Polyethylene Clay Nanocomposites: Modeling and Experimental Investigation of Particle Morphology

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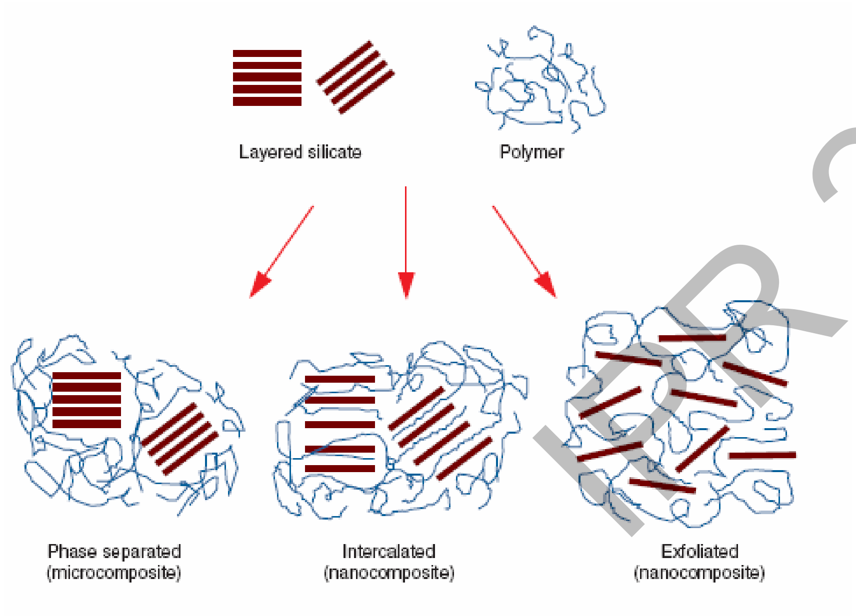
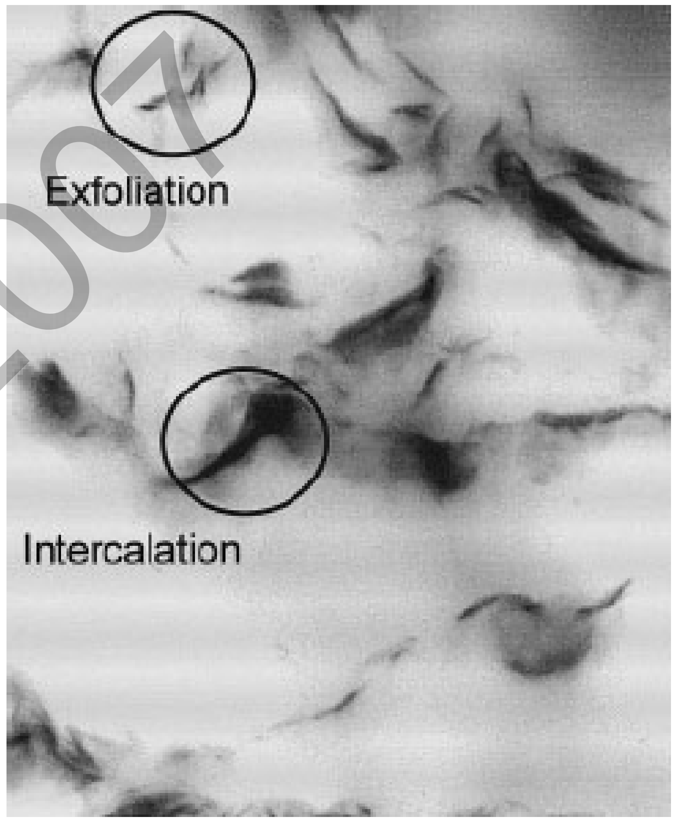
Outline

- **Introduction**
- **Results**
  - ***Modeling***
  - ***Experimental***
- **Conclusions**

Layered Silicate Nanocomposites

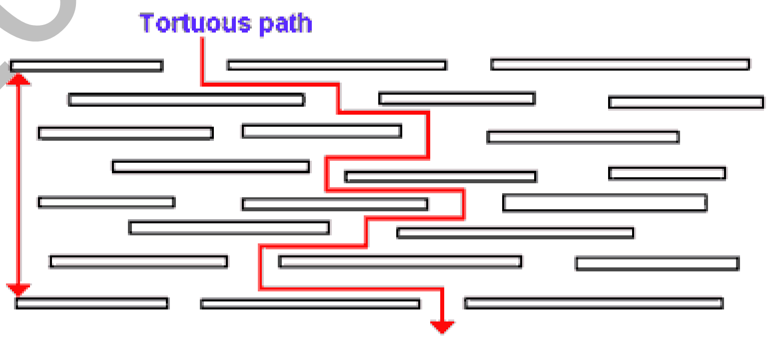




- Shape: Platelet , Size: 1nm thick, 75-150 nm across , Charge: unit cell 0.5-0.75 charge, 92 meq/100g clay, Surface Area: >750 m^2/g, High Modulus: ~170 GPa, Particle: robust under shear, not abrasive

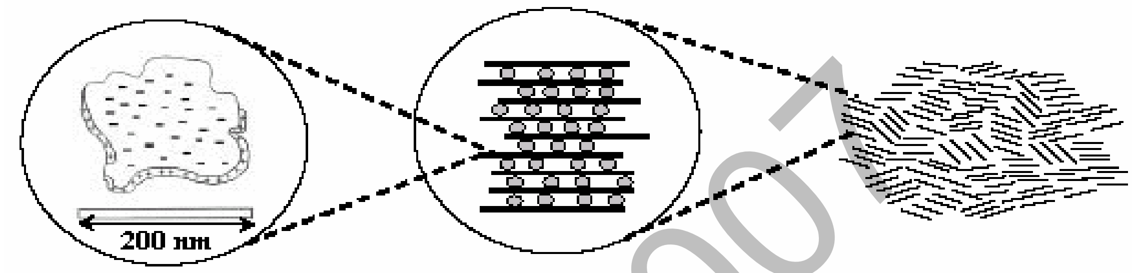
Polymer/Clay Nanocomposites in Brief

- **Scientific facts**
  - High aspect ratio nanofiller
  - High modulus nanofiller
  - Composite theory; torturous path theory
- **Main applications**
  - Reinforcement
  - Barrier
  - Synergistic flame retardant
  - Etc.
- **Basic requirements of using organoclay in nanocomposites**
  - Compatibility
  - Thermal stability



http://www.shu.ac.uk/research/meri/pcas/composites/composites.html

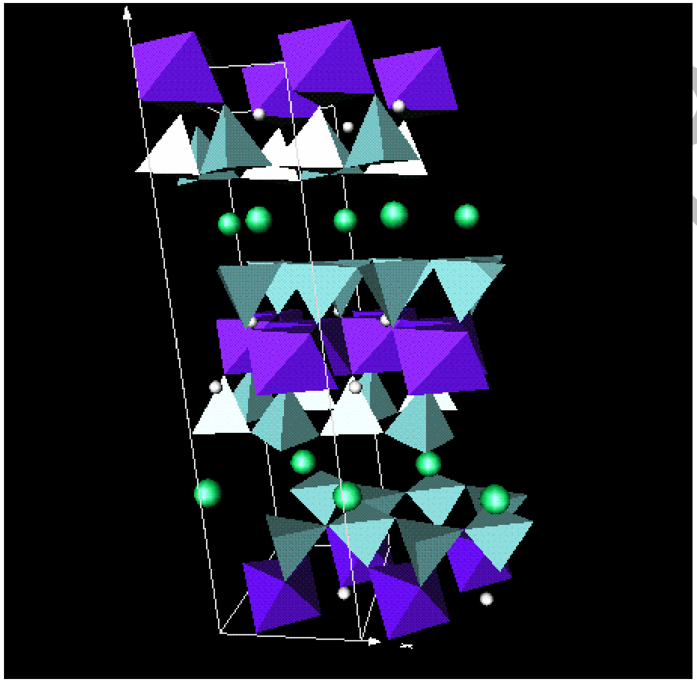
Montmorillonite (Clay): A Layered Structure

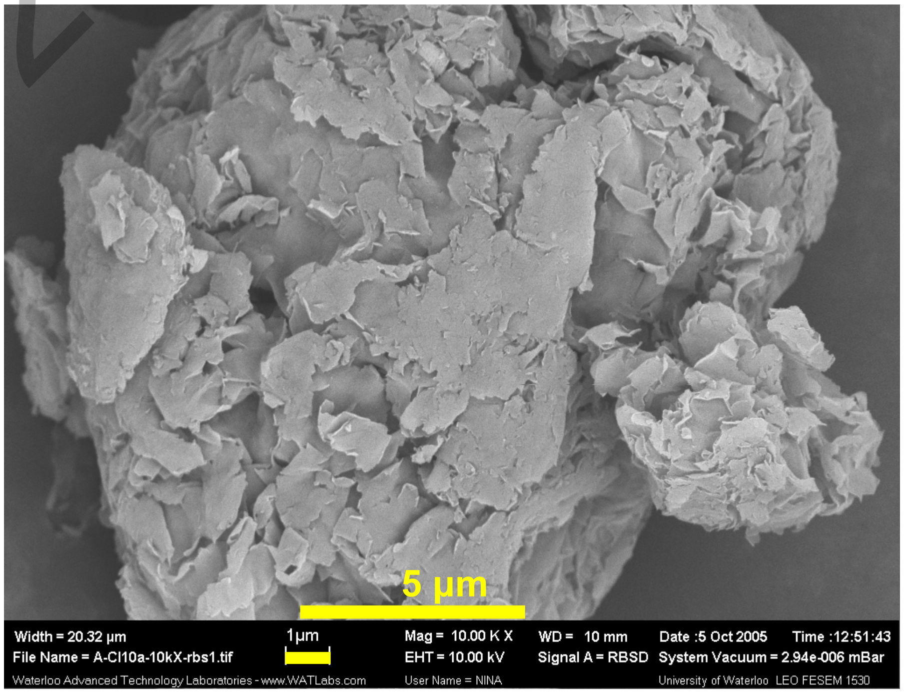


Single Layer
(1 nm)

Primary particle
(8 ~ 10 nm)

Clay powder
(0.1 ~ 10 μm)

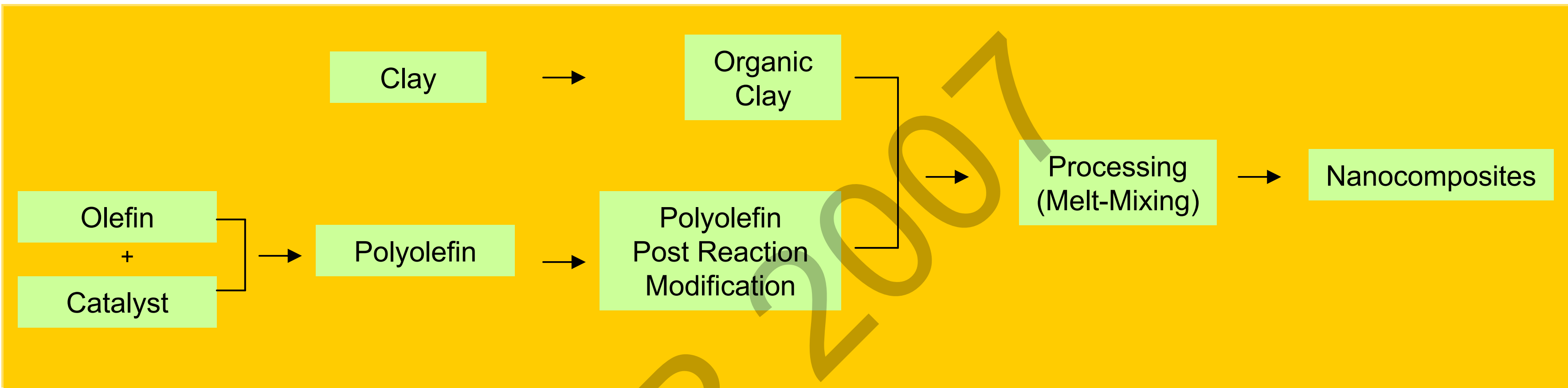


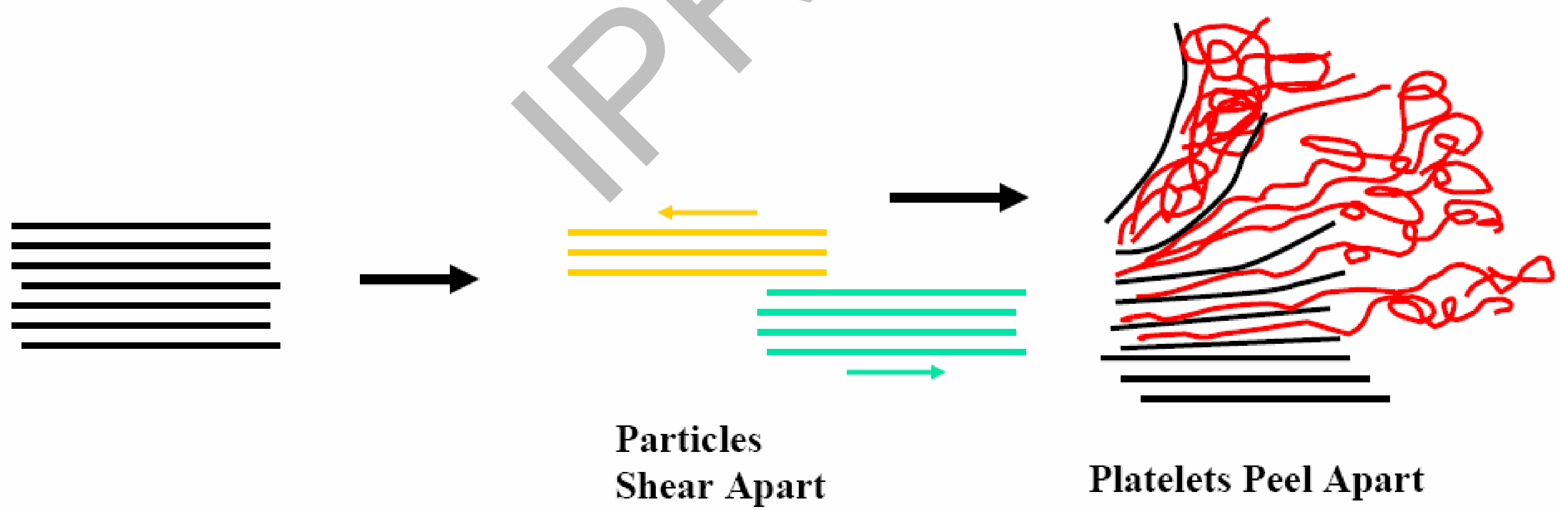


Preparation of Polyolefin-Clay Nanocomposites

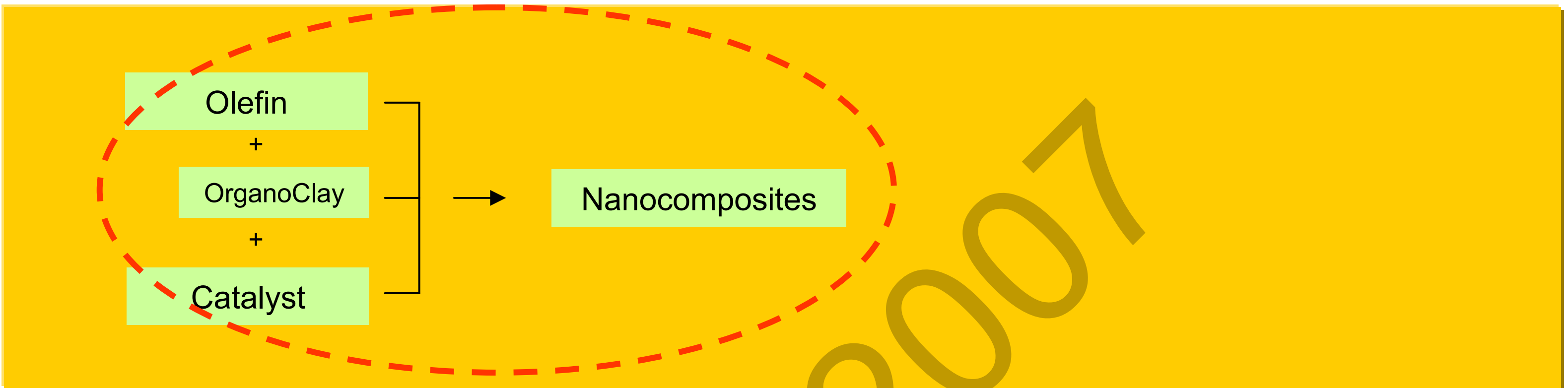
Common Preparation Methods

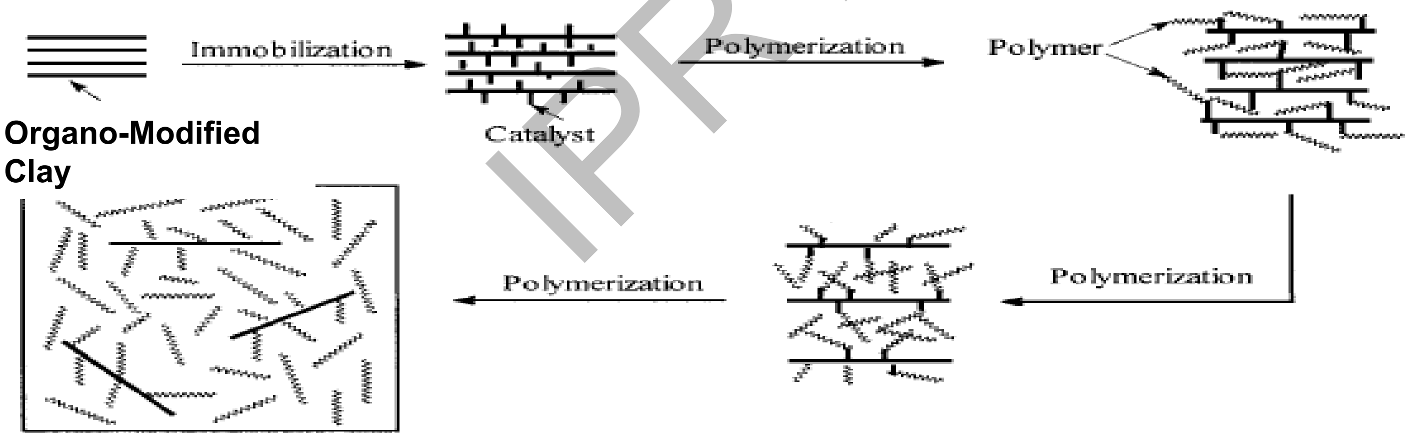
Melt Mixing


Clay
Organic Clay
Olefin
+
Catalyst
Polyolefin
Polyolefin Post Reaction Modification
Processing (Melt-Mixing)
Nanocomposites


Particles
Shear Apart
Platelets Peel Apart

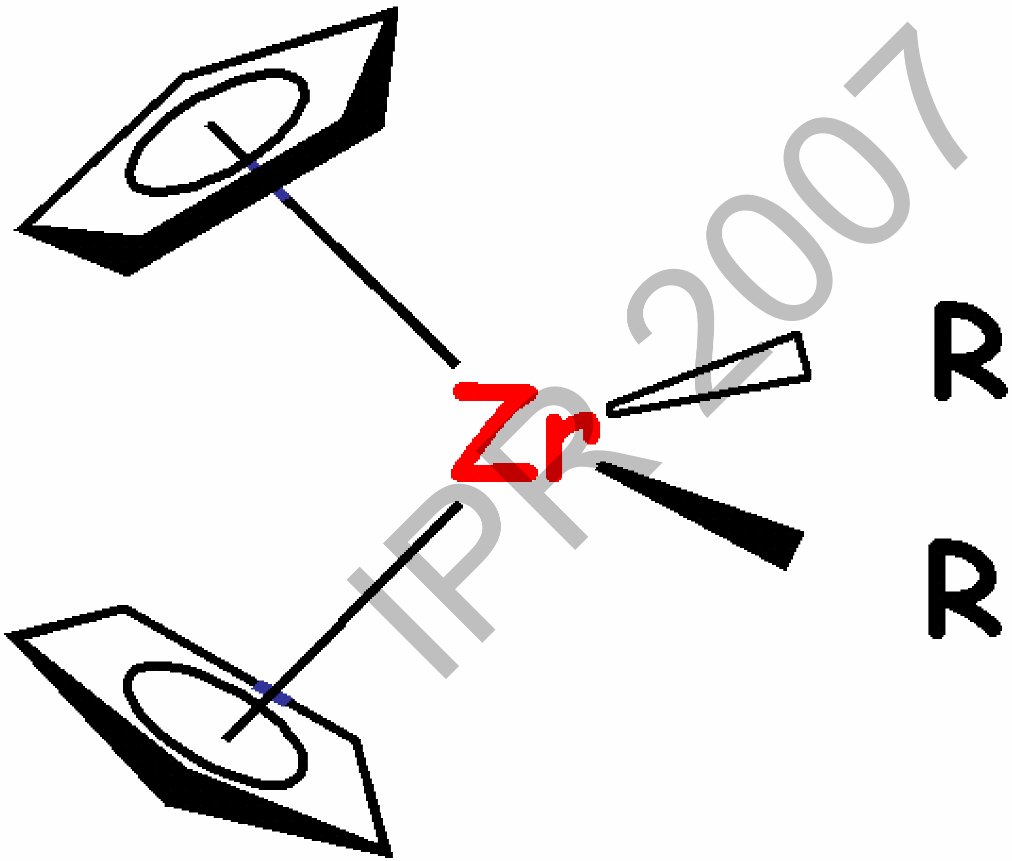
In-Situ Polymerization Method





Scheme 1

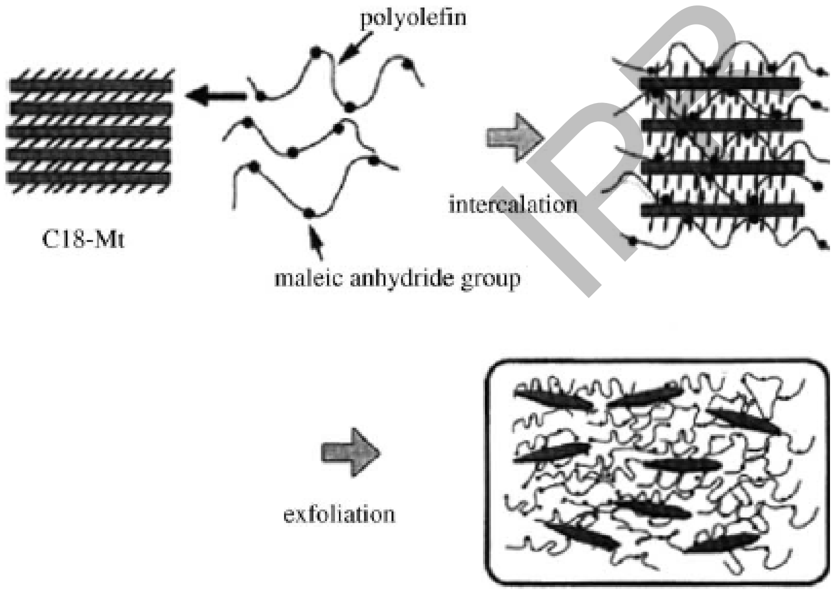
Metallocene Catalyst



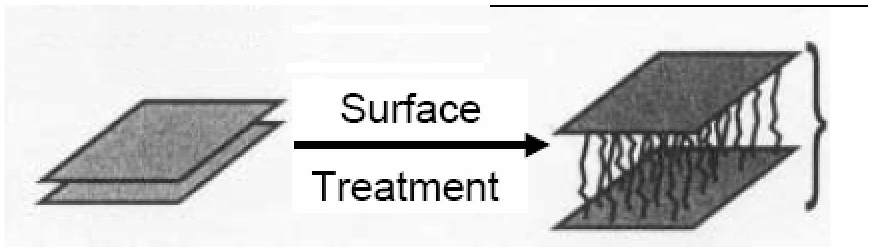
Polymer- clay compatibilization

Polyolefin – clay compatibility

- Needed in processing & production
- Needed for final properties



1. **Polymer compatibilization**
   - Addition of functional groups into the polymer chains
2. **Clay surface treatment**
   - Increased gallery spacing for catalyst supporting
     - Stabilized surface for catalyst supporting
     - Compatibility to monomer & solvent in polymerization system



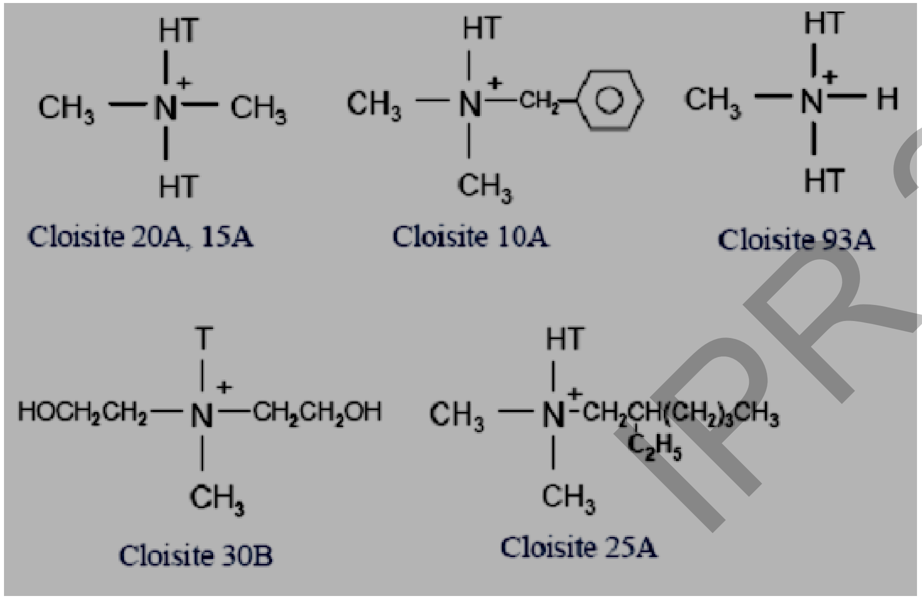
Experimental

- Effect of montmorillonite surface treatment
  - Best treatment selection

Concerns in "In-Situ" Method for Polyolefins

1. **Clay surface compatibility**
   - Catalyst precursors
   - Monomer
2. **Intercalation/exfoliation quality**
   - Extent of intercalation/exfoliation
   - Uniformity
3. **Catalytic activity**
   - Supporting decreases the catalyst activity
   - Supporting efficiency depends on the surface characteristics
   - Some organic treatments might kill the catalyst
4. **Good polymer properties**
   - Molecular weight distribution
   - Melting temperature
5. **Product shape (particle fragmentation)**
   - Powder sizing & bulk density

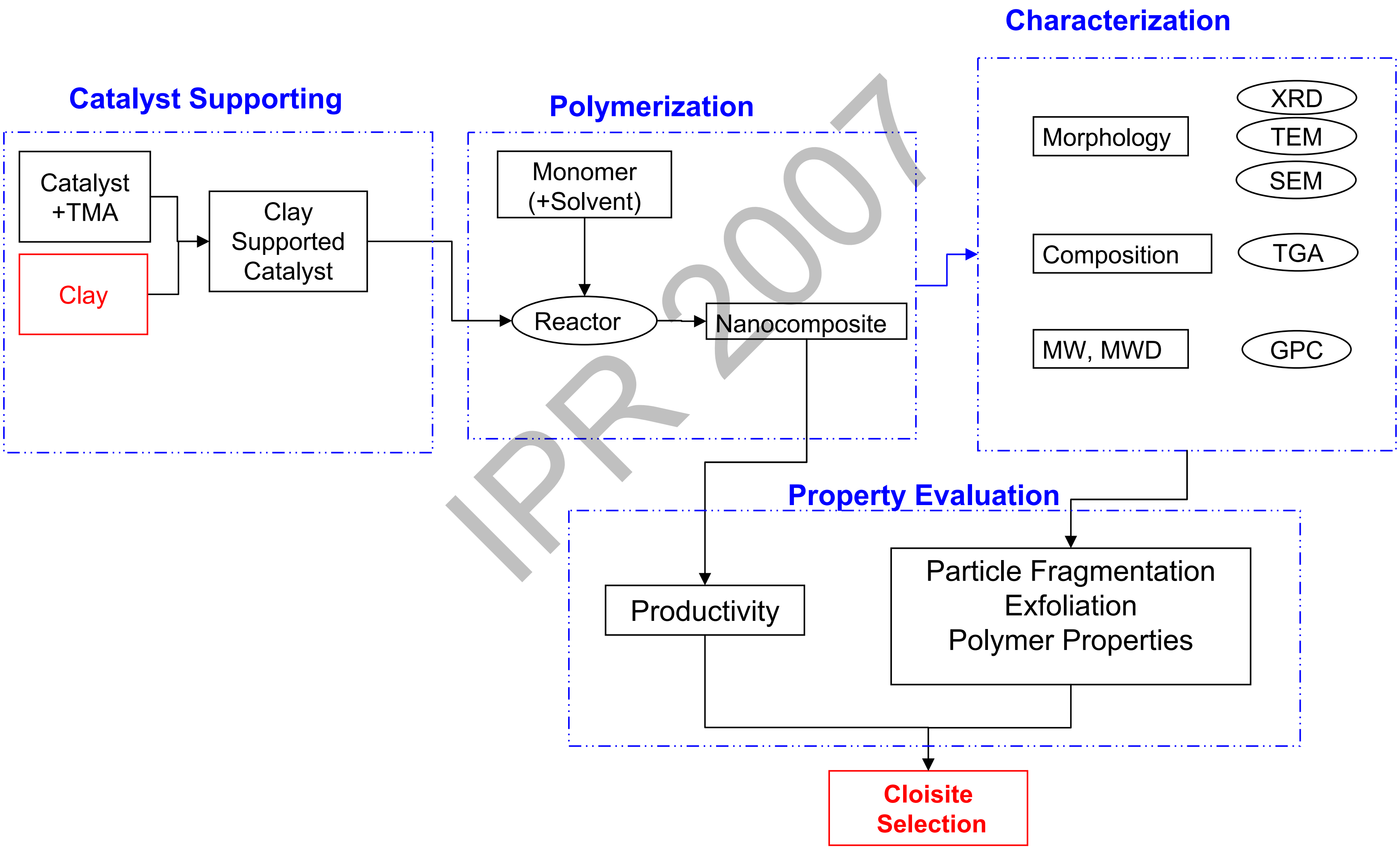
Effect of Montmorillonite Treatment



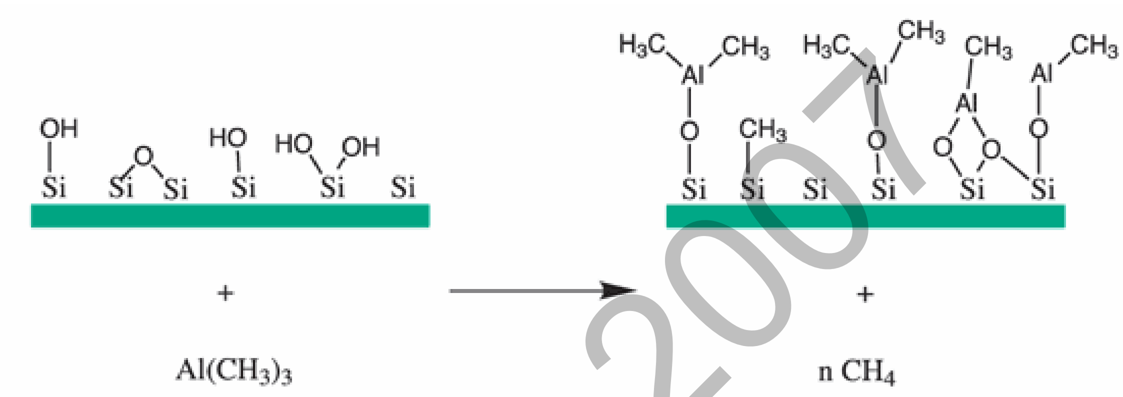
T is Tallow (~65% C18; ~30% C16; ~5% C14)

No.	Montmorillonite Sample	Modifier Concentration (meq/100g clay)	Bulk Density lb/ft^3	d-Spacing (Å)
1	Cloisite® Na^+	92.6	12.45	11.7
2	Cloisite® 30B	90	14.25	18.5
3	Cloisite® 10A	125	10.21	19.22
4	Cloisite® 25A	95	12.08	18.6
5	**Cloisite® 93A**	**90**	**10.56**	**23.6**
6	Cloisite® 20A	95	7.35	24.2
7	Cloisite® 15A	125	10.79	31.5

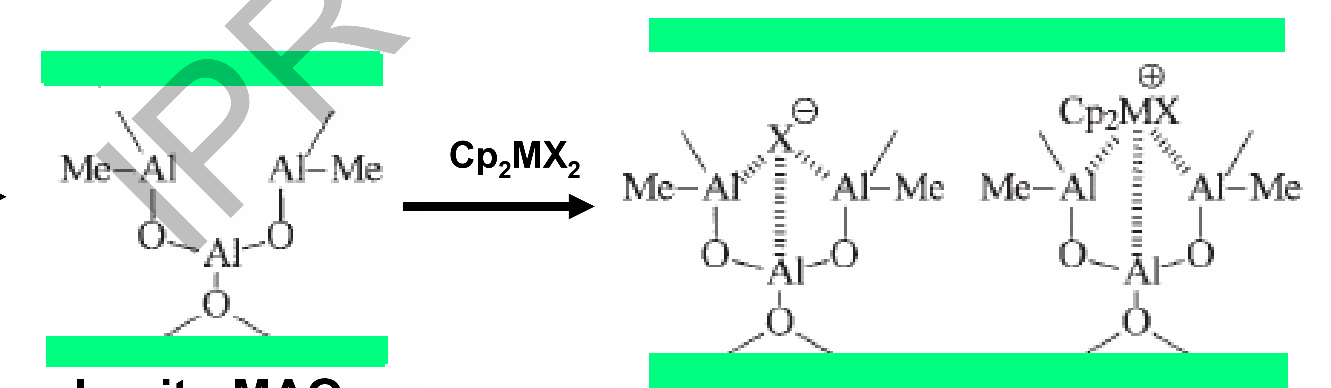
Supporting & Polymerization in glass reactor



Catalyst Supporting on the Cloisite Surface



TMA + Cloisite



In-situ MAO

Ethylene

Polyethylene/Clay Nanocomposite

Screening Results

Clay Sample	Sedimentation Rate	Activity	Polymerization Time (min)	Yield (g)
Cloisite Na^+	Quick (< 2 hr)	Yes	20	**1.87**
Cloisite 10A	Very slow (no precipitation)	N/A	20	-
Cloisite 15A	Very slow (no precipitation)	N/A	20	-
Cloisite 20A	Slow (>24 hr)	N/A	20	-
Cloisite 25A	Moderate(<8hr)	Very small	20	-
Cloisite 30B	Quick (< 2 hr)	Very small (or none)	40	-
Cloisite 93A	Slow (<12 hr)	Good	40	**3.14g**

High Pressure Comparison

Polymerization conditions for screening different supports in slurry phase

Catalyst/Clay ratio	TMA (m mole / g clay)	Ethylene Pressure	Temperature	Polymerization Time
20 micromole metal/gram of clay	6	5 bars	85 ^{o}C	1 hrs

Results

Cloisite 93 A has a better ability to meet primary requirements as support and dispersed phase

- High Activity of Catalyst supported on Cloisite 93A
- Low Activity Of Catalyst Supported on Na+ Cloisite

Sample	No of Runs	Average Normal Yield (g/ g clay/ hr)
Na^{+}	3	3.52
93A	3	78.34

Na^{+} Cloisite

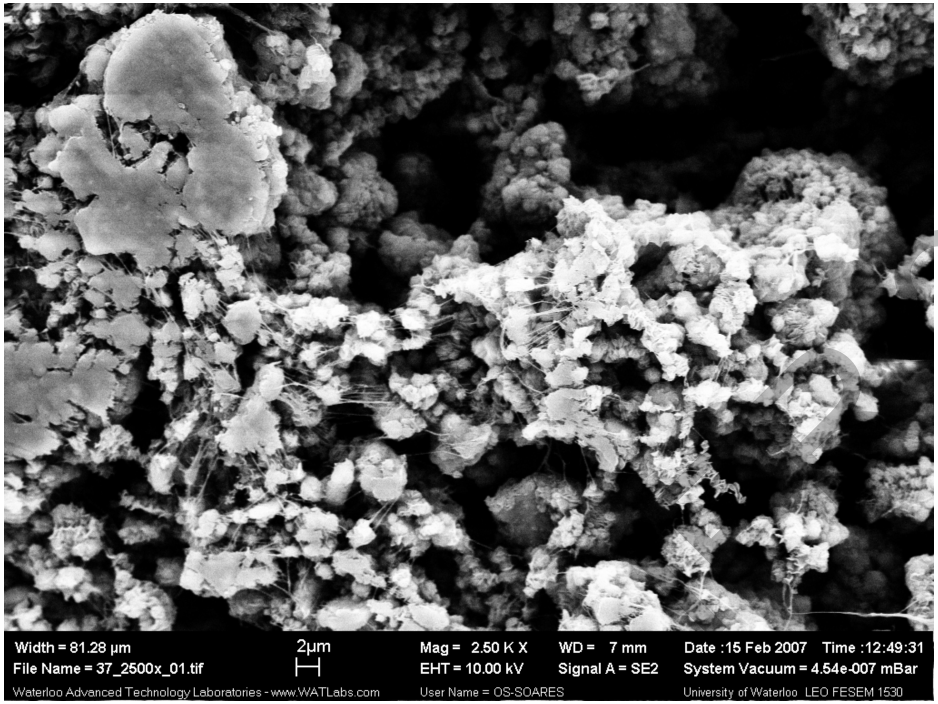


Figure 11- SEM microscopy of PE/Cloisite Na+, – 2, 500X

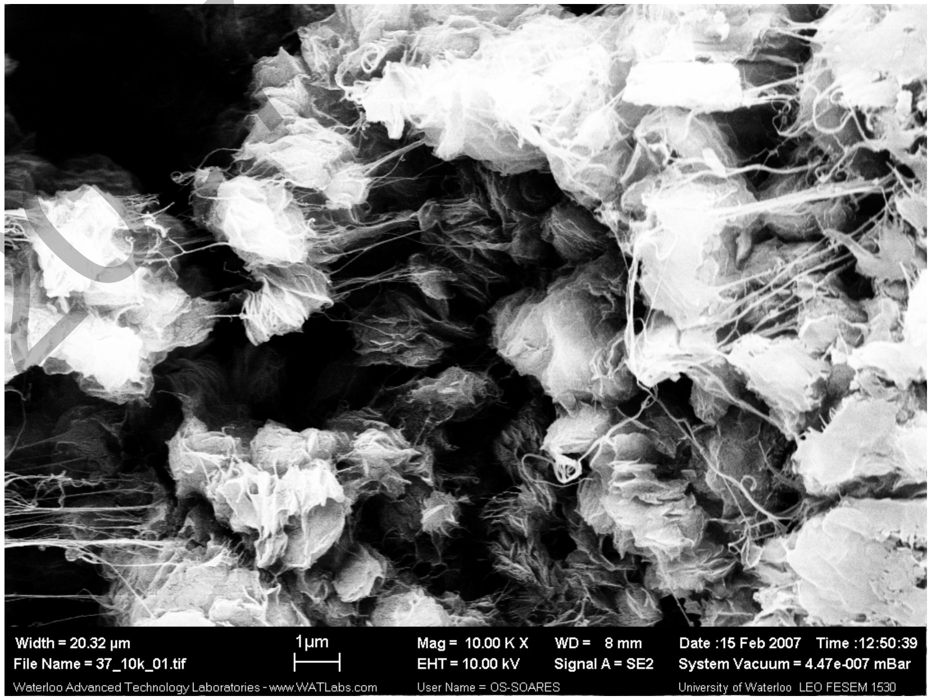


Figure 12- SEM microscopy of PE/Cloisite Na+, – 10, 000 X

High Activity Cloisite 93

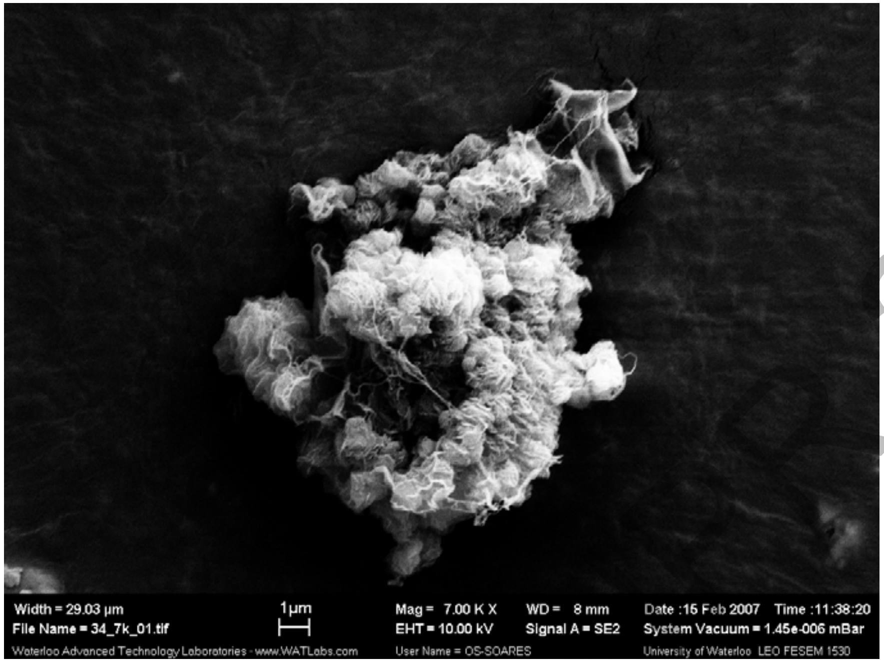


Figure 5- SEM microscopy of PE/Cloisite93, – 7, 000 X

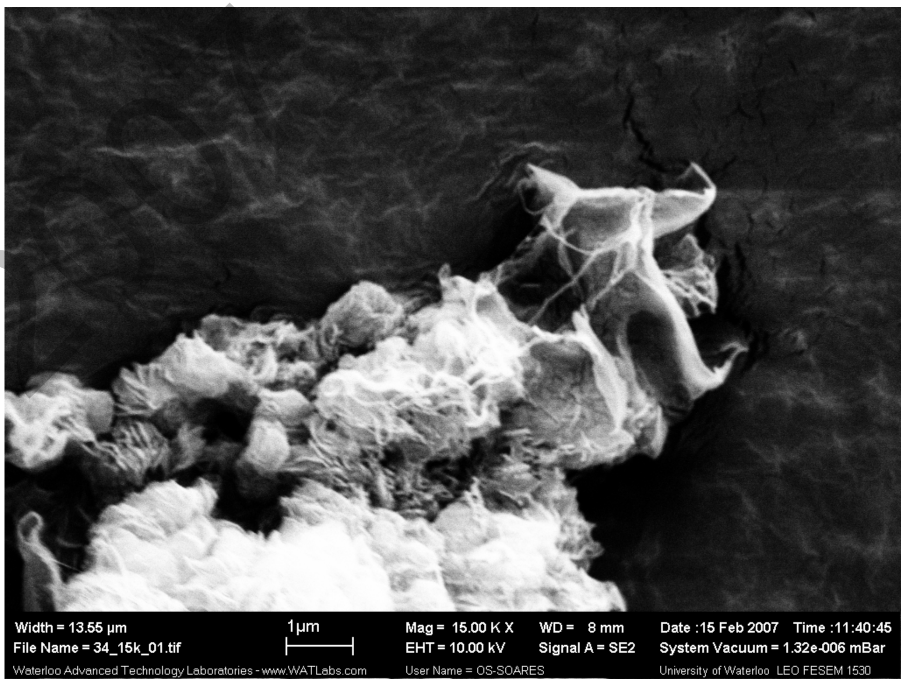
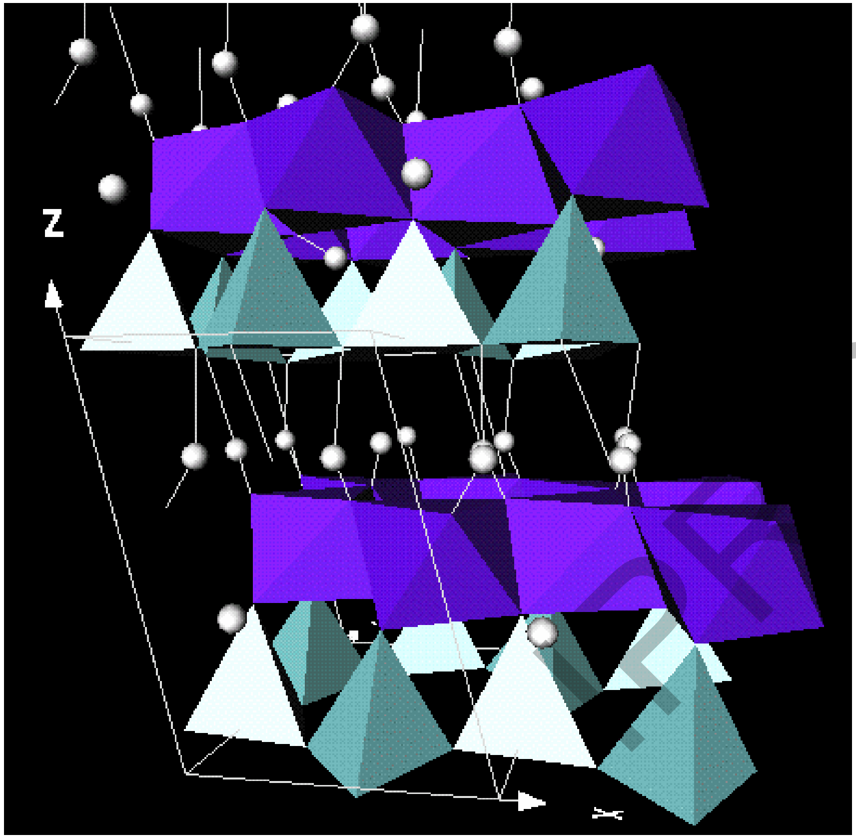
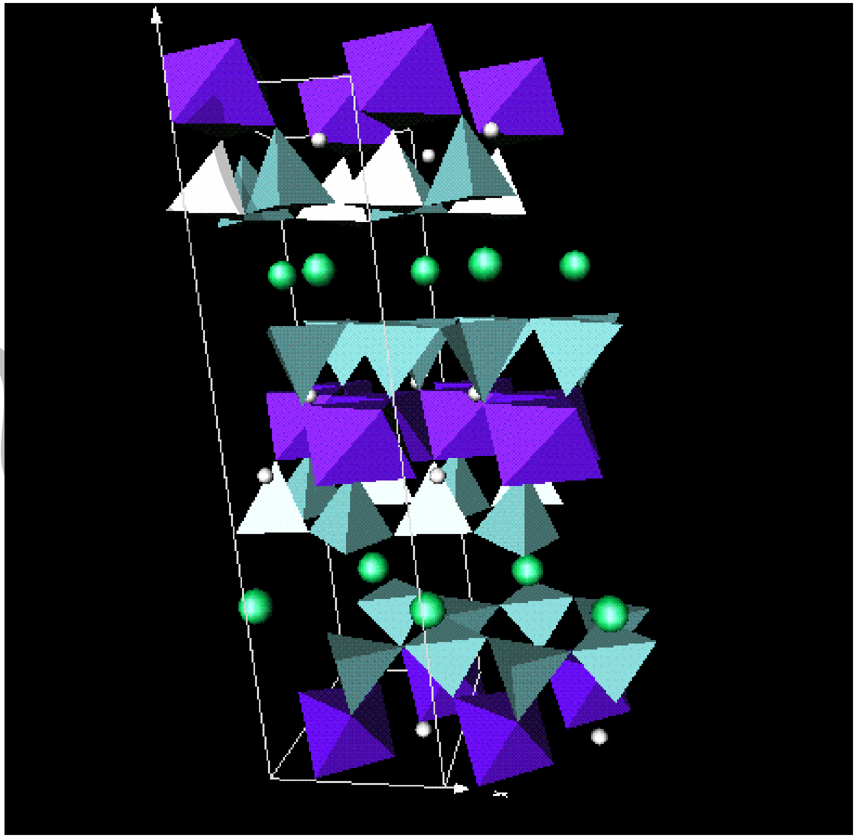


Figure 6- SEM microscopy of PE/Cloisite93, – 15, 000 X

Comparison: Cloisite vs kaolinite





Kaolinite

1:1 layer structure

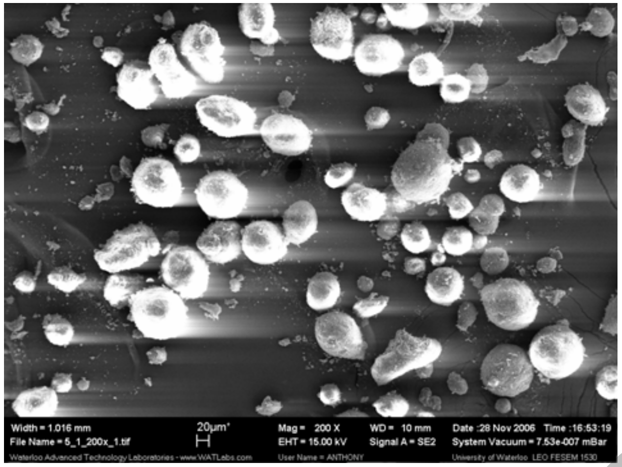
Very low surface charge

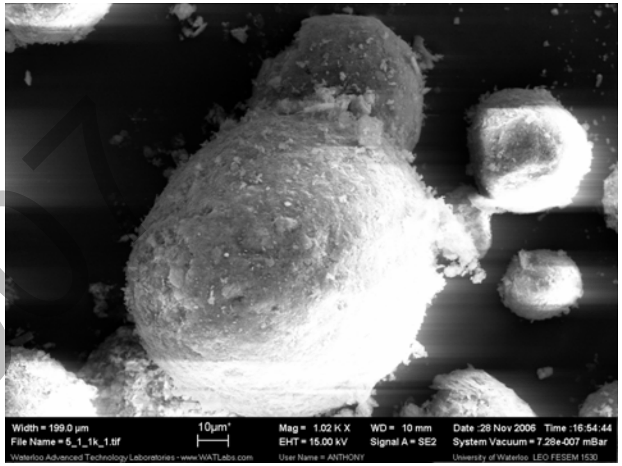
Cloisite

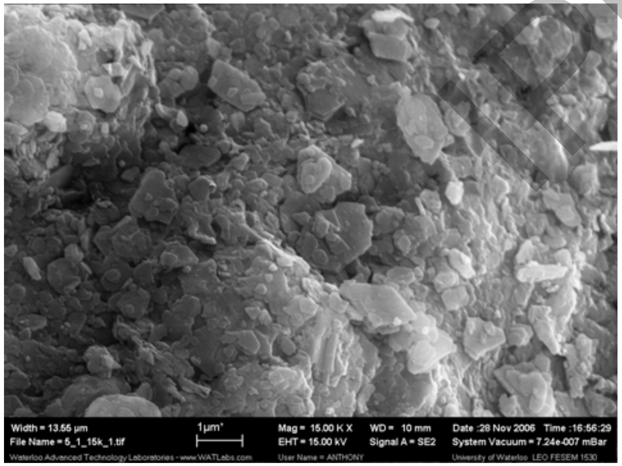
2:1 layer structure

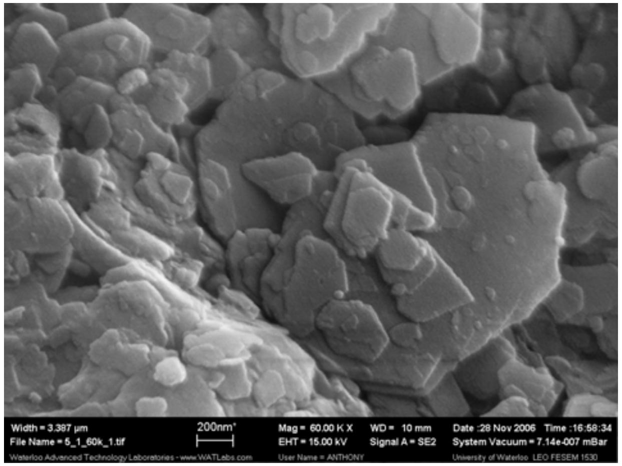
High surface charge

Kaolinite Microstructure

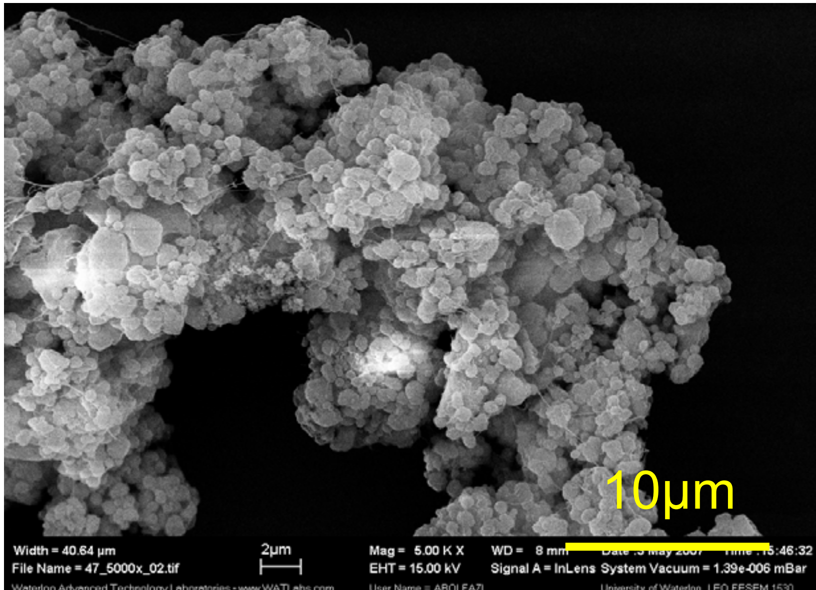


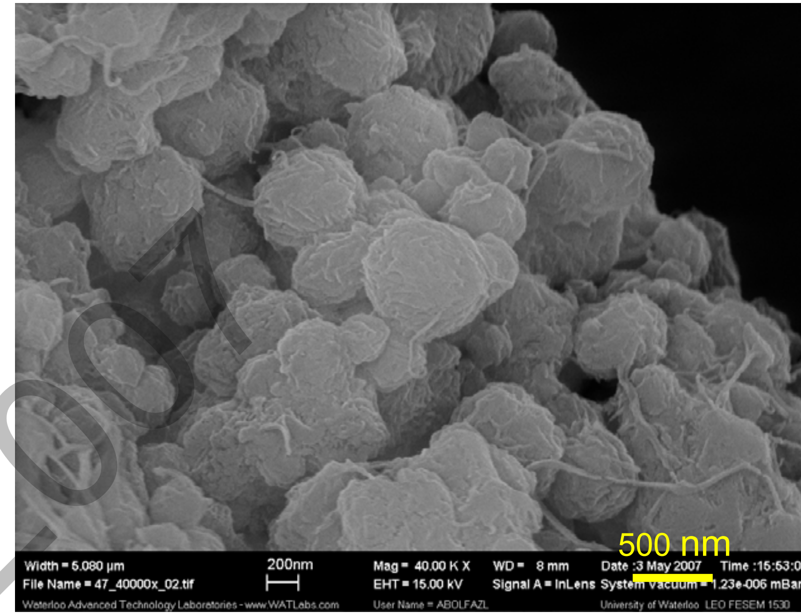




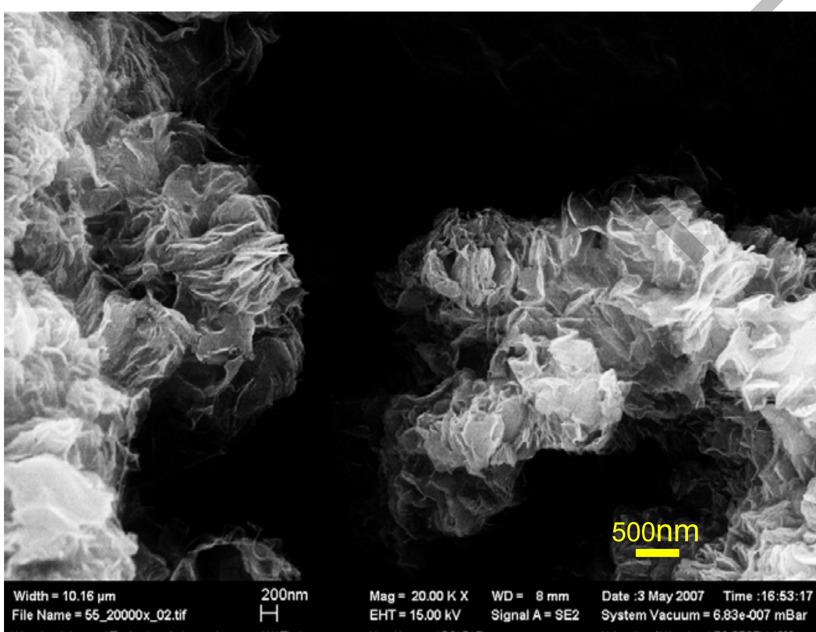


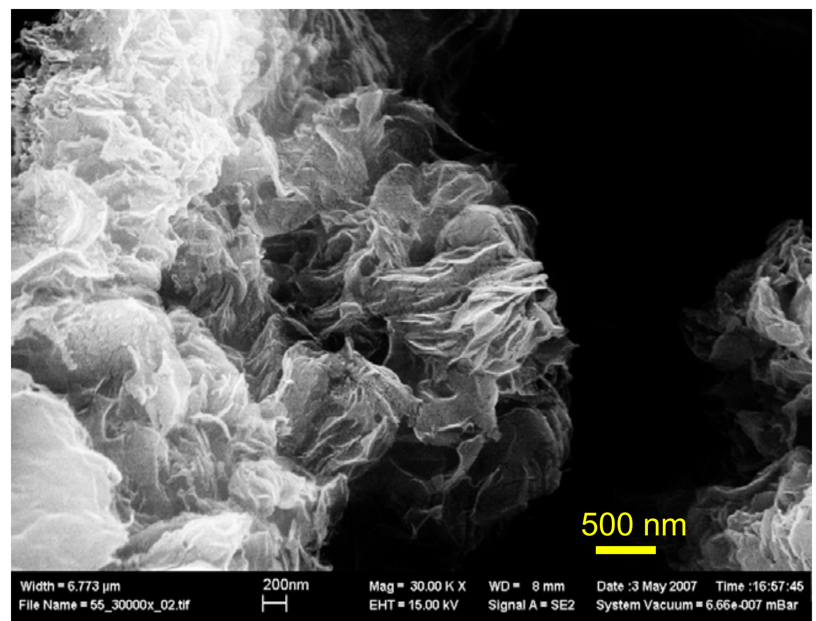
Morphology compared to Kaolinite's





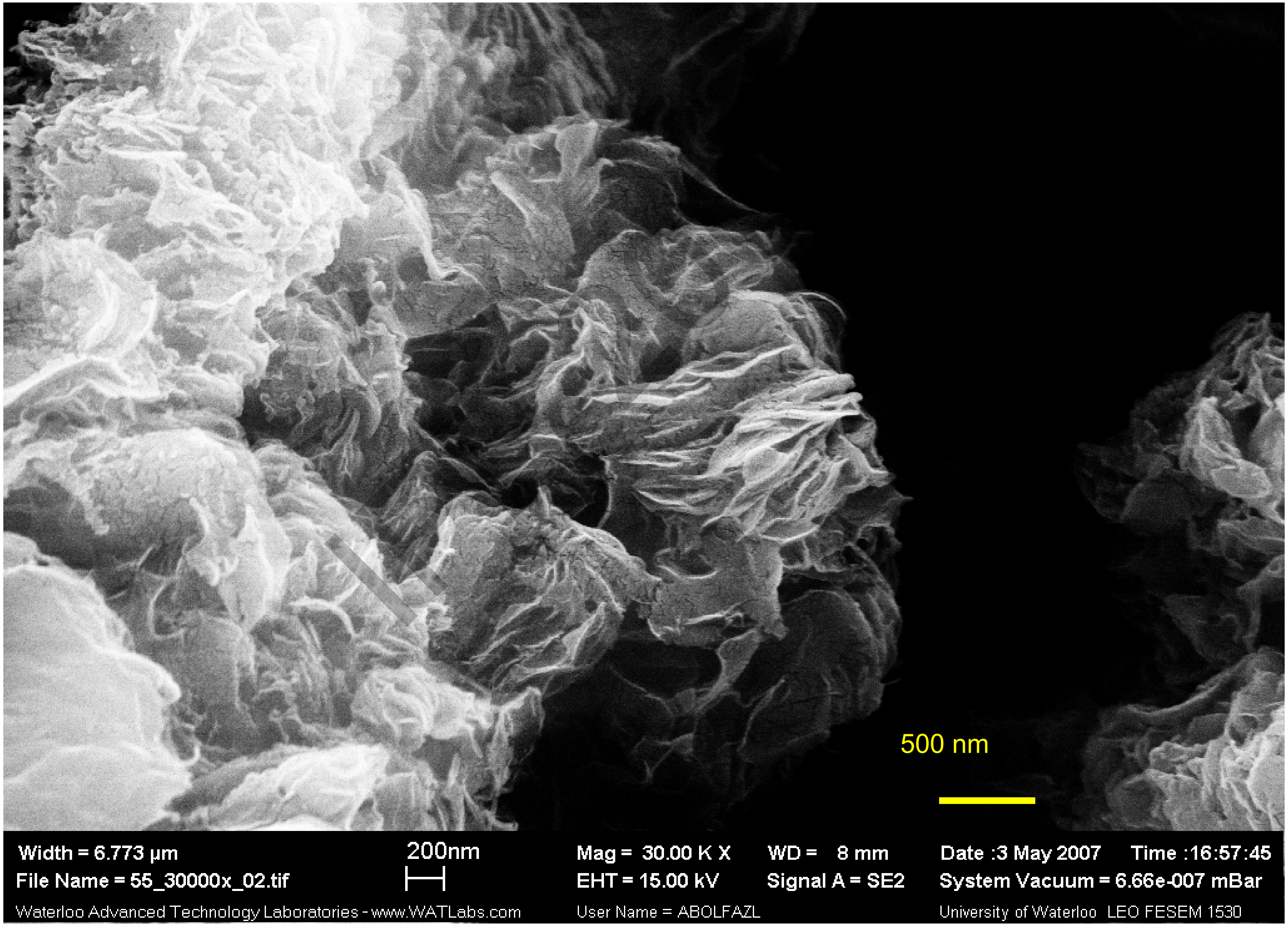
Kaolinite





Cloisite 93 A

Leaf-like Morphology



Interesting Characteristics Cloisite/Metallocene Polymerization System

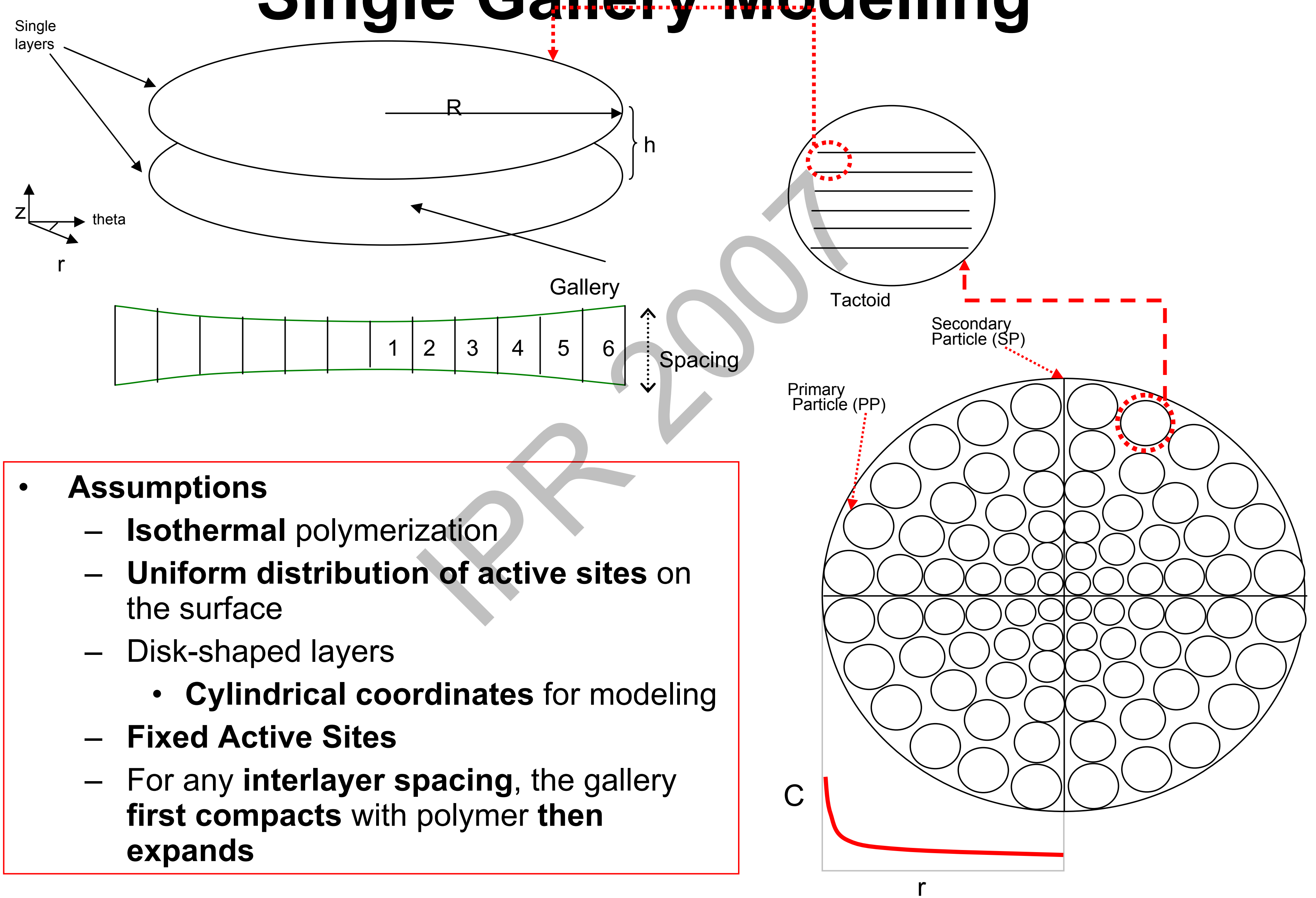
- Relatively High Activity
  - Positive Effect of Clay Surface treatment on the Polymerization Catalyst Activity
- Excellent clay dispersion into polymer matrix down to 0.5 Wt% Clay
- Generally acceptable and controllable powder morphology
- **No MAO**
  - **TMA used to make in-situ MAO**

Benefits of In-situ MAO

- Adsorption water does not have to be removed before supporting
  - Eliminates clay calcination step that might destroy organic modifiers on the clay surface
- MAO does not have to be added to the support or reactor
  - Excess MAO leads to active site removal and two phase polymerization
    - Decreased chance of exfoliation
    - Reactor fouling
- Higher supporting efficiency
  - TMA is smaller than MAO and diffuses better to active the catalyst sites
  - In MAO, the TMA fraction is in charge of catalyst alkylation
- Reduced cost
  - MAO is expensive
  - One of the biggest disadvantages of metallocene catalysts is high level MAO needed for acceptable activities

Mathematical Model

Single Gallery Modelling



- **Assumptions**
  - **Isothermal** polymerization
  - **Uniform distribution of active sites** on the surface
  - Disk-shaped layers
    - **Cylindrical coordinates** for modeling
  - **Fixed Active Sites**
  - For any **interlayer spacing**, the gallery **first compacts** with polymer **then expands**

Conclusions

- We developed a polymerization system that does not require MAO with the following main features:
  - Cloisite 93 A has uses an organic modifier that leads to the best catalyst loading and polymerization activity
  - Clays with lower interlayer spacing produced rigid polymer microparticles
  - Clays with interlayer spacing available produced polymer particles with leaf-like, flaky morphology
  - The layered structures are evident even in clay loading as low as 0.5 Wt%

Thank You!