Detection of Percolating Paths in PMMA/CB Segregated Network Composites Using EFM and C-AFM

Jacob Waddell, Runqing Ou, Sidhartha Gupta,
Charles A. Parker, and Rosario A. Gerhardt

Georgia Institute of Technology

Katya Seal, Sergei V. Kalinin, and Arthur P. Baddorf

Oak Ridge National Laboratory

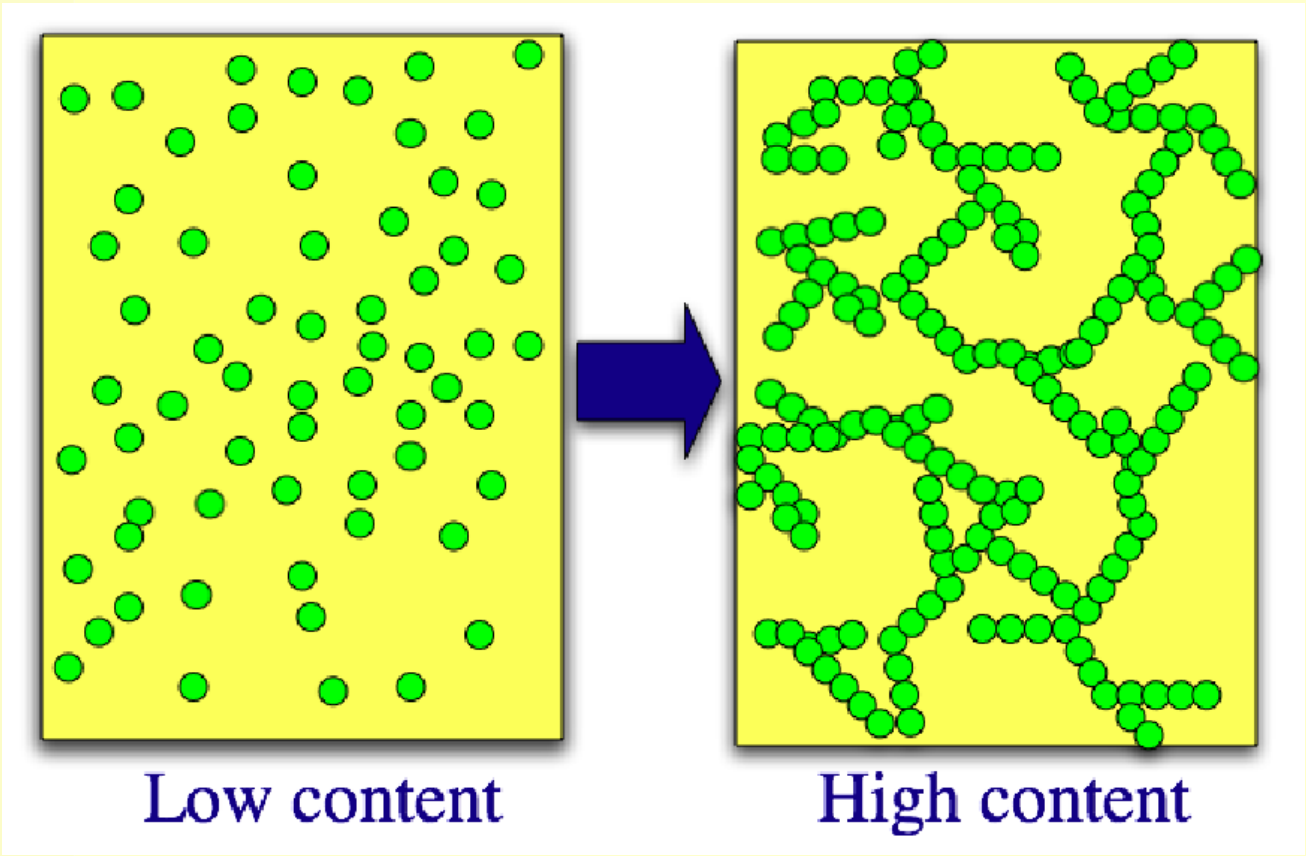
07/30/2009

Outline

- Brief Review of Percolation
- Random Microstructure Vs Segregated Network Microstructure
- Scanning Probe Microscopy Modes
- EFM Detection of Microstructure
- TUNA Detection of Conductive Paths

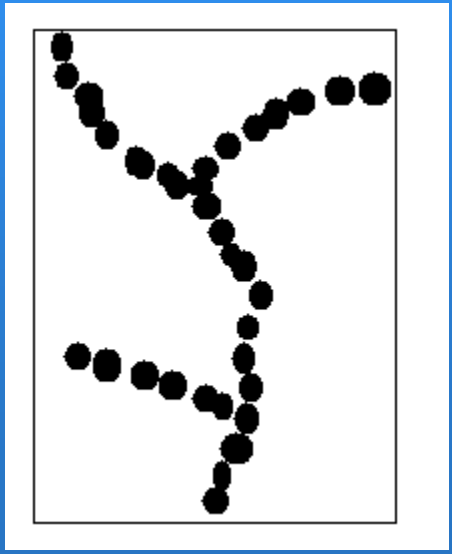
Percolation in Composites

- Percolation is reached when the second-phase forms a connected network in the matrix.

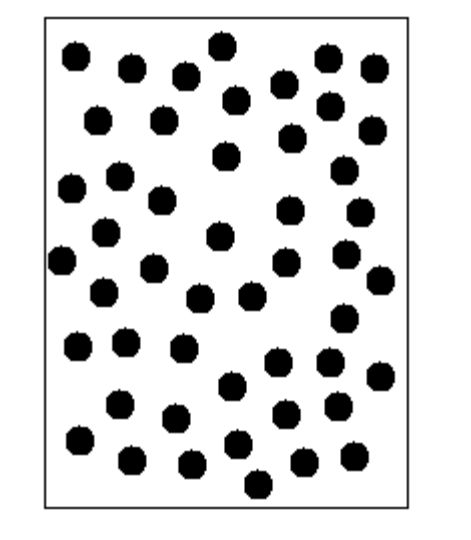


Segregated Vs Random

- Filler-poor and filler-rich regions
- Desired properties with less filler
- Obtained through immiscible polymer blends, and mechanical mixing

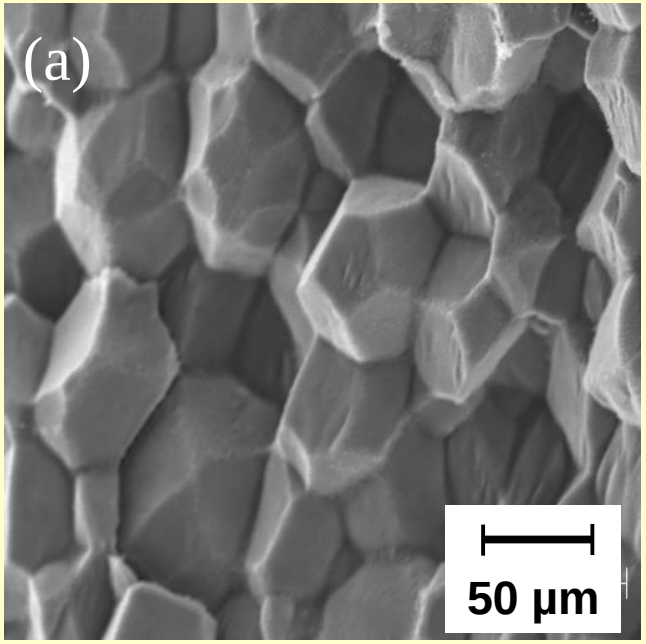


- Evenly dispersed filler
- Homogeneous properties
- Obtained through melt mixing or solution mixing

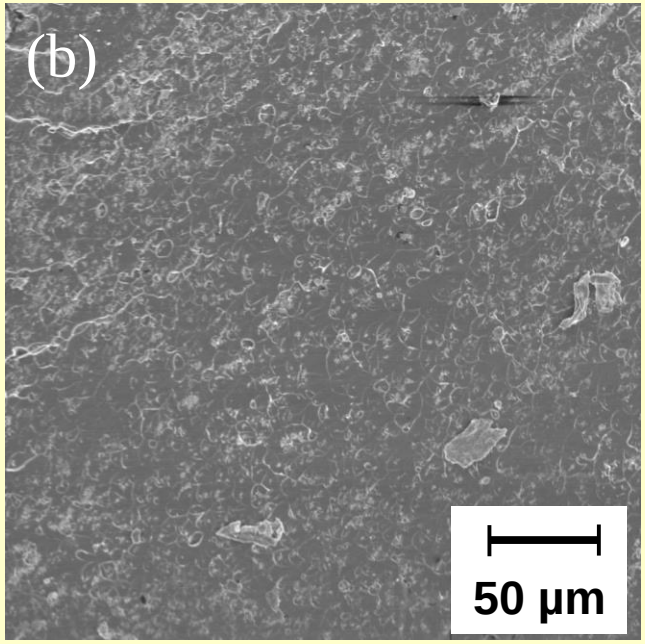


SEM Images of Fracture Surfaces

Carbon Black/ Poly(Methyl Methacrylate) Samples



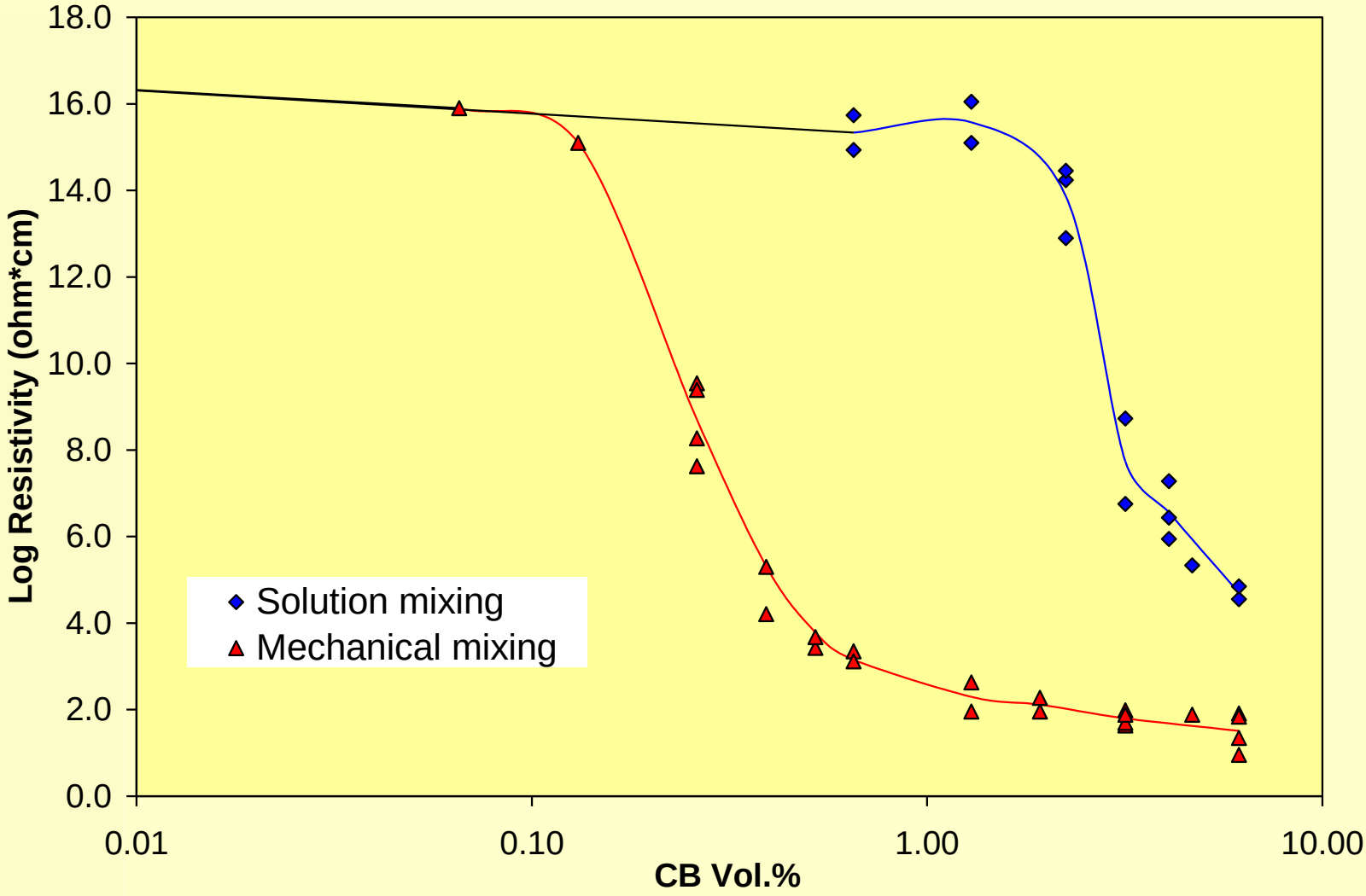
3.17 vol% CB
Mechanically Mixed Sample



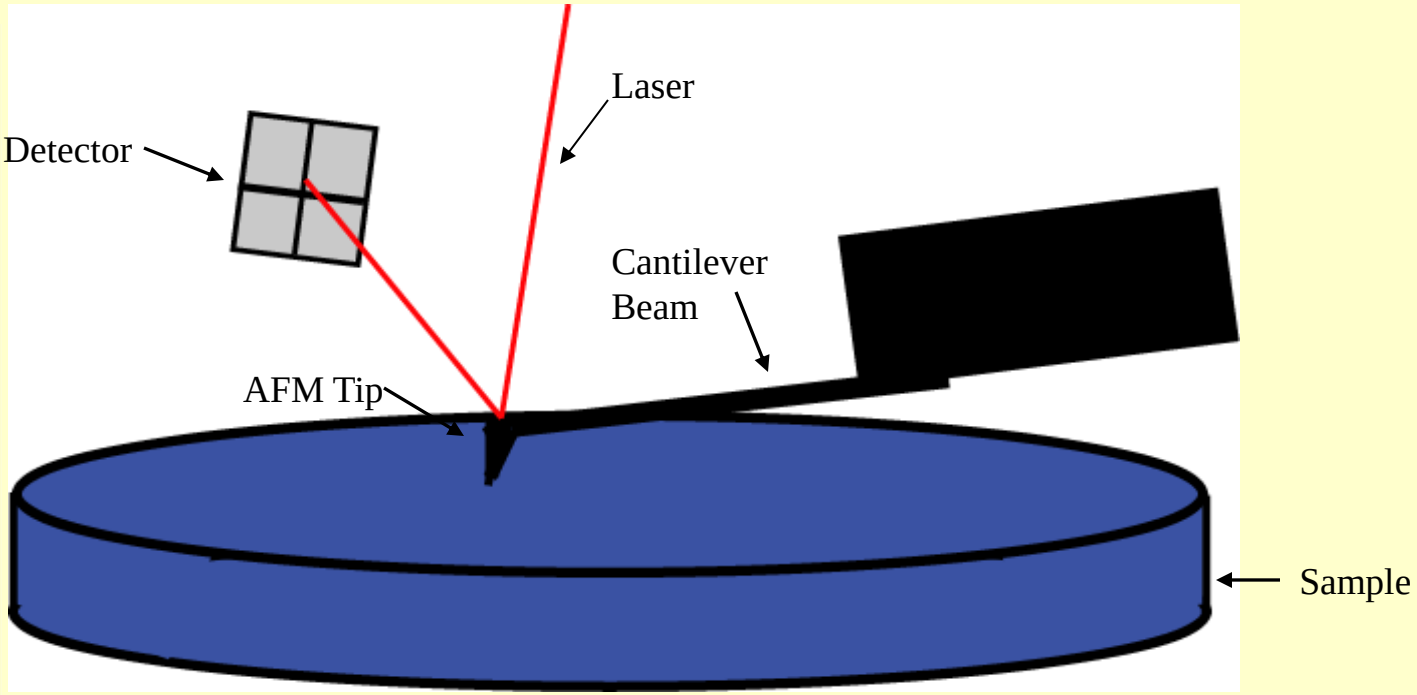
3.17 vol% CB
Solution Mixed Sample

- SEM images allows for good visualization of PMMA structure but it is difficult to determine the location of the carbon black.

Resistivity vs. CB vol.%

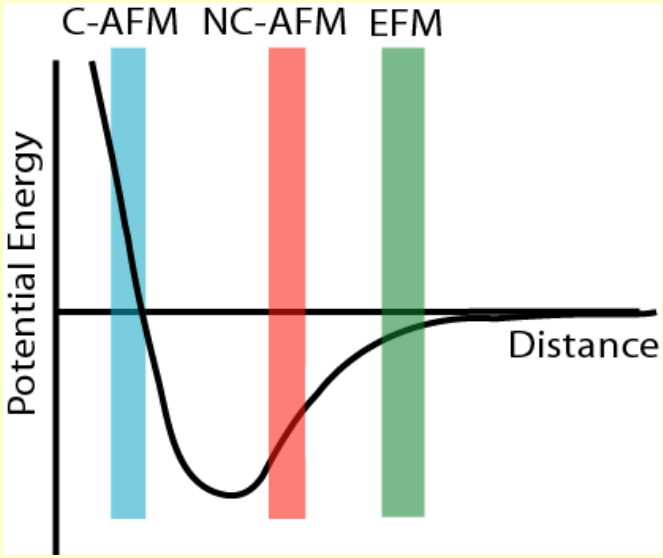


Atomic Force Microscopy



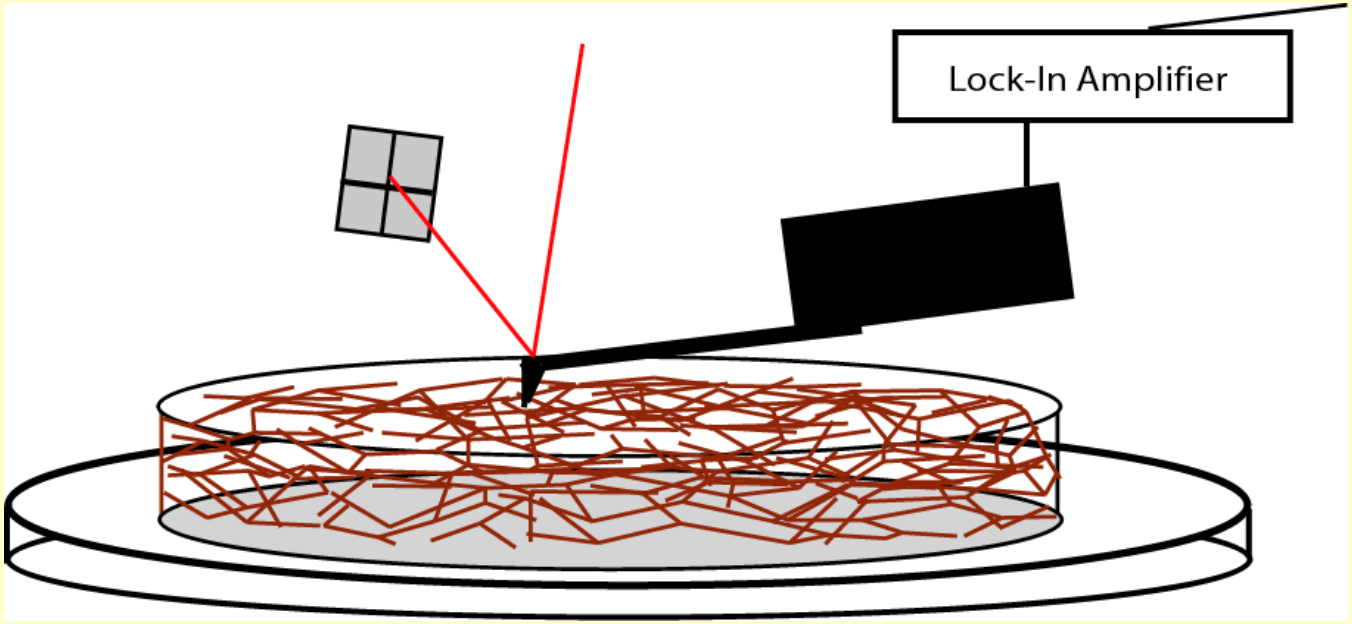
- As the atoms on the AFM tip and the atoms on the sample approach each other, the cantilever beam bends.
- Using a laser aimed at the head of the cantilever beam, the amount of bending can be determined.

Different AFM Modes



- Contact AFM
  - Operates on atomic repulsion
- Non-Contact AFM
  - Operates on atomic attraction
- Electrostatic AFM
  - Operates where atomic interactions are at a minimum but electrostatic forces still exist

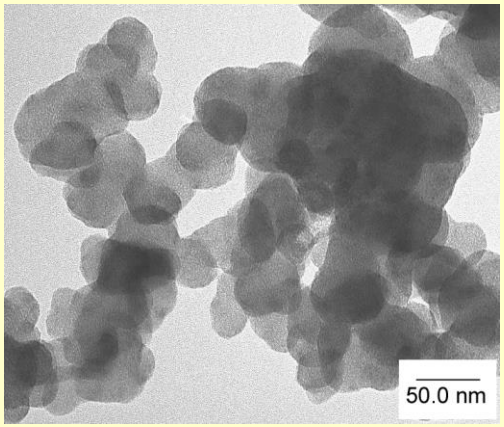
Electrostatic Force Microscopy



- The electrostatic forces of the sample affect the vibration of the EFM tip.
- The signal shows the conductive nature of different regions of the sample at the surface of the material.

Goal of Using EFM

- To determine the location of carbon black in the samples.
- Carbon black regions of the samples should show a larger signal than the surrounding polymer matrix.



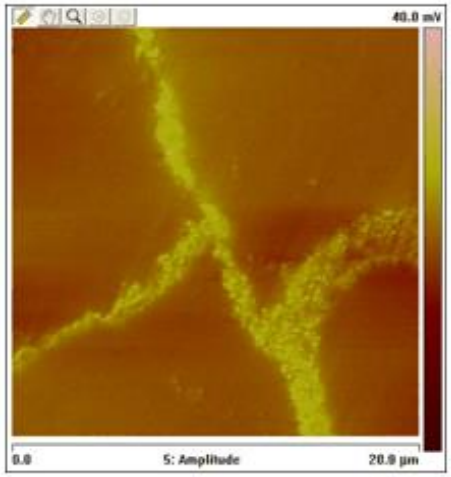
TEM image of highly aggregated CB powder

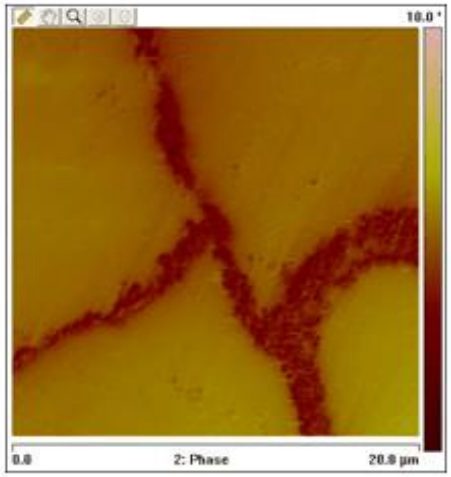
EFM Operating Parameters

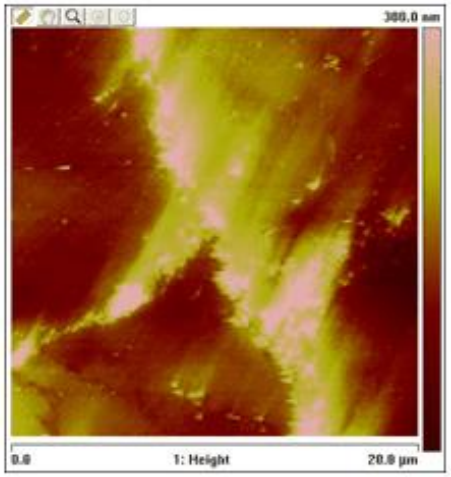
- Instrument – Veeco Dimension V AFM
- Mode - EFM
- Cantilever Tip – NSC35 Cr-Au tip
- Tip Bias - 7 volts
- Frequency – 336 kHz

Segregated Network EFM Images

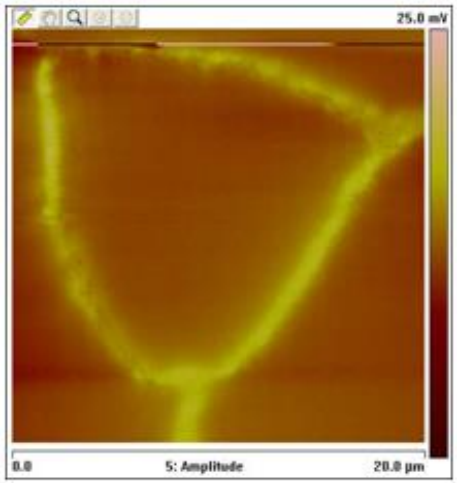
3.17 vol% Carbon Black Sample

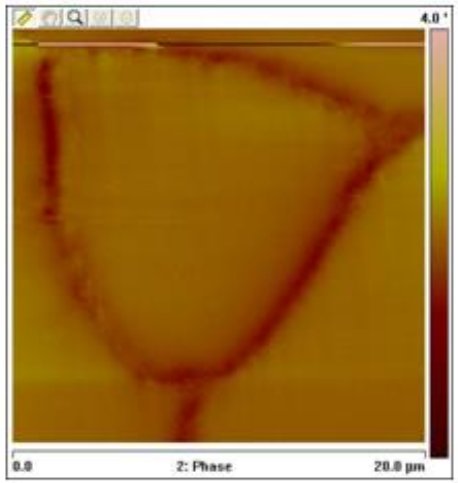


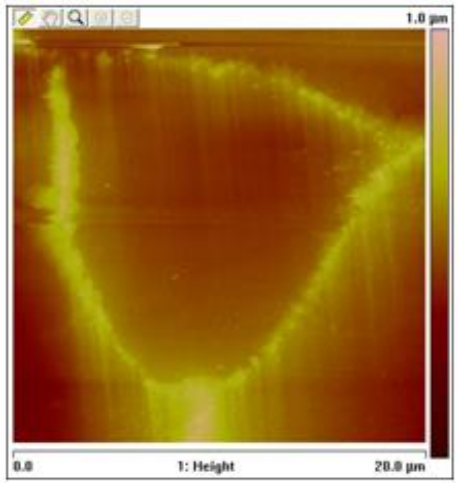




EFM Amplitude EFM Phase Topography





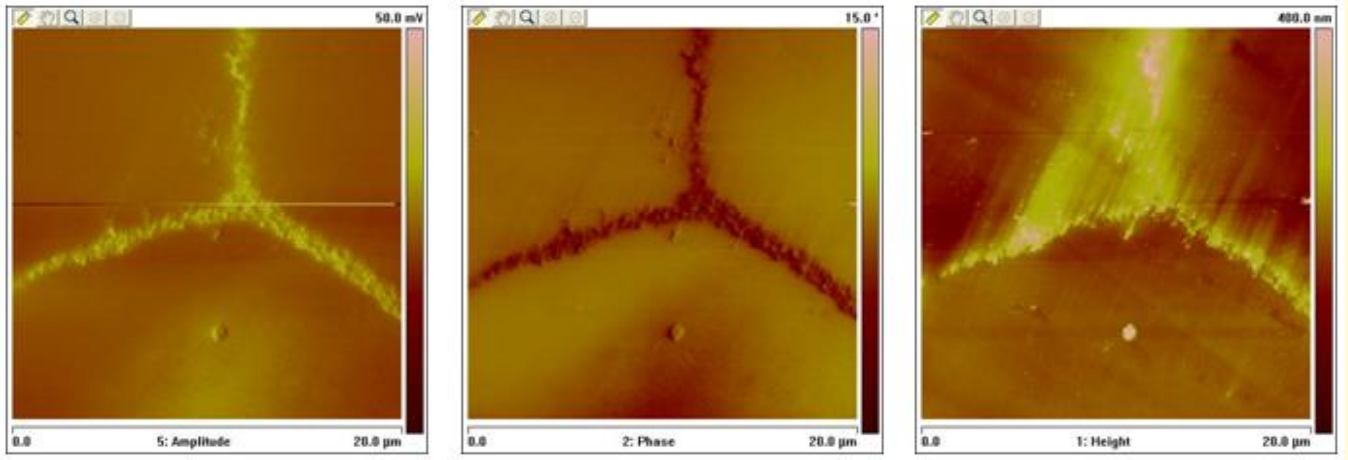


1.93 vol% Carbon Black Sample

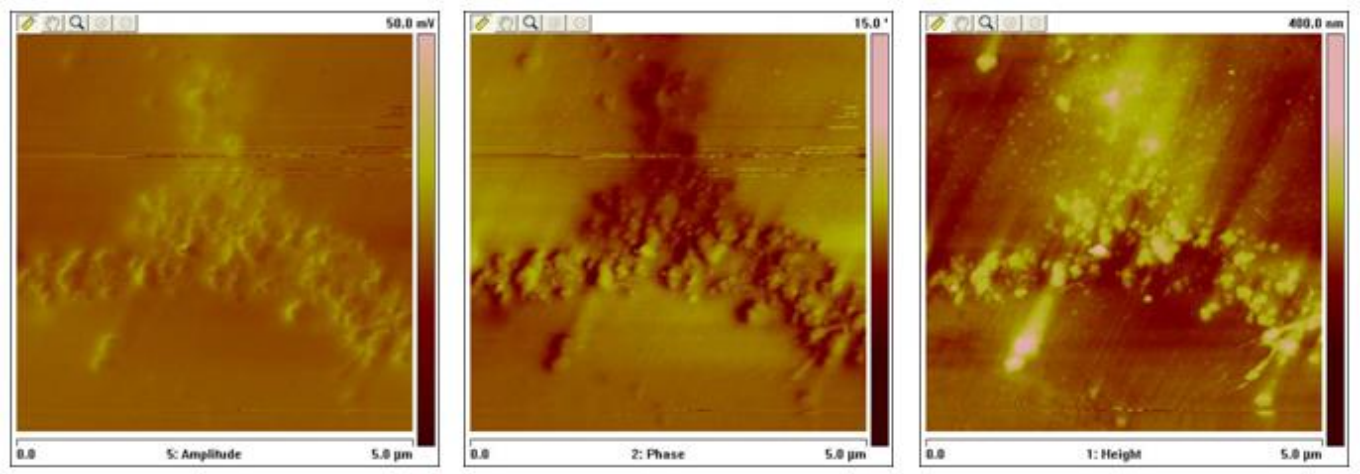
Segregated Network EFM Images (2)

20 X 20 Micron Images

3.17 Vol% CB Samples



EFM Amplitude EFM Phase Topography

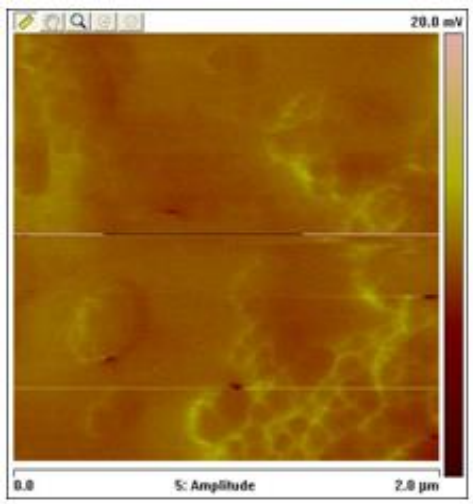


5X5 Micron Images

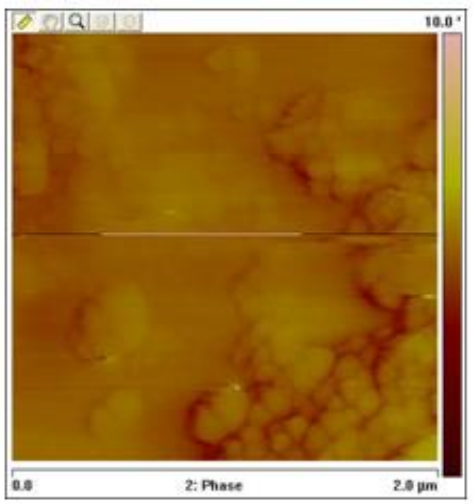
Solution Method EFM Images

4.09 vol% Carbon Black Sample

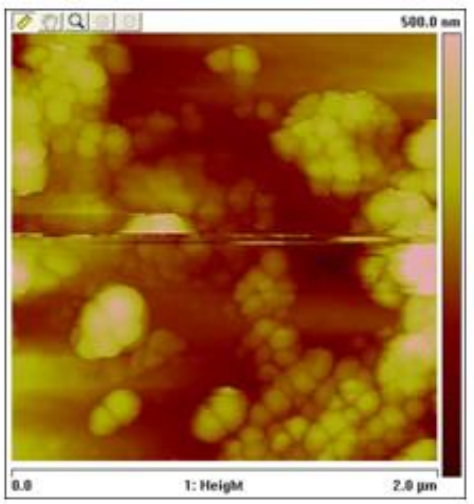
2 X 2 Micron Images



EFM Amplitude

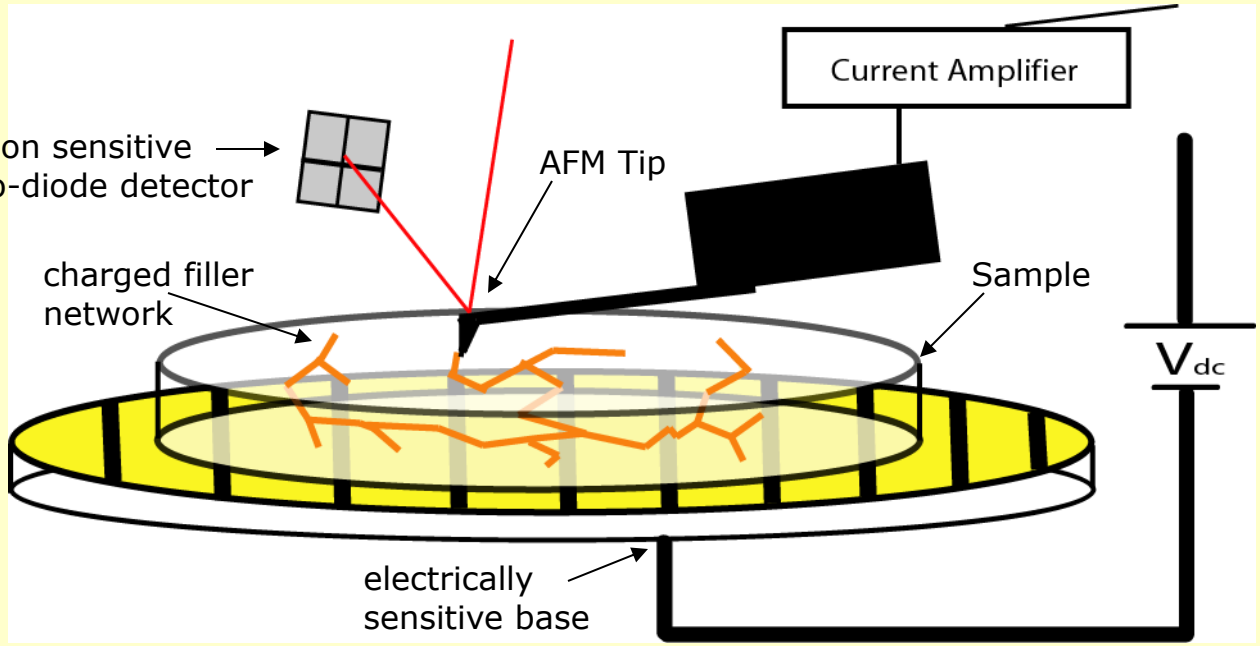


EFM Phase



Topography

Conductive AFM



- In C-AFM, a dc bias is applied to either the base of the sample or the AFM tip and any current that is passed through the sample is measured on the other side.
- TUNA operates like a C-AFM, but is more sensitive. Allowing for detection of currents less than 1 picoamp.

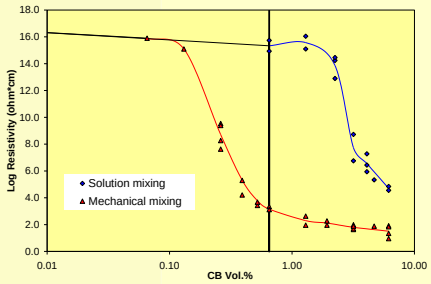
Goal of Using TUNA

- To determine the carbon black on the surface of the sample that is part of a percolated network
- The carbon black that is conducting current will show a higher electrical signal than regions of polymer matrix or carbon black that is not part of a percolated network

TUNA Operating Parameters

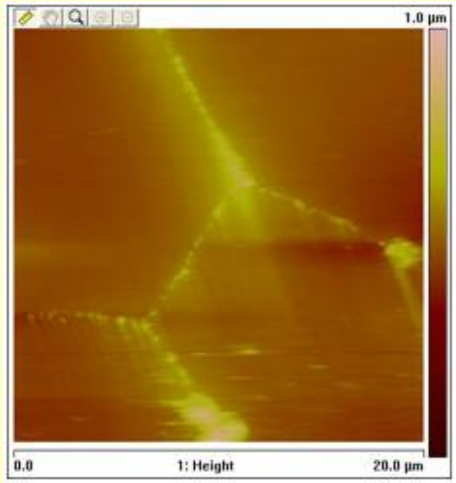
- Instrument – Veeco Dimension V AFM
- Mode – TUNA
- Cantilever Tip – CSC36 Cr-Au tip
- Applied Voltage – 2 V

Segregated Network TUNA Images

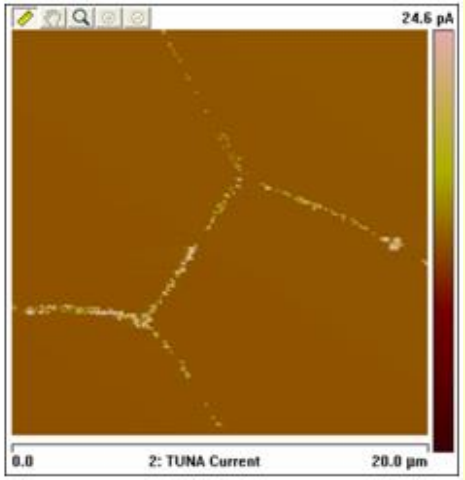


0.65 vol%
Carbon Black

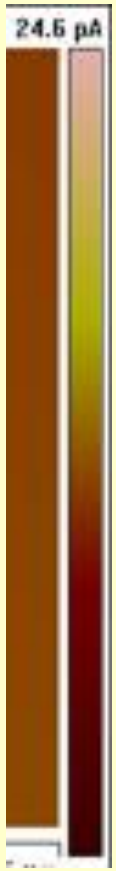
20 X 20 Micron Scan

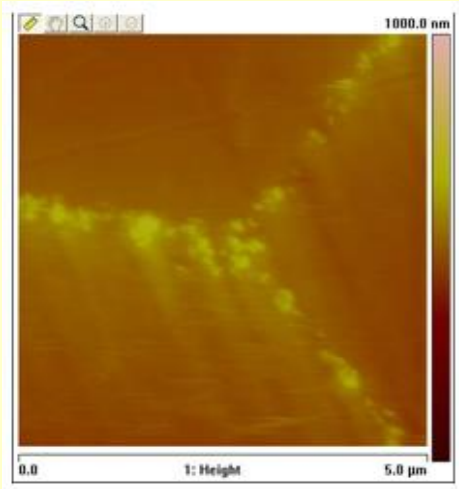


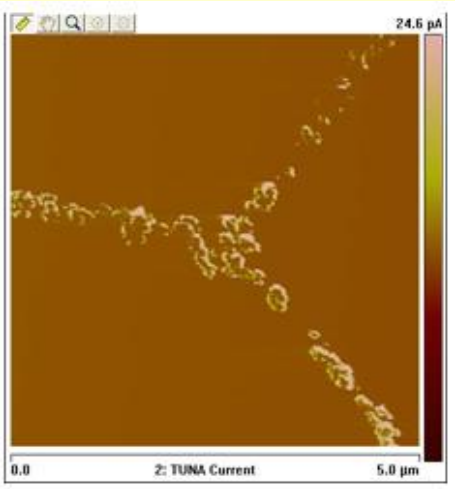
Topography



TUNA Image



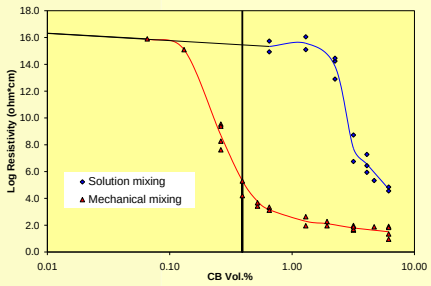




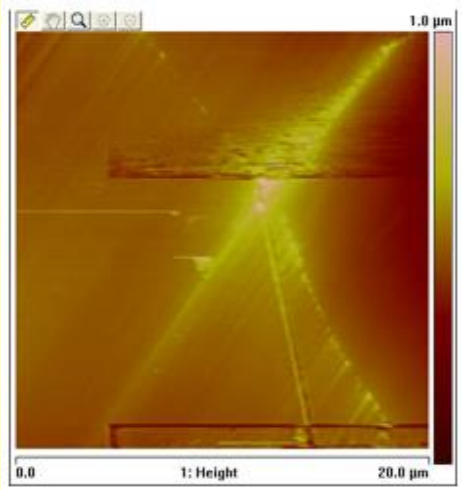
5 X 5 Micron Scan

Segregated Network TUNA Images (2)

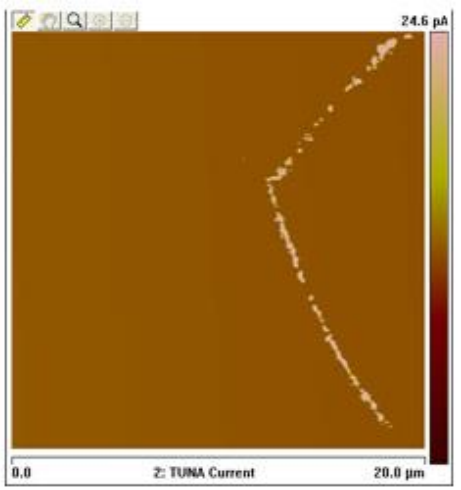
20 X 20 Micron Scan



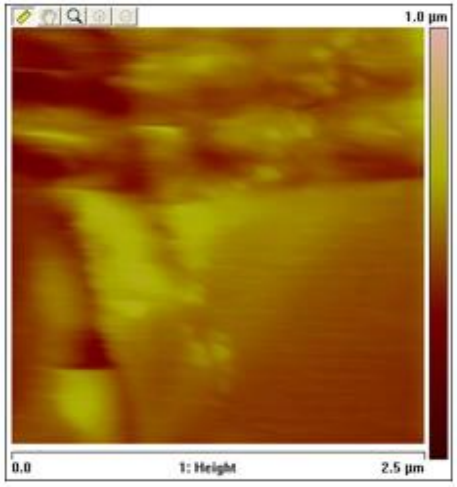
0.39 vol%
Carbon Black

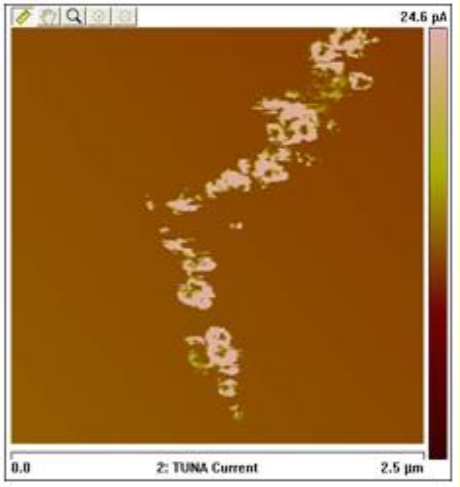


Topography



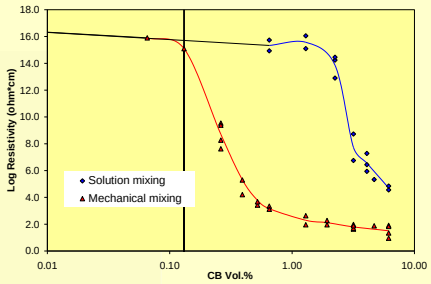
TUNA Image





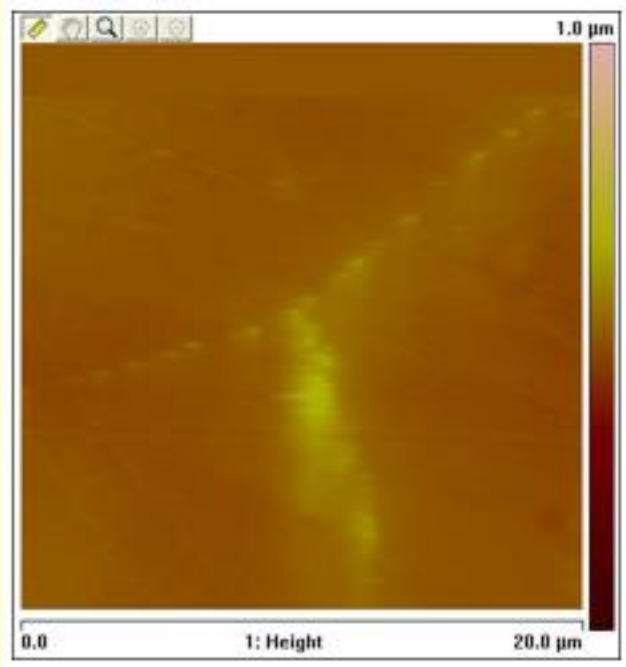
5 X 5 Micron Scan

Segregated Network TUNA Images (3)

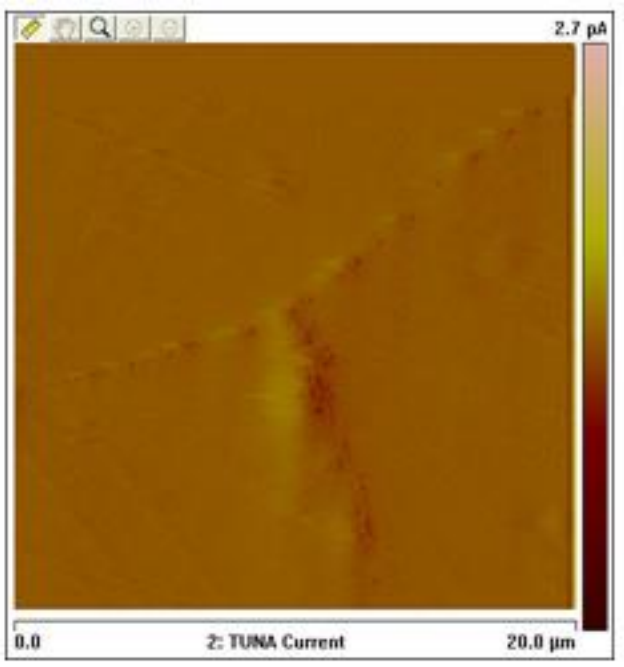


0.13 vol% Carbon Black

20 X 20 Micron Scan

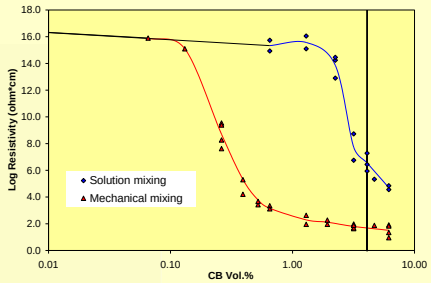


Topography



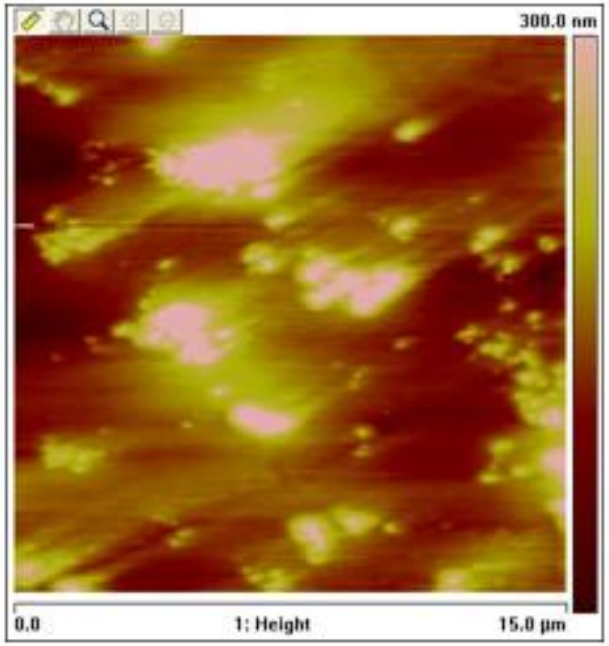
TUNA Image

Solution Method TUNA Images

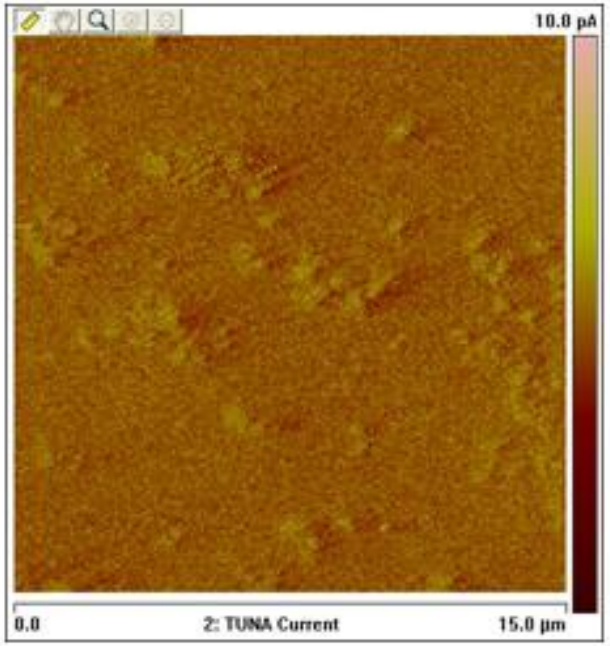


4.09 vol% Carbon Black

15 X 15 Micron Scan



Topography



TUNA Image

Summary

- EFM effectively detected the presence of the carbon black at the boundaries of polymer grains in the mechanically mixed samples.
- EFM also showed the random distribution in the solution mixed samples.
- TUNA images detected carbon black that was part of a percolated network.
- EFM and TUNA imaging allowed for confirmation of the microstructures of the mechanical mixed and solution mixed samples.

Acknowledgments