PolyInsight

Expert Vision for a Changing World

MidAtlantic Rubber & Plastics Group

Surface Characterization and Internal Structure of Rubber & Plastics Using Atomic-Force Microscopy (AFM)

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Agenda

- Brief History of PolyInsight
- Atomic-Force Microscopy (AFM)
  - Surface characterization technique
  - Internal structure technique
- Using AFM as a Problem Solving Tool
  - Roughness of multi-polymer extruded film
  - Morphology of thermoplastic elastomers (TPE)
- Using AFM for Certification/Validation/QA
  - Measuring sub-micron rubber particle size in thermoplastic packaging films
- Summary / Q & A

PolyInsight

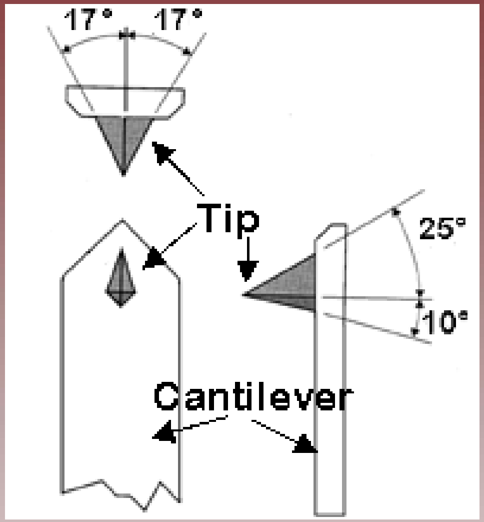
- Small team of experts in the physical and chemical structure of rubber and plastics
- Laboratory operation with several microscopes and related sample preparation equipment in-house
- Located in Akron, Ohio at the Akron Global Business Accelerator
  - Part of NEOinc, The Northeast Ohio Incubator Collaborative for new entrepreneurs/start-ups
  - Partnerships with The University of Akron, and other regional laboratories

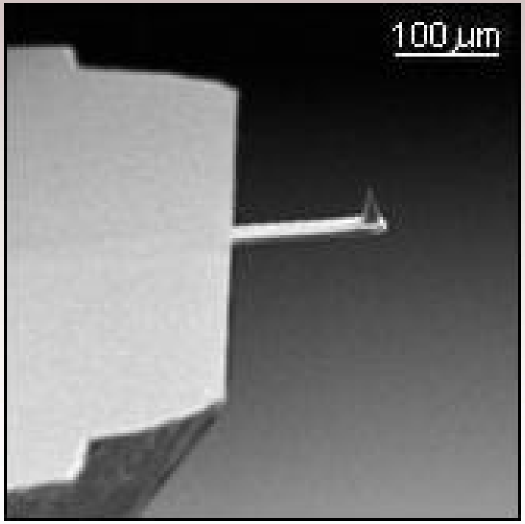
PolyInsight (cont'd)

- Continuous operation since July 2003
- Provide failure analysis, R&D testing, consulting/expert witness, and product certification services to the rubber and plastics industry
- Developed a portfolio of over 50 clients nationally and overseas
- Medical/Healthcare, Automotive, Industrial Coatings, and Consumer Products

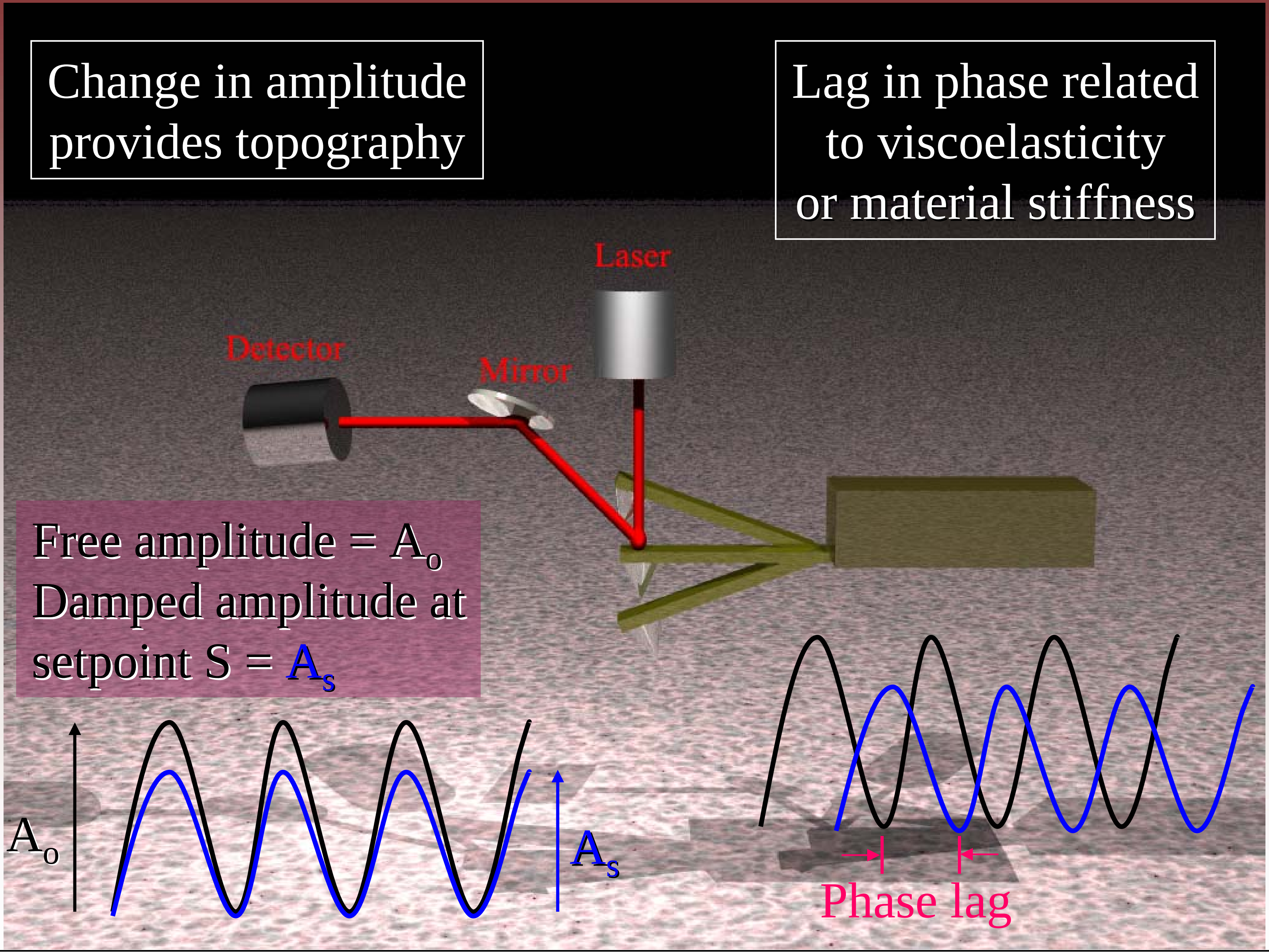
Atomic-Force Microscopy (AFM)

- High spatial resolution imaging of surface topography
- Similar to stylus profilometry, except 1 nm resolution
- Probe interacts with surface to reveal mechanical properties at high resolution



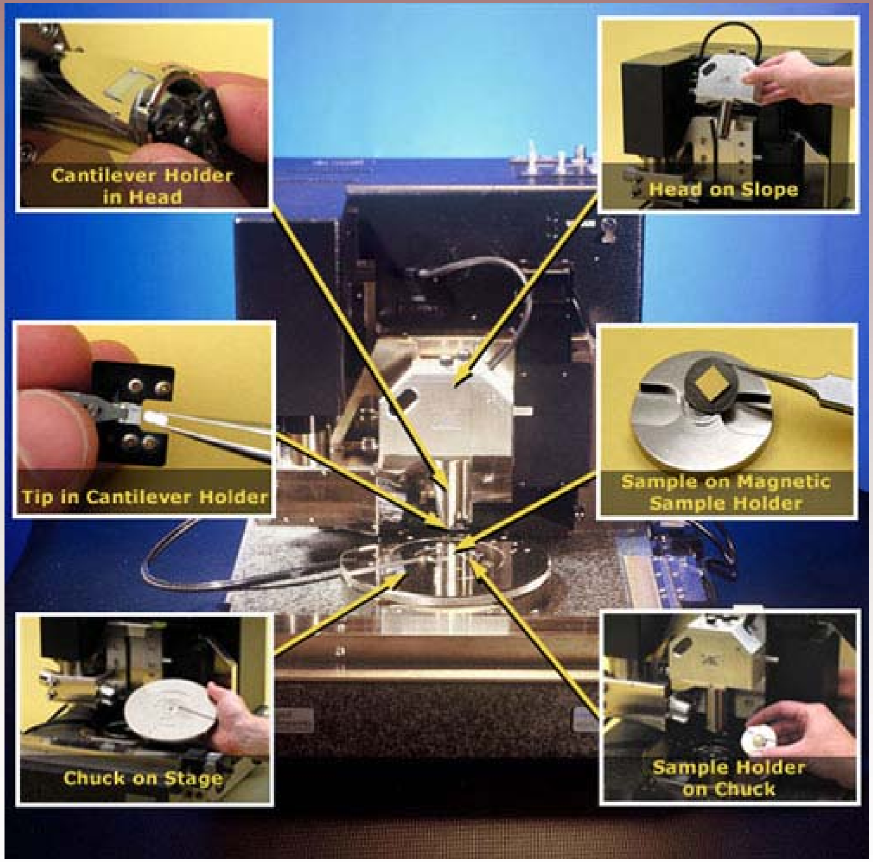


Atomic-Force Microscopy (AFM)

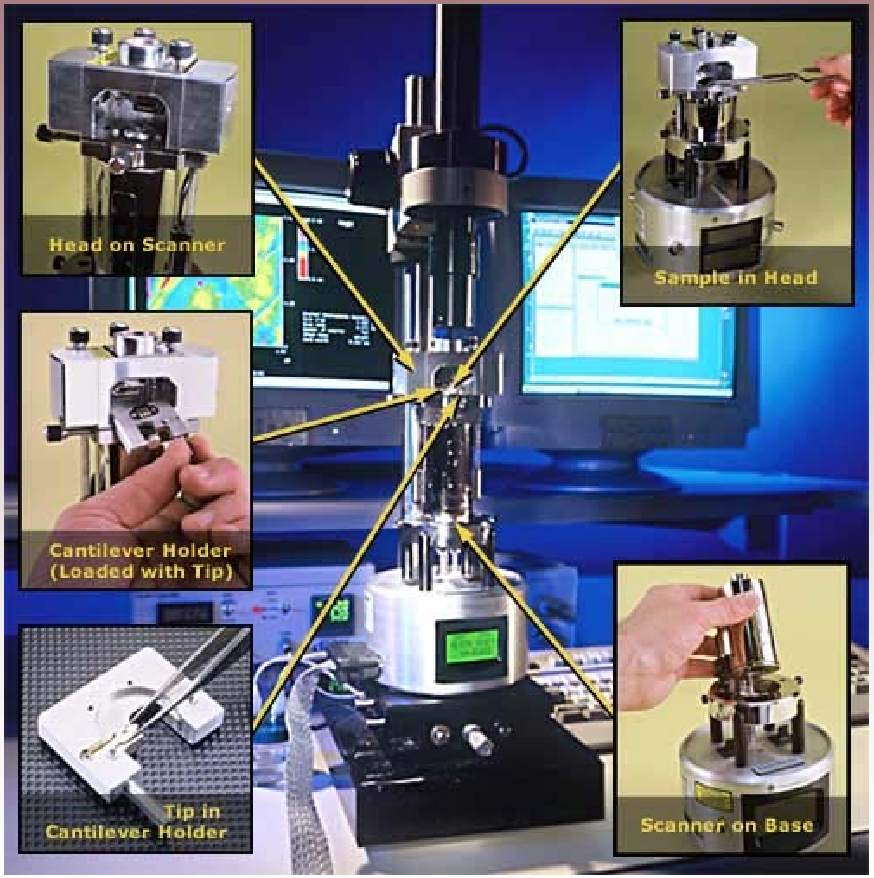


Atomic-Force Microscopy (AFM)

Veeco Dimension 3000 AFM (large sample sizes)



Veeco MultiMode AFM (highest spatial resolution)

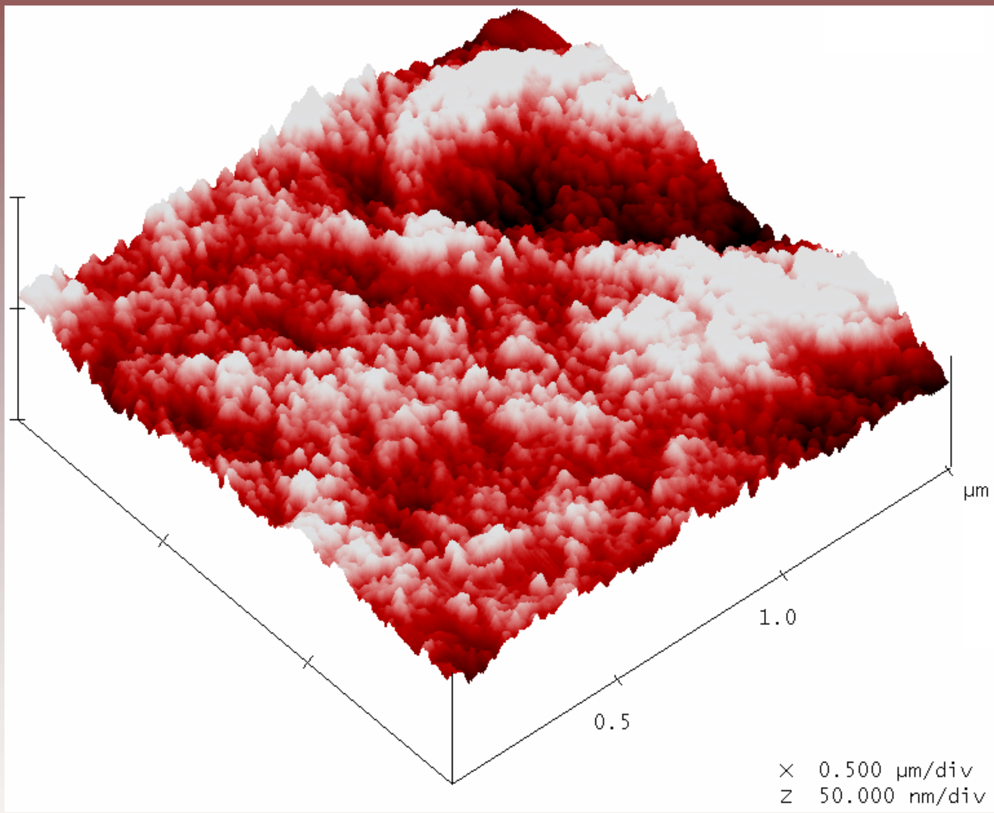


Surface Characterization via AFM

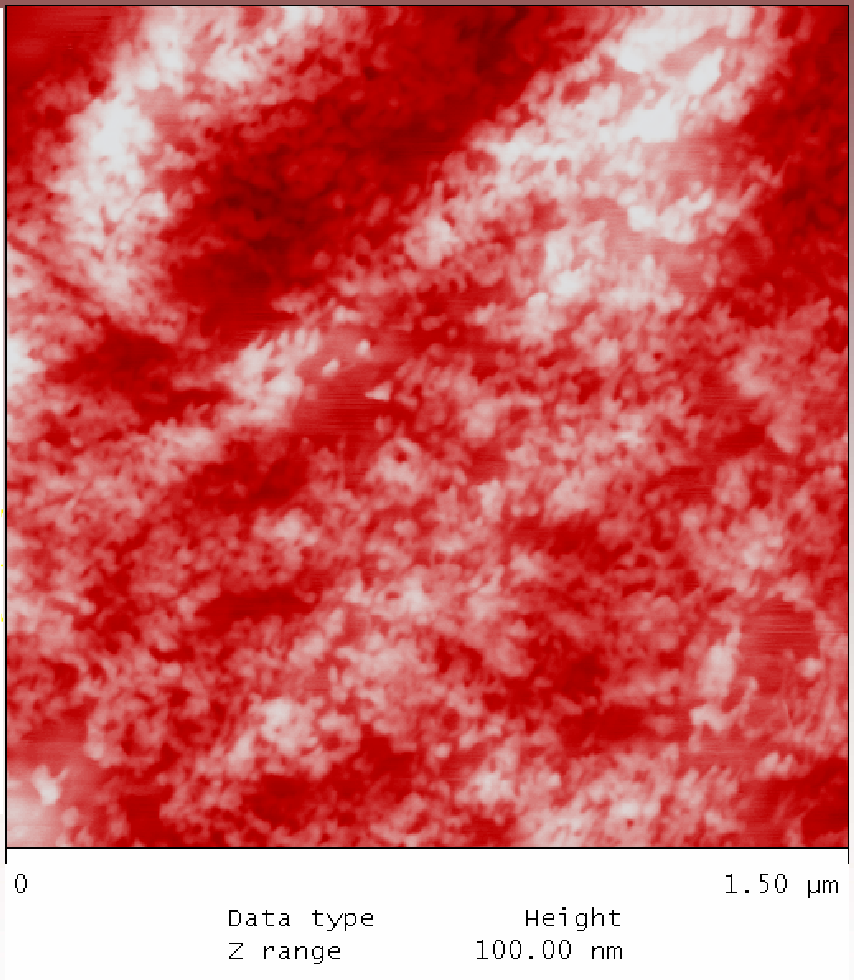
- The height of surface features can be measured quantitatively with 0.1 nm resolution
- Atomic step heights on crystals, DNA molecules, proteins, semiconductor lithography applications
- Maximum height of features allowed is ~ 6 μm, so surfaces must be "smooth"

Surface Characterization via AFM

3D Surface Projection



2D Surface Projection



Surface Characterization via AFM

Roughness Analysis

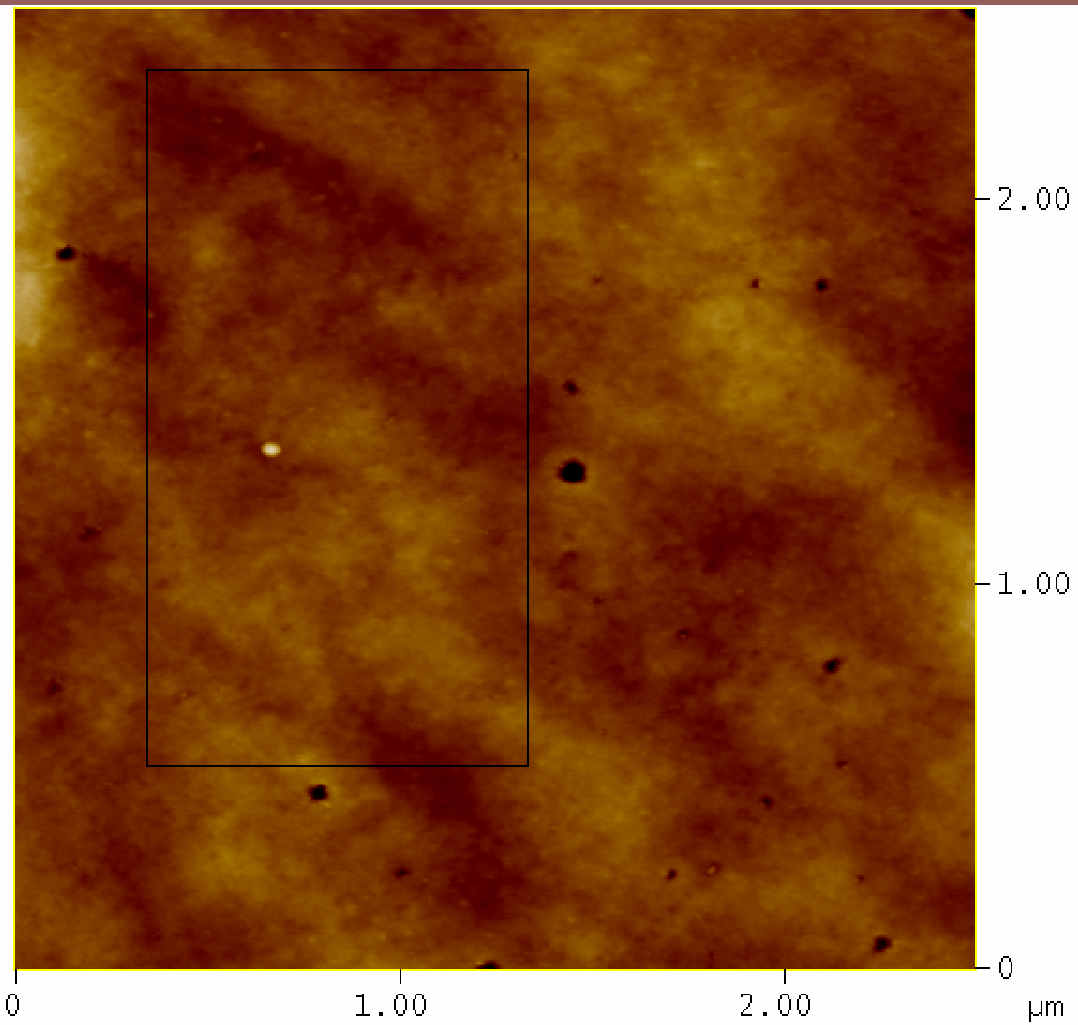


Image Statistics

Img. Z range	33.532 nm
Img. Rms (Rq)	1.563 nm
Img. Ra	1.209 nm
Img. Rmax	33.532 nm
Img. Srf. area	6.265 µm²
Img. Prj. Srf. area	6.250 µm²
Img. Srf. area diff	0.237 %

Box Statistics

Z range	14.970 nm
Rms (Rq)	1.199 nm
Mean roughness (Ra)	0.965 nm
Max height (Rmax)	14.293 nm
Surface area	1.806 µm²
Proj. Surf. area	1.803 µm²
Surface area diff	0.185 %

Internal Structure

- Classic technique for examining the structure of composite materials is Transmission-Electron Microscopy (TEM)
- Materials must be thinned to ~ 100 nm or less to be electron transparent
- Image contrast is based on either electron diffraction (crystalline materials) or mass-density (amorphous materials)

Internal Structure of Polymers

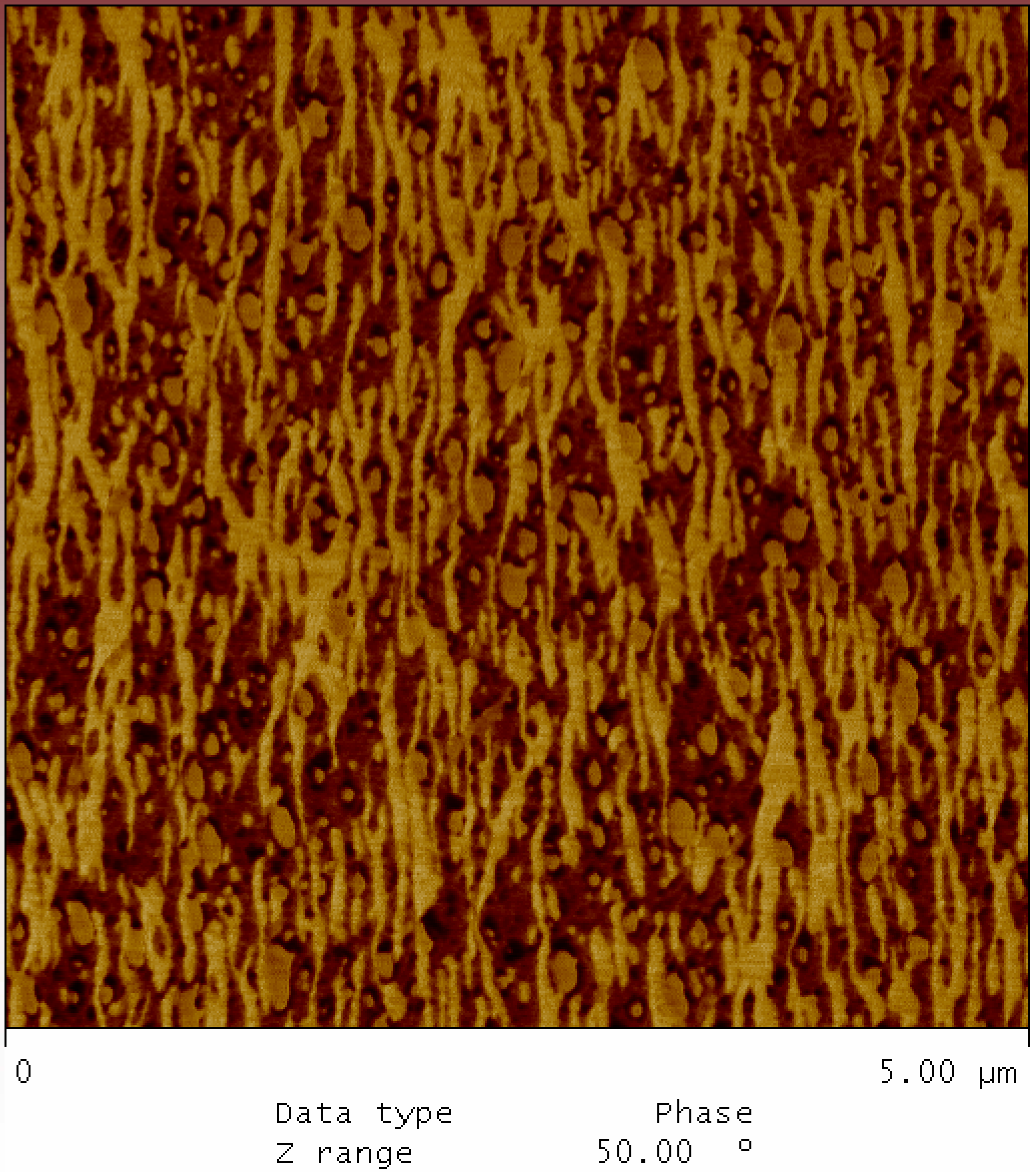
- Sample preparation technique for obtaining electron transparent thin sections is cryoultramicrotomy
- Mass-density image contrast is enhanced by using heavy-metal stains, such as RuO_2 or OsO_4
- TEM offers highest spatial resolution possible at < 0.1 nm, plus chemical ID techniques
- Time-consuming sample preparation ($$$)
- Difficulty with complex multi-component systems

Internal Structure of Polymers via AFM

- Probe interaction with the surface can image "mechanical property" distribution with high spatial resolution (1-5 nm)
- Cryoultramicrotomy must be used to expose the internal structure – cut open in cross-section and look at the surface
- Relies on surface structure being representative of internal structure (just like polished sections)

Internal Structure of Polymers via AFM

- Incompatible 4 component polymer blend can be imaged
  - PP (brightest)
  - PA (round, less bright)
  - PE (dark orange)
  - SEBS (black, surrounds PA)



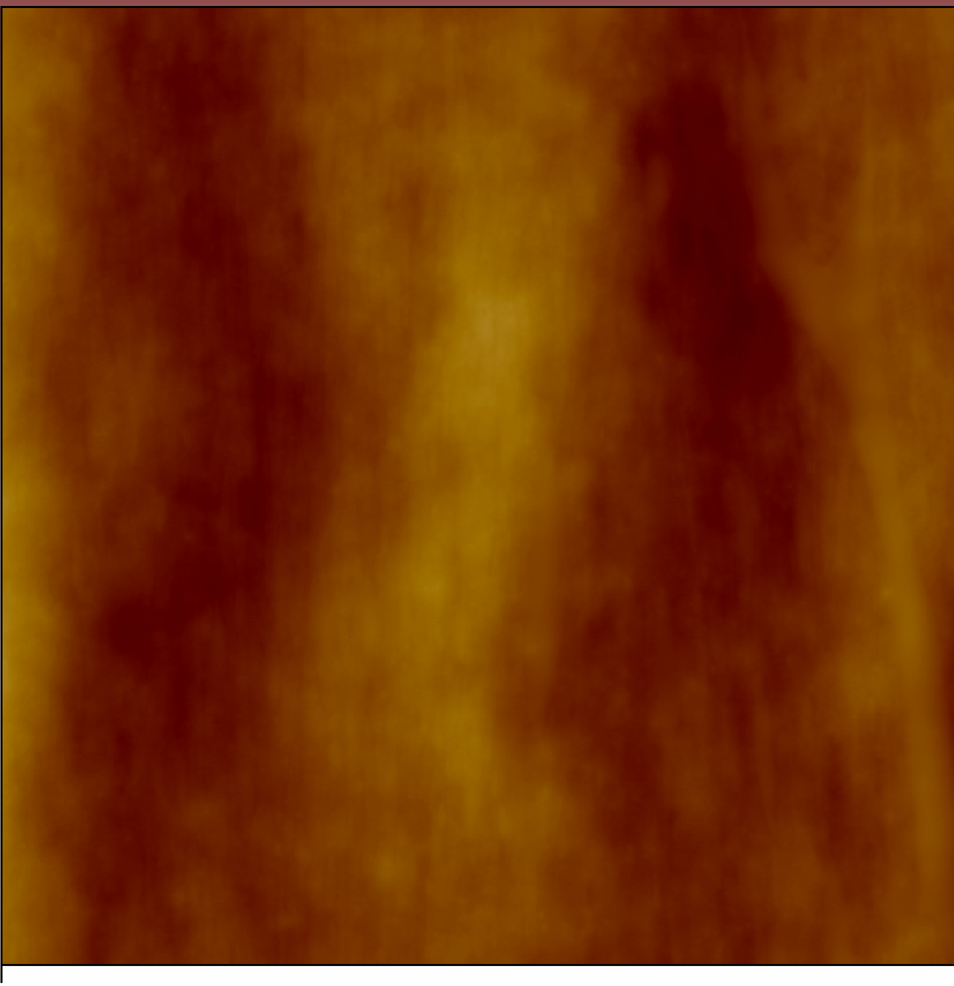
Review of AFM Capabilities

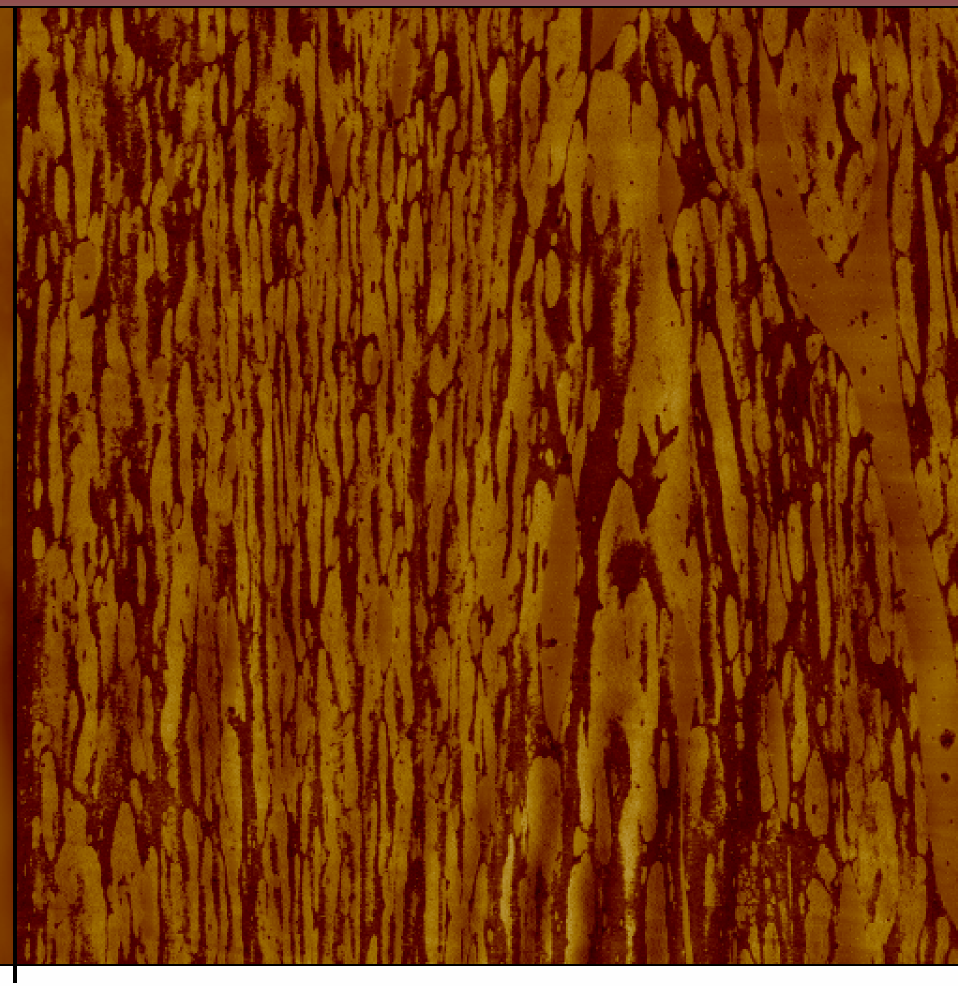
- High spatial resolution imaging of surface structures
- Quantitative measurement of surface roughness
- Imaging of internal structure based on mapping of mechanical properties
- Complex polymer blend morphology can be imaged, no stains required

Using AFM as a Problem Solving Tool

- Surface morphology of a multi-polymer extruded film
  - Client experiences “orange peel” film surface defects
  - “Nothing Changed”
- Internal structure of thermoplastic elastomers (TPE)
  - Client experiences flow problems, dimensional inconsistencies with part
  - “Nothing Changed”

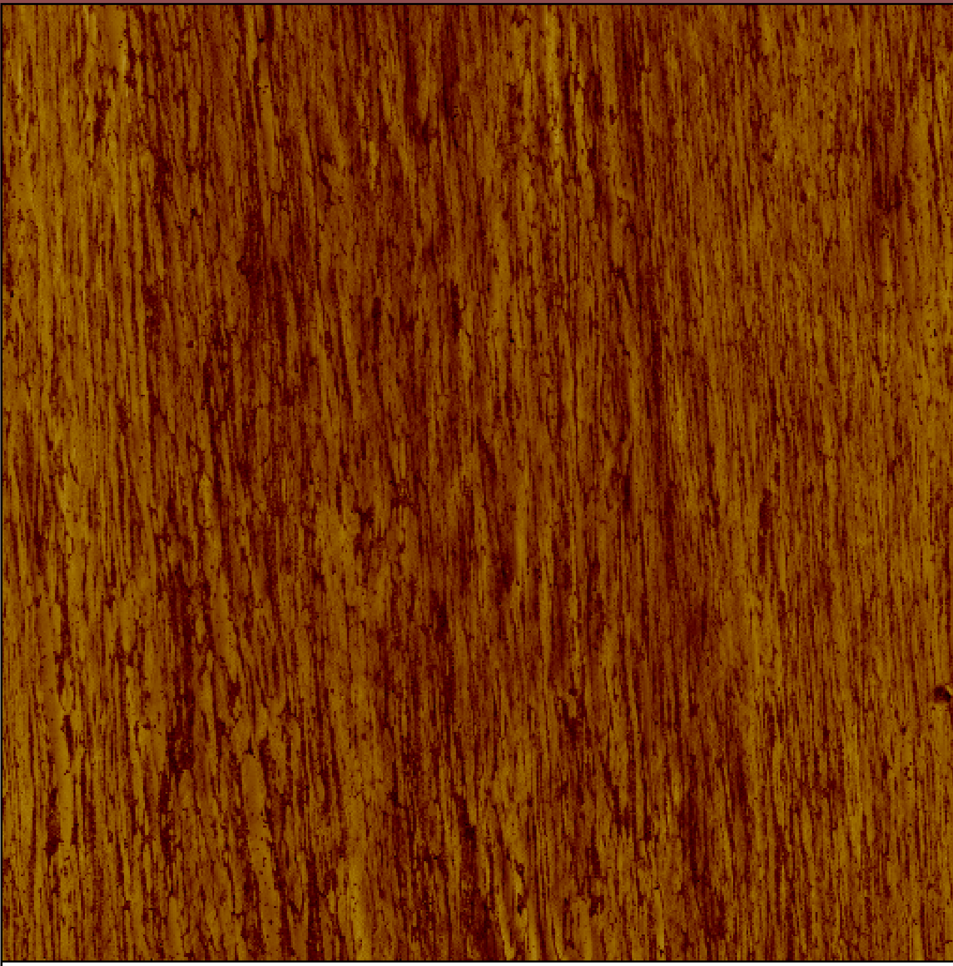
Orange Peel Surface Defect for PP/PE/PA films



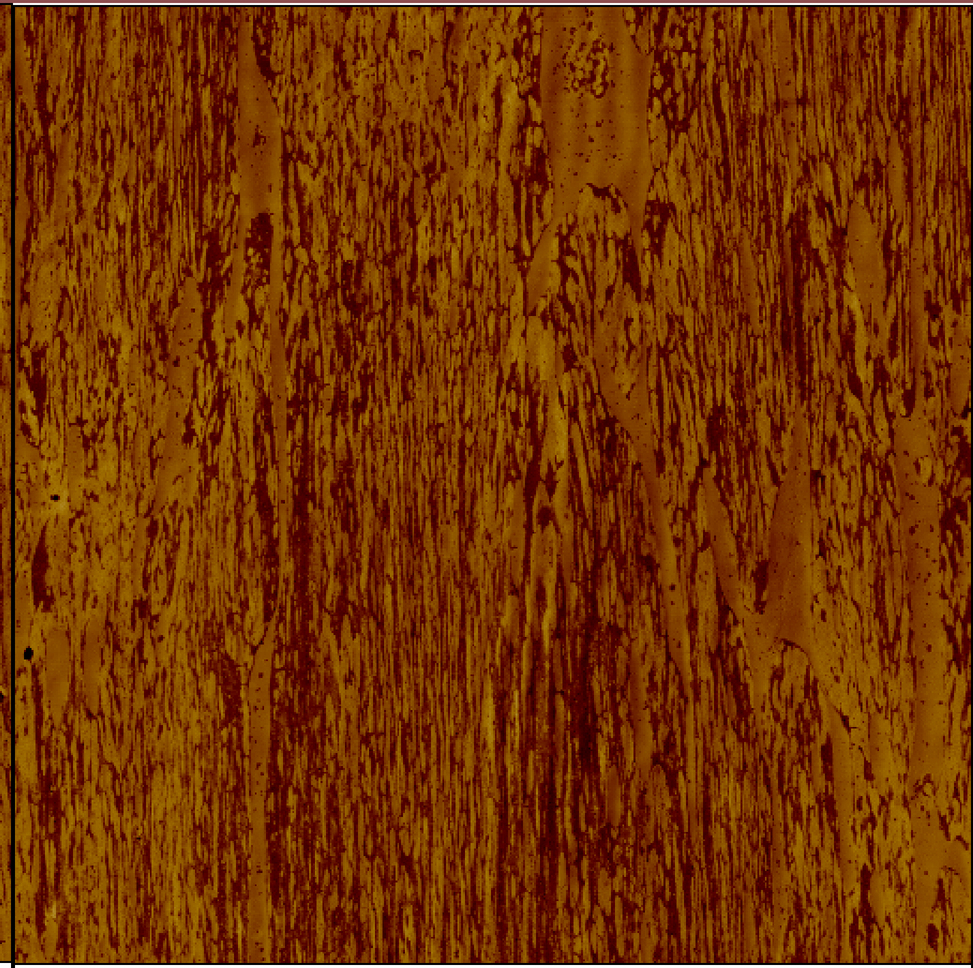


Orange Peel Surface Defect for PP/PE/PA films

Good

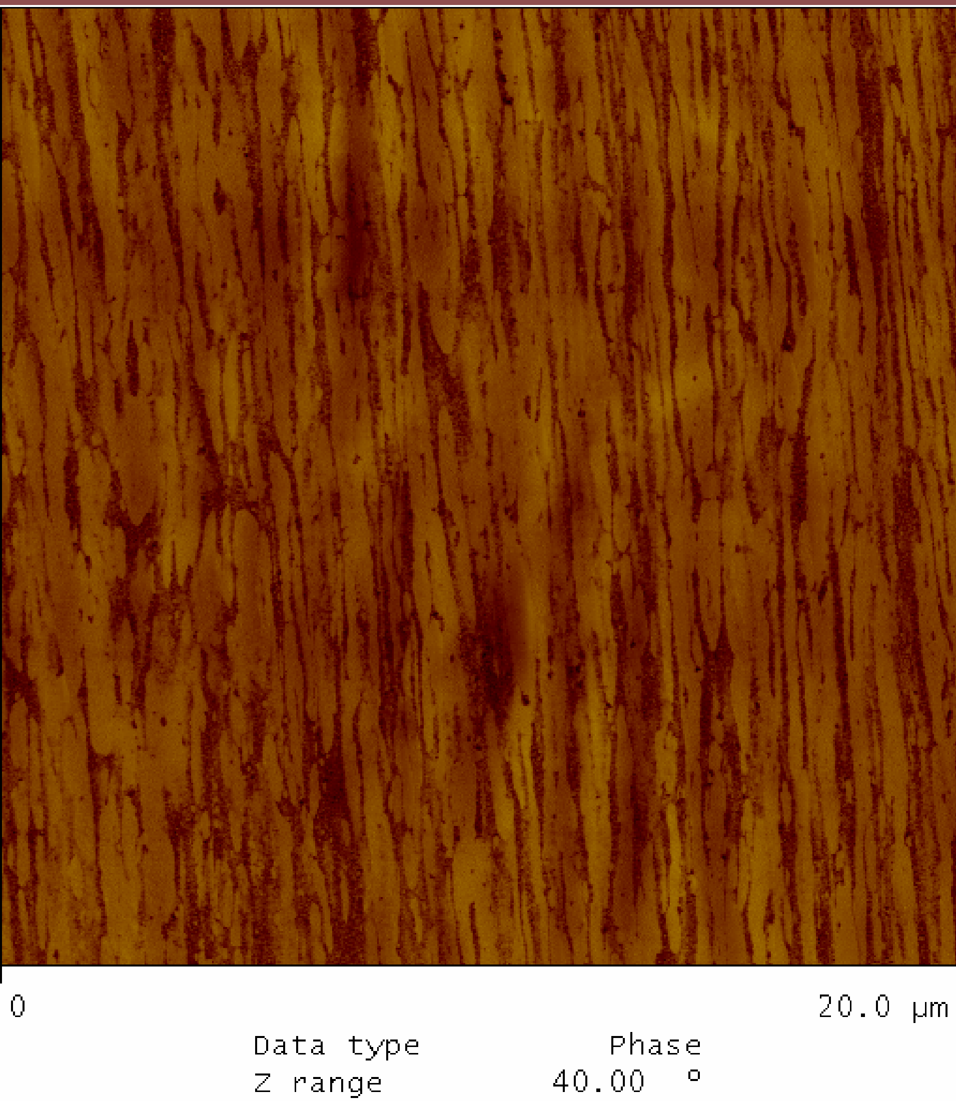


Orange Peel

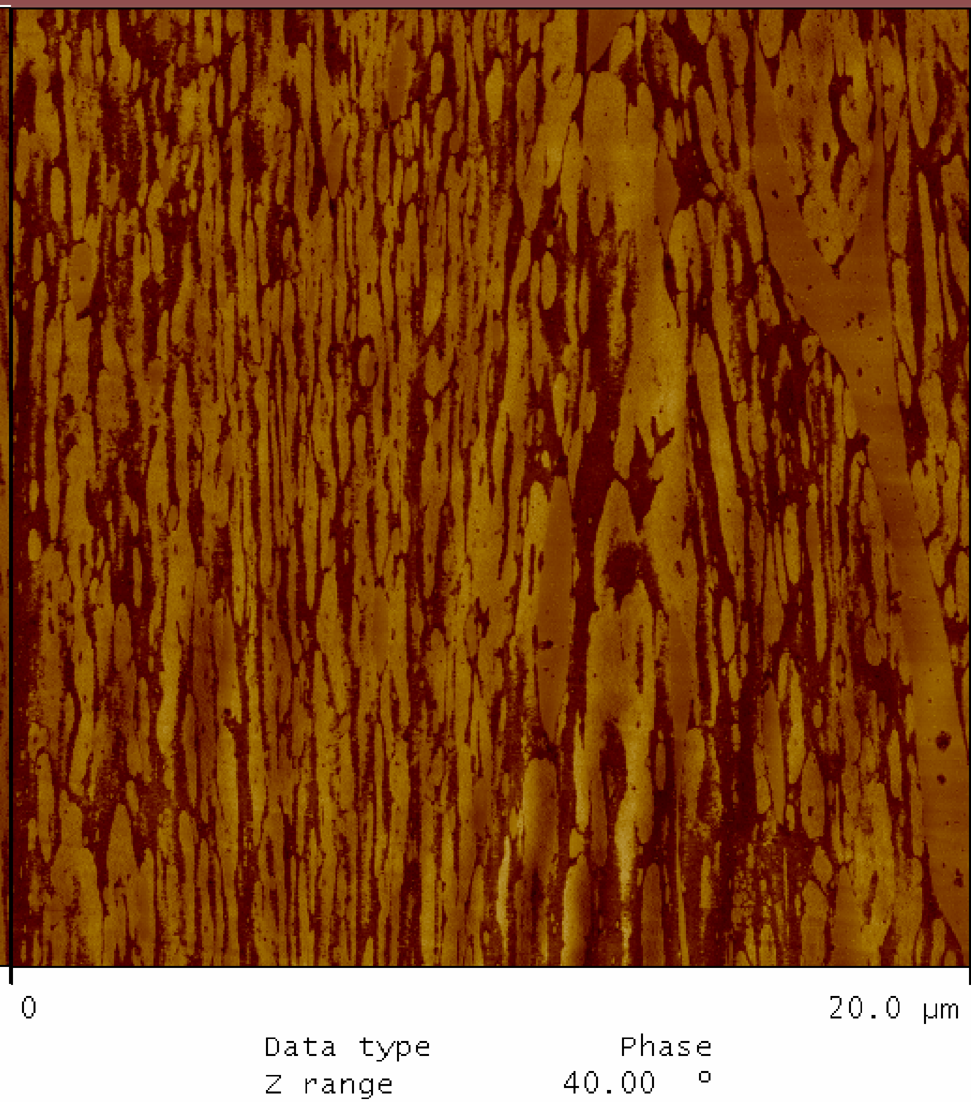


Orange Peel Surface Defect for PP / PE / PA films

Good



Orange Peel

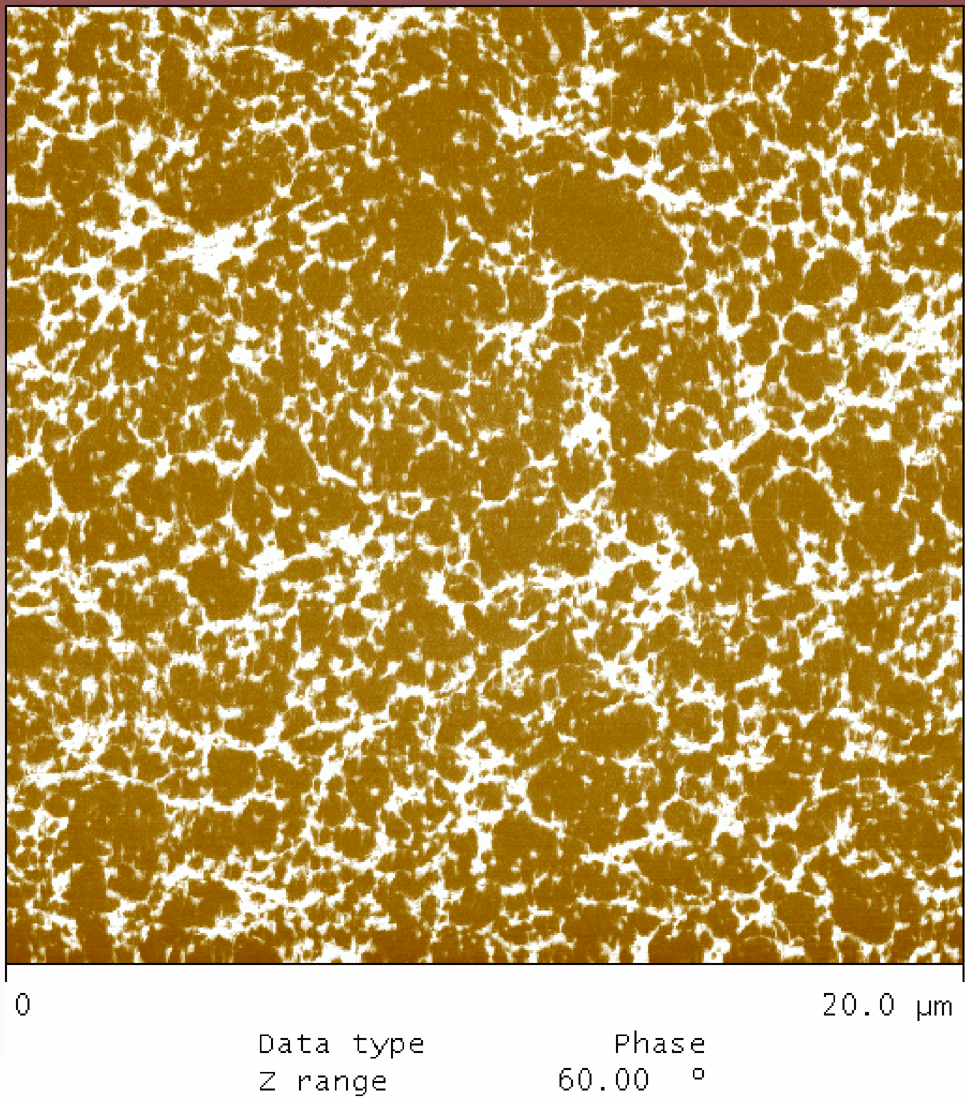


Orange Peel Surface Defect for PP/PE/PA films

- Good film surface: even distribution of all three polymer strands on surface
- Orange peel defect: higher levels of exposed PE, large irregular PA domains on surface
- PA supplier suspected, higher amine number for new lot was discovered

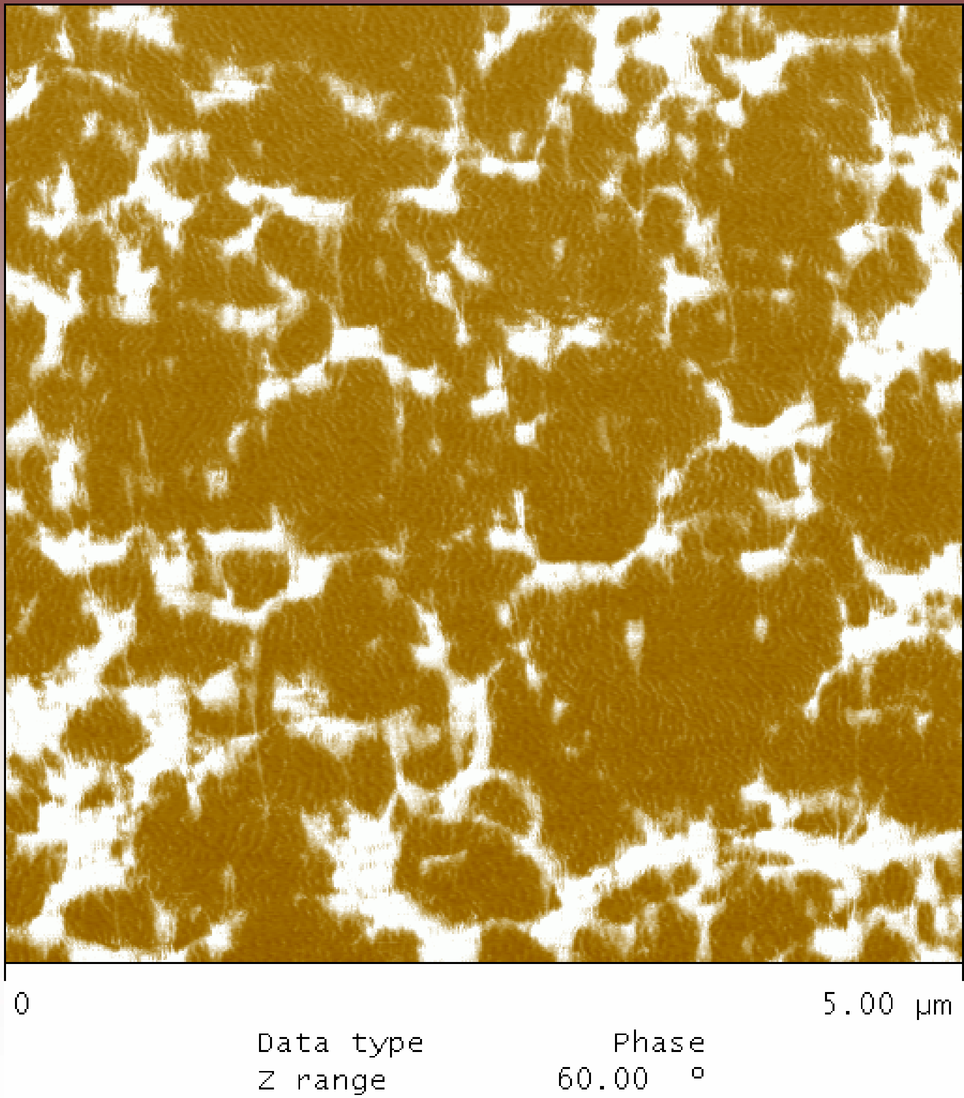
Internal structure of thermoplastic elastomers (TPE)

- TPEs (TPVs) rubber material that can be processed like a thermoplastic and doesn’t need to be cured
- Morphology is rubber “particles” in thermoplastic matrix



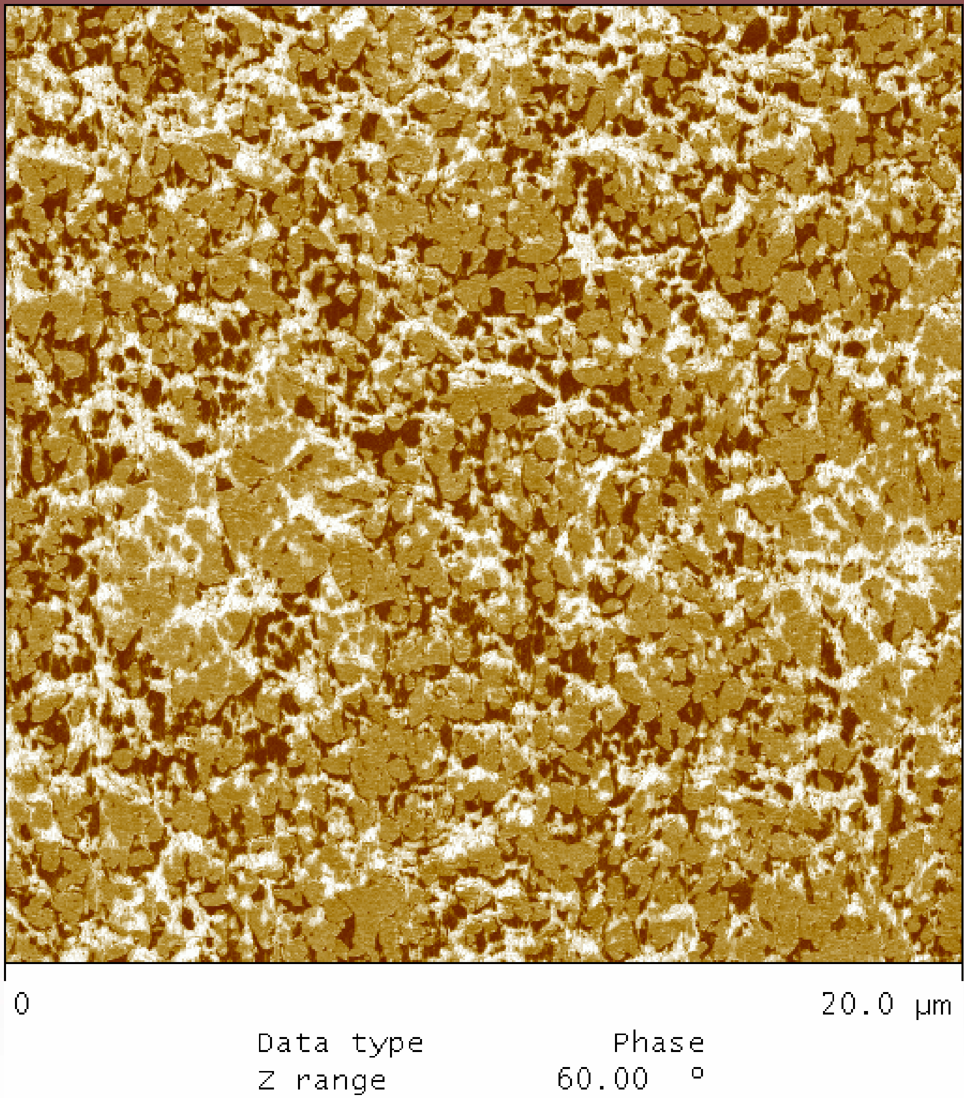
Internal structure of PP/SEBS

- Higher magnification image of PP/SEBS
- Block co-polymer structure for SEBS clearly resolved
- This is the BAD sample!



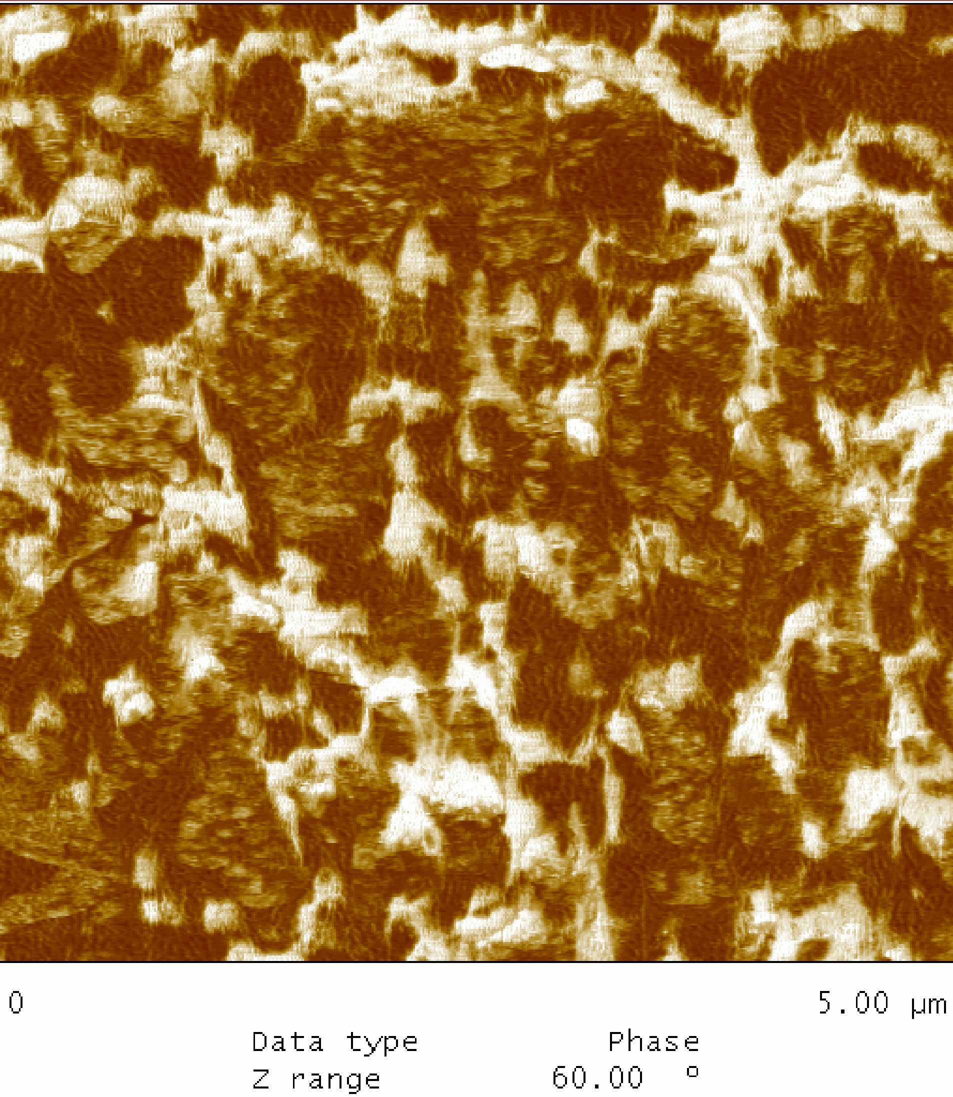
Internal structure of PP/SEBS

- Typical TPE composition: plastic + rubber + OIL
- Oily phase segregates to surface created by cryomicrotomy
- This is the GOOD sample

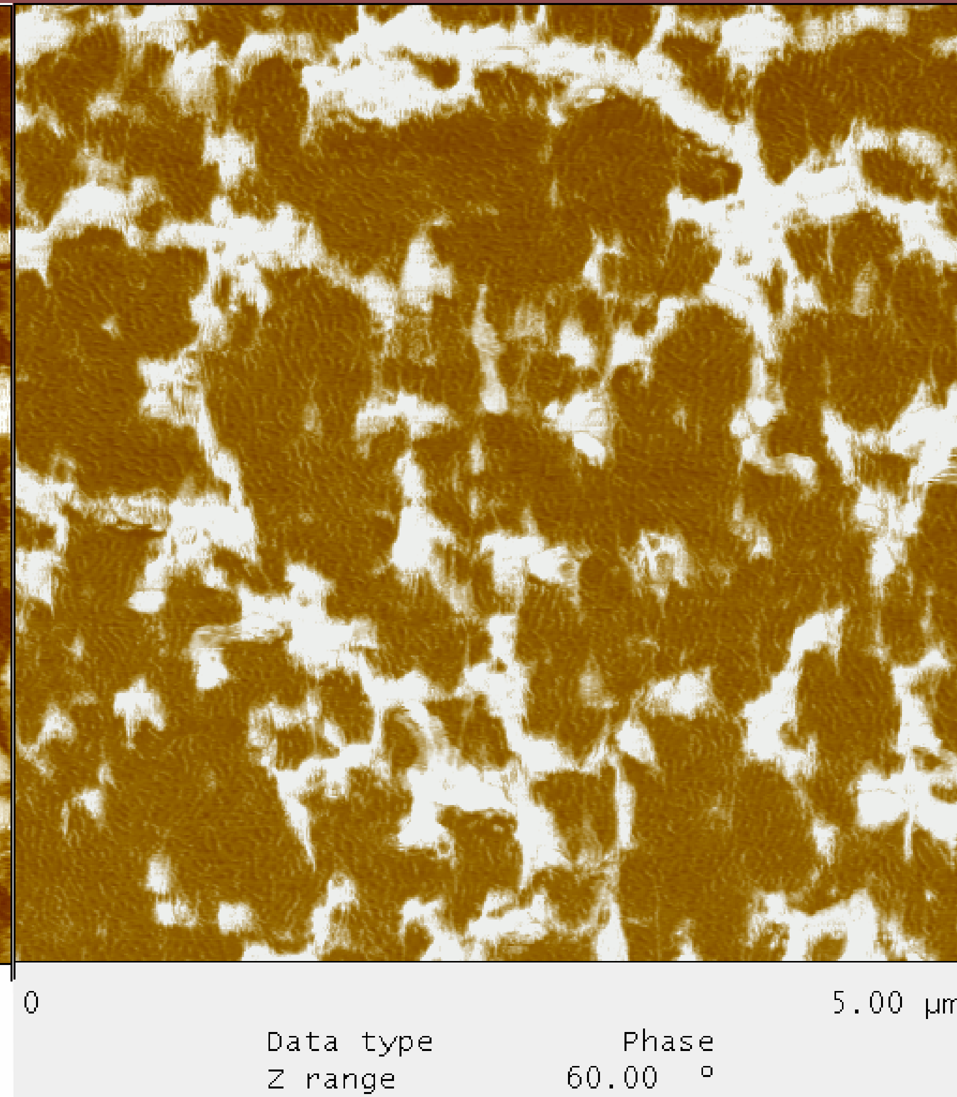


Internal structure of PP/SEBS

1st scan pass

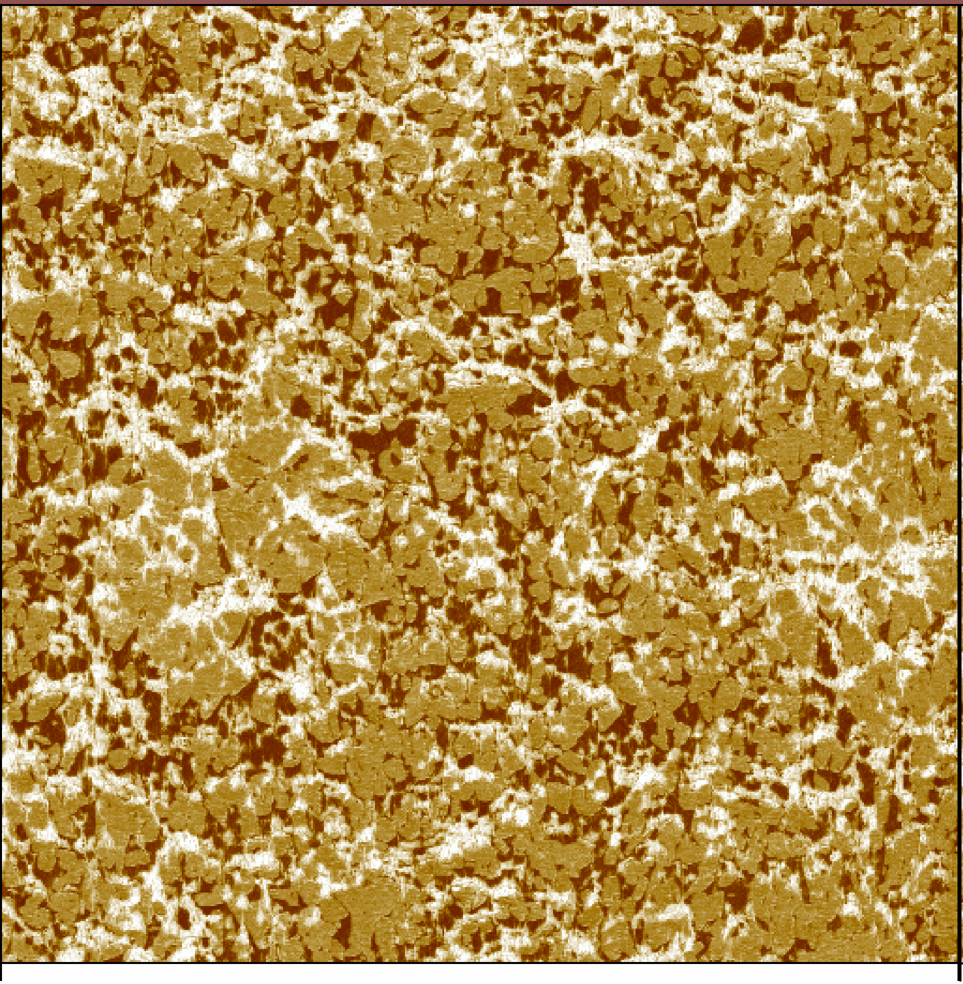


2nd scan pass



Internal structure of PP/SEBS

Before

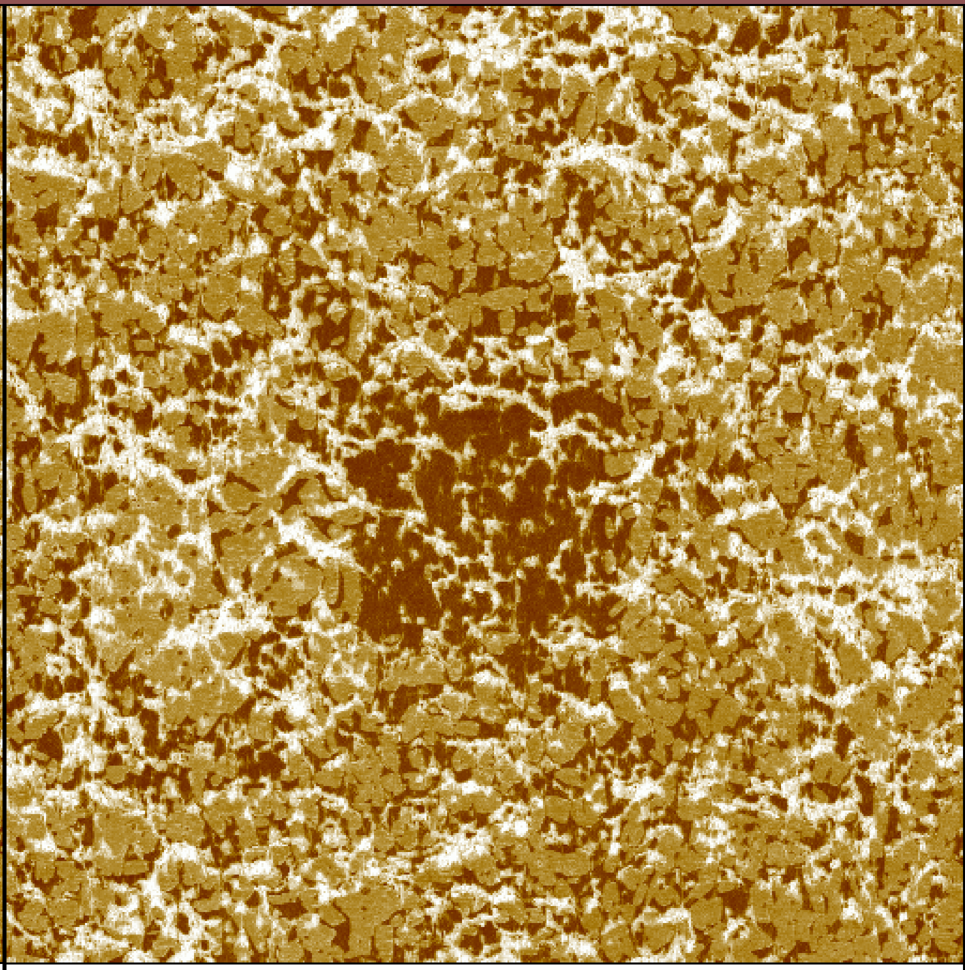


0 20.0 µm

Data type Phase

Z range 60.00 °

After



0 20.0 µm

Data type Phase

Z range 60.00 °

Internal structure of PP/SEBS

- Oily phase mobility to surface is typical behavior
- Good and Bad samples displayed different “oily phase” behavior – but same blend morphology
- Only AFM could reveal this difference!
- Slight difference in oil was not a “drop in the slot” – oil solubility in the polymer was affected

AFM for Certification/Validation/QA

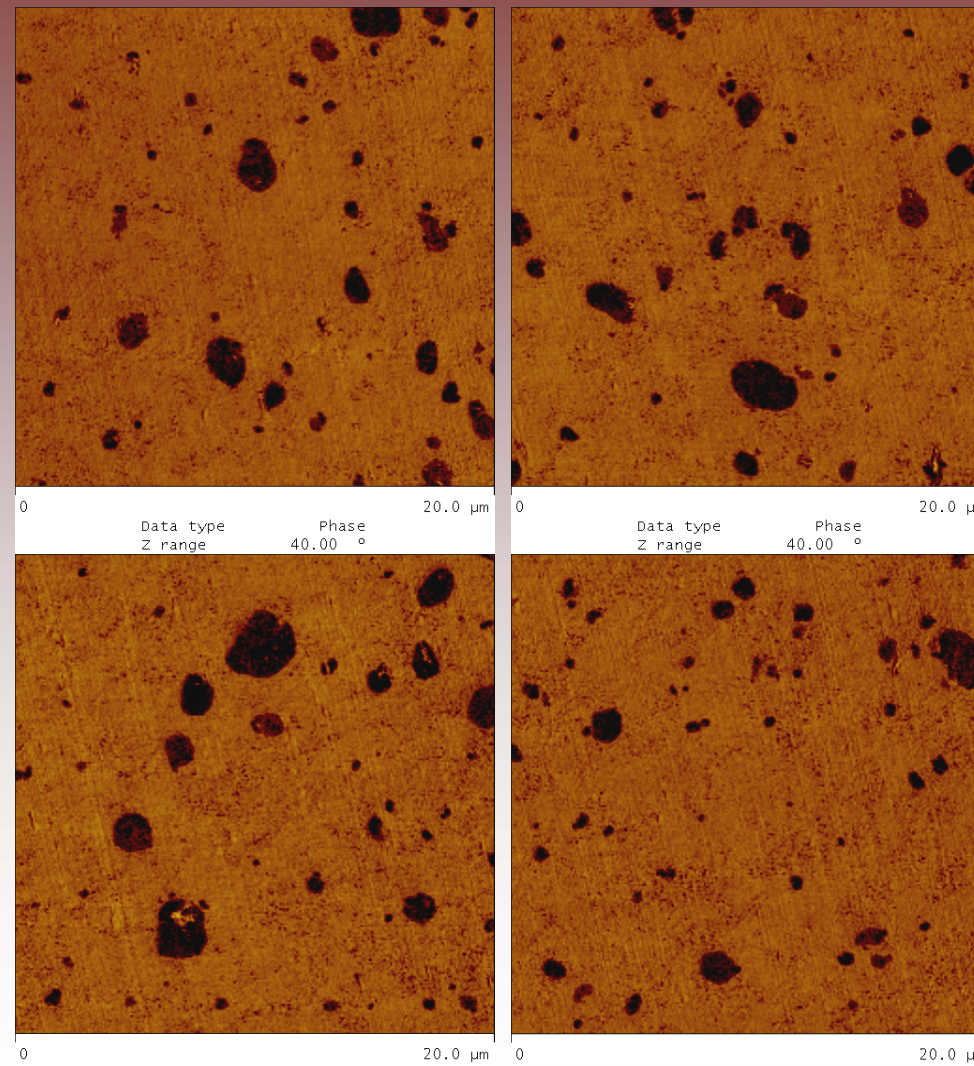
- Typical QA tools can not detect changes in structure which effect ultimate performance – focus on composition and physicals
- Polymer/rubber composites are becoming increasingly complex with performance depending on “nanostructure”
- No adequate QA tools for sub-micron structure exist

AFM for Certification/Validation/QA

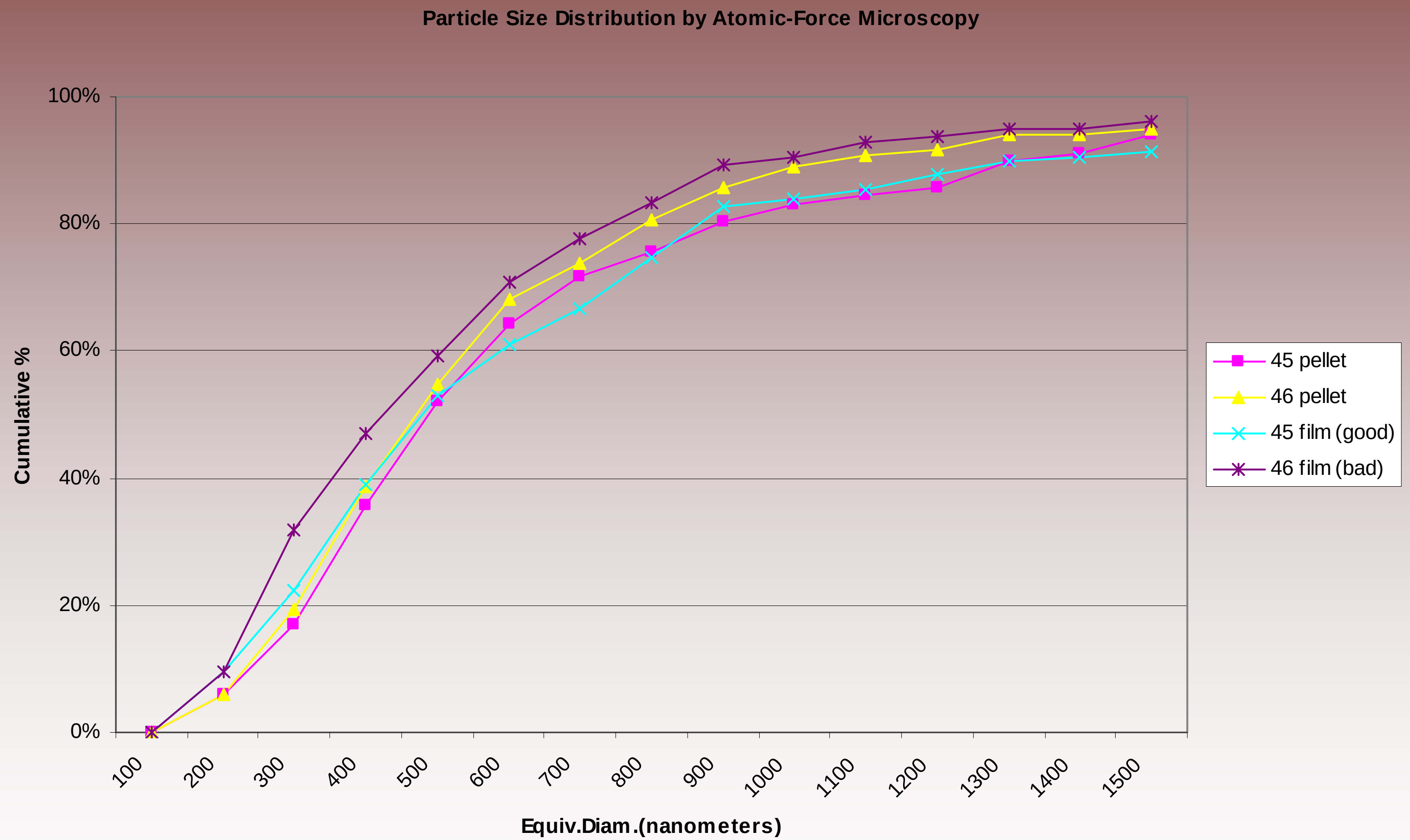
- Catch problems before they leave the plant
- Reduce returns/recalls/adjustments
- Save $$$
- Build customer satisfaction / quality reputation
- Unbiased 3rd party laboratory advantages

Rubber particle size in thermoplastic packaging films

- PE film with TPV rubber particle modifier
- AFM used to image the rubber particles
- Image analysis measures the particle size distribution



Rubber particle size in thermoplastic packaging films



QA tool for particle size distribution

- Large TPV particle fraction: necessary for feel, translucency
- Smaller PSD achieved with higher work screw: films became transparent and had snakeskin defect
- Extruder/blender adjust to dial in proper particle size distribution for PE/TPV blend

Summary

- AFM has unique strengths as a high resolution microscopy technique
- Routine use as a problem solving tool is possible: can “see” things that other techniques cannot
- Great potential as a certification/validation/QA tool for today’s complex materials