Propellant-Insulant Bonding in Rocket Motors

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Introduction

• Motor case liner (insulant) critical to the success of a rocket motor
  – rocket motors generate hot gases at temperatures (1750 and 3750°C) and high pressures (2.8 to 30 MNm\(^{-2}\))
  – propellant burns from the conduit to the chamber wall
  – heat could melt or weaken the combustion chamber body
  – pressure chamber failure; motor explodes; damage platform

Fig. 1. Cross-section of a typical rocket motor. A, chamber; B, head end dome; C, nozzle; D, igniter; E, nozzle convergent portion; F, nozzle divergent portion; G, port; H, inhibitor; I, nozzle throat insert; J, lining; K, insulation; L, propellant; M, nozzle exit plane; N, SITVC system; O, segment joint.

Rao et al Engineering Failure Analysis, 12(2), 325-336, 2005
Introduction

• **Catastrophic failure is prevented by using an insulant**
  – complex composition consisting of fillers, polymers and other additives
  – manufacture, performance and effectiveness are a function of synergistic interactions

• **Adhesives used in several motor components**
  – discussing issues with insulant-propellant
Insulant Requirements

• Requirements for motor case lining processes and material
  – insulant performance
  – insulant mechanisms
  – new materials and new processes
  – availability and cost
  – adhesion of the propellant with the insulant
  – compatibility issues (reaction of additive with propellant)

• Interactive interactions – generally no “drop-ins”
Insulant Requirements

• The components of the insulant are chosen to limit heat transmission – function of the propellant characteristics
  – high specific heats (acting as a heat sink)
  – low thermal conductivity
  – undergo endothermic processes such as phase changes (melting, vaporising) and/or decomposition
  – produce effective boundary layers generated from gaseous molecules insulating the insulants from the flame
  – cause transpiration cooling (transport of gaseous molecules through hot char cooling it down)
  – effective, resilient char formation
  – propensity of char formation rather than gas/volatile formation
  – fibres to reinforce/retain the char during ablation

• The propellant and insulant characteristics limit material choice for effective adhesives
Insulant Problems

• Bonding between the insulant and propellant
  – can be poor
  – significant failure mode

• When the propellant detaches from the polymeric insulant
  – additional propellant surface forms
  – upon ignition an extra burning surface forms
  – over-pressurisation, rupturing the rocket motor case
General Approach to Bonding Insulants

• Nominally two types of solid propellant
  
• Composite propellant
  – plasticised polymeric binder filled with a crystalline filler such as ammonium perchlorate
  – use addition type curing such as isocyanate-hydroxyl reaction to form polyurethanes
  – have reactive isocyanate available

• Double base propellant
  – nitroglycerine/nitrocellulose gels (sometimes crosslinked)
  – potential for reactive chemistry with the nitrocellulose hydroxyl species

• Ideally don’t want mobile low molecular weight side products
  – migration can cause degradation and changes in mechanical properties
General Approach to Bonding Insulants

• Ideally want to exploit the propellant chemistry to form
  – covalent bonds by reaction crosslinking species with the insulant surface
  – diffusion bonds from intermingling swelled polymers

• Diffusion processes can be difficult to achieve
  – bond temperature > glass transition temperature
  – entropy of mixing of similar polymers is low
  – diffusion line poor

• Typical insulants consist of
  – low Tg polymers
  – low surface energies
  – low reactivity
Primers for Composite Propellants

- Development of insulant rocket primer
  - bonding EPDM insulant to HTPB/NCO based propellant

- Used T-peel test to assess the peel strength
  - optimise the composition
  - optimise the cure time
  - measure effect of oxidative ageing 60°C upto 6 weeks

<table>
<thead>
<tr>
<th>LRP3 Material</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTPB</td>
<td>70.9 to 63.0</td>
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<tr>
<td>Chain extender diol</td>
<td>6.4 to 5.7</td>
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<tr>
<td>Fumed silica</td>
<td>12.0 to 10.7</td>
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<tr>
<td>Hindered phenol antioxidant</td>
<td>0.7 to 0.6</td>
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<tr>
<td>Trifunctional isocyanate</td>
<td>10 to 20</td>
</tr>
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</table>

- Combination of covalent and diffusion bond
  - reaction of propellant hydroxyl with primer
Primers for Composite Propellants

- EPDM is a low energy surface
  - can be difficult to bond to

- Rather than rely on inter-diffusion of polymers, considered in-situ polymerisation of inter-penetration of polymers as a bonding mechanism

- Solid state NMR of EPDM based insulant
  - 27 to 30% of the ethylidene norbornene had converted to a crosslinked species
  - therefore double bonds available for further reaction
Primers for Composite Propellants

• 5-ethylidene norbornene
  – ring opening metathesis polymerisation
  – oxidation/hydrolysis

• Paint EDPM surface with functionalised norbornene
  – apply ROMP catalyst
  – in-situ polymerisation

• Followed polymerisation reaction by DMA
  – painted surface with norbornene/catalyst

• Poly(norbornenes) penetrate to 0.4mm of EPDM
  – surface enriched with functional groups
Primers for Composite Propellants

• Six EPDM-based liners
  – no treatment
  – roughen surfaces
  – chemically treated (poly(5-ENB, oxidised/hydrolysed), roughened

• All liners compatibility with composite propellant

• Bonding agent/primer increased the peel strength ten fold
  – failure mode propellant-liner interface

• Inert propellant model
  – failure mode in propellant near liner interface
Primers for Composite Materials

- **Surface treatment systems for polybutadiene-based insulants**
  - exploit the reactivity of the polybutadiene alkene backbone
  - based on silane
  - painted onto **fully cured** liner (low energy surface, no residual crosslinking species)

- **Five primers/bonding agents**
  - 1,4-bis(di-methylsilyl)benzene + Pt(0) catalyst;
  - octadecylsilane + Pt(0) catalyst;
  - 1,4-bis(di-methylsilyl)benzene + Pt(0) catalyst + HTPB LM20;
  - 1-(2-(1-aminoethyl)-dimethylsilyl)-4-(dimethylsilyl)-benzene; and
  - 1-(2-(1-aminoethyl)-dimethylsilyl)-4-(dimethylsilyl)-benzene + 1,4-bis(di-methylsilyl)benzene + Pt(0) catalyst + HTPB

Treatment 4 caused the liner and propellant binders to act as a monolithic material.
Novel Insulants

• Motor case liner programme – redevelop current and design novel insulant systems

• Literature survey 100s of insulant formulation

• Further down-selected to nine
  – NBR/PVC filled with carbon fibre and silica (vulcanised)
  – NBR/PVC filled with vapour grown carbon fibre and silica (vulcanised)
  – Silicone filled with carbon fibre and silica (addition cure)
  – Silicone filled with alumina fibre and silica (addition cure)
  – Silicone filled with vapour grown carbon fibre and silica (addition cured)
  – EPDM filled with carbon fibre and silica (vulcanised)
  – EPDM filled with alumina fibre and silica (vulcanised)
  – EPDM filled with alumina fibre and silica (peroxide cure)
  – EPDM filled with carbon fibre and silica (peroxide cure)
### Small Scale Evaluation of Insulants

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Density/g cm⁻³</th>
<th>Casting Liquid Uptake/%</th>
<th>Phenolic Bonding</th>
<th>DMA – Tg/°C</th>
<th>Tensile – Strain ambient/%</th>
<th>Tensile – Strain -60°C/%</th>
<th>Tensile – strength/MPa</th>
<th>Tensile – P₁₈₀</th>
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<td>ST359901</td>
<td>Silicone/silica/carbon fibre (addition cured)</td>
<td></td>
<td>&lt;1.3</td>
<td></td>
<td></td>
<td>&gt;500</td>
<td>&gt;500</td>
<td>&gt;6.9</td>
<td>&gt;4</td>
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<td></td>
<td></td>
<td></td>
<td>&gt;1.3, &lt;1.5</td>
<td></td>
<td></td>
<td>&lt;500</td>
<td>&lt;500</td>
<td>&gt;6.9</td>
<td>&gt;2.5</td>
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<td></td>
<td></td>
<td>&gt;1.5</td>
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<td></td>
<td>&lt;100</td>
<td>&lt;100</td>
<td>&gt;4</td>
<td>&lt;4</td>
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<td>&lt;5</td>
<td>&lt;5</td>
<td>= adhered</td>
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<td>&lt;60</td>
<td>&lt;60</td>
<td>&lt;500</td>
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<td>&lt;100</td>
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<td>ST35A101</td>
<td>Silicone/silica/vapour grown carbon nanofibre</td>
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<td></td>
<td></td>
<td>&lt;2.5</td>
<td>&lt;2.5</td>
<td>&lt;4</td>
<td>&lt;100</td>
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<td>(addition cured)</td>
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<td></td>
<td>&lt;2.5</td>
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<tr>
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<td>&lt;2.5</td>
<td>&lt;2.5</td>
<td>&lt;4</td>
<td>&lt;100</td>
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<td>&lt;2.5</td>
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<td>cured)</td>
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<td>&lt;2.5</td>
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<tr>
<td>ML057V3</td>
<td>PVC/polybutadiene-nitrile /silica/ vapour grown</td>
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<td>&lt;2.5</td>
<td>&lt;2.5</td>
<td>&lt;4</td>
<td>&lt;2.5</td>
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<tr>
<td></td>
<td>carbon nanofibre(sulphur cured)</td>
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<td></td>
<td></td>
<td>&lt;2.5</td>
</tr>
</tbody>
</table>

- Requirement to bond to a phenolic film ("sticks" to anything)
- Silicone bonding poor
  - low energy surface
  - low reactivity
Adhesion with Phenolic Film

*Phenolic cure is a condensation reaction – water produced. Cure under high pressure.
Novel Insulant Application/Processing

• Novel insulant processes for mixing liquid insulants
  – mixing using an acoustic mixer
  – resonant vibrating platform

• LabRAM ® mixer mixed silicone/silica/fibre
  – approximately 4 times faster
  – as no impellers/blades, the time to clean the LabRAM mixing vessel was 10 times faster than the horizontal mixer
  – additionally very little waste was produced
  – mixing caused self heating, described by a simple internal friction/cooling model

Bad mix

Good mix
Novel Insulant Application/Processing

- Would like to automate insulant manufacture

- Partner demonstrated that
  - a carbon-fibre filled silicone could be moulded into a metal tube producing liners 2mm thick and 500 mm long
  - insulant can be cured in-situ
  - the former can be removed from the mould without damaging the insulant surface

- However, analysis of the liners has shown that there were areas of concern
  - dimensional tolerance, porosity and inhomogeneity

- Additional work would have to be performed to produce flawless insulants
Silicone Insulant Bonding

• Originally silicone bonding poor

• Investigated a number of primer systems
  – Epoxides such as Epikote 828
  – Silicon containing species such as polydimethysiloxane diglycidyl ether, 1,3-divinyltetramethyl disolaxane, polydimethylsiloxane hydride, glycidoxypropyltrimethoxysilane, poly(hydromethylsiloxane)
  – polybutadiene-co-acrylonitrile carboxy terminated with epoxides and radicals
  – Two component base silicone
  – 5-Ethylidene norbornene + ruthenium ROMP catalysts

• 5-ENB and poly(hydromethylsiloxane) pre-treatments best primers
  – others treatments poor

• Pendant ethylidenes react with phenolic species in phenolic film creating a good bond
  – cf EPDM cure process with electron deficit phenolic resins (DG Guillot, AR Harvey, EPDM Rocket Motor Insulation, US patent 6787586 B2.)
Insulant Bonding

- Mechanical testing was performed using button test pieces
  - three temperatures; hot, ambient and cold
  - ML041 v1 and V2 failed in mostly in propellant
  - 5-ENB primed silicone need better adhesion with metal

ST363901, hot film/rubber

ML041V1, hot propellant/film
Conclusions

- **Insulants are critical to the success for motor performance**
  - consists of filled rubbers that limit heat transfer to the pressure chamber body
  - they have low Tg, low surface energy, most insulants have low polymer backbone reactivity

- **Adhesion of the propellant to the insulant is also critical**
  - need to prevent the formation of extra burning surfaces that could over-pressurise the motor and cause it to explode

- **Approach to bonding insulant to propellant is to use primers that form covalent or physical networks**

- **Achieved bonding by**
  - using isocyanate primer systems
  - exploiting of the liner reactivity and reaction with silanes
  - in-situ polymerisation creating novel inter-penetrating networks
  - converting non-reactive insulant surfaces to functionalised surfaces
Acknowledgements

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  – Roxel
  – Artis
  – BD Technical polymers
  – MoD
  – DSTL

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Any Questions?