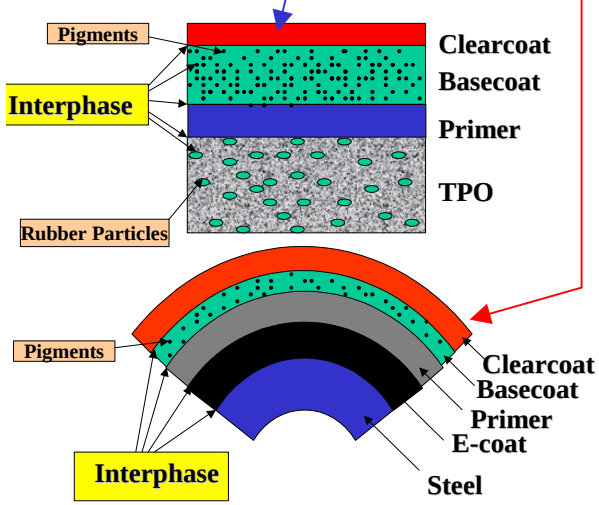
Polymer Interphases Consortium (PIC)
Phase I Research

An Overview of Research Areas & A Summary of Accomplishments

- **Industrial Partners:**
  - DOW Chemicals
  - Visteon Corporation
  - PPG Industries, Inc.
  - MTS Systems Corporation

- **NIST**
  - Building and Fire Research Laboratory
  - Chemical Science and Technology Laboratory
  - Materials Science and Engineering Laboratory

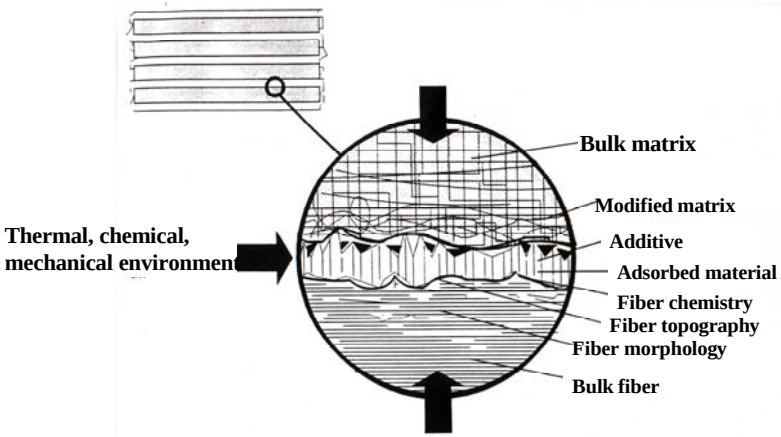
Motivations



Plastic Parts

Metal Parts

Conceptual Fiber/Matrix Interphase



(After L. Drzal)

Rationale

The polymer/substrate interphase region plays a fundamental role in the performance and durability of polymeric materials and systems: nanocomposites, particle-filled materials, paints on plastics and metals, and fiber-reinforced polymer composites. However, little knowledge is available on the understanding of the chemical, physical and morphological properties of the interphase.

Consortium:

Characterization and Modeling of Polymeric Materials and Systems Interphases,

or Polymer Interphases Consortium (PIC)

Officially formed in January, 2001

Participants

INDUSTRY: DOW Chemical, Visteon (FORD), PPG Industries, MTS Systems Corporation

NIST: BFRL, MSEL, CSTL

Major Objectives of PIC

1) To develop advanced measurement and modeling techniques for studies of polymeric materials interfaces/interphases.

2) To better understand morphological, chemical, and physical properties of the interphases formed between polymer films and substrates.

3) To better understand how the interphases change with environmental and mechanical stresses.

4) To develop standards and standards reference materials for testing and characterization of polymer/substrate interfaces/interphases.

Research Areas

Project 1: Characterization of Surface Deformation and Quantification of Mar Resistance of Polymeric Materials and Systems

Principal Investigators: Mark R. VanLandingham, Lipiin Sung, Peter Drzal

(BFRL Leads)

Project 2: Development of Models and Computer Program(s) for Predicting Interphases in Multi-Phase Polyolefin Systems under Shear Flow and Temperature.

Principal Investigators: Charles Han, Howard Wang, Fred Felan, and Nicos Martys

(MSEL Leads)

Project 3 : Characterization and Modeling of Interfaces and Interphases between Polymer Coatings and Substrates.

Principal Investigators: Chris Michaels, Tinh Nguyen, Lipiin Sung, and Forest Landis

(CSTL Leads)

Project 1: Nanoindentation and Scratch and Mar Resistance of Polymeric Coatings

Drs. Mark R. VanLandingham, Lipiin Sung, and Peter Drzal (BFRL Leads)

Major Accomplishments:

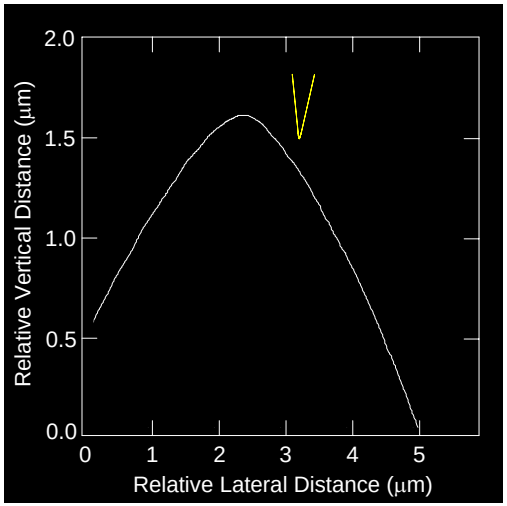
1. Completed a critical review on scratch measurements of polymeric materials.
2. Developed procedures to characterize and reconstruct nanoindentator tip shape.
3. Developed protocols for nanoindentation of polymers and coatings used for the consortium.
4. Developed preliminary protocols for scratch testing of polymers and coatings (used for the consortium) using a nanoindentor .
5. Completed initial optical scattering measurement of scratched samples.
6. Constructed a light scattering laboratory for studies of appearance of scratched deformation.
7. Physical models are being developed for predicting polymeric materials performance during scratch and mar testing.
8. Model(s) is being developed for linking surface deformation to optical scattering properties.
9. Seven papers have been published/submitted to journals.

Performed Extensive Scratch/Mar Literature Review

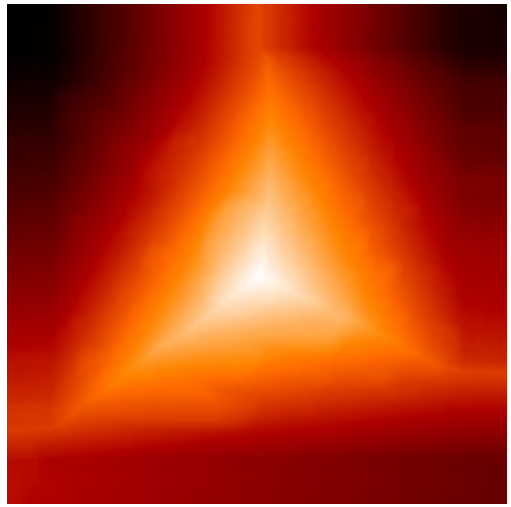
Variation in Testing Parameters

Test/System	Tip material	Tip geometry	Force Range	Depth Range	Speed/length
AFM	Diamond	Non-ideal < 0.1 μm radius	(1 - 400) μN	(10 –250) nm	(1-70) μm/s (1 –70) μm
AFM	Diamond	90° cone 1 μm radius	50 μN - 4 mN	50 nm - 1 μm	(35-70) μm/s 70 μm
Ford	Steel	sphere 500 μm radius	(0.6 - 7) N 30 N	(0.5 –10) μm	100 mm/s ?
LTDS	Diamond	Berkovich pyramid < 0.1 μm radius	(1 – 7) N	50 μm	500 μm/s (1 – 10) mm
CSM	Diamond	Sphere 2 μm radius	(0 - 5) mN	(0.5 – 1) μm	5 μm/s ?
CSM	Diamond	Sphere 200 μm radius	(0.5 – 10) N	?	200 μm/s ?
CSM	Diamond	? 10 μm radius	(0 – 190) mN	(0 – 20) μm	50 μm/s 3 μm
DuPont	Diamond	60° cone, 3 μm radius ?, (1-2) μm radius	(0 – 8) mN	(1 – 4) μm	25 μm/s (1 – 10) mm
MTS	Diamond	Berkovich pyramid < 0.1 μm radius	(0.02 – 16) mN	(0 – 1.5) μm	(10-25) μm/s 500 μm
MTS	Diamond	Cube corner pyramid (0.5-2) μm radius	(0.02 – 16) mN	(0 – 2.5) μm	25 μm/s 500 μm

Developed Tip Shape Estimation Procedures

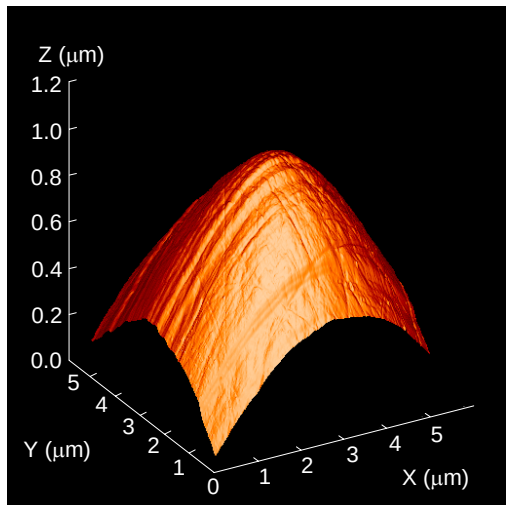


Scan tip using AFM



AFM image of Berkovich tip

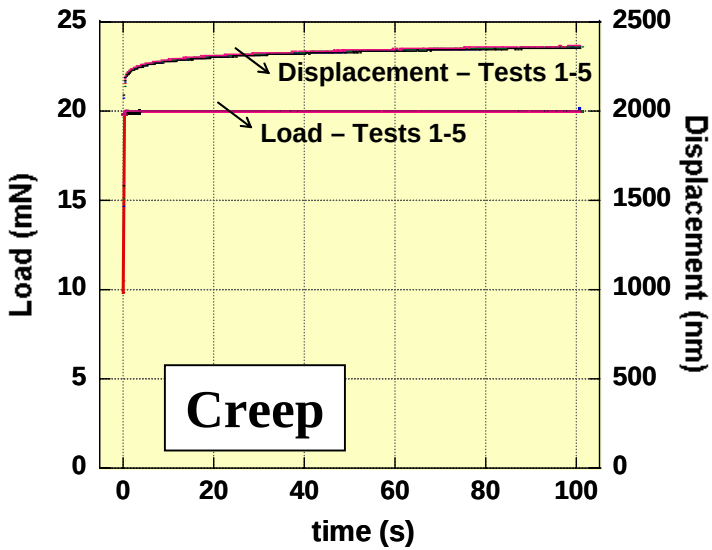
- **AFM imaging yields 3-D tip geometry**
  - **Directly related to strain levels imposed during indentation and scratch testing.**
  - **Reveals tip non-idealities**

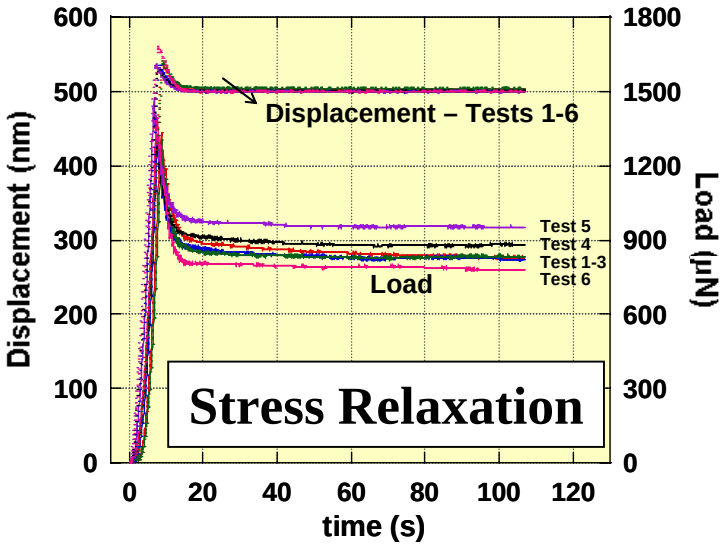


3-D view of rounded cone

Indentation Test Method Development

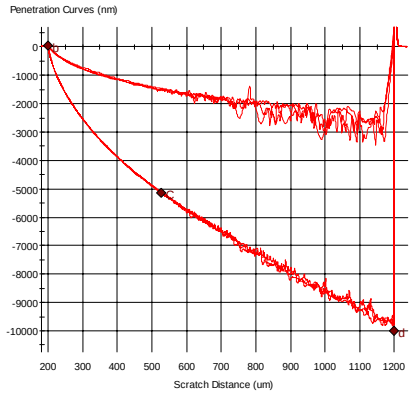
- **Creep Method**
  - Employs a hold segment at beginning of test
  - Holds at prescribed force
  - No loading segment
    - Prescribed force reached in ~ 0.1 s
  - First 5-10 s of data not used
    - CSM data takes several seconds after step loading to settle down
  - Alternate several polymer test set with a fused silica test set.
    - Estimate thermal drift relative to creep rates.
- **Stress Relaxation Method**
  - employs a loading ramp segment at beginning of test
  - Holds at prescribed displacement, h_0
    - Reached in ~ 6 s
    - Slight overshoots of 5-10% of h_0 for XP, 1%-3% of h_0 for DCM
    - An additional 6-8 s needed to adjust, after which variations in h_0 were ± 1-2 nm for both systems



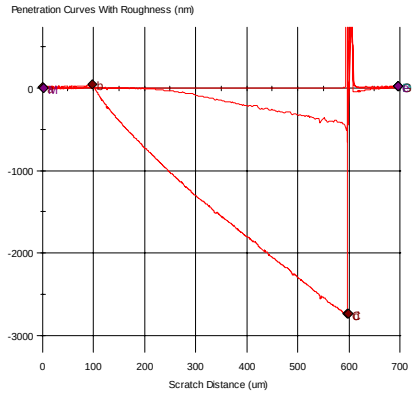


Scratch Testing Development

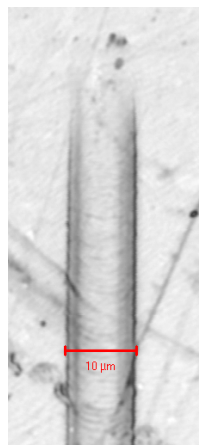
- **Developed Preliminary Scratch Testing Protocols for Polymers**
  - **Use progressive force tests to identify scratch test parameter ranges of interest.**
  - **Use constant force tests to study important ranges of scratch behavior**



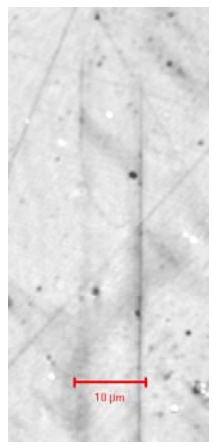
1 μm radius tip



10 μm radius tip



1 μm/s



10 μm/s

- **Important Parameters**
  - **Tip geometry**
  - **Scratch velocity**
  - **Force level.**

Nanoindentation and Scratch Measurements of PIC Materials

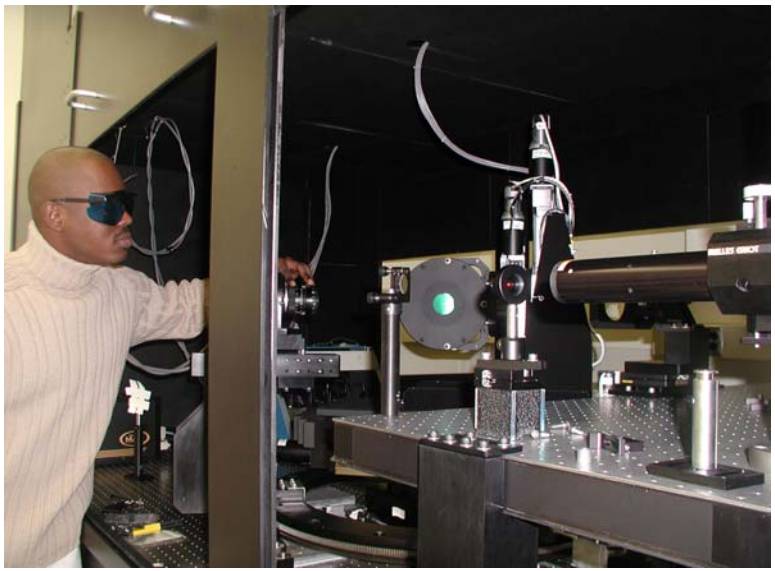
•Measured static, quasi-static, and dynamic properties of heterogeneous commercial systems (filled, unfilled, pigmented) over three indenter tip length scales. Approximately ~5000 nanoindentation tests and ~ 300 scratch tests conducted.

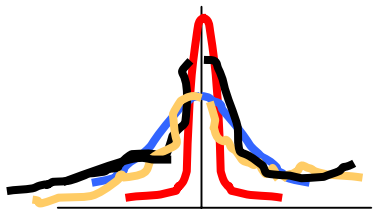
	DCM					XP						
Sample Class	Creep	Stress Relaxation	Standard	Constant Loading Rate	Constant Strain Rate	Creep	Stress Relaxation	Standard	Constant Loading Rate	Constant Strain Rate	Progressive Scratch	Constant Load Scratch
PVDF	X	X	X	X	X	X	X	X	X	X	X	X
HCPP	X	X	X	X	X	X	X	X	X	X	X	X
TPO	X	X	X	X	X	X	X	X	X	X	X	X

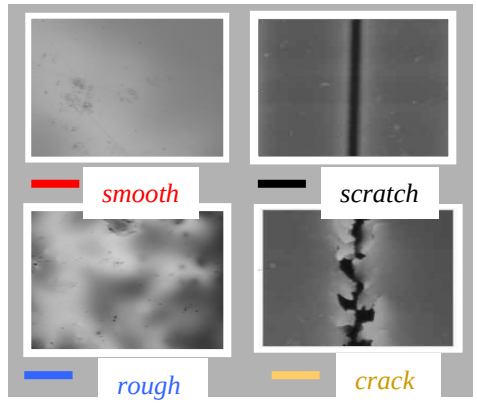
•DCM – Berkovich

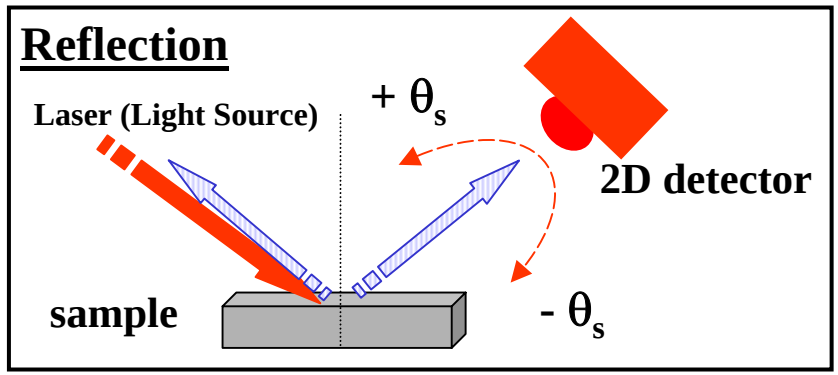
•XP mode – 1 µm 90° conical, 10 µm 90° conical

Constructed a Light Scattering Laboratory for Appearance Measurements of Scratch and Mar









Reflectance measurement

- various scattering angles
- specular, off-specular
- in-plane and out-of-plane measurements
- polarization measurements for detecting craze and other surface deformation

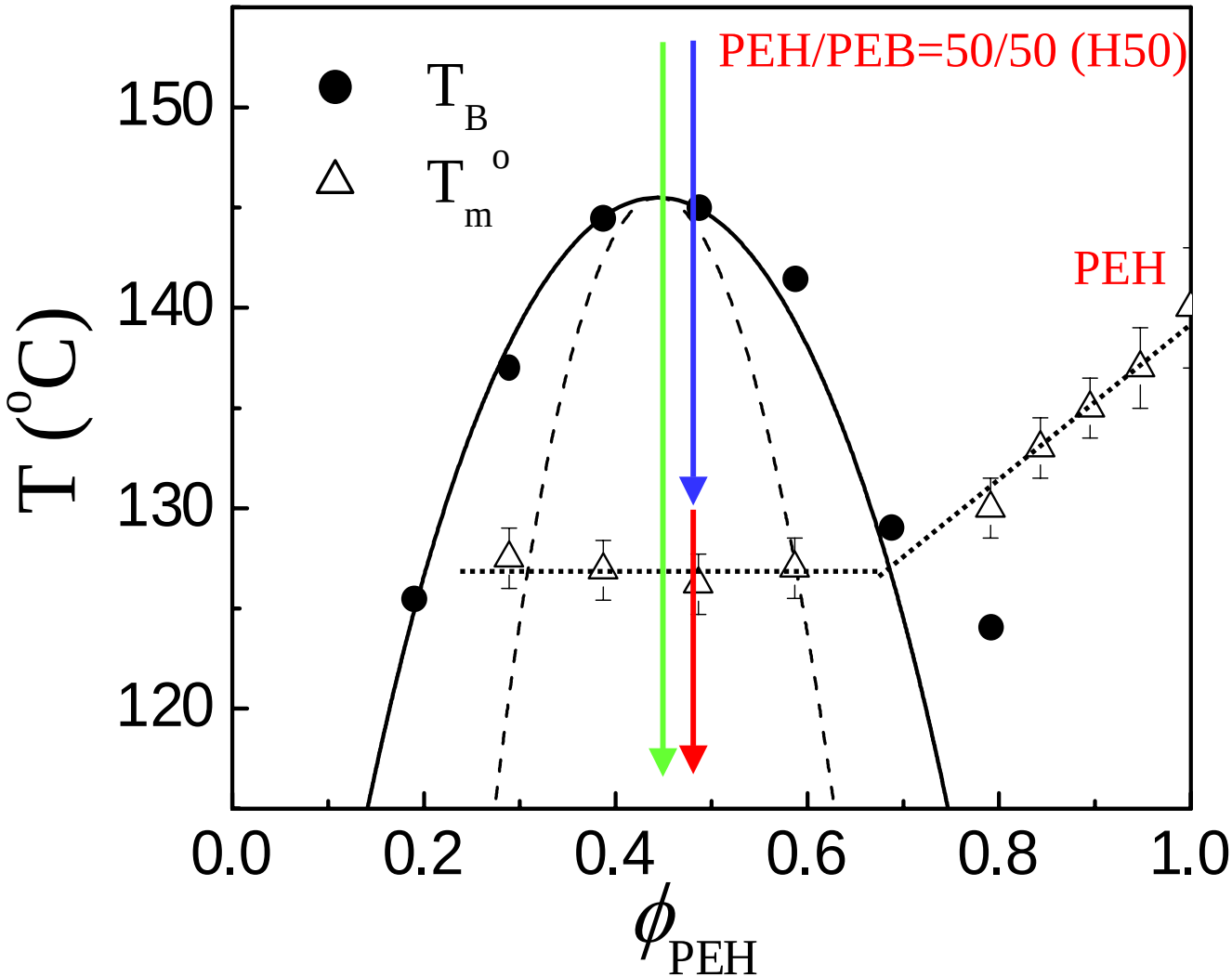
Project 2: Development of Models and Computer Program(s) for Predicting Interphases in Multi-Phase Polyolefin Systems under Shear Flow and Temperature.

Principal Investigators: Charles Han, Howard Wang, Fred Felan, and Nicos Martys (MSEL Leads)

Major Accomplishments:

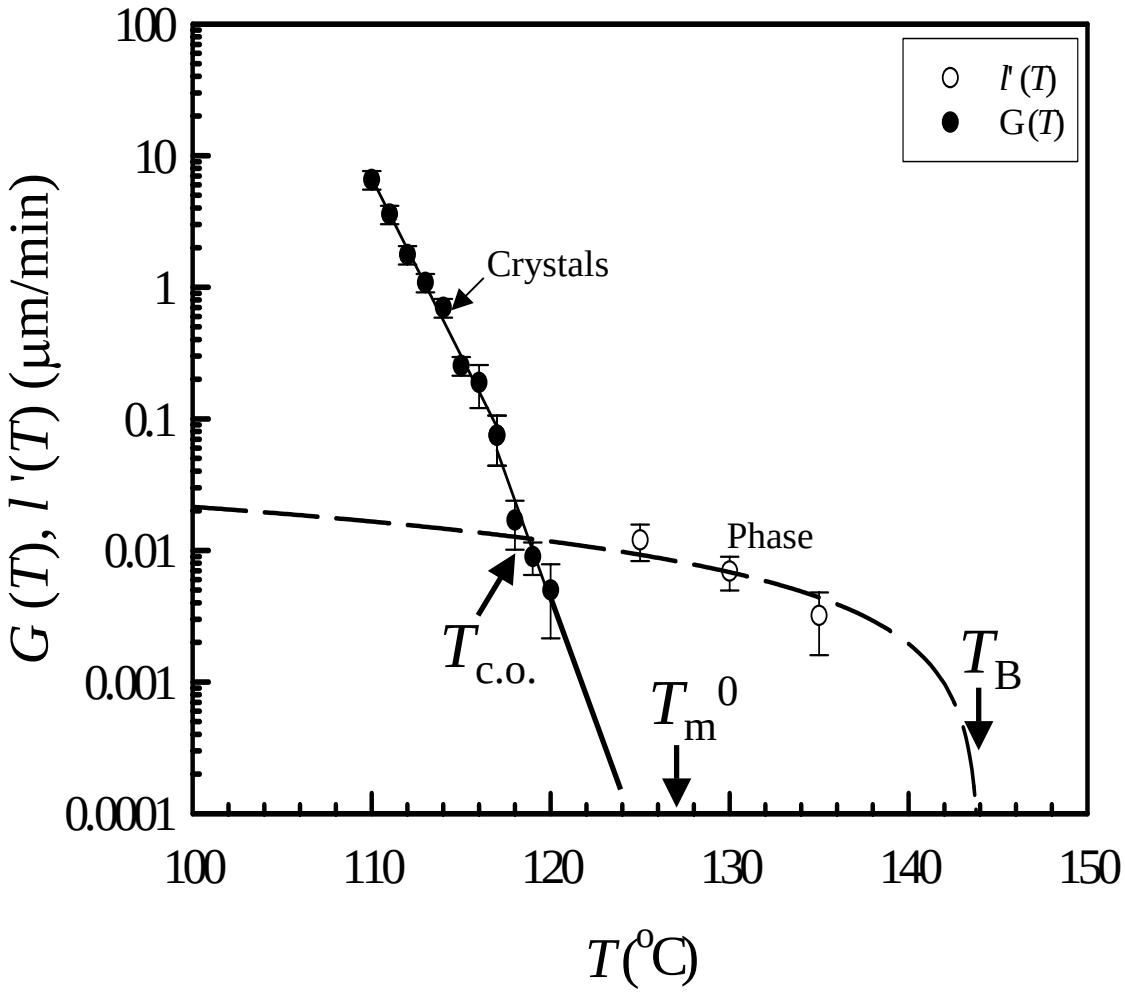
1) Established phase diagram, phase separation kinetics and morphology.
2) Completed measurements of crystallization kinetics and crystal morphology.
3) Completed investigation of interplay between phase separation and crystallization.
4) Completed measurements of shear-induced crystallite orientation and melting.
5) Completed studies on droplets deformation, phase inversion under shear.
6) Completed measurements of rheological properties of blends with complex morphology.
7) Seven papers have been published/submitted to journals.
8) **Models for predicting surface and interphase properties have not been done.

Measured the Phase Diagram of PEH/PEB Blend



Wang et al., Macromolecules, 35, 2002

Revealed Kinetic Cross-Over during Late Stage Phase Separation and Crystallization



Scaling argument for the late-stage spinodal decomposition:

$$l \propto \frac{\sigma}{\eta} t$$

$$\sigma \propto \frac{K_B T}{\xi^{d-1}}$$

$$\tilde{t} = (T_s - T)/T_s$$

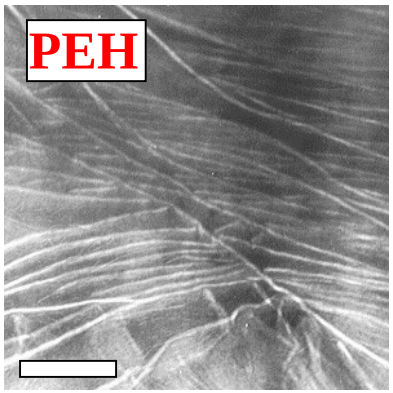
$$l' = \frac{l}{t} \propto \tilde{t}$$

Wang et al, J. Chemical Phys., 116, 2002

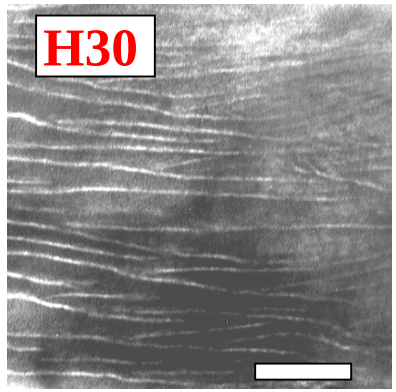
Studied Morphologies of Phase Separation and Crystallization

TEM

T_{iso}=120°C for 2 days, quench

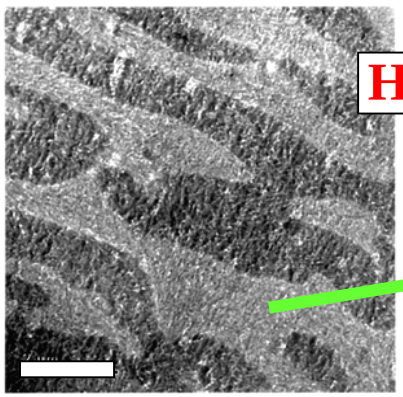


200 nm

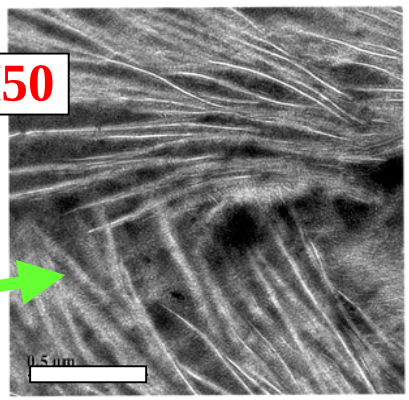


200 nm

23 h @ 130°C, 2 h @ 115°C, quench



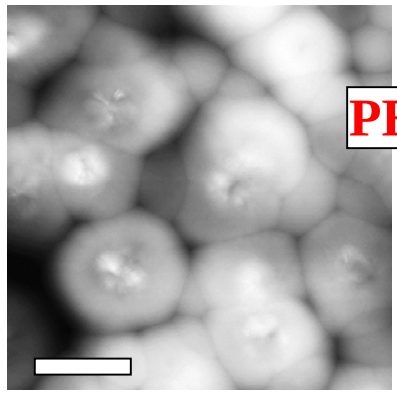
2 μm



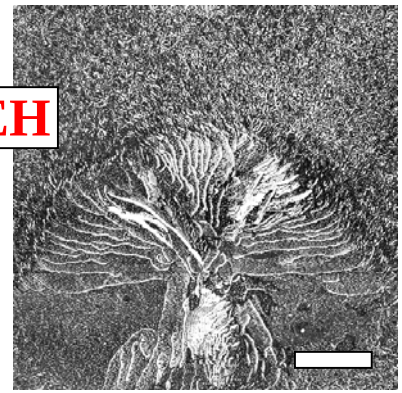
500 nm

AFM

T_{iso}= 118°C for 120 min, quench

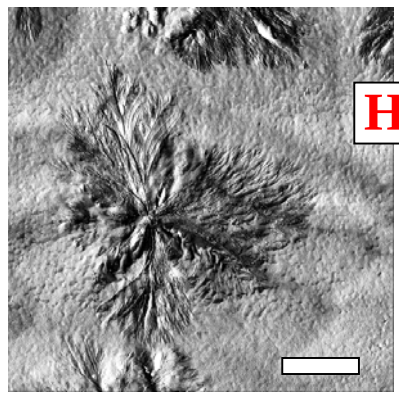


15 μm

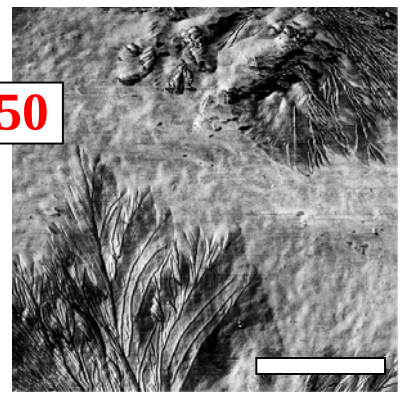


2 μm

T_{iso}=113°C for 10 min, quench

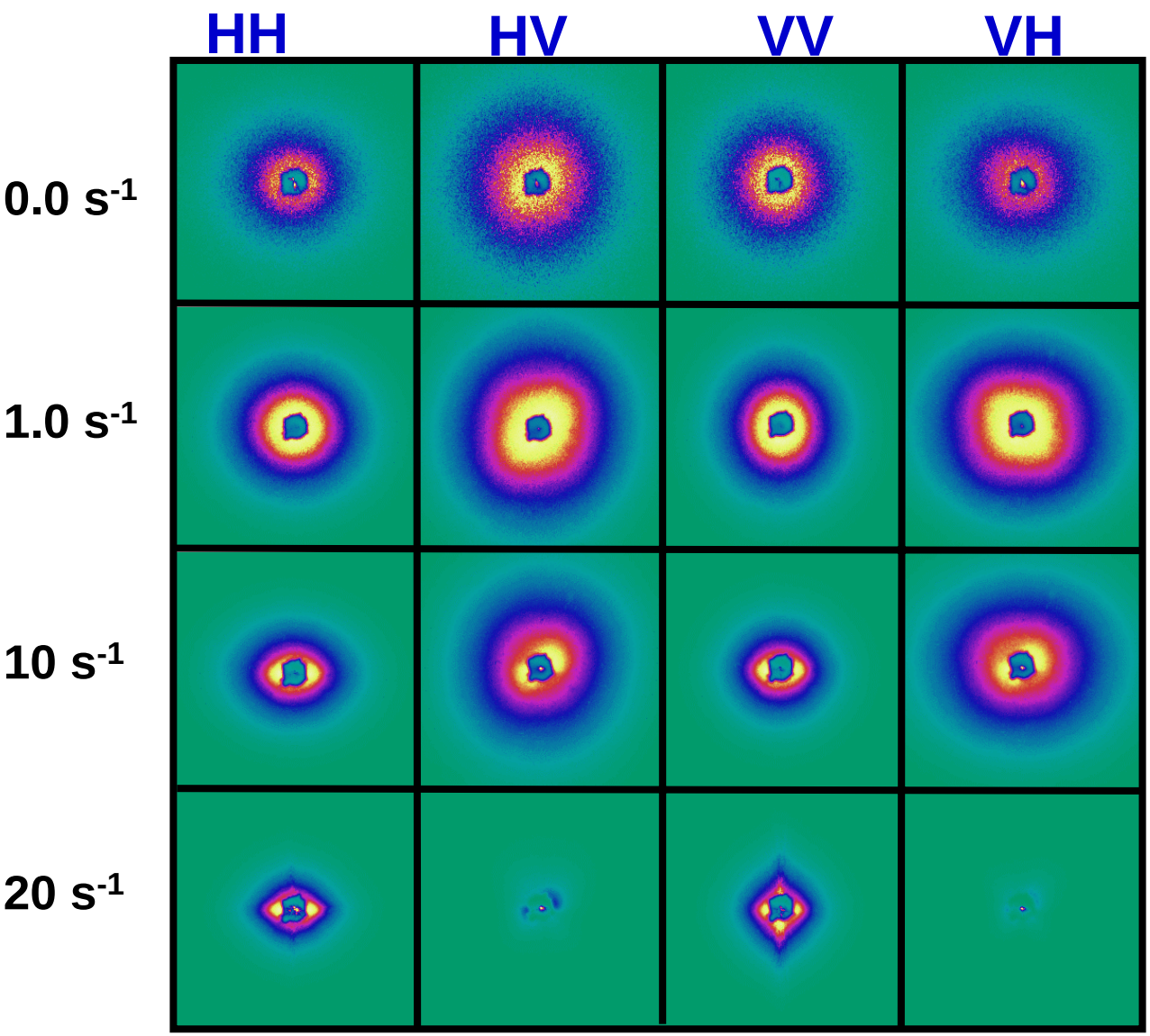


7 μm



5 μm

Shear Light Scattering Study



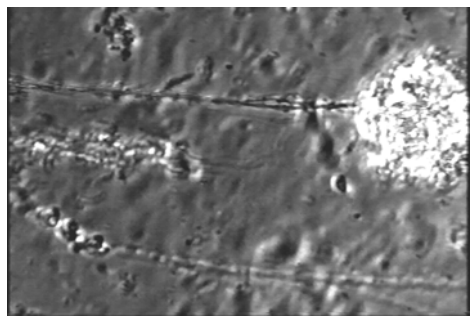
Shear direction requires additional polarizer/analyzer configuration.

At quiescence, crystals are randomly oriented.

At low shear rate, superstructural crystals orient giving rise to the isotropic scattering patter.

At higher shear rate, lamella align along the vorticity.

At even higher shear rate, crystal superstructures dissolve, whereas the remaining crystals aggregate to form necklace.



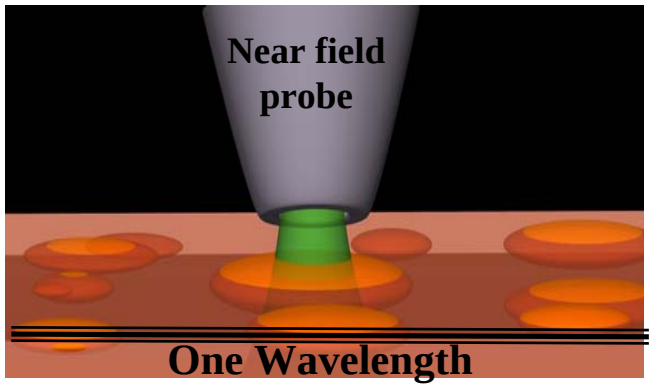
Project 3 : Characterization and Modeling of Interfaces and Interphases between Polymer Coatings and Substrates

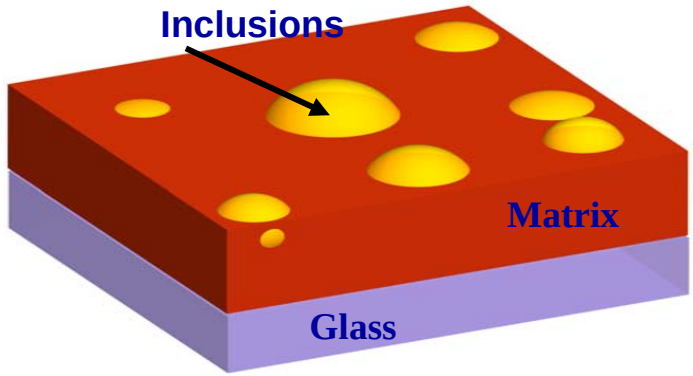
Principal Investigators: Chris Michaels, Tinh Nguyen, Lipiin Sung, and Forest Landis (CSTL Leads)

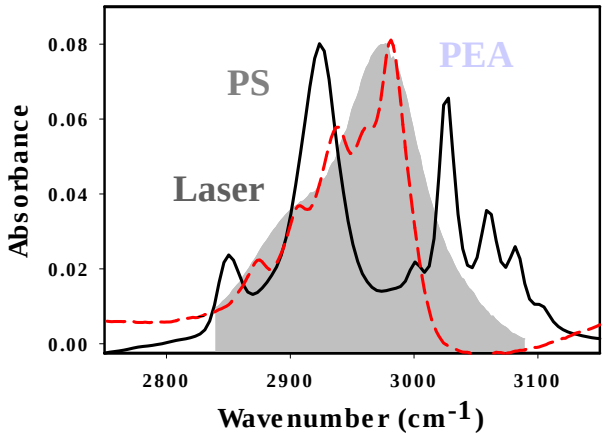
Major Accomplishments

1. Assessed the application of infrared near field scanning optical microscopy (NSOM) for nanoscale chemical studies of polymeric systems.
2. Constructed a confocal Raman microscope for chemical composition studies of surface and interphase of polymeric systems. Utilized this confocal Raman microscope for chemical imaging of consortium materials.
3. Conducted experiments to provide surface and interphase data to better understand the good outdoor and adhesion performances of PVDF-based coatings.
4. Assessed the weathering resistance of PVDF-based coatings exposed to NIST specially-designed UV exposure cells and chamber.
5. Completed investigation of effects of chemical composition and crystallization temperatures for PVDF/acrylic copolymer blends.
6. 12 papers published.

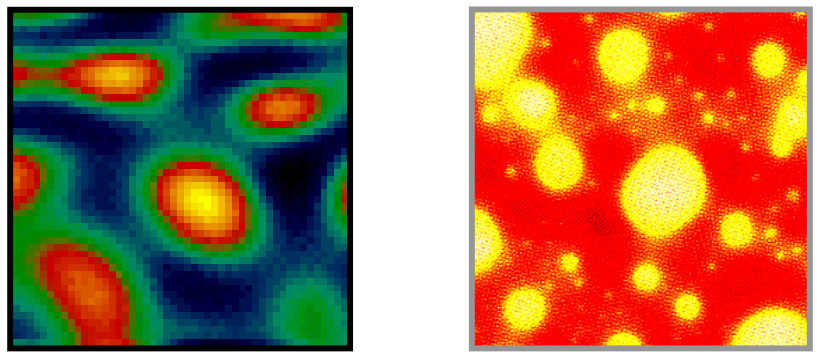
Near_field Infrared Imaging of Heterogeneous Organic Thin Films







Near-field transmission Topography

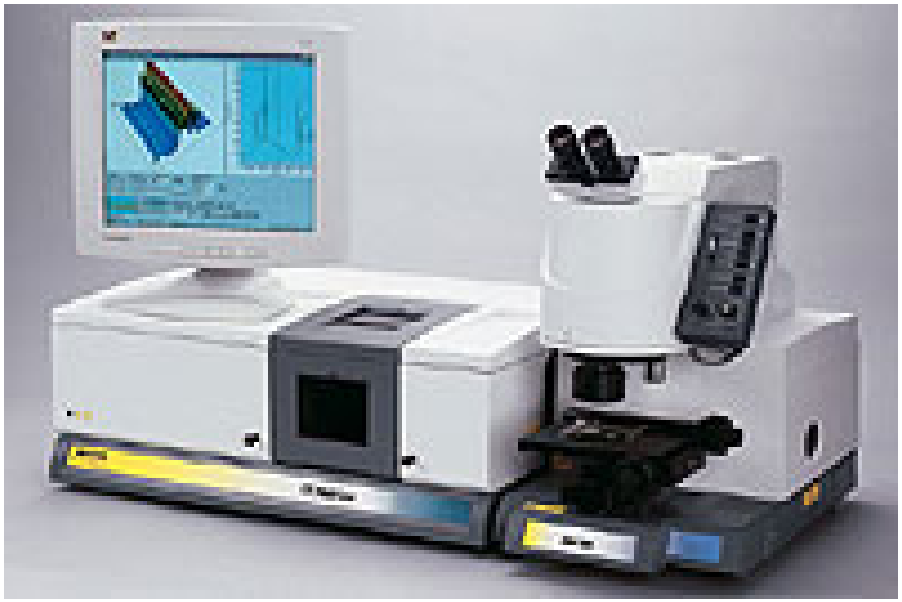


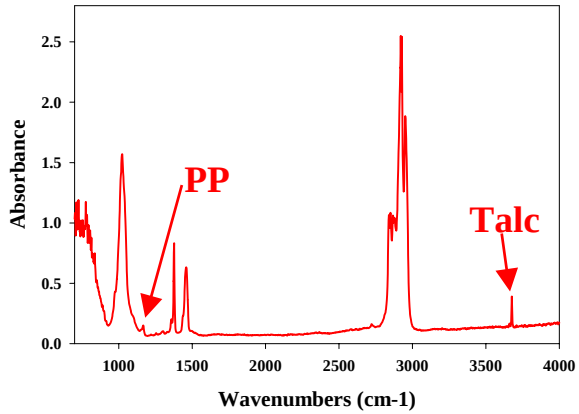
8 mm Images

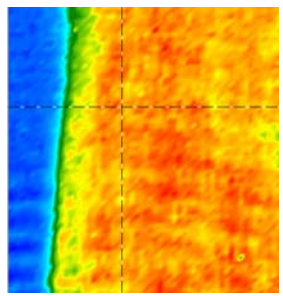
Infrared NSOM

Sub-diffraction spatial resolution of near-field imaging coupled with Chemically selective contrast mechanism ⇒ resonant absorption of long wavelength (2.5-20 μm) photons.

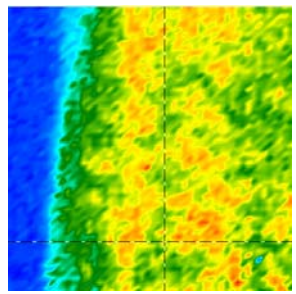
Chemical Characterization of TPO Microstructure: Infrared Mapping of PP and Talc



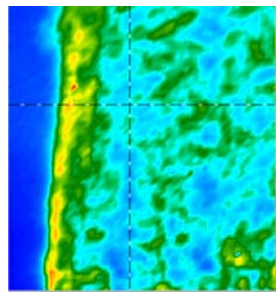




PP



Talc



Talc (norm)

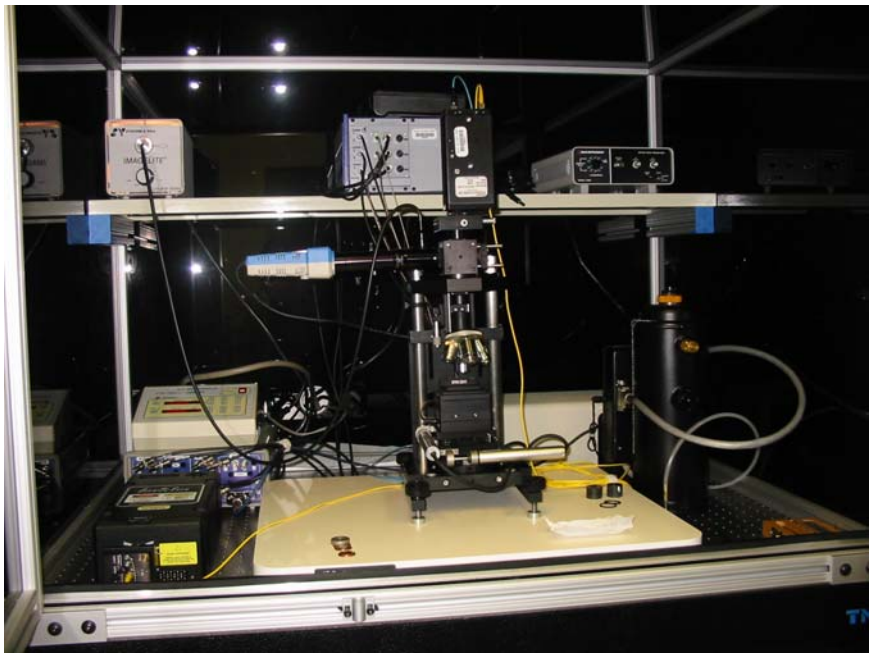
<u>Confocal IR Microscopy</u>

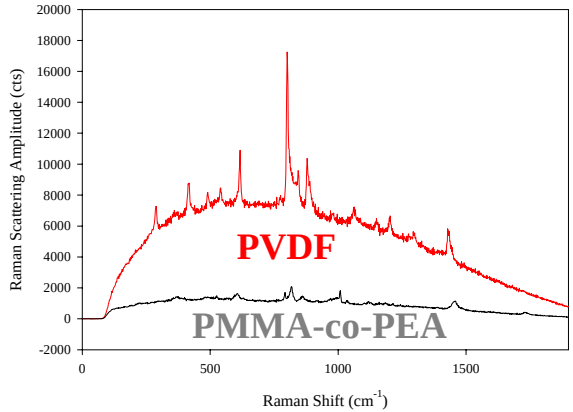
Imaging based on IR Array detector

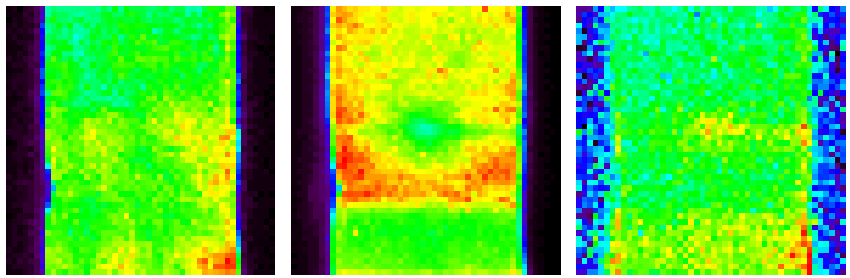
Chemical composition information from vibrational spectra

Multiple sampling strategies possible (Trans, Ref, ATR)

Confocal Raman Microscopy of PMMA-co-PEA/ PVDF Blend Cross Sections: PVDF Mapping







CF_2 Fluorescence Normalized CF_2

Confocal Raman Microscopy

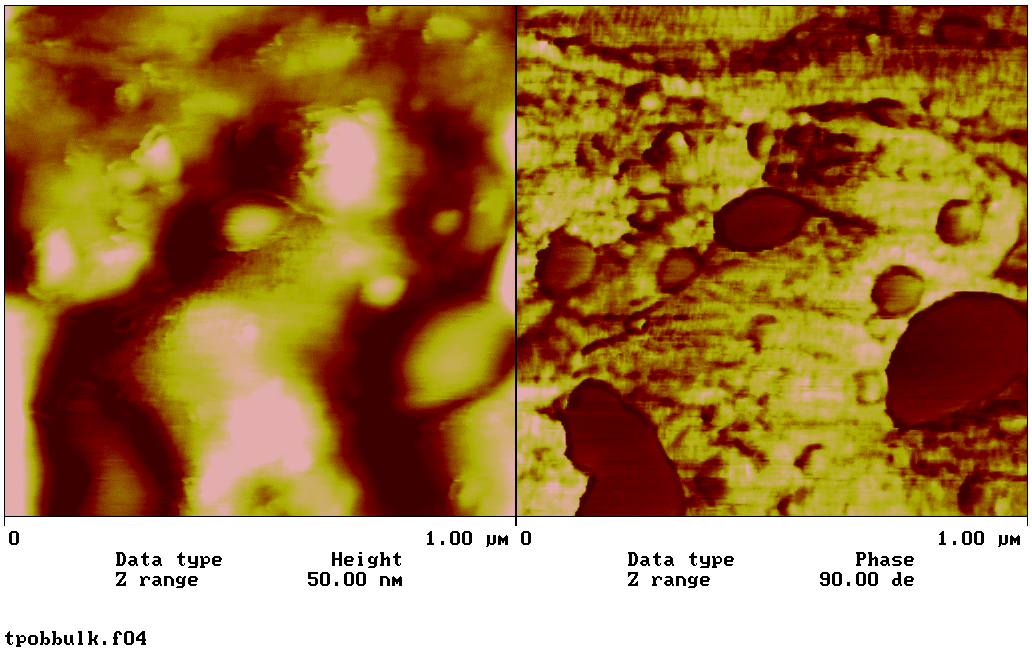
Diffraction-limited spatial resolution Lateral ~ l/2NA

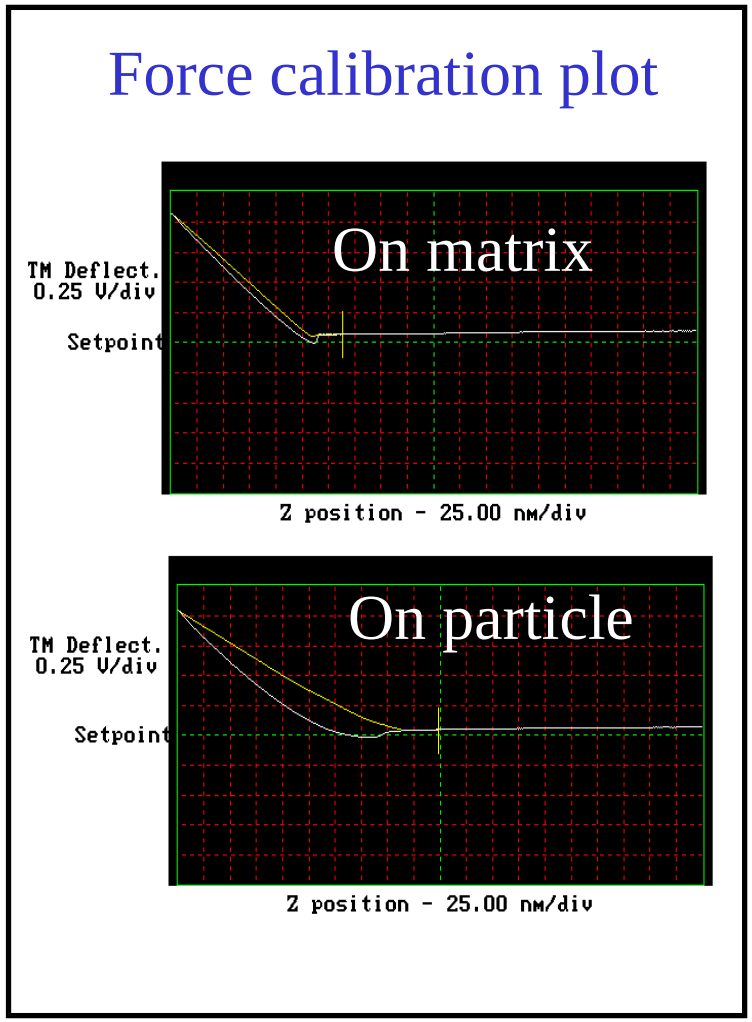
Confocal collection reduces 'out-of-focus Raman signal ⇒ depth profiling

Chemical composition information from vibrational spectra

Structural information from vibrational spectra (e.g. crystallinity, strain)

Imaging and Indentation on TPO



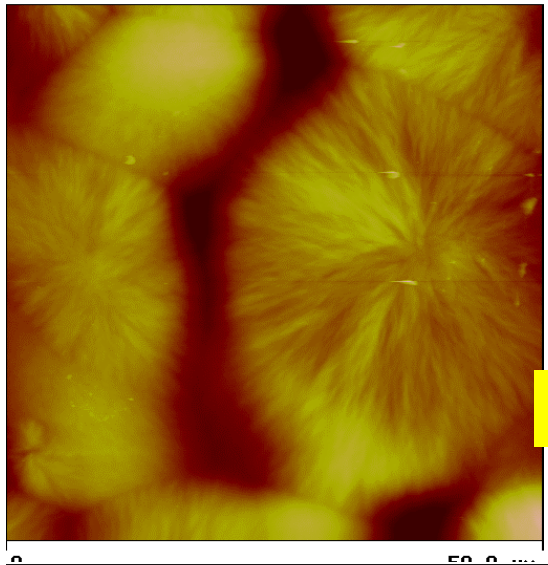


- **Darker particles in phase image show larger hysteresis and deeper trough in force curves, which are characteristic of more compliant materials compared to the matrix.**

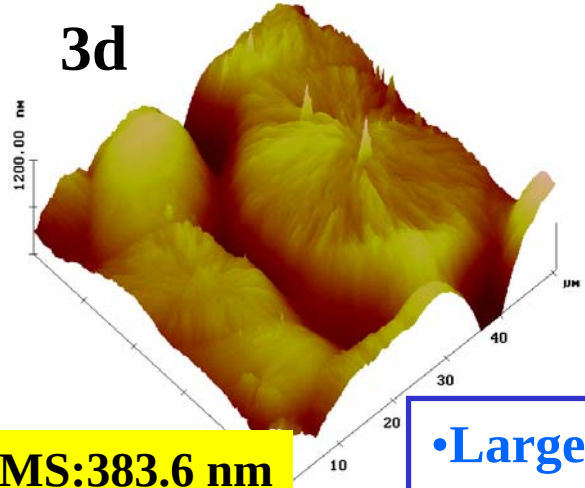
PVDF/PMMA-co-PEA: 70/30; Virgin

Height 2d

3d



50 μm

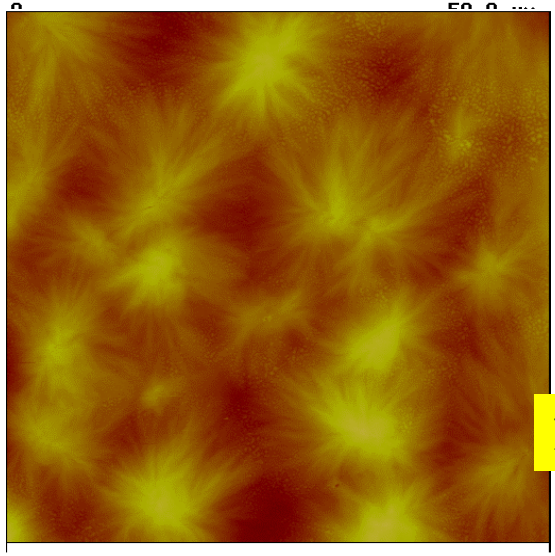


Surface

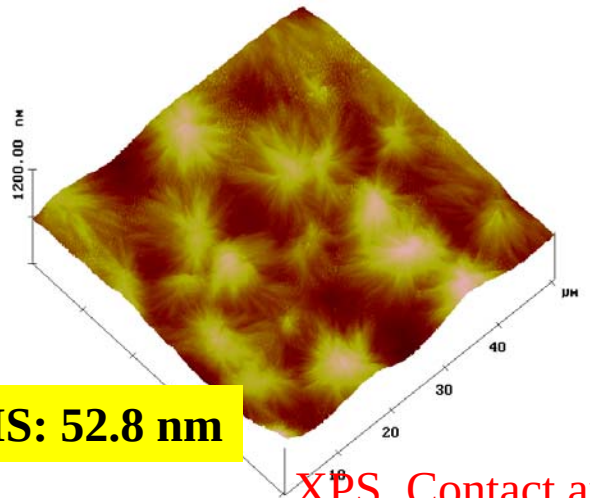
RMS:383.6 nm

600 nm

- Larger spherulites
- Rougher topography



50 μm



Interface

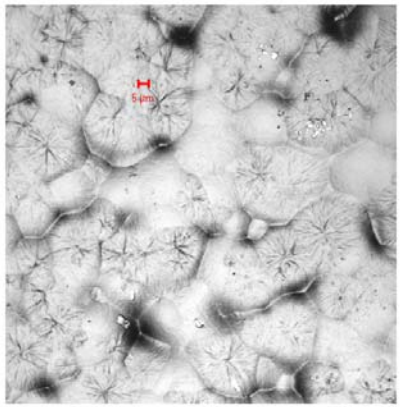
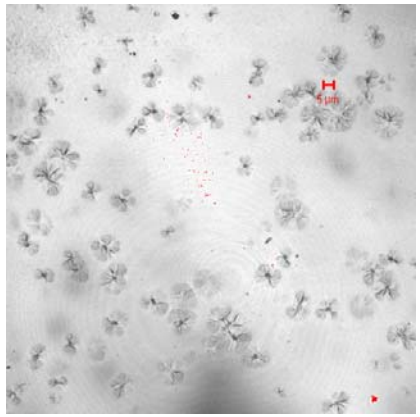
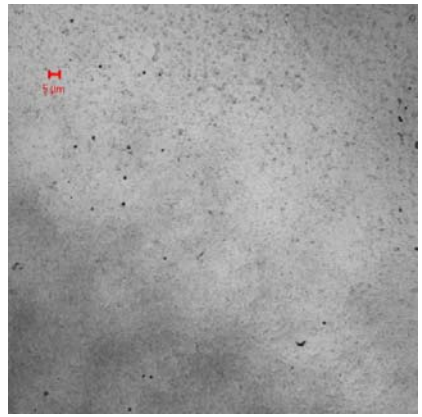
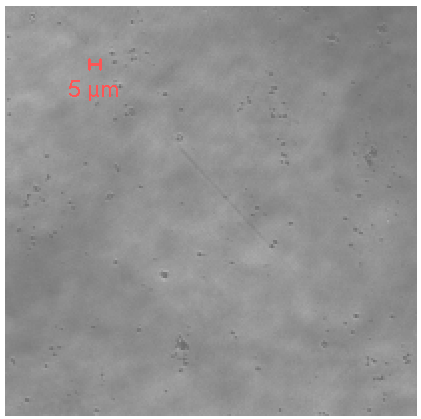
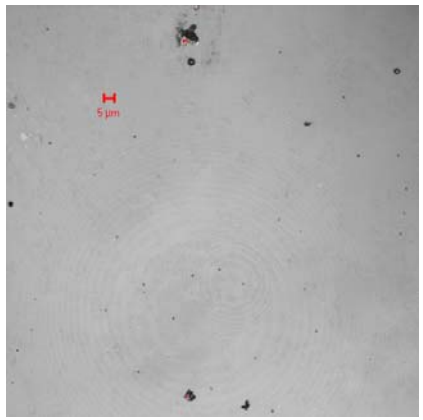
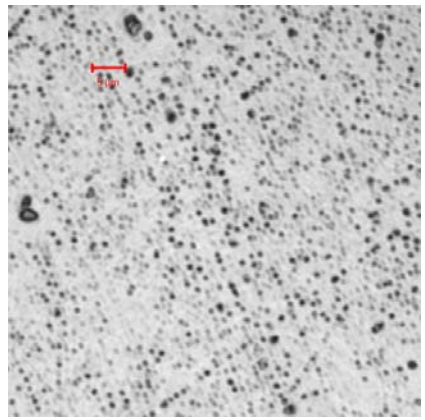
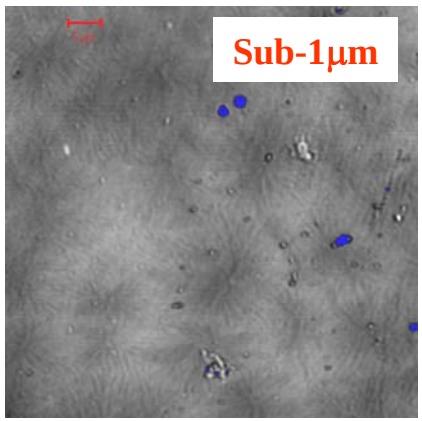
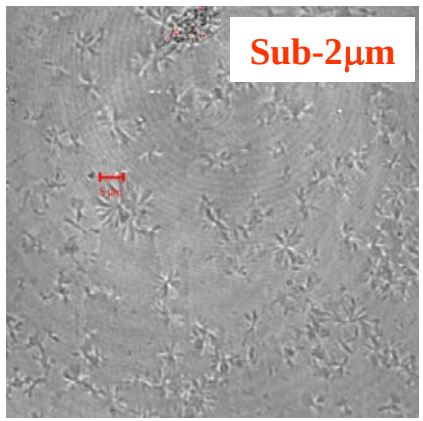
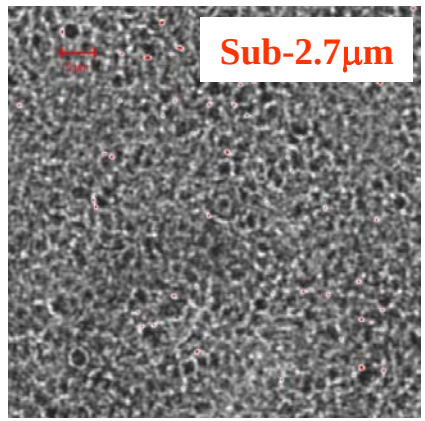
RMS: 52.8 nm

XPS, Contact angle, FTIR-ATR, SALS, confocal, …

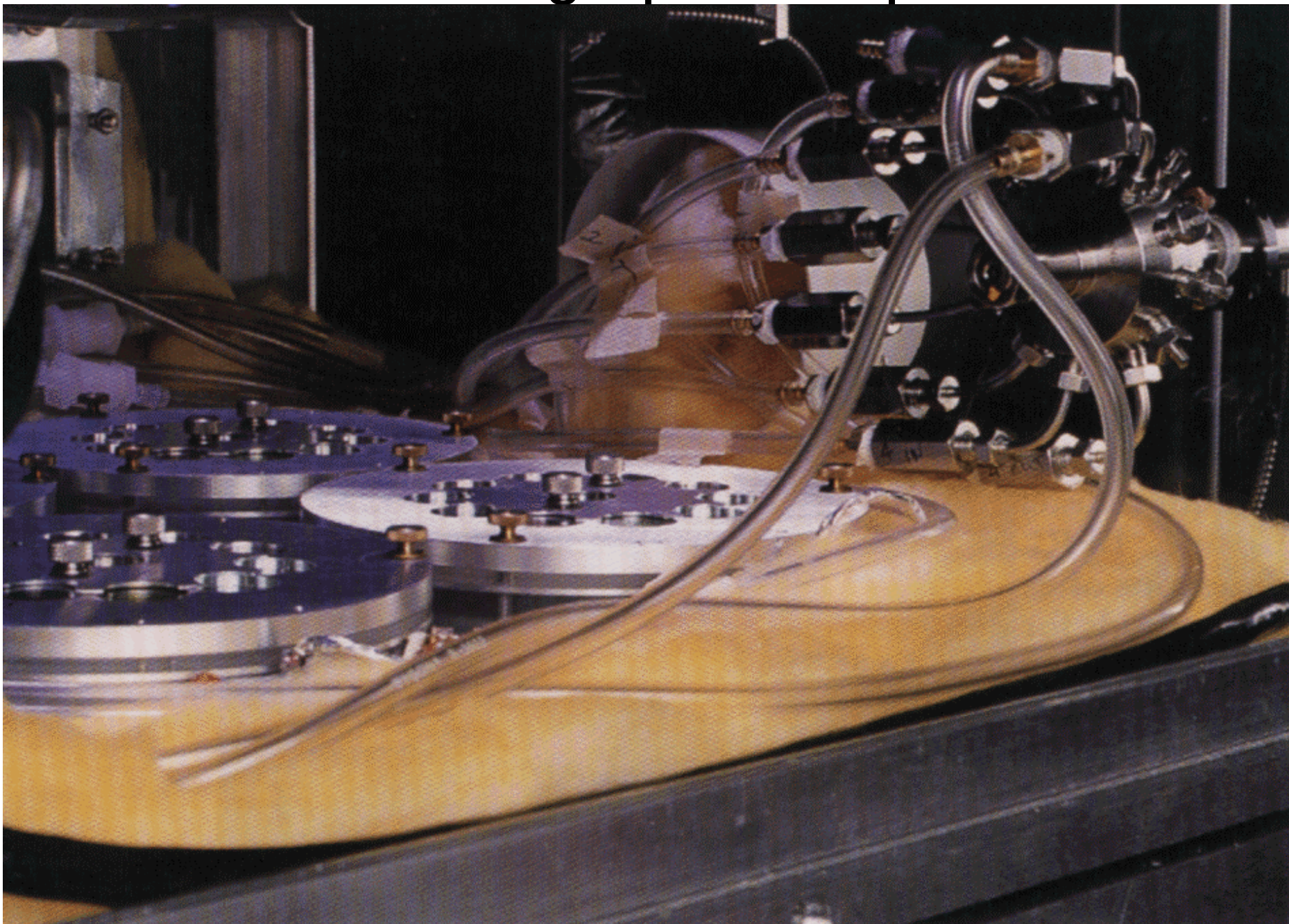
- PVDF crystals mostly dominate the surface

PVDF/ PMMA-co-PEA

(Confocal microscopy)

	70/30	60/40	50/50
Surface			
Interface			
Sub-interface			

Photograph of Exposure Cells



PVDF/PMMA-co-PEA: 50/50; Surface

Height Phase Phase

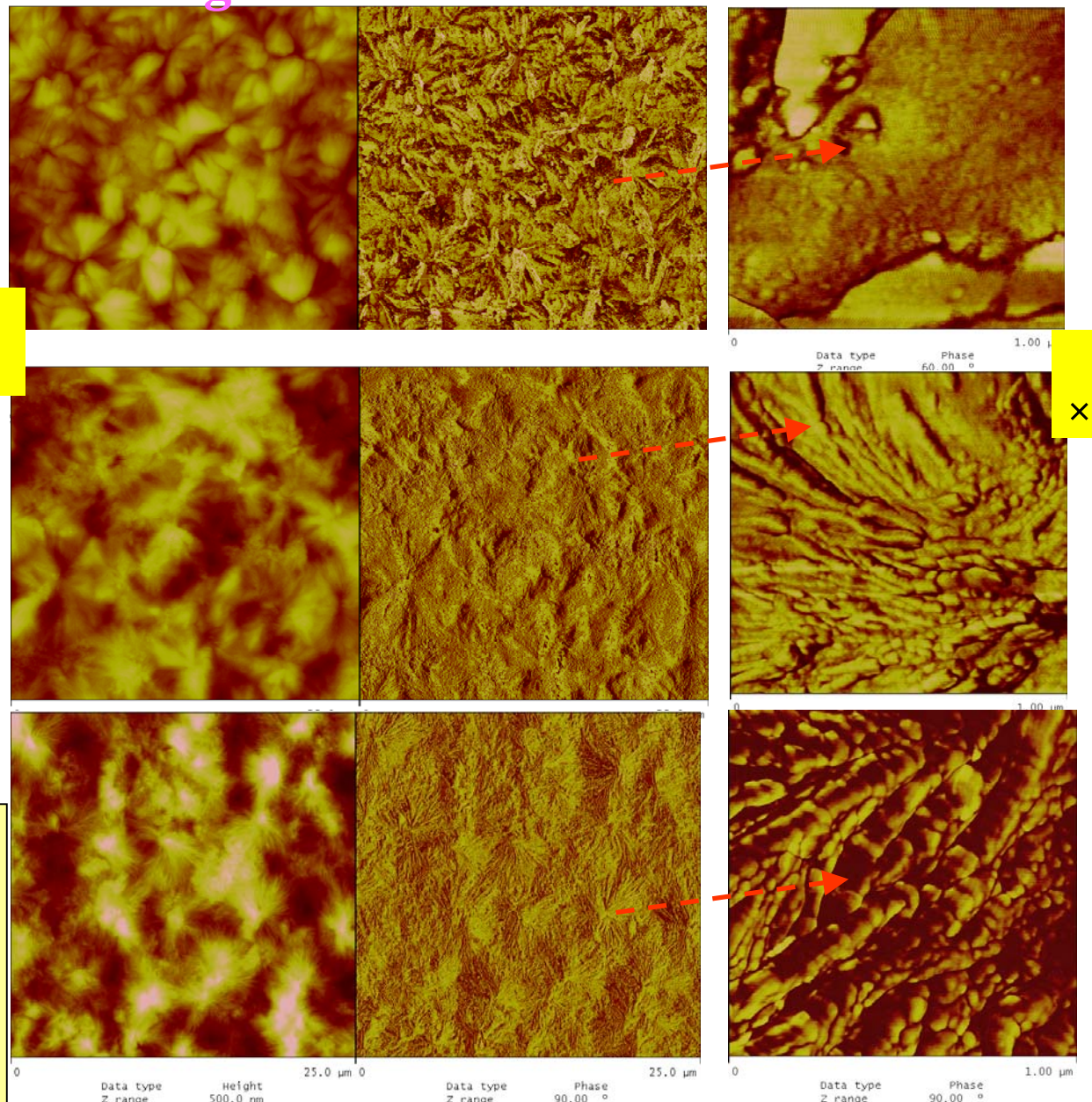
Virgin

2 month exposure

7 month exposure

25μm× 25μm

1.0μm × 1.0μm



- Crystal *size* appears *larger* after exposure.
- *Lamellae* structures are more obvious.

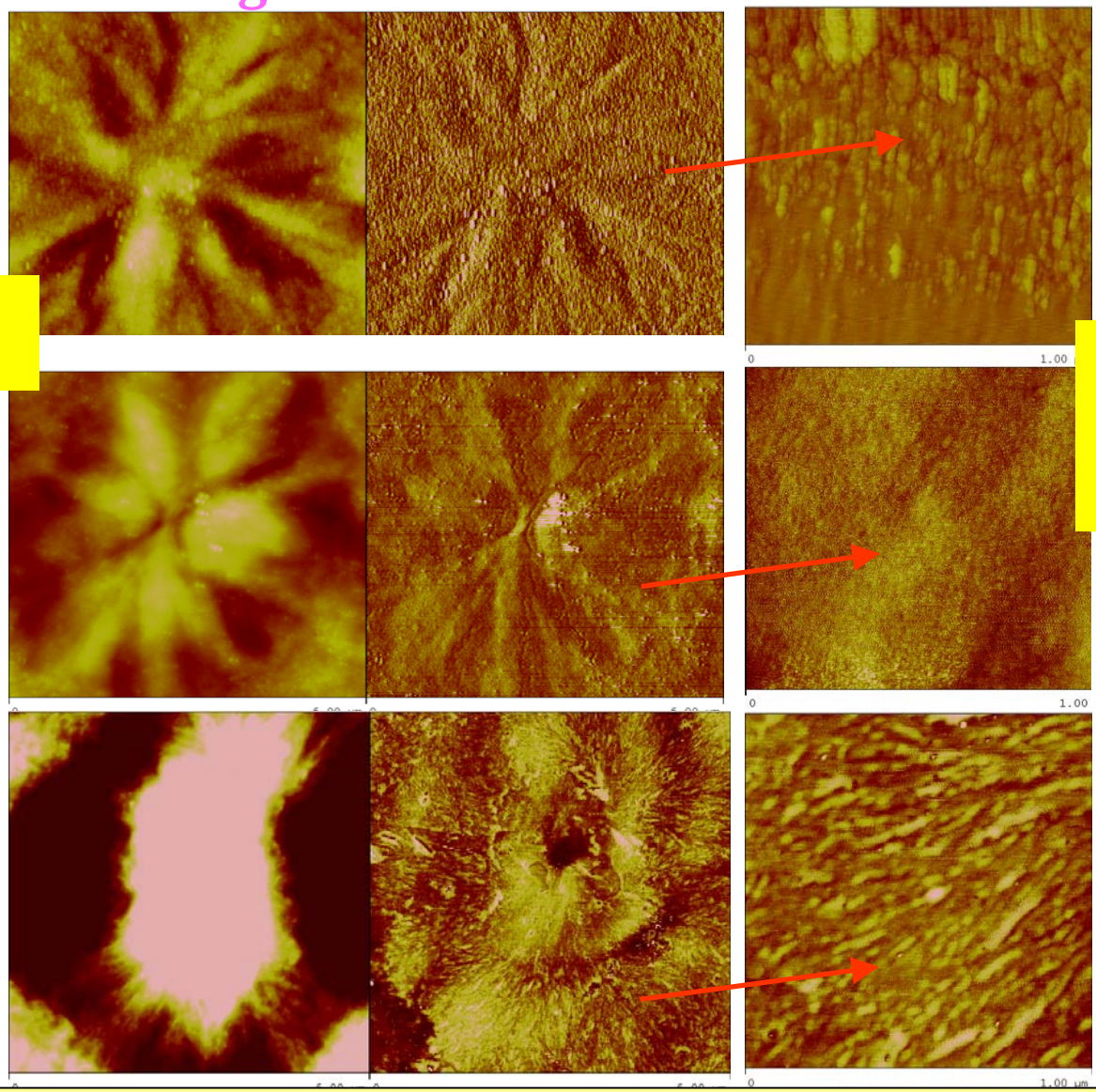
PVDF/PMMA-co-PEA: 60/40; No UVA, Interface

Height | Phase | Phase (Facing down)

Virgin

2 month exposure (50°C/75%RH)

7 month exposure (50°C/75%RH)



More organized microstructure is observed after 7 month exposure.

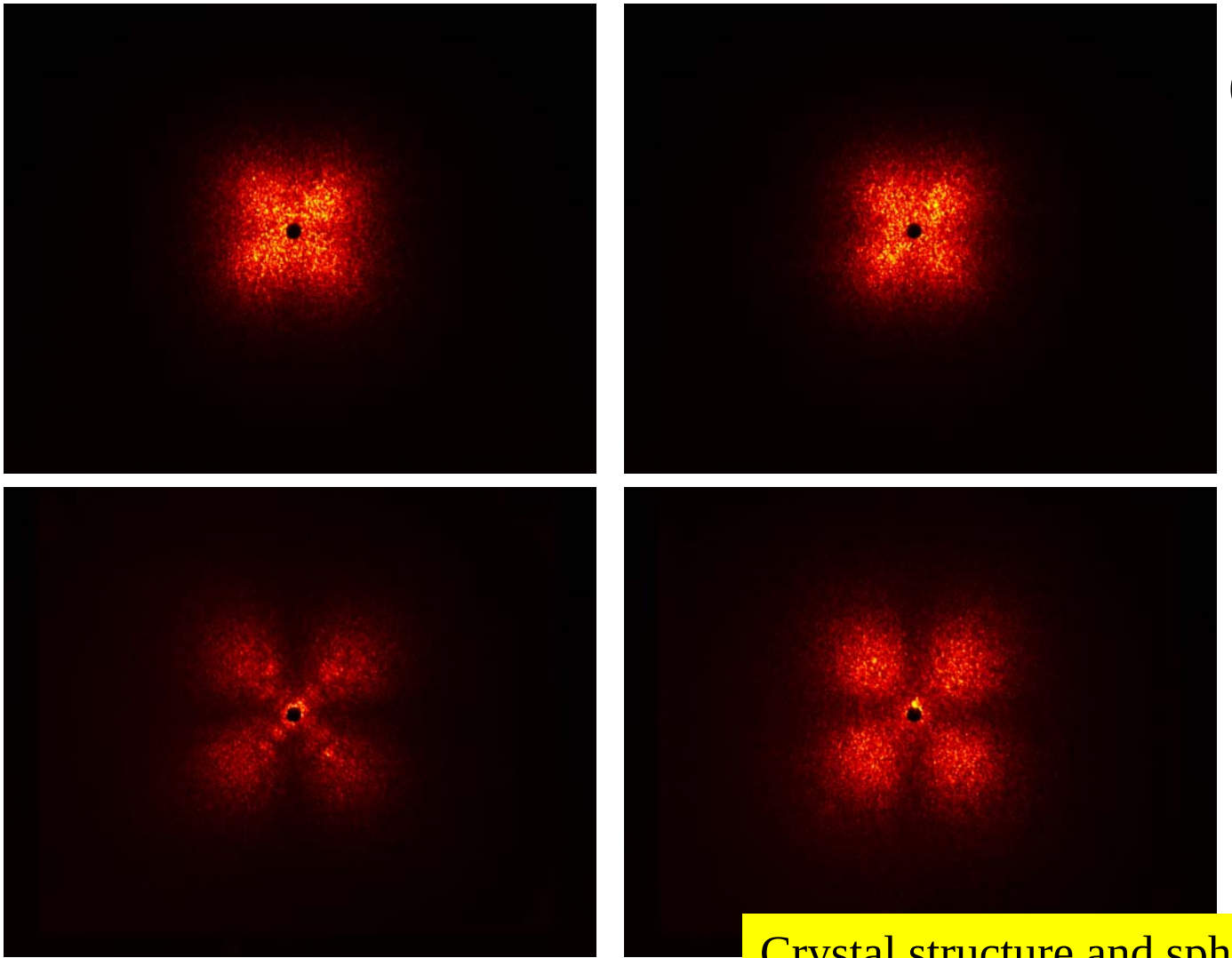
Small-angle Light Scattering Images of PVDF/PMMA-*co*-PEA

BULK

Initial | After 6 months

PVDF

60/40



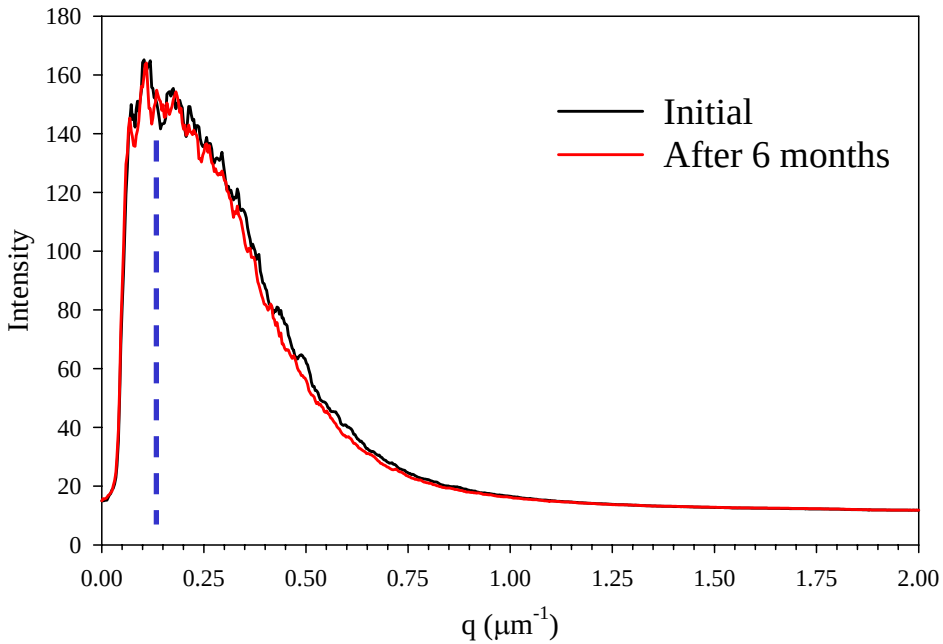
(Exposure to UV)

0.5 μm^{-1}

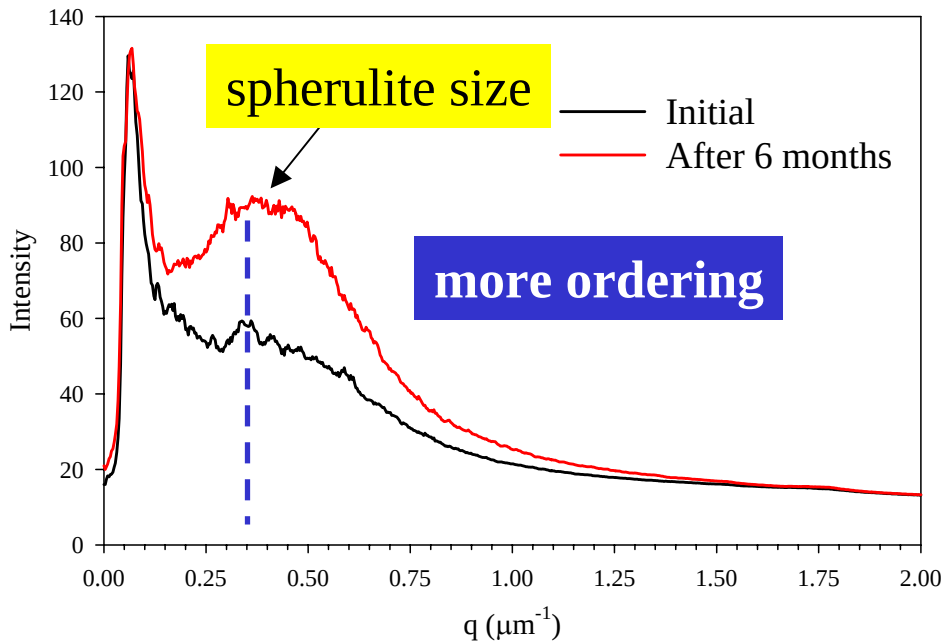
Crystal structure and spherulite size

Small-angle Scattering Profiles of PVDF/PMMA-*co*-PEA blends

BULK



PVDF



PVDF/PMMA-co-PEA, 60/40

- PVDF sample shows no change in spherulitic morphology after degradation.
- No significant change in the size of the spherulites with degradation.
- Scattering peak in the 60/40 sample increases with degradation – **more ordering (increase in PVDF concentration or/and chain reorganization)**

List of Publications and Manuscripts Generated from PIC Projects

Project 1

1. M. R. VanLandingham; "A Review of Instrumented Indentation," *J. Res. Natl. Inst. Stand. Technol.* **108**(4) (2003) 249-265.
2. M. R. VanLandingham, N.-K. Chang, T. Y. Wu, L. Sung, V. D. Jardret, S.-H. Chang; "Relating Instrumented Indentation to Scratch and Mar Resistance of Polymers," *J. Coatings Technol*. (2004), submitted.
3. M. R. VanLandingham, J. S. Villarrubia, R. Camara; "Measuring Tip Shape for Instrumented Indentation Using Atomic Force Microscopy," *J. Mater. Res.* (2004) submitted.
4. M. R. VanLandingham, N.-K. Chang, C. C. White, P. L. Drzal, S.-H. Chang; "Viscoelastic Characterization of Polymers Using Instrumented Indentation – I. Quasi-Static Testing," *J. Polym. Sci. B: Polym. Phys.* (2004) to be submitted.
5. C. C. White, M. R. VanLandingham, P. L. Drzal, N.-K. Chang, S.-H. Chang; "Viscoelastic Characterization of Polymers Using Instrumented Indentation – II. Dynamic Testing," *J. Polym. Sci. B: Polym. Phys.* (2004) to be submitted.
6. M. R. VanLandingham; "Scratch and Mar of Polymeric Materials," Service Life Prediction: Challenging the Status Quo (2004) to be submitted.
7. M. R. VanLandingham, Neng-Kai Chang, Tsun Yen Wu, L. Sung, V. D. Jardret, and Shuo-Hung Chang, "*Measurement Approaches to Develop a Fundamental Understanding of Scratch and Mar Resistance*," FSCT·ICE 2003 Proceedings of the 81th Annual Meeting Technical Program, Pennsylvania Convention Center, Philadelphia, PA, Nov. 12-14, **2003**.

Project 2

1. G. Matsuba, K. Shimizu, H. Wang, and Han, C. C., "*The Effect of Phase Separation on Crystal Nucleation Density and Lamellar Growth in Near-Critical Polyolefin Blends*", ***Polymer***, submitted.
2. G. Matsuba, K. Shimizu, H. Wang, and C. Han, "*Kinetics of Phase Separation and Crystallization in Poly(Ethylene-Co-Hexene) and Poly(Ethylene-Co-Octene)*", ***Polymer***, **44**, 7459 (2003).
3. A.J. Müller, M.L. Arnal, A.L. Spinelli, H. Wang, and Han C. C. "*Morphology and Crystallization Kinetics of Melt Miscible Polyolefin Blends*", *Macromolecular Chem. and Phys.*, 204, 1497 (2003).
4. H. Wang, E.K. Hobbie, K. Shimizu, and Han, C. C., "*Competing Kinetics in Simultaneously Crystallizing and Phase-separating Polymer Blends*", *J. Chem. Phys.*, 116, 7311 (2002).
5. H. Wang, K. Shimizu, E. Hobbie, A. Karim, and C. Han, "*Phase Diagram of a Nearly Isorefractive Polyolefin Blend*", ***Macromolecules*, 35,** 1072 (2002).
6. H. Wang, C. Han, B. Hsiao,"*Simultaneous SAXS and WAXS study of the Isothermal Crystallization in Polyolefin Blends*", *Polymeric Materials: Science & Engineering, Preprint*, 85, 427 (2001).
7. G. Wang, H. Wang, K. Shimizu, K., and C. Han, "*Early Stage Crystallization in Poly(ethylene-co-hexene) by SAXS/WAXS, DSC, OM and AFM*", *Polymeric Materials: Science & Engineering, Preprint*, 85, 435 (2001).

Project 3

1. T. Nguyen, X. Gu, M. Van Landingham, M. Giraud, R. Dutruc-Rosset, R. Ryntz, and D. Nguyen. Characterization of Coating Systems Interphases with Phase Imaging AFM Proceedings, Adhesion Society Meeting, J. A. Emerson, Ed., 24, 68, (2001).
2. T. Nguyen, X. Gu, M. Van Landingham, and D. Nguyen, Surface and Interface Microstructure of Coatings Systems and Their Implication on Durability, Proceedings, International Conference on Durability of Building Materials and Components, Brisbane, Australia, March, 2002.
3. X. Gu, T. Nguyen, D. Nguyen, and M. VanLandingham, Surface and Interface Properties of PVDF/Acrylic Copolymer Blends, Proceedings, Adhesion Society Meeting, Orlando, February, 2002, pp 497-499.
4. T. Nguyen, X. Gu, M. VanLandingham, Rose Ryntz, D. Nguyen, and J. Martin, Nanoscale Charcaterization of Coatings Surface Degradation with Tapping Mode Atomic Force Microscopy, Proceedings, *Adhesion Society Meeting*, Myrtle Beach, SC, February, 2003, p 508.
5. X. Gu, T. Nguyen, L. Sung, M.R. VanLandingham, Y.C. Jean, and J. W. Martin, "*Advanced Techniques for Nanocharacterization of Polymeric Coating Surfaces*," FSCT·ICE 2003 Proceedings of the 81th Annual Meeting Technical Program, Pennsylvania Convention Center, Philadelphia, PA, Nov. 12-14, 2003; submitted JCT (2004).
6. X. Gu, L. Sung, D.L. Ho, C.A. Michaels, D. Nguyen, Y.C. Jean, and T. Nguyen, "*Surface and Interface Properties of PVDF/Acrylic Copolymer Blends Before and After UV exposure*," FSCT·ICE 2002 Proceedings of the 80th Annual Meeting Technical Program, Oct. 30 – Nov 1, New Orleans, LA. (2002).
7. X. Gu, L. Sung, D.L.Ho., C.A. Michaels, D. Nguyen, J. Jean, and T. Nguyen, Surface and Interface Properties of UV-Exposed PVDF/PMMA-co-PEA Blends, Proceedings, *Adhesion Society Meeting*, Myrtle Beach, SC, February, 26, 505 (2003).
8. S. J. Stranick, D. B. Chase, and C. A. Michaels, "Chemical Imaging with Near-Field Scanning Optical Microscopy," *Proc. SPE ANTEC* (2001).
9. C. A. Michaels, X. Gu, D. B. Chase, and S. J. Stranick, "Near-field Infrared Imaging and Spectroscopy of a Thin Film PS/PEA Blend," *Appl. Spec*, **58** (2004).
10. S. J. Stranick, D.B. Chase and C. A. Michaels, "Chemical Imaging with Scanning Near-Field Microscopy and Spectroscopy," Rubber Chemistry and Technology, (2002).
11. S. J. Stranick, D.B. Chase and C. A. Michaels, "Near-Field Microscopy for Chemical and Material Analysis on the Nanoscale," *Poly. Mat. Sci. and Eng.* **87**, (2002).
12. C.A. Michaels, D.B. Chase, and S.J. Stranick, "Chemical Imaging of Thin Film Polymer Blends with Near-Field IR Microscopy," *Poly. Mat. Sci. and Eng.* **88**, 188 (2003).

Interphase Consortium - Research Areas:

Project 1

Title: **Characterization of Surface Deformation and Quantification of Mar Resistance of Polymeric Materials and Systems.**

Principal Investigators: **Mark R. VanLandingham, Lipiin Sung, and Peter Drzal (BFRL)**

Objectives:

1) To develop advanced measurement techniques for evaluating mar and scratch resistance of polymeric materials and systems,
2) To relate material properties and deformation behaviors.
3) To relate surface deformation (mar) and appearance.

Products:

1) **Techniques and models for characterization of mar and scratch resistance of polymeric coatings and systems.**
2) **Standards reference materials.**
3) **Standards for mar and scratch measurements.**
4) **Correlation of deformation scales from molecular to visual.**

Interphase Consortium - Research Areas

Project 2

Title: Development of Models and Computer Program(s) for Predicting Interphases in Multi-Phase Polyolefin Systems under Shear Flow and Temperature.

Principal Investigators: Drs.Charles Han, Howard Wang, Fred Feland, and Nicos Martys

Objectives:

1) To develop computer modeling program(s) for prediction of polymer multi-phases under shear flow and temperature gradients,
2) To carry out measurements for obtaining inputs for the modeling;
3) To develop characterization techniques and protocols for evaluating the interphase structure and its formation during processing of a polymer coating on a structured substrate surface.

Products: a) Techniques for characterizing polymer multi-interphases.

b) Models for predicting polymer interphases properties.

c) Data base of parameters for interphases optimization.

Interphase Consortium - Research Areas:

Project 3

Title: Characterization and Modeling of Interfaces and Interphases between Polymer Coatings and Substrates.

Principal Investigators: Drs. Chris Michaels (Lead), Tinh Nguyen, Lipiin Sung, and Forest Landis

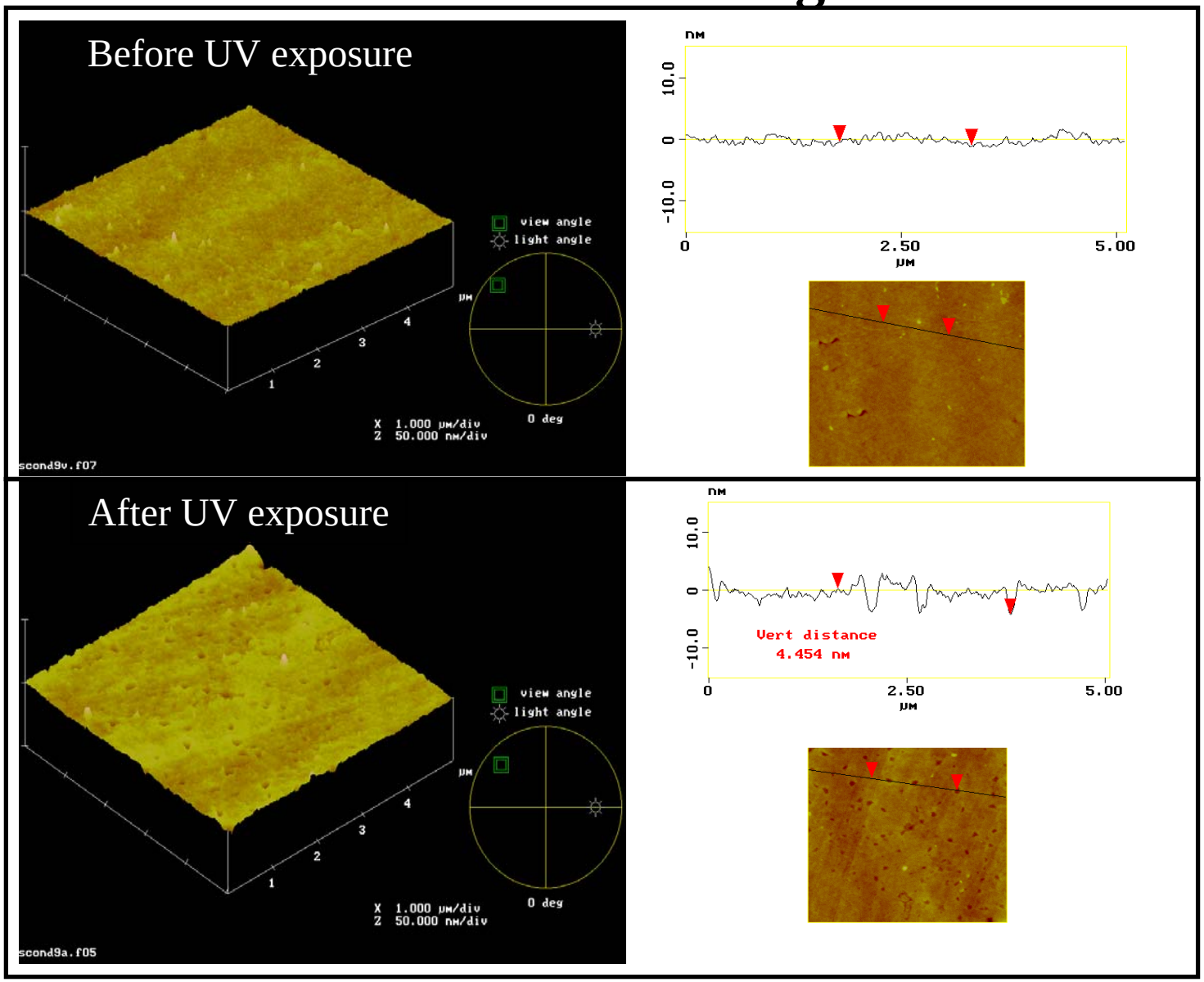
Objectives:

1) To develop nanoscale chemical and mechanical probes for characterizing the interphase region in polymer coating/substrate systems,
2) To model interphase development, and
3) To develop a database of important parameters for optimizing polymer/substrate interface/interphase formation.

Products:

1) Techniques for nanoscale characterization of polymer/substrate (organic and inorganic substrates) interphases.
2) Models for polymer/substrate interphases development.
3) Database of parameters for optimization of polymer/substrate interphases.

Automotive Coating Surface



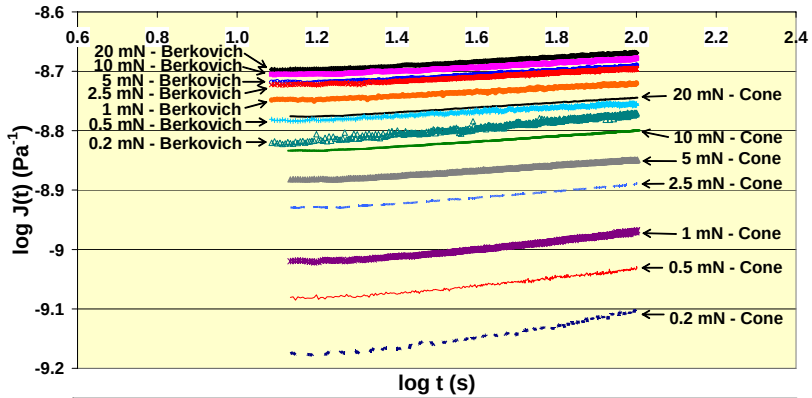
RMS 0.776 nm

RMS 1.056 nm

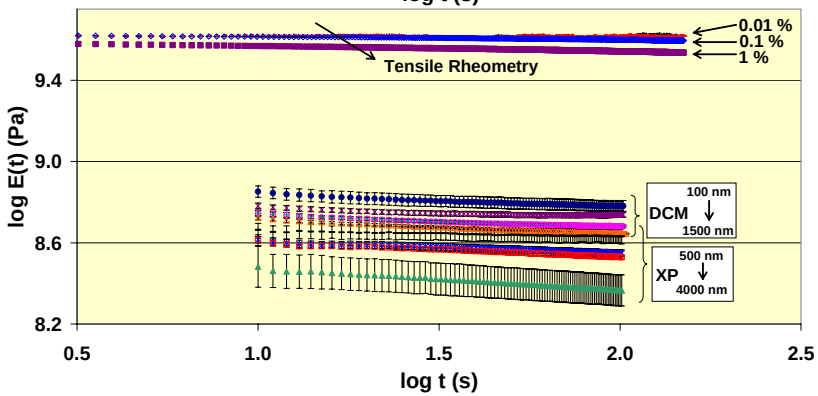
- Many pits developed on the surface of the sample after UV exposure.

Viscoelastic Characterization

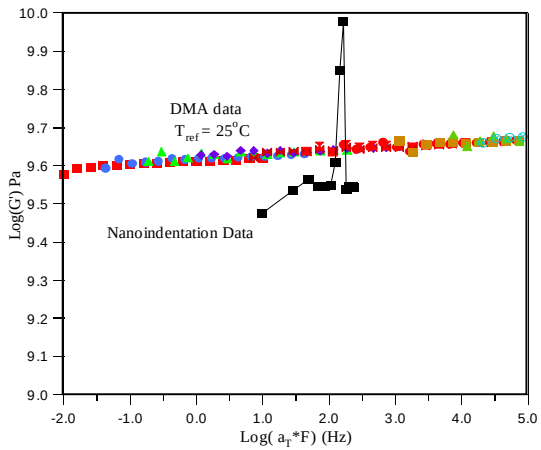
- **Creep Compliance**
  - **Establish time and stress dependence under contact forces**



- **Stress Relaxation Modulus**
  - **Establish time and strain dependence under contact forces**



- **Dynamic Moduli**
  - **Establish frequency (short time) dependence under contact forces in terms of energy storage and loss**



Forms basis for constitutive models