Reactivity of ADN with PolyButadiene in Air

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1 Introduction

MoD (UK) is funding a Novel Propellants programme developing rocket propellants

Current composite rocket propellants usually contain ammonium perchlorate (AP)

• toxic
• stealth issues

Aim to develop rocket propellants using chlorine-free oxidisers

• ammonium dinitramide (ADN)
• 1,1-diamino-2,2-dinitro-ethylene (FOX-7)
1 Introduction

Aim to measure and understand ageing of ADN in binders

Advantageous to fill polybutadiene (HTPB) with ADN

• polymer has a proven track record as a binder system in AP composite propellants
• exhibits good mechanical properties
• low glass transition temperature

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADN</td>
<td>69.4</td>
</tr>
<tr>
<td>Polybutadiene</td>
<td>30.6</td>
</tr>
</tbody>
</table>

Subjected HTPB/ADN composite to a minimal ageing trial

• three temperatures (60, 70 and 80°C)
• dry conditions
2 Bulk Ageing

Oxidised at a faster rate than expected in air

• darkened rapidly (within two weeks) to form a hard skin
• inhomogeneous
• brown banding at the ADN/polybutadiene interface
• downward trend in the sol fraction – oxidative crosslinking
2 Bulk Ageing

Understand ageing
- Quantify rate
- Nature of reaction

Identify additives
- Stabilisers
- Antioxidants

Prolong life
- Decrease costs
- Increase safety
3 Experimental

Diffuse reflectance infrared spectroscopy (DRIFTS)

- optimised for trans-flection

Coated aluminium sample holder base with thin coat

- dried in vacuum for 10 minutes prior to kinetic measurement
- ADN/HTPB (uncured) ratio 50:50
- heated in holder exposed to dry air
- collected IR spectrum every 5 minutes
4 Aged HTPB (no stabiliser)

Cured HTPB undergoes autocatalytic oxidative crosslinking (40 microns thick)
- hours to days depending on temperature

Forms new carbonyl and hydroxyl bearing species
4 Aged HTPB (no antioxidant)

R45M

- uncured with minor amounts of antioxidant (AO)
- 80°C, dry air, ~2.4 days maximum oxidation rate
- Fits autoxidation scheme

Initial dip in the OH content

- due to hydrogen abstraction reactions of OH

\[
A \xrightarrow{k_{a1}} B + C + S \\
A + B \xrightarrow{k_{a2}} B + C + S \\
k_2 = k_{a2} \cdot [A]_0 \\
k_1 = k_{a1}
\]
5 Aged HTPB + ADN (no stabiliser)

Addition of ADN

- degradation does not follow classic auto-oxidation scheme
- HTPB oxidises at a faster rate in the presence of ADN
- time to maximum auto-oxidation rate was ~ 90 minutes

Different oxidation products

- carbon-multiple bond-nitrogen species (2223cm$^{-1}$) – probably a conjugated nitrile – reaction of ADN with oxidising HTPB
6 Effect of Antioxidant

Addition of Calco2246 AO

- increased the time to maximum auto-oxidation
- linear

BUT still a fast oxidation process at 80°C

<table>
<thead>
<tr>
<th>Mass % Calco2246</th>
<th>Time to max oxidation/days</th>
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<tbody>
<tr>
<td>0</td>
<td>0.06</td>
</tr>
<tr>
<td>0.25</td>
<td>0.2</td>
</tr>
<tr>
<td>0.25</td>
<td>0.4</td>
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<tr>
<td>0.5</td>
<td>0.6</td>
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<tr>
<td>1</td>
<td>1.1</td>
</tr>
<tr>
<td>2</td>
<td>3.0</td>
</tr>
<tr>
<td>3</td>
<td>4.4</td>
</tr>
<tr>
<td>5</td>
<td>7.3</td>
</tr>
</tbody>
</table>
6 Effect of Antioxidant

Extrapolation to lower temperatures (Arrhenius) – still fast oxidation process

<table>
<thead>
<tr>
<th>Mass % AO</th>
<th>Temperature/°C</th>
<th>Time to max oxidation / days</th>
<th>Time to max oxidation / years</th>
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</thead>
<tbody>
<tr>
<td>0.5</td>
<td>80</td>
<td>0.3</td>
<td>0.001</td>
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<tr>
<td>0.5</td>
<td>60</td>
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</tr>
<tr>
<td>0.5</td>
<td>20</td>
<td>105</td>
<td>0.29</td>
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<tr>
<td>1</td>
<td>80</td>
<td>0.5</td>
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</tr>
<tr>
<td>1</td>
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<td>2.6</td>
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<td>60</td>
<td>18</td>
<td>0.05</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>1224</td>
<td>3.4</td>
</tr>
</tbody>
</table>
7 Effect of Stabiliser and Antioxidant Type

Addition of stabiliser pNMA at 80°C
• 0.2% - no affect
• 0.5% appears to accelerate oxidation

Change antioxidant to
• Irganox 1520 - (4,6-bis (octylthiomethyl)-o-cresol)
• less efficient antioxidant than Calco2246
8 Effect of Polybutadiene Type

R45M – 20% vinyl, 60% trans, 20% cis (minor antioxidant)
Krasol LBH2000 (vinyl-HTPB) – 65% vinyl, 22.5% trans, 12.5% cis (minor antioxidant)
Aldrich HTPB (cis-HTPB) – 1% vinyl, 27% trans, 72% cis (no observable antioxidant)

Reactivity

Vinyl HTPB << R45M < cis-HTPB
8 Effect of Polybutadiene Type

Vinyl HTPB + minor AO - extrapolated oxidative ageing to room temperature

- longer life

Disadvantage Vinyl HTPB

- higher glass transition temperature (-46°C versus -75°C for R45M)

Formation of the conjugated nitrile after maximum oxidation rate

<table>
<thead>
<tr>
<th>Temperature/°C</th>
<th>Time to max oxidation / days</th>
<th>Time to max oxidation / years</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>0.8</td>
<td>0.002</td>
</tr>
<tr>
<td>70</td>
<td>3</td>
<td>0.008</td>
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<tr>
<td>60</td>
<td>~13</td>
<td>~0.04</td>
</tr>
<tr>
<td>50</td>
<td>~64</td>
<td>~0.2</td>
</tr>
<tr>
<td>40</td>
<td>~339</td>
<td>~0.9</td>
</tr>
<tr>
<td>30</td>
<td>~2010</td>
<td>~5.5</td>
</tr>
<tr>
<td>20</td>
<td>~13441</td>
<td>~36.8</td>
</tr>
</tbody>
</table>
9 Conclusions

HTPB/ADN propellant, with small amounts of antioxidant, ages rapidly

- highly inhomogeneous process

Followed oxidation of thin ADN/HTPB R45M samples using IR spectroscopy

- does not follow the classic autoxidation kinetic scheme
- much faster than pure HTPB R45M
- evidence of ADN reaction with oxidising HTPB - formation of a conjugated nitrile species

Addition of antioxidants mitigates degradation

- inefficient additives

Stabiliser pNMA does not improve oxidation rate

Oxidation depends on polymer backbone

- vinyl HTPB<<R45M<cis HTPB
The authors thank the DSTL's Programme and Delivery Directorate (MoD, UK) for funding this work.

Thank you for your attention!