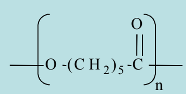
Chapter 3.1 : second example

Polyester matrices : role of clays and organo-modification

Biodegradable Polyester Layered Silicate Nanocomposites

Biodegradable Aliphatic Polyesters

Poly(ε-caprolactone) :



PCL

- Biocompatible and bioresorbable materials
- Biodegradable polymers with controllable life-time

  Via enzymatic/hydrolytic chain cleavage and ultimate bioassimilation

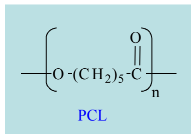
- Miscible with numerous commercial thermoplastics…

  e.g., PVC, SAN, ABS, CPE, nitrocellulose, polycarbonate, (PE),…

Industrial production of PCL by Solvay, Dow (Union Carbide), Daicel,…

Nanocomposites : organic-inorganic materials

Poly(ε-caprolactone) **layered-silicate** ***(few wt%)***



nanometer scale dispersion

Objectives :

First : to improve properties of PCL : *stiffness, gas barrier, thermal behavior,…*

Second : to use highly filled PCL/clay nanocompositions as « masterbatch » in various thermoplastic matrices,

i.e., PCL behaves as a clay-surface compatibilizer

Two main methods for PCL nanocomposite synthesis

- **melt intercalation**

poly(caprolactone) + clay —△→ mixing in the molten state

- ***in-situ* intercalative polymerization**

ε-caprolactone + clay + catalyst ⟶ ring-opening polymerization

Clay = Montmorillonite

$Na_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$ [CEC = 80-100 mequ./100 g]

from Southern Clay Products or Süd Chemie

Poly(ε-caprolactone) nanocomposites by melt intercalation

commercial PCL
Mn = 50,000 $g.mol^{-1}$

+

Montmorillonite (modified)
3 wt%

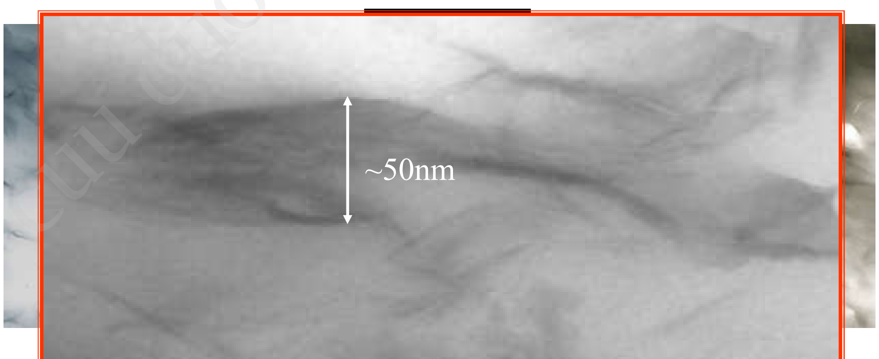
melt blending on a two-roll mill at 130°C for 10 minutes

code	Ammonium cation (organic fraction wt.-%)[a]		basal spacing (d, Å) in clay	basal spacing (d, Å) in PCL composite[b]	
Mont-Na	Na^+	(-)	12.1	12.3	microcomposite
Mont-COOH	$HOOC\text{-}C_{11}H_{22}NH_3^+$	(11.2)	13.8	13.7	microcomposite
Mont-C_{18}	$C_{18}H_{37}NH_3^+$	(14.1)	18.7	25.6	Intercalated nanocomposite
Mont-Alk	$(CH_3)_2N^+(C_{18}H_{37})_2$	(28.9)	ca. 29.0 (broad)	36.0	Intercalated nanocomposite
Mont-$(OH)_2$	$(CH_3)(C_{18}H_{35})N^+(CH_2CH_2OH)_2$	(20.1)	18.4	31.0	Intercalated nanocomposite

a) determined by TGA
b) PCL composite filled with **3wt.-%** of layered silicates (precluding the organic layer)

Pantoustier et al., e-Polymer, 9 *(2001)*

T.E.M. of melt intercalated nanocomposi



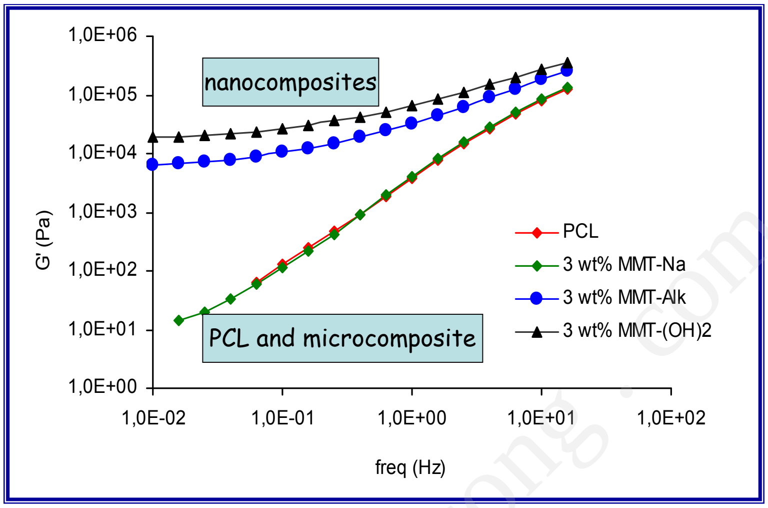
Mont-C_{18}	Mont-Alk	Mont-$(OH)_2$
$C_{18}H_{37}NH_3^+$	$(C_{18}H_{37})_2N^+(CH_3)_2$	$(C_{18}H_{35})(CH_3)N^+(CH_2CH_2OH)_2$
(Nanofil 848)	*(Nanofil 15)*	*(Cloisite 30B)*

Exfoliation of the silicate sheets in PCL never complete, it remains some stacks of silicate layers whatever the alkylammonium cations considered

semi-intercalated/semi-exfoliated structure

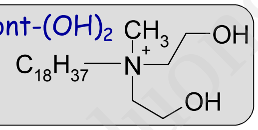
Rheological propertie

[Strain controlled rheometer](#) :
-parallel-plate geometry
-25mm diameter, 1mm thickness
-80°C, 1% deformation



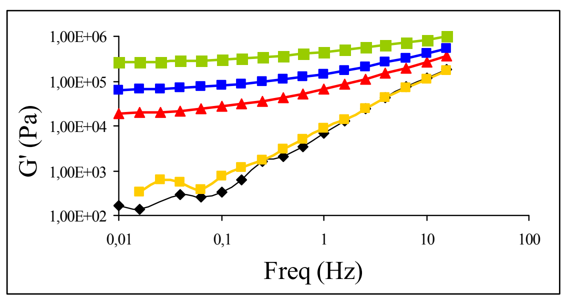
Lepoittevin et al., Polymer, 43 *(2002)*

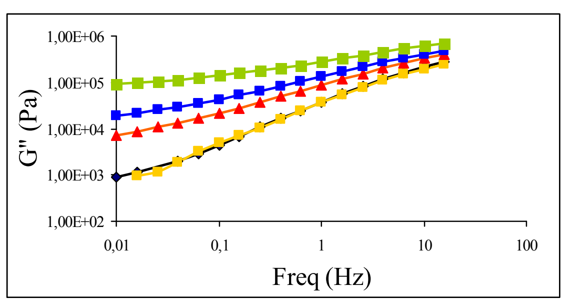
Mont-$(OH)_2$



Rheological properties (at 80°

— PCL 50K
— PCL + 1% clay
— PCL + 3% clay
— PCL + 5% clay
— PCL + 10% clay

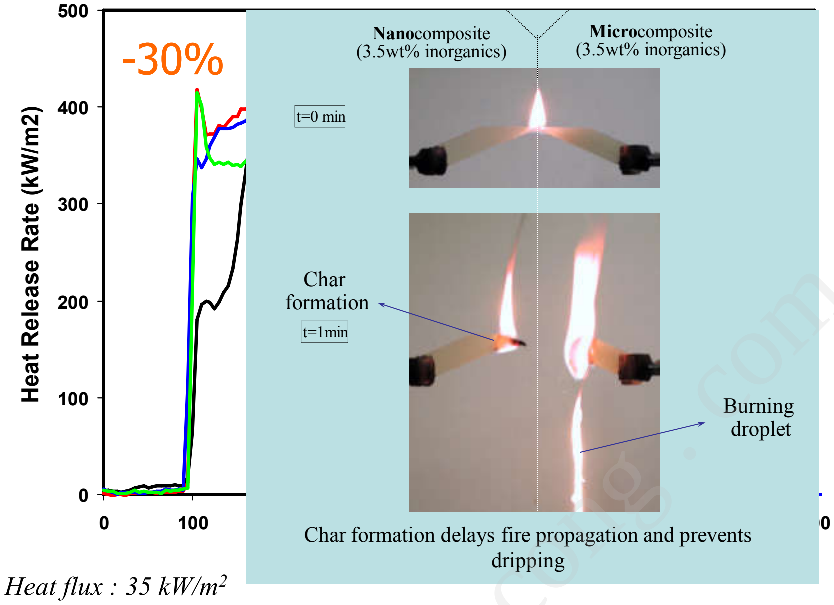




% clay ⇑
G' et G'' ⇑

Lepoittevin et al., Polymer, 43 *(2002)*

Cone Calorimetry (nanofiller =Mont-$(OH)_2$)

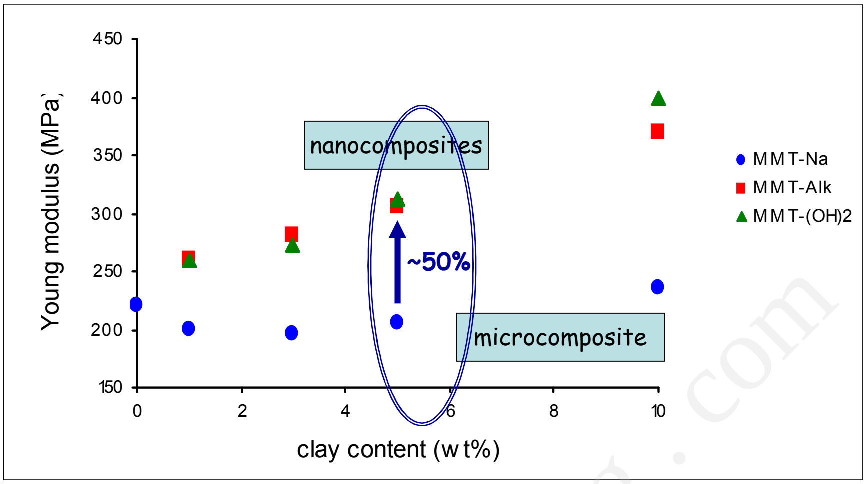


Heat flux : 35 kW/m²

Cone Calorimetry (nanofiller =Mont-$(OH)_2$)

Charring effect with clay content

Effect of clay content on elastic modu



Tensile tests with a constant deformation rate : 50 mm/min

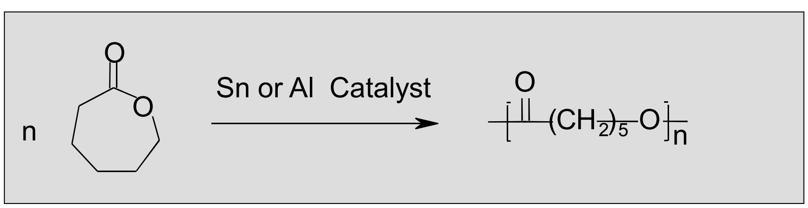
(638 type V ASTM norm)

Pantoustier et al., e-Polymer, 9 *(2001)*

Poly(ε-caprolactone) nanocomposites by ***in situ* polymerization**

- clay (montmorillonite) 1 to 10 wt-%
- slurry in ε-caprolactone (in bulk : no solvent)

Activation : Sn or Al-based catalyst



Effect of (organo)clay?
Intercalation/exfoliation?

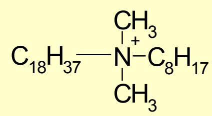
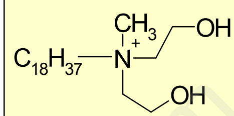
Pantoustier et al, Polym. Eng. Sci., 42 *(2002)*

In-situ polymerization

[monomer]/[Sn(Oct)$_2$] = 300

3 wt-% clay

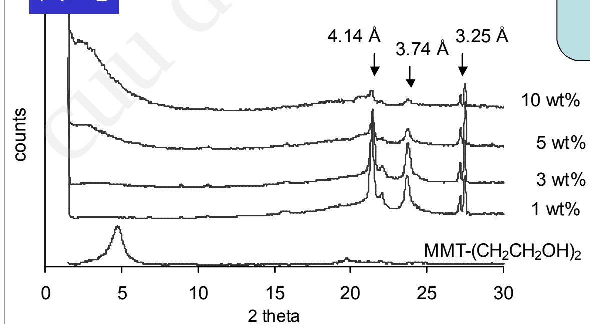
analysis by X-ray diffraction

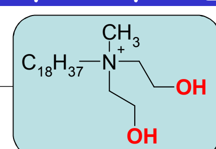
Montmorillonite	Montmorillonite	Montmorillonite
Na^+		
d = 12 Å	**d = 18.5 Å**	**d = 20 Å**
↓	↓	↓
intercalation	intercalation	**exfoliation**
d = 19 Å	**d = 27 Å**	**no peak**

Pantoustier et al, Polym. Eng. Sci., 42 *(2002)*

In-situ polymerization : catalysis by $Bu_2Sn(OM$

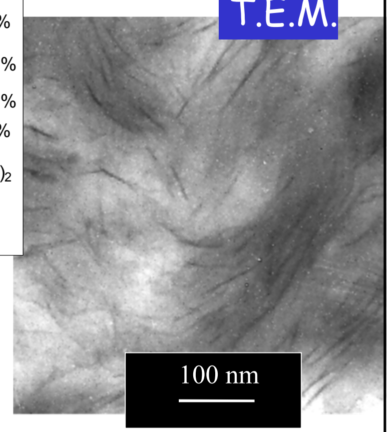
XRD





Mont-(OH)$_2$

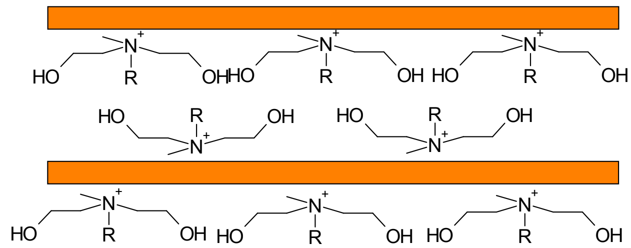
T.E.M.



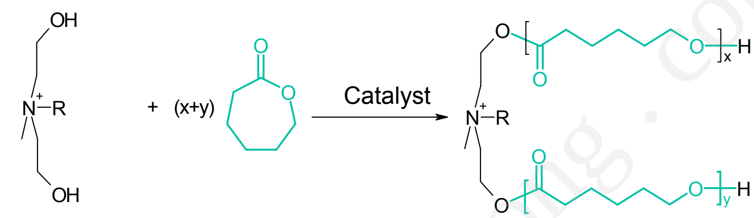
Complete exfoliation

Lepoittevin et al., Macromolecules, 35 *(2002)*

Why exfoliation with MMT-$(OH)_2$?



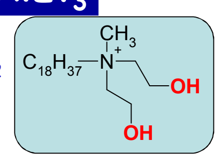
$R=C_{18}H_{35}$



In-situ polymerization : catalysis by $AlEt_3$

room temperature, 24 h
$[ROH] = [AlEt_3]$

Mont-$(OH)_2$



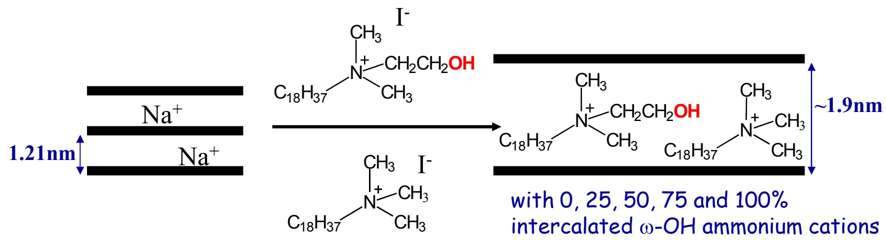
$$\text{Mont-(OH)}_2 + AlEt_3 \longrightarrow \text{Mont-(OAlEt}_2)_2 + C_2H_6 \uparrow$$

Clay wt-%	conversion %	M_n g/mol	M_w/M_n	$M_{n,th}$ g/mol
1	92	85,300	2.0	116,000
3	91	41,700	1.8	39,500
5	91	27,400	1.9	22,700
10	72	6,000	- [a]	8,200

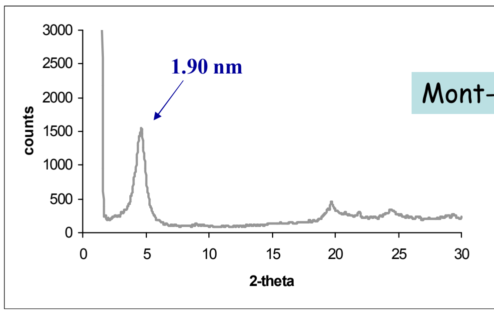
[a] Bimodal molecular weight distribution

CL-« grafted » clay nanohybrids : grafting density contr

By **co-intercalation** (in H_2O at 85°C) of hydroxy-functionalized and non functionalized ammonium cations :



with 0, 25, 50, 75 and 100% intercalated ω-OH ammonium cations (ca. 21~wt-% organic modifier)

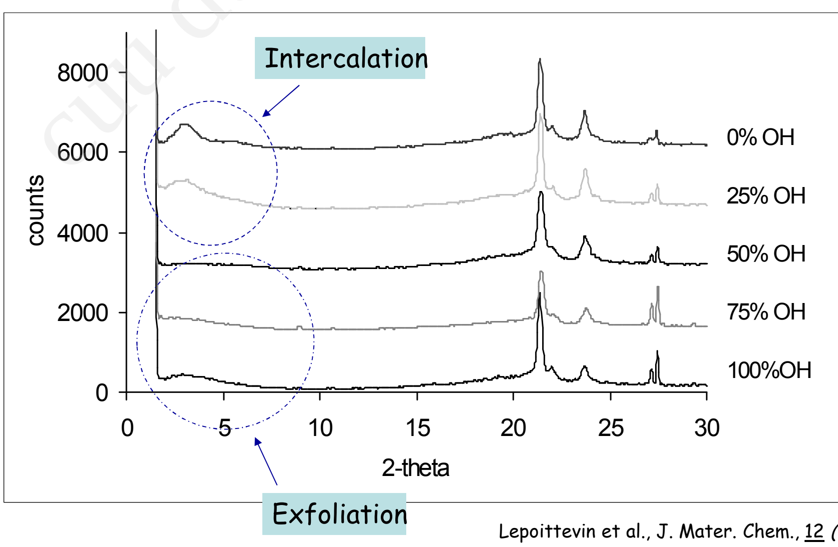


Mont-OH with 100% OH

Lepoittevin et al., J. Mater. Chem., 12 *(2002)*

PCL-« grafted » clay nanohybrids : grafting density control

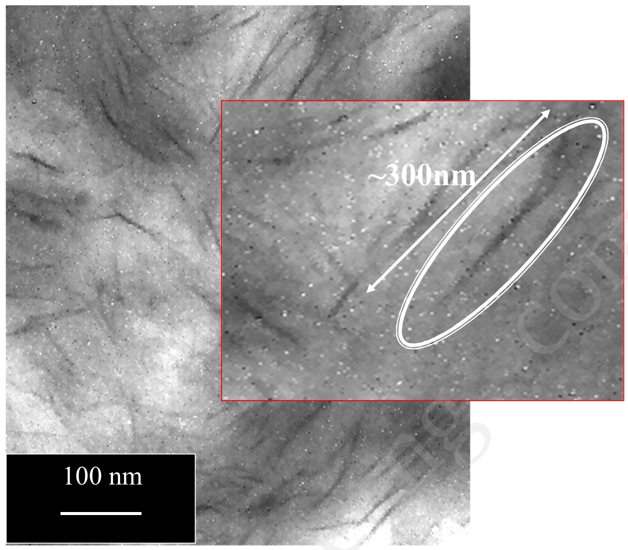
3 wt-% Mont-OH$_{(x\%)}$



Lepoittevin et al., J. Mater. Chem., 12 *(2002)*

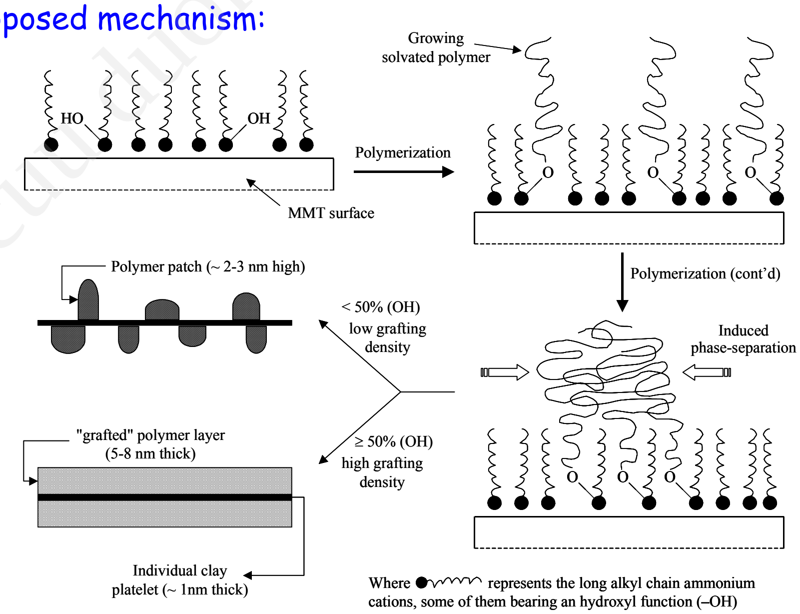
PCL-« grafted » clay nanohybrids : grafting density control

3 wt-% Mont-$OH_{(100\%)}$



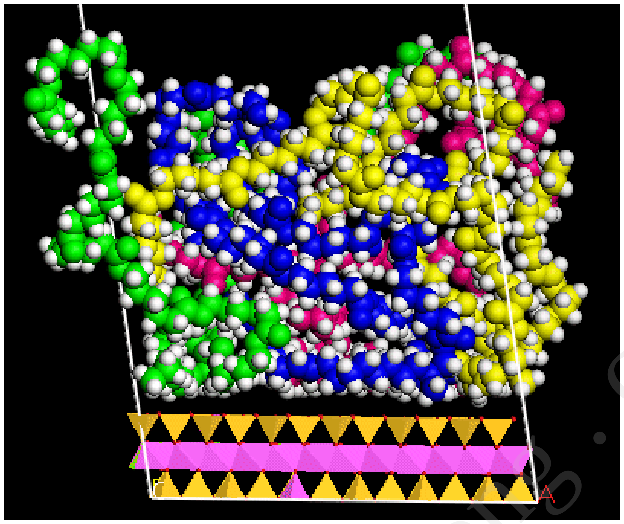
Controlled polymer grafting on clay platelets

Proposed mechanism:



Viville et al., J. Amer. Chem. Soc., *2004*

MD simulation of the exfoliated system

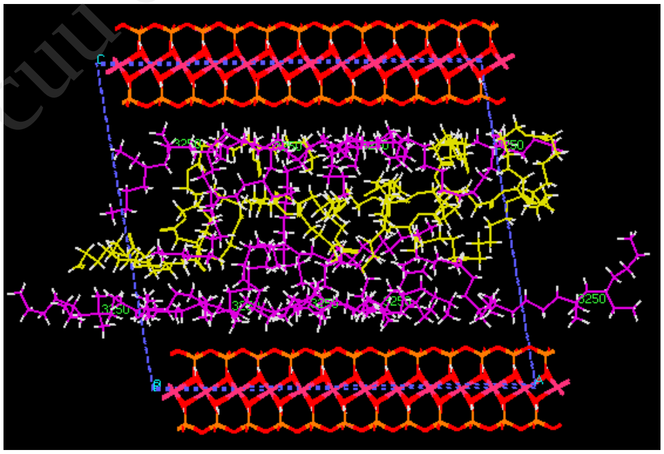


NVT 300 K
UFF force field
Periodic cond.

8 PCL chains grafted to OH-substituted surfactants

MD simulation of the intercalated system

PCL + alkylammonium-Montmorillonite



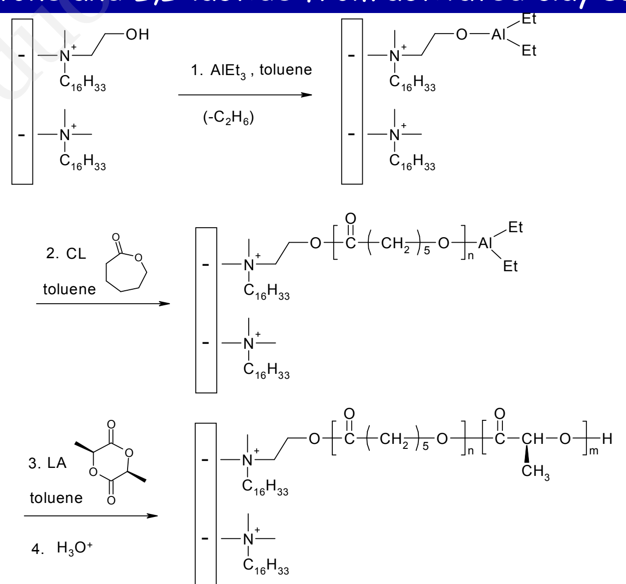
Interlayer distance: 2.9 nm

NVT 300 K
UFF force field
Periodic cond.

Stabilization of the polyester chains in the cavity

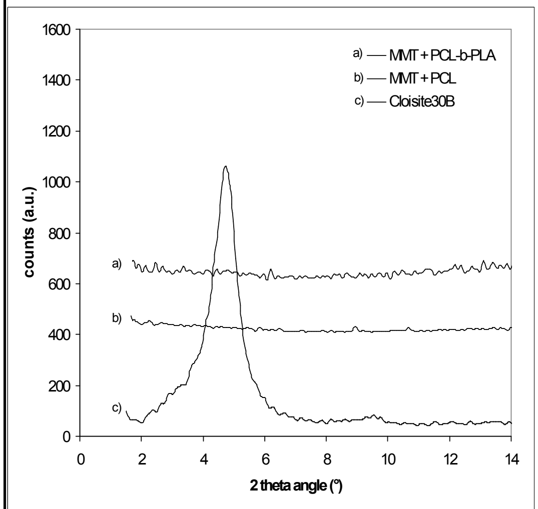
- Hydrophobic interactions with alkyl groups of the ammonium ions
- Polar interactions between the (- O – CH_2 -) groups of PCL and the aluminosilicate surface

Nanohybrids by sequential copolymerization of ε-caprolactone and L,L-lactide from activated clay surface



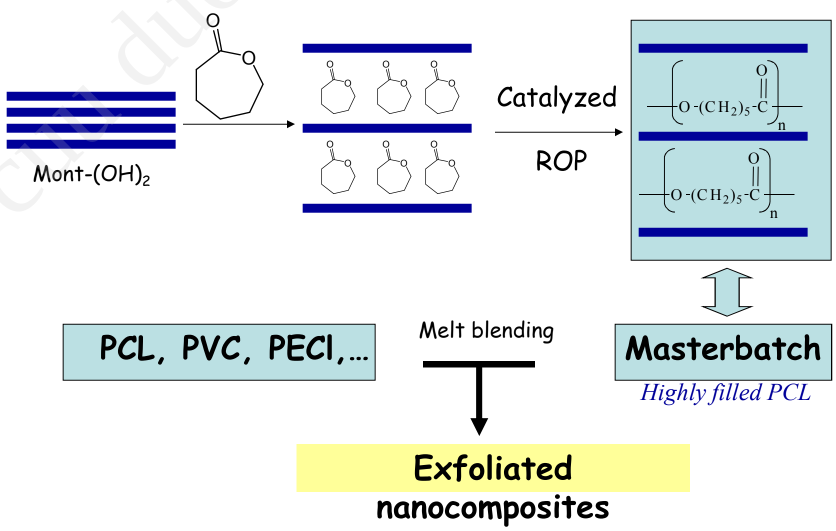
Pollet et al., Macromol. Chem. Phys., *2004*

Nanohybrids by sequential copolymerization of ε-caprolactone and L,L-lactide from activated clay surface



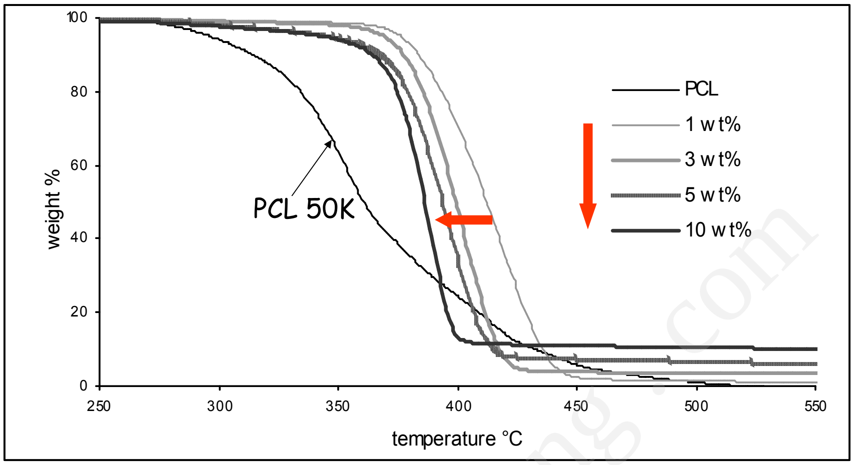
Pollet et al., Macromol. Chem. Phys., *2004*

PCL nanocomposite « masterbatch » by in-situ polymerization



Lepoittevin et al., Polymer, 44 *(2003)*

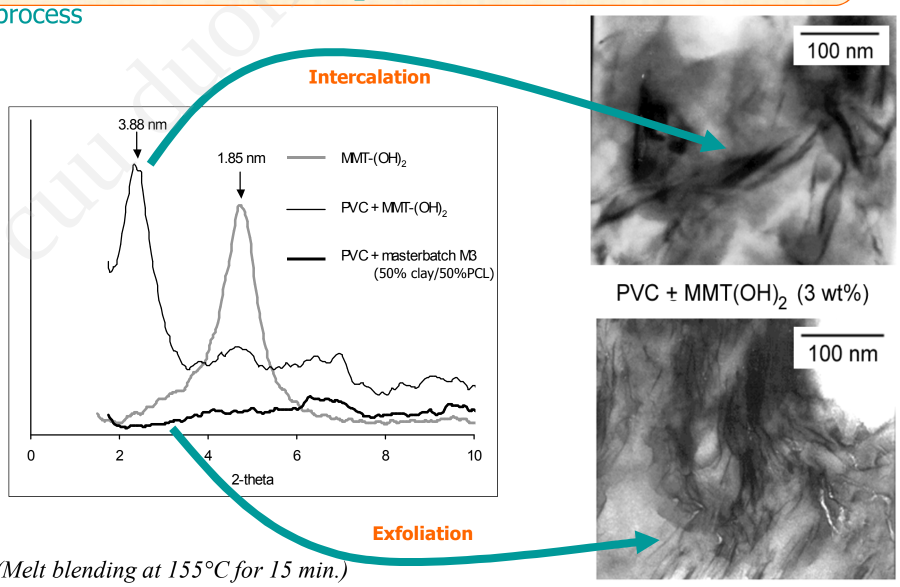
Thermogravimetric analysis of PCL-grafted Mont-$(OH)_2$ exfoliated in PCL via « masterbatch » process : **effect of clay**



Conditions : 20°C/min. under air flow

Lepoittevin et al., Polymer, 44 *(2003)*

PVC / (PCL-grafted) Mont$(OH)_2$ nanocomposites via « masterbatch » process



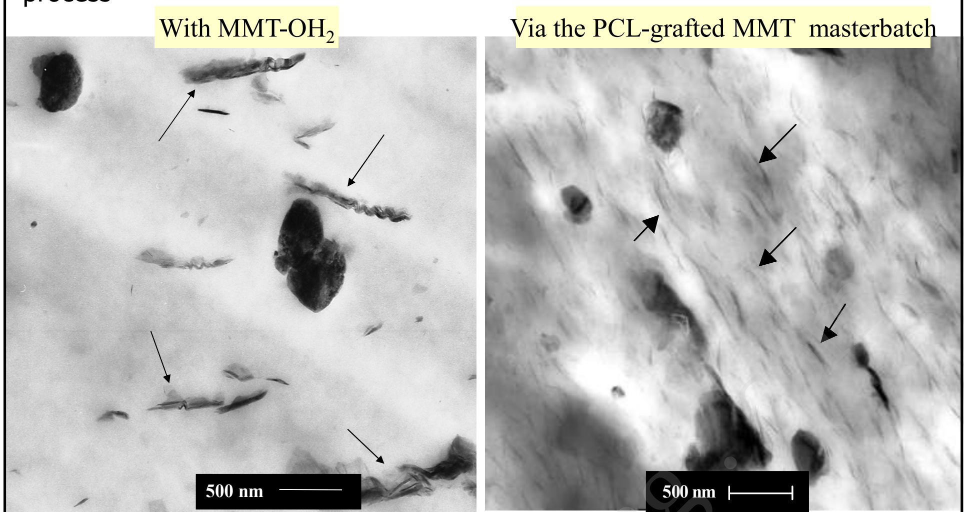
PVC + $MMT(OH)_2$ (3 wt%)

(Melt blending at 155°C for 15 min.)

PVC + masterbatch M3 (3 wt%)

Lepoittevin et al., Polymer, 44 *(2003)*

CPE / (PCL-grafted) Mont(OH)$_2$ nanocomposites via « masterbatch » process



Nanocomposites based on 3wt% clay dispersed in stabilized CPE matrix

The large "round" particles are additives within the commercial CPE matrix

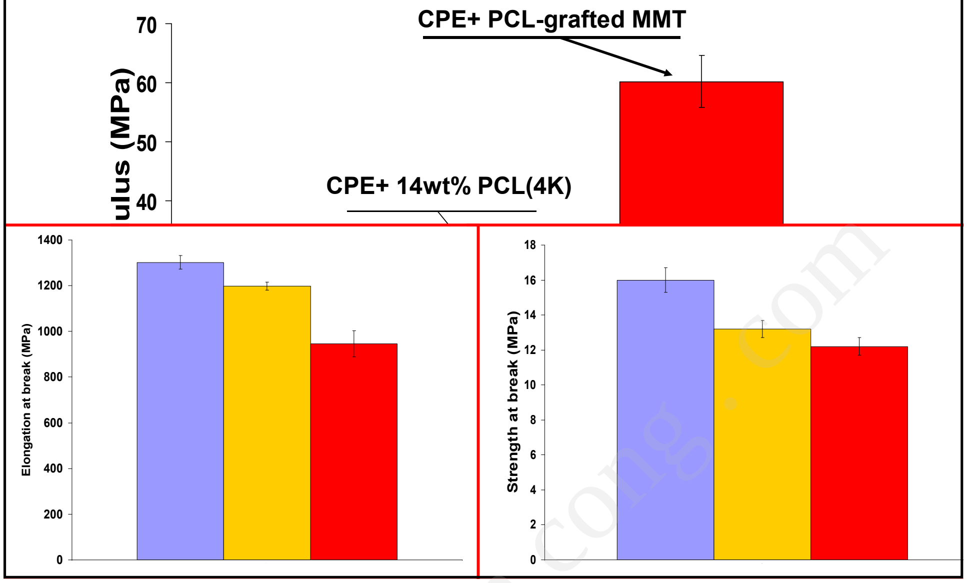
Tensile properties of unfilled CPE, and CPE added with 3wt% in clay (melt blending at 175°C; ASTM D638 typeV)

Blends	Elongation at break (%)	Young's modulus (MPa)
CPE	1302 ± 29	4.3 ± 0.3
CPE + Cloisite 30B	1219 ± 38	8.1 ± 0.8
CPE + masterbatch*	1111 ± 63	14.3 ±3.0

* PCL-grafted MMT-OH$_2$ masterbatch (with 25 wt% clay)

CPE with 36wt% chlorine (Tyrin®3652) from Dupont Dow Elastomers and stabilised by 4 phr Lankroflex® E2307 (epoxidized soybean oil)

Tensile properties of CPE added with 5wt% in MMT-$(OH)_{0.75}$
(melt blending at 175°C; ASTM D638 typeV)



masterbatch process : application to PLA nanocomposites

1. ***Highly filled*** (53 wt%) Cloisite®30B / PLA nanocomposite — ***In situ* polymerisation**

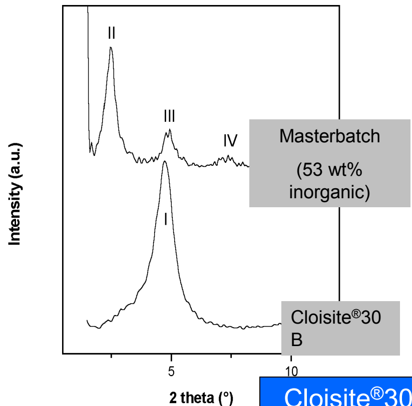
2. ***Melt blending*** — ***Preformed PLA*** (commercial matrix) PLA (70% *S*-lactic acid)

→ Cloisite®30B / PLA nanocomposites with ***3 wt% of loading***

Paul et al., Macromol. Chem. Phys., *2005*

PLA nanocomposites via masterbatch process

Morphology



Cloisite®30B / PLA nanocomposites with ***3 wt% of***

Exfoliation of clay platelets

Biodegradation tests

Weight loss of PCL/clay composites films (5x5 cm and 100 μm thick) in natural composting environment

The biodegradability tests were performed in a laboratory scale compost.

The compost composition was approximately as follow :

- 41% shredded leaves
- 21% food waste (bread, dry milk, vegetables…)
- 15% paper
- 11% cow manure
- 8% sawdust
- 3% urea

The total dry weight of compost was ~ 5kg.

The moisture content was maintained by periodic addition of water.

To avoid anaerobic conditions, the compost was constantly aerated with oxygen.

The temperature of the compost was about ***48°C (± 2°C).***

The biodegradability was determined by measuring the weight loss of composted samples after washing them with water and drying under vacuum until constant weight.

Conclusions

Polymer layered silicate nanocomposites :

New family of performant materials
- readily accessible by Melt intercalation
  In situ intercalative polymerization
- easily melt processed and shaped
- with much improved properties

(barrier, thermal, mechanical, rheological, flame retardant,…)

Key-example : Biodegradable polyester-based nanocomposites
- next generation of thermoplastic materials
- main targeted applications : packagings