

Polytechnique
2019

Material Reduction and Biobased Materials Use For More Sustainable Polymer Packaging

Abdellah Ajji et al.
3SPack NSERC-Industry Research Chair
CREPEC, Chemical Engineering Department
Montreal, QC, Canada

Sustainability in Packaging

Packaging Performance is Paramount/Priority requirement

- Must have performance to protect the economic and environmental investment in the product as well as the package.

Reduce, Replace, Recycle, Reuse, ...

- May still be room for further performance and cost optimization,
- New opportunity to further optimize with sustainability driver: better performing resins at comparable total system cost.

Renewable (biobased), biodegradable, compostable

- Developments in processing,
- New modifiers to improve performance (processing, end use),
- New renewably sourced polymers with performance benefit.

Nanotechnology/Nanoparticles in Polymer Applications

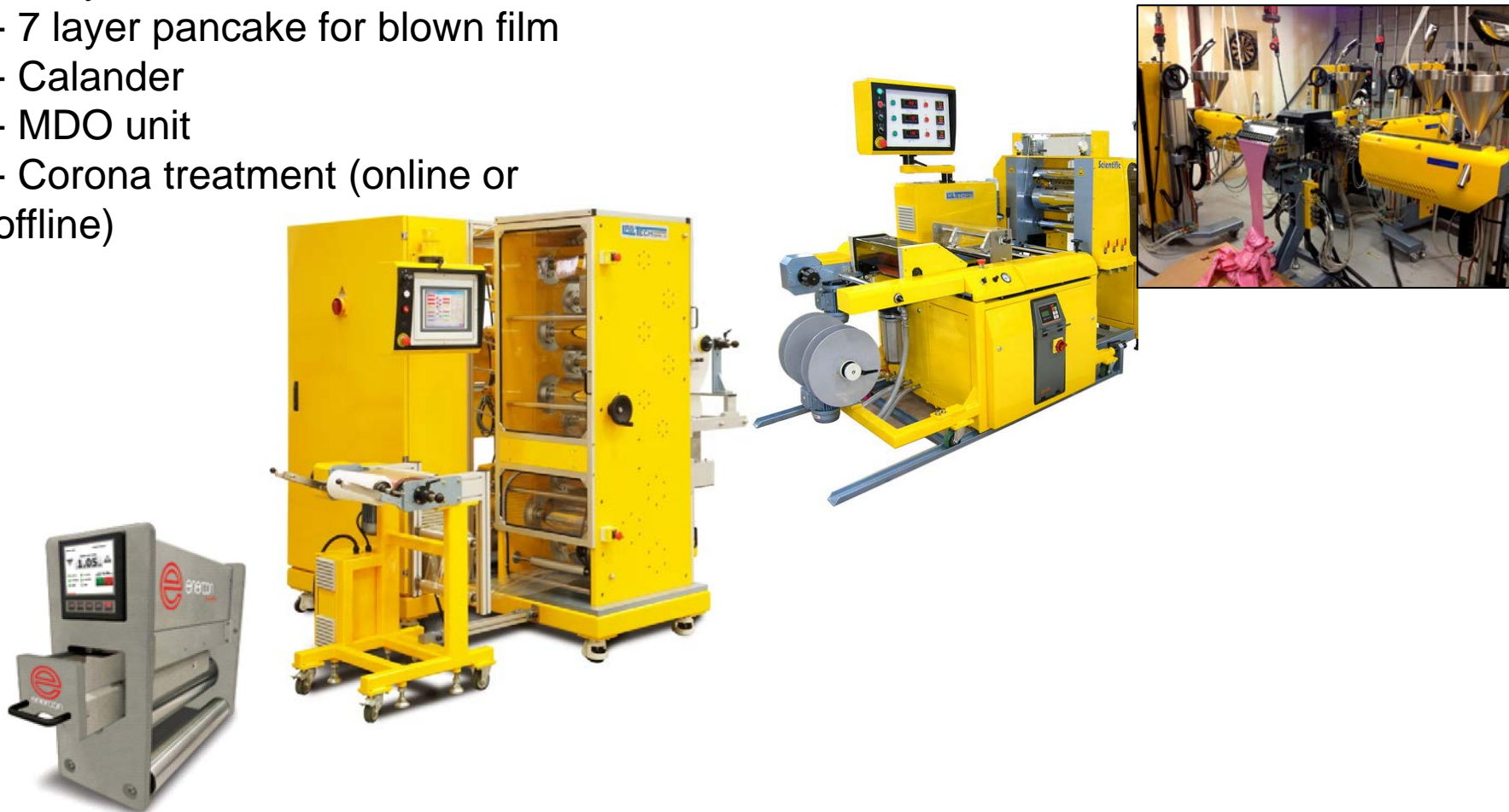
- Addition of nanoparticles: taking advantage of surface area, shape, functionality, ...
- Nanoparticles (nanocomposites) can be used in some packaging applications: Barrier, Oxygen scavenging, antibacterial,....
- Issues: regulation

I- FILM PROCESSING

3S *pack* 

What we already have :

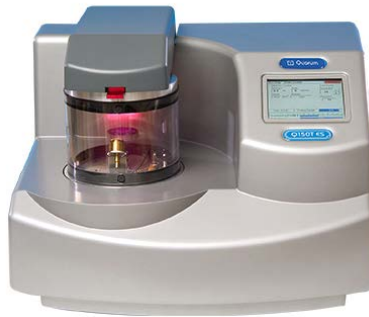
- 4 extruder cast film and blown film line, 1 twin screw extruder
- 9 layer feedblock for cast
- 7 layer pancake for blown film
- Calander
- MDO unit
- Corona treatment (online or offline)



II- FILM MORPHOLOGY ANALYSIS AND BARRIER

3S *pack*

- Tabletop Scanning Electron Microscope from Hitachi with EDX
- Carbon/Chromium Sputter/Coater from Quorum
- Ultracryo microtome for SEM and TEM sample preparations



- Oxygen Transmission Rate Equipment (3) with and without Moisture control
- Water Vapor Transmission Rate Equipment (2)

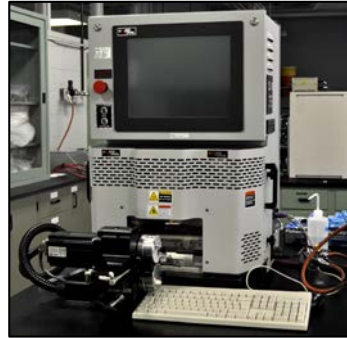


II- FILM CHARACTERIZATION MECHANICAL CHARACTERIZATION AND

3S *pack*

SEALABILITY

- Seal/Hot tack Tester
- Flex Crack Tester
- Abrasion Tester
- Mechanical Properties Tester with environmental chamber
 - Tension mode,
 - Compression mode,
 - Puncture,
 - Cycling (fatigue)



II- FILM CHARACTERIZATION

OTHER CHARACTERIZATIONS

3S *pack*

- FTIR with microscope
- Conductivity /Resistivity Tester
- Helium Pycnometer
- Oxygen, CO₂ and Ethylene Reader



II- OTHER PROCESSING AND CHARACTERIZATION EQUIPMENTS

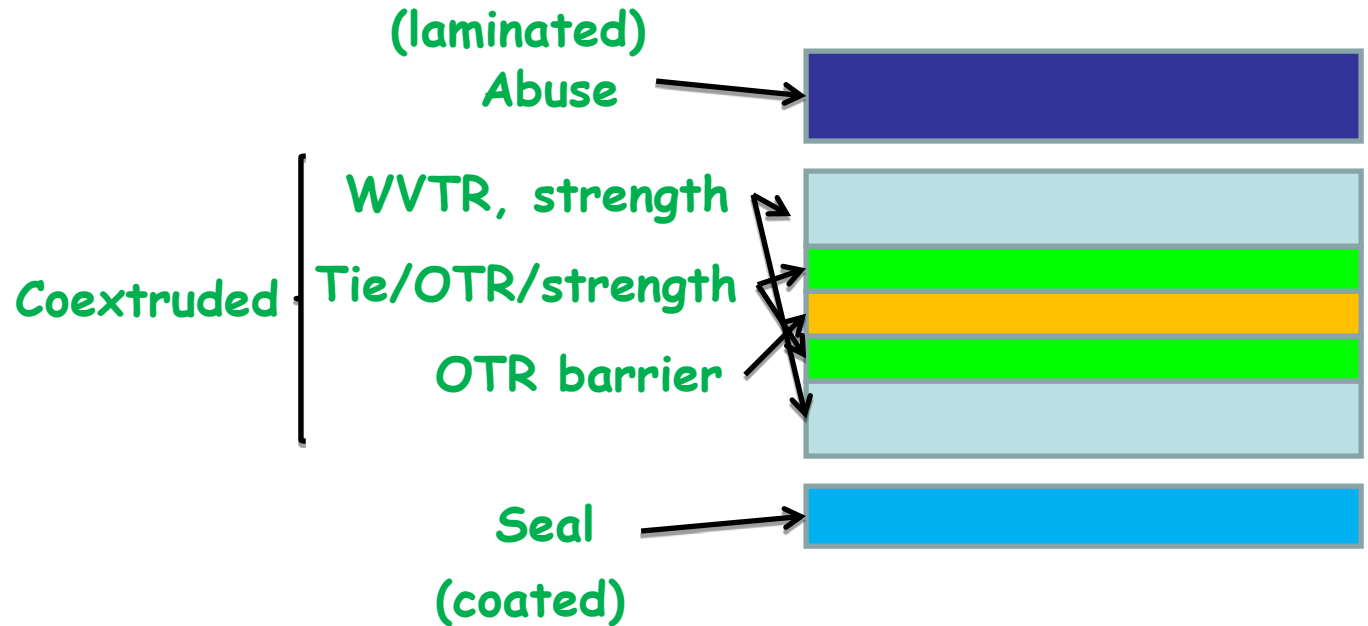


Available in CREPEC, Department and Polytechnique:

- Internal batch Mixer
- Injection Molding Machine, thermoforming.
- Single Screw and Twin Screw extruder (lab scales)

- DSC (Differential Scanning Calorimetry)
- TGA (ThermoGravimetric Analysis)
- DMA (Dynamical Mechanical Analysis)
- Rheology
- Impact Tester
- Tear Tester
- Dart impact Tester
- HDT (Heat Deflection Temperature) Tester
- TEM (Transmission Electron Microscope)
- AFM (Atomic Force Microscopy)
- XPS, SIMS,...
- Environmental chamber, Solvent and Water Ovens
- ...

Typical Packaging Structure

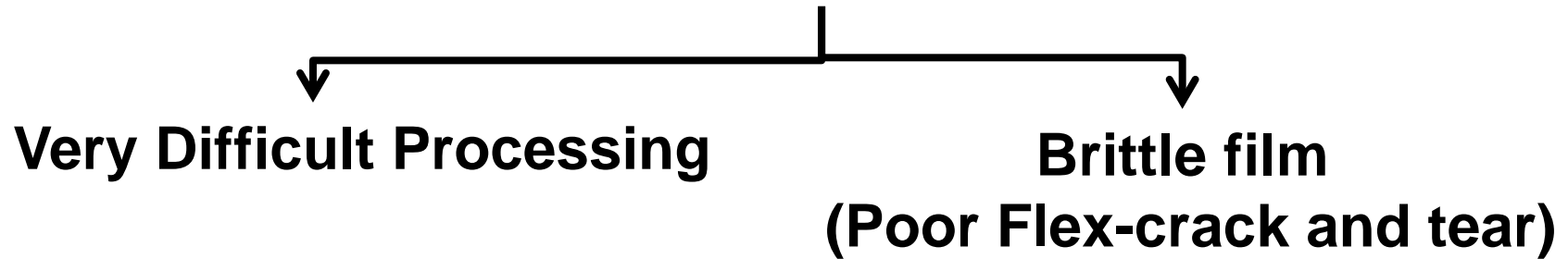


Nanostructures and Functionnality can be involved in all these layers

PLA based films for packaging



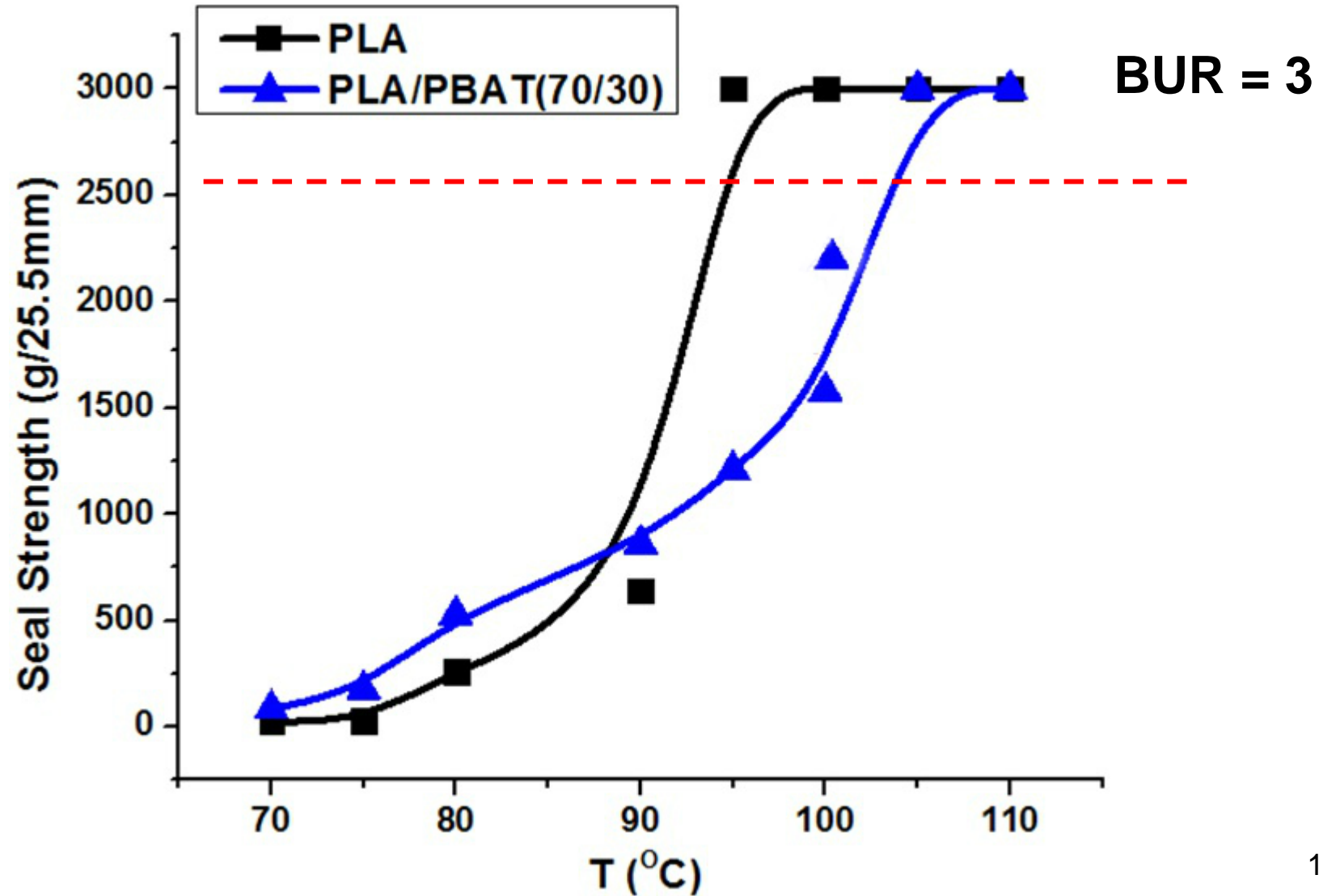
PLA in Packaging



PLA/PBAT blends

Produce Bio-based or compostable sealant films for environmental friendly packages.

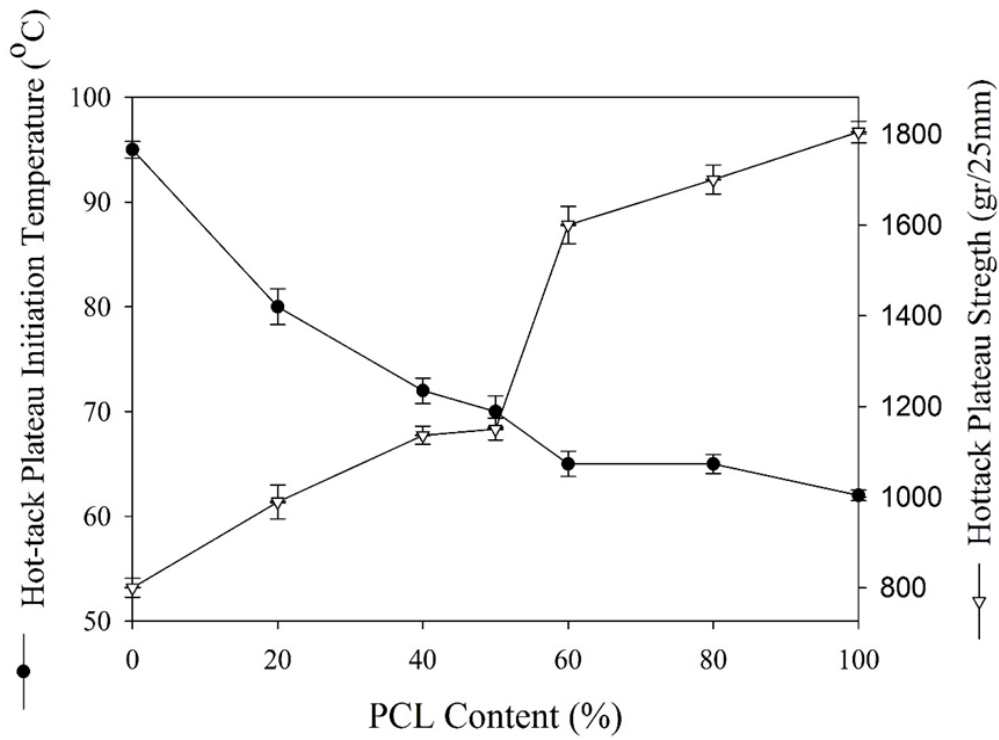
Bioplastic sealants



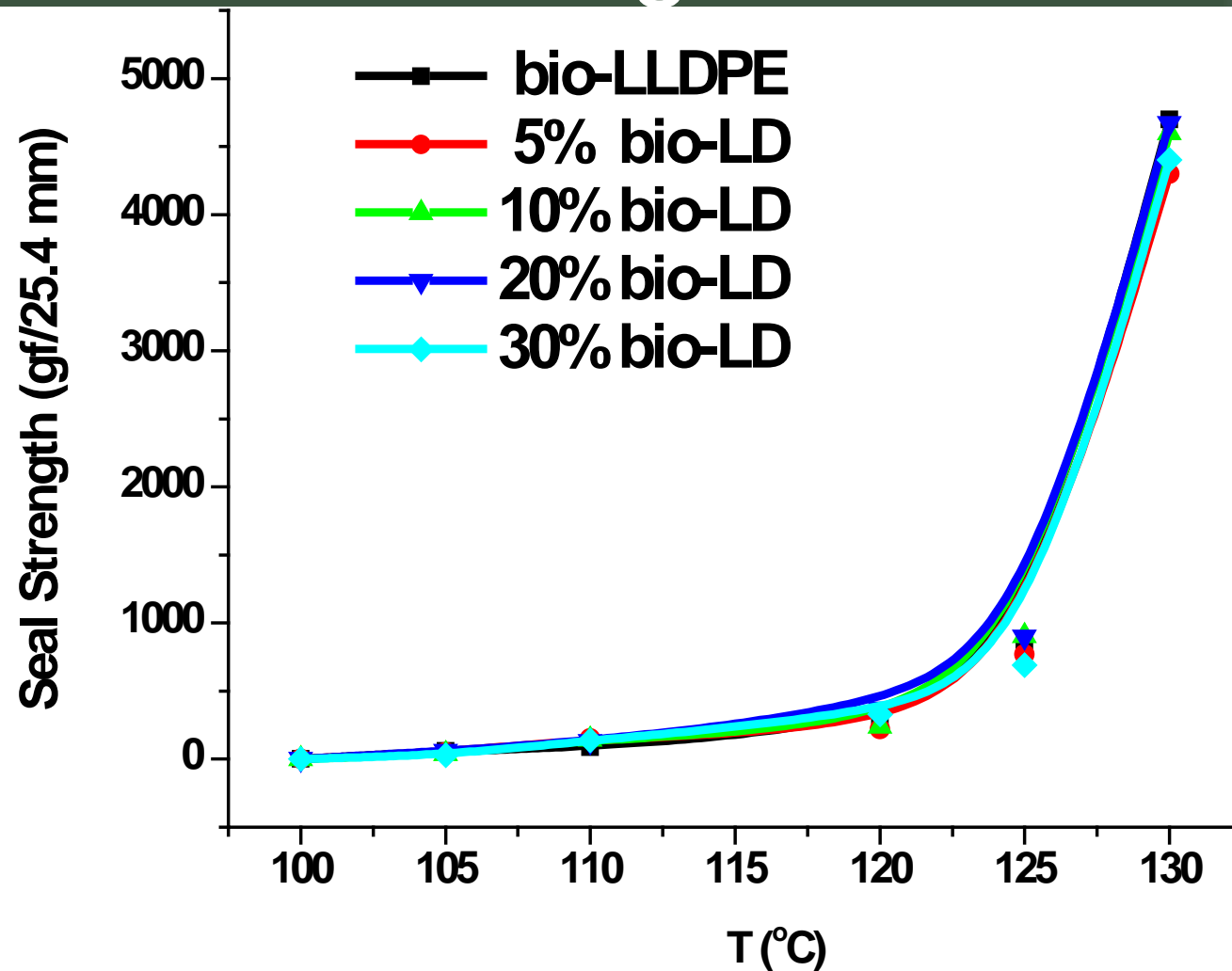
Result: Mechanical Properties and seal behavior of blends

3S pack

- ❖ Hottack Plateau initiation temperature Decreases up to 30 °C
- ❖ Hottack Strength increases up to twice



Seal Strength*



- *Sealing were done at 40 psi and 0.5 s dwell time*
- *Peeling was done at 33 mm/s*

Nanoparticles addition (Nanacomposites) or coatings for Barrier Enhancement.

Nanocomposites

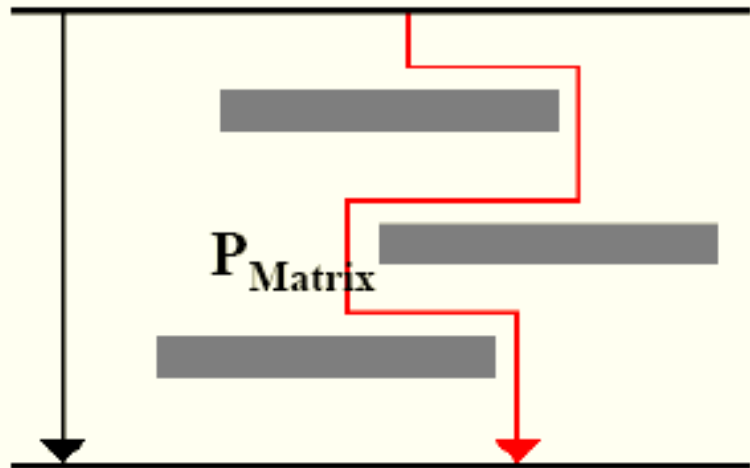
PNC based on layered silicates have received very much attention because of their potential to improve:

- Stiffness, strength and impact resistance
- Barrier properties
- Dimensional and thermal stability



Advantage for layered silicate: low content.

Barrier Enhancement: Tortuous Path



What does it take to reduce
50% permeability?

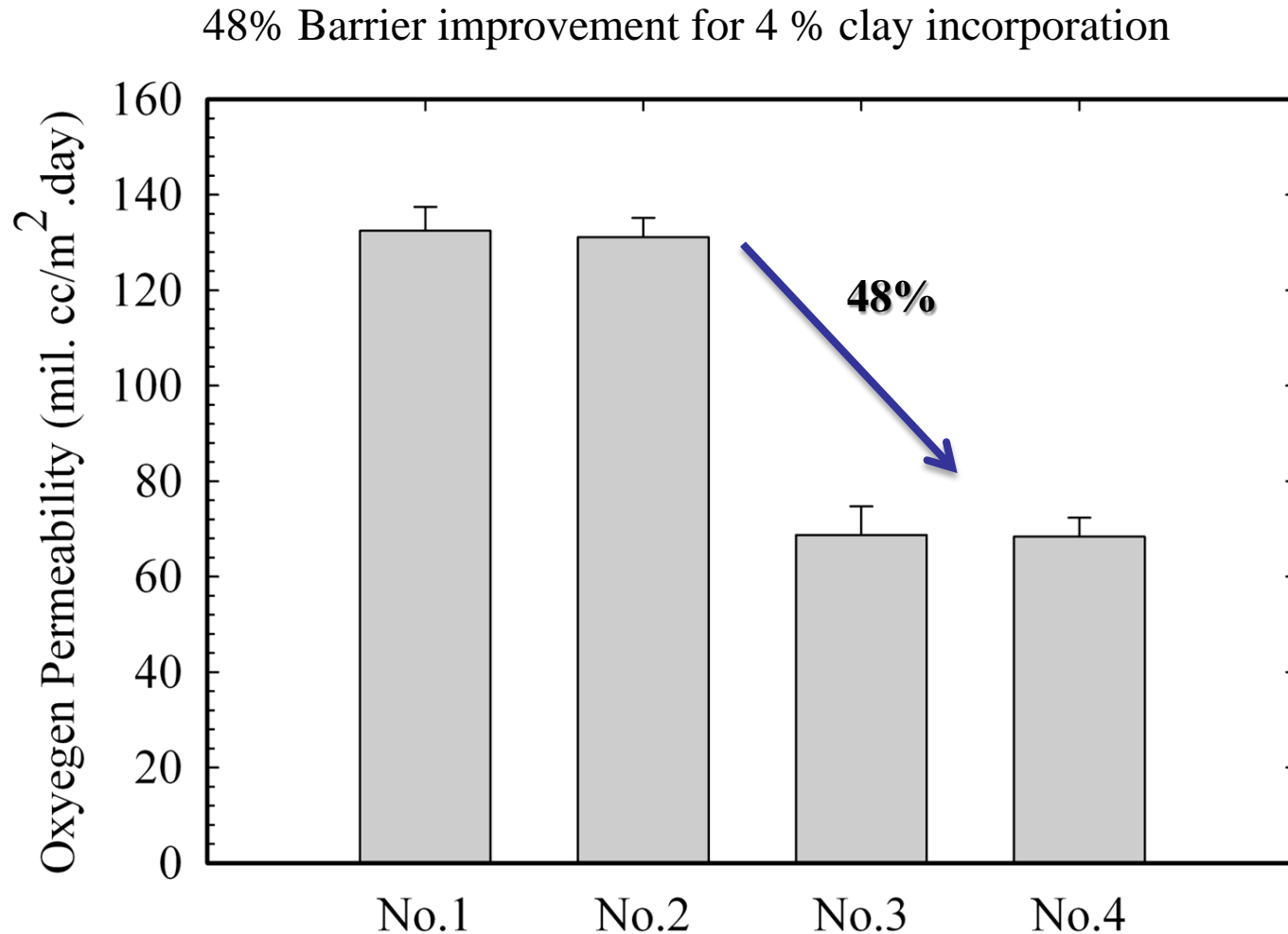
Aspect ratio	Volume %
20	9%
200	1%
400	0.5%

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

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

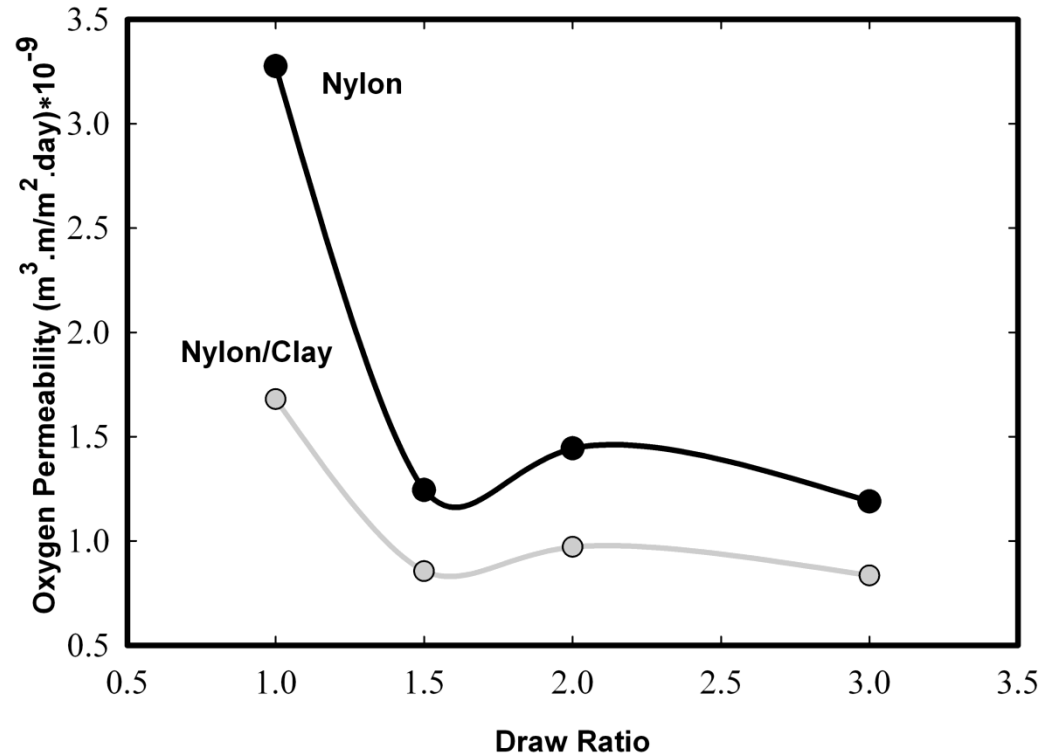
PA-6 Nanocomposites: Oxygen permeability

The values are normalized



Total thickness: 50 μm , sample 1: PA 6 μm , 2: PA 12 μm

MDO Effect on Barrier



Oxygen permeability for multilayer films with nylon and nanocomposite

Layer by layer film deposition technique

3S *pack*

Main characteristics for MMT: Orientation and intercalation

Good properties

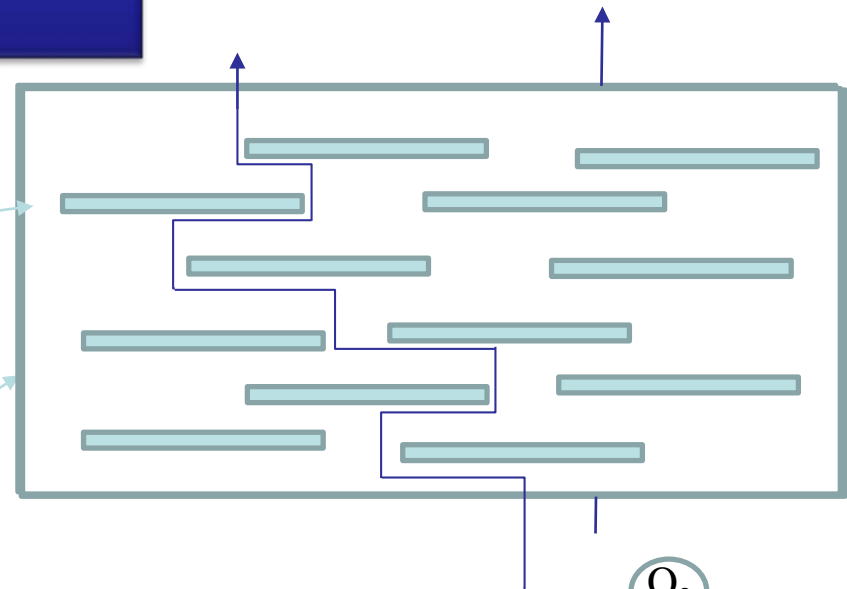
Availability

Nontoxicity

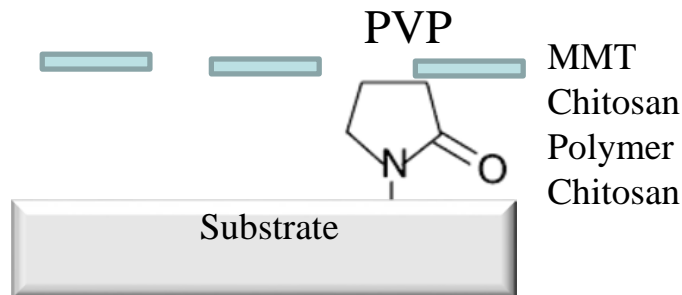
MMT: improve polymer barrier

MMT
nanoparticles

Polymer



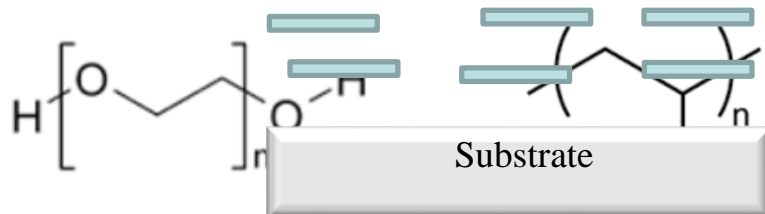
Hydrogen bonding



Quadlayer structure

PEO

PVA

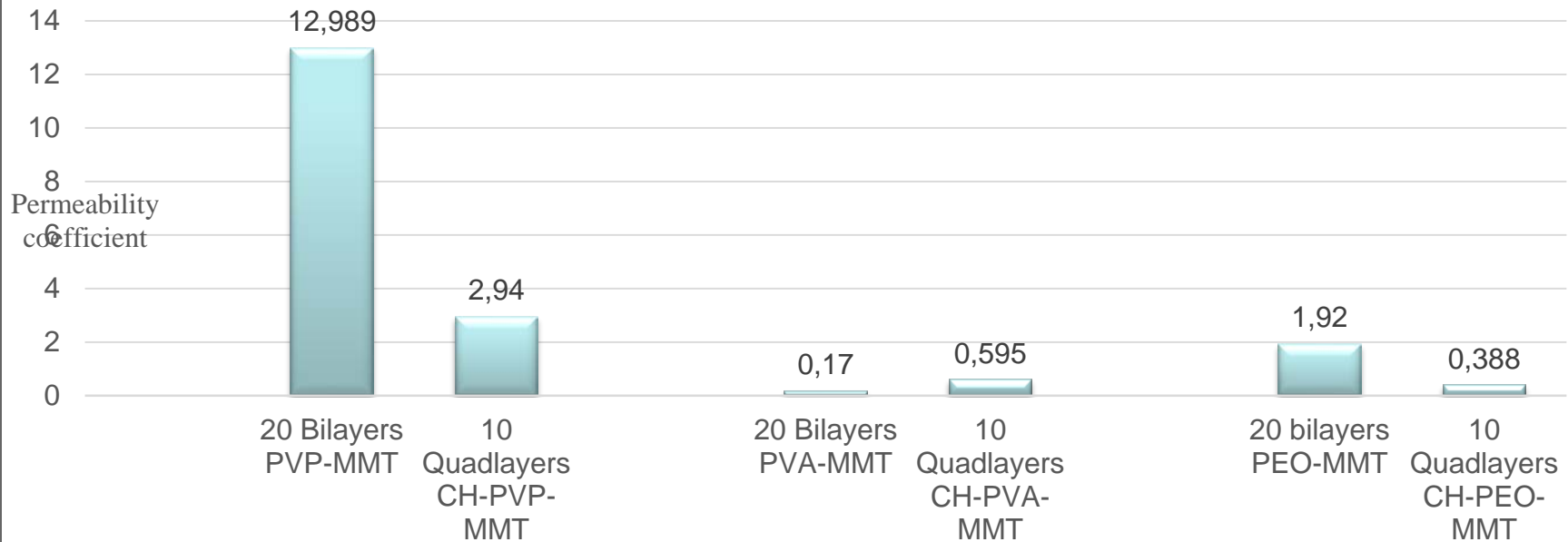


MMT
Polymer

Bilayer structure

Parameters optimization and main results **3S pack**

Dipping time	Polymer solution (% wt)	MMT suspension (% wt)	CS solution pH
1min	0.1	0.5	6



Conclusions - Barrier Layer

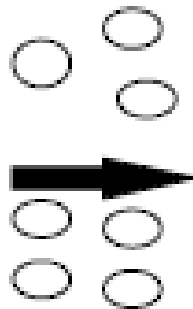


- Barrier properties of polymers can be improved using nanocomposites,
- Clay intercalation/exfoliation plays a significant role in barrier properties improvements,
- Barrier coatings are good alternatives, if process and moisture allow,
- LBL technique is promising, but needs developments for large scale applications.

Active Packaging:
Antibacterial and Oxygen
Scavenging Films: Less wasted
food, product sustainability.

Active layer using OS

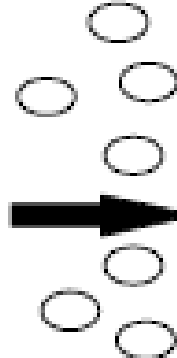
Outside
Container



Inside
Container



Outside
Container



Inside
Container

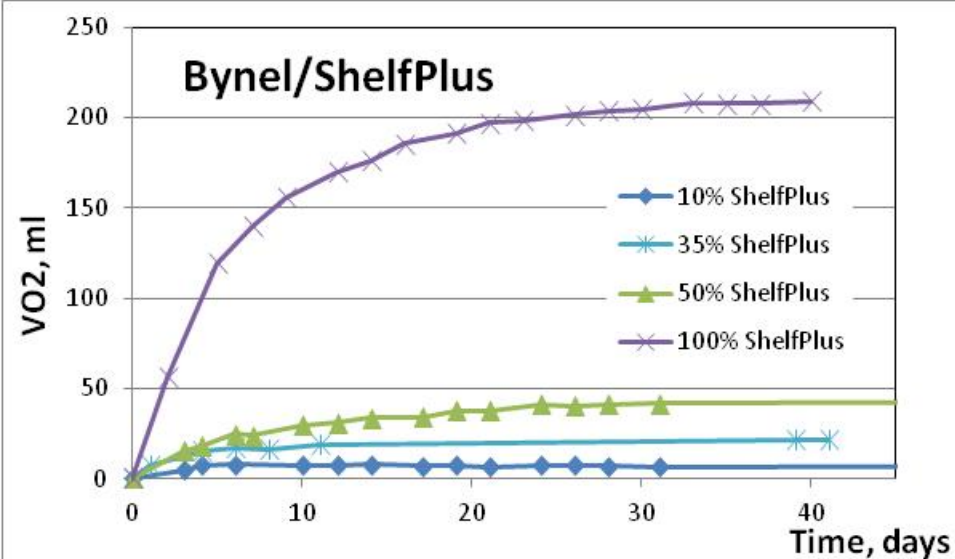
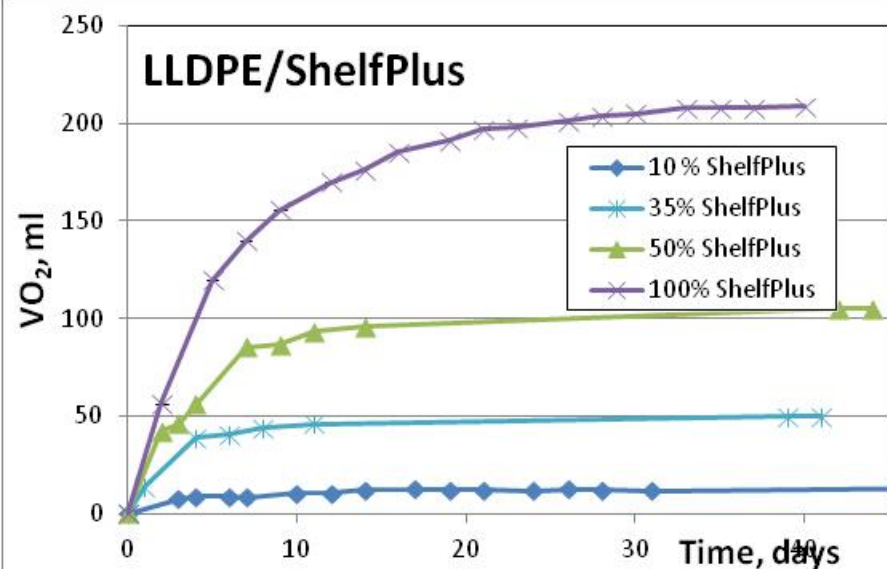


= Oxygen molecule initially outside container



= Oxygen molecule initially inside container

Evaluation of ShelfPlus: Main findings



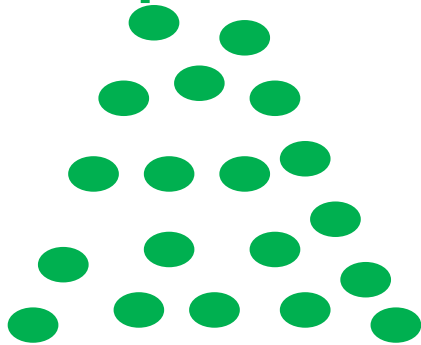
- Blends with LLDPE have better oxygen depletion behavior.
- Shelfplus blended with Bynel exhibit lower OS.
- EVOH+ShelfPlus lowest effect.

Grade	<u>FPS 317A+ ZnO Novachemicals</u> 4 g/10min			<u>LLDPE/AM (Tie layer)</u> <u>Bynel 42E703 Du Pont</u> <u>6,4 g/10 mn</u>
Sample	3	4	5	5
Temperature	190	200	1-4 :200 5-9: 220	1-4 :200 5-9: 220
<u>Thikness μm</u>	70			

Spray of ZnO nanoparticles on the LLDPE films

3S *pack*

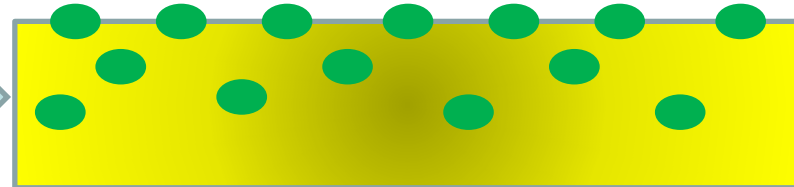

ZnO
nanoparticles



Extruded LLDPE
films

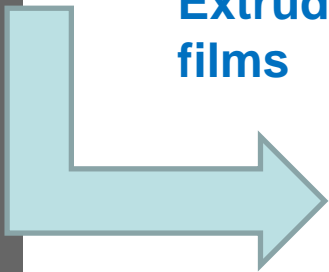


Cooling



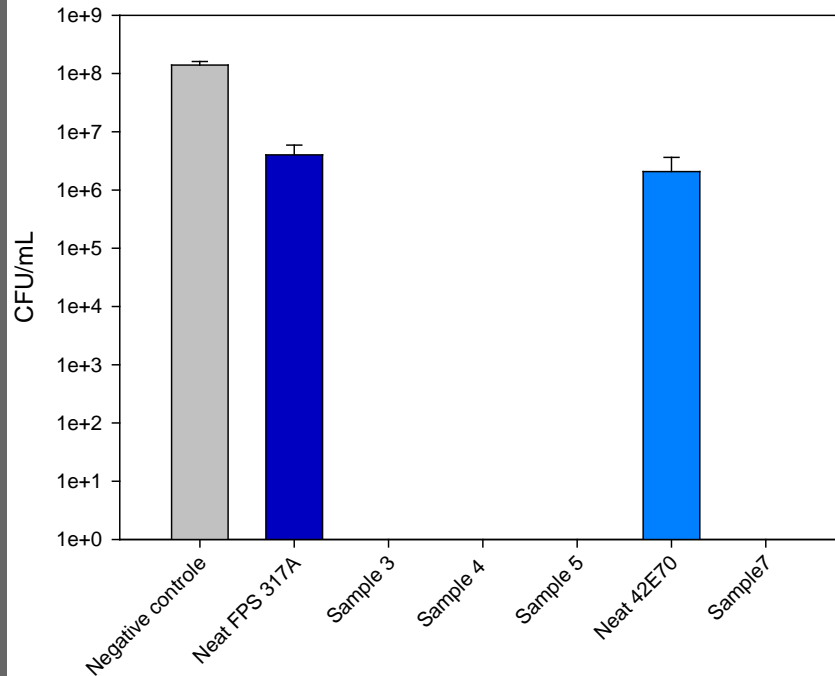
LLDPE/ZnO films

Twin-Screw Extrusion



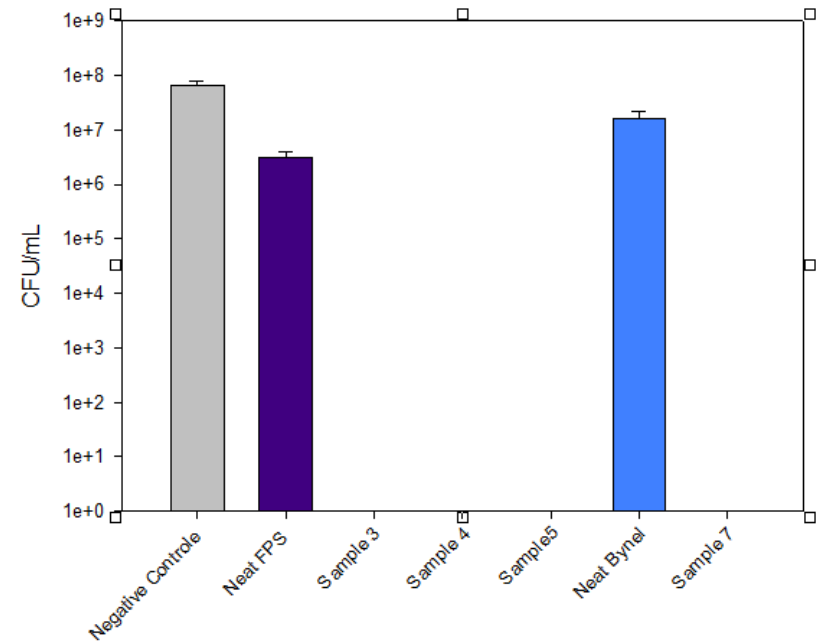
Exit of the
die

E.coli- 1 month



November 2016

E. Coli - 5 months



March 2017

Selective Degradation of Biodegradable Blends in Simulated Laboratory Composting



Submitted to polymer degradation
and stability

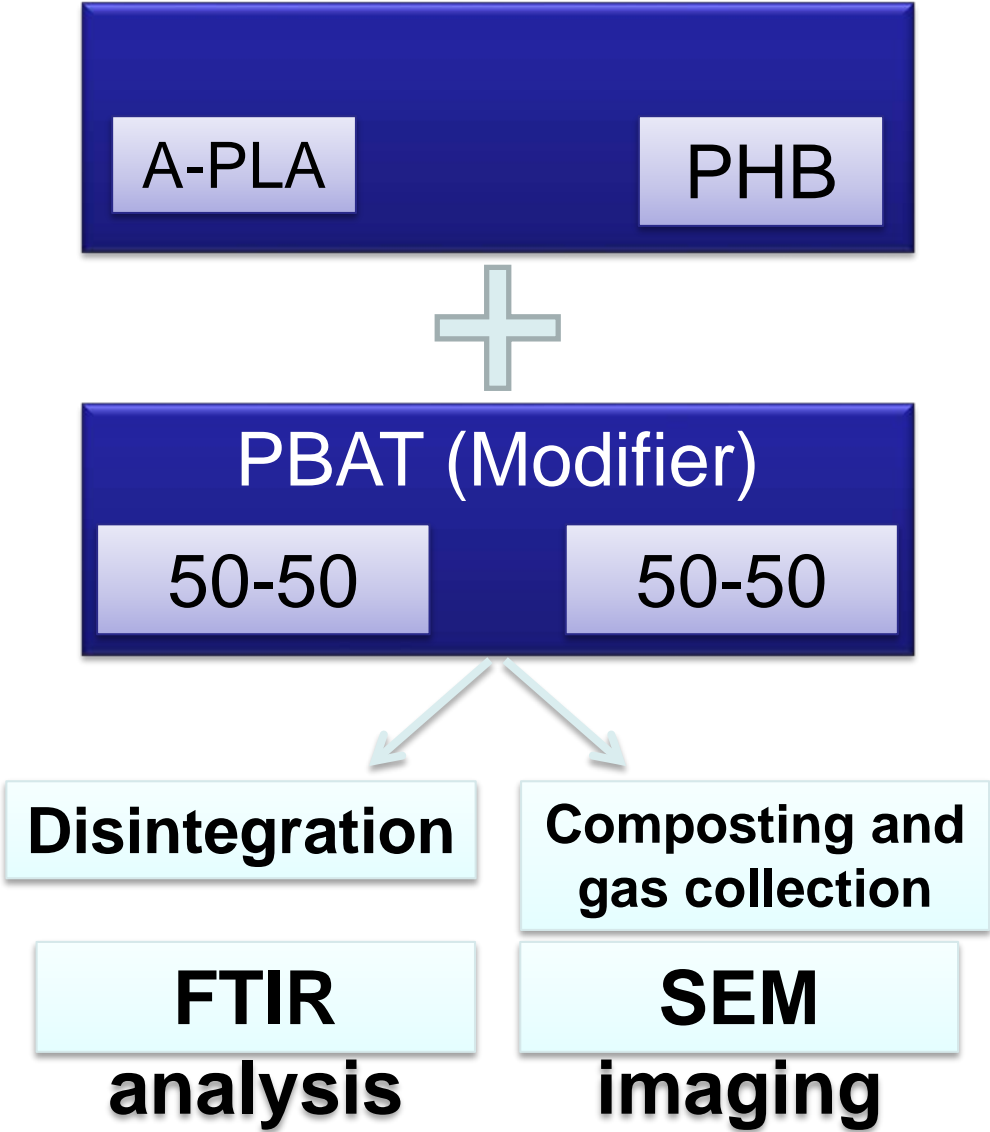
Materials



PLA Natureworks
4060D

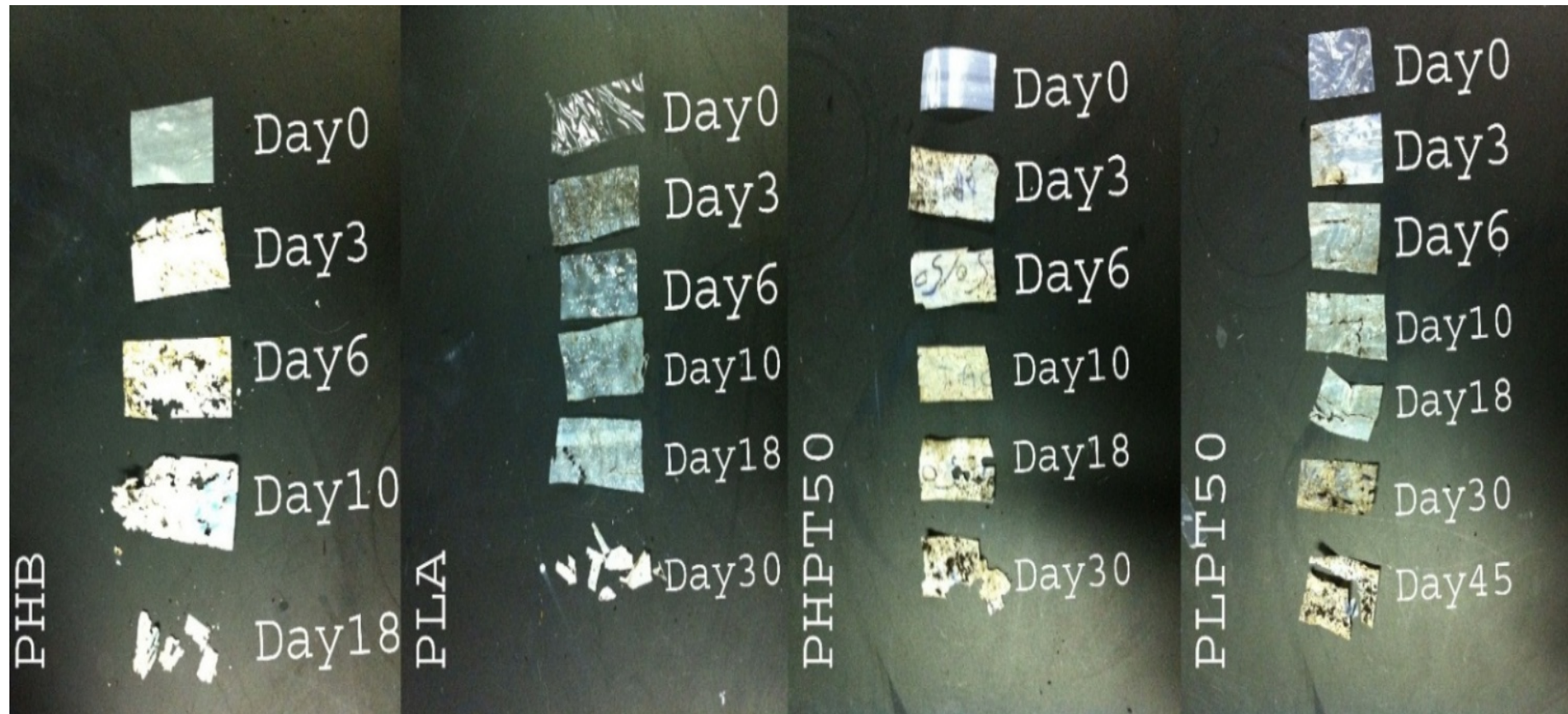
PBAT F Blend
C1200

PHB P290 Biomer



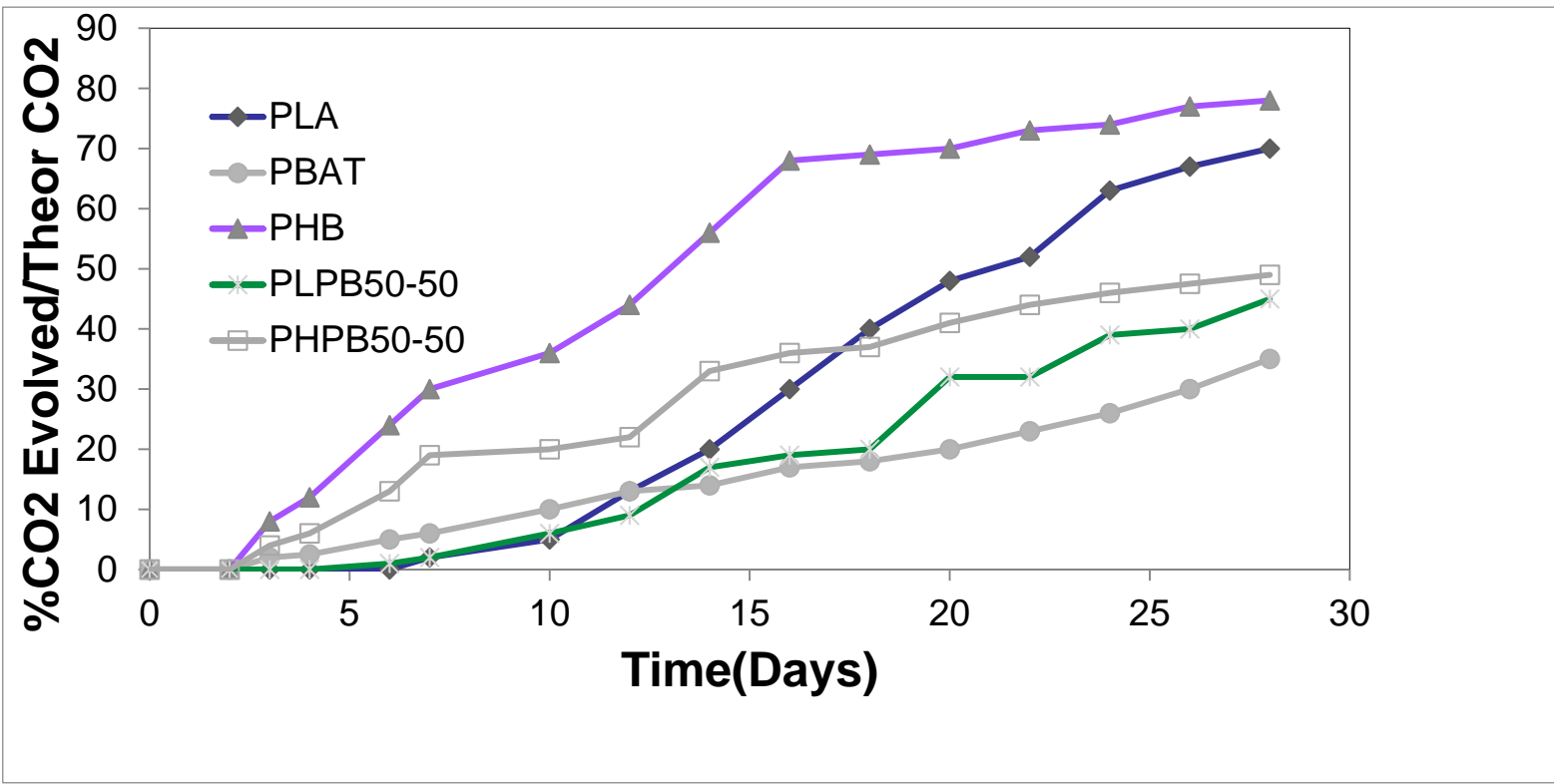
Result: Disintegration and mechanical strength

3S *pack*
🟡 🟢 🟠



Integrity of samples are lost \Rightarrow loss of mechanical properties

Result: Composting and gas collection



Faster bacterial digestion ⇒ Larger amount of CO₂ evolved

Concluding Remarks:

- Many challenges still remain for the development of more sustainable packages with the use of nanoparticles / nanostructures in Packaging:
 - Dispersion,
 - Manipulation and Regulation,
 - Appropriate Performance.