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Intercalation/Exfoliation and Performance of Clay-Poly(lactic acid) Nanocomposites

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Intercalation/Exfoliation and Performance of Clay-Poly(lactic acid) Nanocomposites

M-T. Ton-That , W.Leelapornpisit, J.Denault

Bioplastics 2006
Montreal, Quebec, Canada
September 27th-29th, 2006

National Research Council Canada / Conseil national de recherches Canada

Canada

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Presentation outline

- Introduction
- Objectives
- Melt compounding; effect of clay chemistry and PLA structure
- Characterization
  - X-ray
  - SEM
  - TEM
  - Mechanical properties
    - Tensile tests
    - Impact
    - HDT
- Conclusions
- Future works

Green Processing of Strong, Lightweight Polymer Foams from Renewable Resources

Objective → *Foam manufacturing from bio-based (PLA, PHA…) polymer nanocomposites*

In Summary

Value: 1.7 M$
Duration: 3 years
NRC Partners: IMI and ICPET
Sponsor: Climate Change Technology and Innovation (PERD/OERD)

Our Responsibilites

Respond to our needs for materials in the 21st century

- Environmental issues and economic concerns due to limited oil supply
  - ✓ To cope with limitation of resources supply
  - ✓ Synthetic polymers are highly durable materials (200-500 yrs) mostly used in short-term applications
  - ✓ Non-biodegradable plastic represent 11% of the municipal solid waste in USA (data 2001).
  - ✓ Incineration of synthetic plastic produces CO_2 contributing to global warming





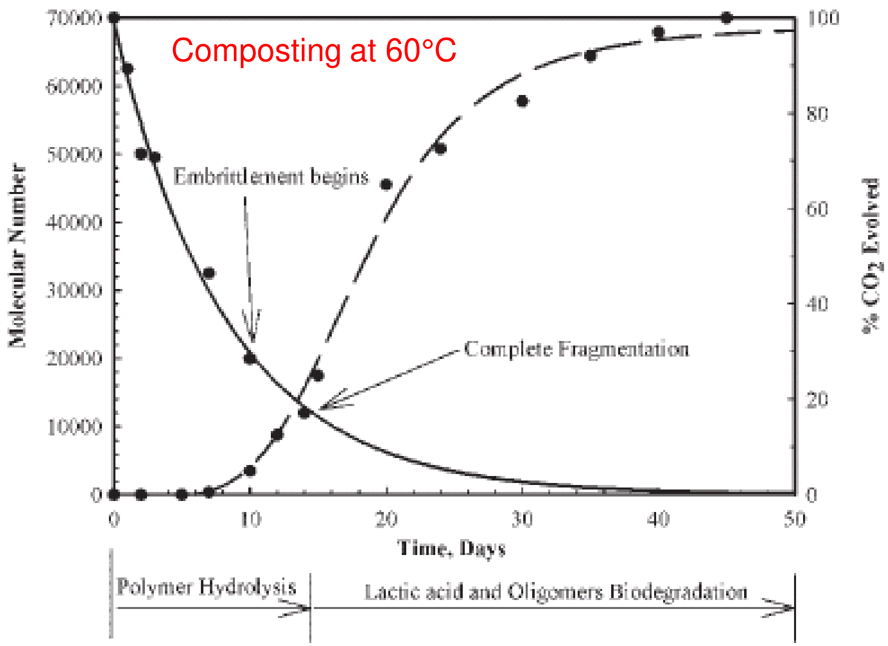
Why Biopolymer ?

Biopolymers are now available at large scale and reasonable cost.

- PLA example
  - ✓ In US, NatureWorks has a 300 million pound PLA plant with a cost of 1U$/pound.
  - ✓ NatureWorks is able to supply large-scale company like Coca-Cola, Dunlop Pacific, etc.
  - ✓ Unitika in Japan.

Biopolymer Advantages

- **Made from renewable ressources (sustainable)**
- **Biodegradable and recyclabe after service**
- **PLA advantages**
  - High clarity and gloss
  - High stiffness
  - Easy to process on standard equipment
  - Good film forming properties
  - Properties similar to Polystyrene
  - Good taste and aroma barrier
  - Cost competitive to PET



From R. Auras et al, *Macromol. Biosci.*, **4**, 835 (2004)

PLA Applications

- **Medical field**
  - Drud delivery systems
  - Healing products
  - Surgical implant devices
- **Packaging materials**
  - Food containers
  - Agriculture
  - Waste bags
- **Non-woven structure**
  - Filtration
  - Hygiene products
  - Protective clothings

Biopolymer Applications

Dream of Henry Ford in 1930

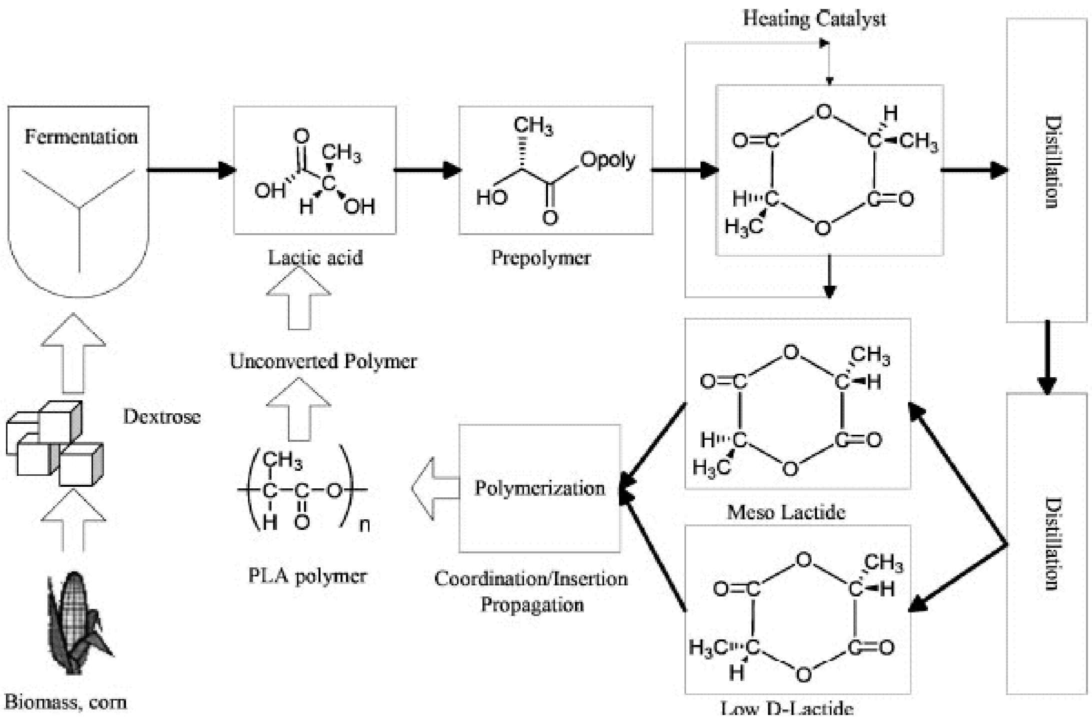
- ''Growing a car like a crop''
- Use soy-based polymer for knobs and body panels
- Water absorption problem causes excessive body panels warpage
- Was replace by synthetic polymer after the World War II because of economy and durability

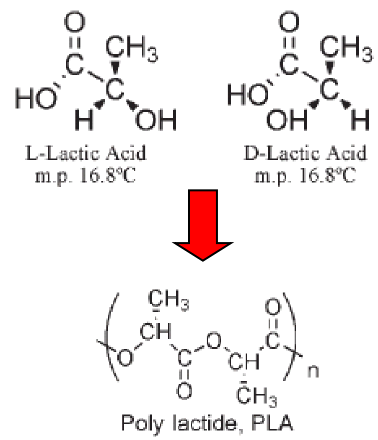
➢ *Now such durability becomes a problem*

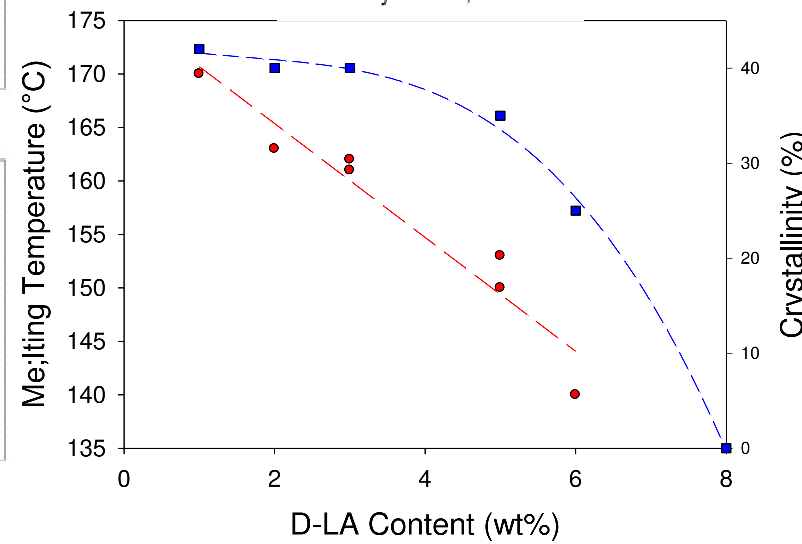
Henry Ford in 1937

PLA: Synthesis and Structure

NatureWorks Manufacturing Process:







From R. Auras et al, *Macromol. Biosci.*, **4**, 835 (2004) and
G. Schmack et al., *JAPS*, **91**, 800 (2004)

93%+ L-LA = Semi-Crystalline PLA
50-93% L-LA = Amorphous PLA

Challenges with PLA

- **Acceptance in the market place**
- **PLA must be competitive on a cost-performance basis**
- **Property limitations**
  - High density 1.25 g/cc
  - Low Tg (50°C) and HDT
  - Low crystallinity and slow crystallization
  - Brittleness
  - Heat resistance lower than PET
  - High moisture absorption
  - Limited barrier to moisture and gases (O_2 and CO_2)
- **Nanotechnology and foam process can upgrade PLA properties**

Objectives

- Develop formulations of Poly(lactic acid) Nanocomposites by melt compounding technologies
- Optimize processing
- Control the micro-nanostructure
  - intercalation vs exfoliation
- Maximize performance
- Minimize cost

PLA Nanocomposites Materials and Processing

Polymer

PLA 2002D, (NatureWorks)

T_m=148°C → ~ 5-7% D-LA (amorphous)

Nanoclays

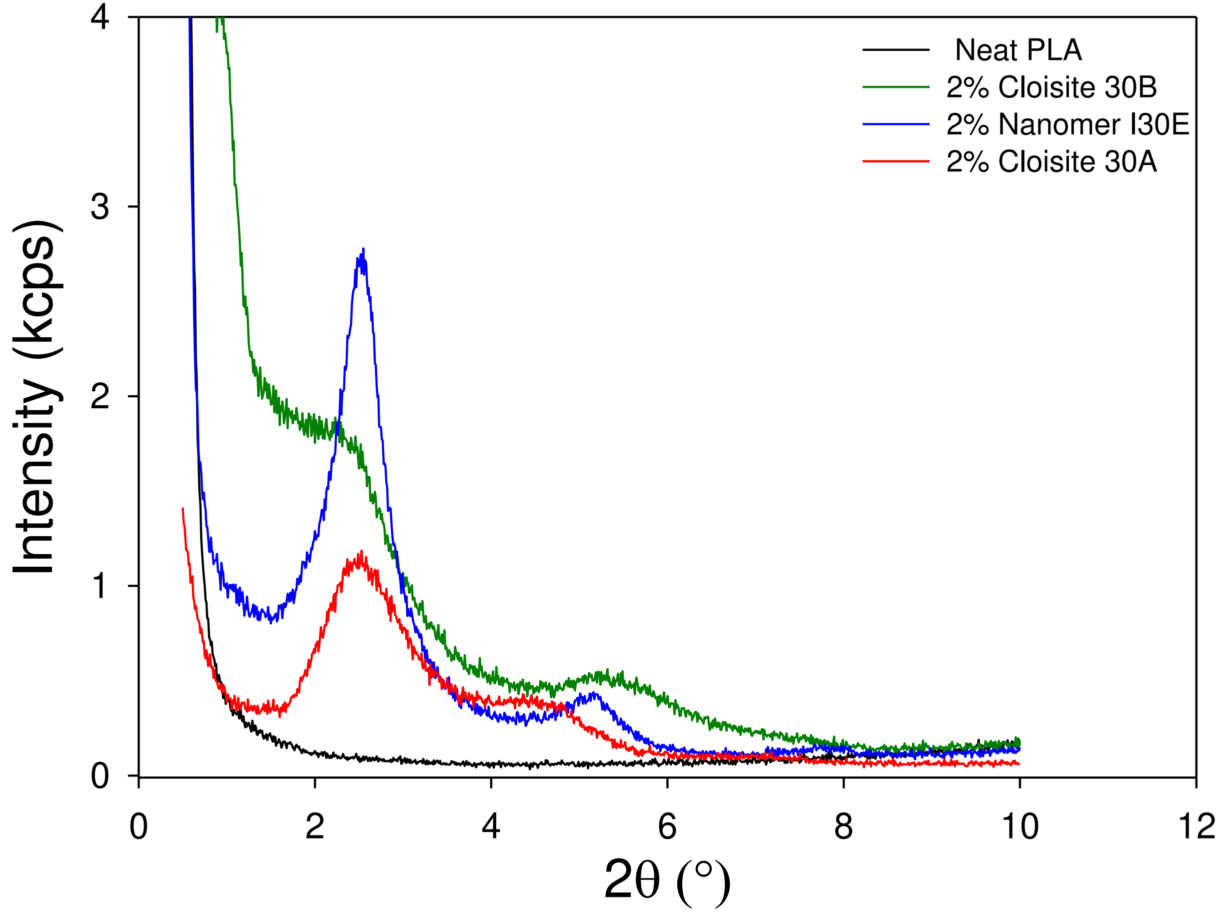
Cloisite Na+ (Southern Clay Products)
Cloisite 20A (Southern Clay Products)
Cloisite 30B (Southern Clay Products)
Nanomer I30E (NanoCor)

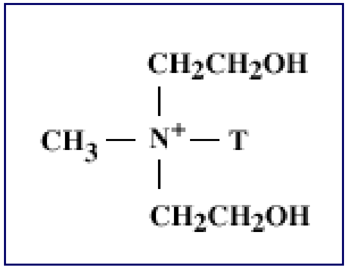
Conditions

Haake conical counter-rotating TSE
N= 100 rpm
T_{melt} = 190-230°C
t = 5-20min

Haake's Mini-twin screw extruder

PLA Nanocomposites Structure -XRD

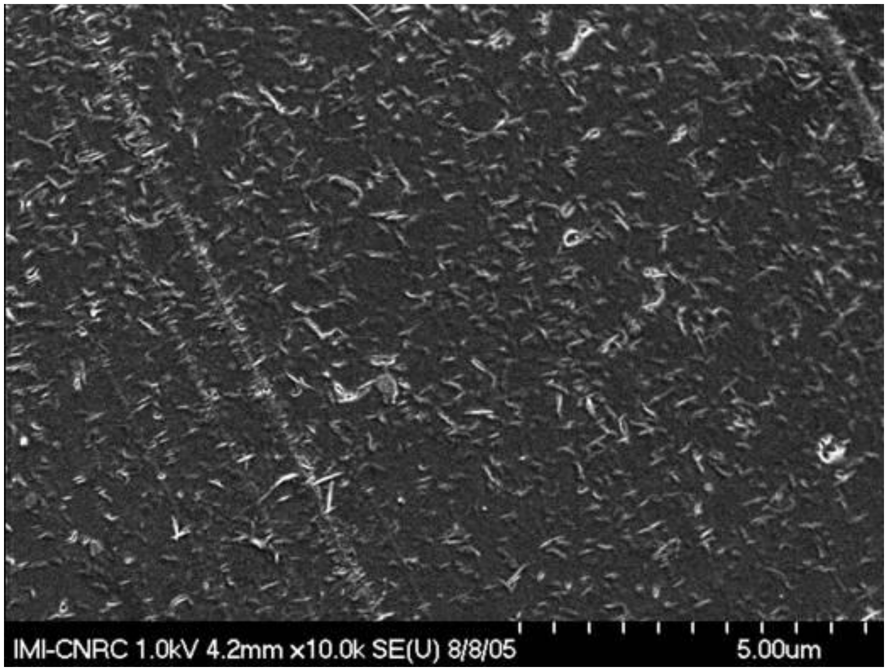


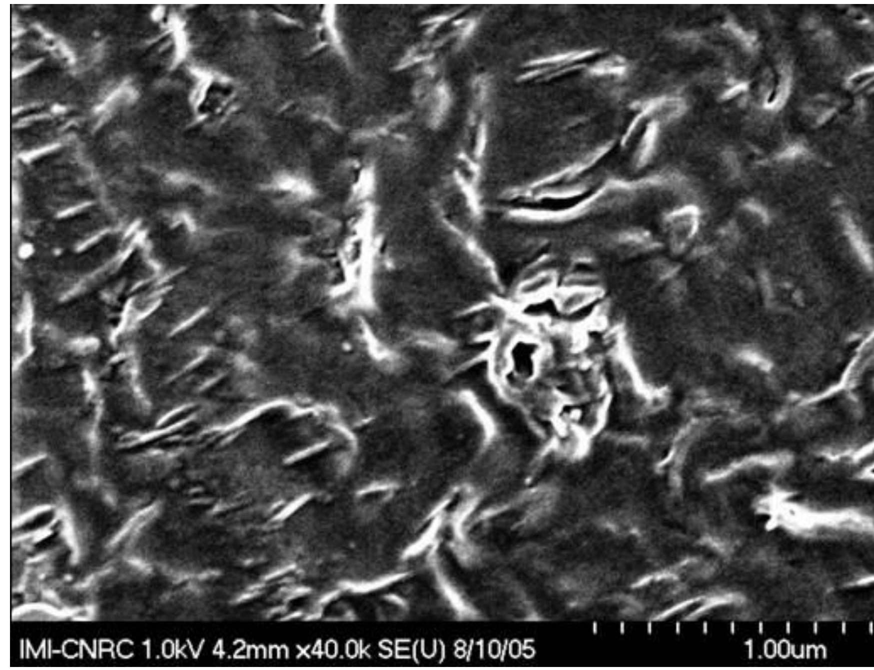


Cloisite 30B
MT2EtOH: methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium

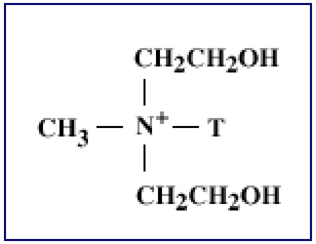
Cloisite 30B provides a better intercalation and exfoliation (asymmetric peak) because of the hydroxyl group in the intercalant

PLA Nanocomposites Structure - SEM



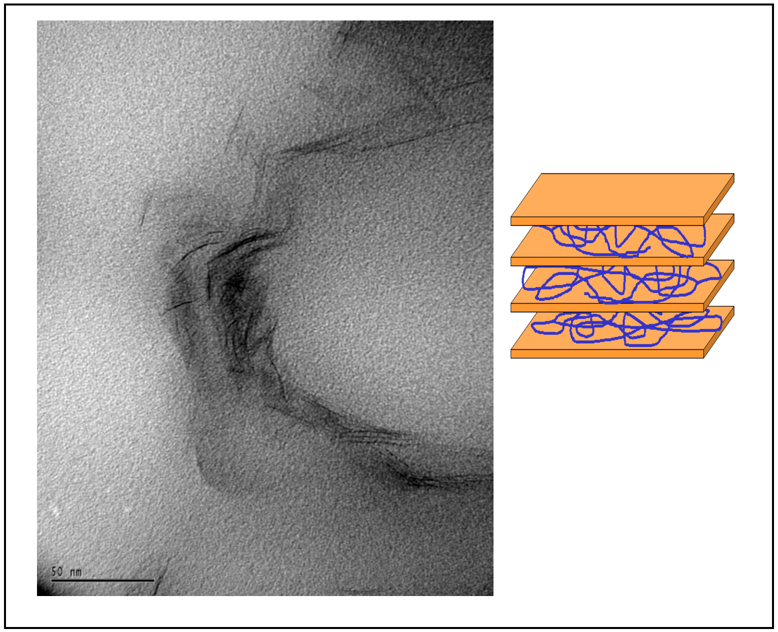


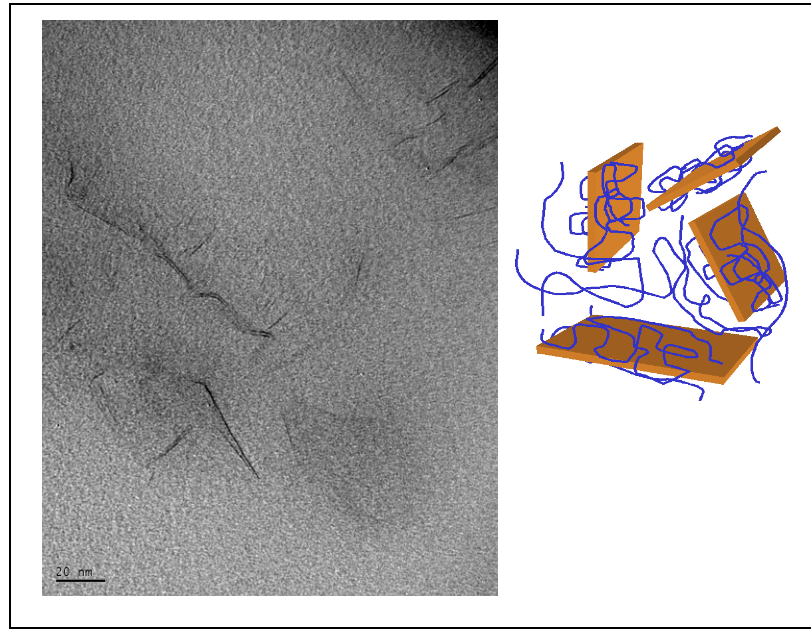
Cloisite 30B provides a very good micro-dispersion even in the low shear rate of the mini-compounder



Cloisite 30B
MT2EtOH: methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium

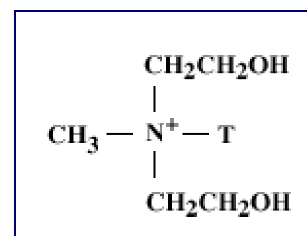
PLA Nanocomposites Structure - TEM





Cloisite 30B provides a fairly good intercalation and exfoliation even in the low shear rate of the mini-compounder

→ Cloisite 30B is chosen for further studies

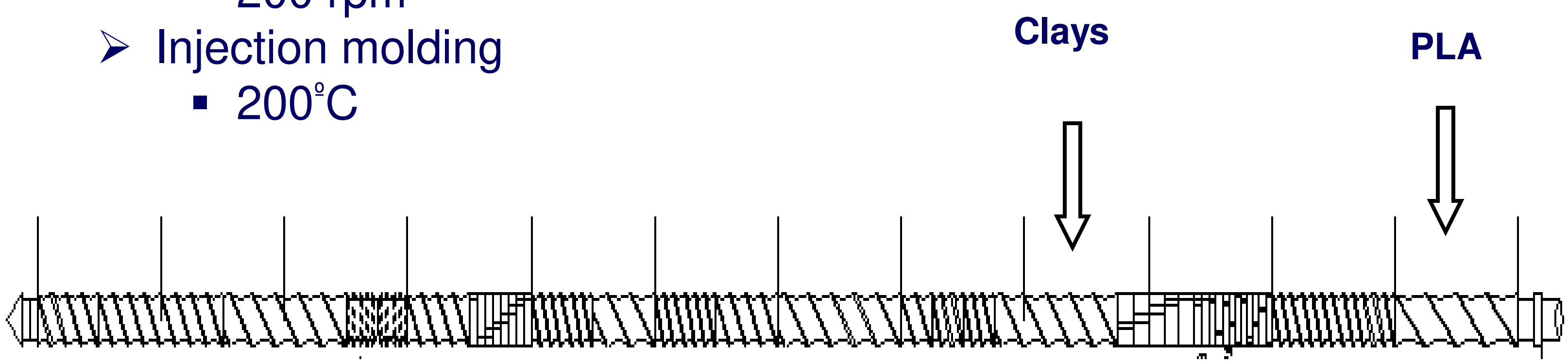


Cloisite 30B
MT2EtOH: methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium

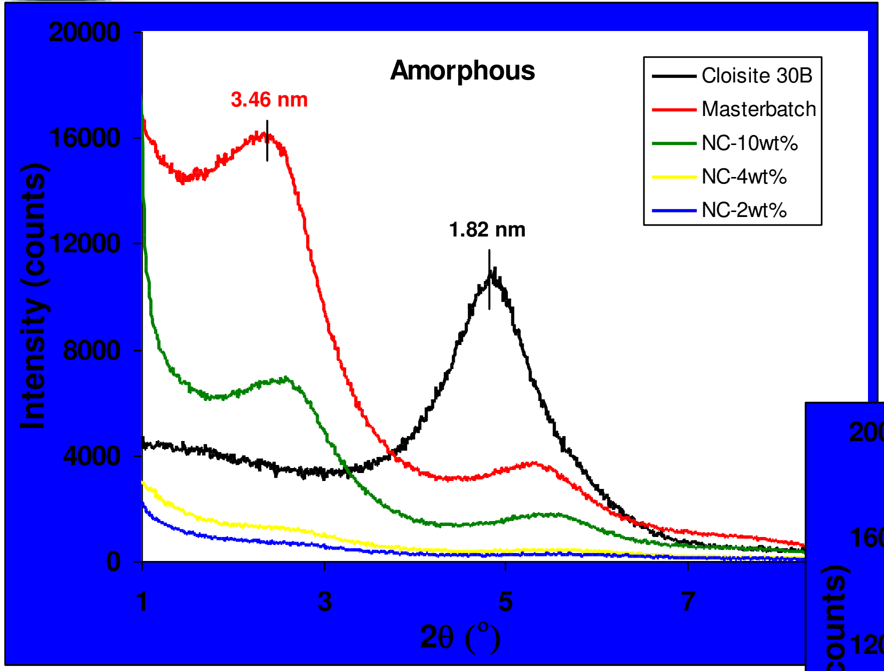
PLA Nanocomposites with a Twin-screw Extruder

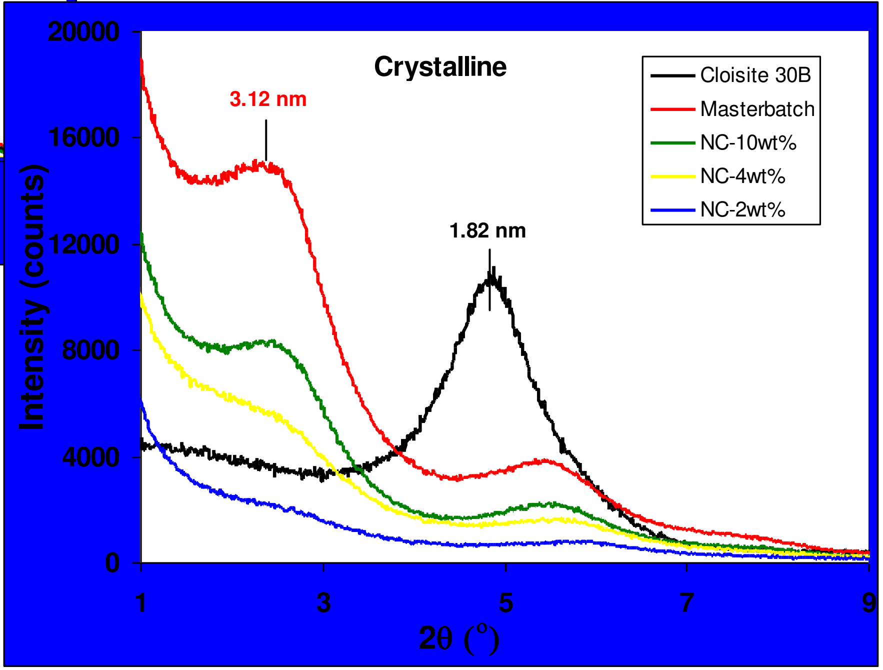
- Materials
  - Clay: Cloisite 30B (SCP)
  - PLA 8302D (PLA-A-amorphous) (9.85% d-Lactic acid)
  - PLA 4032D (PLA2-C-crystalline) (1.40 % d-Lactic acid)

- Melt process
  - Twin-screw extruder
    - Side-feeding
    - 200°C
    - L/d = 40
    - 200 rpm
  - Injection molding
    - 200°C



XRD Analysis





- Only very lightly difference in term of intercalation
- At 2wt% clay, exfoliation took place in both PLA matrices
- But better exfoliation for amorphous PLA

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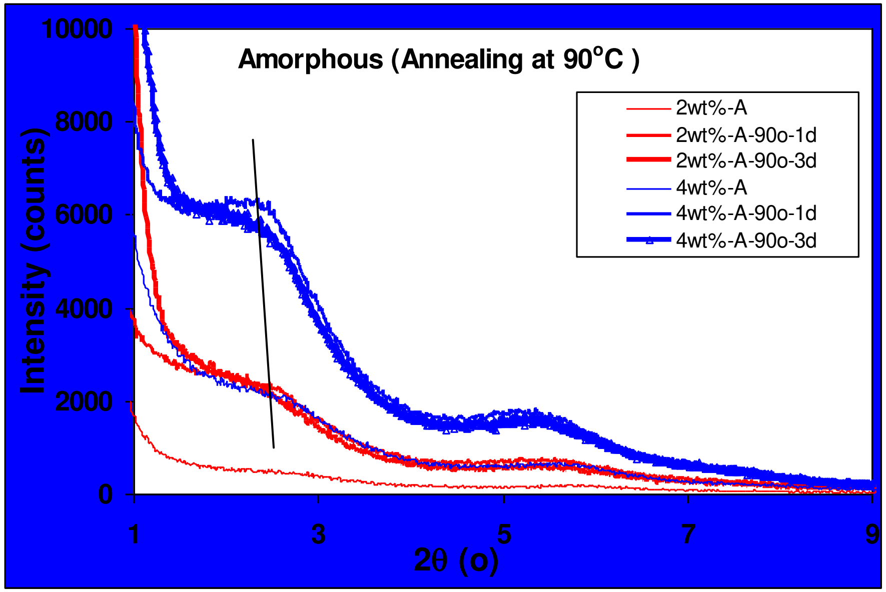
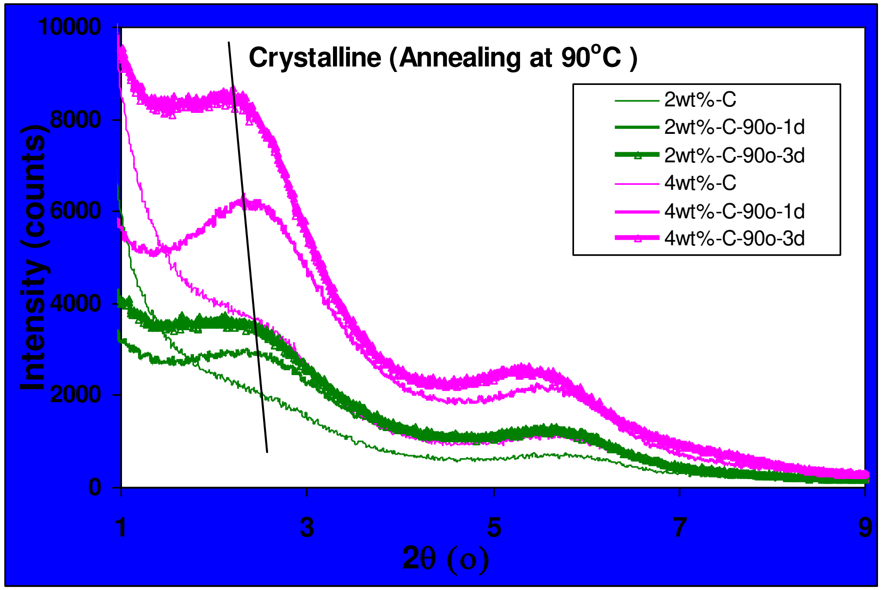
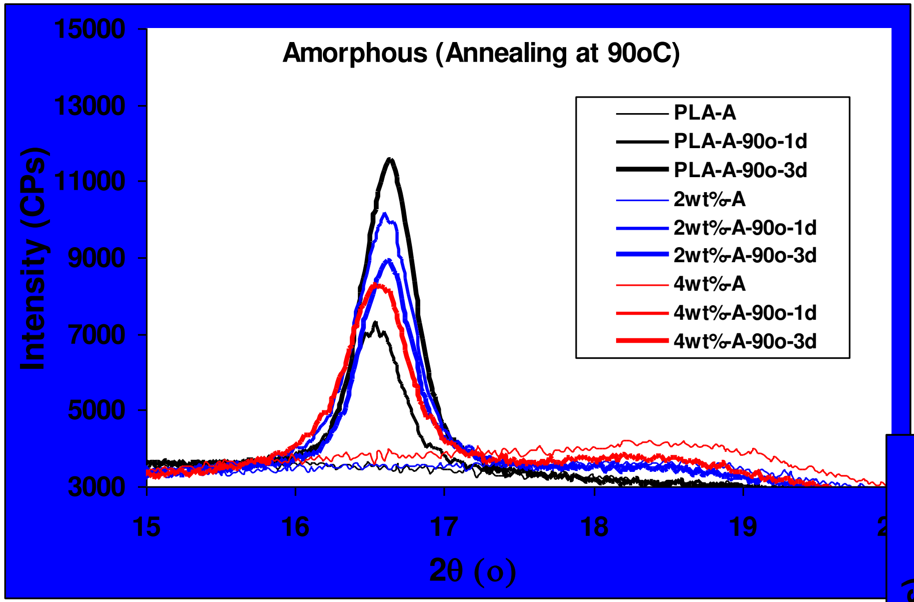
Annealing effect
Clay structure

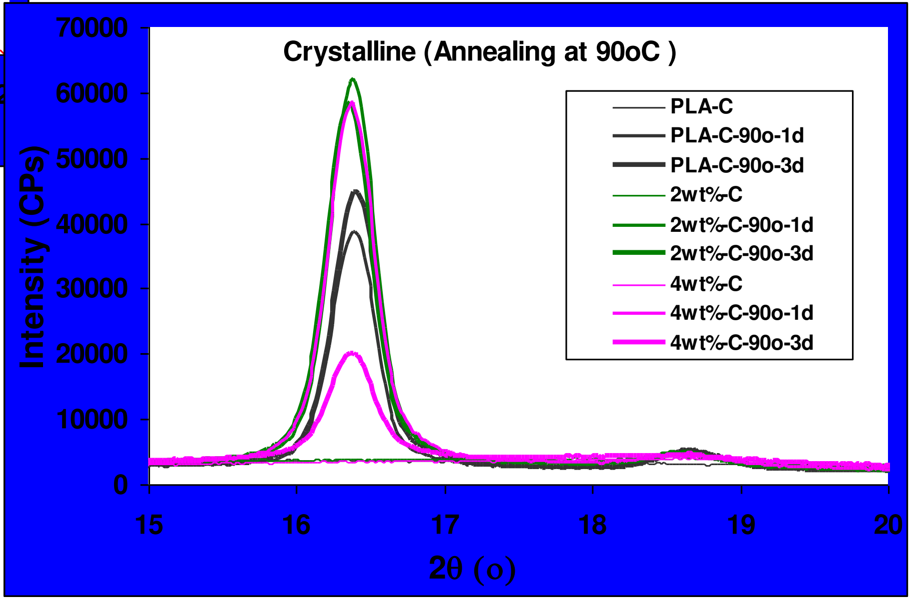


- Annealing seems to decrease the intercalation-exfoliation of clay and more evidence in the PLA crystalline systems as a result of crystallization



Annealing effect PLA structure

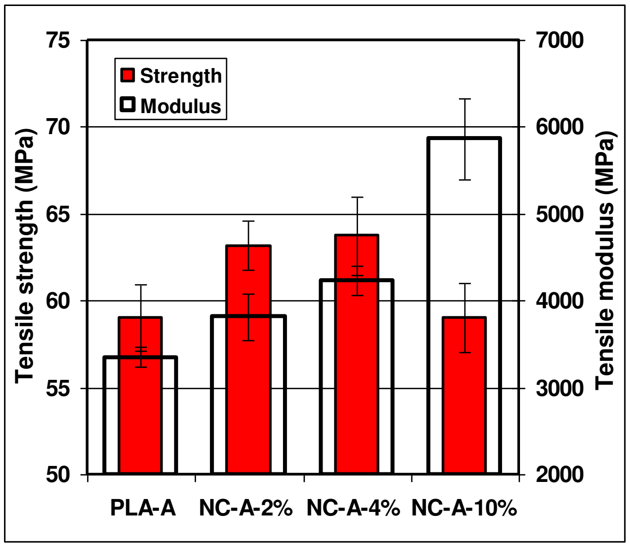


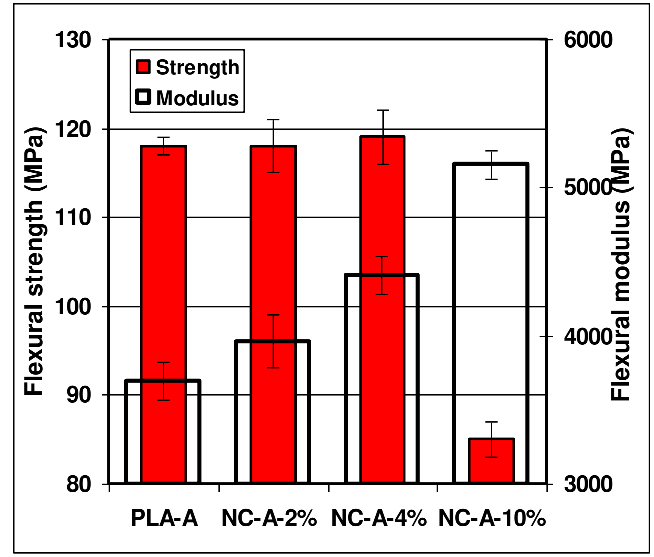


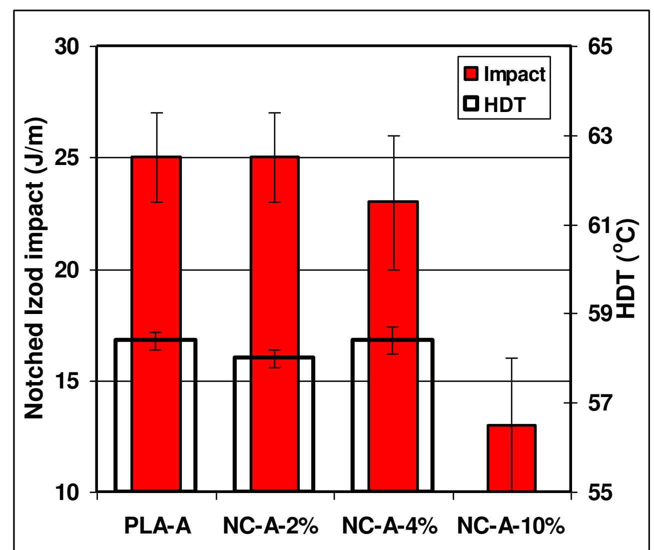
- Annealing leads to higher crystallinity
- Effect is more important in the low D content PLA; clay seems to favor the crystallization

Mechanical Properties

Amorphous PLA



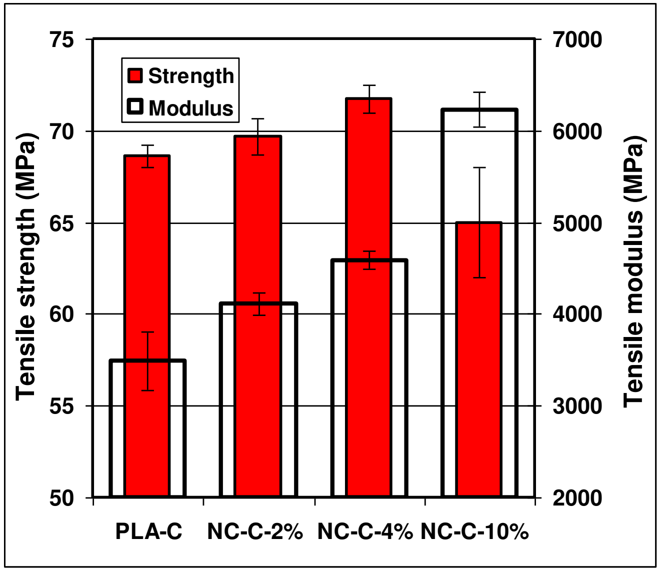


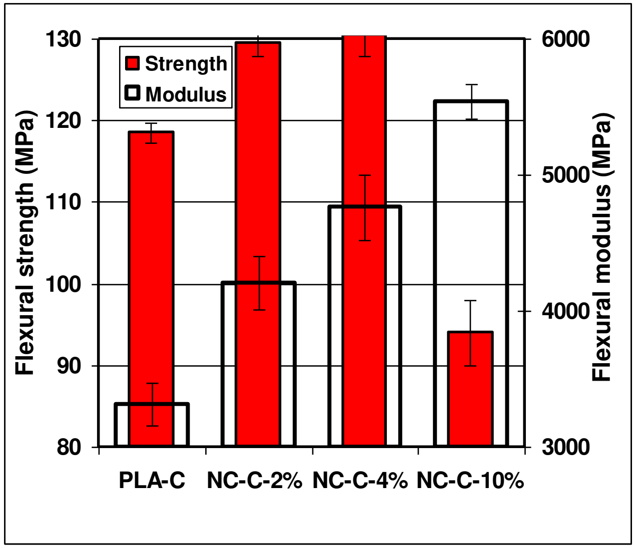


- Clay improves strength and modulus and does not affect the impact and HDT
- At high clay concentration of 10%: loss in tensile and impact strength are noticeable

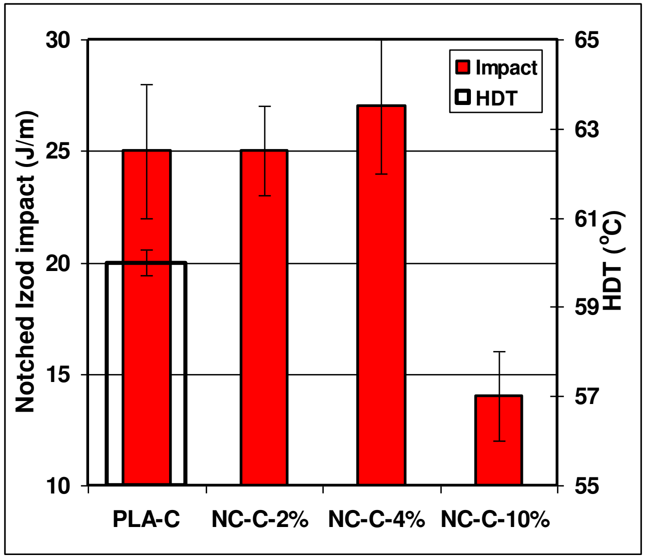
Mechanical Properties

Crystalline PLA





- Similar observation as for amorphous systems:
- Clay improves strength and modulus and does not affect the impact
- At high clay concentration of 10%: loss in tensile and impact strength are noticeable



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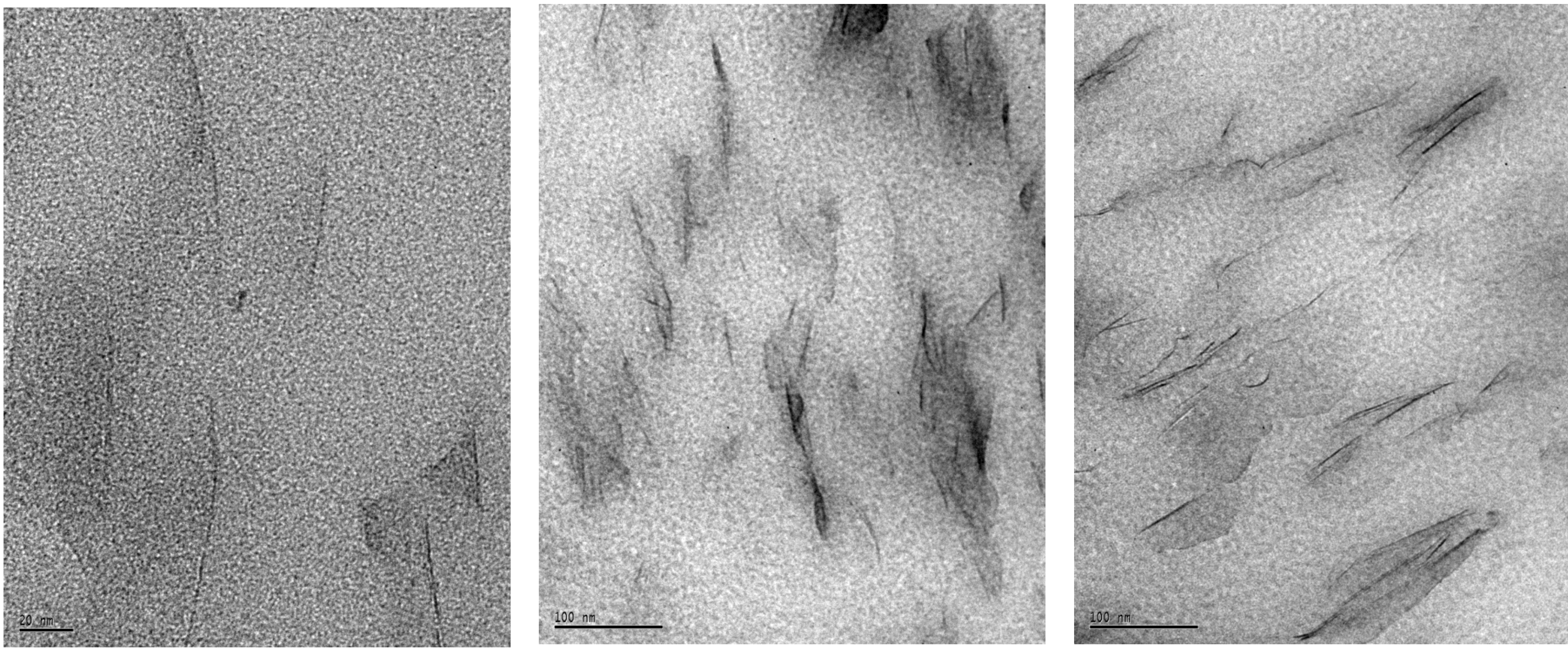
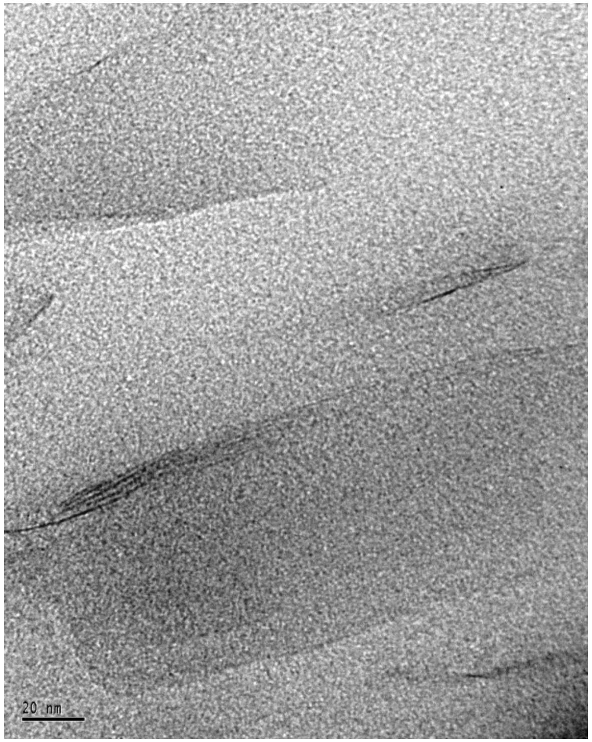
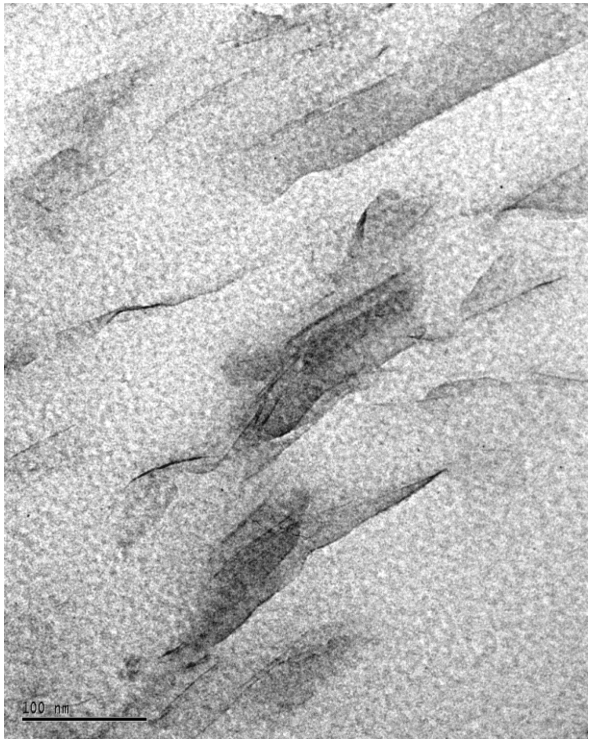
Amorphous PLA



- ❑ Good exfoliation has achieved although very few multiple stacks remain (may be due to the imperfection of clay treatment or clay degradation)

Crystalline PLA





- Good exfoliation has achieved as in the amorphous systems

Summary and Conclusions

- Cloisite 30B is the most appropriate commercial organo-clay for the fabrication of PLA nanocomposites by melt compounding
- Good exfoliation can be achieved with Cloisite 30B by melt-compounding (but processing parameters play a very important role)
- With the addition of less than 5wt% clay, strength and modulus of the PLA matrix are improved why impact strength is not affected
- Amorphous PLA seems to give better intercalation-exfoliation structure
- However HDT is not improved

  - Problem of clay-PLA interaction?
  - Intercalant degradation?
  - PLA degradation?

Future work

- ❑ Optimize of the processing procedure to minimize intercalant and PLA degradation and optimize clay-PLA interaction
- ❑ Better understanding the crystallinity effect in the intercalation/exfoliation and the mechanical performance

  - ✓ Extrusion parameters
  - ✓ Use more thermally stable intercalant
  - ✓ Use of coupling agent if necessary

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Science at work for Canada

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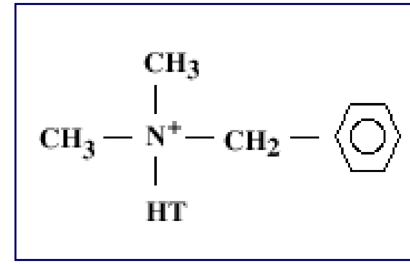
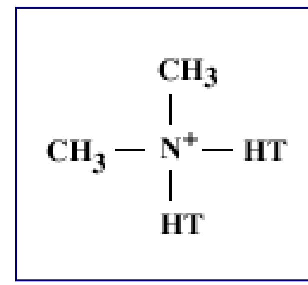
Commercial nanoclays

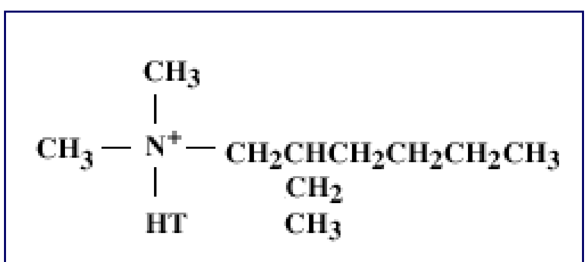
- Southern Clay Products, Inc.
  - MMT: 92.6 meq/100g
  - Intercalant:
    - **Cloisite 10A (2MBHT)**
    - **Cloisite 15A, 20A (2M2HT)**
    - **Cloisite 35A (2MHTL8)**
    - **Cloisite 30B (MT2EtOH)**
    - **Cloisite 93A (M2HT)**



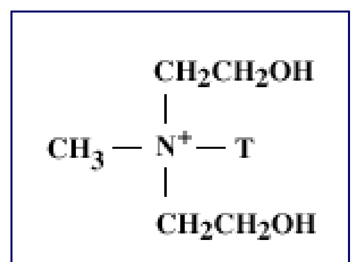
2MBHT: dimethyl, benzyl, hydrogenatedtallow, quaternary ammonium



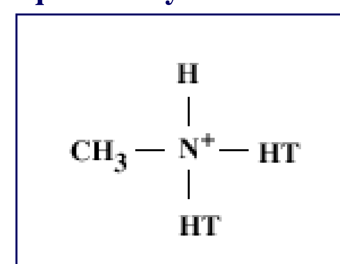
2M2HT: dimethyl, dihydrogenatedtallow, quaternary ammonium



2MHTL8: dimethyl, hydrogenatedtallow, 2-ethylhexyl quaternary ammonium



MT2EtOH: methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium



M2HT: methyl, dihydrogenatedtallow ammonium