F)/RDX 10/90</td>
<td>100-150nm</td>
</tr>
</tbody>
</table>

SEM images:

- AP nanocryogel
- RDX nanocryogel

Physical characterizations
Energetic characterizations

Drop-weight results: impact behavior

<table>
<thead>
<tr>
<th></th>
<th>$H_{50}$ (mm) / $P_{MAX}$ (bars)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Macro</td>
</tr>
<tr>
<td>P/NP(7/3)F/AP 20/80</td>
<td>215 / 1.06</td>
</tr>
<tr>
<td>(P/NP 7/3))F/RDX 25/75</td>
<td>138 / 2.11</td>
</tr>
<tr>
<td>(P/NP 7/3))F/RDX 10/90</td>
<td>170 / 4.85</td>
</tr>
<tr>
<td>RDX</td>
<td>Various crystal sizes</td>
</tr>
</tbody>
</table>

Nanosized AP formulations:
- Better mix between oxidizer and reductant
- Matrix protects AP towards aggression

RDX formulations:
- Sensitivity is controlled by intrinsic RDX sensitivity
- Strong effects of dispersion/dilution of RDX under 90% wt

AP nanodispersions are less sensitive and more powerful than mixture of powders

RDX nanodispersions are as sensitive as mixture of powders
Energetic characterizations on AP cryogels

Closed-chamber combustion: combustion behavior

2 g pellets in a 64 cm³ chamber

Pressing sequence: 60°C + 3x1000 bar

\[ \rho = 1.65 \text{ g/cm}^3 \]

- Burning rate of the nanosized formulations is two to three times higher than mixtures of powders
- Nanostructuration guarantees a stable combustion all over the explored pressure range (pressure exponent < 1)

Strong assumptions

Crack of the pellet: Deconsolidative burning
Energetic characterizations on AP cryogels

- **Ultrasound measurement method (ONERA):** combustion behavior

  10 g pellets in a 0.6L chamber

  Pressing sequence: 
  - nano = 60°C + 3x1100 bar
  - macro = 60°C + 3x1500 bar

  \[ \rho = 1.78 \text{ g/cm}^3 \]

  Echantillons nanostructurés (2107 et 2108)
  
  \[ y = 7.639x^{0.5195} \]
  \[ R^2 = 0.9685 \]

  Echantillons macrostructurés (2074 et 2075)
  
  \[ y = 1.9161x^{0.8996} \]
  \[ R^2 = 0.7427 \]

  Noise (homogeneity defects of the combustion behavior in the pellet)

- **Confirm closed chamber combustion results**

  burning rate \(_{nano}\) = 2 to 3 x burning rate \(_{macro}\)

  pressure exponent \(_{nano}\) < pressure exponent \(_{macro}\)
Energetic characterizations on RDX cryogels

Small-scale gap test: detonation initiation behavior of RDX formulations

- Classical run: 30 to 50 tests (up-and-down method)
- Determination of the barrier thickness ($e_{50}$) driving to the sample initiation probability of 50%

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Reference HMX/TATB/phenoxy (45/52/3) 98 TMD%</th>
<th>Nano RDX/(P/NP7/3F) (90/10) 95 TMD%</th>
<th>HMX/TATB/technoflon (65/30/5) 98 TMD%</th>
<th>Macro RDX/(P/NP7/3F) (90/10) 95 TMD%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_{50}$ (mm)/confidence limits</td>
<td>&lt; 1</td>
<td>1.84 [1.52-2.09]</td>
<td>1.88 [1.78-2.00]</td>
<td>2.84 [2.50-3.10]</td>
</tr>
</tbody>
</table>

✓ Strong improvement of shock-sensitivity when nanostructuring,
✓ RDX nanoformulation is as insensitive as a formulation containing TATB despite more nitramine content, more porosity and lack of binder.
✓ Need to be validated with more shots (only 10 on each formulation until now)
Conclusions

- A formulation process able to produce nanodispersions of AP or RDX (up to 90wt%) in a nanostructuring matrix has been developed

- Propellant application: AP formulations
  - Nanodispersions are less sensitive than mixture of powders (impact sensitivity)
  - When they decompose, AP nanocryogels are more powerful than mixture of powders
  - Combustion of AP nanocryogels shows improved propulsion performances (burning rate and combustion stability) compared to mixture of powders

- Explosives application: RDX formulations
  - No effect of nanosizing on impact sensitivity (intrinsic to RDX)
  - Strong improvement of shock-sensitivity for nanostructured formulation
Prospects

- Optimizations of the nanodispersion process (step simplification and duration, drying, get rid of the residual porosity)

- Propellant application: AP formulations
  - Classical propellant formulations are under way (SAFRAN partner)

- Explosives application: RDX formulations
  - Detonation characterizations to be completed
  - Direct use without further processing for high-energy detonators (exploding wire or slapper)
  - Development of formulations with binder for booster or loading explosive applications
Acknowledgements

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