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2009 Symposium on Nanomaterials for Flexible Packaging

Nanocomposite Materials for Packaging Film Applications

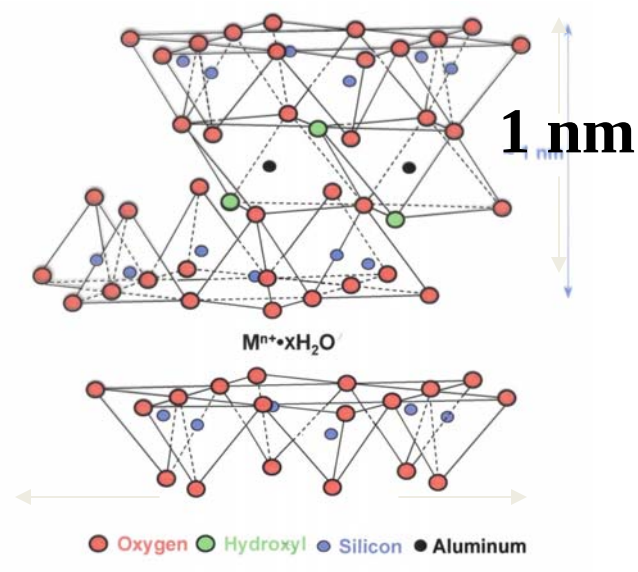
Tie Lan
General Manager
Nanocor, Inc.

Outline

- Concept of Nanocomposites
- Manufacturing and Processing Technologies
- Enhanced Barrier Properties
- Applications in Packaging

Nanoclay As Passive Barrier materials

Montmorillonite



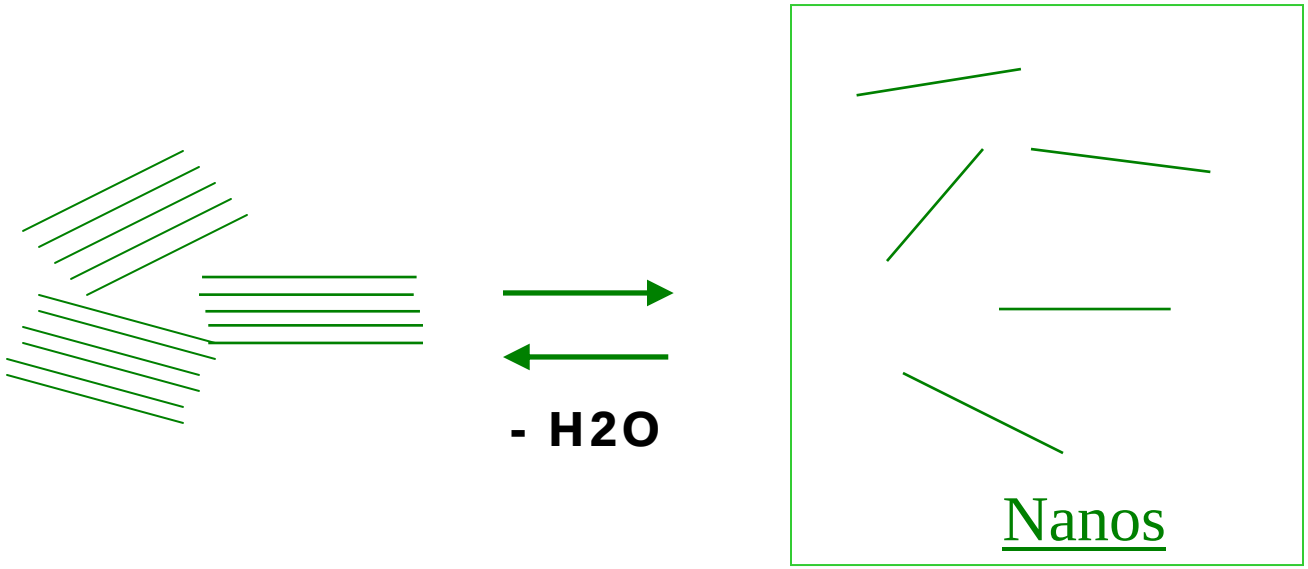
100 to 500 nm

High aspect ratio impermeable silicate layers, <u>200-300</u>

Chemical reactivity for inner surface modification

Nanoclay platelets are one-ten thousandth the diameter of a human hair!!

Nanoclay

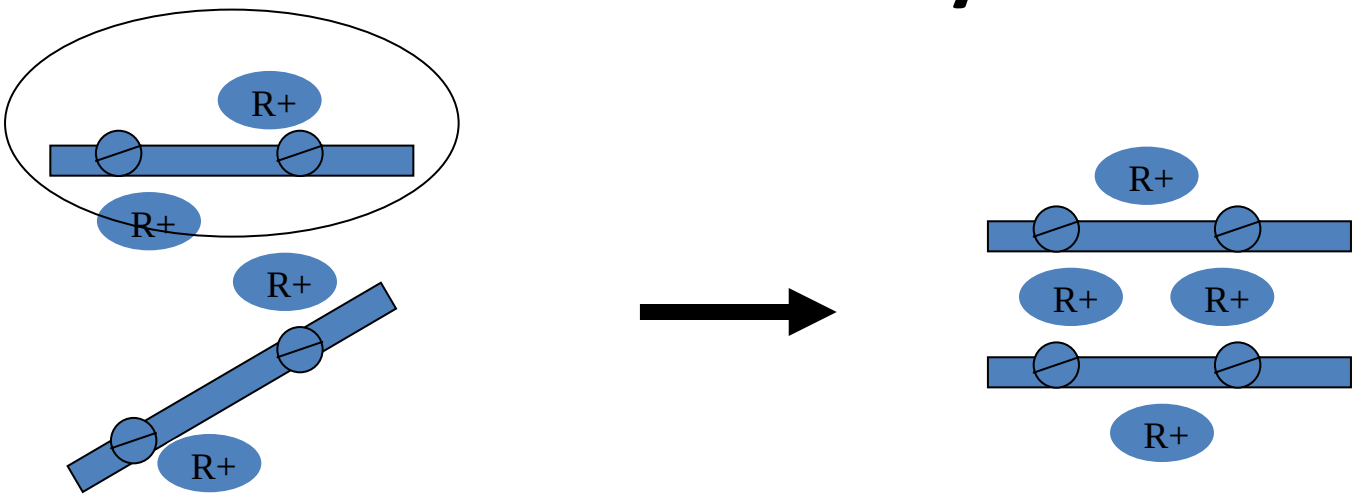


Na-montmorillonite

Water Dispersion

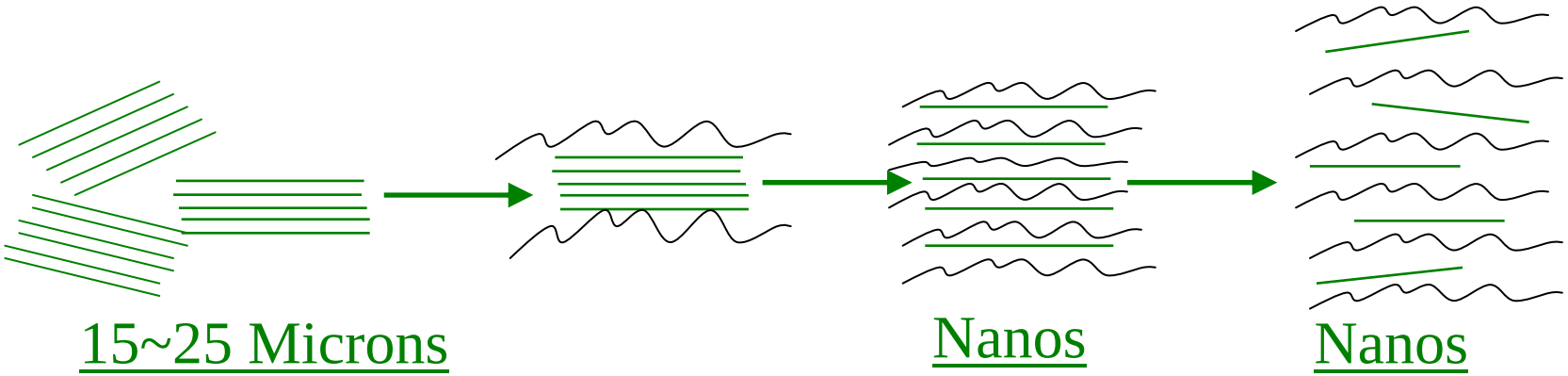
BEST DISPERSED NANOCLAY

Nanoclay



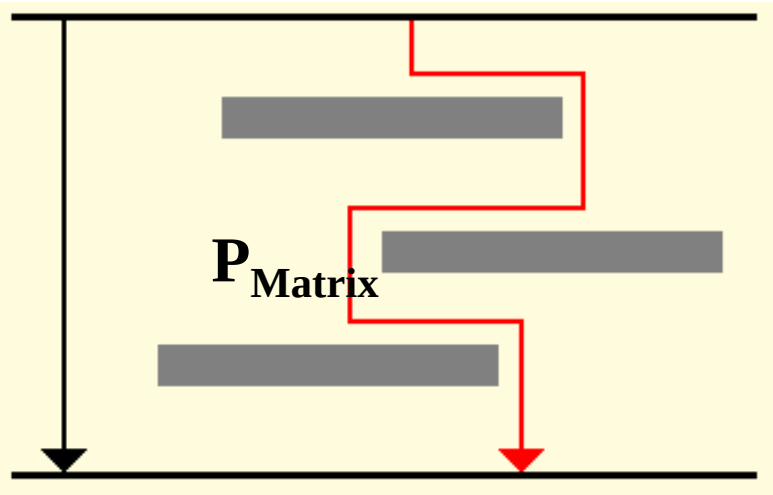
It is **<u>impossible</u>** to supply single layer nanoclay particles

Nanoclay



Resin Solvation Nanocomposite

Nanoclay: Barrier Enhancement

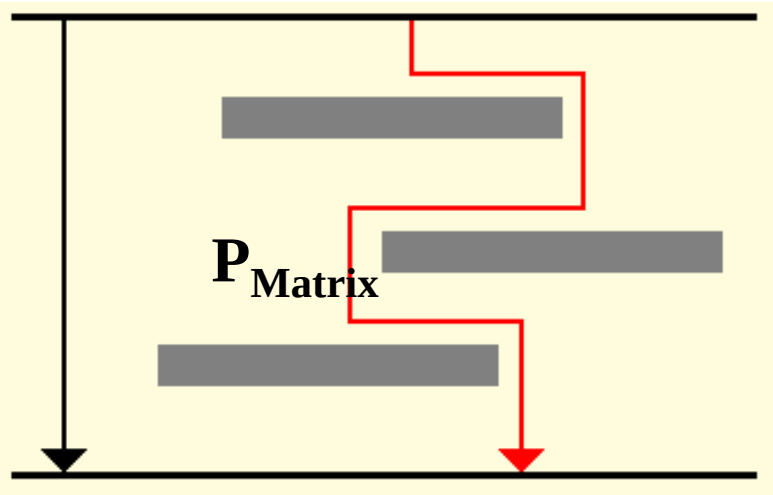


Clay Platelets Create Tortuous Path

$$P_{nanocomposite} = \frac{(\textit{Matrix Volume Fraction})*(P_{matrix})}{1 + (\textit{Clay Volume Fraction})*(\textit{Clay Aspect Ratio})/2}$$

L. E. Neilson, J. Macromol. Sci. (Chem.), A1(5), 929-942 (1967)

Nanoclay: Barrier Enhancement



What does it take to reduce 50% permeability?

Aspect ratio	Volume %
20	9%
200	1%
400	0.5%

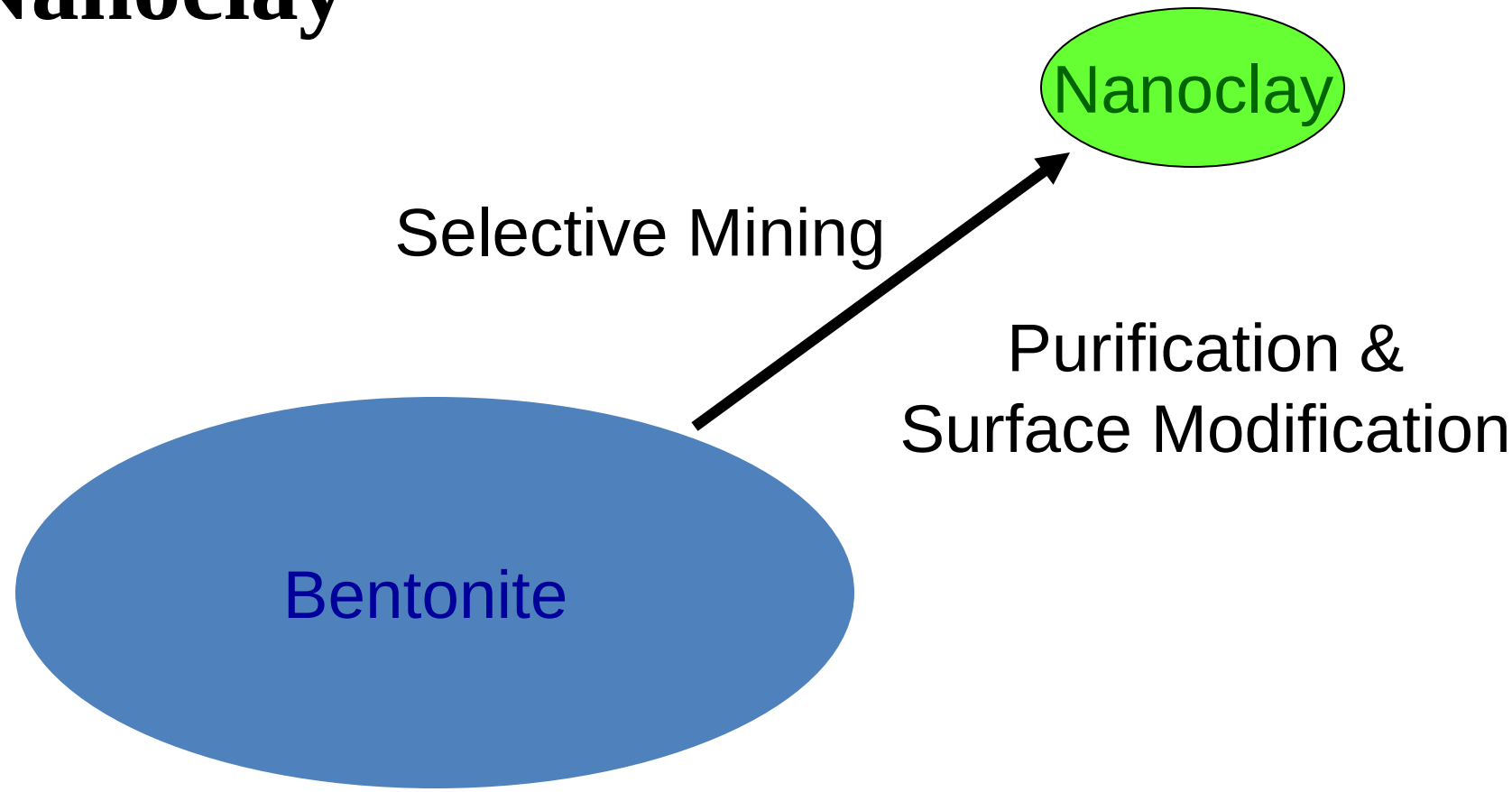
$$P_{nanocomposite} = \frac{(\textit{Matrix Volume Fraction})*(P_{matrix})}{1 + (\textit{Clay Volume Fraction})*(\textit{Clay Aspect Ratio})/2}$$

L. E. Neilson, J. Macromol. Sci. (Chem.), A1(5), 929-942 (1967)

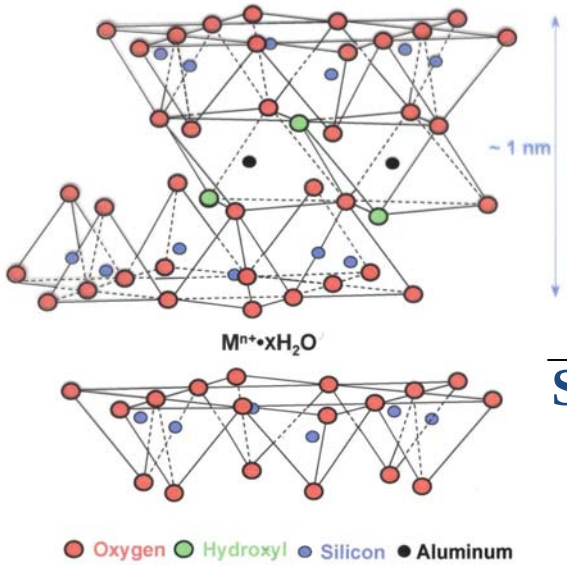
Nanocomposites

- **Low addition level of nanoclay enhances the barrier of the base resin**
- **Development from lab to pilot to production**

Nanoclay

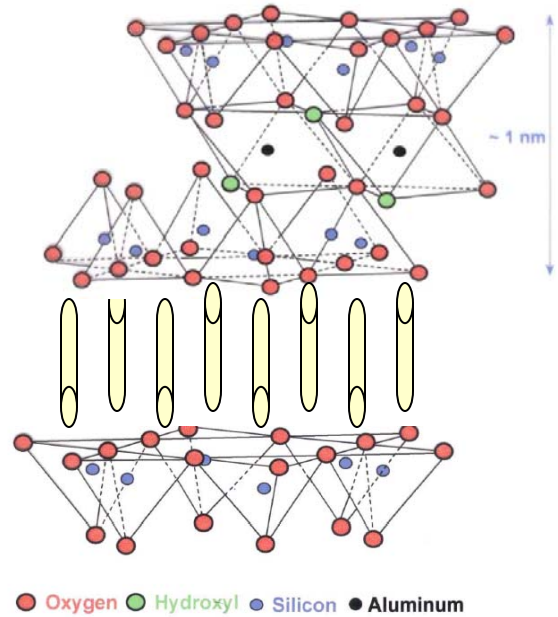

Nanoclay
Selective Mining
Purification &
Surface Modification
Bentonite

Nanomer® Formation



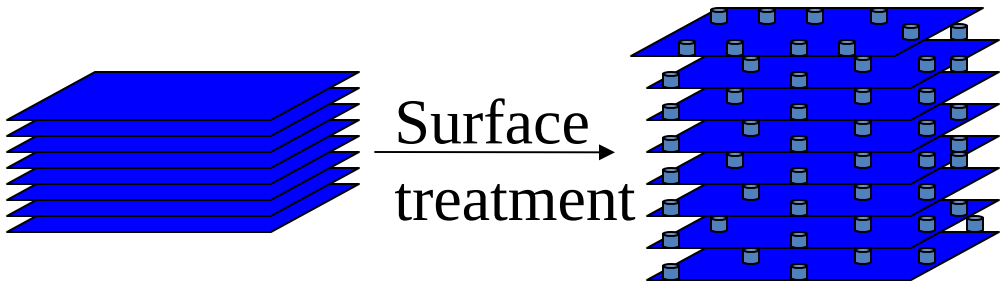
High Aspect Ratio

Surface Treatment



Hydrophilic

Hydrophobic

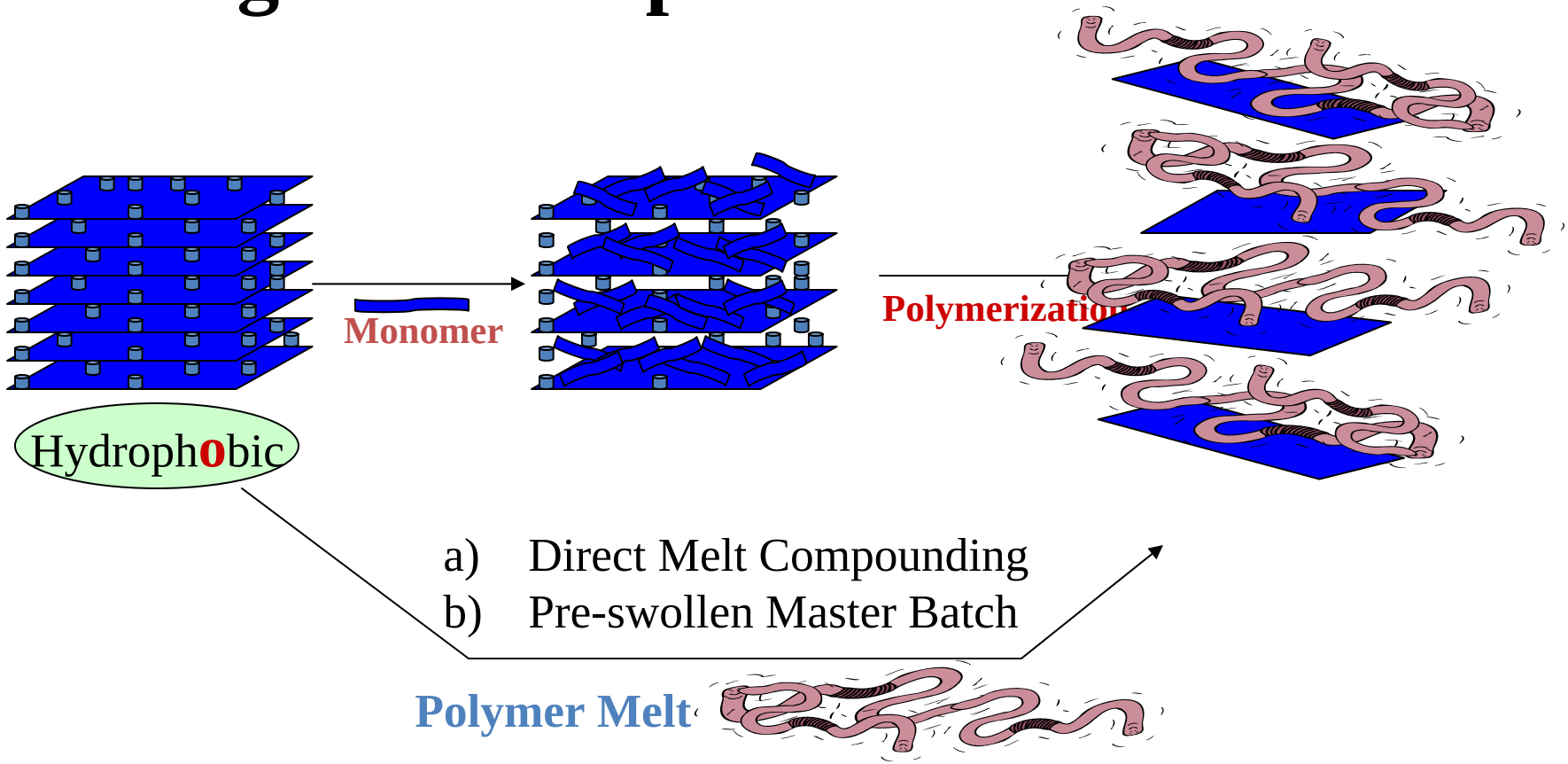


Requirement For Food Packaging

Regulatory Compliance of all materials/processes

- Montmorillonite is considered GRAS
  (Generally Recognized As Safe, 21CFR184.1155)
- Clay surface treatment agents have various FDA status.
- Migration of the surface modifier is the concern
- Minimize surface treatment is the key to obtain good regulatory status.
- Detailed information on package film structure, packed food, storage condition, pack conditions, etc...
- KH letter, FCN with FDA, etc....

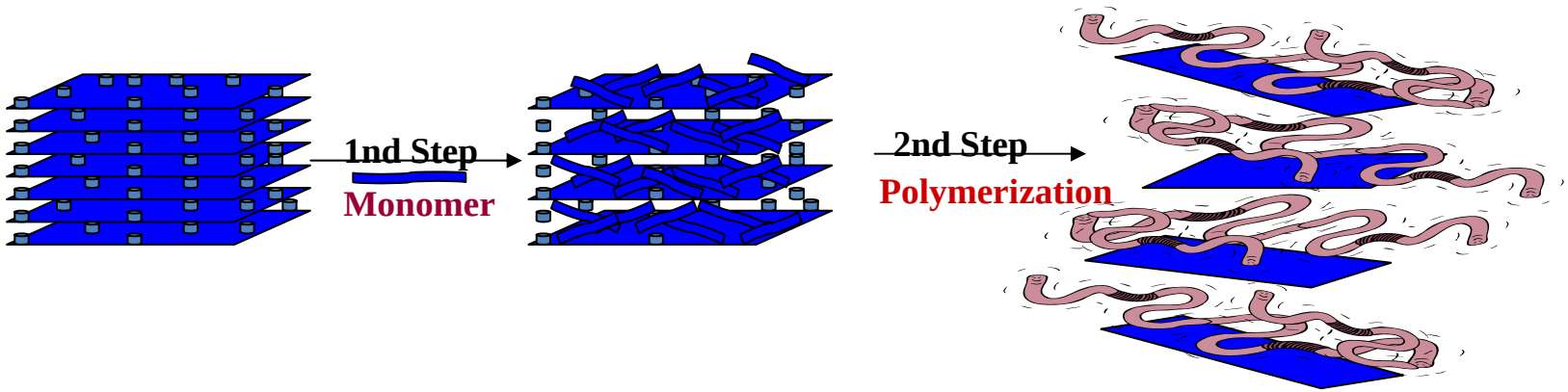
Making Nanocomposites



Nanomer® → **Nanocomposite**

Nanocomposite Formation

In Situ Polymerization



Monomer intercalation into clay inner layer regions

Anchor polymerization catalyst into the clay layer resin

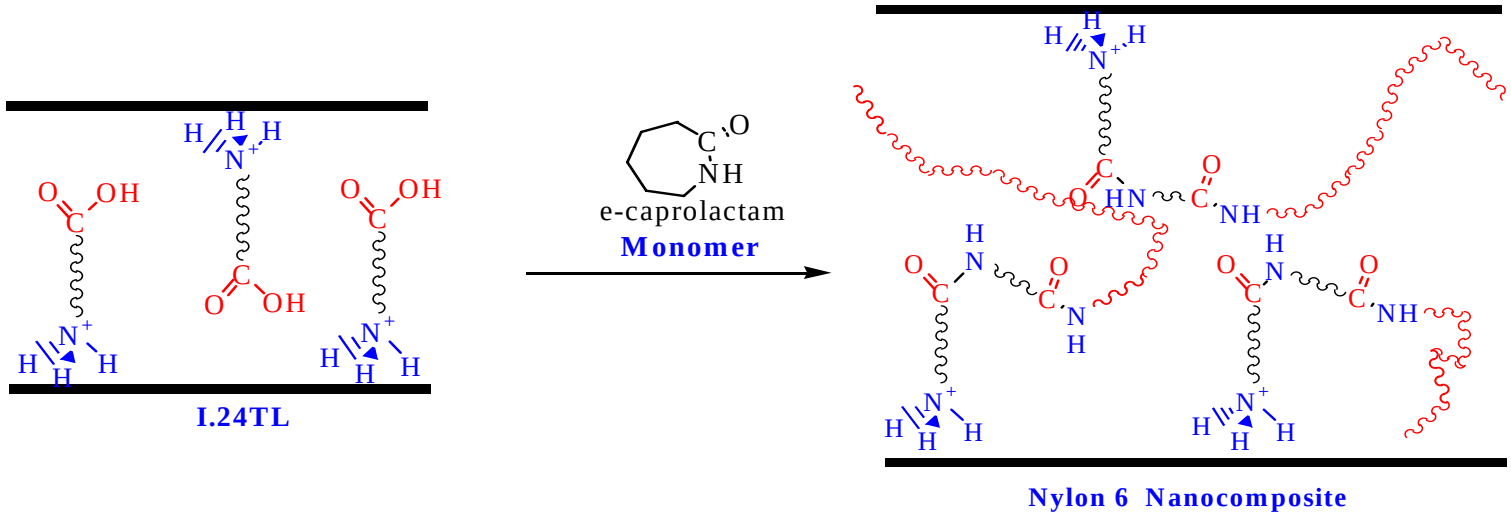
Initiate polymerization via heat or UV

PA6, epoxy, urethane, PP and PE

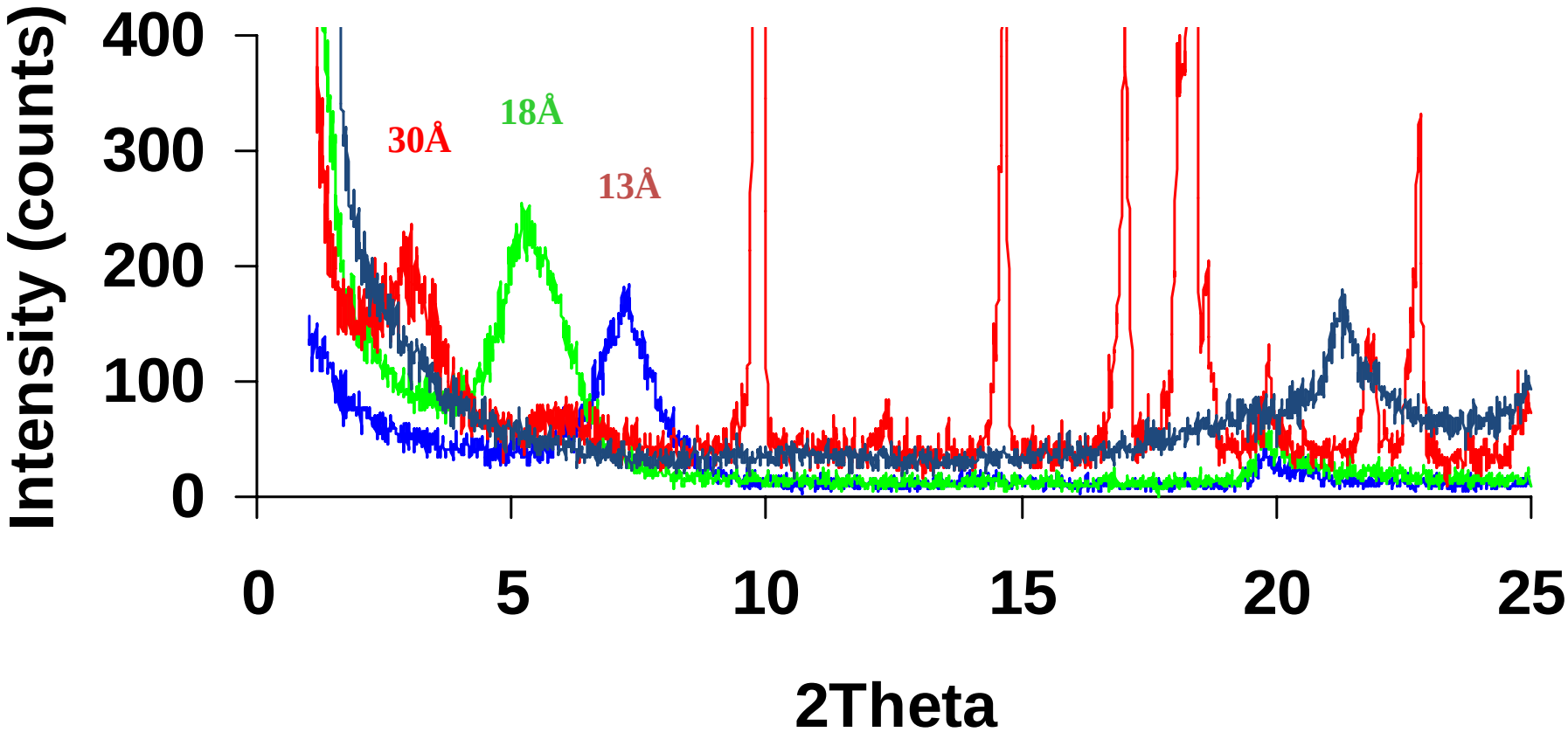
Nanocomposite Processing

In situ polymerization: Nano-PA6

- In situ polymerization process with patented technology
- No extractable surface modifiers
- FDA/EU approval status for direct food contact

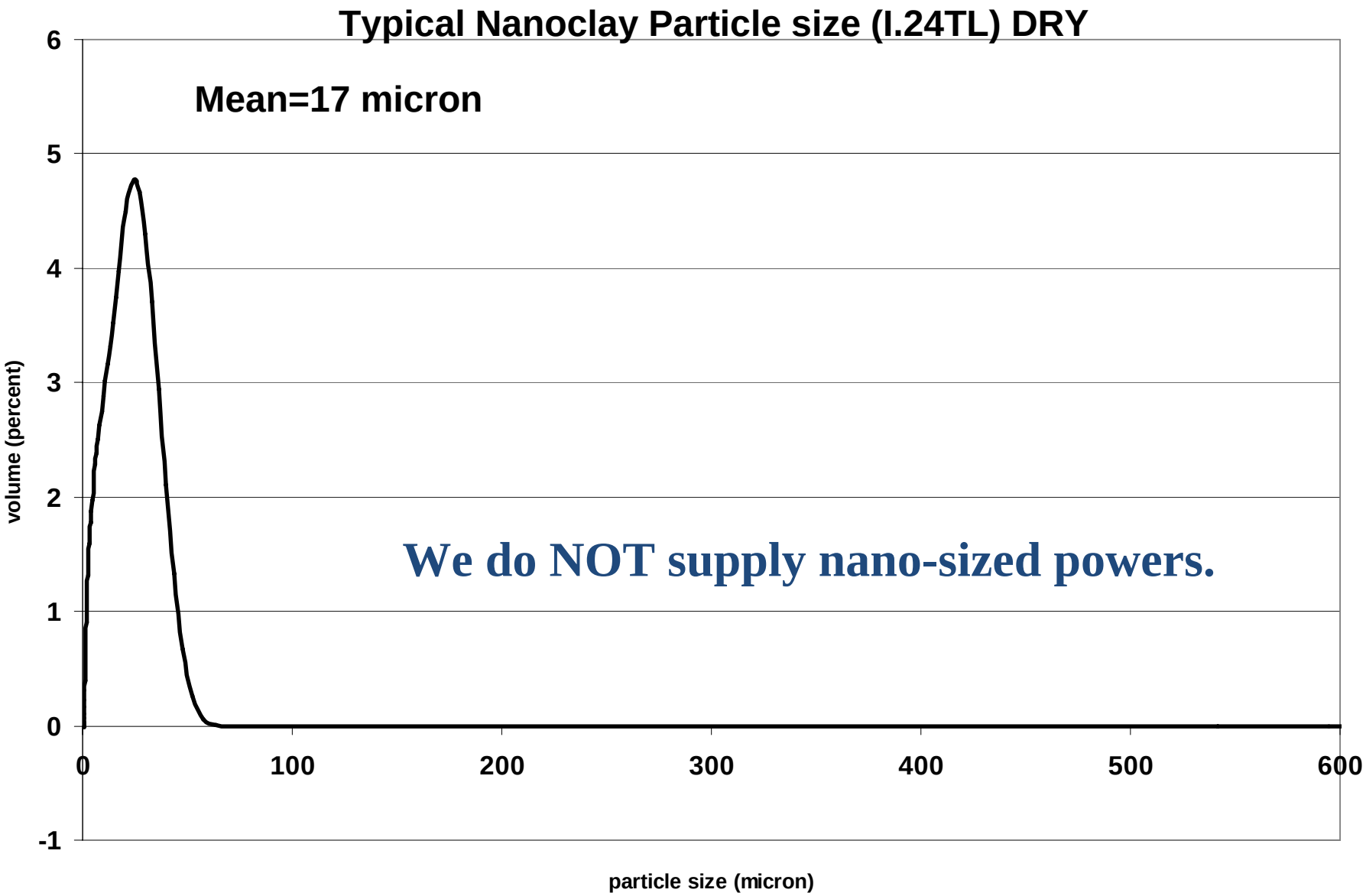


Nanoclay Phase Change in nano-PA6 Formation process

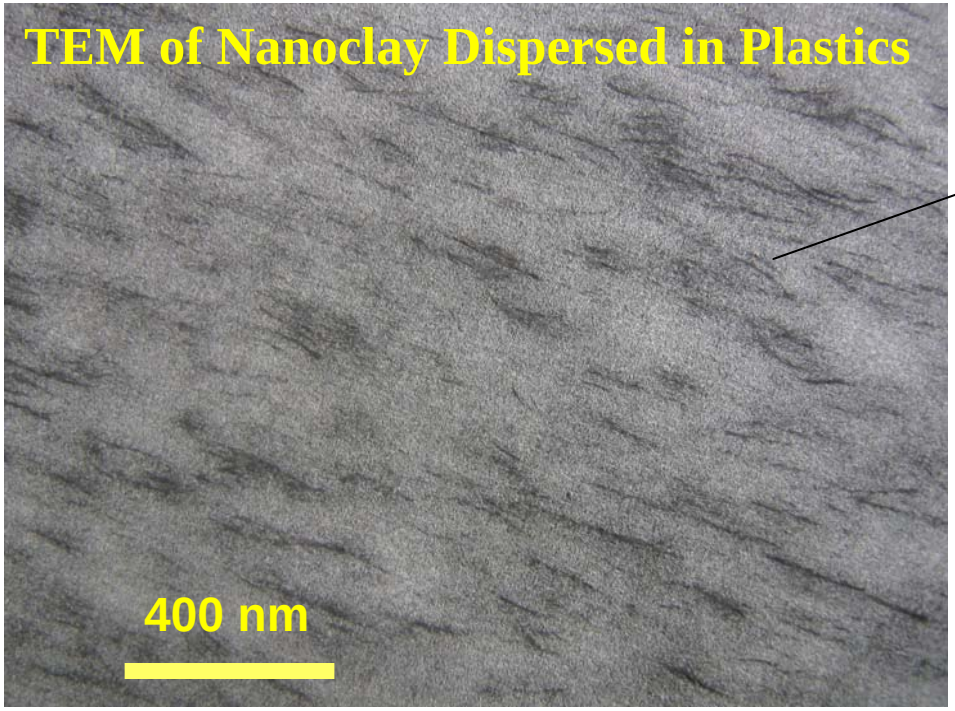


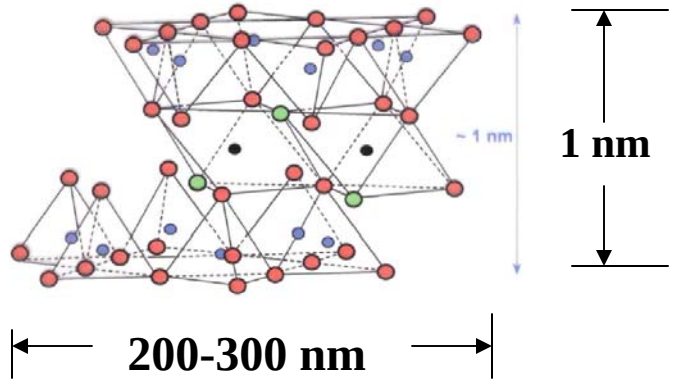
Nanoclay Morphology-PSD

- Produced nanoclay
- Fully Dispersed nanoclay in plastics
- Burning of plastic resin
- Char of nanocomposite


Typical Nanoclay Particle size (I.24TL) DRY
Mean=17 micron
We do NOT supply nano-sized powers.
volume (percent)
6
5
4
3
2
1
0
-1
0
100
200
300
400
500
600
particle size (micron)

Nanocomposite



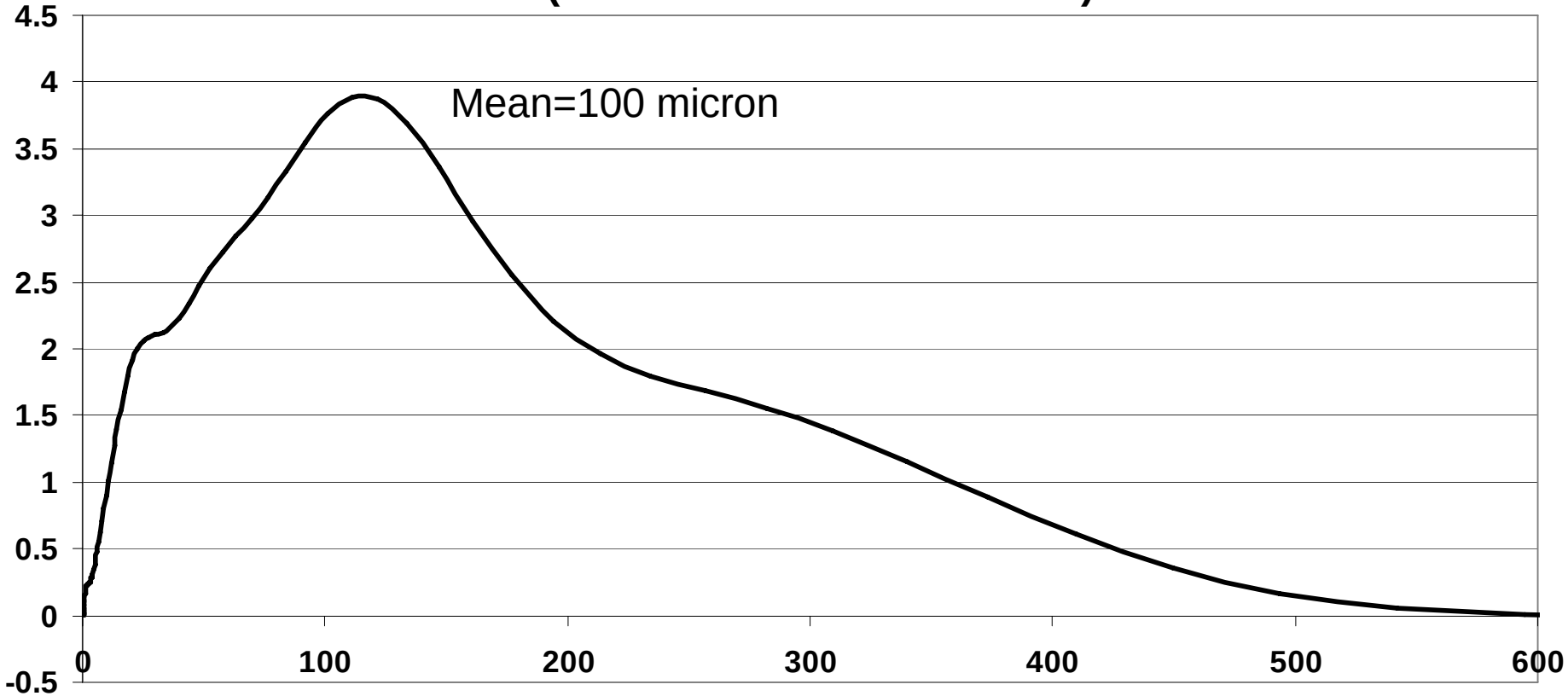


Nanoclay platelets are one-ten thousandth the diameter of a human hair!!

NANO-PA6

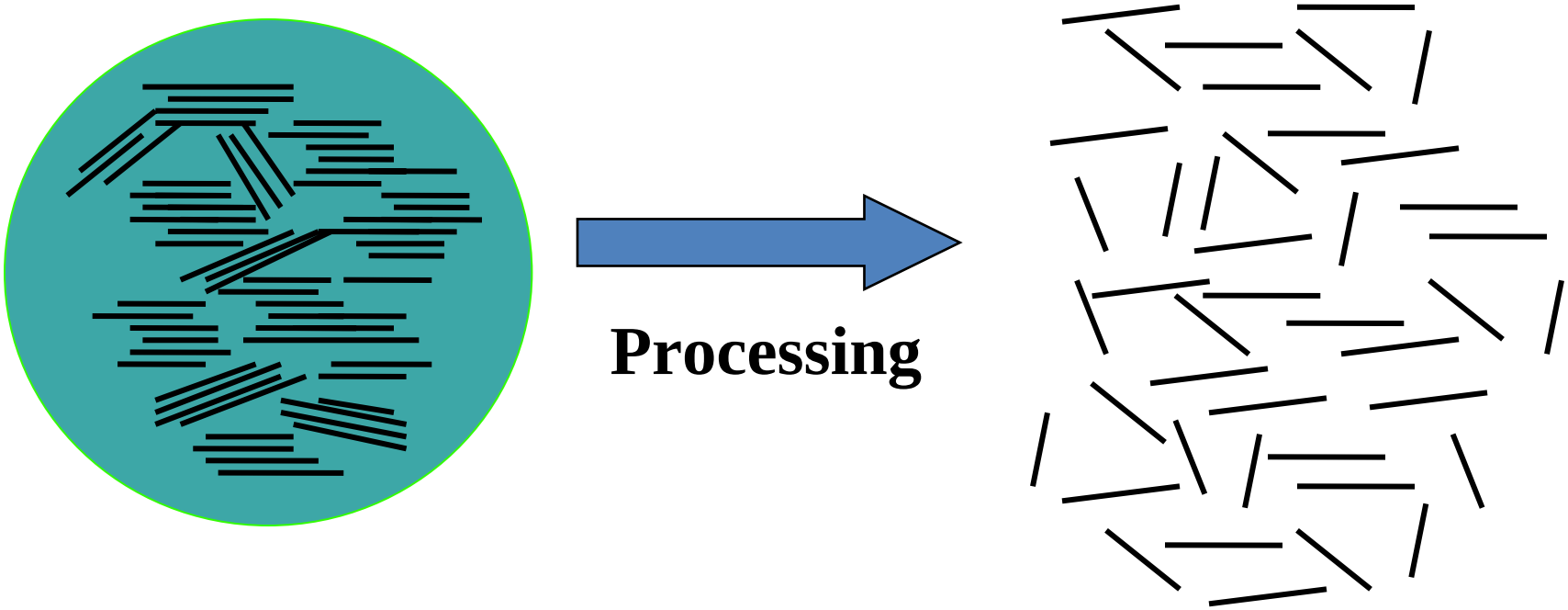
AFTER BURNING (950C) FOR 30 MINS

PARTILCE SIZE OF RESIDUAL ASH AFTER BURING OF NANO-PA6 (MECHANICALLY GROUND)



Nanocomposite Processing

Melt Compounding

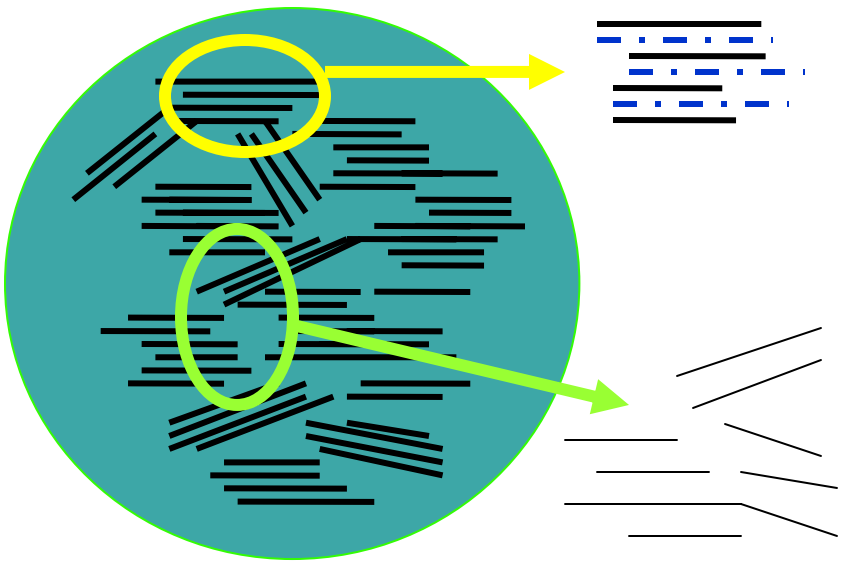


15 µm Particle **>1 Million Platelets**

We do NOT supply nano-sized powers.

Nanocomposite Processing

Melt Compounding



It is easy for polymer to enter clay interlayer region

It is difficult to break the clay agglomerates

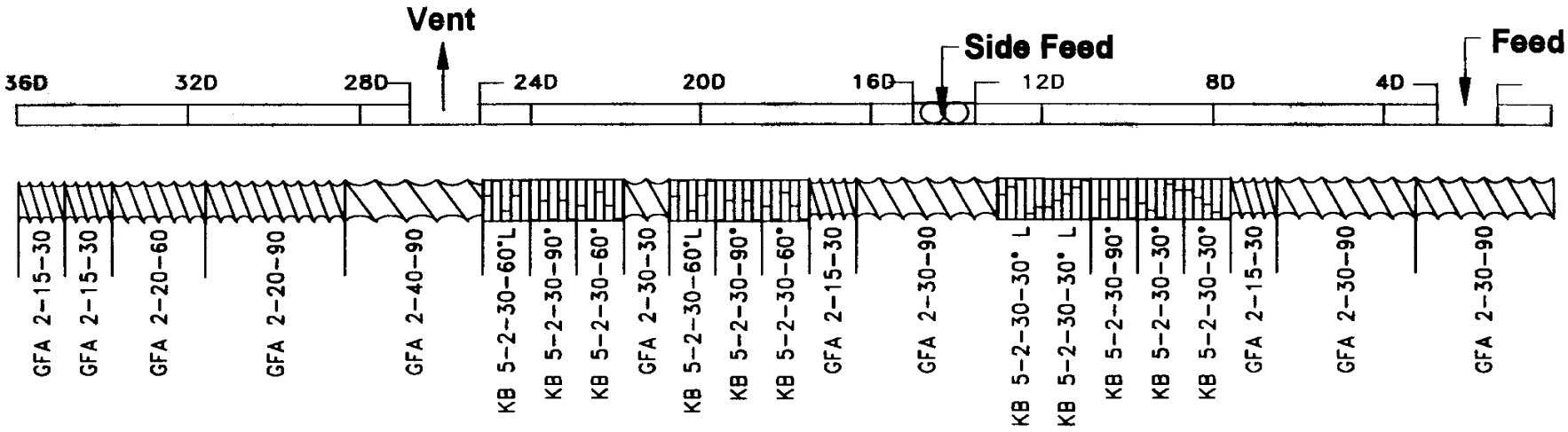
Edge-surface chemistry

Polymer shear stress is more important in clay dispersion.

Nanocomposite Processing

Melt Compounding

Screw Design-Twin Screw Extruder (27 mm, 36 L/D)



Nanocomposite Processing

Melt Compounding

High Shear Stress Processing Equipments

TSE-JSW

SUPERTEX α II NIC

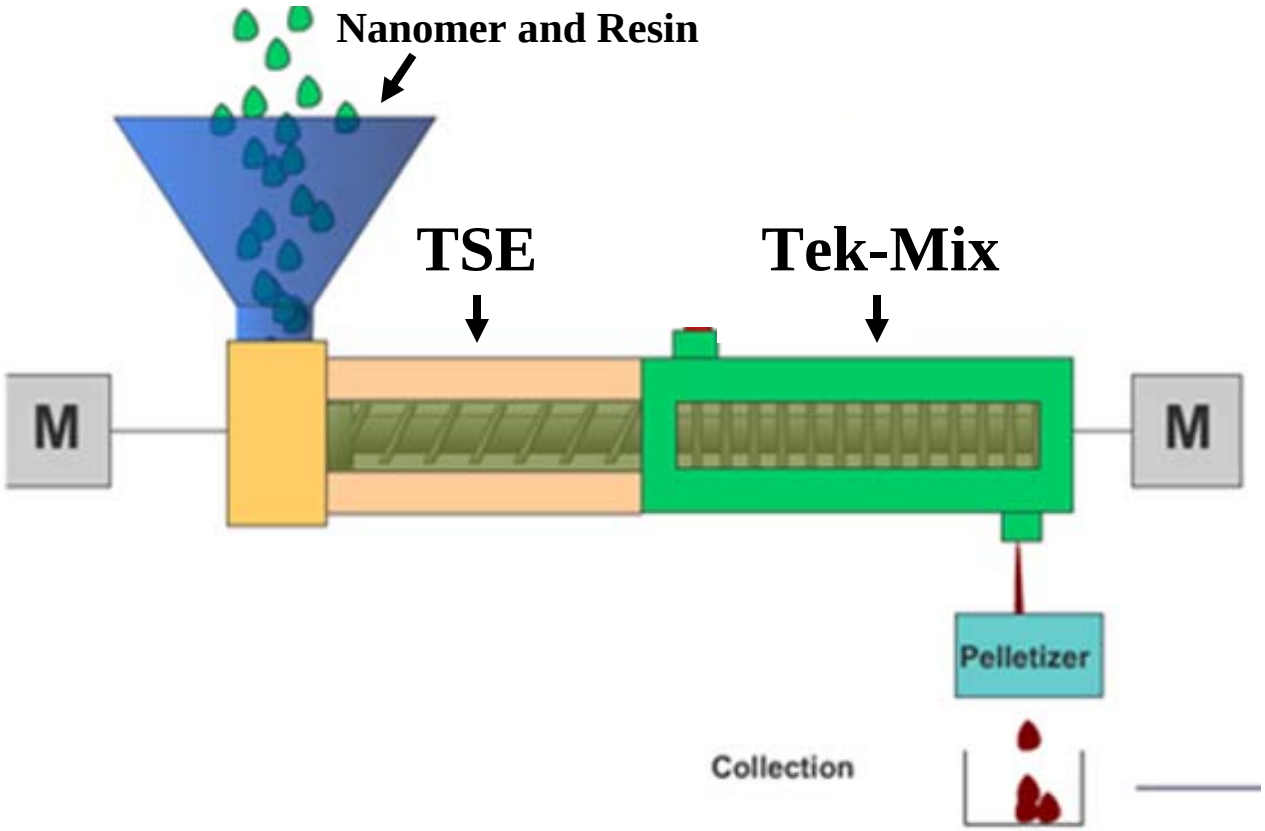
TKR-F

STRATEK PLASTIC LTD

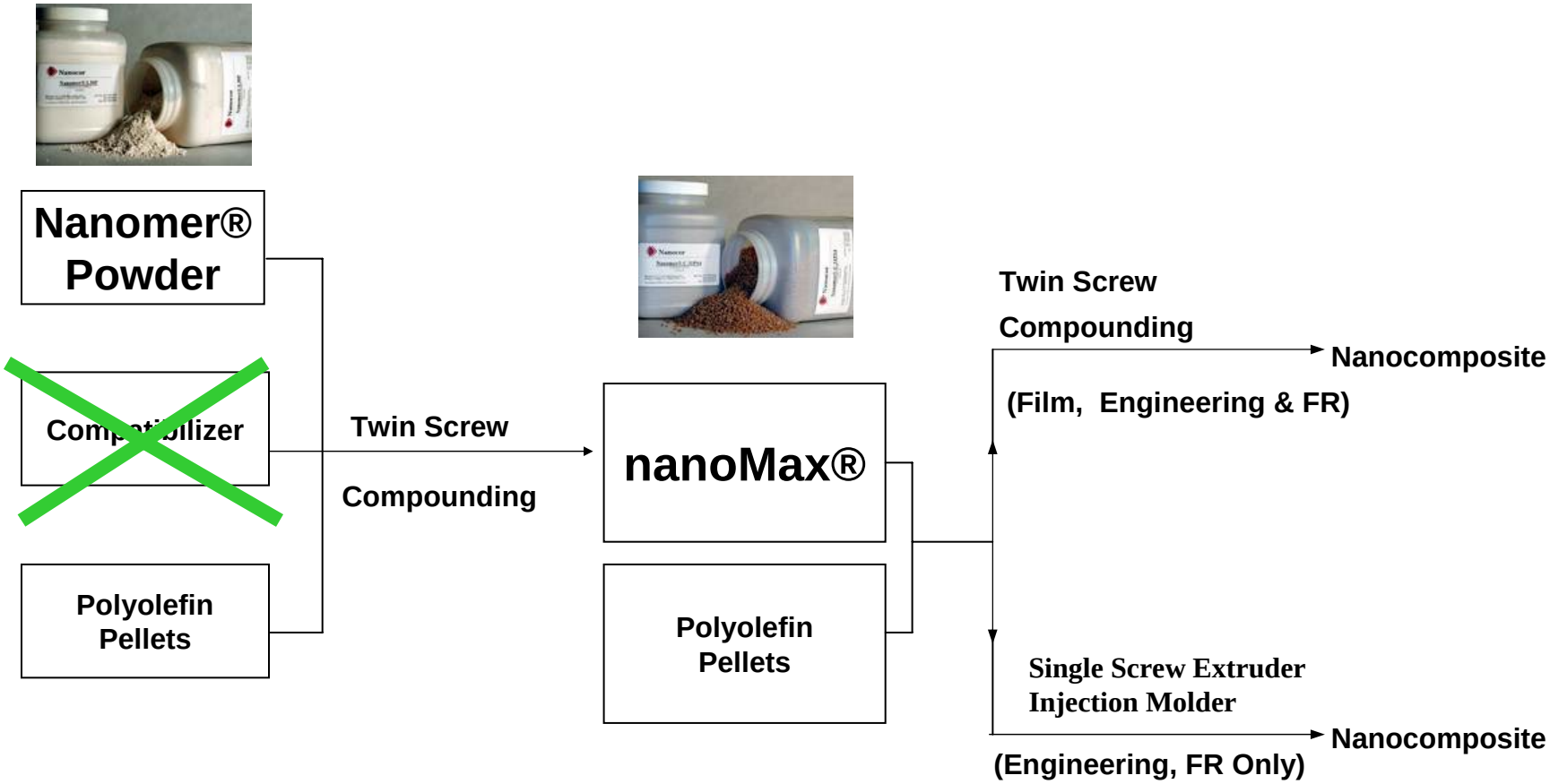
Tek-Mix: an Extensional flow Mixer that attaches to any extruder

STRATEK PLASTIC LTD

Tek-Mix: an Extensional flow Mixer that attaches to any extruder



Nanocomposite Processing



Nanocomposite Processing

Melt Compounding

Elimination of Polyolefin Compatibilizers (PP-g-Ma, PE-g-Ma):

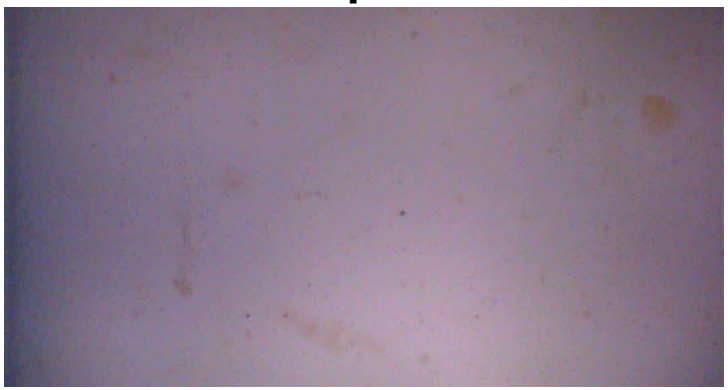
- **In favor for food contact applications**
- **Remove additional cost to the formulation**
- **Reduce negative effect on melt rheology**

Nanocomposite Processing

Melt Compounding

Regular MB with Ma-PE, Tek-Mix MB without Ma-PE

30-140 µm



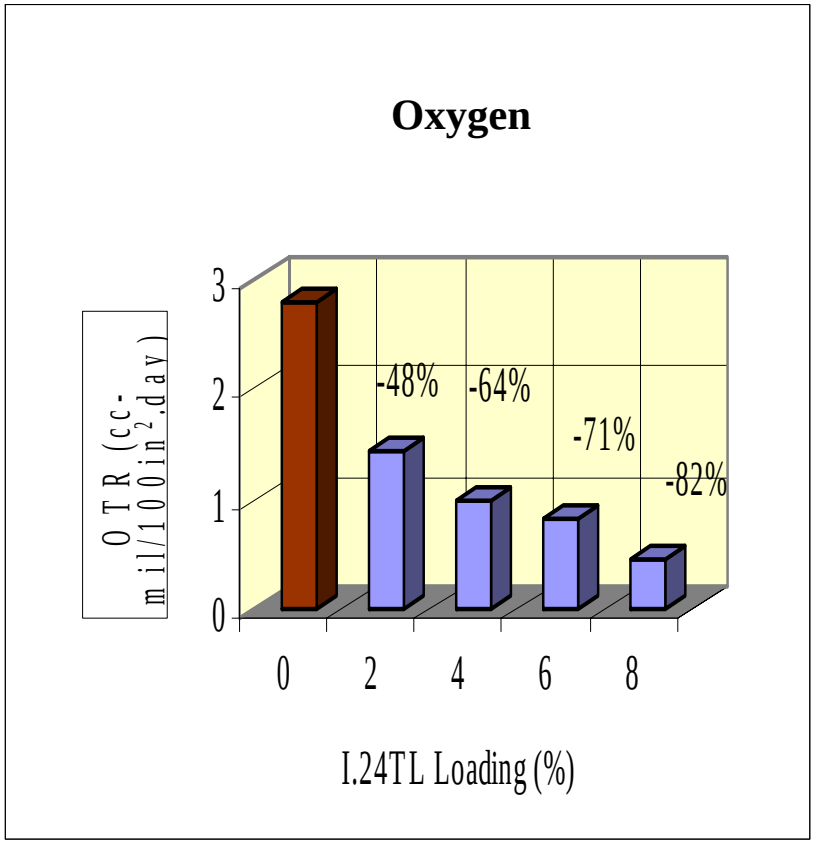
13-22 µm

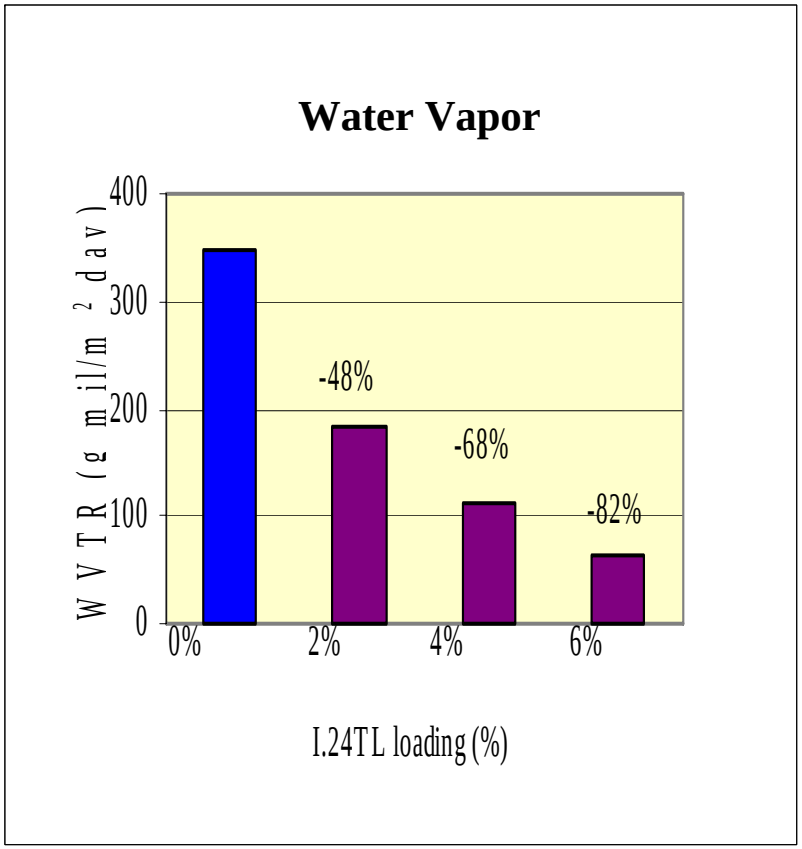
Barrier Improvement of nanocomposites

- Nano-PA6
- Nano-Nylon MXD6
- Nano-PP and nano-PE

(Cast Films)

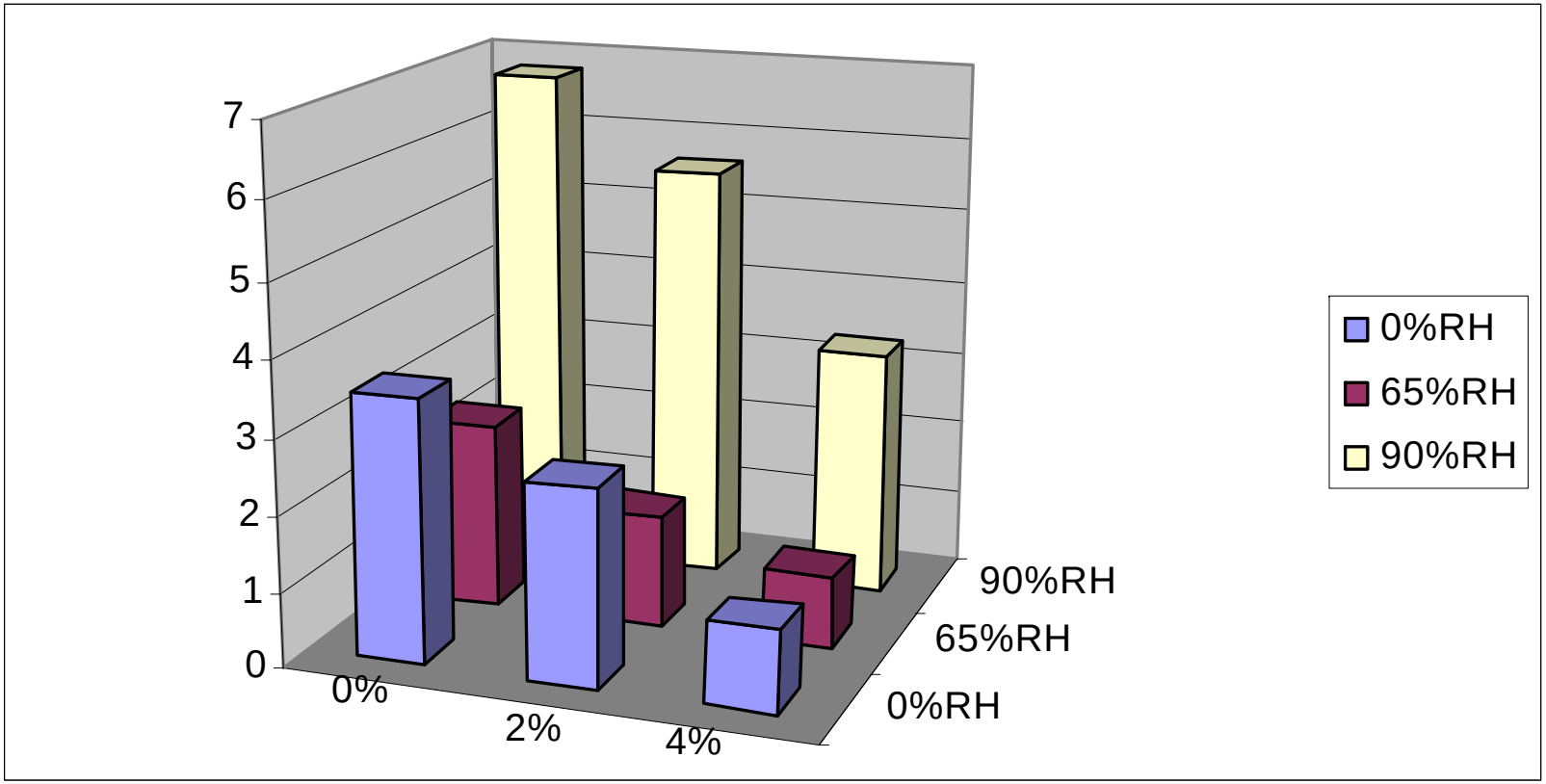
Barrier Improvement of nano-PA6





(Cast Films)

Barrier Improvement of nano-PA6



Film Mechanical Properties of Nano-PA6

Cast Monolayer Films (20-30 micron)

Flow Direction

Testing Sample	%Nano Loading	Young's Modulus (Mpa)	Yield Strength (Mpa)	Strain @ break (%)
Nylon 6 B135WP	n/a	150	12	700
Nano-PA6	3%	270	35	650

Perpendicular Direction

Testing Sample	%Nano Loading	Young's Modulus (Mpa)	Yield Strength (Mpa)	Strain @ break (%)
Nylon 6 B135WP	n/a	200	16	600
Nano-PA6	3%	380	28	550

Nanocomposites

- **Same Tm, Tg ---Same processing**
- **Smart design**

Use less resin ---same strength and barrier

PE//PA6//PE = 40//20//40

PE//nano-PA6// = 40//10//40

10% saving in film weight

Nanocomposites can save cost!

Nanocomposites

Next Generation ready to ta

Extruder with barrier nanofilm counts chickens

By Dan Hockensmith
PLASTICS NEWS STAFF

Next Generation Films Inc. is applying nanotechnology literally on top of the chickens lying in grocers' meat aisles.

The Lexington, Ohio-based extruder of three-layer films is marketing a new ultrathin oxygen barrier for food packaging that consists of a layer of nanonylon sandwiched between two layers of polyethylene.

The 14-year-old company has made three-layer bags using nanotechnology for more than a year, founder and Chief Executive Officer David Frecka said in an

pending technology, those com-

in a 260,000-square-foot campus,

"The bio-based films, you can't recycle," "With nano [film], you can use fewer layers – it's still as strong and it can be recycled."

- David Frecka, CEO, Next Generation Films

Windmoeller & Hoelscher Varex three-layer blown film line running in one of its four bays, cranking out as much as 2,100 pounds of film per hour. An 87-inch W&H Varex three-layer line is scheduled to be installed this summer.

Once that machine — the company's third W&H line — is in

he said.

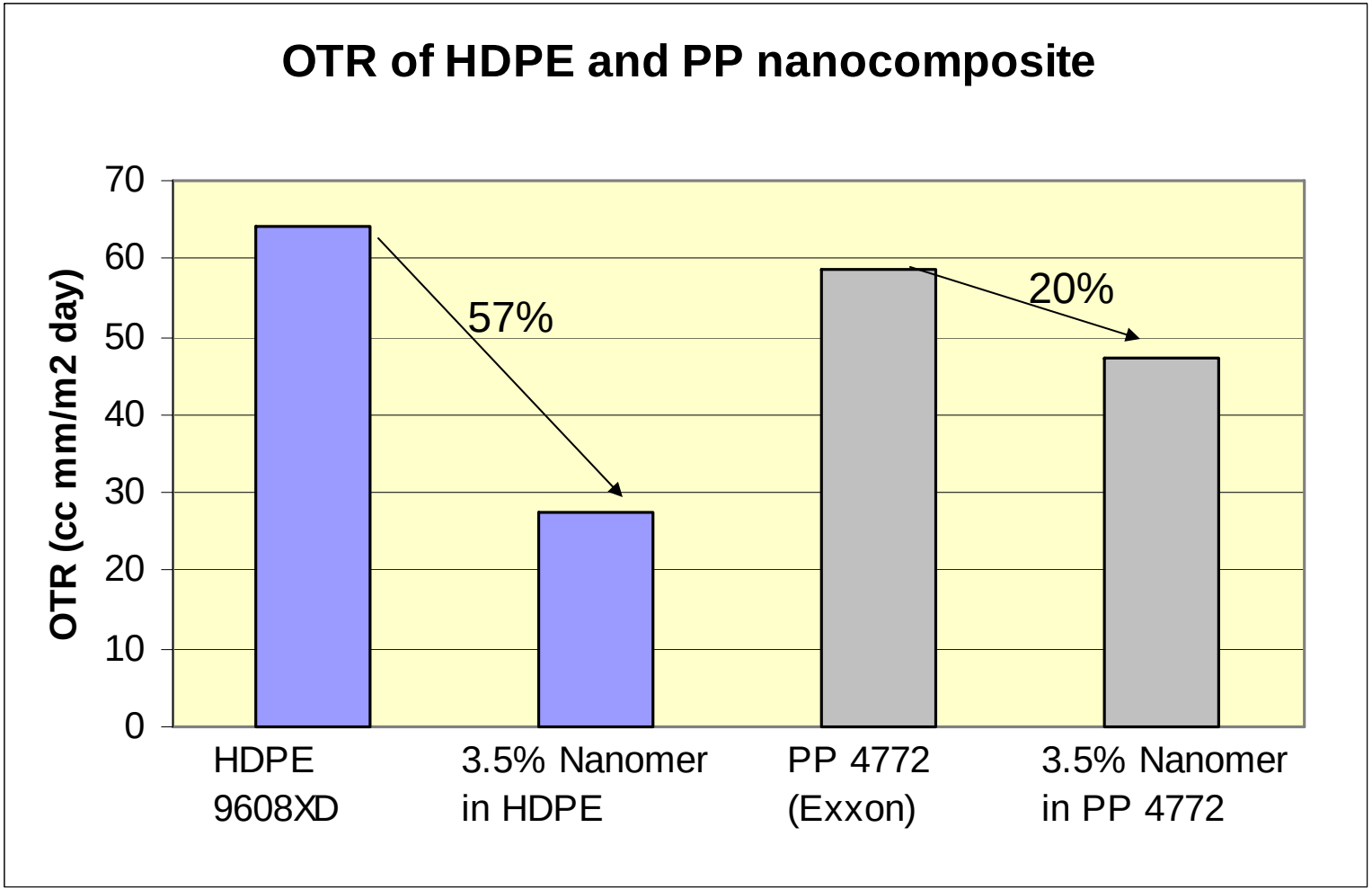
Next Generation's sales are about $80 million, Frecka said, though he wouldn't give the actual amount. He said he gets "a phone call a day" from private equ

Nano-Nylon MXD6 Barrier Properties

Property	Units	MXD6 a)	Imperm a)
OTR (23ºC, 60%RH)	cc·mm/m²·day·atm	0.09	0.02
CO_2TR (23ºC, 60%RH)	cc·mm/m²·day·atm	0.30	0.15
WVTR (40ºC, 90%RH)	g·mm/m²·day	1.36	0.58

a) Non-oriented monolayer film

PP and HDPE Nanocomposites



Summary

- **Nanoclays are effective additives to plastics to enhance barrier properties.**
- **Plastic nanocomposites are the same class of plastics but with better properties**
- **Nanocomposites offer material saving option and higher performance product design**
- **It is possible and practical to have regulatory approval to use nanocomposite plastic as food packaging materials**

Thank You