

Formulation-Derived Interface Characteristics Contributing to Failure in Plastic-Bonded Explosive Materials

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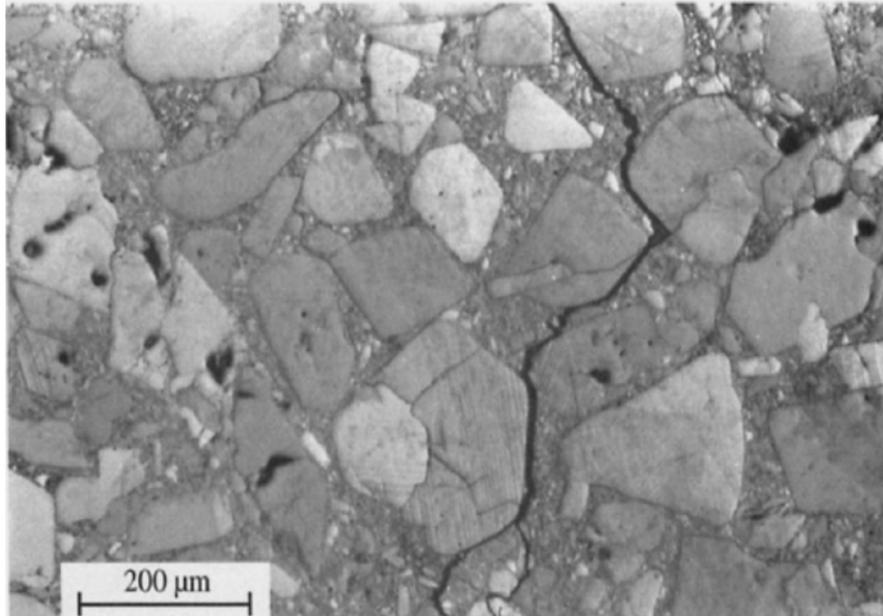
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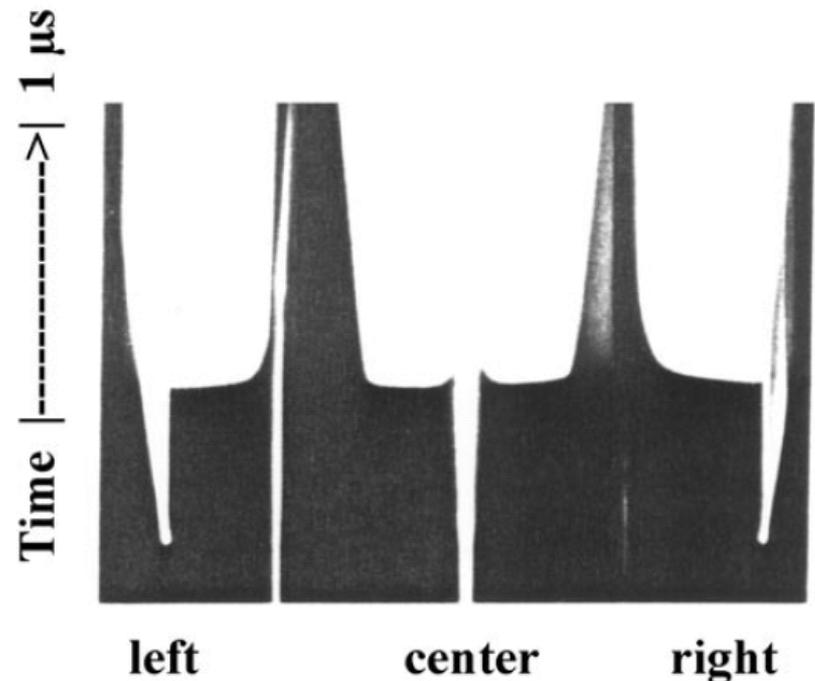
Slide 1

Interfaces Affect Sensitivity & Performance of PBXs

- Crystal-binder interfaces implied for adhesion, durability, aging, sensitivity...
- Back of envelope calc: a golf ball sized piece of PBX 9501 contains ~27 million particles. This yields a total HE surface area of ~1.5m²!
- Low tensile stresses (< 5 MPa) can cause fracture and increase the chance of off-normal detonation

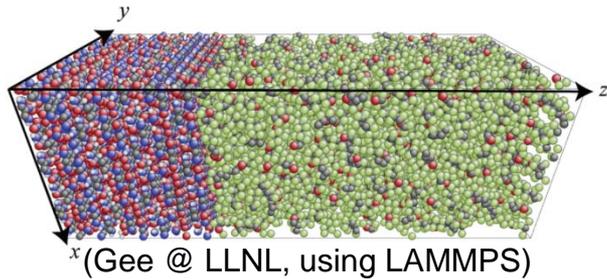


Rae *et al.*, 2002



Souers *et al.*, 2006

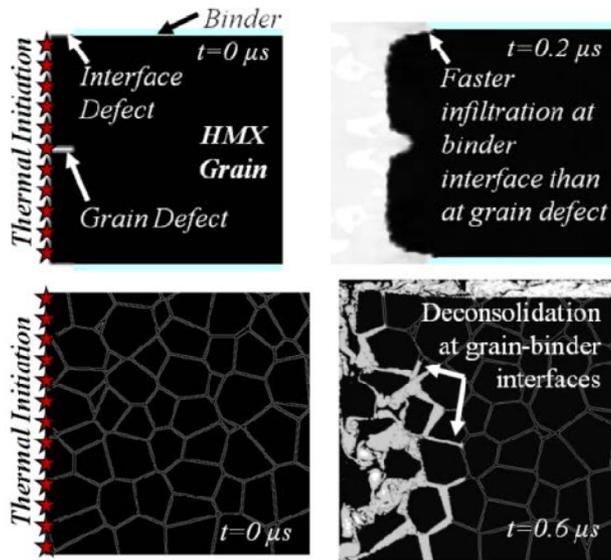
Example HE models which incorporate “interfaces”



Molecular dynamics (MD) simulations often assume infinitely smooth interfaces. “Bonding sites” are determined from force potential calculations, assuming periodic binder structure.

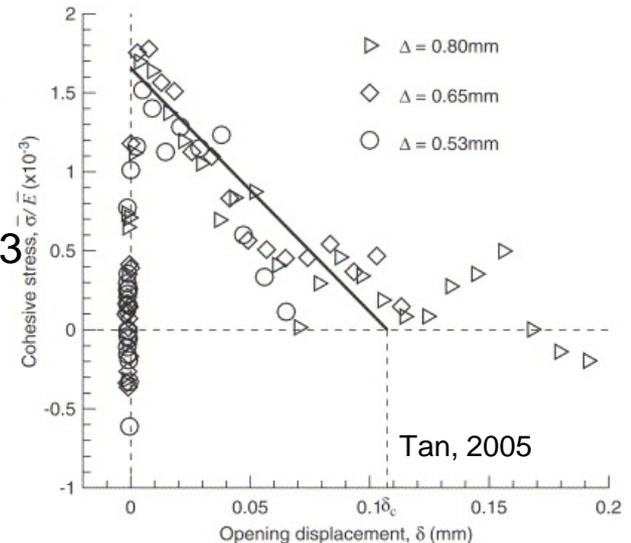
Recent efforts have highlighted the necessity of describing crystal-binder interfaces in grain-scale models.

- Interface defects propagate faster than grain defects
- Interfaces break up or “deconsolidate” faster than the grains under reactive burning



(Springer @ LLNL, using ALE3D)

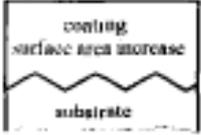
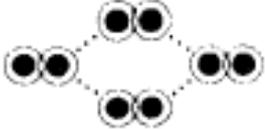
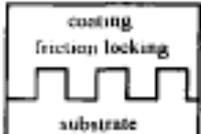
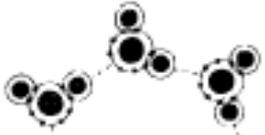
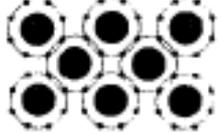
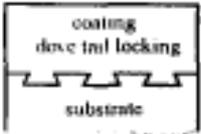
Complex composites like PBX 9501 do not exhibit simple cohesive zone behavior. PBX 9501 has 3 stages of decohesion!



Real PBX interfacial fracture is anisotropic, dependent on many factors, and there often is not available experimental information in the literature

Crystal – Polymer Interfacial Properties

- **Characterization of the interface is necessary**
 - Fracture
 - Wetting / adhesion
- **Key questions:**
 - **What factors are most important to adhesion?**
 - Surface roughness
 - Surface energy
 - Interphase region
 - **How can we quantify the adhesion?**
 - **What effect does solubility have during processing and in the resulting microstructure?**

Roughness	Surface energy	Interphase
mechanical interlocking 	physical bonding van der Waals bonds 	chemical bonding ionic bonds 
	hydrogen bridge bonds 	atomic bonds 
		metallic bonds 

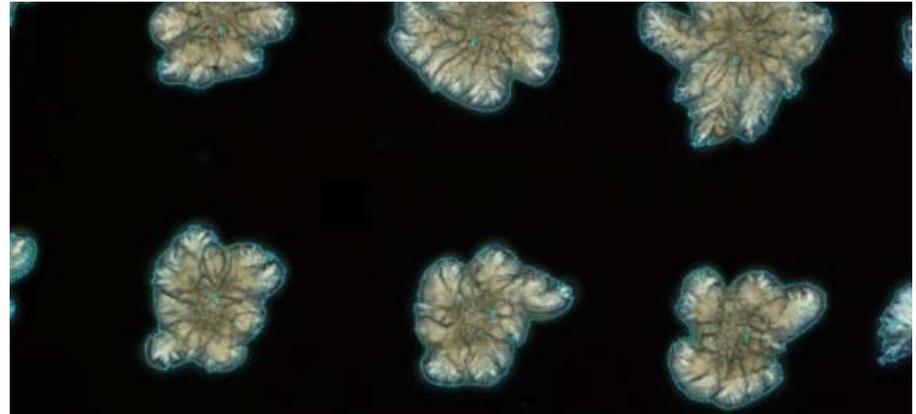
(Weiss, 1995)

PBX microstructure is affected by formulation processes

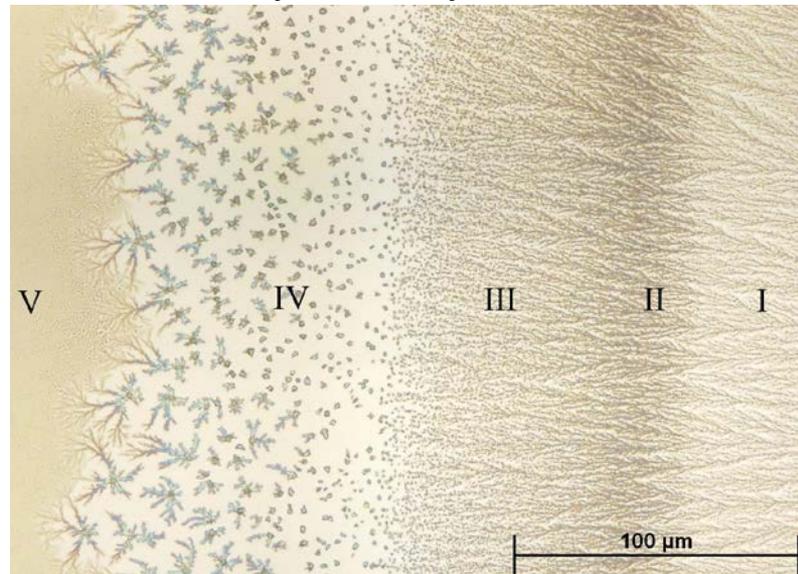
- **Most PBXs are formulated with a slurry casting process**
 - Energetic crystals of some specified size and size distribution are suspended in water or other non-solvent
 - Suspension is mixed with polymer dissolved in organic solvent(s)
 - Drastic alteration of solubility conditions causes the polymer to “crash” out of solution and coat the energetic crystals
- **We have years of historical data and anecdotal evidence that this procedure must be tightly controlled to produce specified PBX**
 - Composition A-3 (RDX-PE) exhibits wide varieties of properties, usually due to incomplete surface coverage (McGann et al)
 - New production procedure for binders like Kel-F 800 (Hoffman et al)
- **Even when the product is as specified, the finished composite does not always have the anticipated microstructure**
 - HMX particle size distribution in pressed parts is not as specified (Skidmore et al)

Interactions often occur between the multiple formulation constituents

- Usually, the energetic crystal has some solubility in the polymer solvent
- Sometimes the crystal also has solubility in the polymer itself
- Interphase regions between the crystal and binder can be formed (“dirty binder”)
- Solubility thermodynamics and kinetics are both important for crystal stability

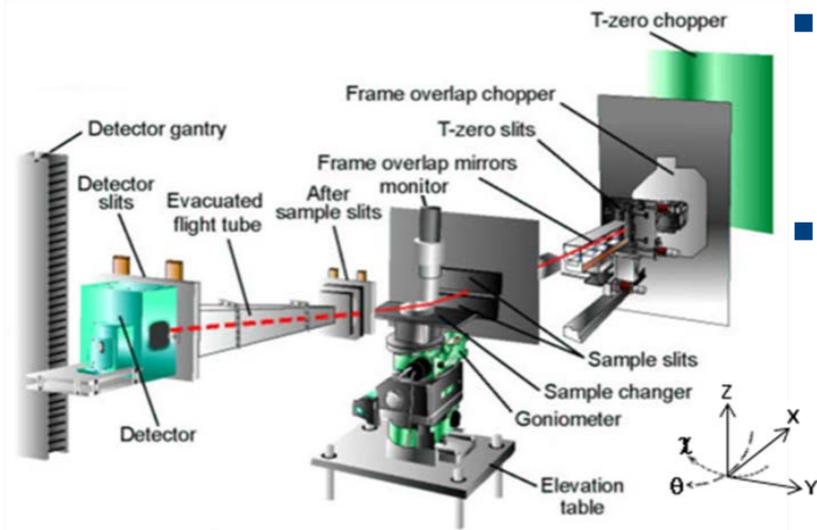


Inert molecular crystal recrystallization from binder



HMX (I) coated with NC (II) showing regions of dissolution and recrystallization (III-V)

Neutron Reflectometry: Study of Films and Interfaces



- Neutrons can be advantageous as a probe

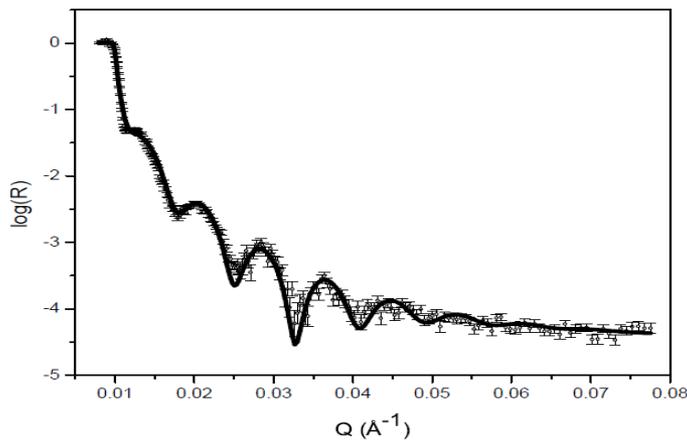
- Buried interfaces
- Nucleic scattering

- High resolution of chemistry through-thickness by modeling scattering length density (SLD)

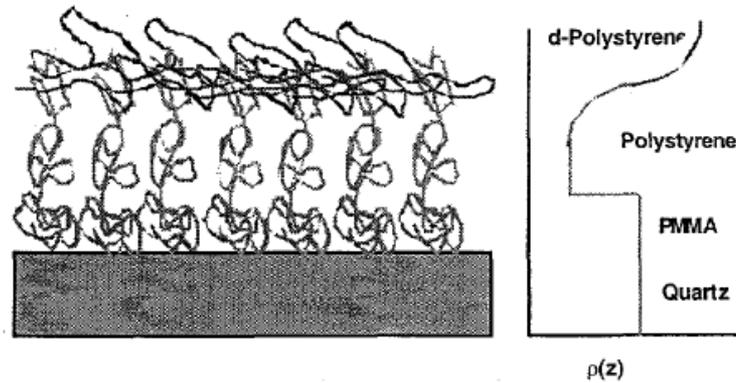
- SLD is a function of scattering cross section b (e.g. chemistry) and molecular volume (e.g. density)

- SLD can be plotted as a function of depth into the sample

$$R = \frac{I_{out}}{I_{in}} = \frac{k_{out}}{k_{in}} Q_z = \frac{4\pi \sin(\theta)}{\lambda}$$

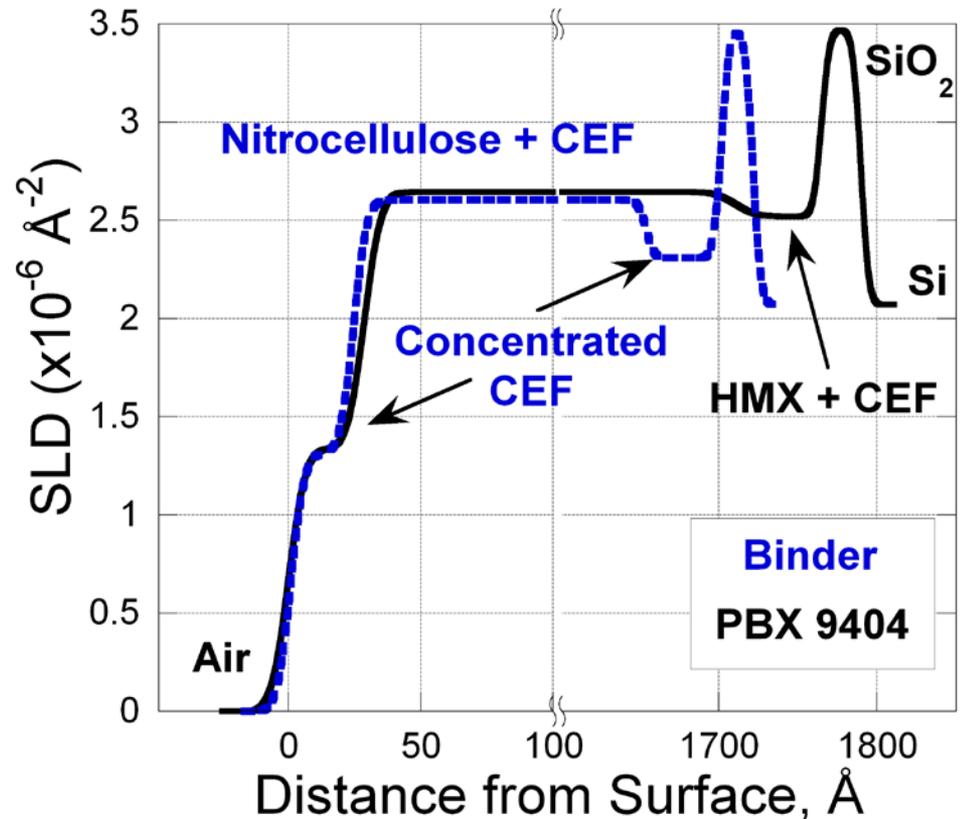


$$SLD = \sum \frac{n_i b_i}{V} \approx \frac{\text{atoms}}{\text{volume}} \times \text{chemistry}$$



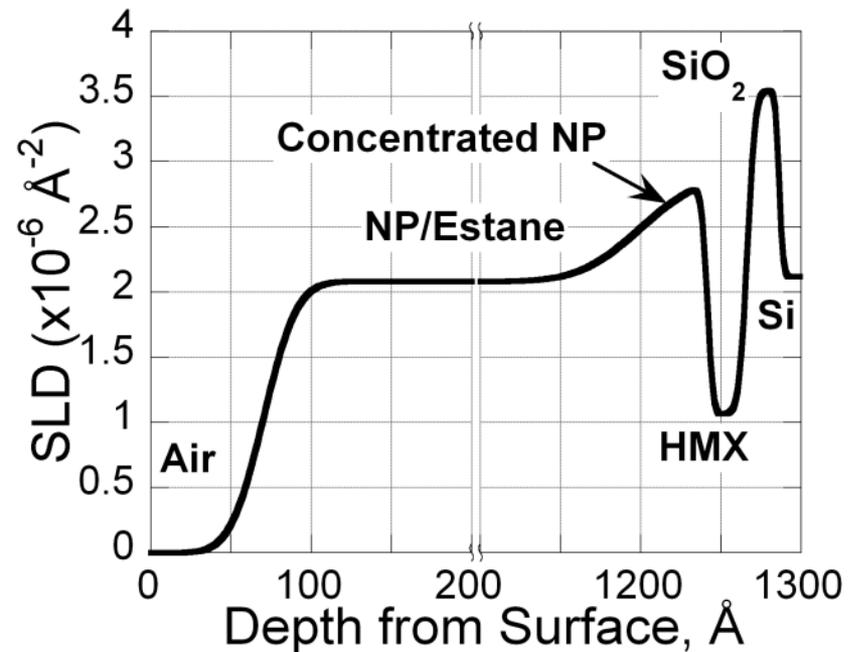
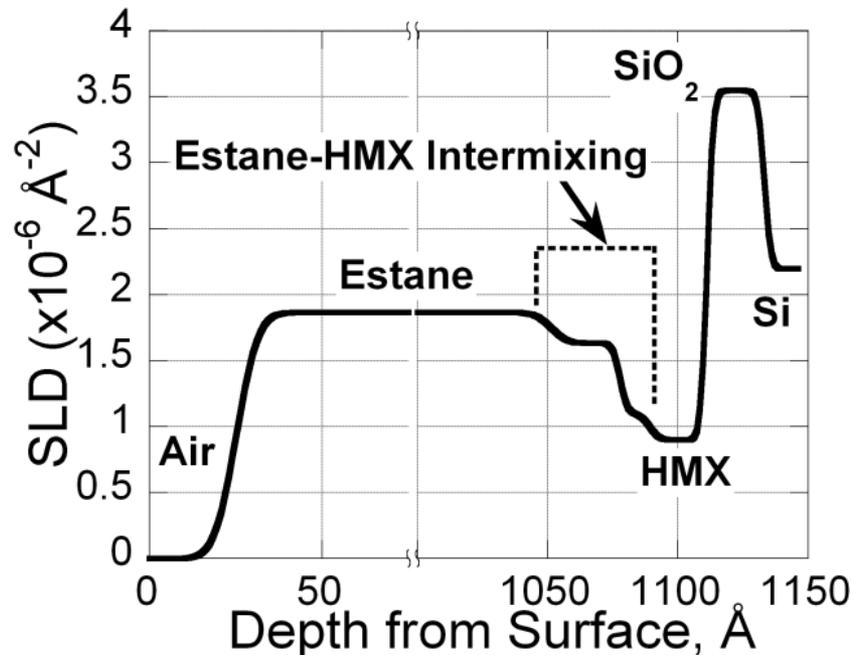
NR of PBX 9404 (NC + CEF Plasticizer + HMX)

- CEF plasticizer is observed to segregate at substrate interface and at air interface
- Plasticizer migration and evaporation is tied to mechanical damage and aging in NC-containing propellants (Pesce-Rodriguez et al)
- Reflectometry shows that the 9404 binder deposition process dissolves HMX film, confirming microscopy
- SLD of plasticizer-rich region and main binder slightly higher, indicating HMX diffuses to a large extent throughout the sample



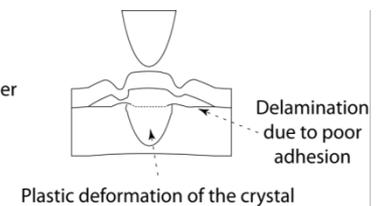
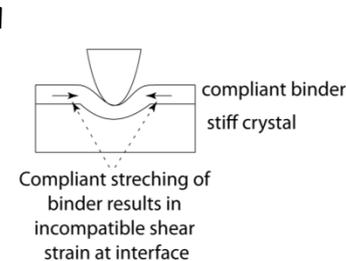
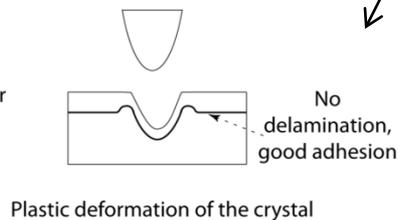
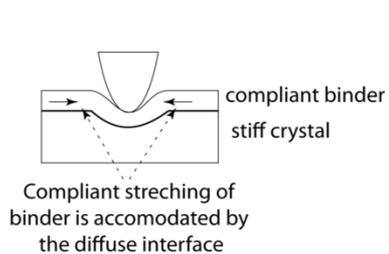
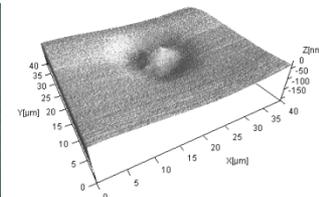
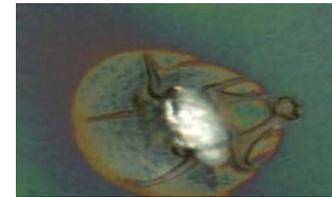
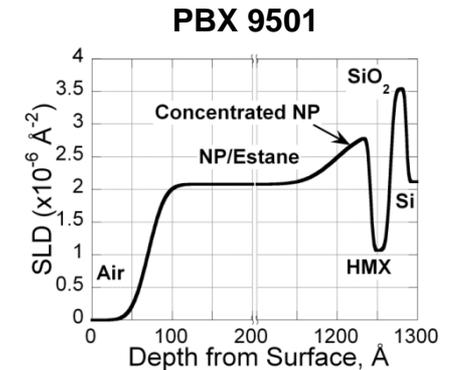
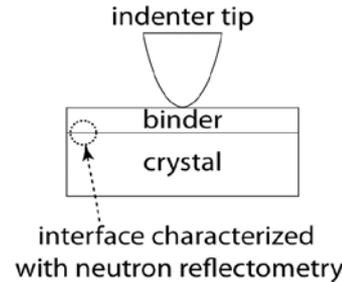
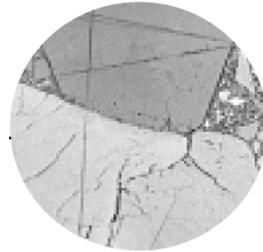
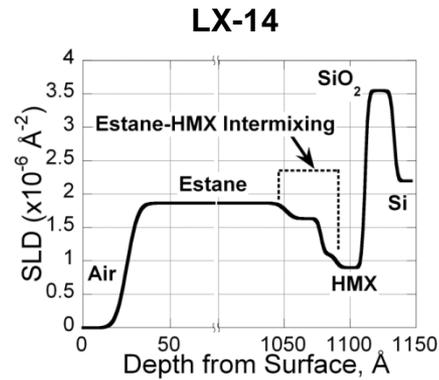
NR of HMX-Estane: Plasticizer Effect

- HMX coated by Estane (LX-14) and by NP/Estane (PBX 9501)



- HMX dissolves into the polymer to create an interface of varying composition – an *interphase* region
- When NP is included it segregates to the interface, hindering dissolution
 - NP is a much smaller molecule than the polymer chains

Post-deformation analysis revealed that *fracture behavior depended on interfacial structure!*

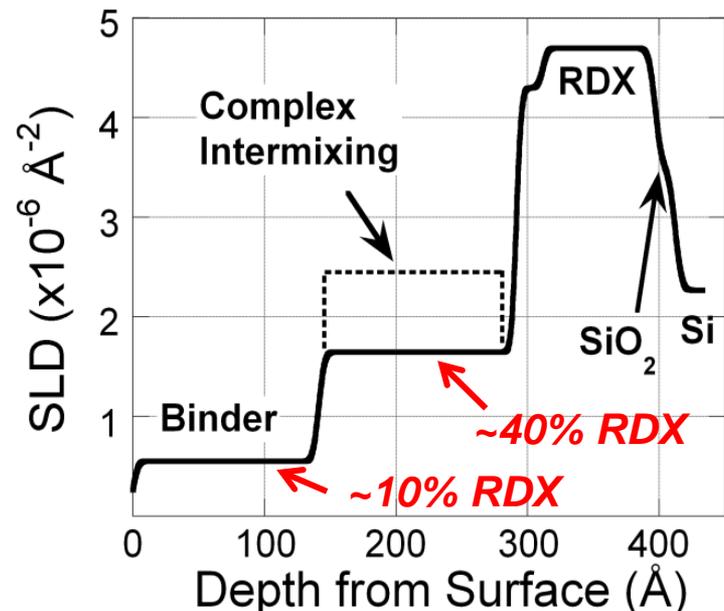


Interfacial composition affects properties & performance!

Significant heterogeneity observed in Composition A-3 materials (RDX-Wax) and in layered film systems

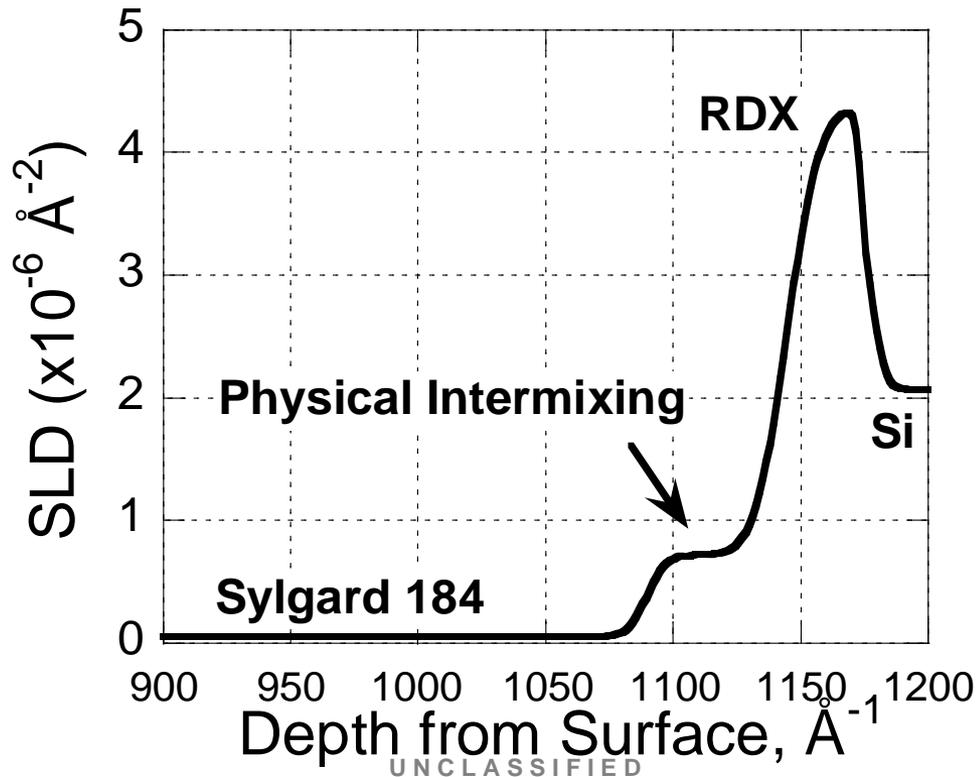
- Surface energy determination showed that residual chemicals have higher attraction to RDX than the binder
- Some of the residual chemicals can dissolve RDX
- Neutron reflectometry confirmed that RDX was being dissolved into the binder to create an interphase

Material	Surface Energy			W_a to RDX
	γ^d	γ^p	γ_s	
AC 656 OPE	29.1 ± 1.3	4.0 ± 2.2	33.1 ± 3.5	80.3 ± 3.5
Emulsion: OPE	29.8 ± 1.6	3.1 ± 2.0	32.9 ± 3.6	79.4 ± 3.6
Emulsion: other	20.1 ± 4.7	39.1 ± 3.7	59.2 ± 8.4	99.9 ± 8.4



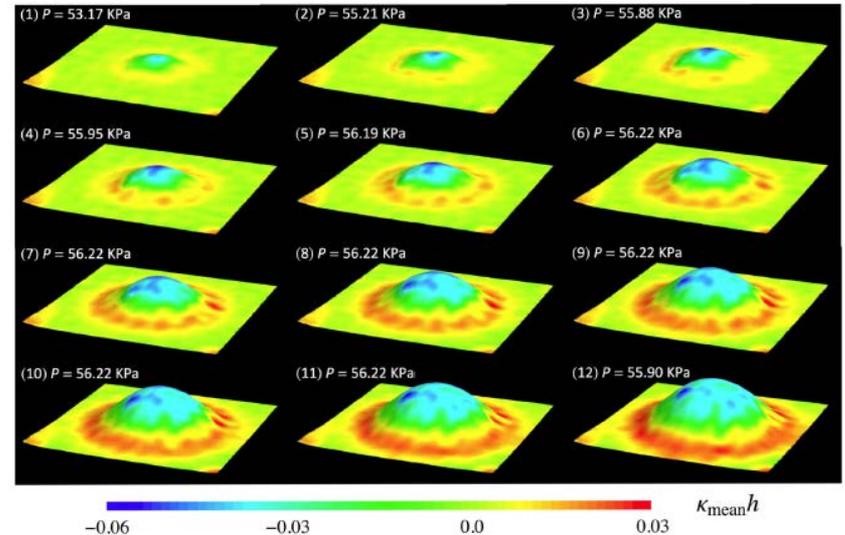
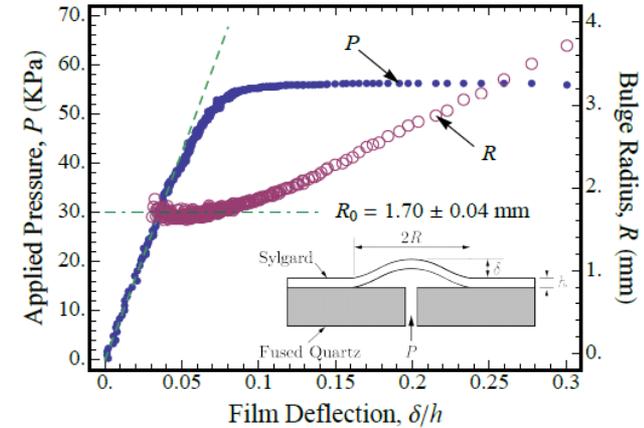
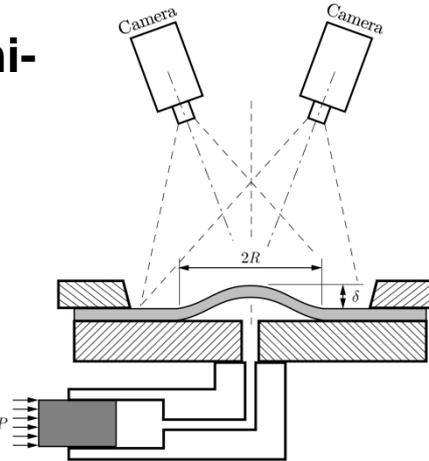
Contrasting Case: Sylgard on RDX

- XTX 8004 (extrudable) showed little interaction between RDX and binder
- “Interface” is smaller (2 – 3 nm)
- Sylgard SLD is not elevated above theoretical value



The Bulge Test: Linking measured interfacial chemistry to true adhesion

- Most adhesion tests are semi-quantitative because they can't accurately assess the energy absorbed by the materials rather than the interface
 - PBX adhesion tests commonly crack the crystal
- The bulge test should only strain the adherent (binder)
- If film thickness is known, bulge area = deformed film + delaminated area
- Bulge size measured with DIC



Conclusions

- **Nano-scale compositional information can be obtained with high fidelity, showing small changes in formulation conditions directly determine the size and composition of crystal-binder interfaces**
- **Nanoindentation experiments demonstrate a measureable effect of these interfaces on adhesive properties.**
 - Semi-quantitative, need better techniques such as bulge testing
 - Are these mechanical properties relevant / noticeable at larger scales?
 - Preliminary data is promising
 - Are sensitivity or performance properties affected?
- **The data can be used for development of grain scale models**
- **The possibility exists to tailor or customize certain PBX properties by intentionally modifying the interface**

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Thank You!
Any Questions?