NANOMATERIALS: NEW MATERIALS AND NEW PARADIGMS

Nanotech Colloquium

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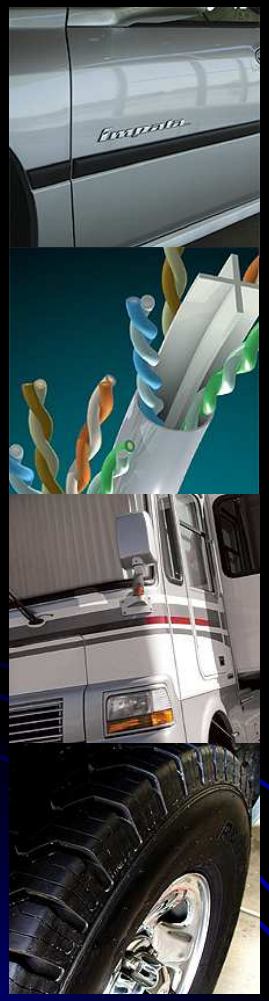
Texas State University

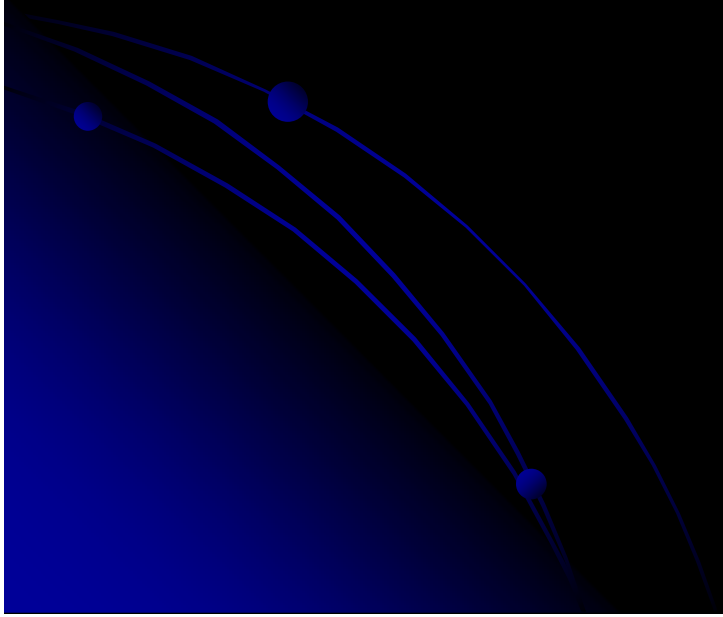
NANOCOMPOSITE: NANO-PARTICLE/POLYMER COMPOSITE WITH ENHANCED PROPERTIES



- One nanometer = 1/100,000 the width of a human hair
- Molecular level modification with 1 to 3% of a nano-sized additive.

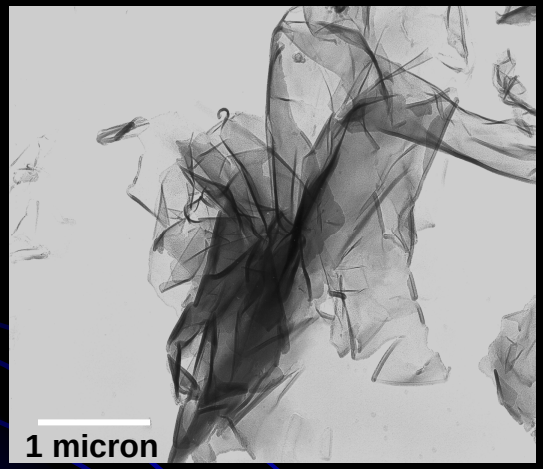
Property Improvements	Applications
I. Physical Properties	Composites and Coatings
II. Barrier	Coatings, Packaging, Automobile tires
III. Flame Retardancy	Composites and Coatings
IV. Rheology Control	Coatings, Cosmetics, Paper Making
V. Conductivity	Electrical / Electronic

I. STRUCTURE / PROPERTIES OF NANOCOMPOSITES



NANOCLAY
TYPICAL PROPERTIES

TEM OF REFINED MONTMORILLONITE

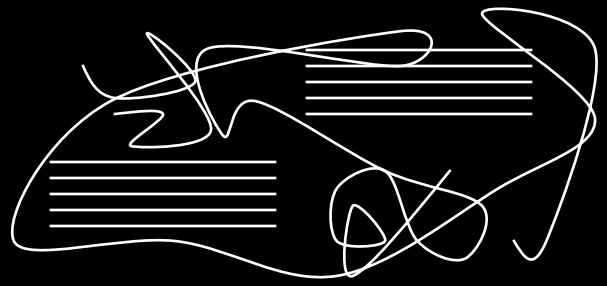


- **SMECTITE FAMILY**
  Montmorillonite
- **PARTICLE SIZE**
  1 nm thick by 70-100 nm wide
- **SURFACE AREA**
  > 750 m^2/g
- **Aspect Ratio**
  75-150 nm when exfoliated
- **SPECIFIC GRAVITY**
  1.66 - 2.86 g/cc
- **BULK DENSITY**
  340 kg/m^3 (21 lbs/ft^3)
- **MOISTURE**
  < 2 wt%

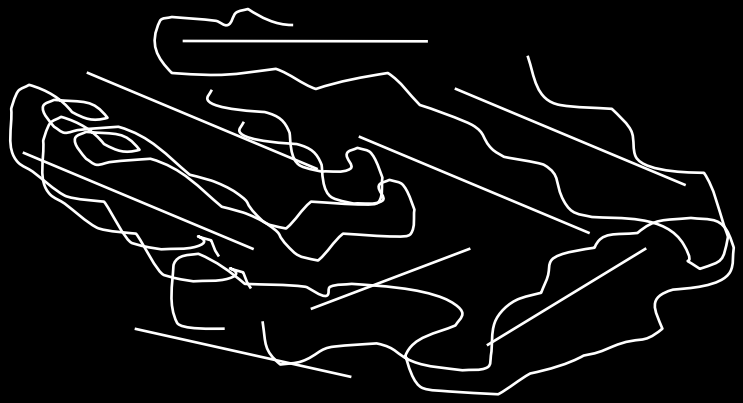
SUMMARY OF CLAY MINERAL PROPERTIES

Secondary mineral	Type	Interlayer condition / Bonding	CEC [cmol/kg]	Swelling potential	Specific surface area [m^2/g]	Basal spacing [nm]
Kaolinite	1 : 1 (non-expanding)	lack of interlayer surface, strong bonding	3 - 15	almost none	5 - 20	0.72
Montmorillonite	2 : 1 (expanding)	very weak bonding, great expansion	80 - 150	high	700 - 800	0.98 - 1.8 +
Vermiculite	2 : 1 (expanding)	weak bonding, great expansion	100 -150	high	500 - 700	1.0 - 1.5 +
Hydrous Mica	2 : 1 (non-expanding)	partial loss of K, strong bonding	10 - 40	low	50 - 200	1.0
Chlorite	2 : 1 : 1 (non-expanding)	moderate to strong bonding, non-expanding	10 - 40	none		1.4
Allophane	-	-	10 - 50	-		-

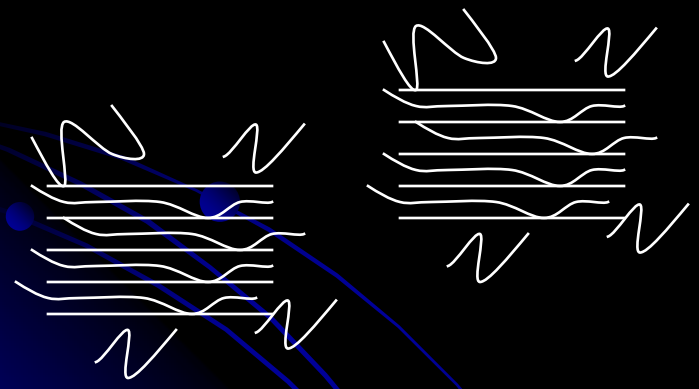
NANOCOMPOSITE MORPHOLOGIES



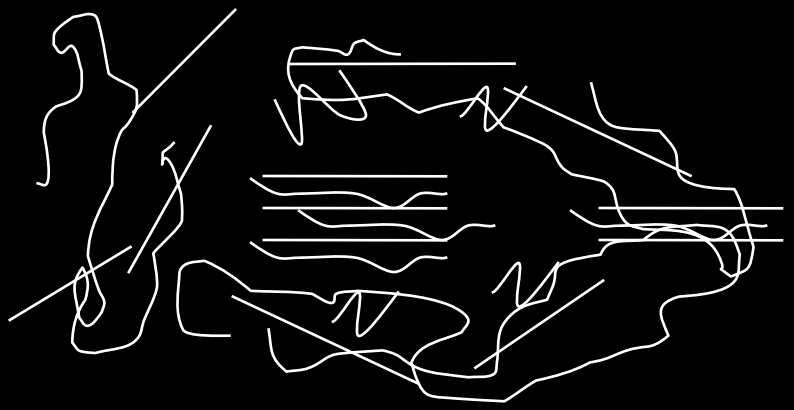
Polymer – Nanoclay



Exfoliated, Delaminated



Intercalated

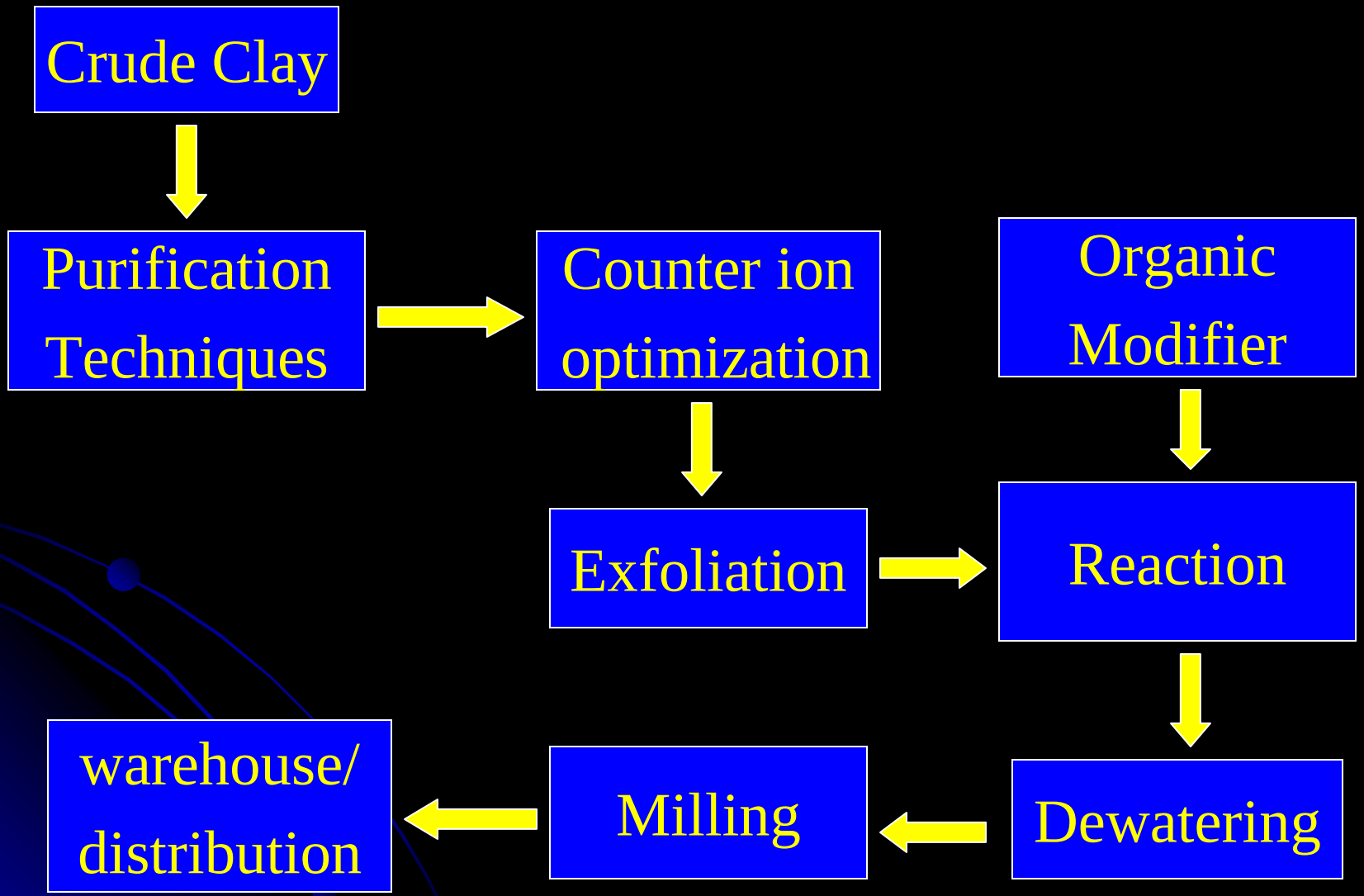


Intercalated mixed w/Exfoliated

VARIABLES AFFECTING MORPHOLOGY

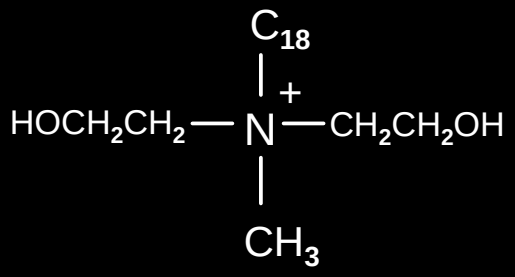
- Clay Type
- Clay Source
- Surface Treatment
- Processing
  - During Clay Manufacture
  - During Nanocomposite Manufacture

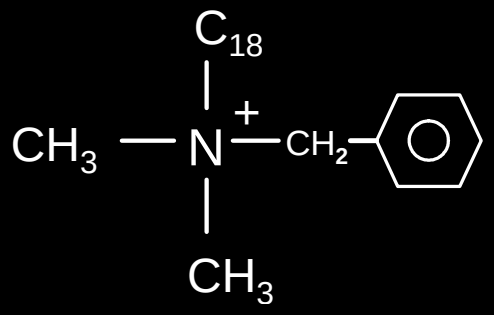
ORGANOCLAY MANUFACTURING PROCESS

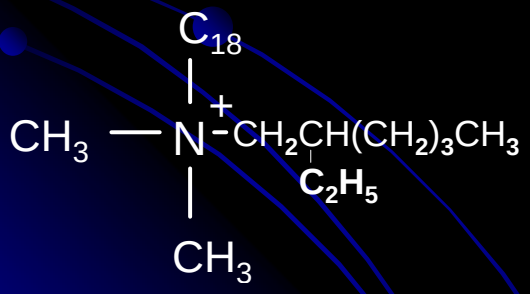


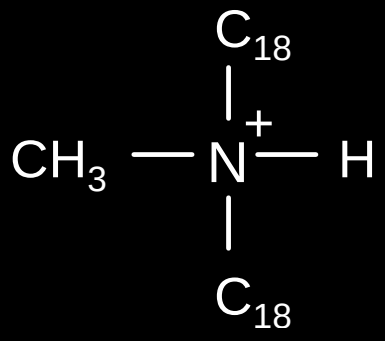
QUATERNARY AMINES: TYPICAL NANOCLAY SURFACE TREATMENTS

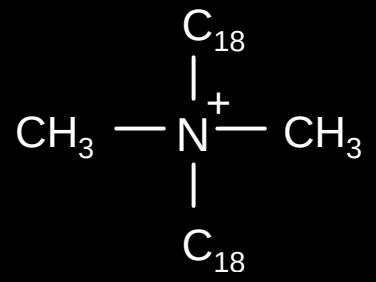
No Surface Treatment; Most Hydrophilic



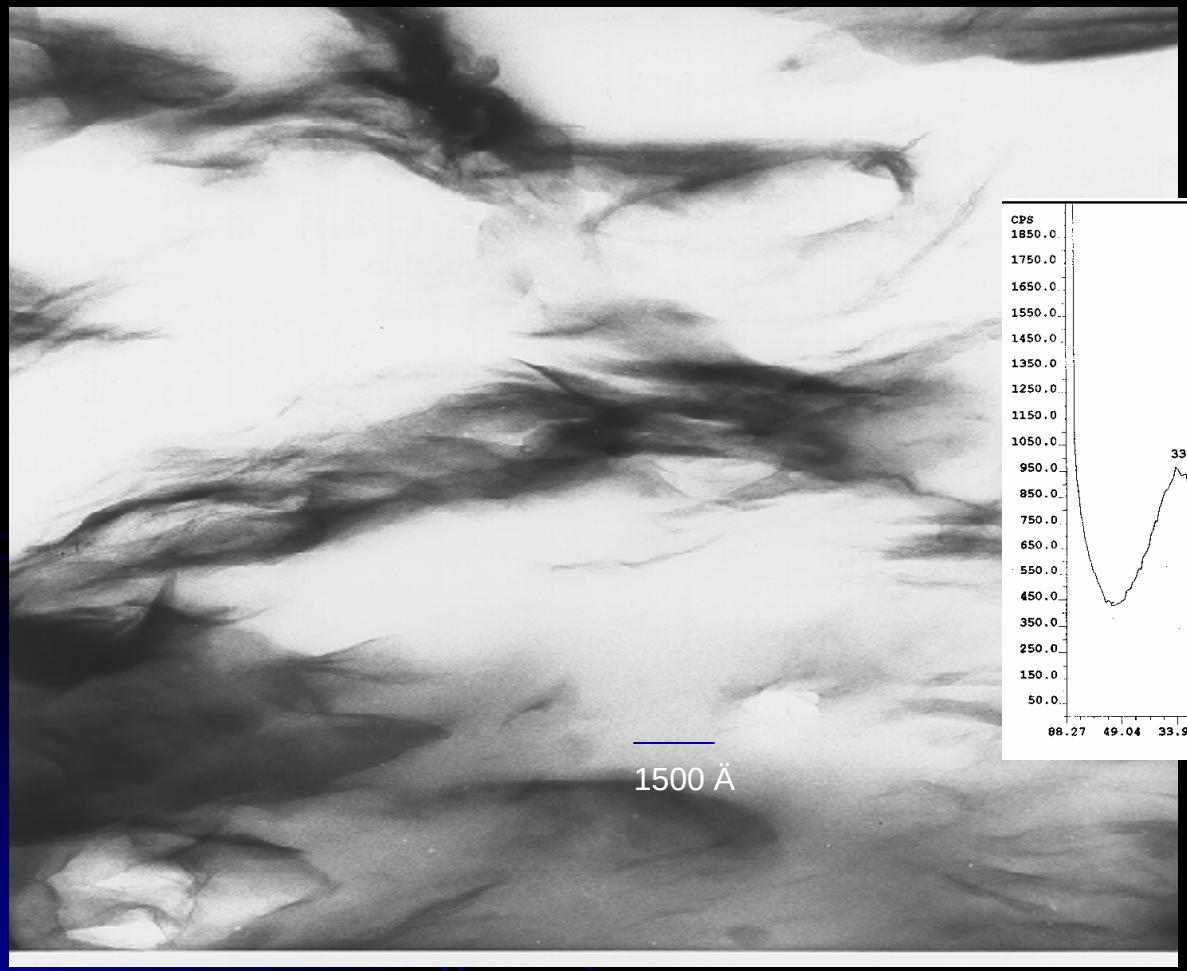


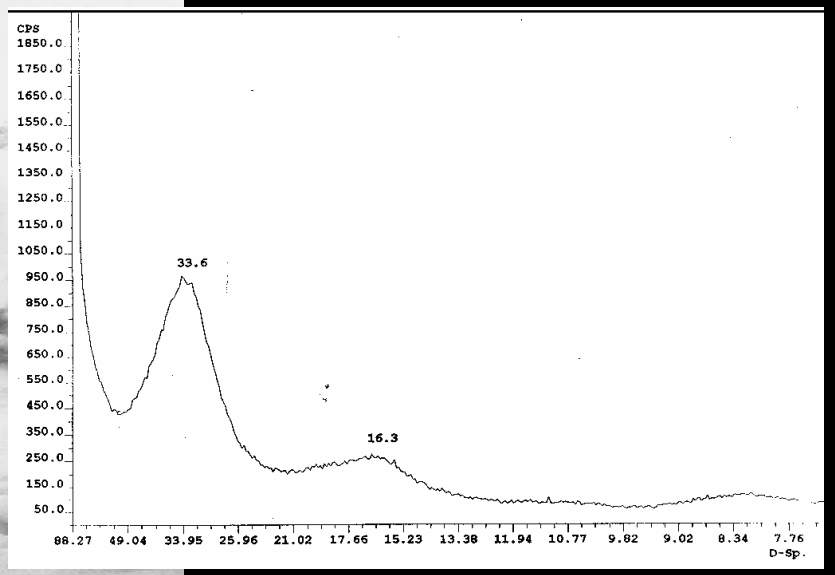




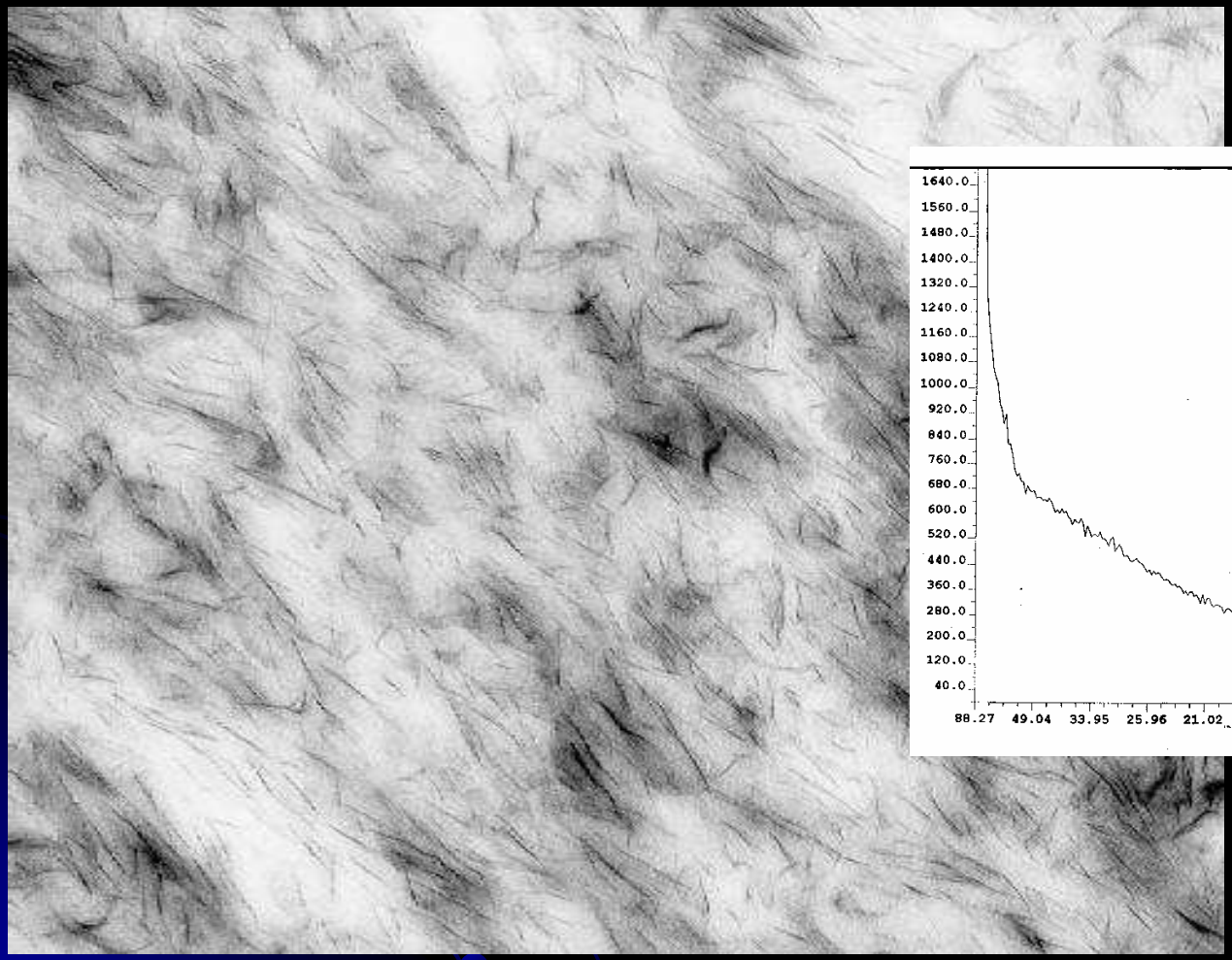


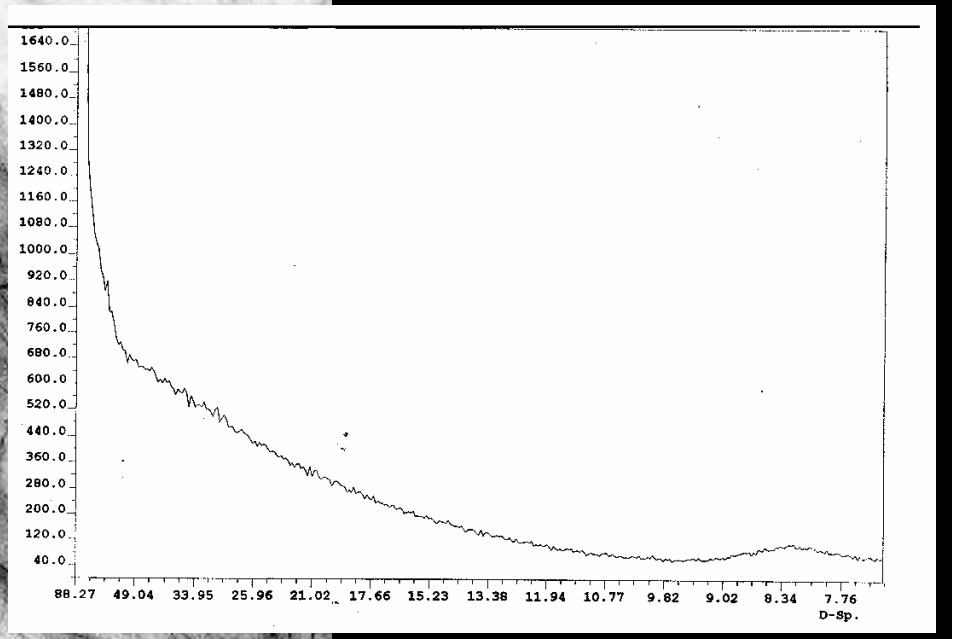
NYLON 6 – NANOCLAY WITH HYDROPHOBIC SURFACE TREATMENT





NYLON 6 – NANOCLAY WITH POLAR SURFACE TREATMENT





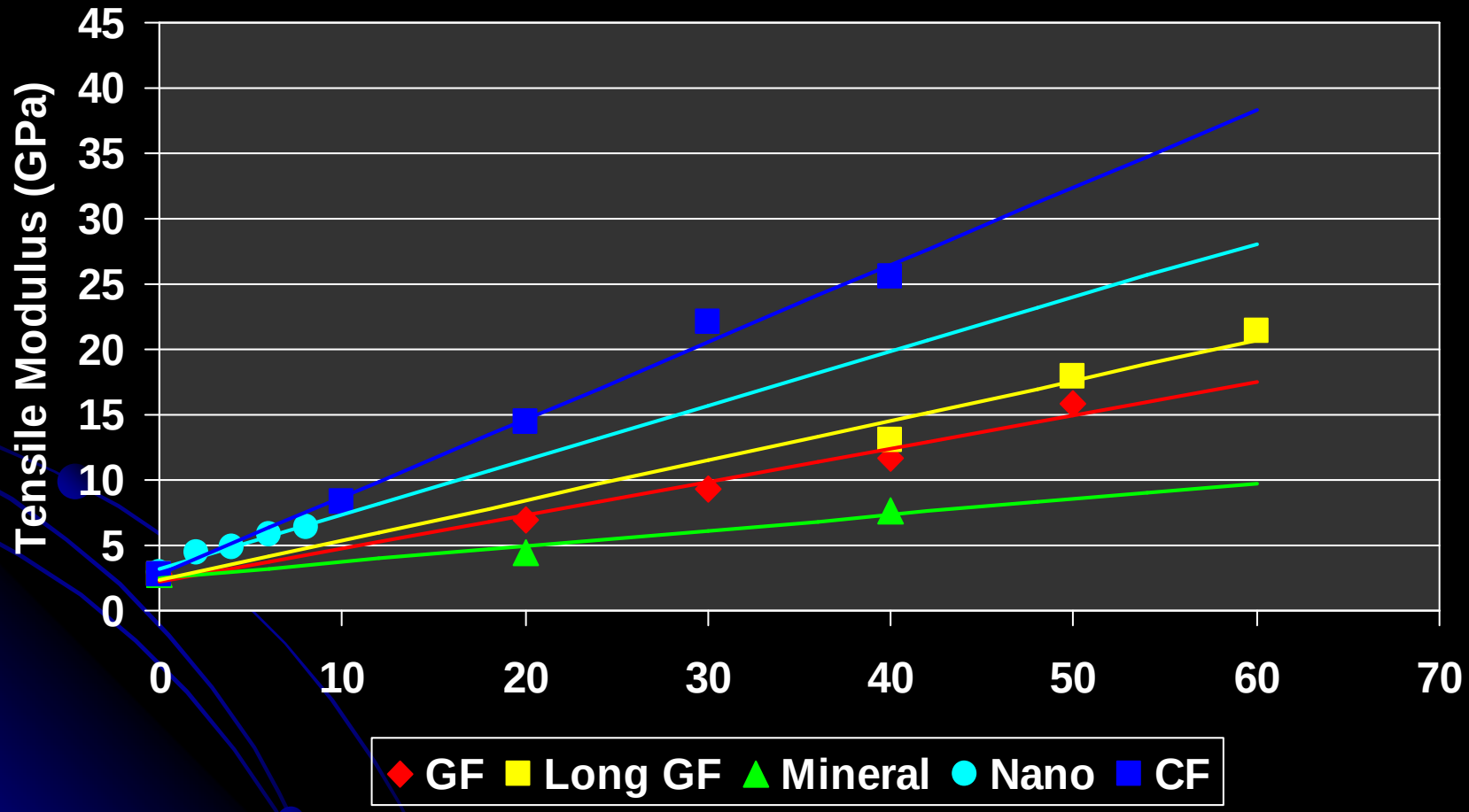
PROPERTIES OF NYLON 6 NANOCOMPOSITES

Nanocor, ANTEC 2001

Nanoclay (wt%)	Flexural Modulus (GPa)	Tensile Modulus (GPa)	HDT (°C)	OTR (cc·mil/m^{2}·day)
0	2.84	2.96	56	35
2	4.33	4.40	125	21
4	4.58	4.90	131	14
6	5.39	5.87	136	11
8	6.13	6.37	154	7

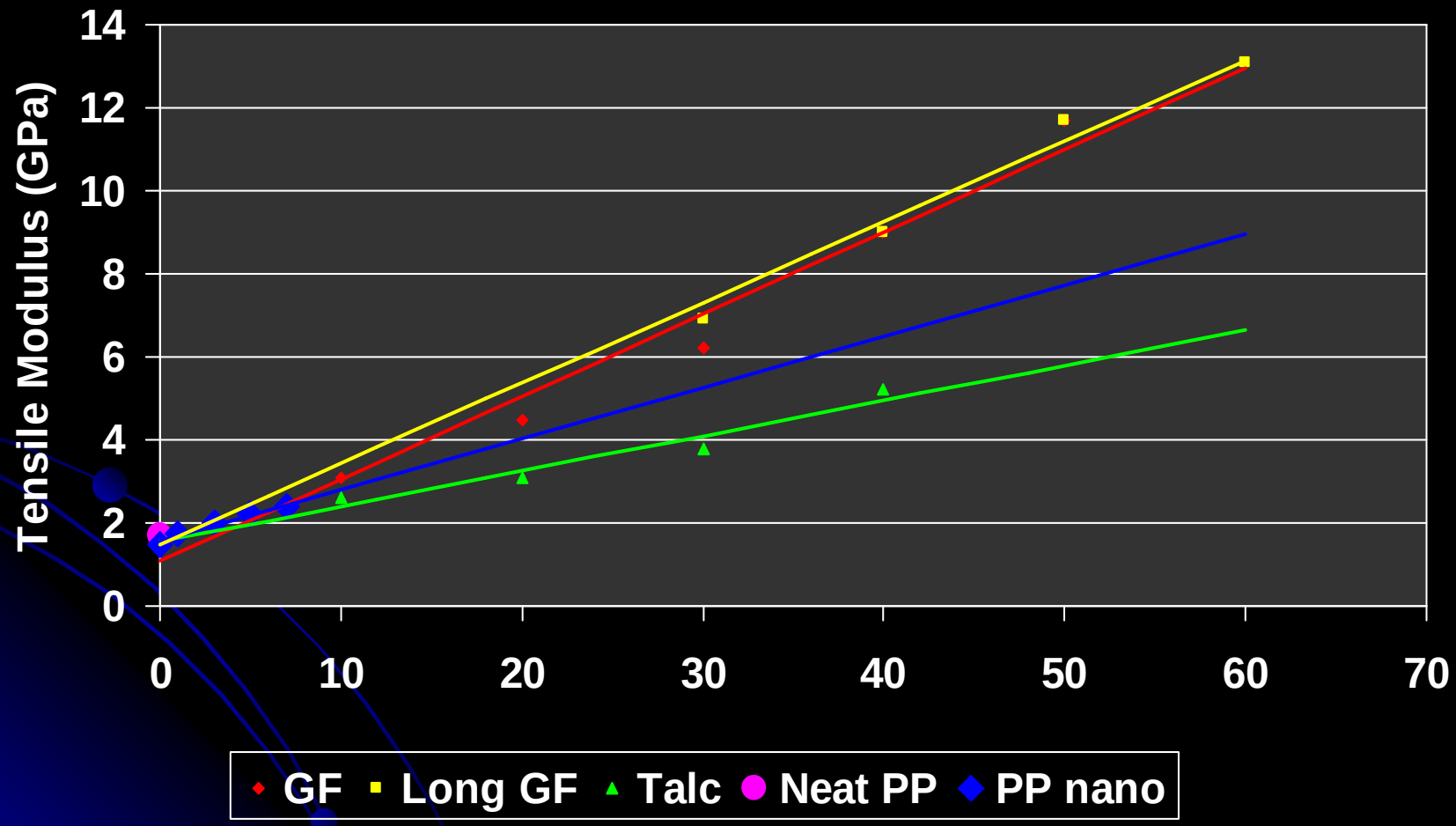
EFFECT OF FILLER TYPE AND CONCENTRATION ON THE TENSILE MODULUS OF NYLON 6 COMPOSITES

(Nanocomposite data from Nanocor; all other data from RTP)



EFFECT PP FILLER TYPE AND CONCENTRATION ON THE TENSILE MODULUS OF PP COMPOSITES

(Nanocomposite data from Paul et. al., Antec 2004 p. 1516; all other data from RTP)



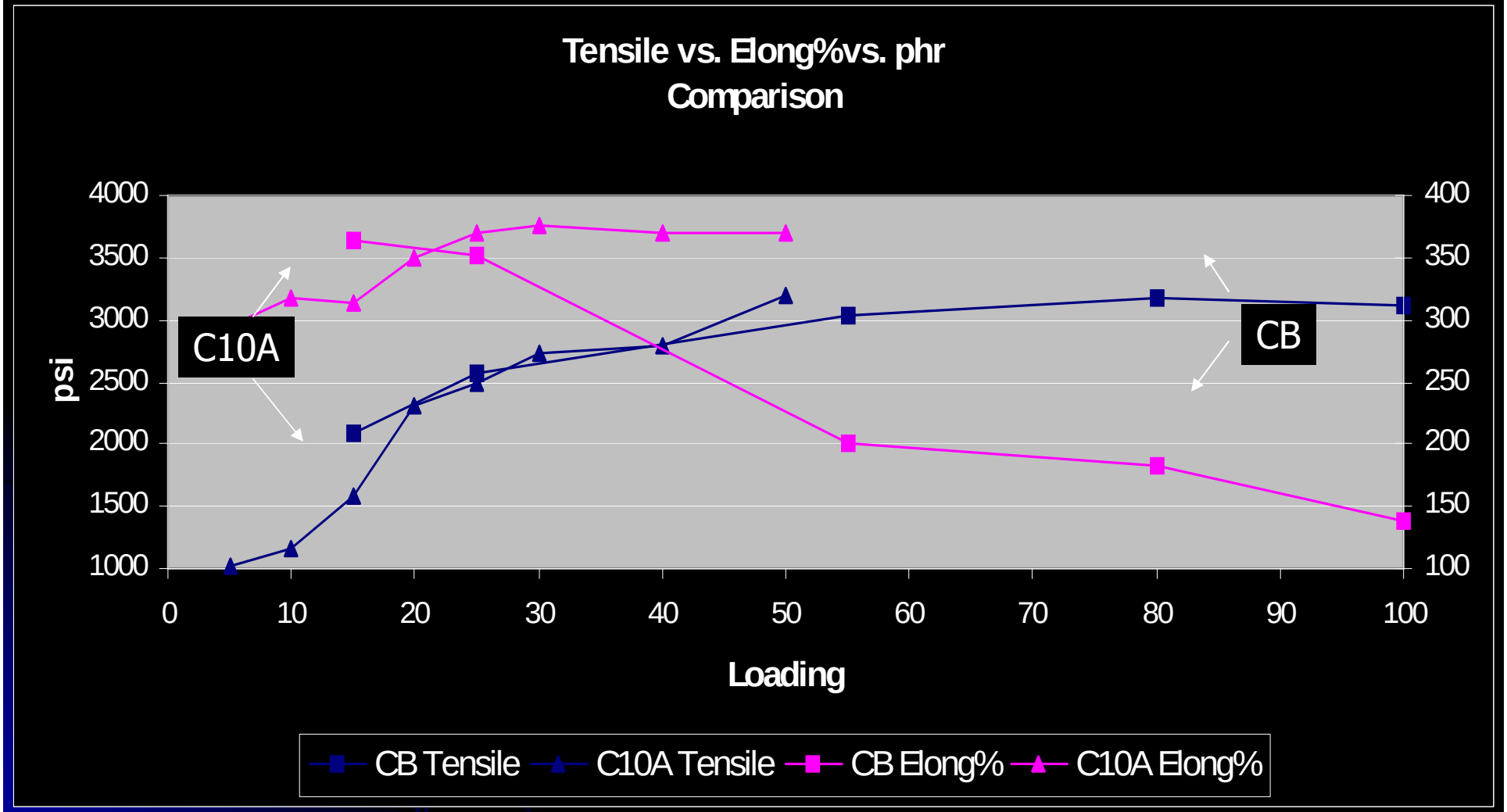
LOW DENSITY SHEET MOLDING COMPOUND PERFORMANCE

Twardowska et. al., Composites 2005

	Steel	SMC (control)	Nano-SMC
Tensile Strength, MPa	331	65 – 90	98
Tensile Modulus, GPa	207	10-12.5	9.7
Specific Gravity	7.86	1.8 – 2.0	1.45

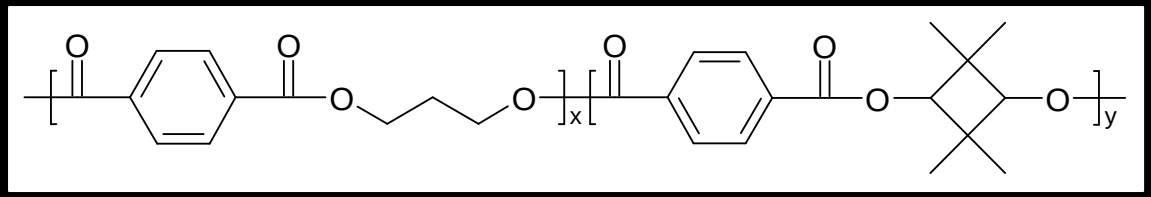
NANOCOMPOSITE PERFORMANCE IN NITRILE RUBBER

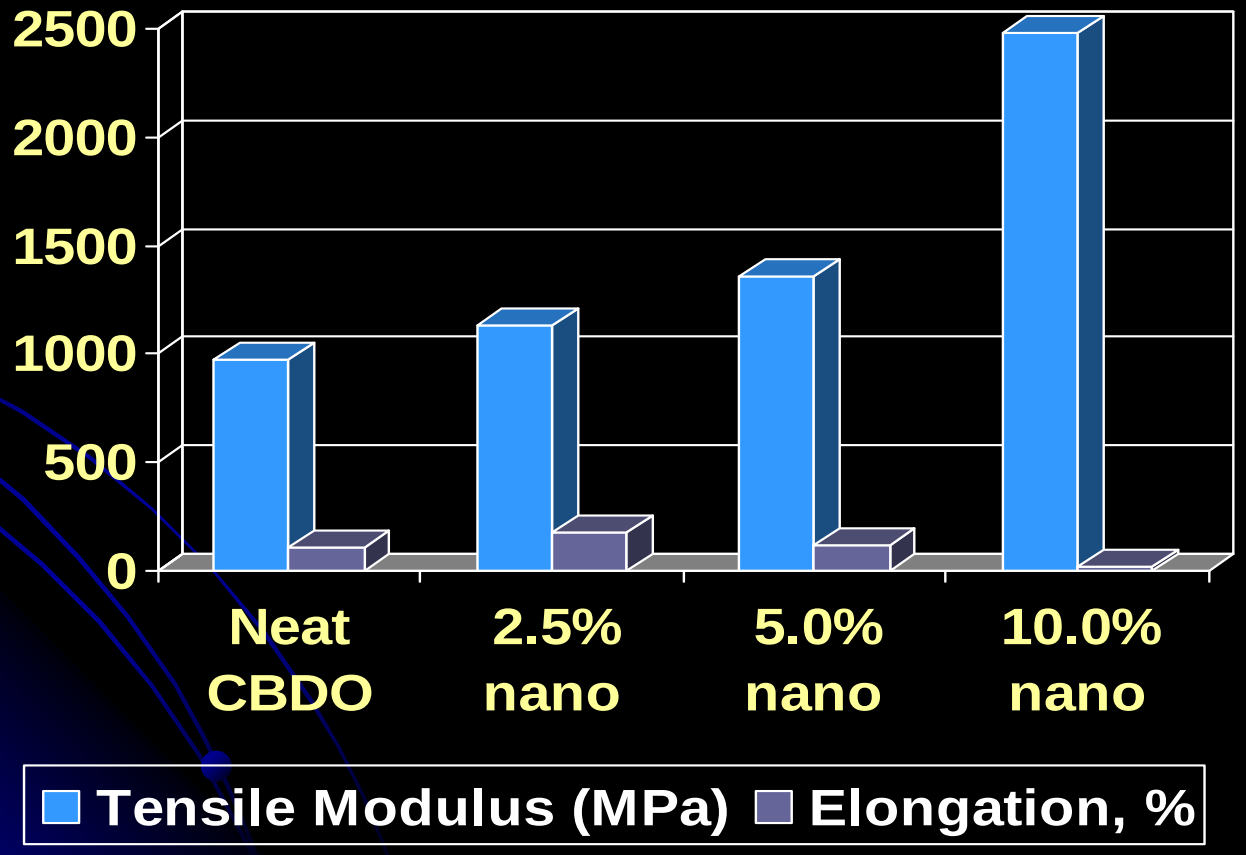
CLOIS POWELL, CLOISITE® NANOCLAY, SOUTHERN CLAY PRODUCTS



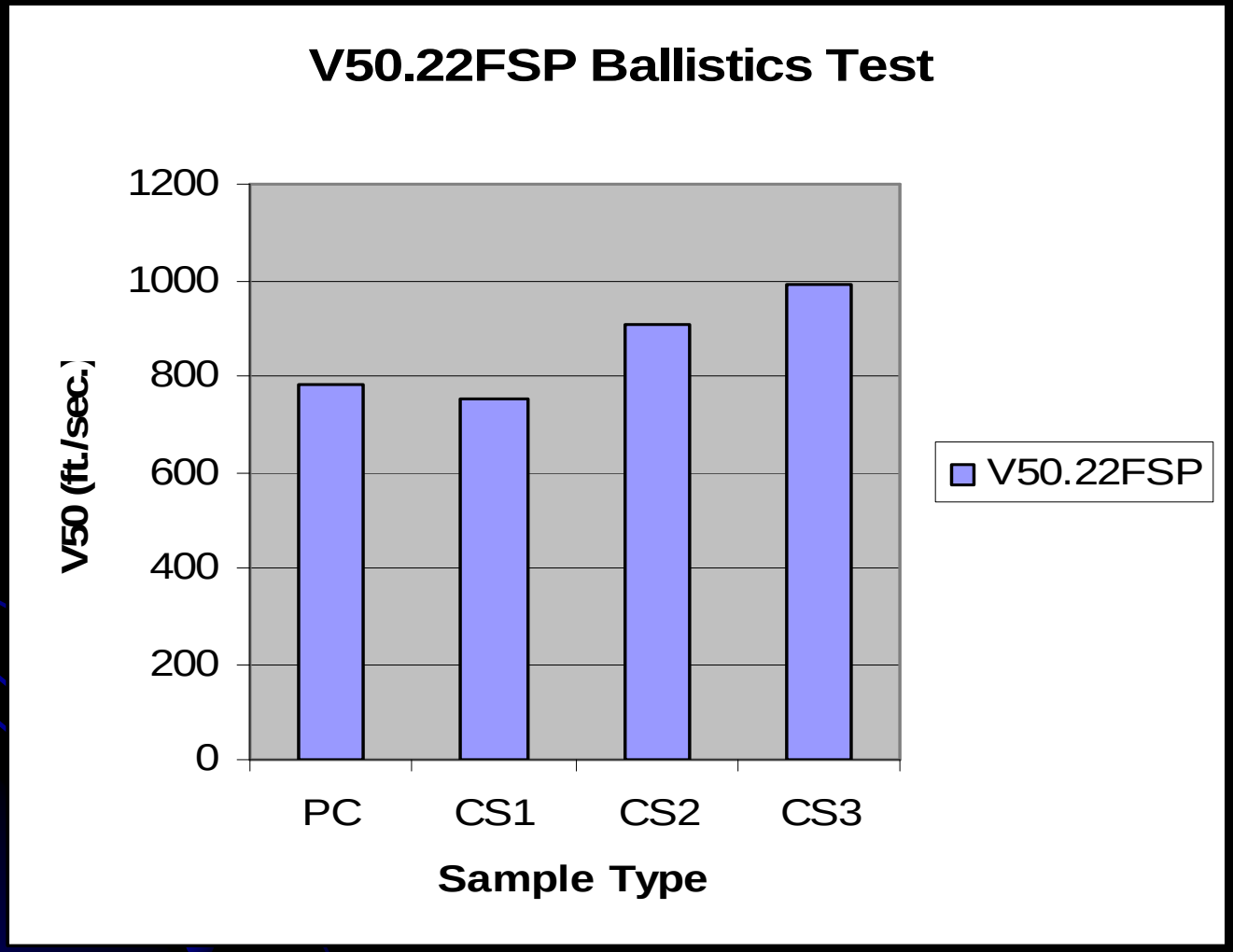
TENSILE PROPERTIES OF CBDO COPOLYESTER NANOCOMPOSITES

BEALL ET. AL., TEXAS STATE UNIVERSITY





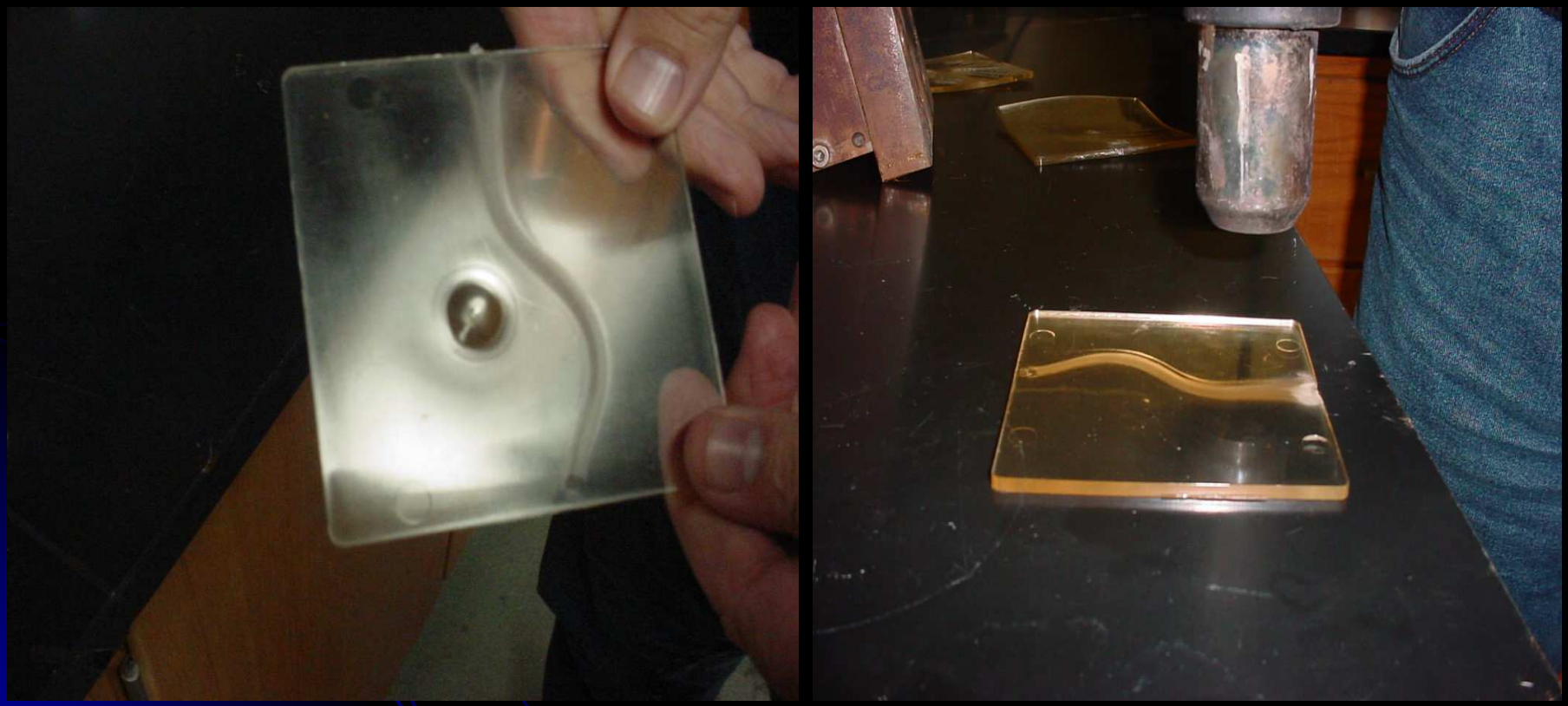
COMPSARISON OF BALLISTIC'S GRADE PC AND CBDO COPOLYESTER



CS1 and CS2 were compression molded
CS3 was extrusion sheet molded

SHAPE MEMORY OF CBDO NANOCOMPSITES

SELF-HEALING OF CBDB COPOLYESTER NANOCOMPOSITES



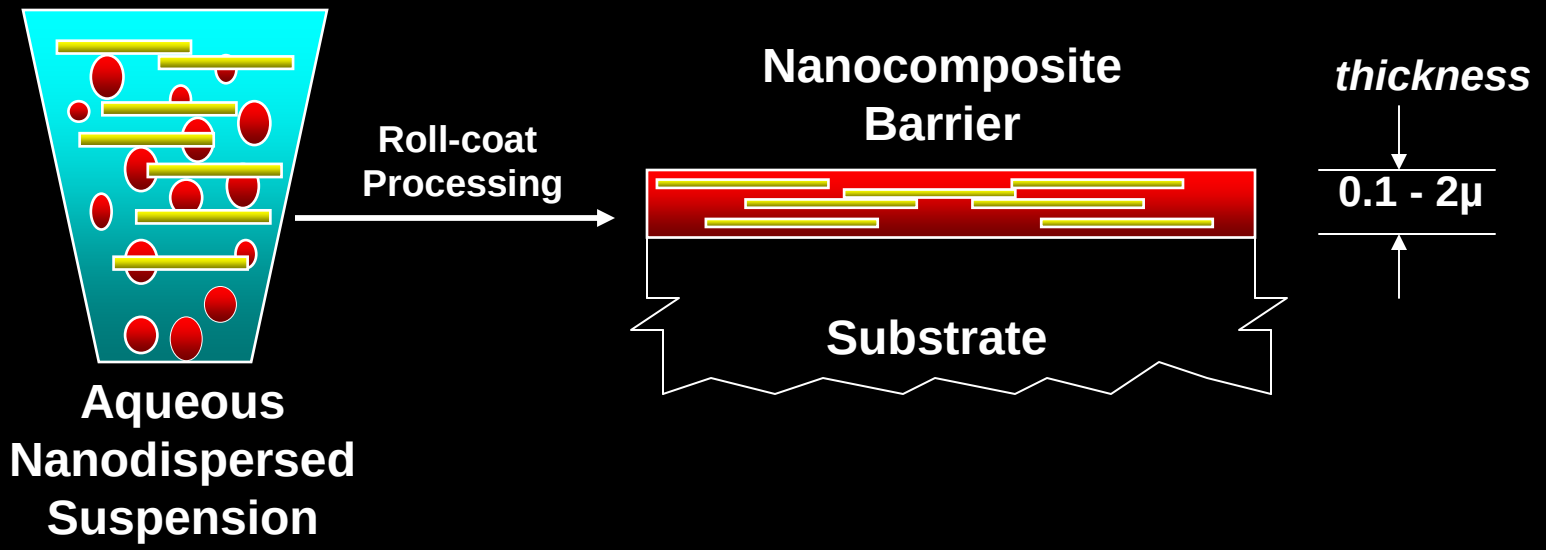
II. BARRIER PROPERTIES OF NANOCOMPOSITES

NANO-NYLON BARRIER TECHNOLOGY

Property	Units	MXD6	Imperm* 103
OTR (23°C, 60%RH)	cc·mm / m^2·day·atm	0.09	0.02
CO_2TR (23°C, 60%RH)	cc·mm / m^2·day·atm	.30	0.15
WVTR (40°C, 90%RH)	g·mm / m^2·day·atm	1.36	0.58

* Developed by an alliance with Nanocor Inc. and Mitsubishi Gas Chemical

NANOLOK™ TECHNOLOGY PLATFORM



- Clay platelets (▬) 1-3 nanometers x 0.3-10μ are dispersed in a water-based resin system (◪).

- Finished coating contains 100s of platelets per micron of coating thickness. Platelets form a tortuous path for gas (O_2, etc.) diffusion. 30-60,000X barrier improvement.

NANOCOMPOSITE BARRIER COATING SYSTEMS

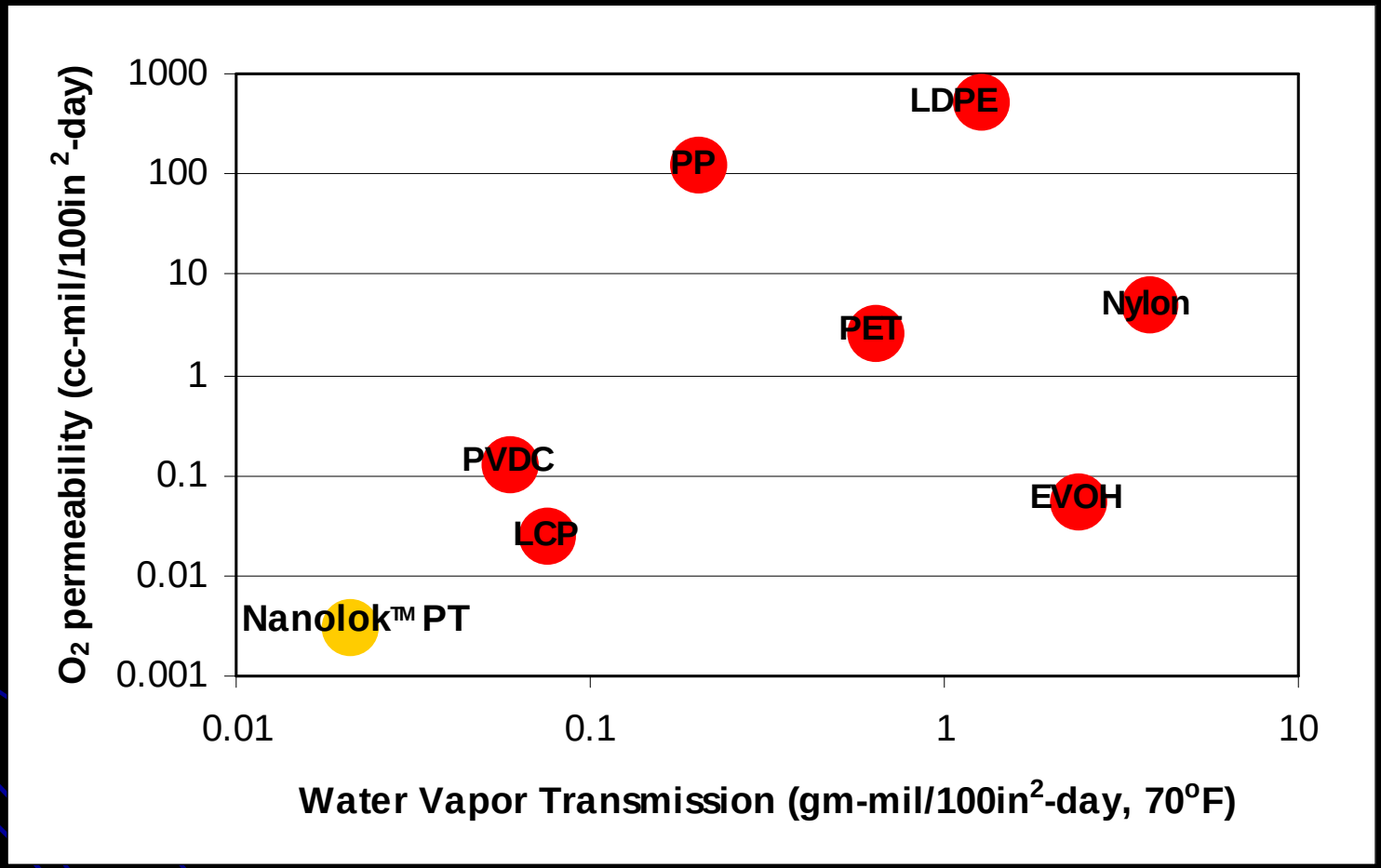
Polymer	Target Applications	Key secondary Properties	Current Status
Butyl	Tires, sport balls,	Flexibility, rubber processing	commercial
Chloroprene	Gloves, rubber hoses	Flexibility, flame resistance, oil resistance	Customer sampling
Nitrile	Gloves, rubber hose, bicycle tubes	Flexibility, oil resistance,	Customer sampling
EPDM	Bicycle tubes, industrial	Flexibility, environmental stability	Limited sampling
Polyester	Rigid and Flex packaging	Transparency, PET and PP adhesion	Customer sampling
Acrylic	Rigid and Flex packaging	Transparency, PP adhesion, chemical resistance	Customer sampling

SUPERIOR O_2 BARRIER

Relative Oxygen Barrier Effectiveness

Least

Most



Nanolok™ PT is a trademark of InMat, Inc.;
it is coating comprised of nano-dispersed silicate
In polyester resin.

III. ENHANCED FLAME RETARDANCY OF NANOCOMPOSITES

EVA / $Mg(OH)_2$ / Nanoclay Compositions and Flame Ratings

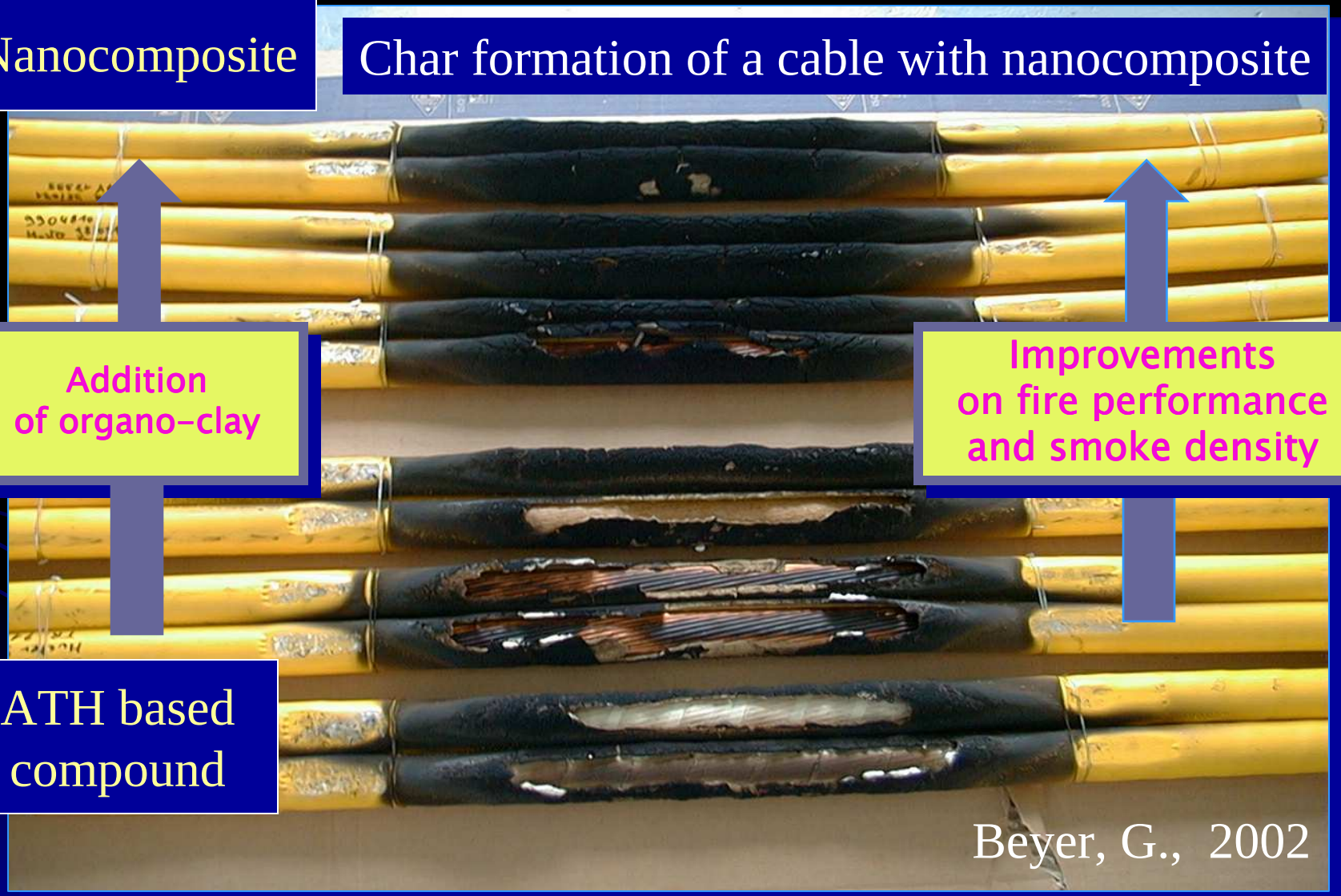
www.Nanocor.com

EVA, wt%	40	45	42	50	47
$Mg(OH)_2$ (wt%)	60	55	55	50	50
Nanomer (wt%)	0	0	3	0	3
UL94 rating	V-0	Fail	V-0	Fail	V-0

NANOCOMPOSITE POWER CABLE

Nanocomposite

Char formation of a cable with nanocomposite



Addition of organo-clay

Improvements on fire performance and smoke density

ATH based compound

Beyer, G., 2002

FLAME RETARDANT NANOCOMPOSITES WITH LAYER DOUBLE HYDROXIDES (LDH)

D'Souza et. al., University North Texas

- LDH are synthetic anionic clays similar to brucite, $Mg(OH)_2$
- Conventionally synthesized LDH's are strongly hydrophilic materials, either amorphous or microcrystalline
- Adjacent layers are tightly bound to each other

FLAME RETARDANT PROPERTIES OF DIFFERENT LDH FILLERS (60 wt%) in EVA

Evans et. al, Chem. Comm., 2006, p. 490

Filler	LOI (%)	Smoke Density
None	21.3	187.4
Mg/Al-CO3	30.0	133.1
Mg/Al-borate	29.2	102.9

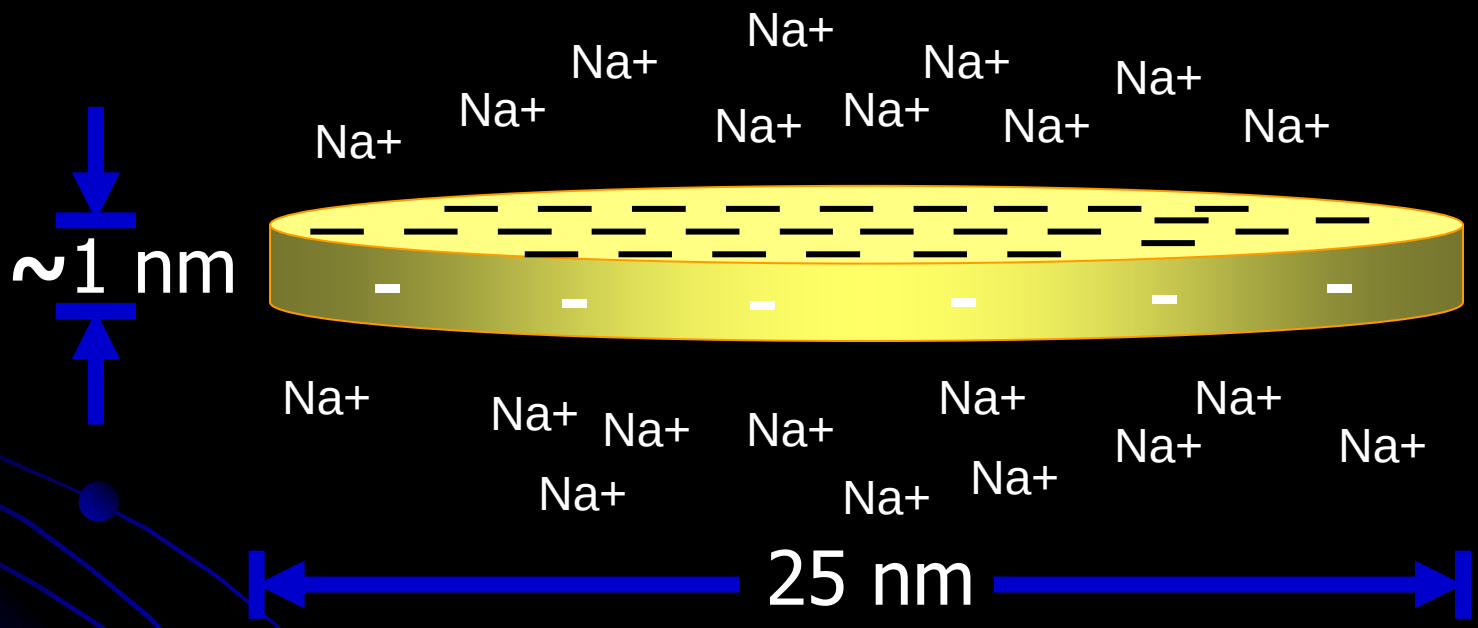
IV. RHEOLOGY CONTROL

LAPONITE® SYNTHETIC SILICATES

- Inorganic Metal Silicate
  - Crystalline White Powder
  - Structure similar to Nature Smectite Clays
- Unique aqueous system character derived from particle size & particle-particle and/or particle-organics interactions
- Synthetic consistency and purity

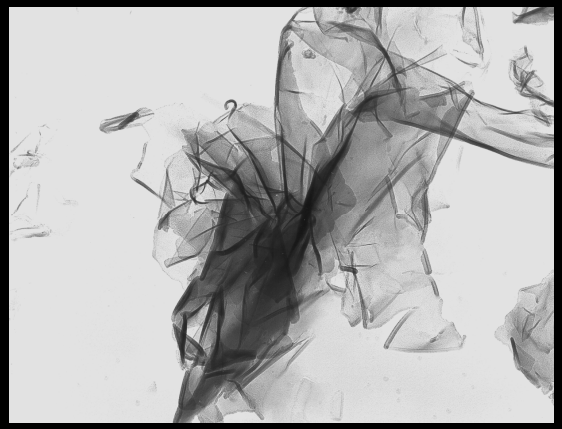
Critical for a reactant!

PRIMARY SYNTHETIC SILICATE PLATELET



Reactivity at the edge by way of the siloxy anion

Isomorphic Structures

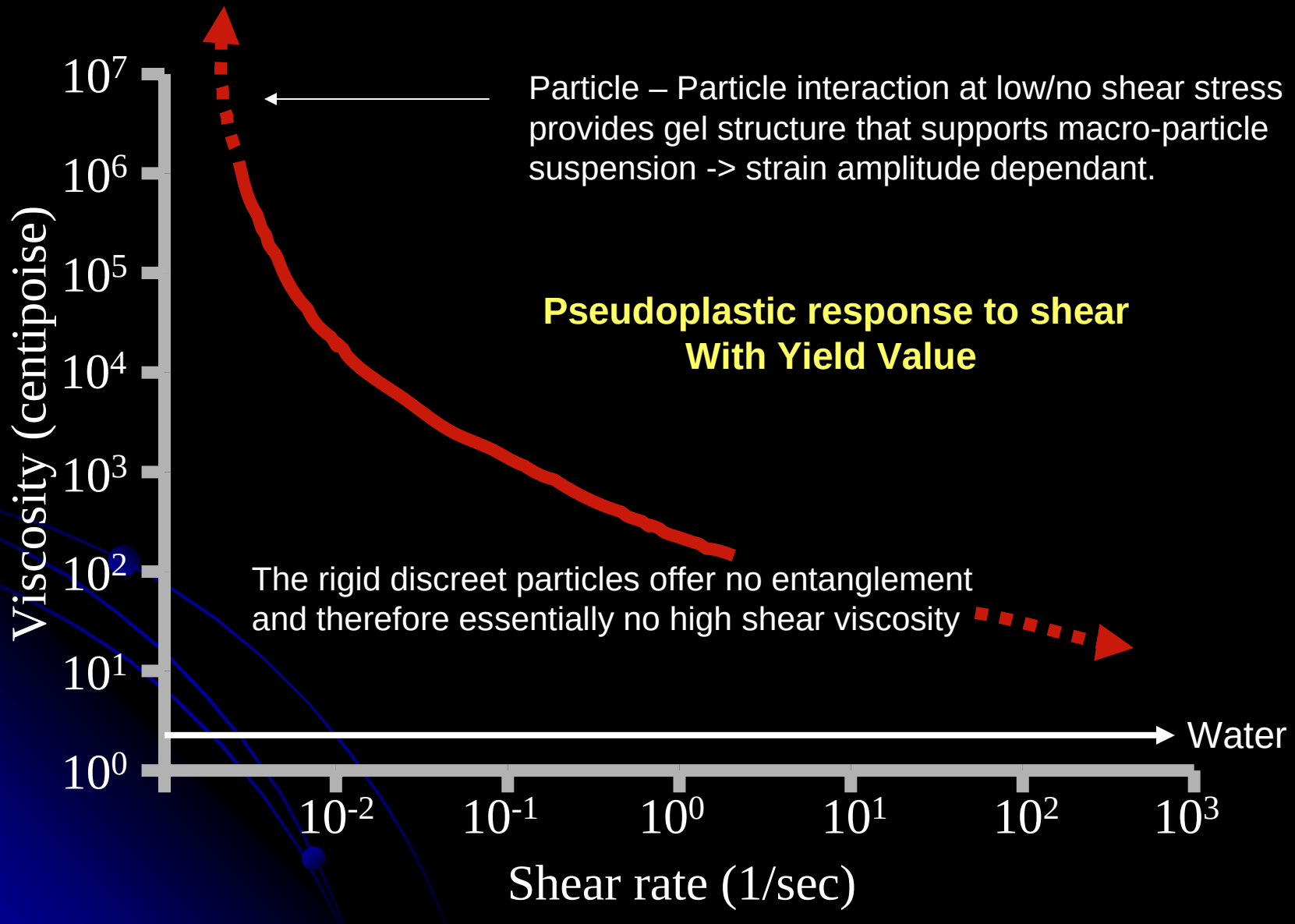


Montmorillonite

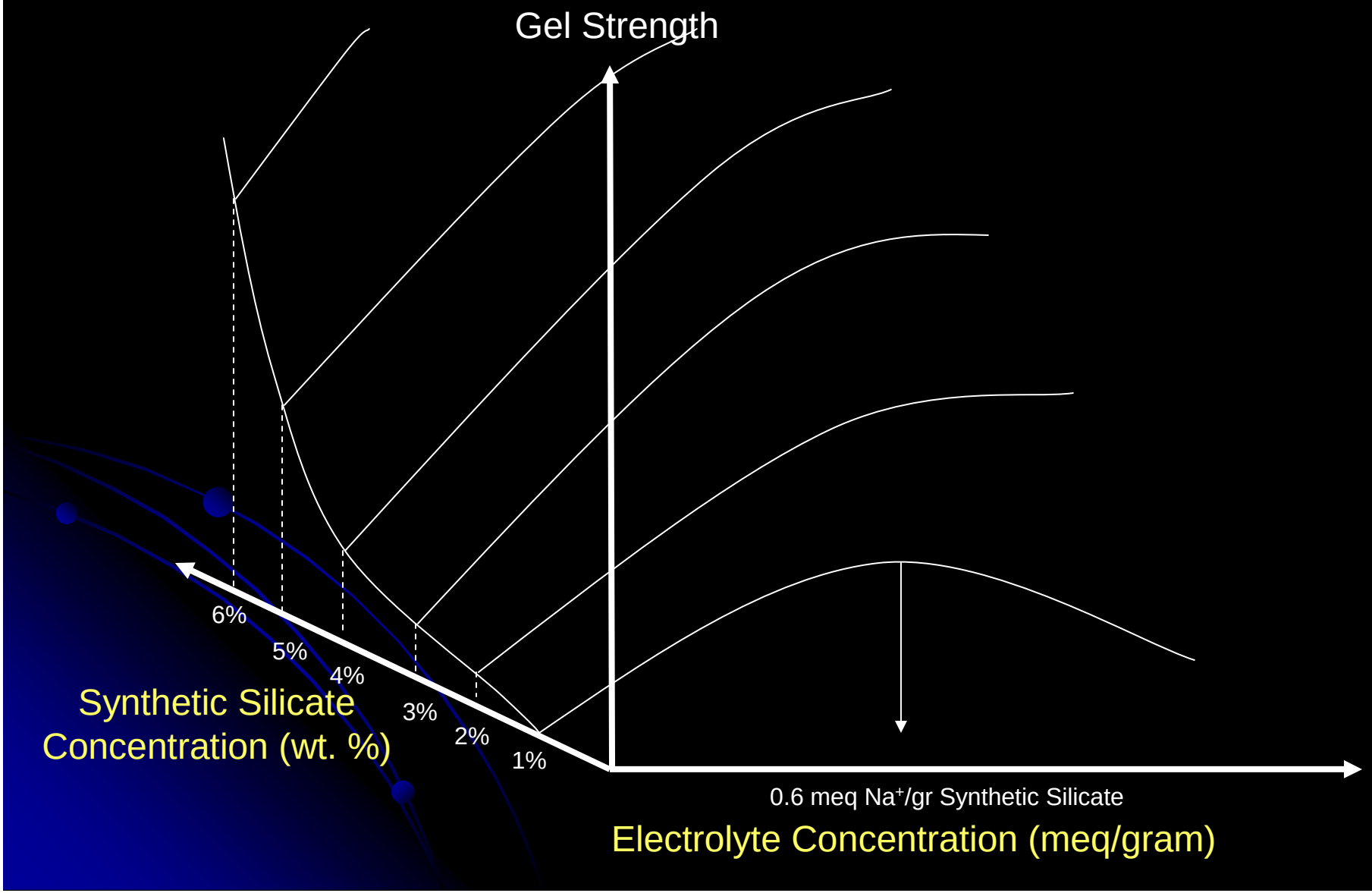
Synthetic Silicate

Hectorite

Rheological Behavior



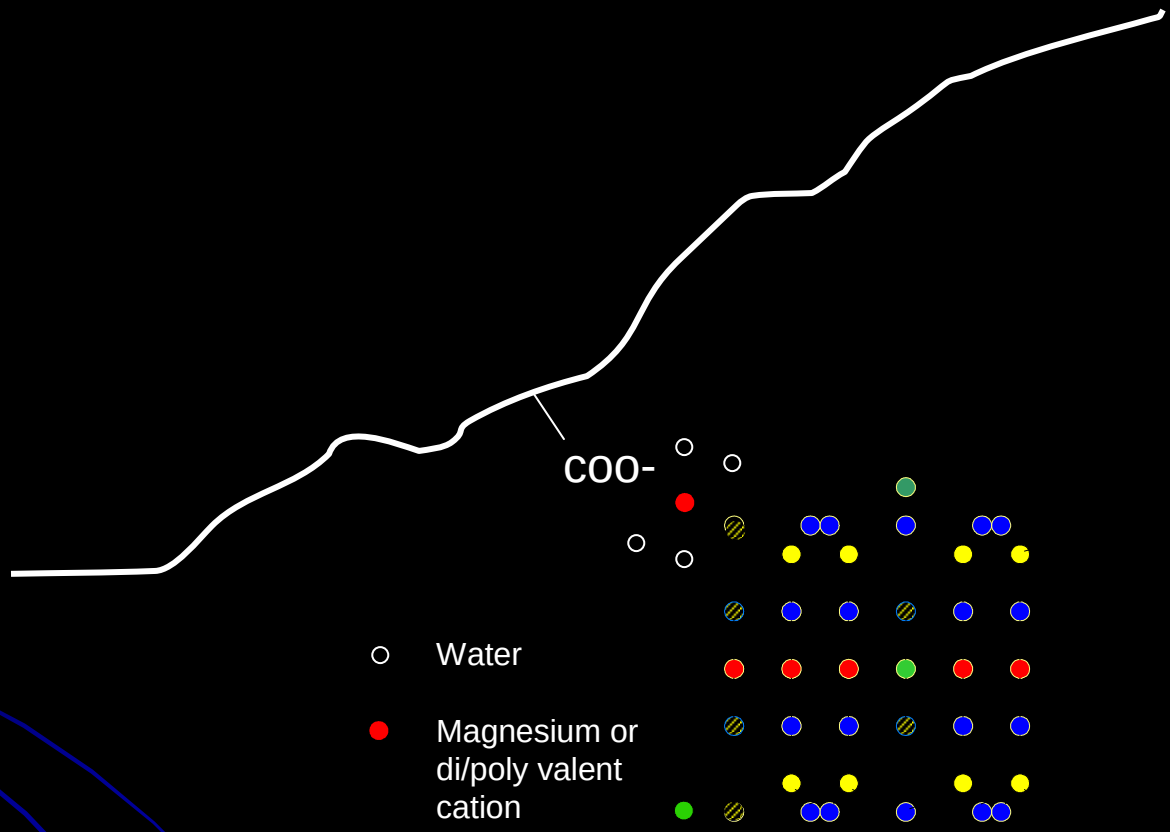
SYNTHETIC SILICATE RHEOLOGY - FUNCTION OF CONCENTRATION AND ELECTROLYTE LEVEL



SYNERGISTIC POLYMERS WITH SYNTHECTIC SILICATES

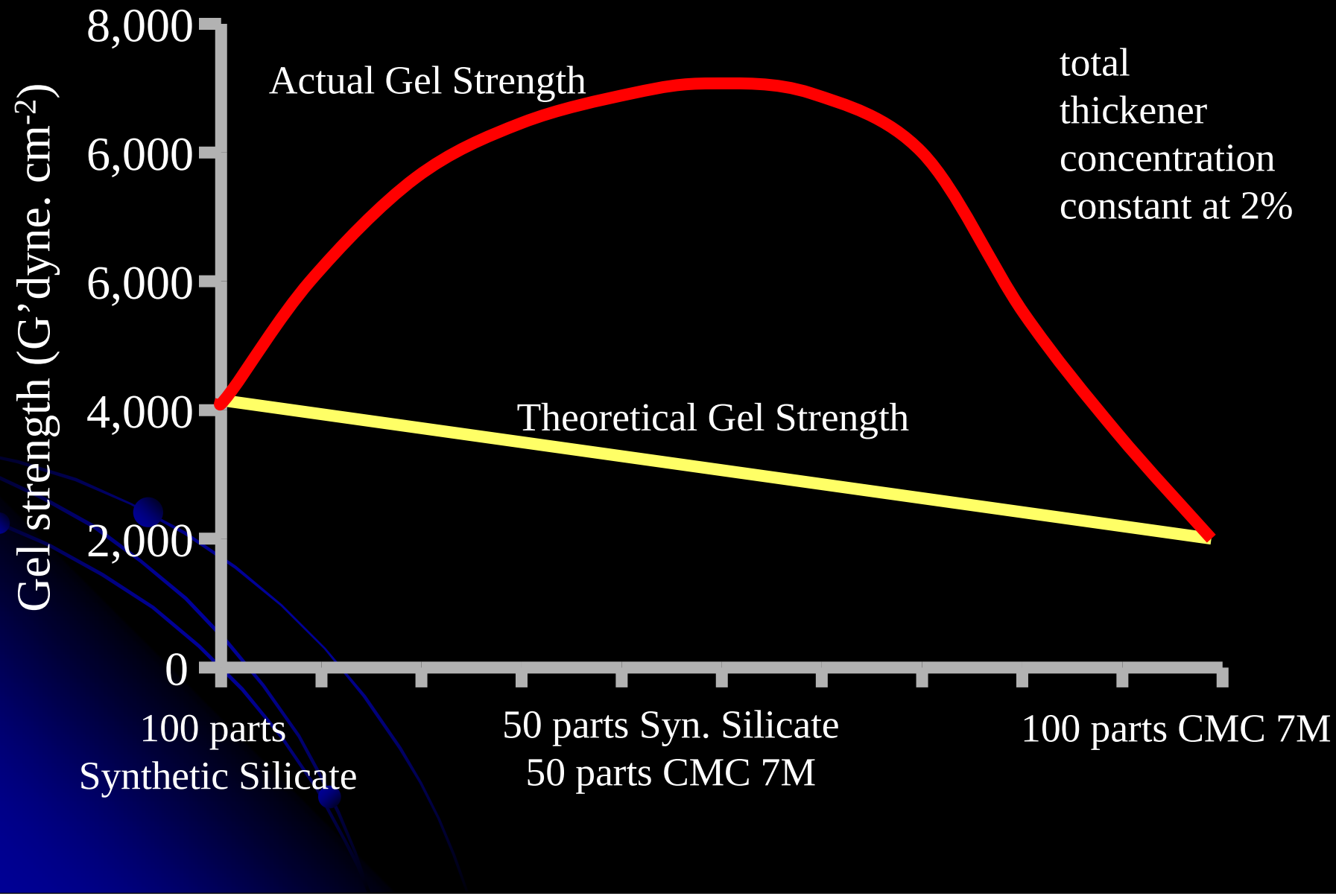
- Polymer must be anionic
  - Ionic polymers chain extend in solution
  - Non-ionics are entangled “ball” – not useful
- Molecular Weight is critical
  - High MW yields more interaction
- pH
  - No lower than pH 7
- Electrolyte in solution
  - Some is needed to suppress the anionic – anionic repulsion
- Divalent Cations
  - “Fortuitous” magnesium from Synthetic Silicate

PLATELET – POLYMER INTERACTION

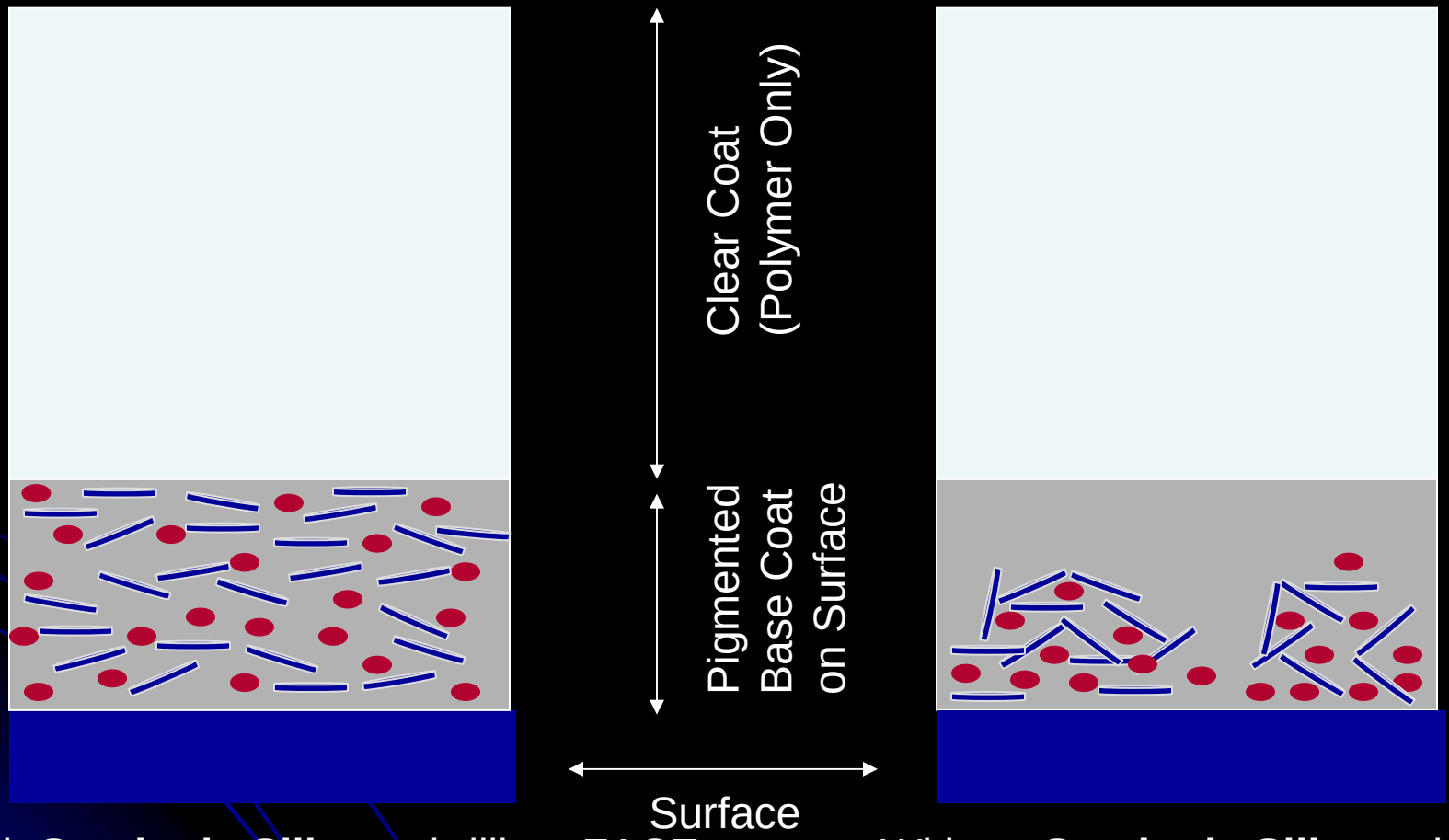


Divalent Cation “Salt” Bridge

SYNERGISTIC VISCOSITY w/ CARBOXY POLYMER



PIGMENT ORIENTATION & DISTRIBUTION CONTROL



With **Synthetic Silicate**, brilliant FACE with dramatic glancing angle FLOP (maximize the pigments potential)

Without **Synthetic Silicate**, less Dramatic reflection from both normal and glancing angle illumination

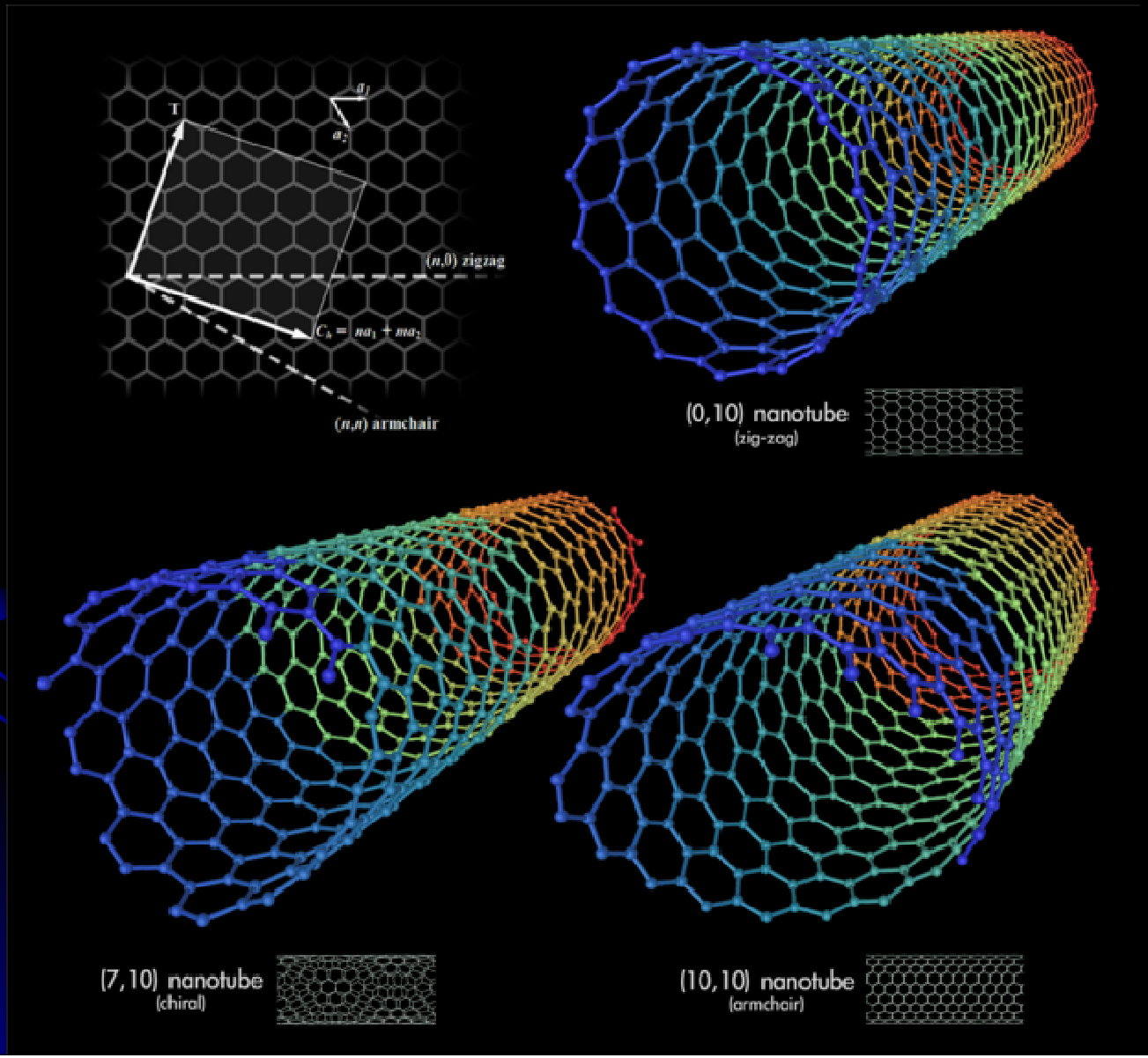
AUTOMOTIVE OEM BASE COATS

Additive for Water Borne Automotive OEM Base (Pigmented) Coat

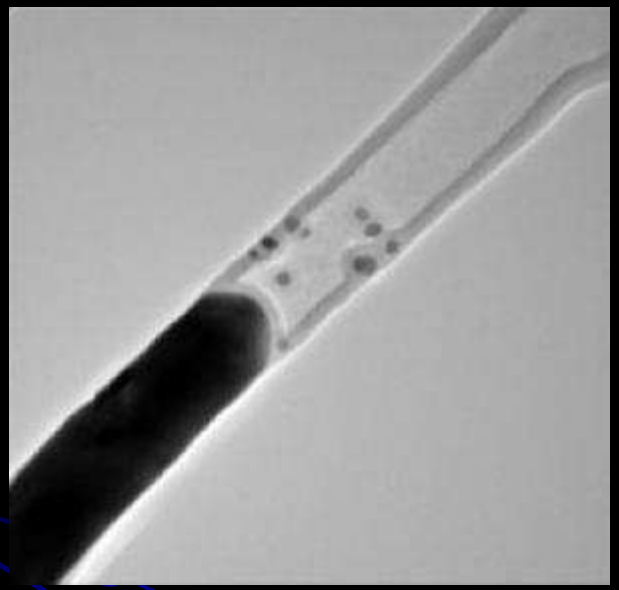
- Uniform dispersion of pigment
- Plate pigment “flip flop” control
- Rheology to allow for spray-ability with superior “edge effect” control
- Excellent consistency
- No interference of color or clarity
- UV and oxidatively stable

V. CONDUCTIVITY

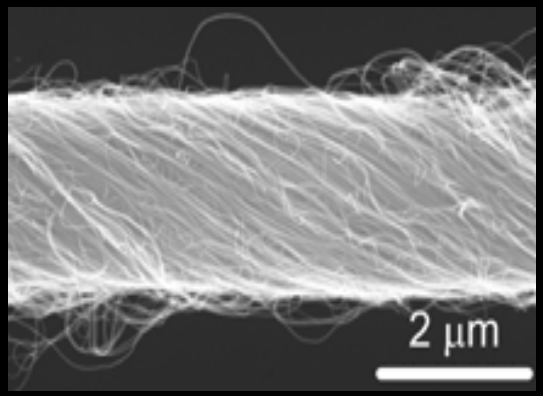
STRUCTURES OF SINGLE WALLED CARBON NANOTUBES (SWCNT)



POTENTIAL APPLICATIONS FOR CNT



Junction between carbon nanotube and gold nanowire; Computer chips, displays, sensors. RPI, January 11, 2007



Carbon nanotube yarn may be used As powerful actuators; exert 100x Force/area of natural muscle. Technology Review, Dec. 8, 2006

BENEFITS OF NANOCOMPOSITES

- **ENHANCED MECHANICAL PROPERTIES**
  - Increased modulus
  - Better impact than highly filled systems
  - Low density formulations
- **IMPROVED BARRIER**
  - Gas
  - Chemical
  - UV
- **SYNERGISTIC FR SYSTEMS**
  - Increased char
  - Reduced smoke
- **IMPROVED RHEOLOGY**
  - Good flow and leveling
  - Pigment suspension stability
- **CONDUCTIVITY**
  - Can tailor conductivity level based upon need of application
  - High aspect ratios give enhanced strength and stiffness

THANK YOU


RESEARCH & DEVELOPMENT
Nanopolymers
Now is not the time to go 'Nano-budgetary' on this.