BIO-BASED NANOCOMPOSITES: CHALLENGES AND OPPORTUNITIES

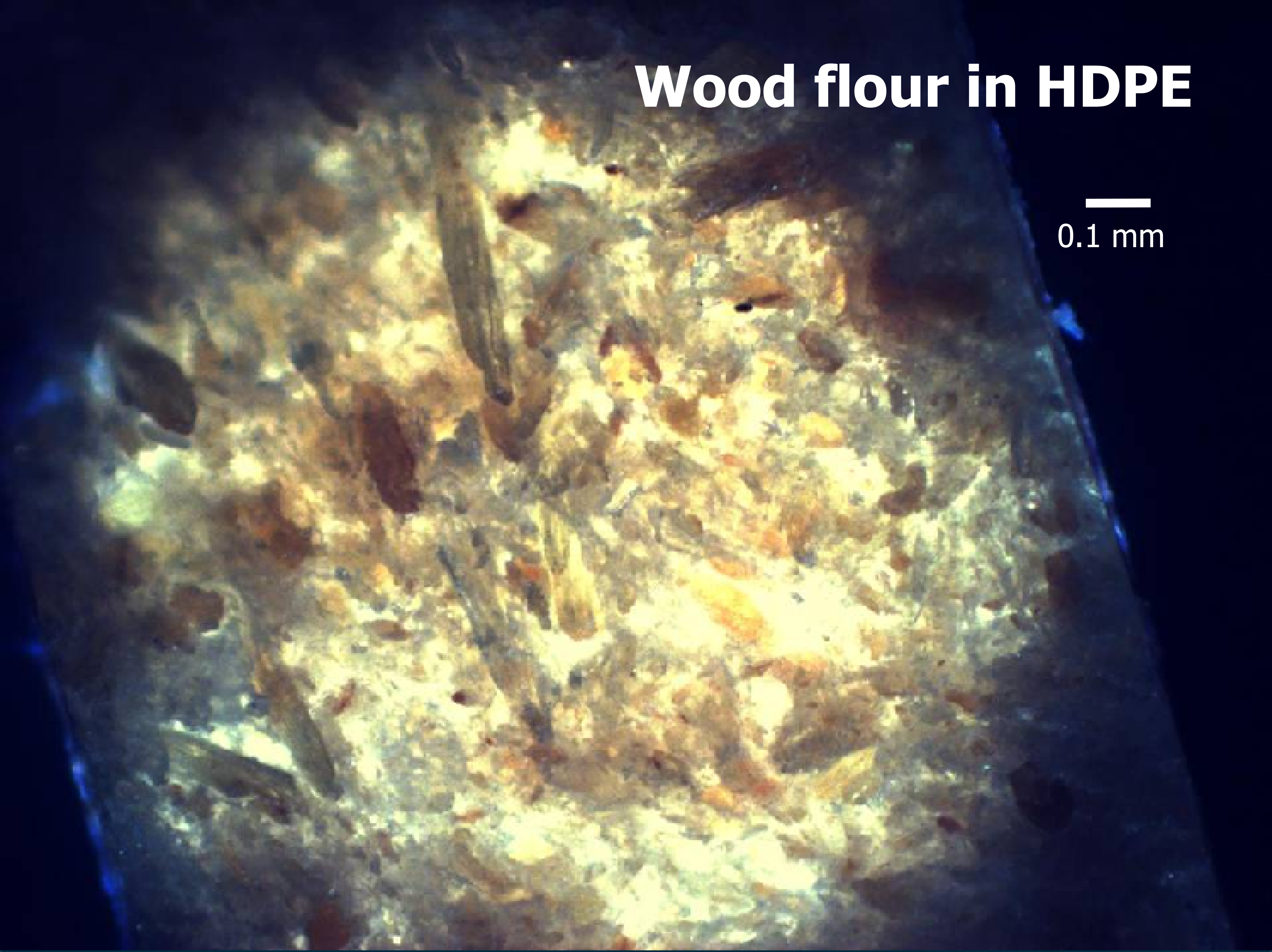
John Simonsen
Department of Wood Science & Engineering
Oregon State University

Outline

- What is the difference between composites and nanocomposites?
- Nanocrystalline cellulose (NCC, CNXL)
- Experimental results
  - Polyhydroxyoctanoate
  - PVOH
  - PUR
  - Polysulfone (PSf)
  - CMC
- Challenges and opportunities
- Acknowledgements

Polymer Composites

- Generally consists of a polymer “matrix” and a particulate “filler”
- Filler (dispersed phase) is dispersed in matrix (continuous phase)
- Can also have continuous filler (graphite fiber pultrusion, used for aerospace, etc.), but not yet used in nanocomposites


Wood flour in HDPE
0.1 mm

Synergism in Polymer Composites

- **Function of matrix:**
  - **Disperse fibers**
  - **Transfer load to filler**
  - **Load sharing between broken and intact filler particles**
  - **Increases toughness**
- **Function of filler**
  - **Carry load, increase properties**
  - **Lower cost**

What makes a nanocomposite different?

Reduced impurities

- As the size of a particle is reduced, the number of defects per particle is also reduced
- Mechanical properties rise proportionately

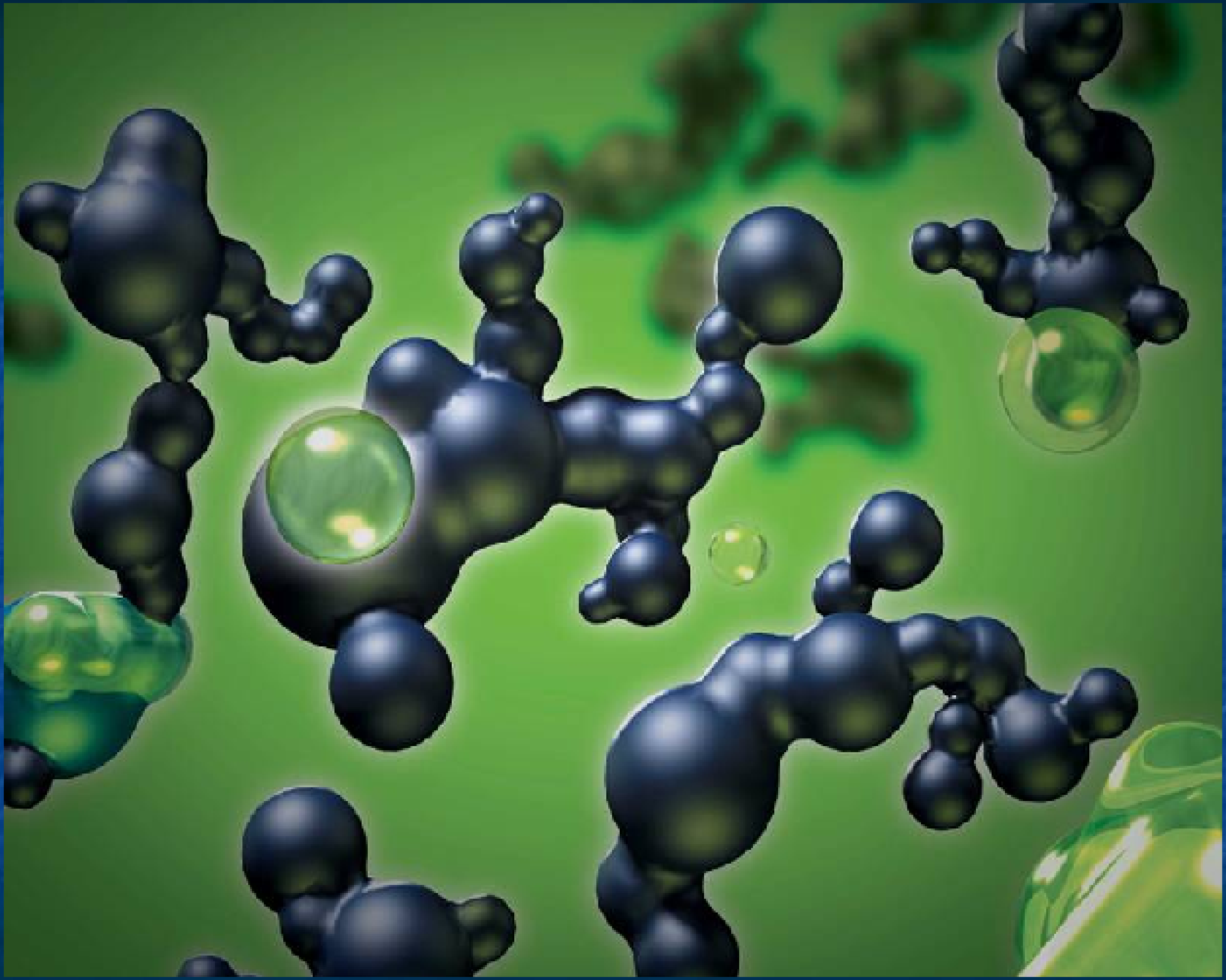
Properties of fibers and nanoparticles

material	Density, g/cm^3 ρ	Theoretical strength, GPa	Whisker strength (S), GPa	Bulk strength, GPa	Specific whisker strength S/ρ
iron	7.68	20	13	4.1	1.68
Carbon (graphite)	1.38	98	21	1.7	12.4

An historical nano-example:

Carbon black

http://www.degussa.com/downloads/en/pictures/product_stories/
2004_06_15_carbon_black.Par.0006.posterImage.jpg



http://www.degussa.com/downloads/en/pictures/product_stories/
2004_06_15_carbon_black.Par.0006.posterImage.jpg

Addition of nano-sized carbon to rubber

- Particle size 10-75 nm
- Strength can increase 1000 X
- Stiffness increases 7 X (in accordance with modified Einstein equation)
- Abrasion resistance 4-5 X
- Without carbon black, tires would not be made from rubber!

Surface Area

	m^2/g
E-glass fibers*	**~1**
Paper fibers	**4**
Graphite	**25-300**
Fumed silica	**100-400**
Fully exfoliated clay	**~ 500**
Cellulose nanocrystals**	**250**
Carbon nanotubes***	**~ 100**

*http://www.jm.com/engineered_products/filtration/products/microfiber.pdf
** Winter, W. presentation at ACS meeting, San Diego, March 2005
***http://www.ipme.ru/e-journals/RAMS/no_5503/staszczuk/staszczuk.pdf.

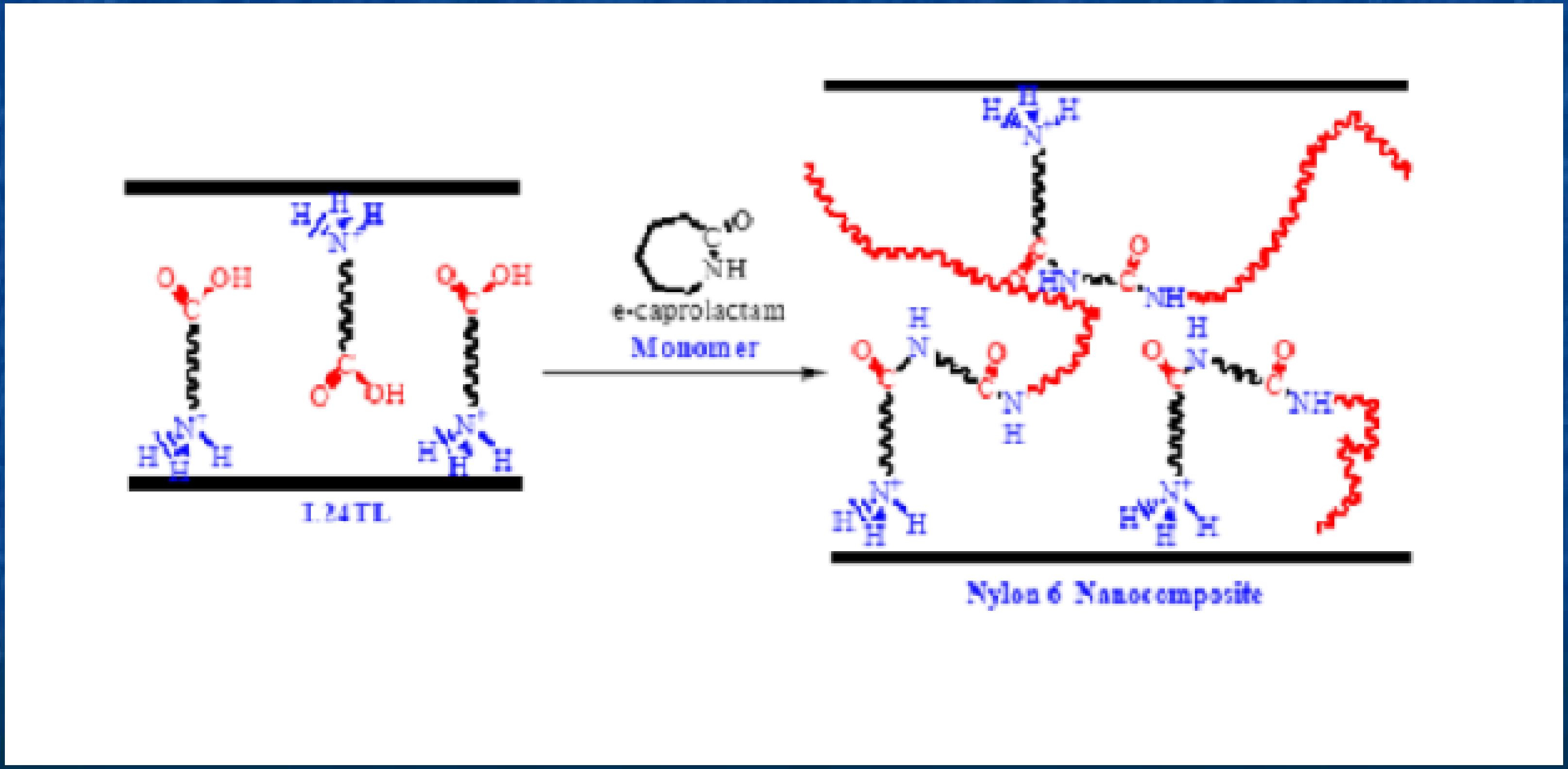
Polymer-clay nanocomposites

mechanical and barrier properties

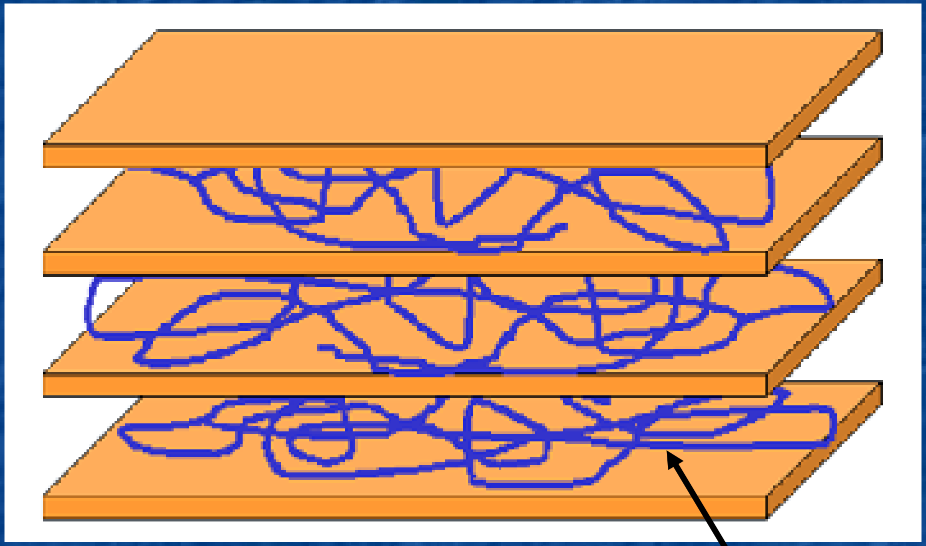
The step-assist on the 2002 GMC Safari (shown) and Chevrolet Astro vans is the automotive industry's first exterior applications for thermoplastic polyolefin-based nanocomposites. The part won General Motors the 2001 Grand Award for plastics innovation from the SPE's Automotive Division. (Photo courtesy of Wieck Photo Database).

http://www.specialchem4polymers.com/resources/articles/article.aspx?id=579

Nano-PA6
Using Nanomer 1.24 TL - *In Situ Polymerization*



Aspect ratio > 100



intercalation

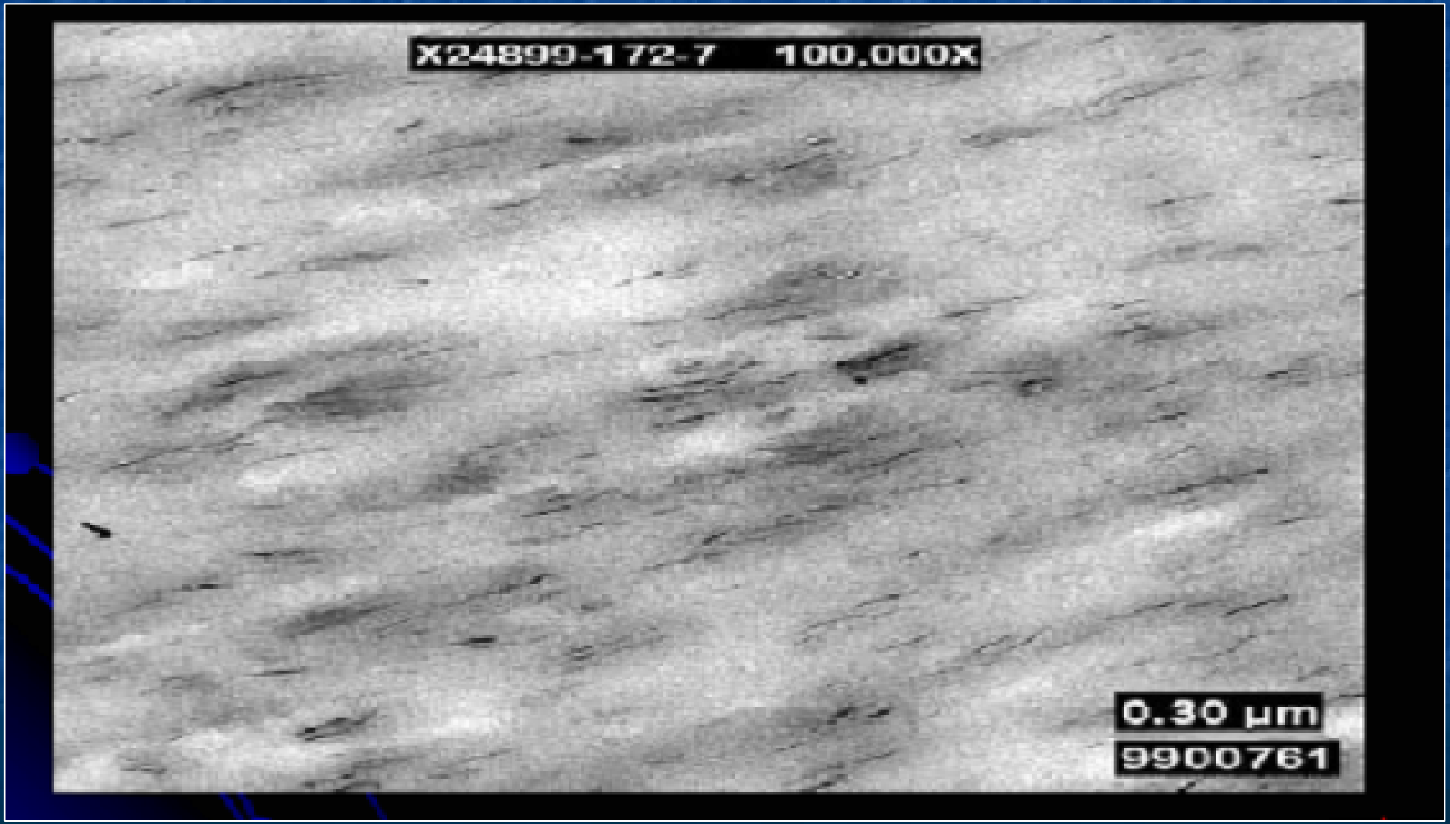
exfoliation

Confined polymer

U. Southern Miss. Macrogalleria http://www.psrc.usm.edu/macrog/mpm/composit/nano/struct2_1.htm

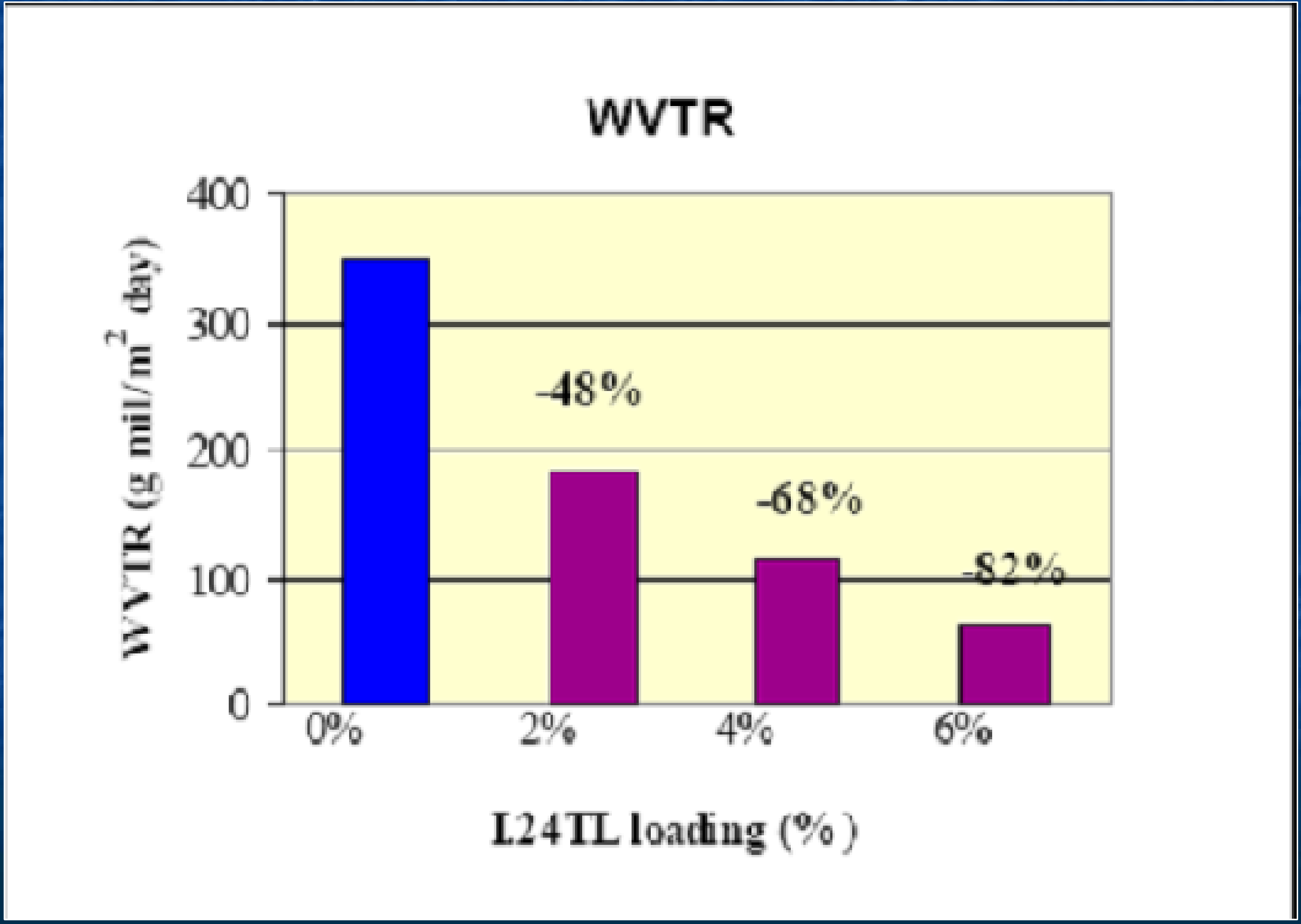
Barrier Platform

Mitsubishi gas chemical and Nanocor Alliance Imperm®
Nano-Nylon MXD6

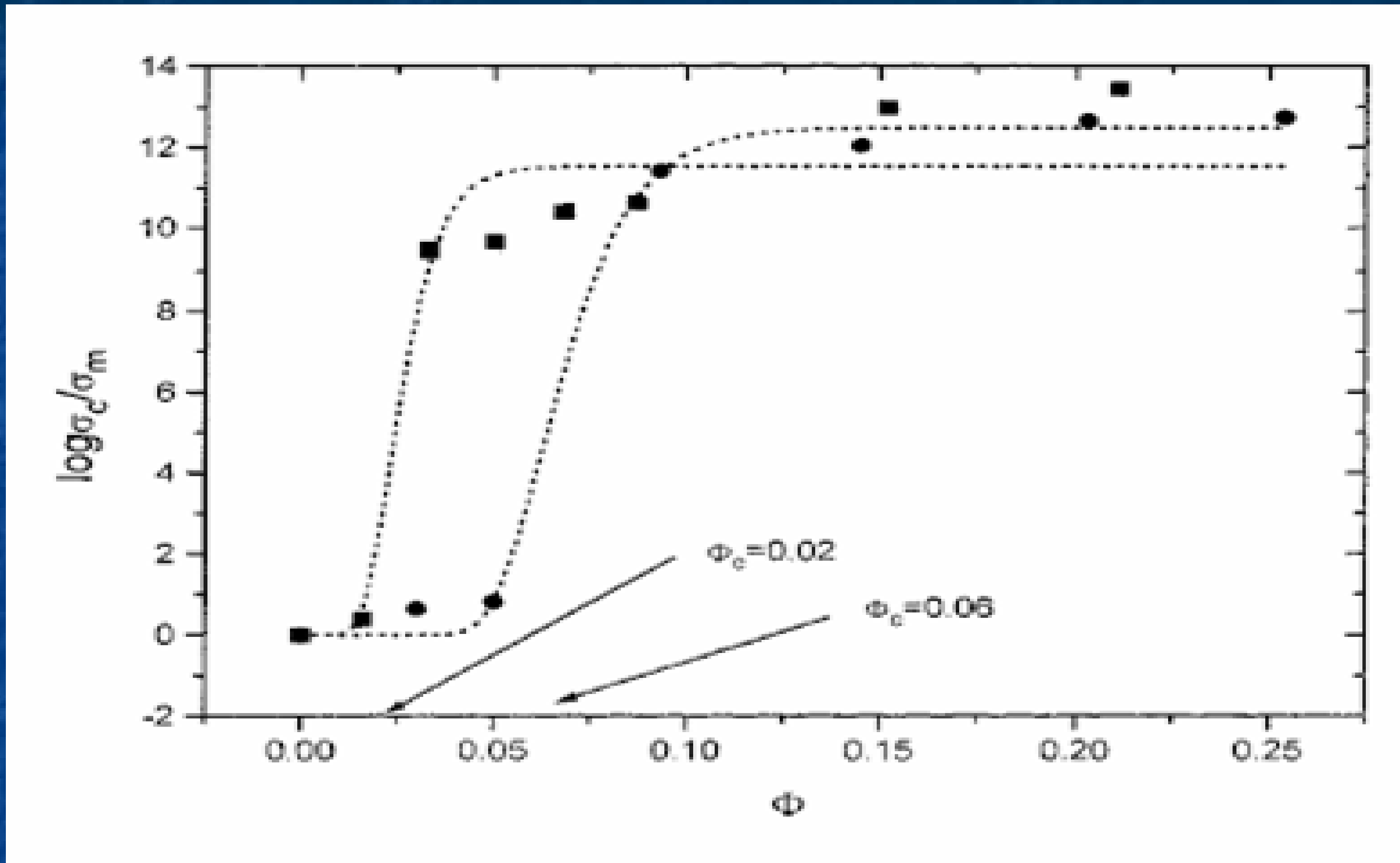


Barrier Film for packaging

Nano-PA6 using Nanomer 1.24 TL - *In situ polymerization*



Percolation



Relative electrical conductivity ($□_c$/$□_m$) of the carbon black filled LDPE (circles) or HDPE (squares) as a function of the filler content (N).

I. Chodak, I Krupa. J. Mat. Sci. Lttrs. 1999 18:1457-1459

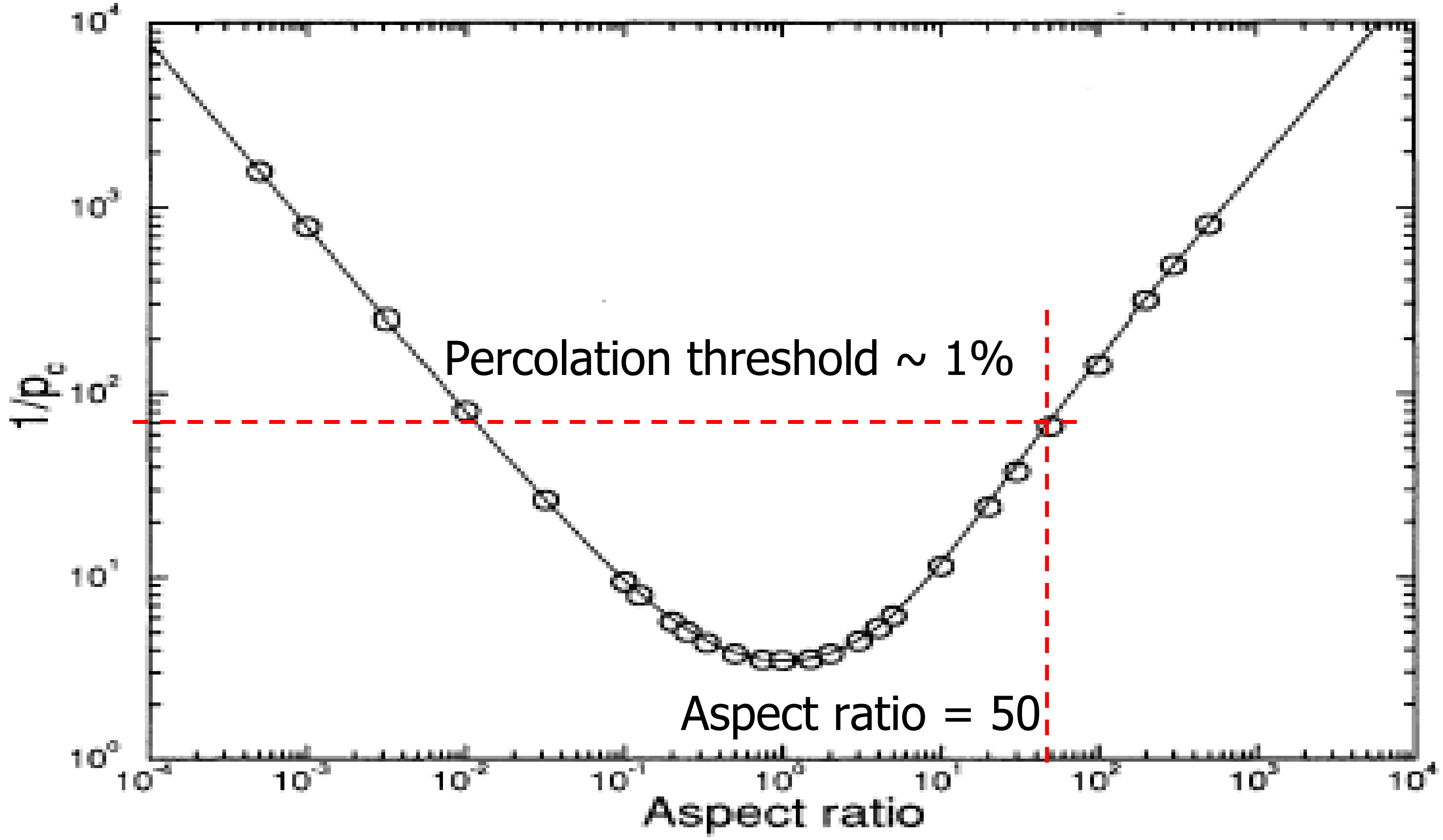


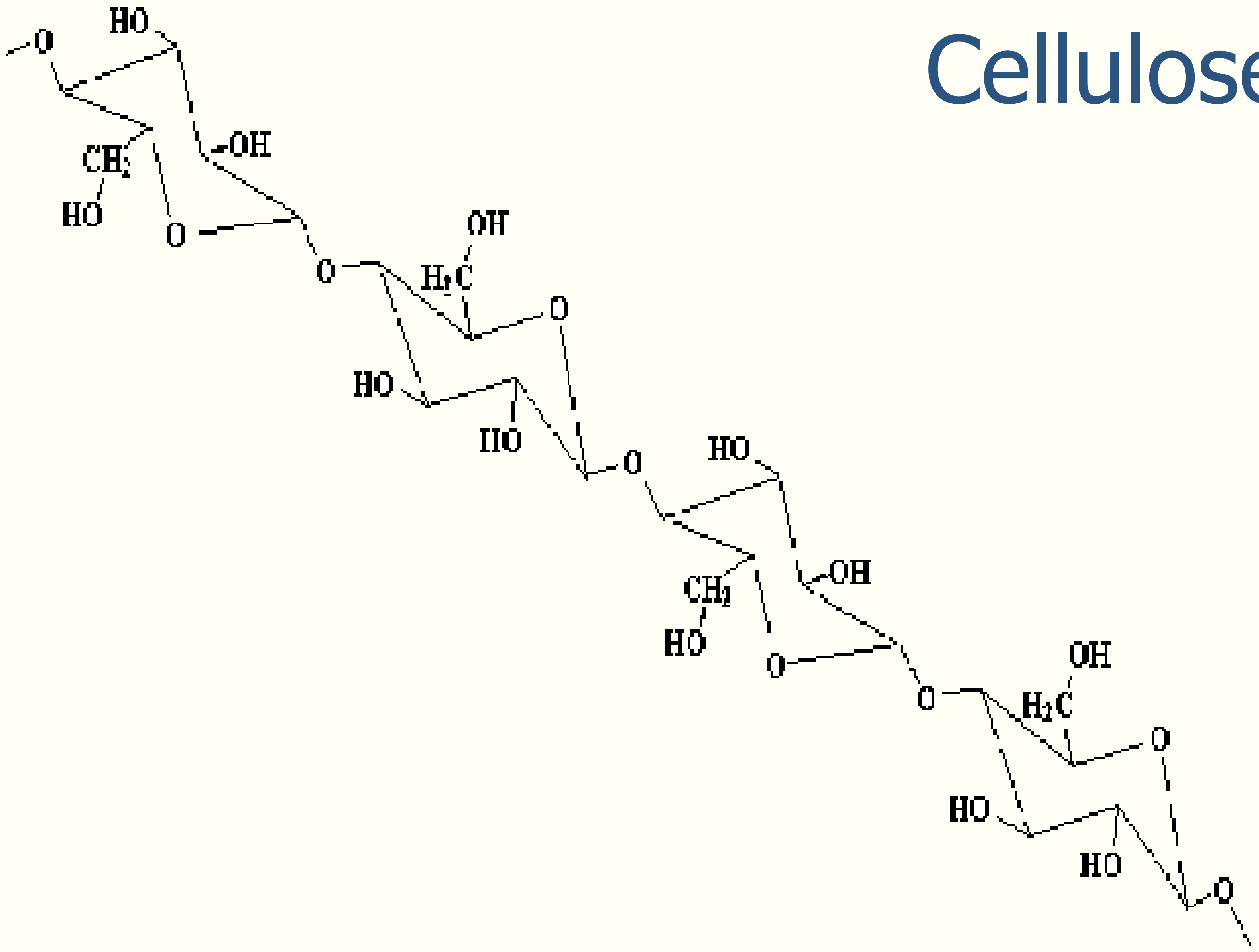
FIG. 3. Inverse of the critical volume fraction for percolation ($1/p_c$) plotted vs aspect ratio of ellipsoids of revolution. The solid line is a Padé-type approximant described in the text. It is fit to both asymptotic limits, the value of $1/p_c$ for the sphere, and is forced to have zero slope at $a/b=1$.

Garboczi, et. al. Phys. Rev. Ltrs. E, 1995, 52(1): 819-828

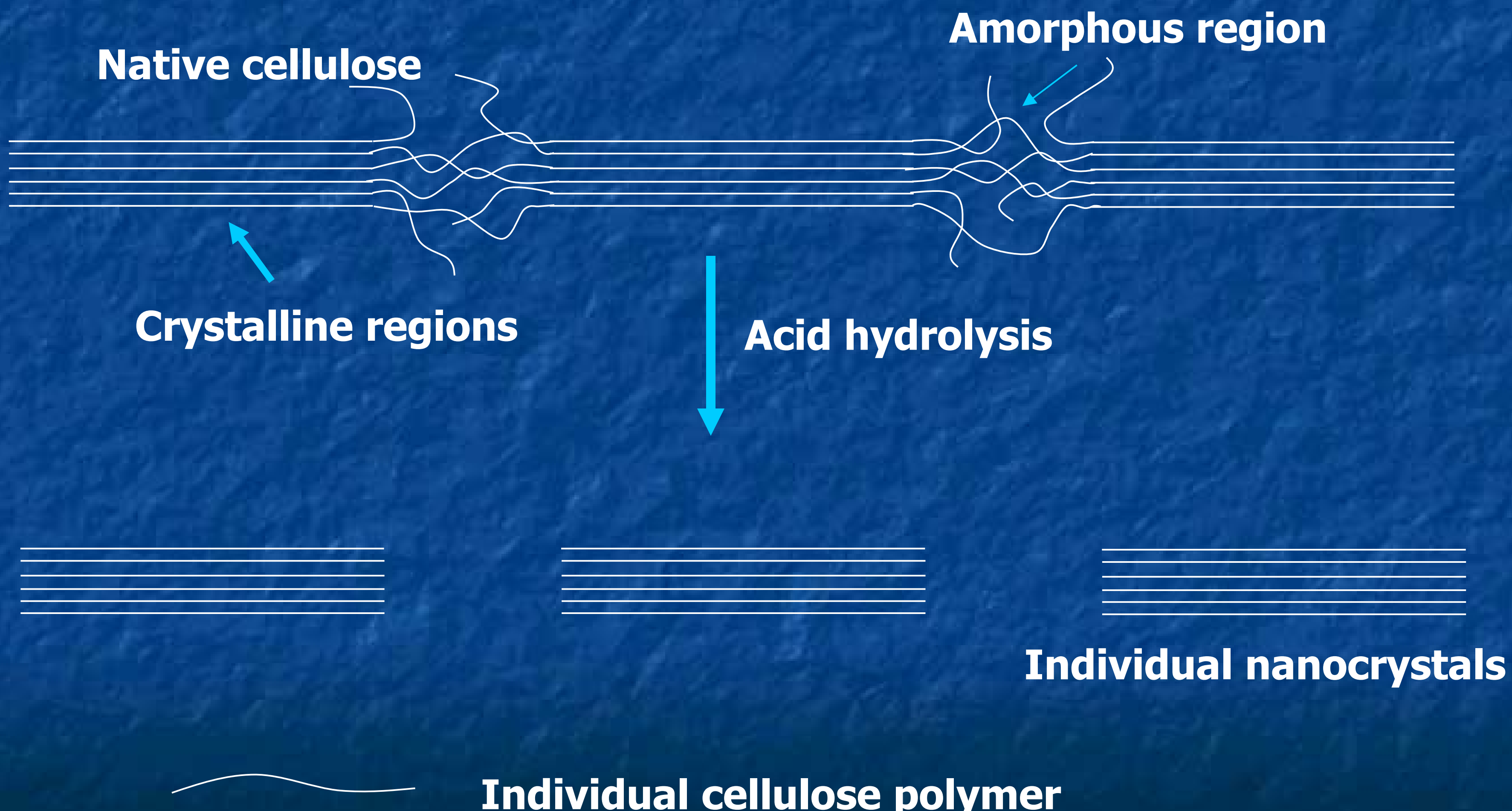
Nanocomposite Concepts

- **Reduced defects**
- **Surface area**
- **Percolation**
- **Interphase volume**
  - **Polymer morphology**

Cellulose



Cellulose Nanocrystal (CNXL) Production



Sources of nanocrystalline cellulose

- Microcrystalline cellulose (wood)
- Bacteria (Nata de coco)
- Cotton
- Ag wastes
- Tunicates

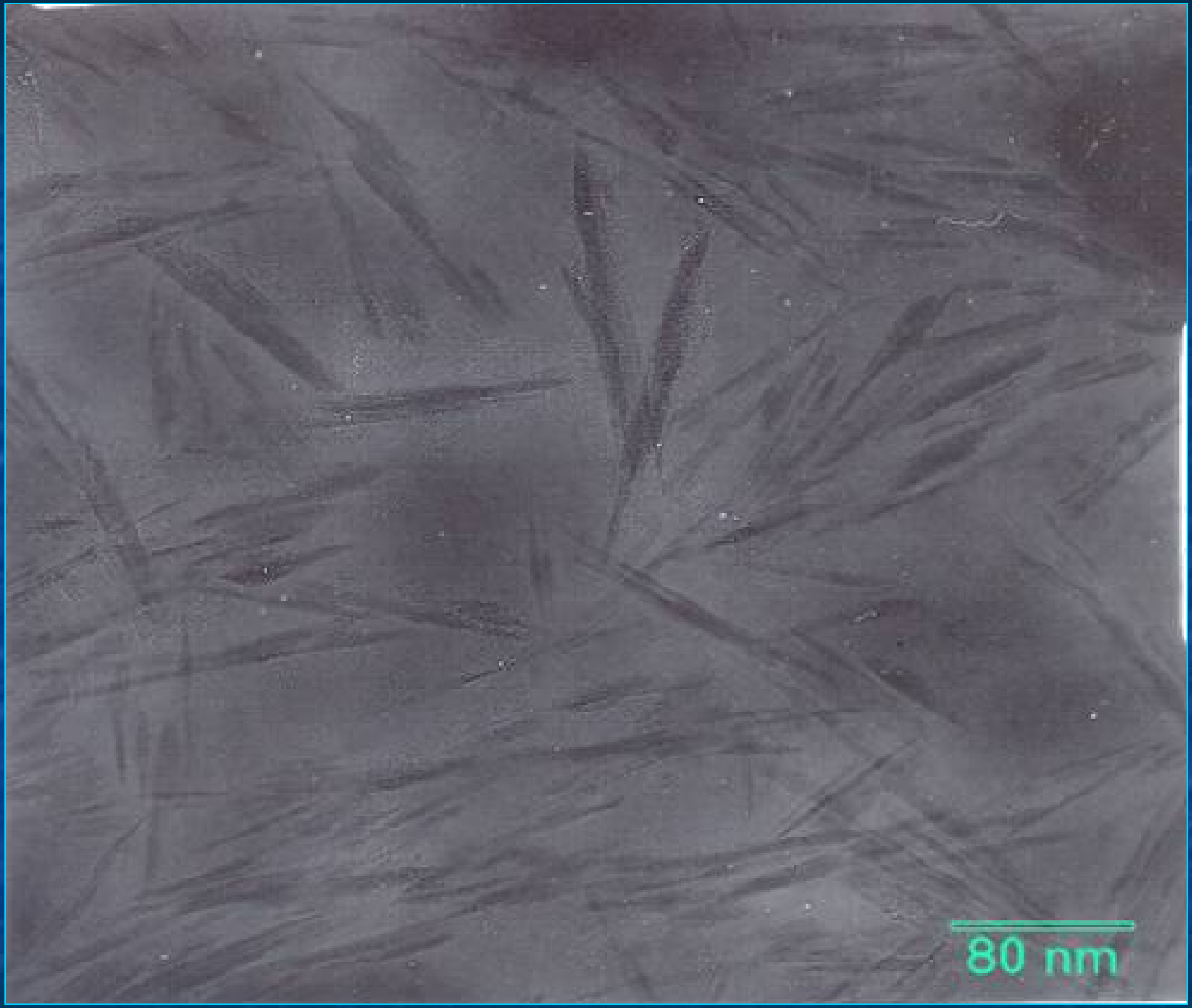
Cellulose nanocrystals

Cellulose source	Length	Cross section	Aspect ratio
Tunicate	100 nm – microns	10-20 nm	5 to > 100 (high)
Algal (Valonia)	> 1000 nm	10 to 20 nm	50 to > 10 nm (high)
Bacterial	100 nm – microns	5-10 x 30-50 nm	2 to > 100 (medium)
Cotton	200-350 nm	5 nm	20 to 70 (low)
Wood	100 – 300 nm	3 – 5 nm	20 to 50 (low)

Beck-Candanedo, et. al. Biomacromol. (2005) 6:1048-1054

COST OF CELLULOSE NANOCRYSTALS

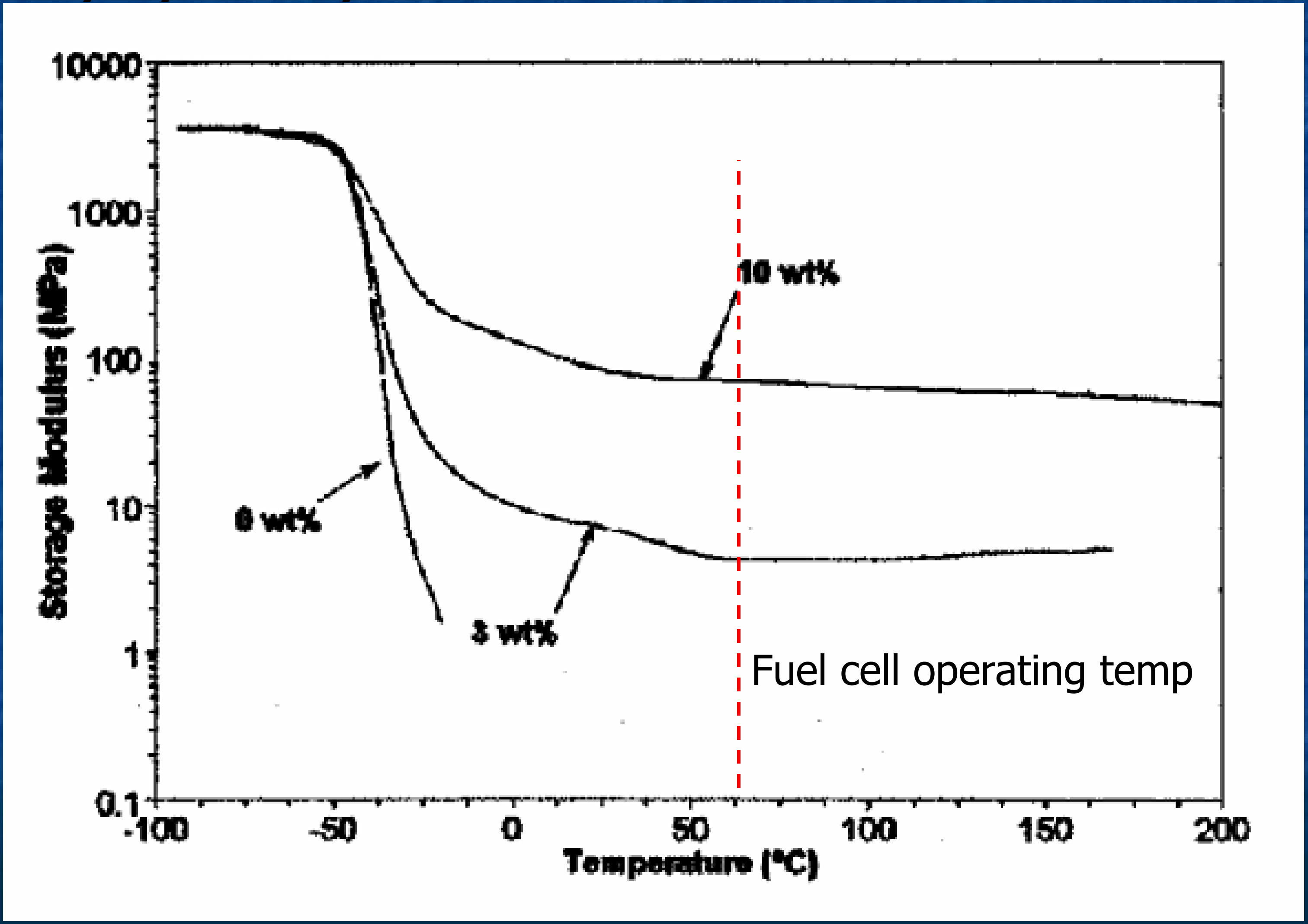
- Microcrystalline cellulose (MCC)
  - ~ $7/kg
  - HCl based process
- Nanocrystalline Cellulose (CNXL)
  - Target ~ $2/kg
  - H_2SO_4 based process
  - Do you need the purity of MCC starting material?
  - Can acid be recovered?
  - Uses for byproduct (sugar in acid)?



TEM image of cellulose nanocrystals

Polymer systems

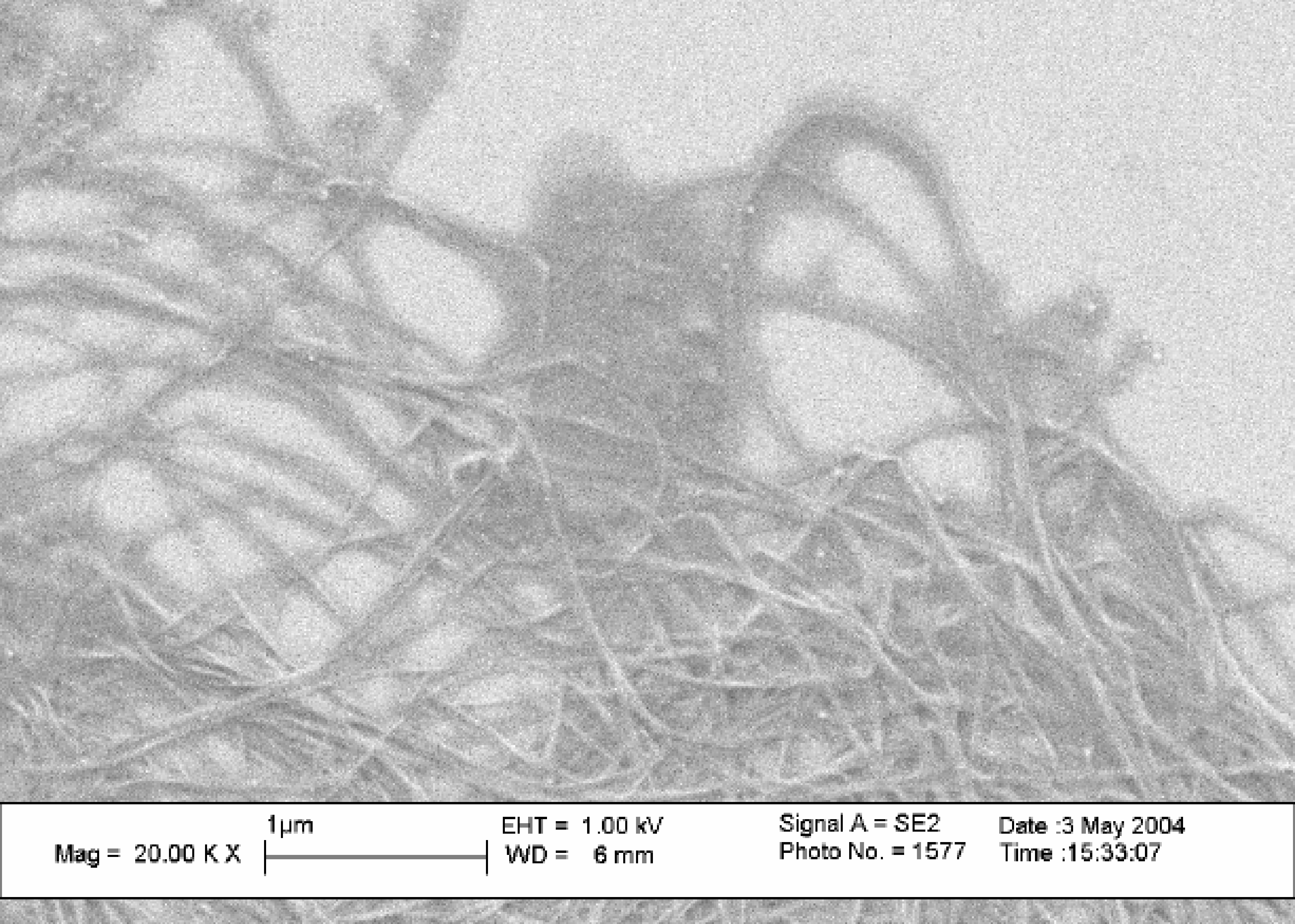
Battery Separator, CNXL in Polyhydroxyoctanoate



M. Samir, F. Alloin, J-Y Sanchez, A. Dufresne, 2004. Macromol. 37:4839-4844

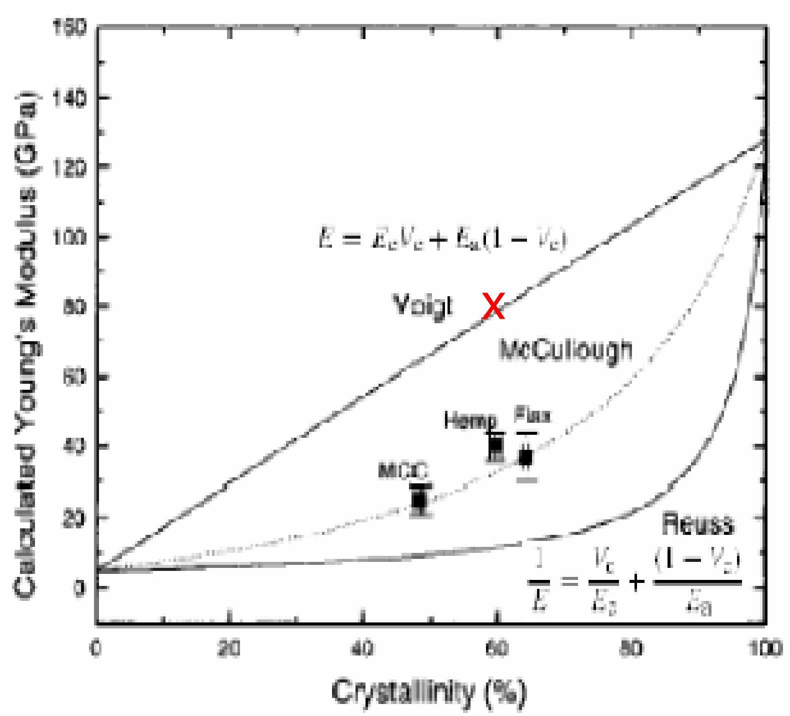
BACTERIAL CELLULOSE/ POLYVINYLALCOHOL

Slide from Wankei Wan, U. W. Ontario, London, ON, Canada



Bacterial cellulose has very high modulus

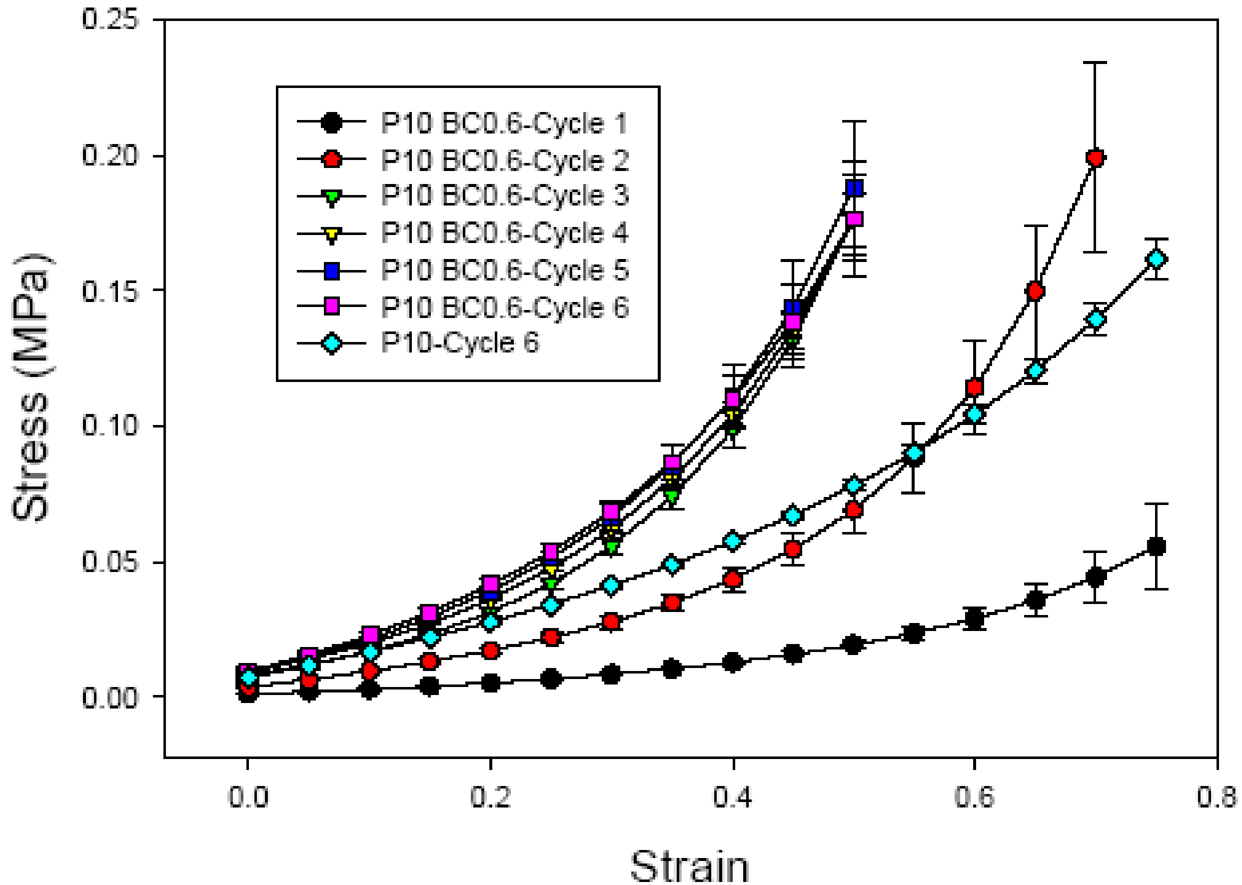
Fiber diameter: 27-88 nm
Crystallinity: 60%
Young's modulus: 78 ± 17 GPa



Eichhorn and Young, Cellulose 8:197 (2001)
Guhados et al., accepted Langmuir (2005)

Slide from Wankei Wan, U. W. Ontario, London, ON, Canada

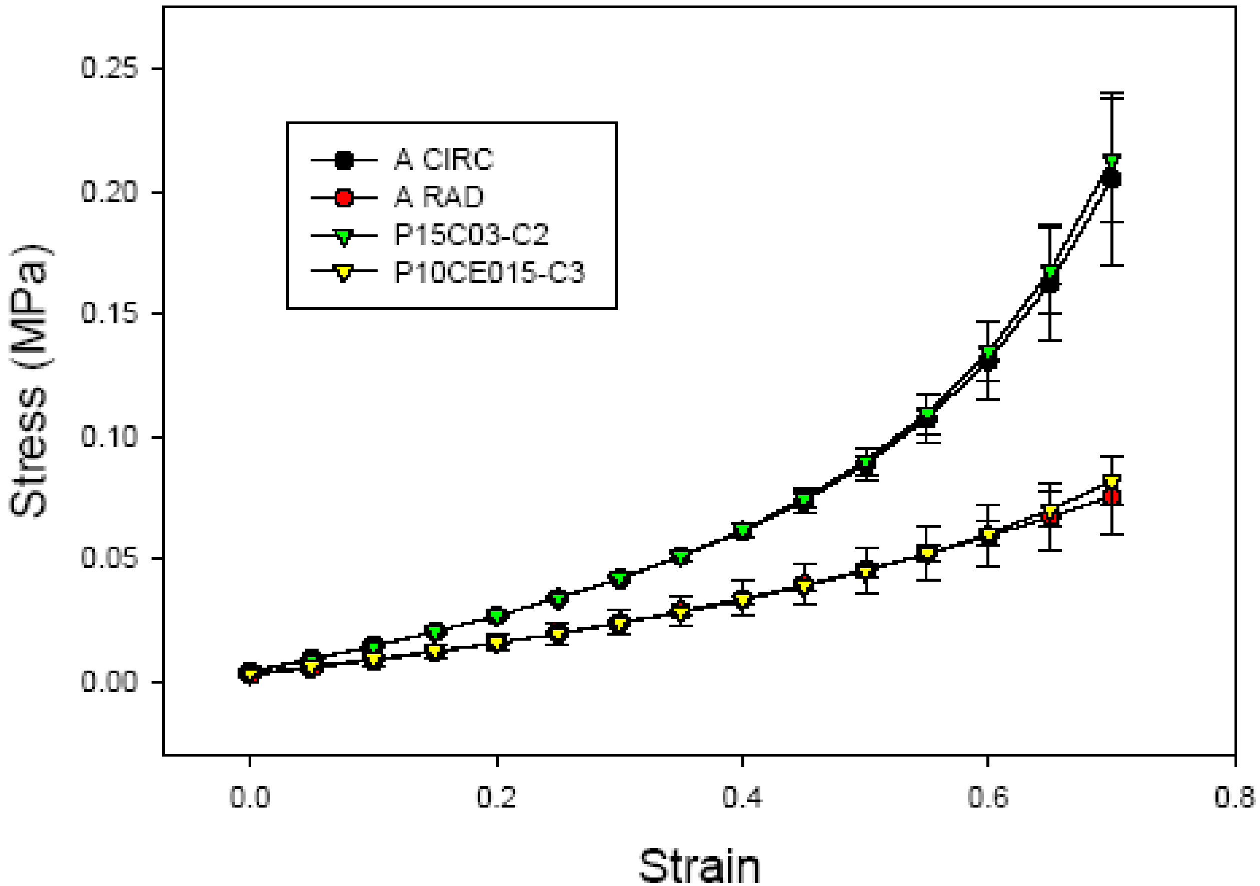
Bacterial cellulose – PVA nanocomposite



Millon et al, submitted to JBMR (B), (2005)

Slide from Wankei Wan, U. W. Ontario, London, ON, Canada

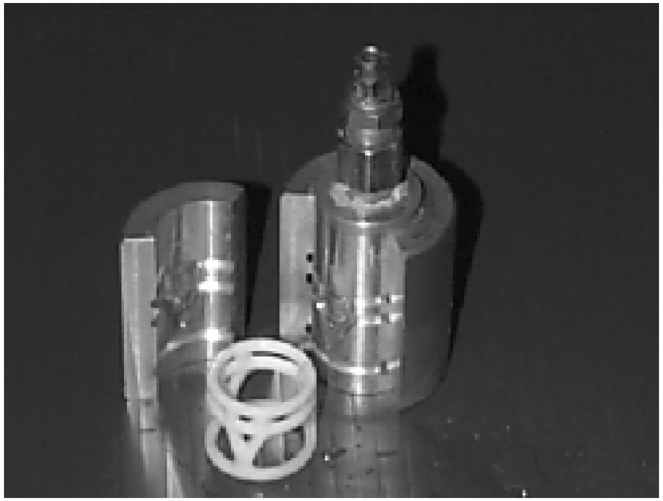
Aorta – tensile properties

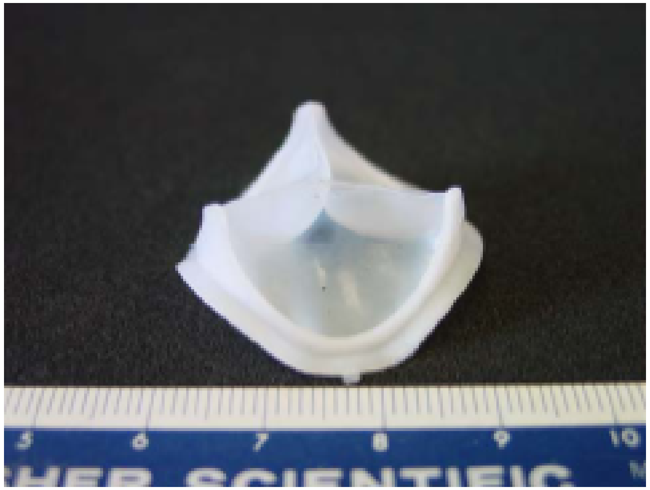


Millon et al, submitted to JBMR (B), (2005)

Slide from Wankei Wan, U. W. Ontario, London, ON, Canada

Some prototypes





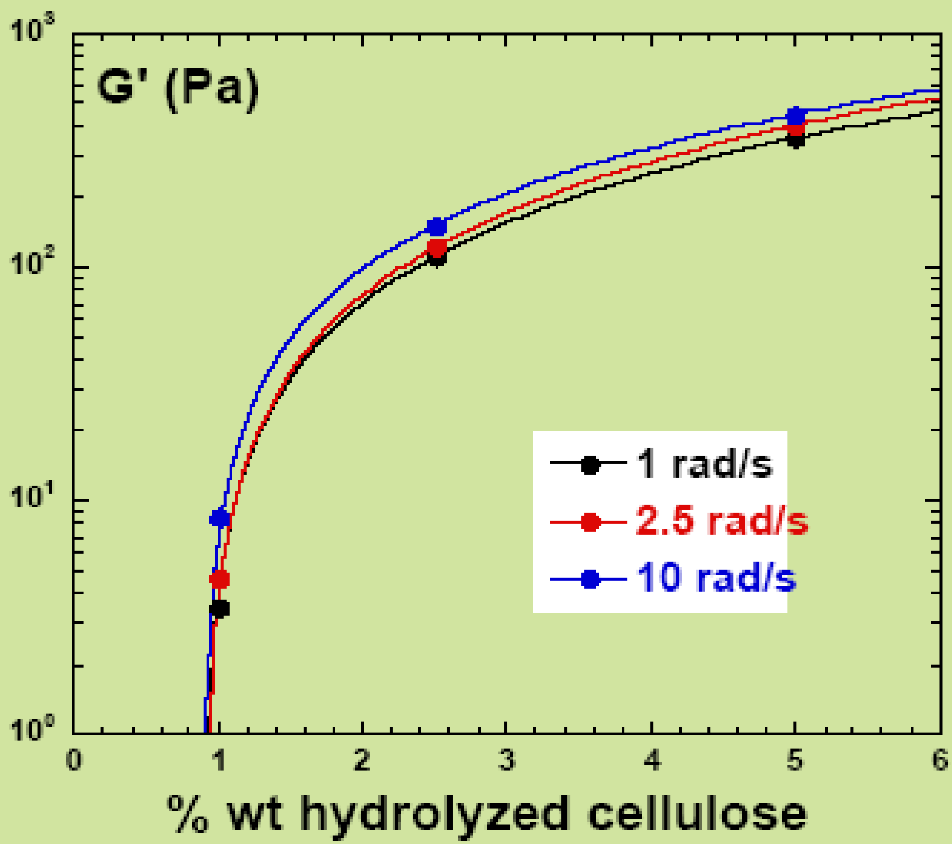
Wan et al, JBMR (B), (2001)
Med Eng Phys, (2004)

Slide from Wankei Wan, U. W. Ontario, London, ON, Canada

Cellulose nanocrystal-filled polyurethane

Composites: Unreacted Mixture

Rheology of the Hydrolyzed Crystals + Polyol Mixture + MDI



$$G' \propto (m - m_{cG'})^{\beta_{G'}}$$

Du et al. Macromol., 37, 9048 (2004)

Calculated parameters

$m_{cG'}$ ~ 0.88 wt%

$\beta_{G'}$ ~ 1.2

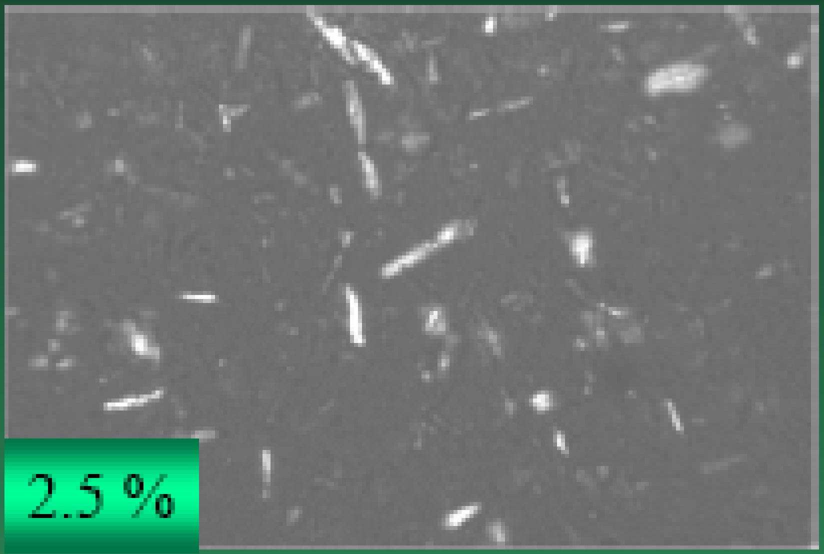
Theoretical Percolation Threshold

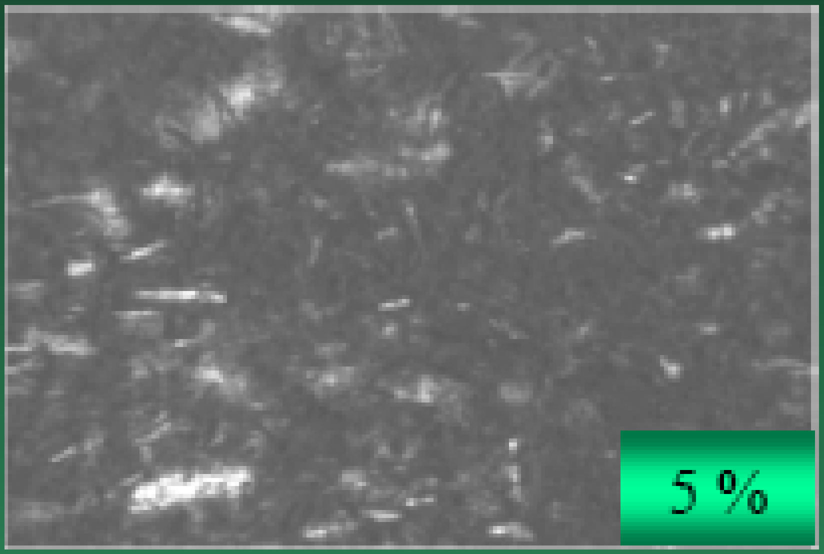
~ 1.07 wt%

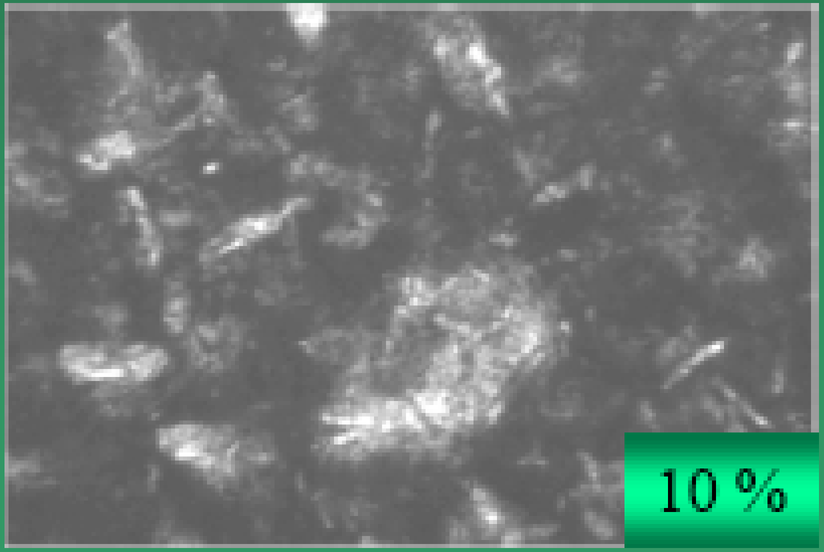
Garboczi et al. Physical Rev. Letters 52, 1995

Cellulose Crystals: Dispersion

Polarized Light (OM)





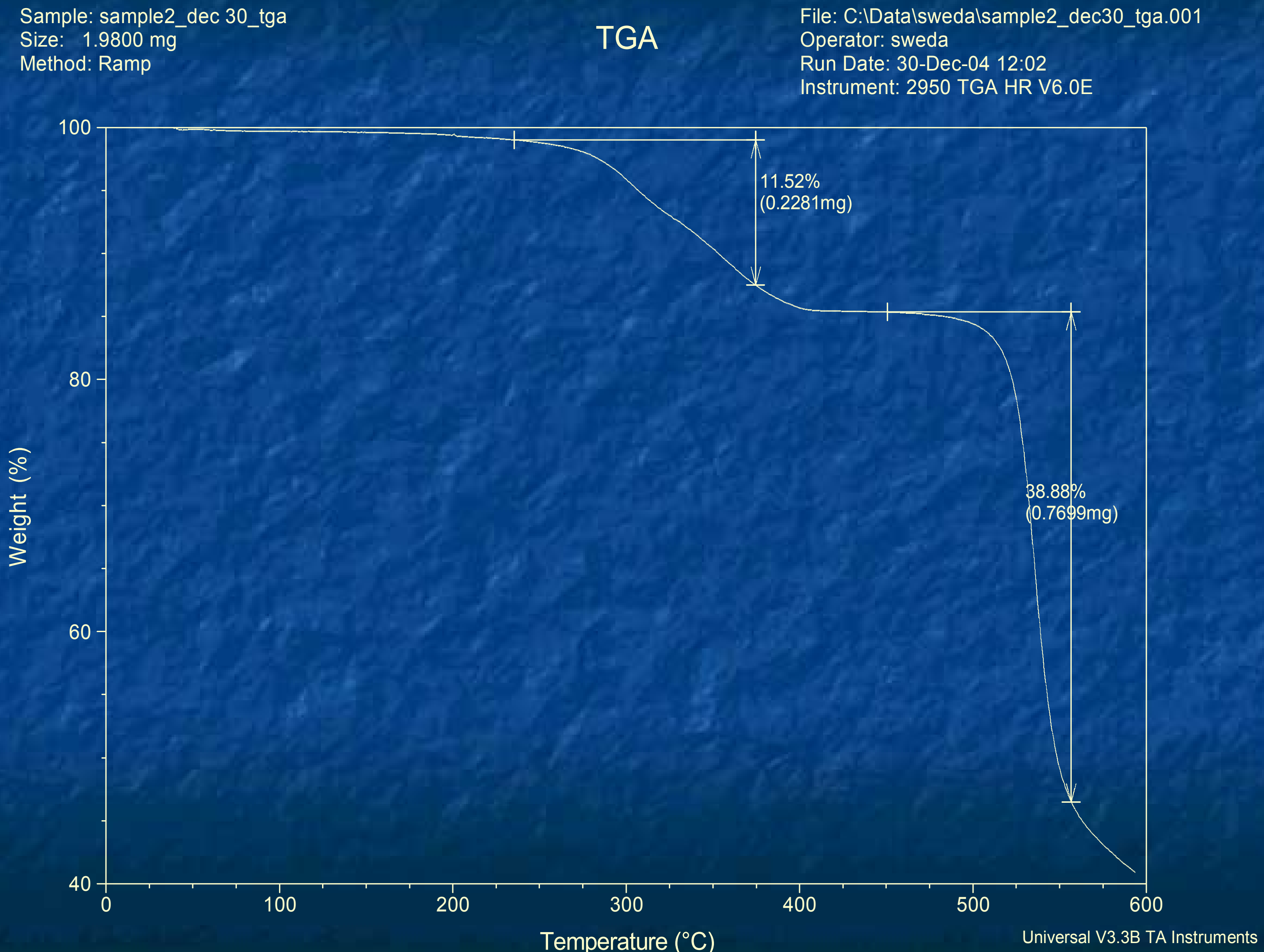


Even after mixing and sonication some "bundles" and aggregates are observed (2.5%). Aggregation becomes an important problem at higher concentrations (see 10 % sample).

Polysulfone/cellulose nanocomposites

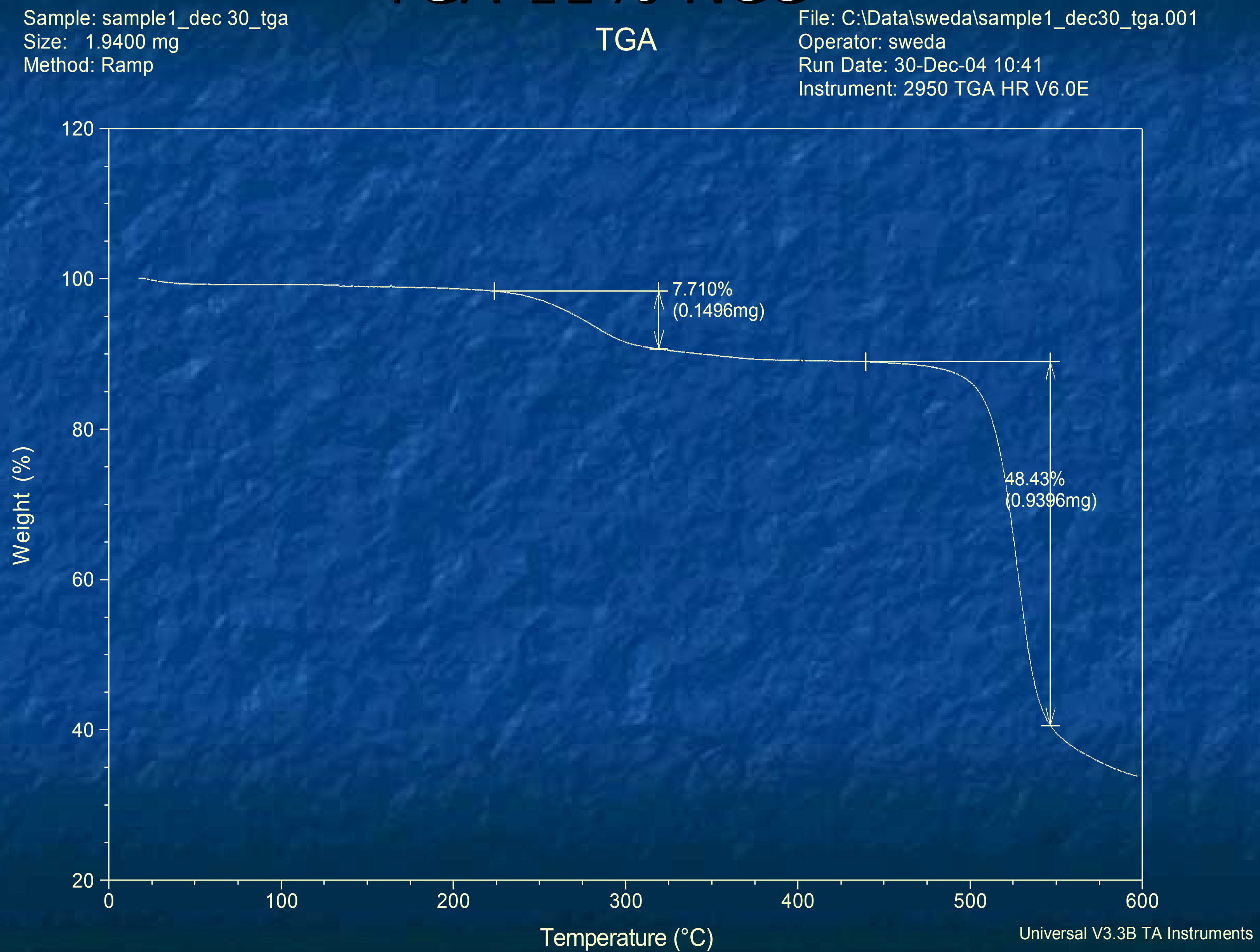
Sweda Noorani
John Simonsen

TGA-16% NCC

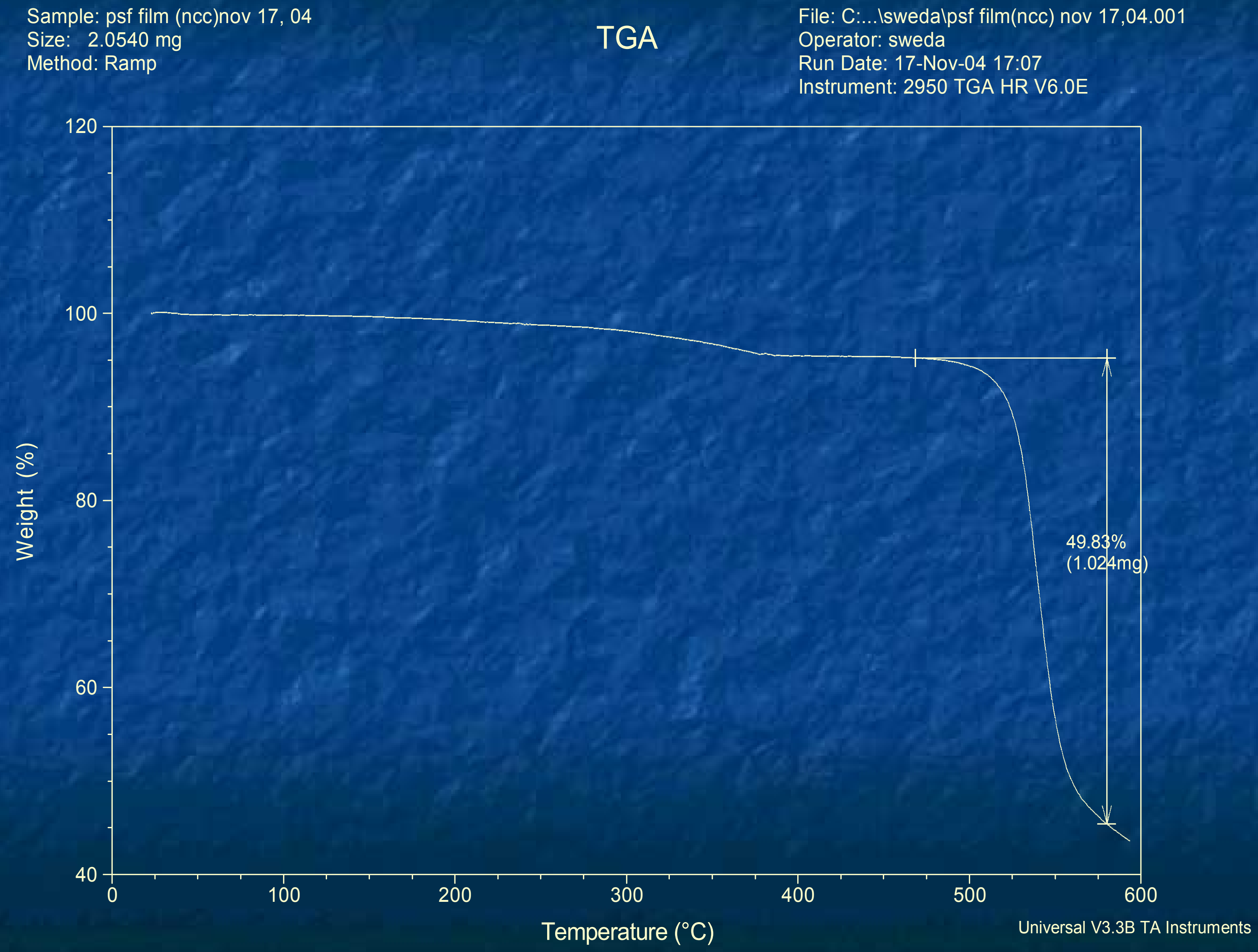


Sample: sample2_dec 30_tga
Size: 1.9800 mg
Method: Ramp
TGA
File: C:\Data\sweda\sample2_dec30_tga.001
Operator: sweda
Run Date: 30-Dec-04 12:02
Instrument: 2950 TGA HR V6.0E
11.52%
(0.2281mg)
38.88%
(0.7699mg)
Weight (%)
100
80
60
40
0
100
200
300
400
500
600
Temperature (°C)
Universal V3.3B TA Instruments

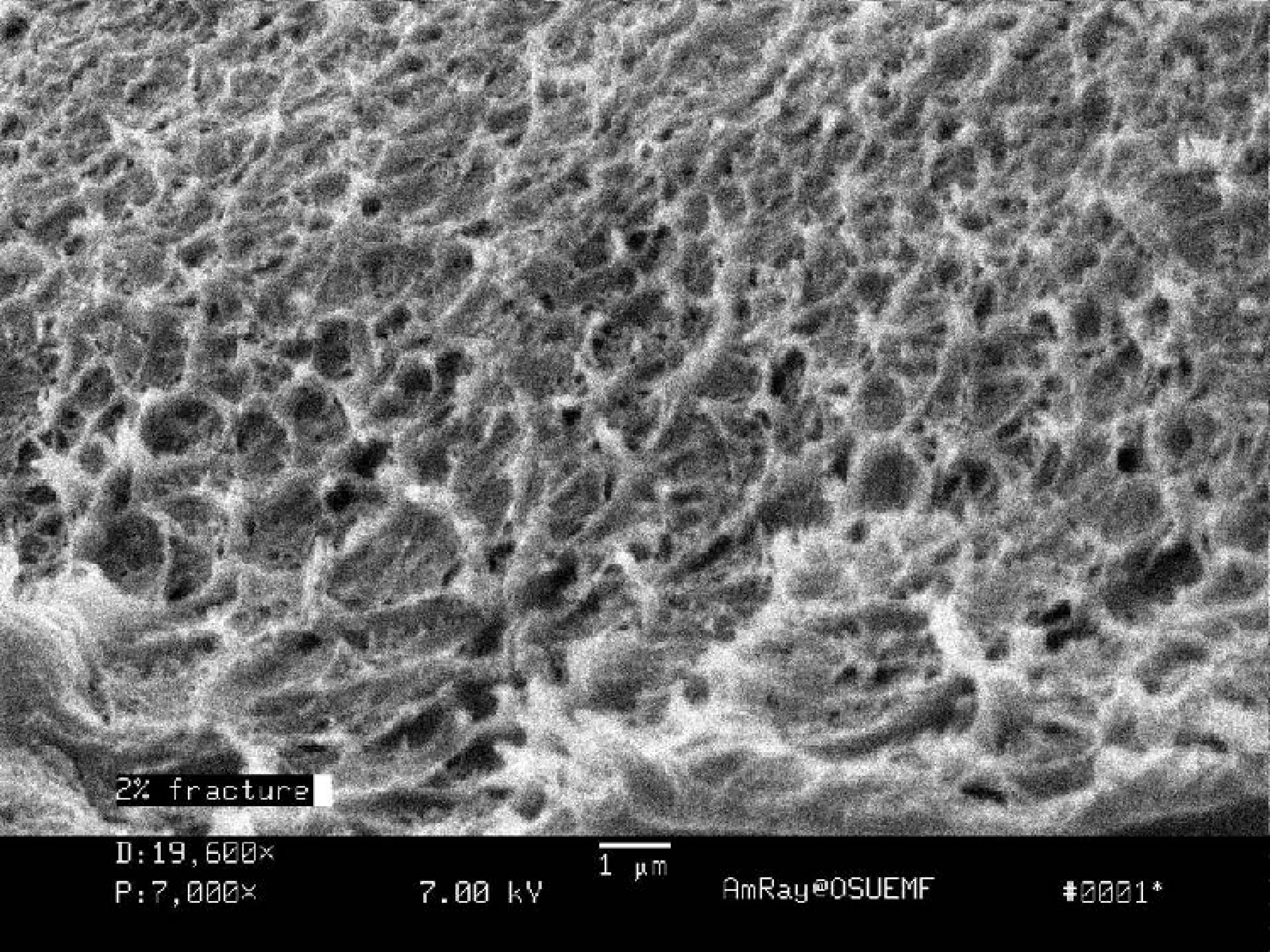
TGA-11% NCC

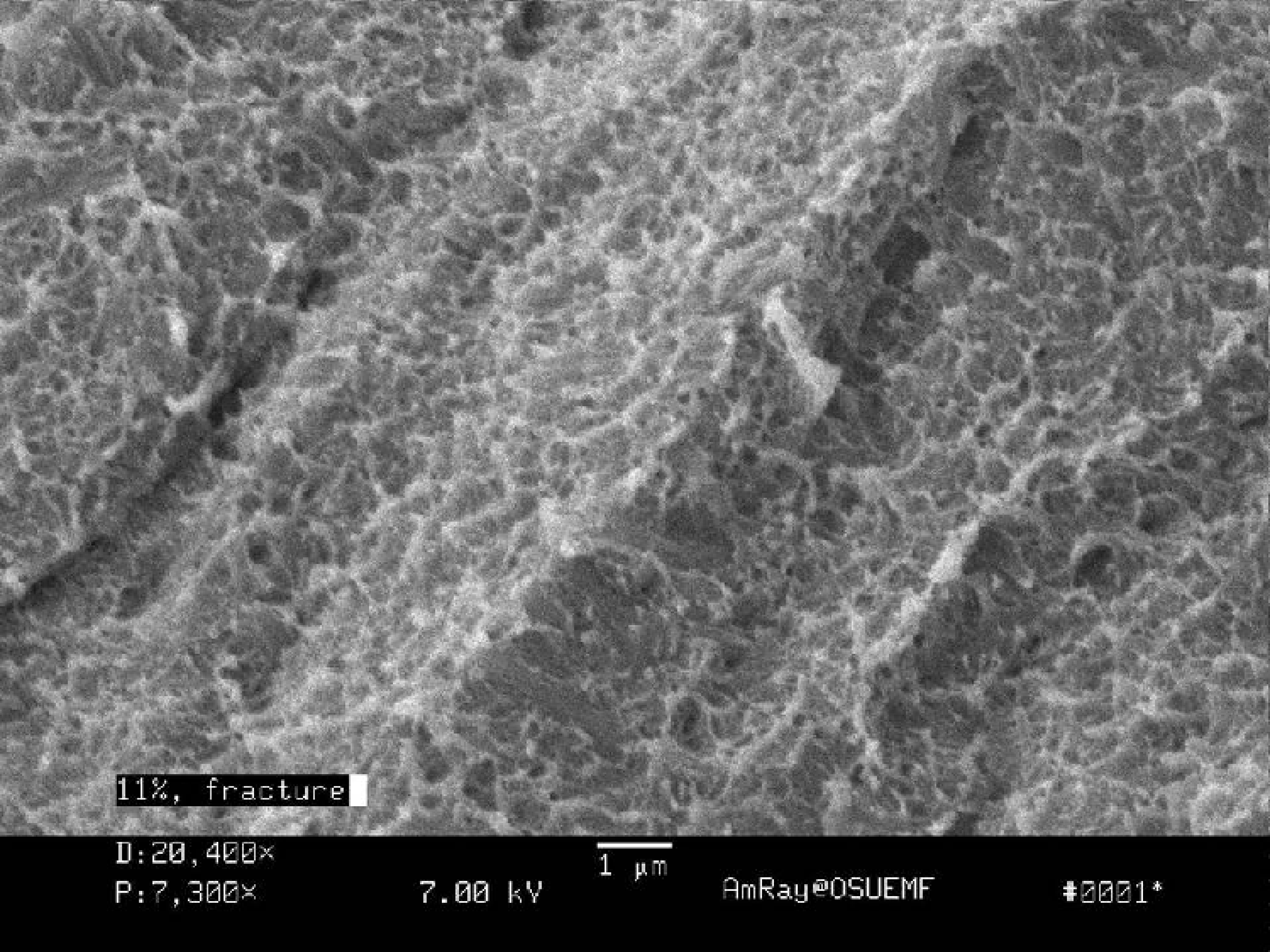

Sample: sample1_dec 30_tga
Size: 1.9400 mg
Method: Ramp
TGA
File: C:\Data\sweda\sample1_dec30_tga.001
Operator: sweda
Run Date: 30-Dec-04 10:41
Instrument: 2950 TGA HR V6.0E
7.710%
(0.1496mg)
48.43%
(0.9396mg)
Weight (%)
120
100
80
60
40
20
0
100
200
300
400
500
600
Temperature (°C)
Universal V3.3B TA Instruments

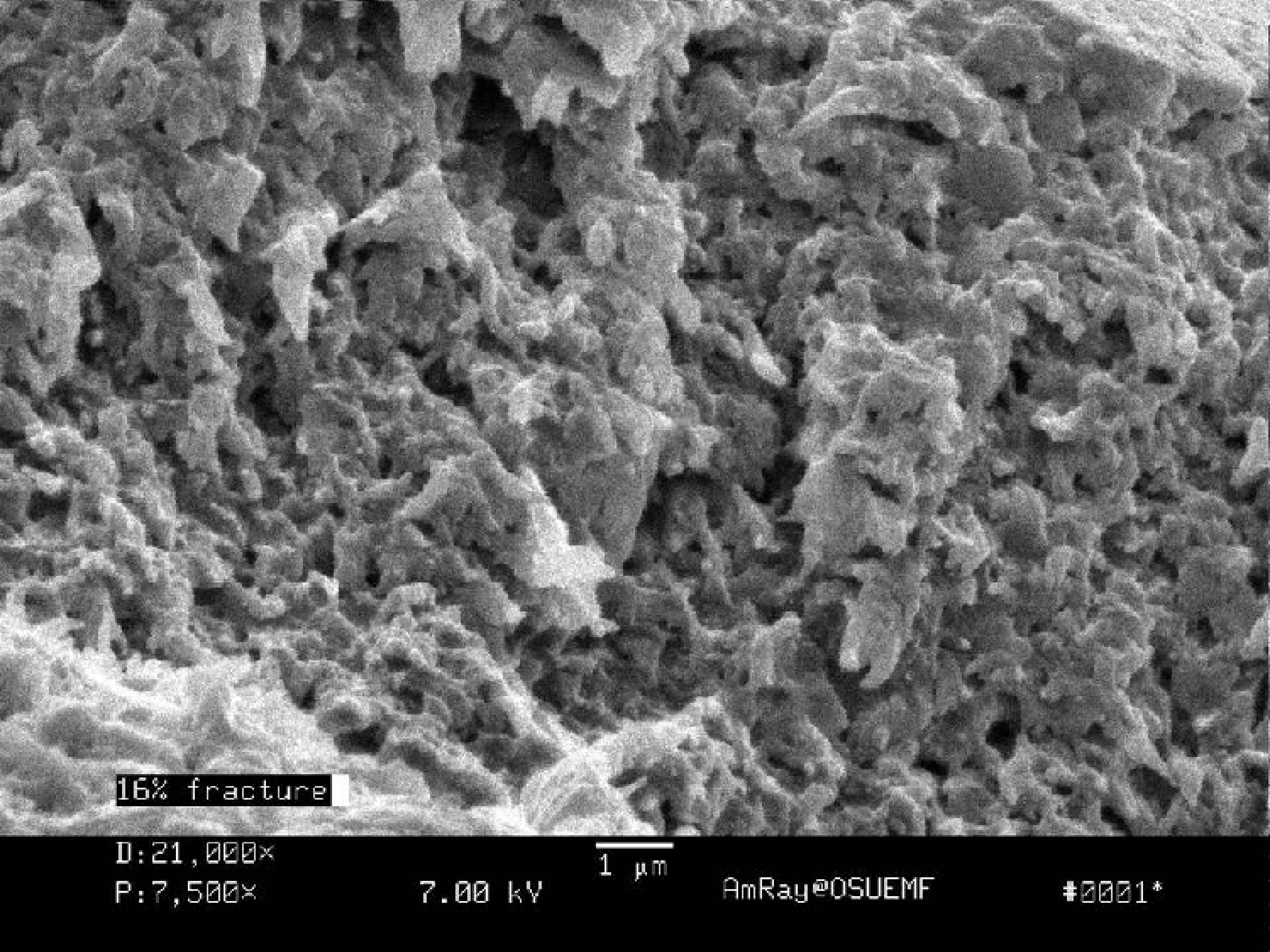
TGA (Psf film with 2% NCC)

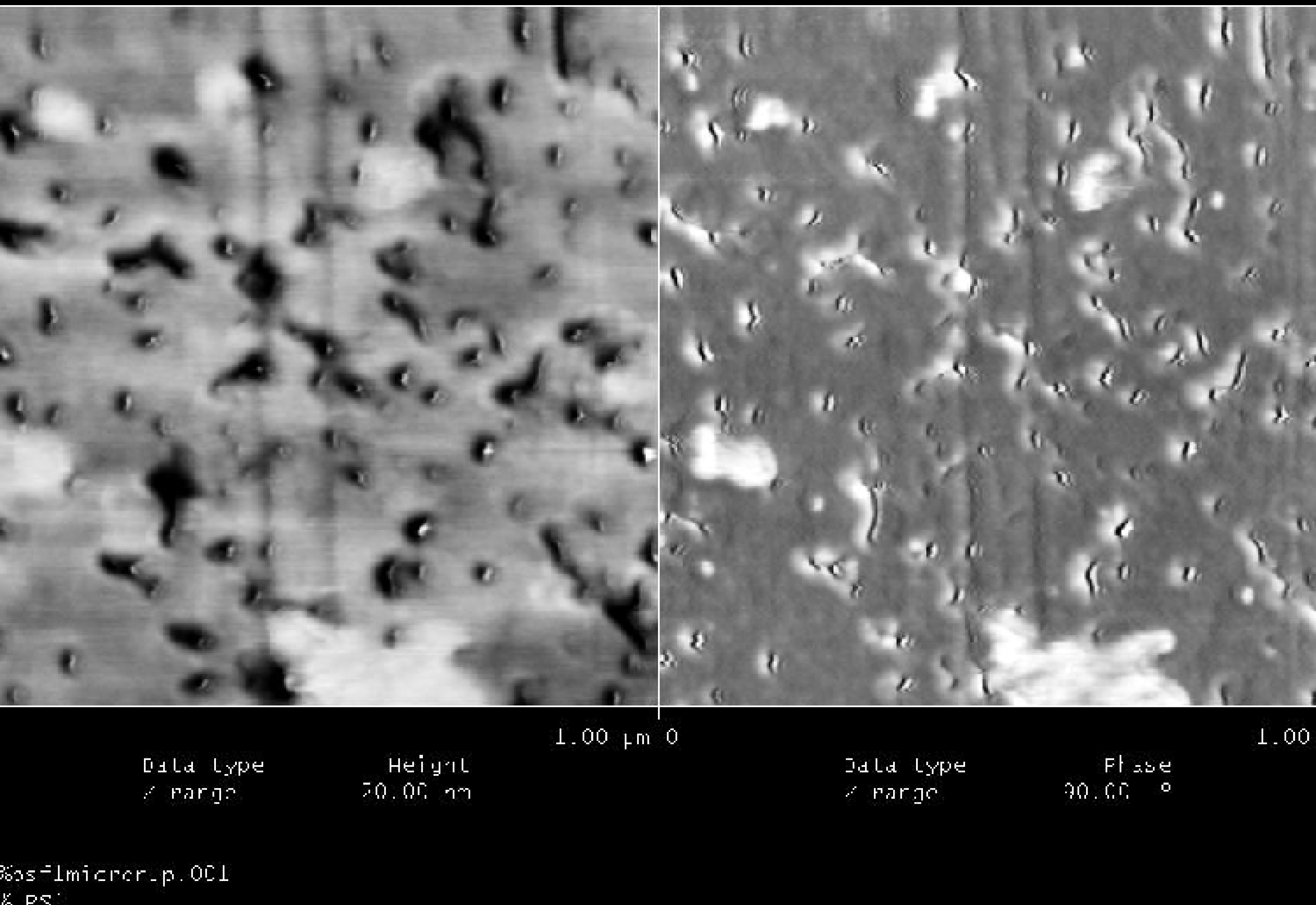


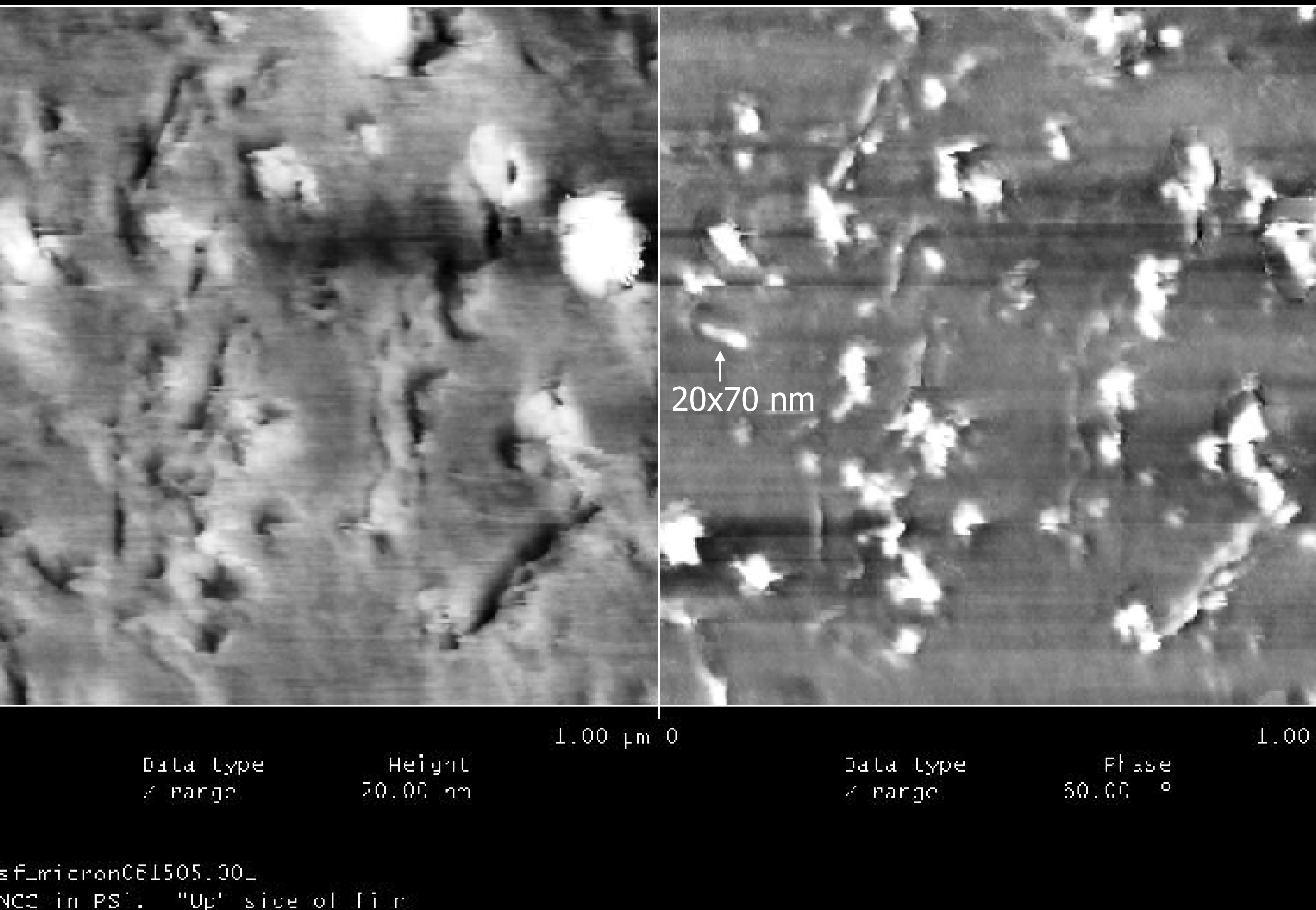

0% fracture
D:14,000×
P:5,000×
1 µm
7.00 kV
AmRay@OSUEMF
#0001*


2% fracture
D:19,600×
1 µm
P:7,000×
7.00 kV
AmRay@OSUEMF
#0001*


11%, fracture
D:20,400×
1 µm
P:7,300×
7.00 kV
AmRay@OSUEMF
#0001*


16% fracture
D:21,000×
P:7,500×
1 µm
7.00 kV
AmRay@OSUEMF
#0001*


1.00 µm 0
1.00
Data type
Height
Z range
70.00 nm
Data type
Phase
Z range
90.00 °
% PS

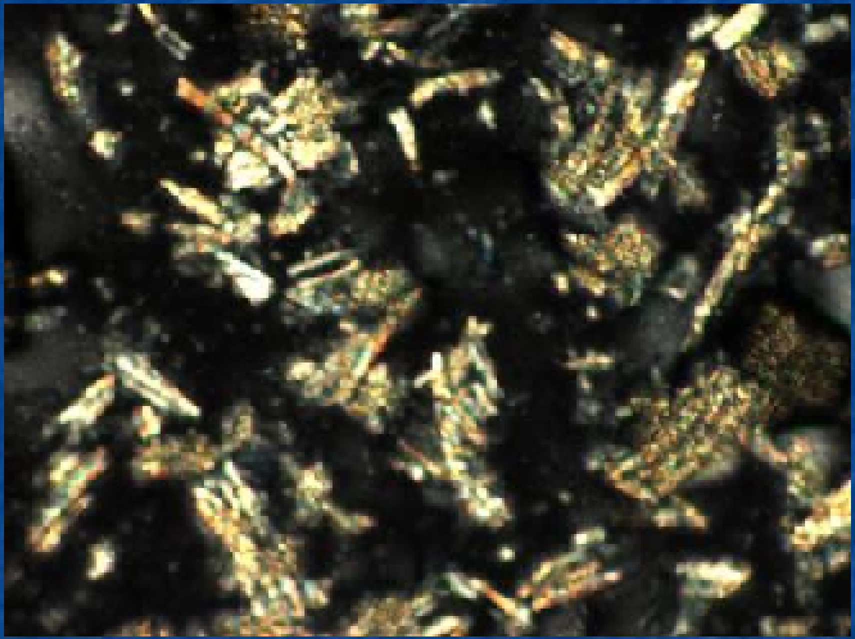


20x70 nm
1.00 µm 0
1.00
Data type
Height
70.00 nm
Data type
Phase
60.00 °
sf_micron061505.001
NCC in PSt. "Up" side of film

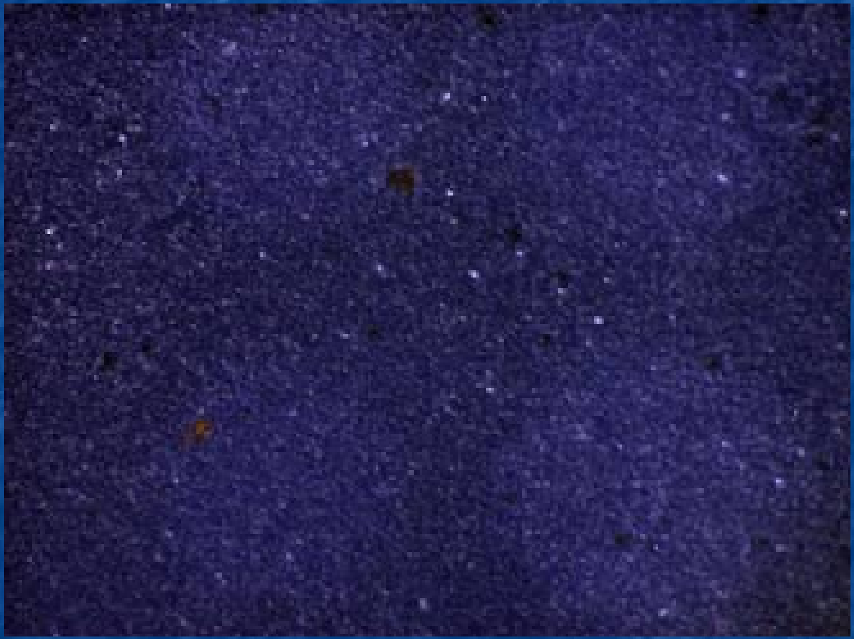
CELLULOSE NANOCRYSTAL-FILLED CARBOXYMETHYL CELLULOSE

YongJae Choi

Comparison of Microcrystalline Cellulose (MCC) to NCC in CMC



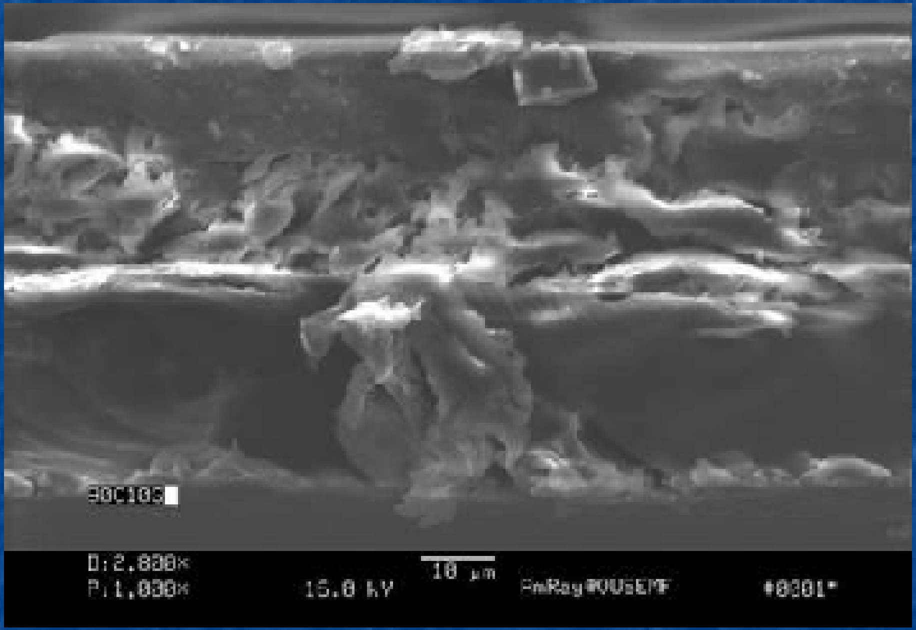
10% MCC



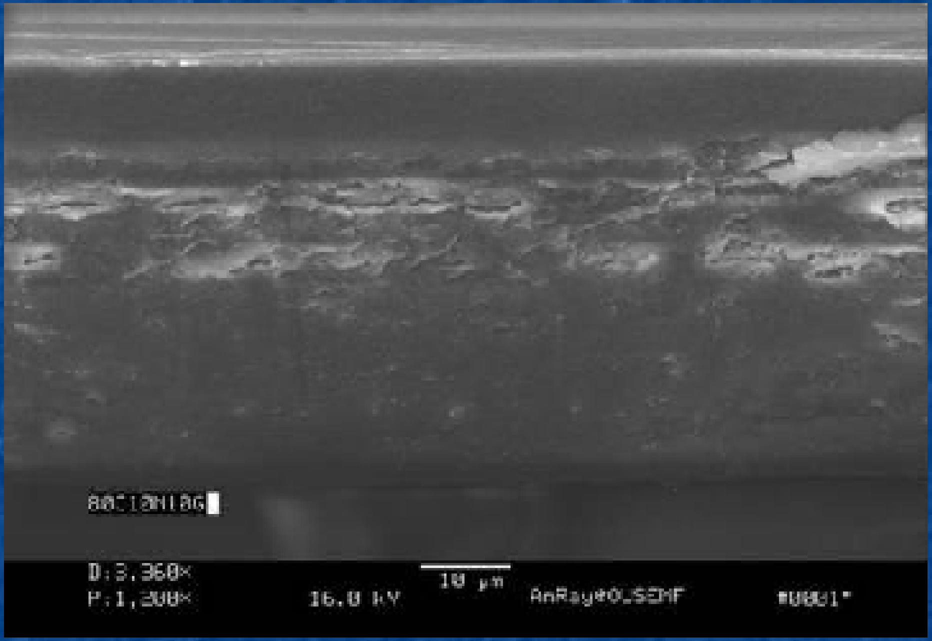
10% NCC

10% glycerin plasticizer
200X optical (crossed polars)

CROSS SECTION OF FILM

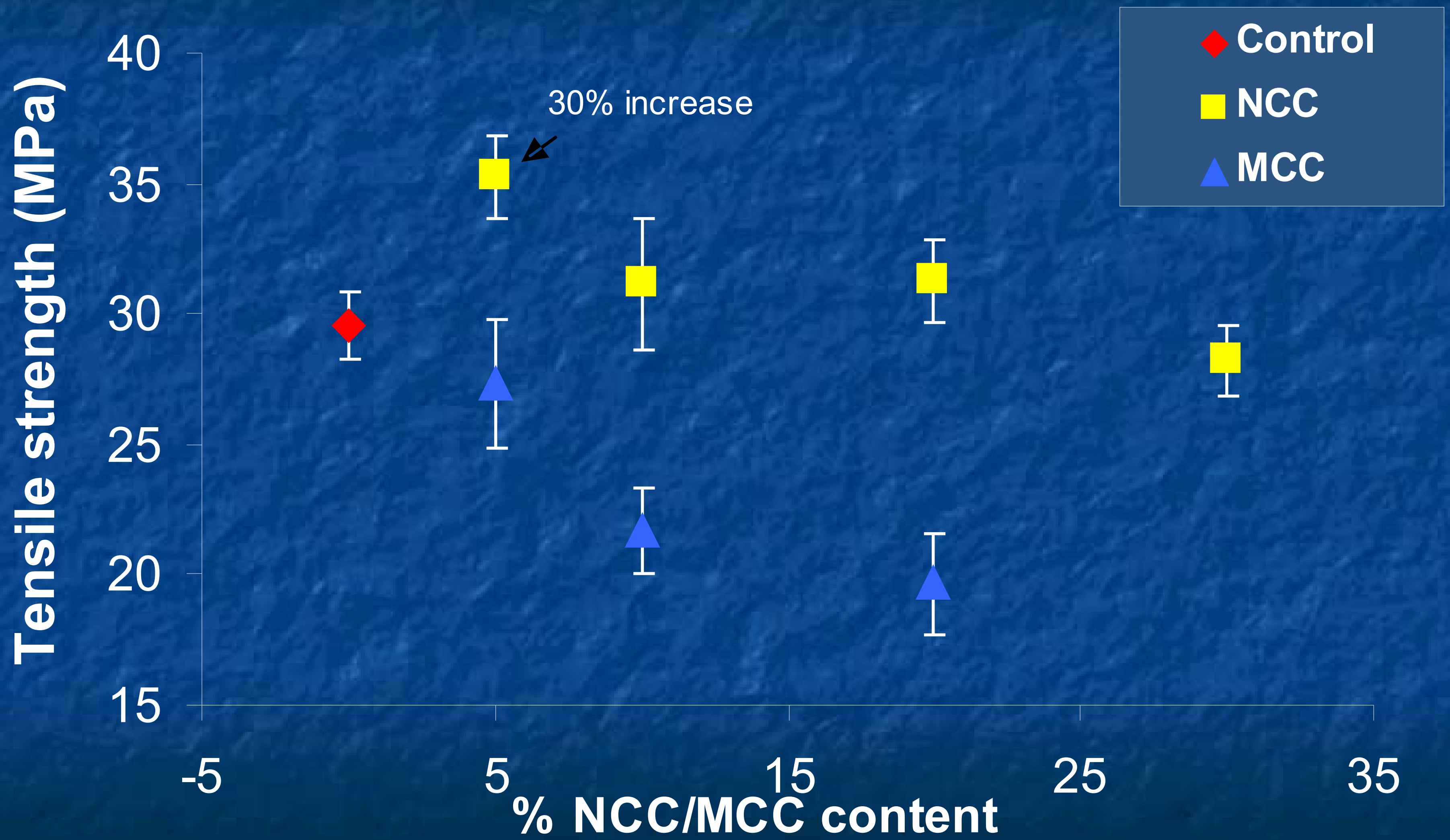


90%CMC/10%Gly

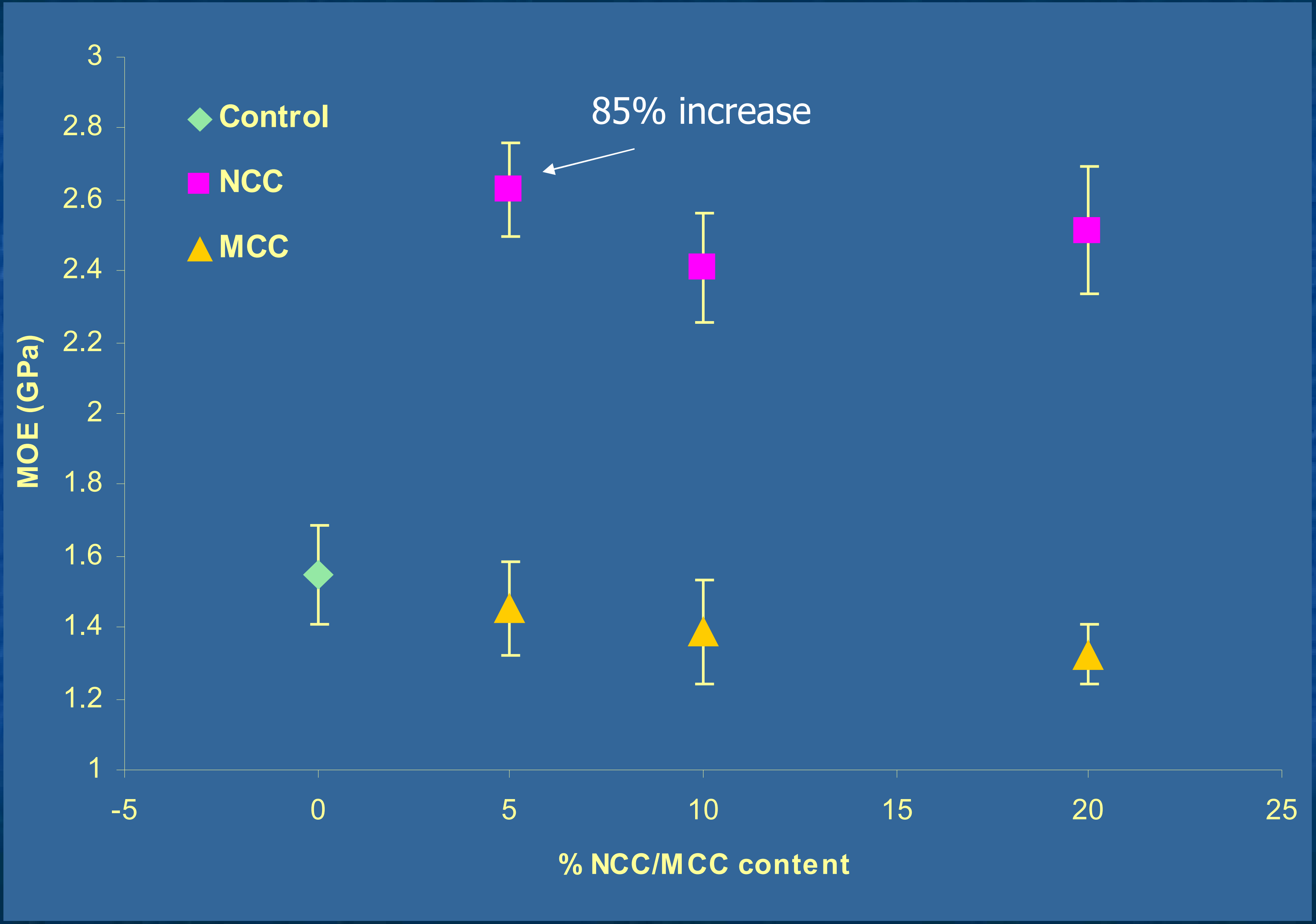


80%CMC/10%NCC/10%Gly

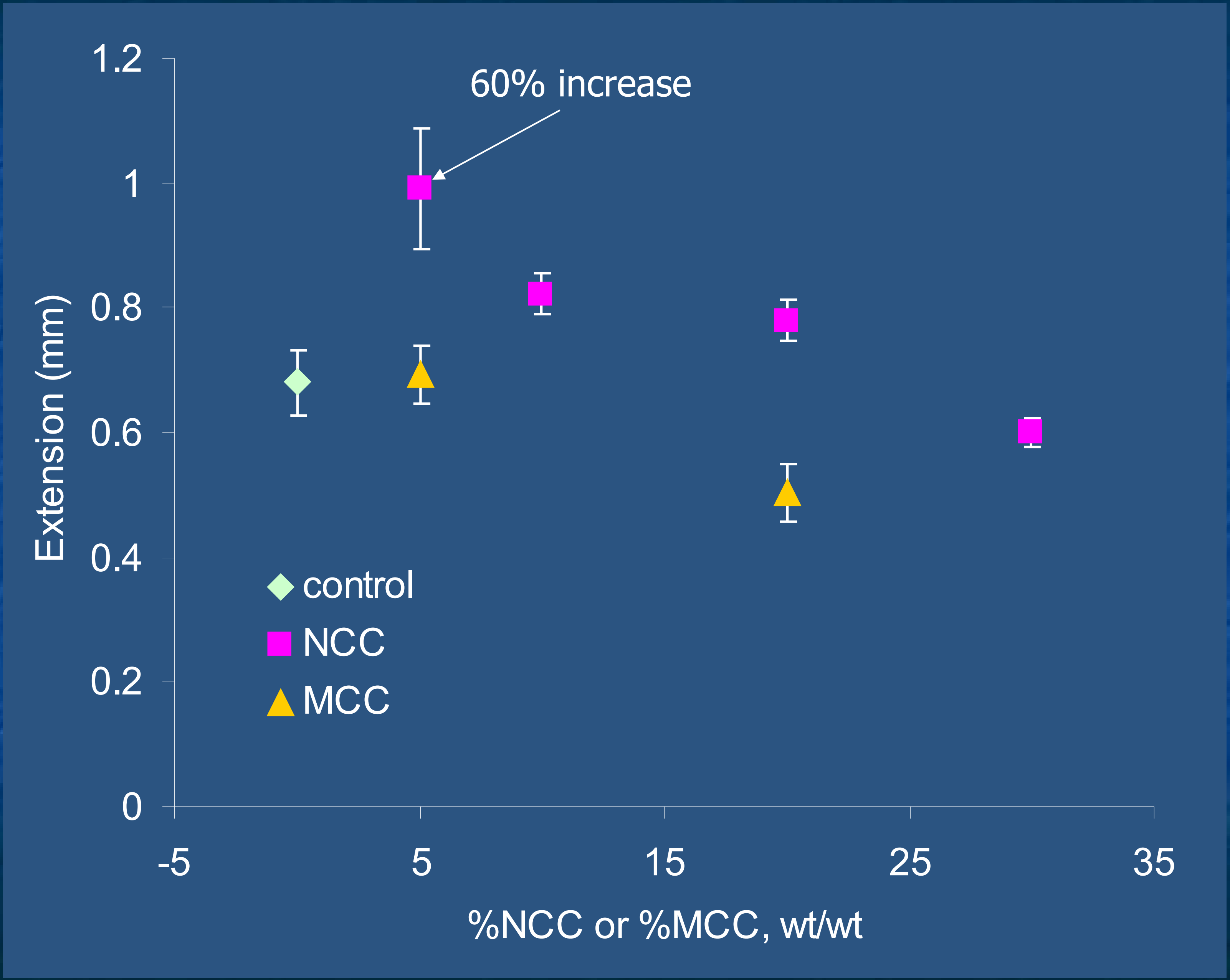
Mechanical properties (MOR)



Mechanical properties (MOE)



Extension at failure

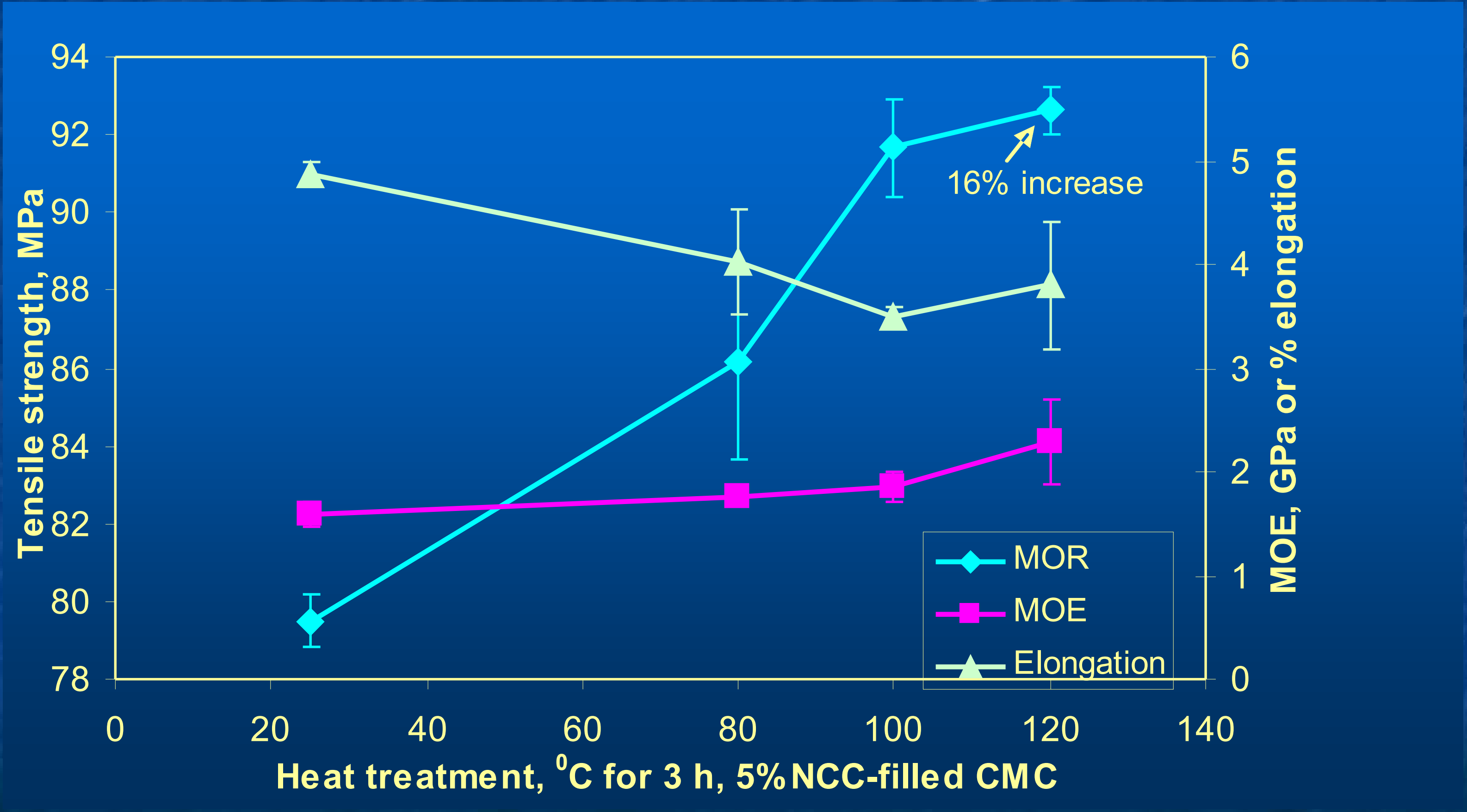


HEAT TREATMENT

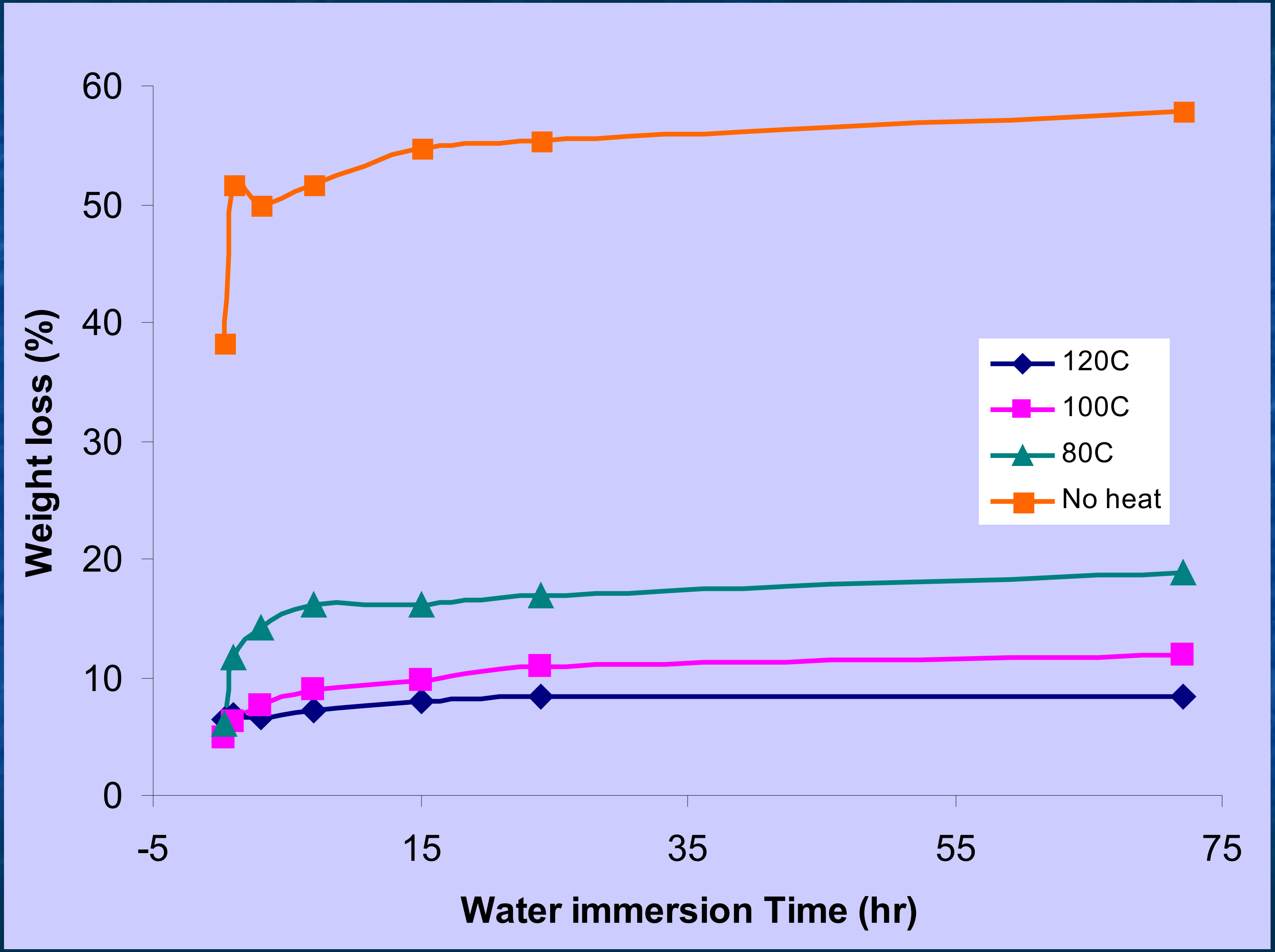
5% NCC in CMC (H form)

No plasticizer

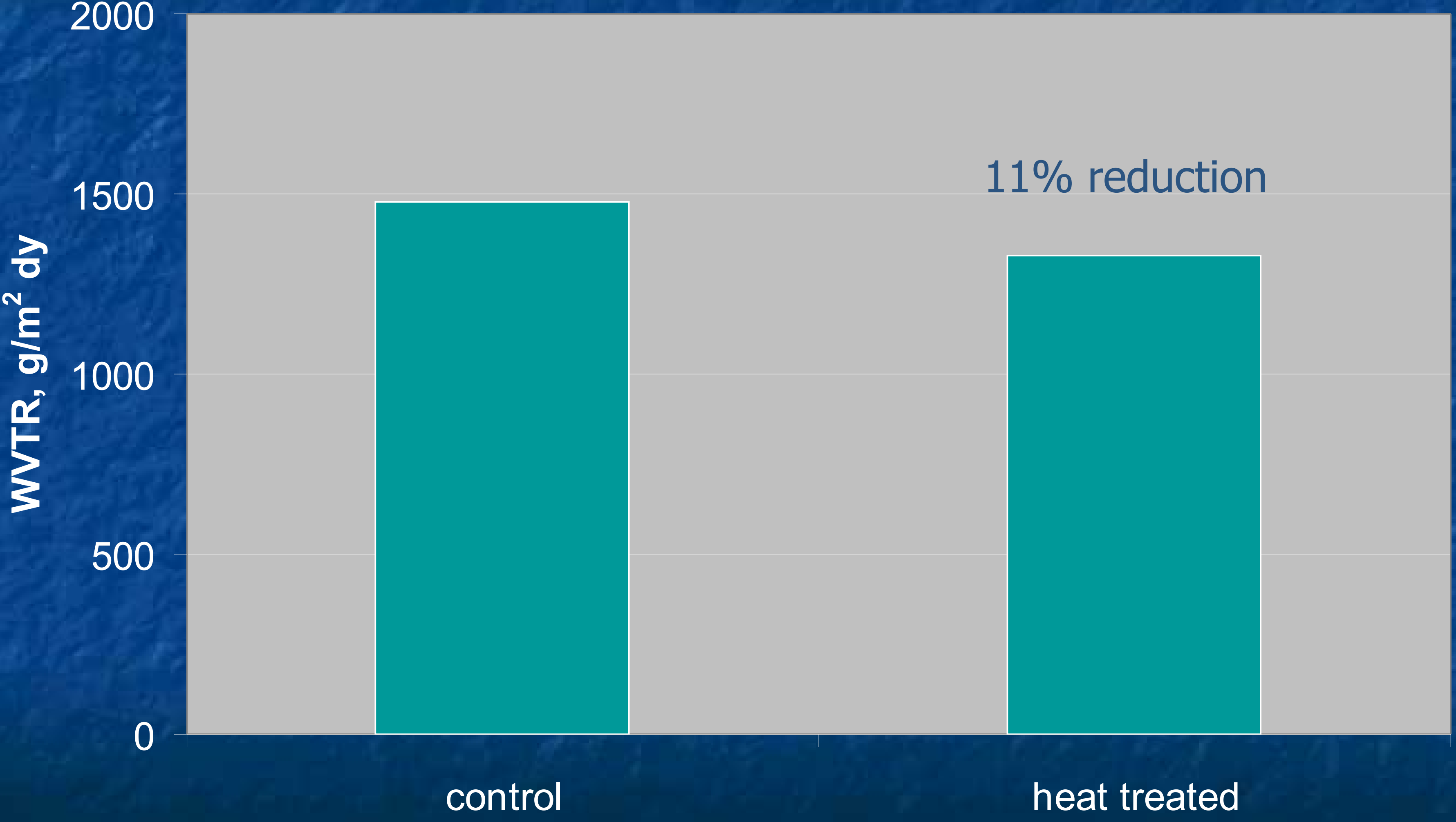
HEAT TREATMENT



Water Dissolution



Water vapor transmission rate



CHALLENGES

- Dispersion of nanoparticles
- Production scale-up of nanoparticles
- Coupling of filler to matrix
- Where are the high stiffness, high strength composites we should have?
- Improving knowledge base to allow intelligent design of products which capture the advantages of this exceptional nanomaterial

OPPORTUNITIES - APPLICATIONS

- Membranes
  - Fuel cells
  - Kidney dialysis
  - Reverse osmosis
  - Protein separation
  - Pervaporation

APPLICATIONS

- Advanced textiles – fibers
  - Again, where are the high stiffness, high strength composites we should have?
- Biomedical
  - Tissue engineering
    - Heart valves
    - bone replacement materials

APPLICATIONS

- Advantages
  - Biocompatible
  - Biodegradable
  - Exceptional mechanical properties
  - Chemical modification straightforward
  - Self-assembling?

Acknowledgements

- This project was supported by a grant from the USDA National Research Initiative Competitive Grants Program

QUESTIONS?