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Title:	Microstructural Characterization of Plastic-Bonded Explosives
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Title: Microstructural Characterization of Simulated Plastic-Bonded Explosives

Plastic bonded explosives (PBX), a mixture of hard, anisotropic grains in a compliant matrix, represent an interesting case for understanding composite mechanical response and failure. The nature of the crystal-polymer interface are important for relating mechanical and explosive properties to the manufacturing process as well as for the development of predictive failure models. Acetaminophen is studied here as an inert substitute for traditional explosive crystals for two reasons: it has similar mechanical and crystallographic properties to explosives, and because acetaminophen – polymer composites are of interest to the pharmaceutical industry. The adhesion of the crystal to several typical polymer binders has been characterized by surface energy measurements and a novel mechanical test. The chemistry of the interface has been analyzed with neutron reflectometry, differentiating between a clean interface and a compositionally graded interphase region. Several other techniques, such as atomic force microscopy and chemical staining, have also been used to obtain information about the interfacial properties, and the results of all these methods will be presented.

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Microstructural Characterization of Plastic-Bonded Explosives

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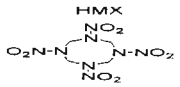
Plastic-Bonded Explosives (PBXs)

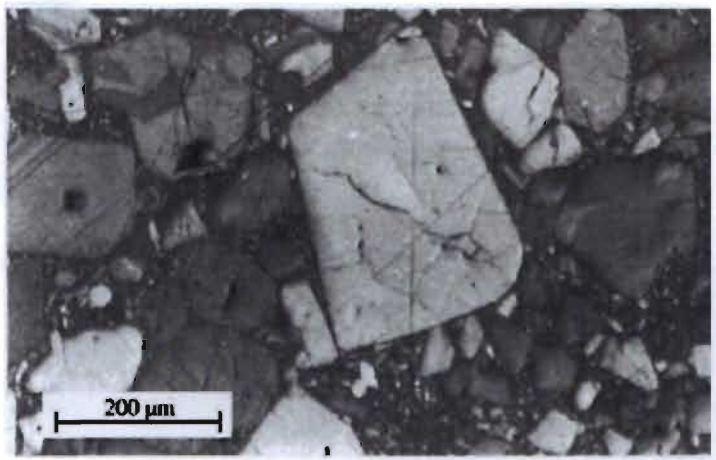
- **Composite materials designed for reliable use in industrial and military applications**
- **Highly loaded explosive crystals (> 85% by weight) in a compliant polymer matrix**
  - Explosives are fragile molecular crystals with low-symmetry structures
  - Commonly referred to as the "binder"
  - Provides physical stability to the explosive crystals and reduces sensitivity

HMX



RDX

TATB



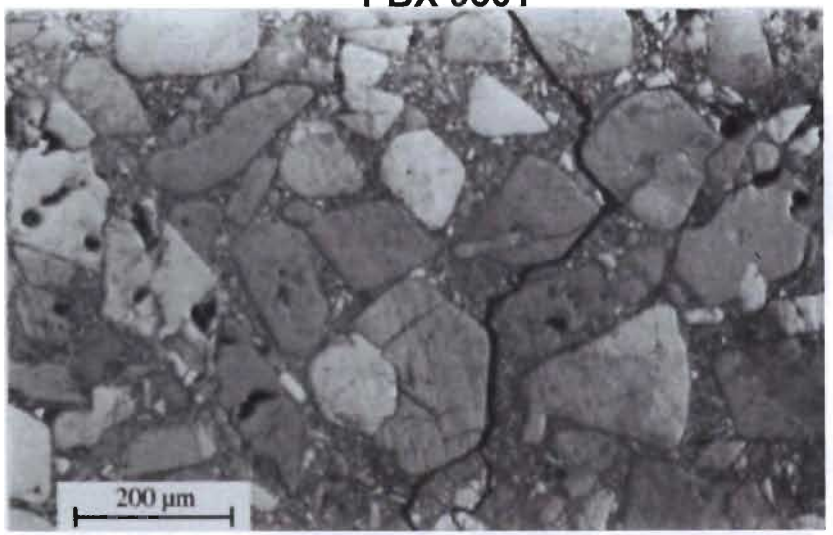
PBX 9501

Rae *et al.*, 2002

Failure of Plastic-Bonded Explosives

- **Relatively low tensile stresses can cause fracture and increase the chance of hot spot formation**
  - Exact failure mode depends on particle size, loading, and polymer properties (Palmer *et al.*, 1993)
  - Most traditional PBXs failed via crack propagation between the crystal and the binder
- **Serious implications for handling safety and application**
- **Leads to unpredictable combustion behavior at shock pressures (Berghout, 2002)**
  - Change pressure necessary for detonation
  - May even change combustion mode

PBX 9501

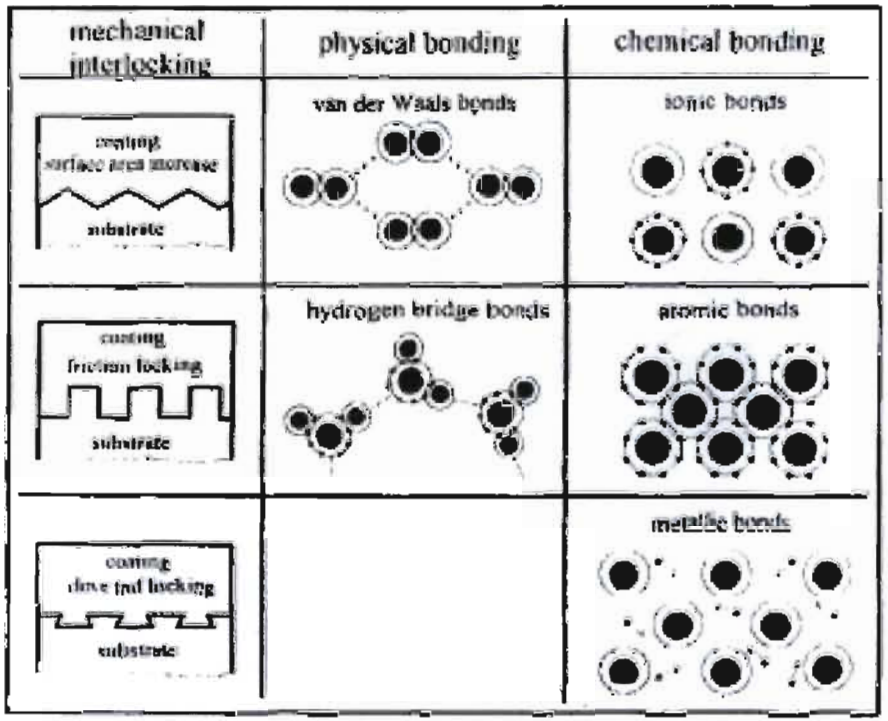


Rae *et al.*, 2002

Crystal-Polymer Interfacial Properties

- **Characterization of the interface is necessary**
- **Key questions:**
  - What factors are most important to adhesion?
    - Surface roughness
    - Surface energy
    - Interphase region
  - How can we quantify the adhesion?
  - Is the polymer at the interface the same composition as in the bulk PBX?

Roughness Surface energy Interphase

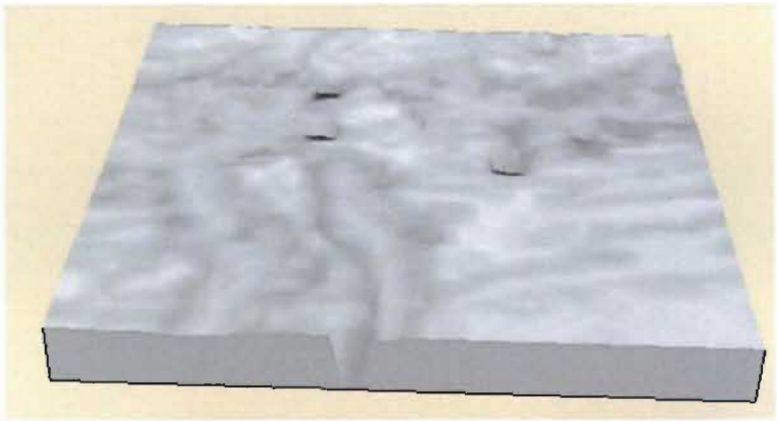


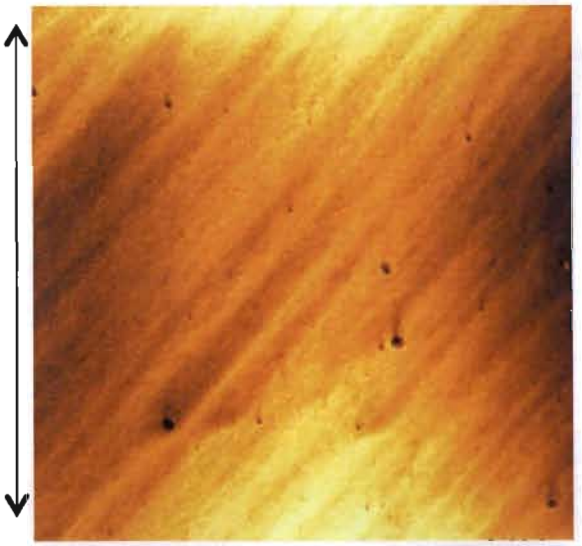
(Weiss, 1995)

Quantifying Surface Roughness

- **Many techniques for measuring roughness**
  - AFM, X-ray scattering, interferometry for very thin films
  - Physical or optical profilometry for thicker films
- **Optical profilometry was used for acetaminophen crystals and dip-coated thick Estane films**
  - Bare crystal roughness – 0.76 μm RMS
  - Coated roughness – 10.2 μm RMS
- **Explosives can be grown very smooth and roughness can be induced precisely (Ramos, private communication, 2010)**

Dip-coated Acetaminophen



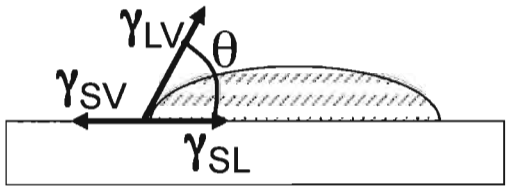


RDX – 3.2 nm RMS

Surface Energy and Work of Adhesion

- **Surface energy may be measured with contact angle experiments**
  - Use 2 or more standard liquids
  - Static or dynamic angles
  - Advancing or receding angles

$$\gamma_{LV}\cos\theta = \gamma_{SV} - \gamma_{SL}$$



- **More accurate to break down energy into polar (p) and dispersive (d) components (Fowkes, 1963)**

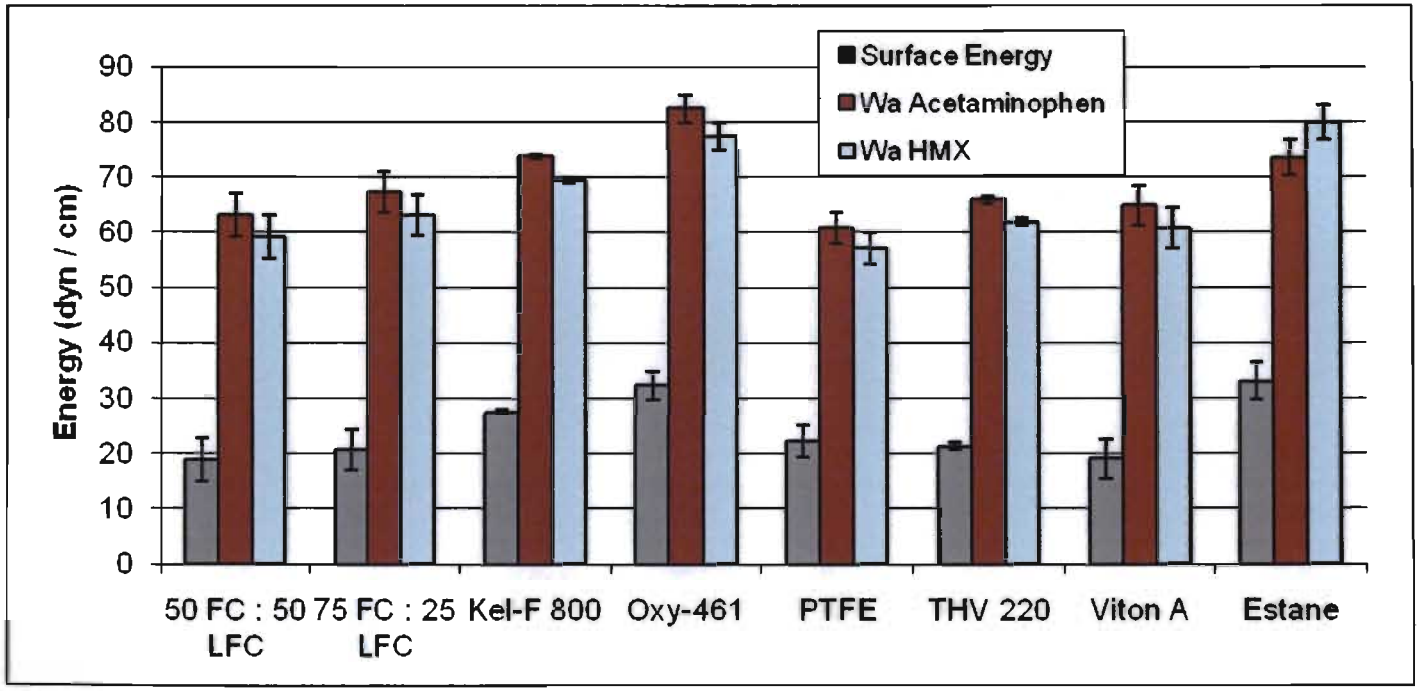
$$\gamma_{LV} = \gamma_{LV}^{p} + \gamma_{LV}^{d} \qquad \gamma_{SV} = \gamma_{SV}^{p} + \gamma_{SV}^{d} \qquad \gamma_{SL} = \gamma_{SL}^{p} + \gamma_{SL}^{d}$$

- **Theoretical work of adhesion can then be calculated, treating the binder as the liquid**

$$W_a = \gamma_{LV} + \gamma_{LV}\cos(\theta) = 2(\gamma_{LV}^{d}\gamma_{SV}^{d})^{1/2} + 2(\gamma_{LV}^{p}\gamma_{SV}^{p})^{1/2}$$

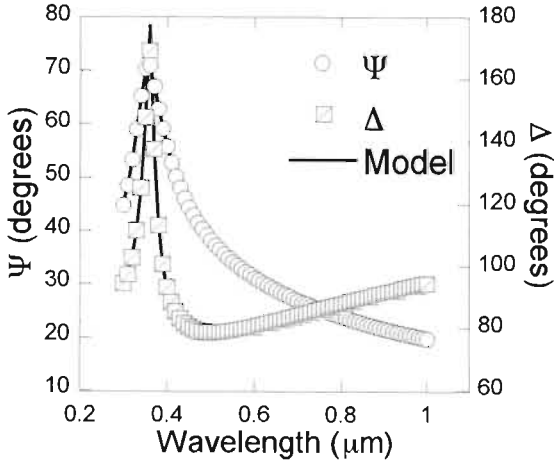
Surface Energy of Potential Binders

- Several fluropolymer binders investigated and compared with Estane
- Theoretical work of adhesion calculated to TATB and HMX using literature values of energy for the explosives

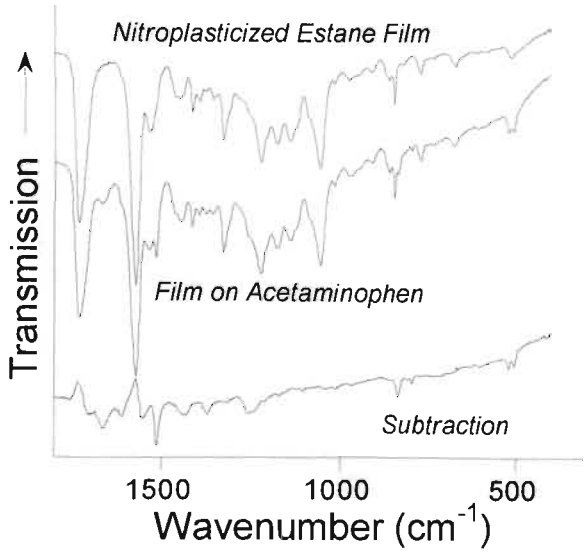


Neutron Reflectometry of Simulated PBX

- **Measured film samples with ellipsometry, IR spectroscopy and NR**

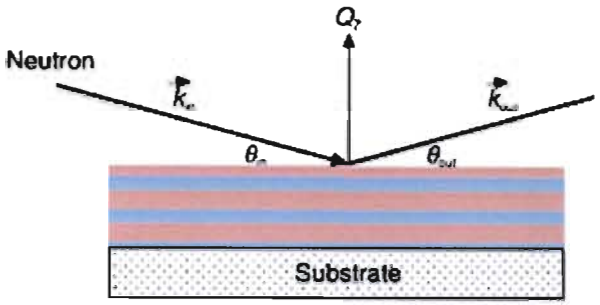


Sample	Coating Speed (mm / min)	Thickness (nm)	Variation (%)	*n*	*k*	MSE fit
BDNPA/F	50	523±2.0	9.55±0.20	1.472	0.002	24.8
Estane 5703	50	67.0±0.01	2.93±0.17	1.489	0.000	2.55
Acetaminophen	50	136±0.29	19.6±0.69	1.568	0.005	20.6
Estane on Aceta.	100	114±0.11	18.7±0.18	1.508	0.001	14.2
NP Estane	100	72.6±0.10	3.09±0.05	1.486	0.006	8.35
NP Estane on Aceta.	100	70.4±0.07	8.89±0.25	1.475	0.005	6.22



Model	Thickness (nm)	n	k	MSE fit
Two layers: Estane (top) Acetaminophen (bottom)	99.8 15.1	1.483 1.529	*0* *0.005*	24.04
Two layers: Aceta. (top) on Estane (bottom)	4.7 108	1.586 1.491	*0.005* *0*	18.43
3 vol% Acetaminophen dispersed in Estane*	113	*1.489* *1.568*	*0* *0.005*	15.83
Two layers: Estane (top) Acetaminophen (bottom)	108 5.9	*1.489* *1.568*	*0* *0.005*	15.37
One homogeneous layer	114	1.508	0.001	14.2
* An Effective Medium Approximation (EMA) was used: the two materials with fixed optical constants were modeled as an isotropic mixture				

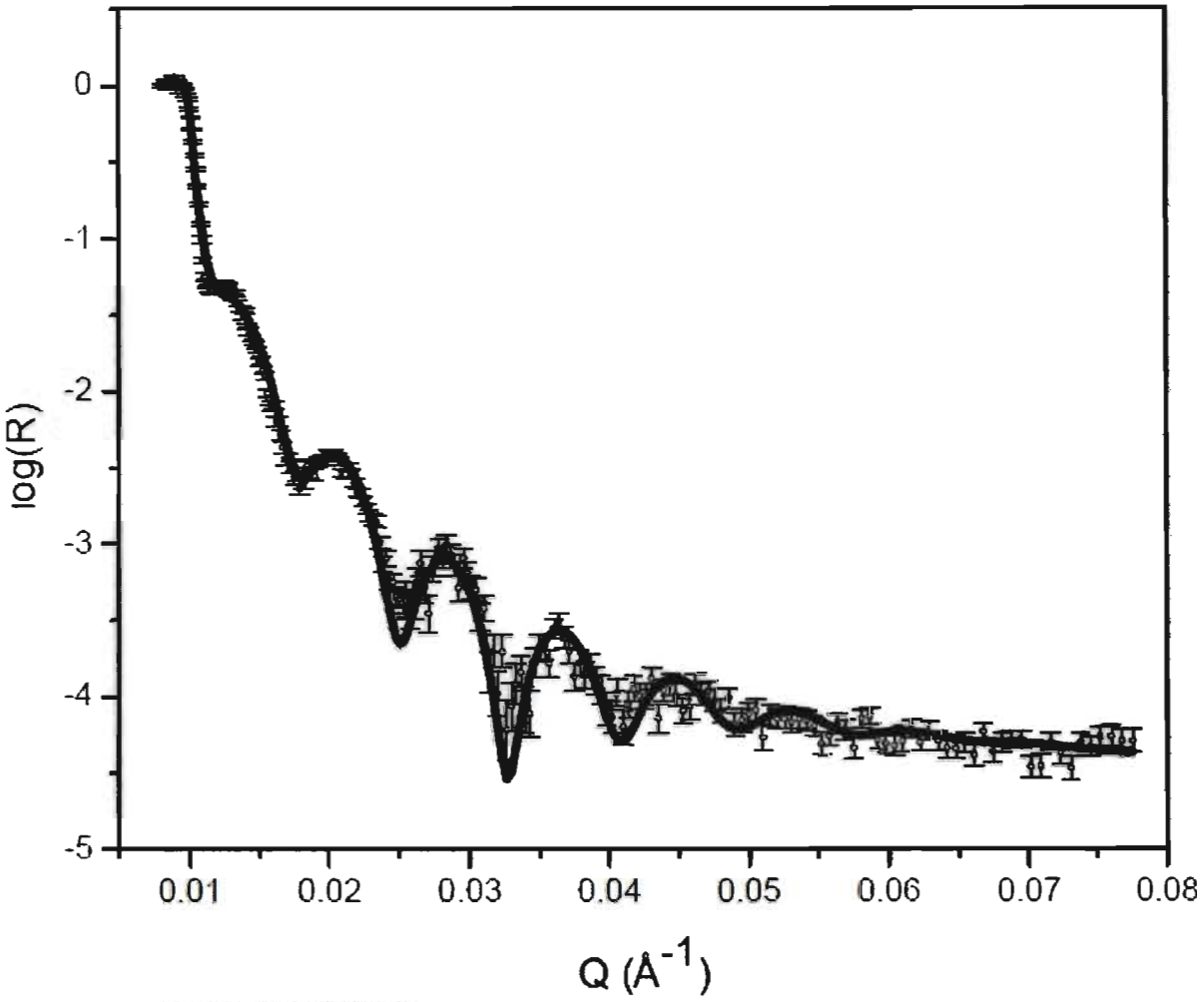
Neutron Reflectometry of Simulated PBX



Specular reflection

$$\theta_{in} = \theta_{out}$$

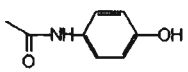
$$Q_z = |\vec{k}_{out} - \vec{k}_{in}| = (2\pi/\lambda)(\sin\theta_{in} + \sin\theta_{out})$$



Neutron Reflectometry of Simulated PBX

- **Two samples – acetaminophen coated by estane with & w/o NP**

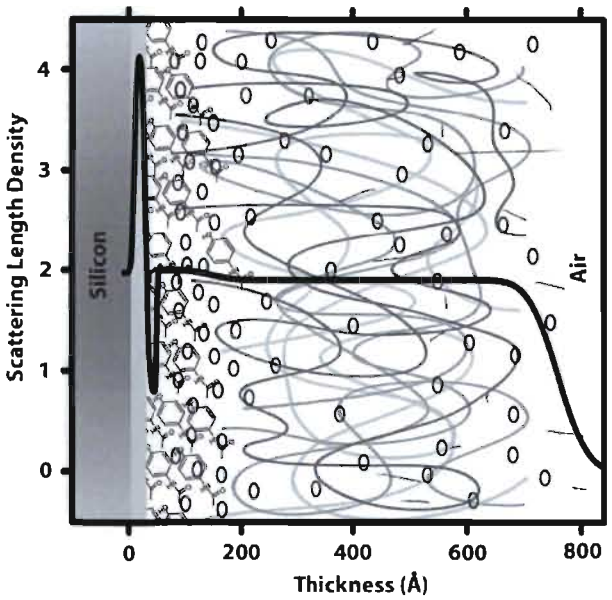
Aceta

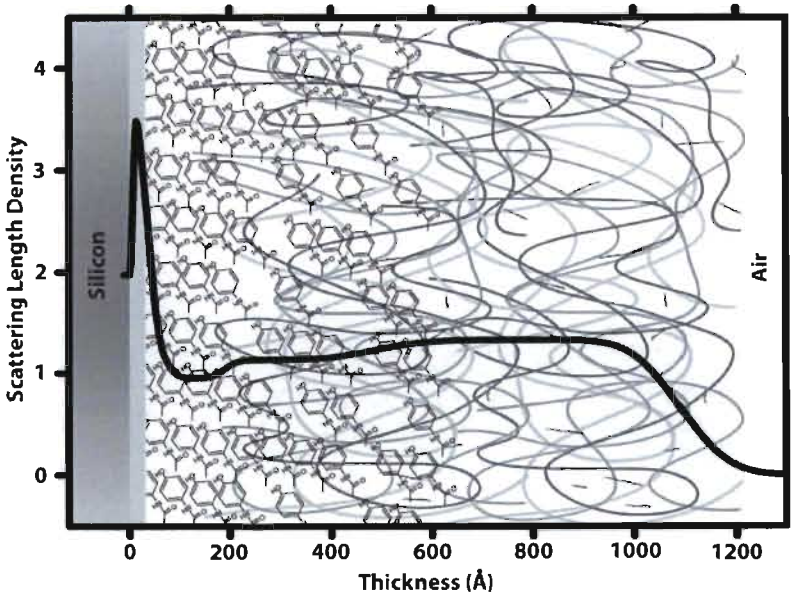


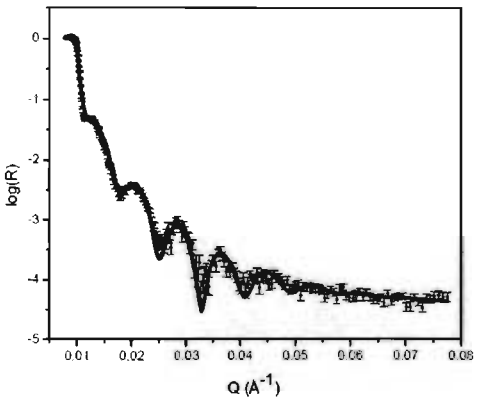
NP

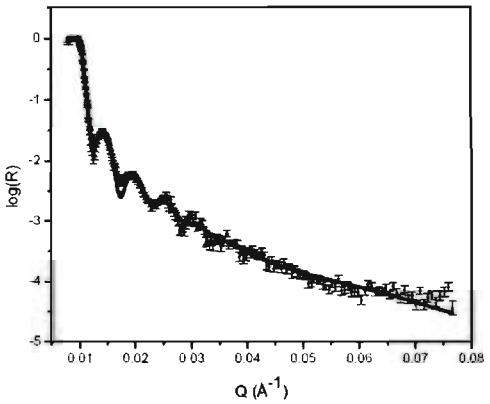
0

Polymer

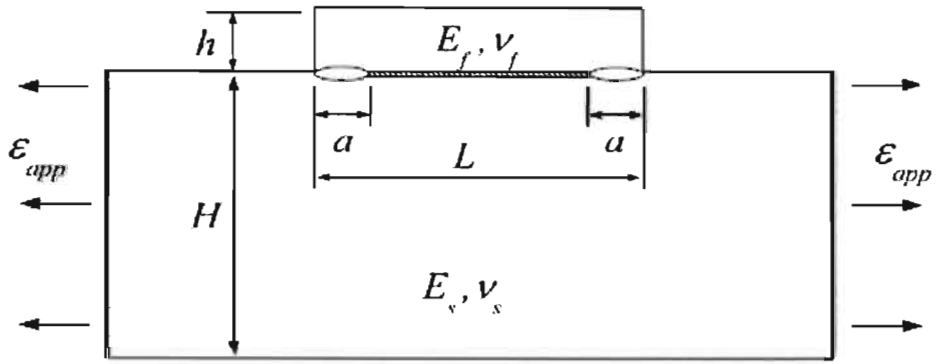






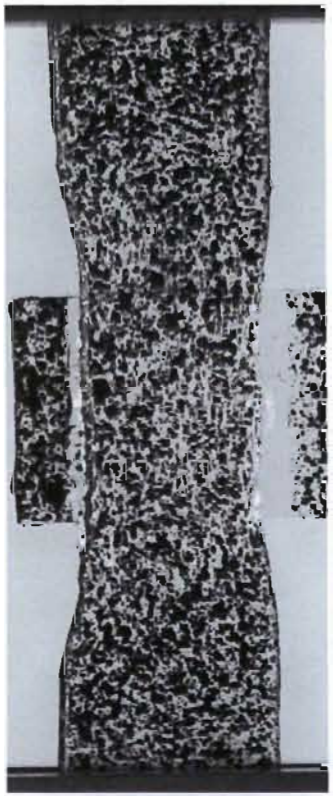


Island Delamination: Digital Image Correlation (DIC)

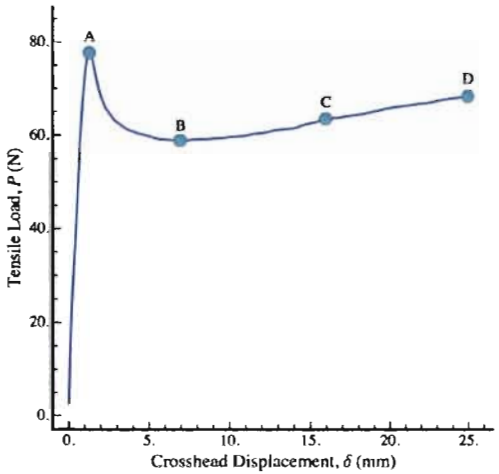


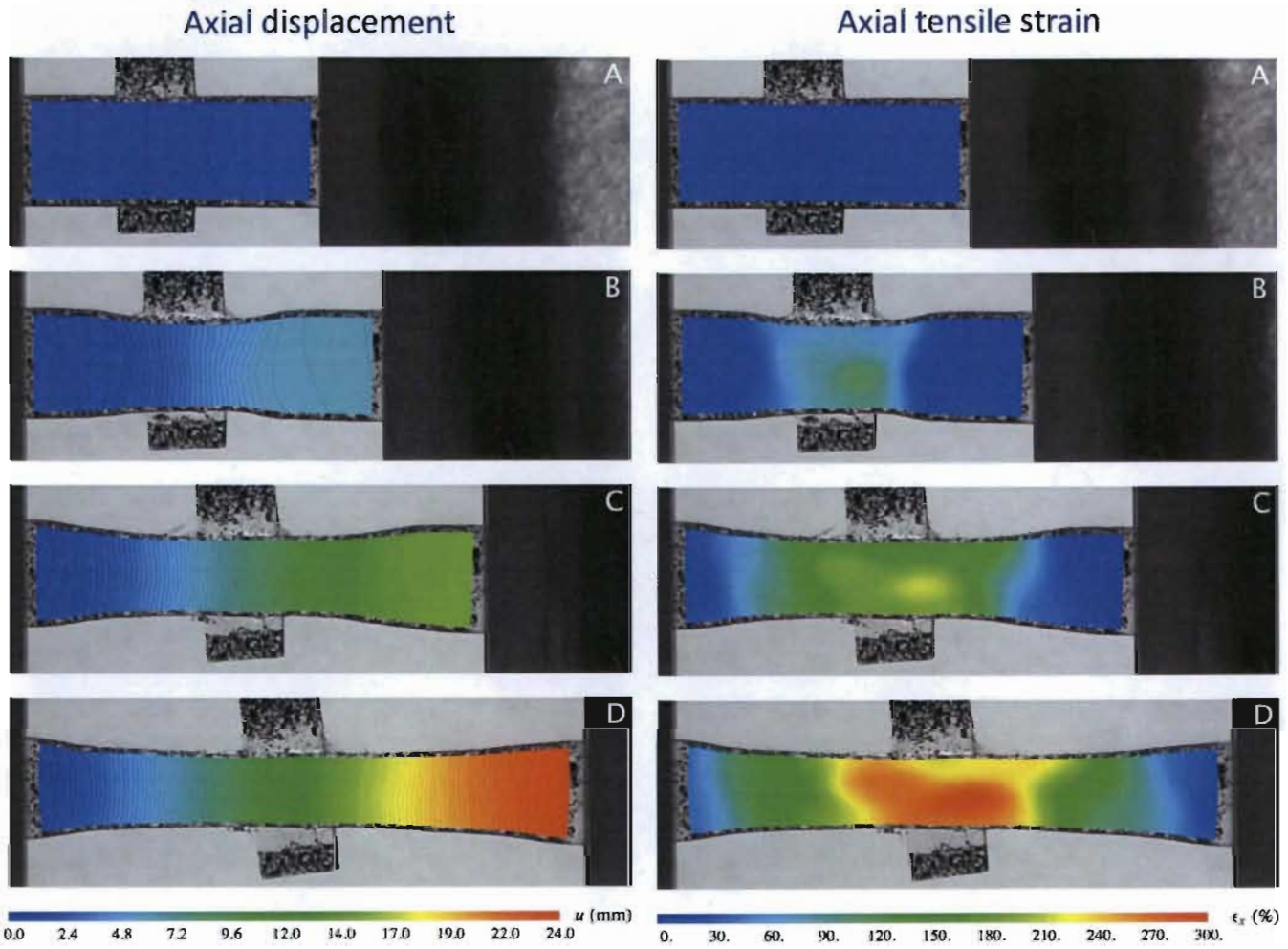
$$G = \frac{\pi}{16} \frac{E_S}{(1-\nu_S^2)} \varepsilon_{app}^2 (L-2a)$$

- Two polymers were tensile tested using digital image correlation to map strain (axial and lateral)
- Glass or acetaminophen crystals were attached to tensile specimens via a softening process



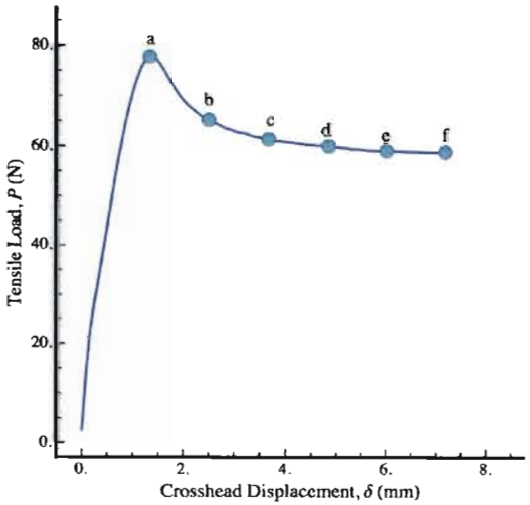
Kel-F 800 Tension: Test No.1



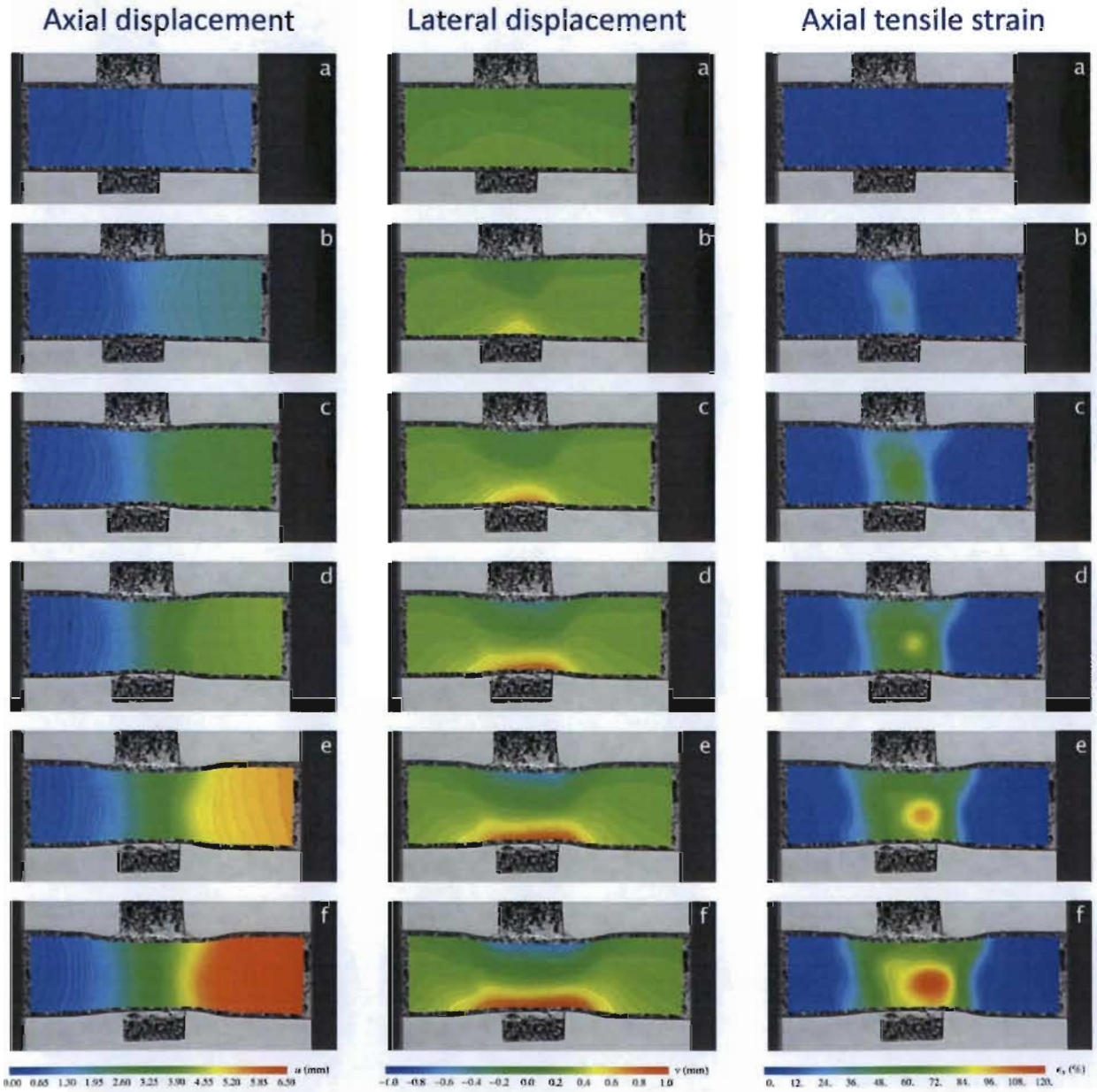


- Crosshead speed: 5 mm/minute.
- At moment D, overall engineering strain is about 94%, but the local (Lagrangian) strain is close to 300%.
- The load drop from moment A to moment B should be the focus of investigation.

Kel-F 800 Tension: Test No.1 (During Stage of Load Drop)

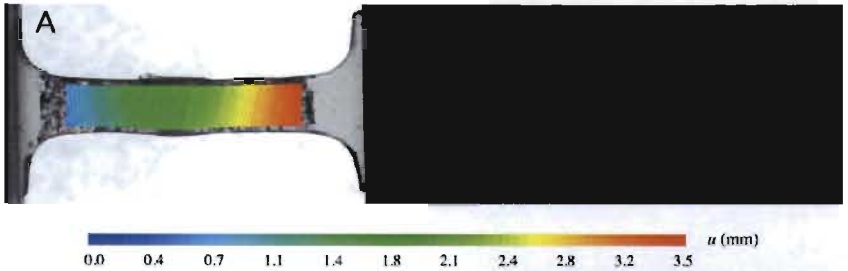


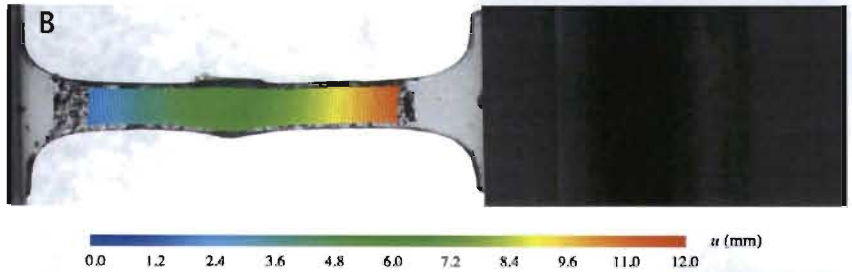
- Prior to moment a (A), uniform deformation in each section.
- Between moments a and f (or A and B), debonding is occurring within the center section.
- After moment f (B), sample behaves like a homogeneous uniaxial tensile specimen.

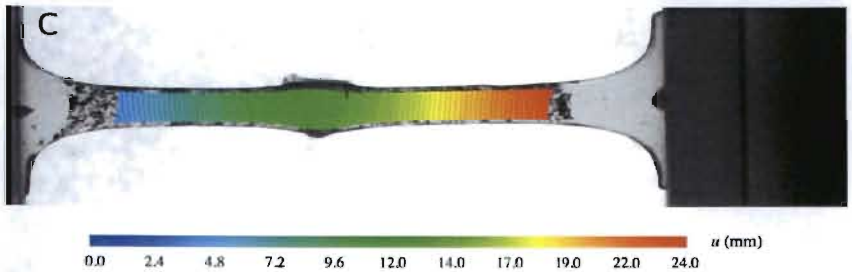


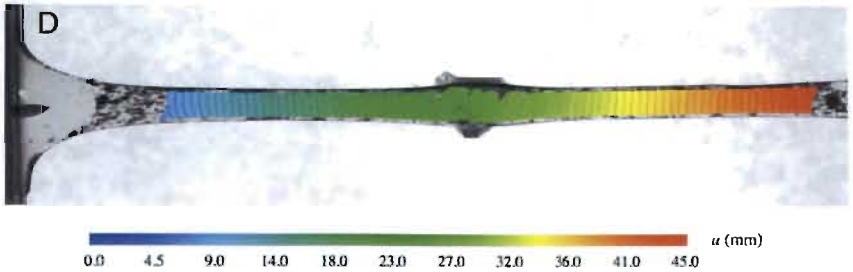
Compare with Estane Binder: Test No.6

Axial displacement

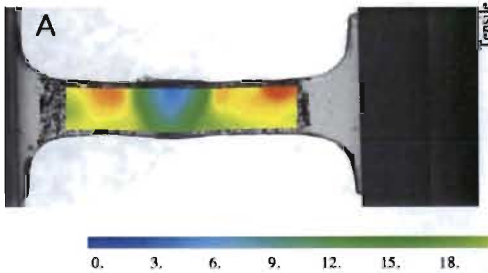


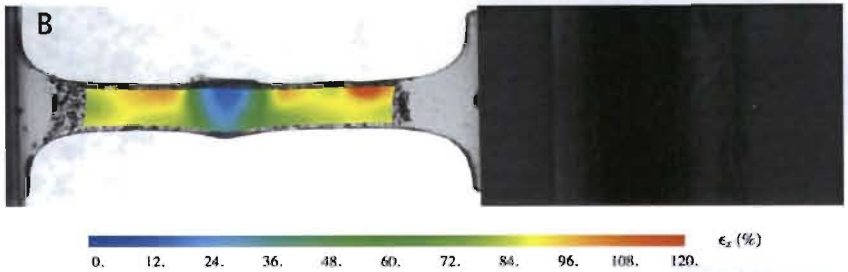


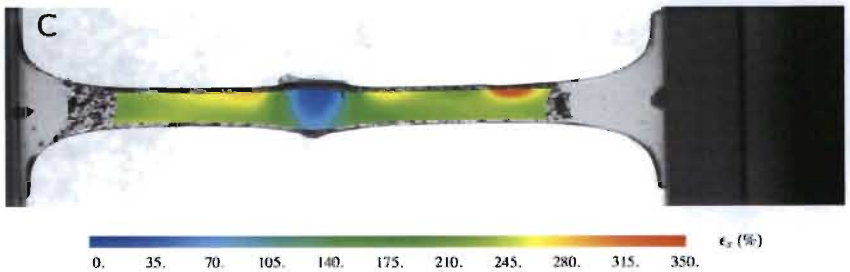


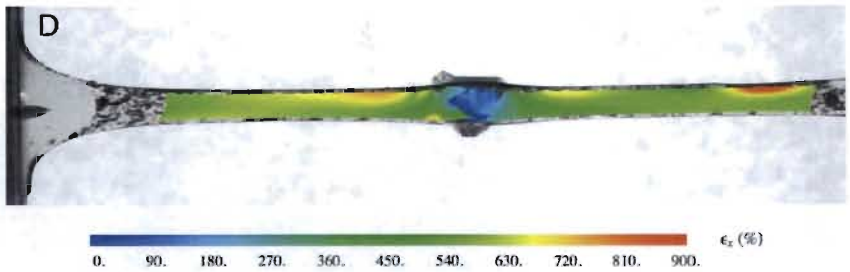


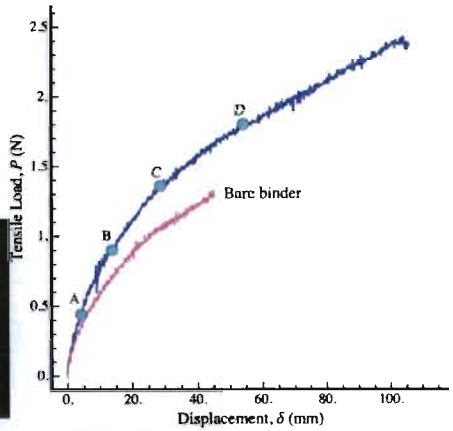
Axial tensile strain











Pop-Off Test Summary

- **DIC is extremely useful and is probably the way to go for measuring local strain**
  - Unfortunately it is still difficult to track debonding
    - Should try with a different, known system to "calibrate"
    - May be possible to determine difference in energy between bonded and bare samples
- **Test shows different results between polymers with large differences in modulus**
  - Plasticized estane ~ 3 MPa
  - Kel-F 800 ~ 1.4 GPa
- **Problems still present:**
  - Rotation of the island may indicate poor bonding from pressing method
  - Polymers tested so far are either complex or have thermal problems
- **Solution: choose a new, simple polymer that has some relevance to acetaminophen**
  - Polyvinylpyrrolidone – well-characterized, no Tg issues, and is often used in pharmaceuticals
    - Try with glass first, then with acetaminophen
    - Complement with other adhesion determining techniques to get a comparison

Summary

- **Surface roughness and interfacial chemistry can be measured for these materials by neutron reflectometry**
  - AFM may not be as useful due to difficult sample prep
  - Infrared spectroscopy in transmission can assist but not uniquely identify location of chemical components
  - Ellipsometry can accurately model film structure but is not as certain as reflectometry
- **Thermodynamic work of adhesion can be calculated from measured surface energy**
- **Processing has been found to have a large impact on measured structure**
  - Polymorphism in organic films
  - Crystallinity (or lack) in binders
- **Bulk mechanical / thermal property measurements have been tested to "proof of concept" level but currently need to be developed**