Polymer (nano)composites
: key-role of chemistry

(Cont.)

Outline

I. Polymer microcomposites filled with microparticles
  - I.1. Mechanical melt blends
  - I.2. Importance of « polymer/filler » interface (tension and adhesion)
  - I.3. "Polymerization-filled composites" PFC's

II. Polymer nanocomposites filled with nanoparticles
  - II.1. Layered silicate as nanofillers
    - Polymer-clay nanocomposites : melt blending *vs. in situ* polymerization
    - Polyolefinic matrices : role of matrices and compatibility
    - Polyester matrices : role of clays and organo-modification
  - II.2. Carbon nanotubes as nanofillers
    - Polymer-CNTs composites : production and properties
    - « Melt blending » technique, e.g., in elastomeric matrices
    - *in situ* polymerization, e.g., in thermoplastic matrices

III. General conclusions et outlook

Chapter 2.1 : first example

Polyolefinic matrices :
role of matrices and compatibility

Polyethylene Layered Silicate Nanocomposites

Polyolefin/clay nanocomposites : facts

The three main preparative techniques have been used to tentatively prepare polyolefin/clay nanocomposites

- Exfoliation adsorption :

PE + clay organomodified with protonated dodecylamine, dissolved in xylene/benzonitrile (80:20 wt%) then precipitated in THF ⟹ Result : **at best little intercalation** H.G. Jeon et al, Polym. Bull., 41, p.107 (1998)

PE + clay organomodified with hexadecyltrimethylammonium, dissolved in toluene (autoclaved at 170°C) then solvent evaporation ⟹ Result : claimed exfoliation (?) L. Song et al, J. Mater. Chem., 12, p.3152 (2002)

Processes involving organic solvents, no study of the nanocomposite stability if melt processed

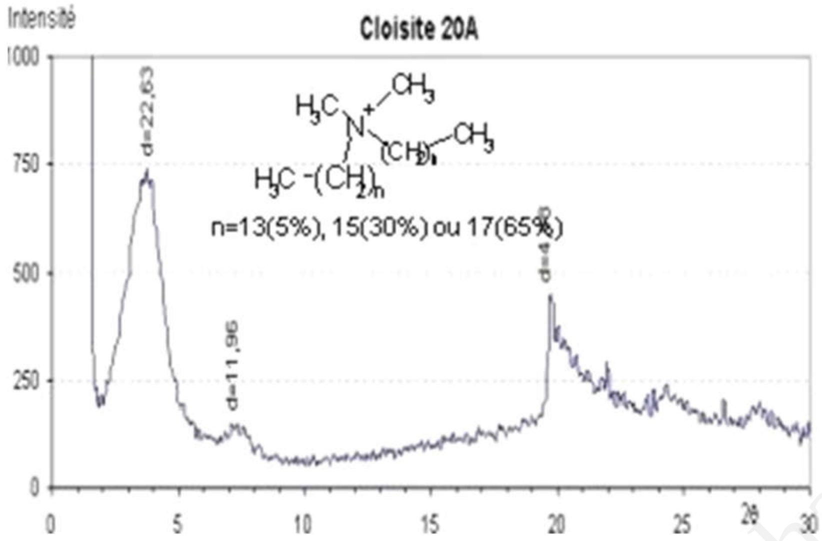
- Melt intercalation/exfoliation :

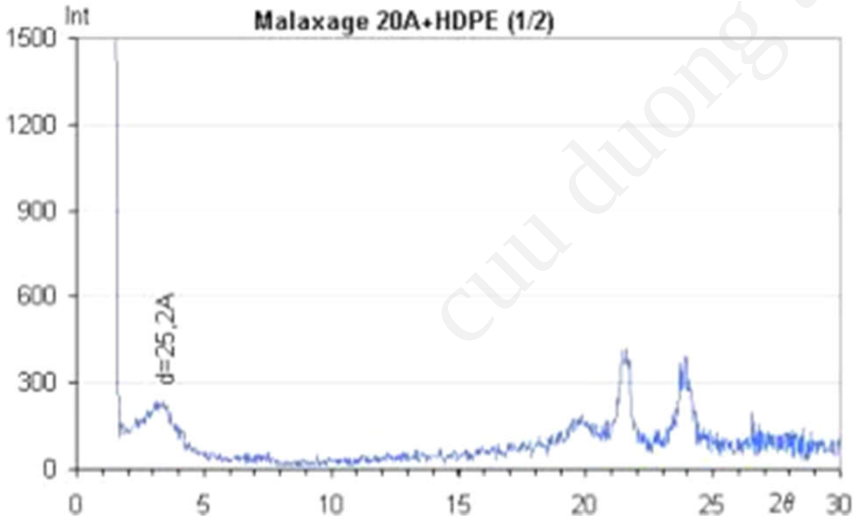
A large amount of research deals with this technique, easily implemented in industry (melt processing)

- In situ intercalative polymerization :

Numerous studies mainly based on ethylene and ethylene/α-olefin (co)polymerization

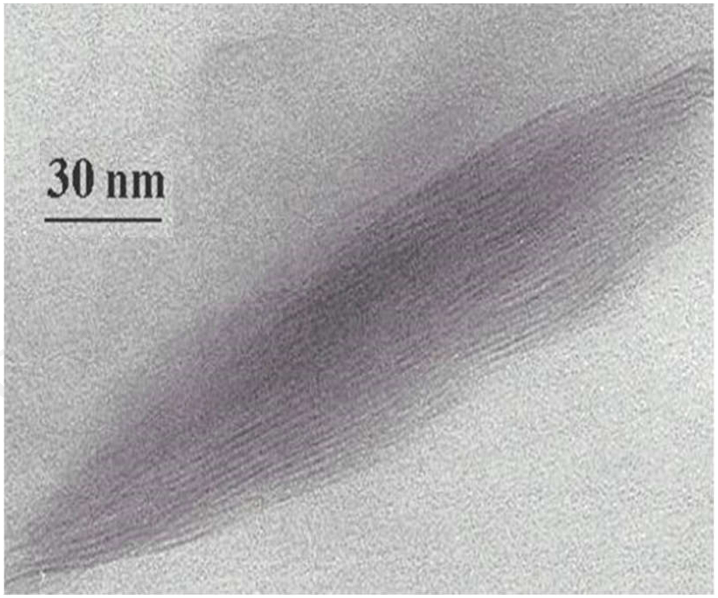
Polyethylene/clay based nanocomposites : melt blend of HDPE and organoclay





M. Mainil, Ph.D. thesis, UMH (2005)

TEM picture of a stack of Cloisite 20 in HDPE



No intercalation

No exfoliation

Whatever the shear (internal mixers, extruders,…)

Need to bring polarity in the PE matrix

Melt intercalation with **polyolefins** : generalities

PE and PP do not spontaneously intercalate in classical organomodified clays ⇒ intrinsically immiscible

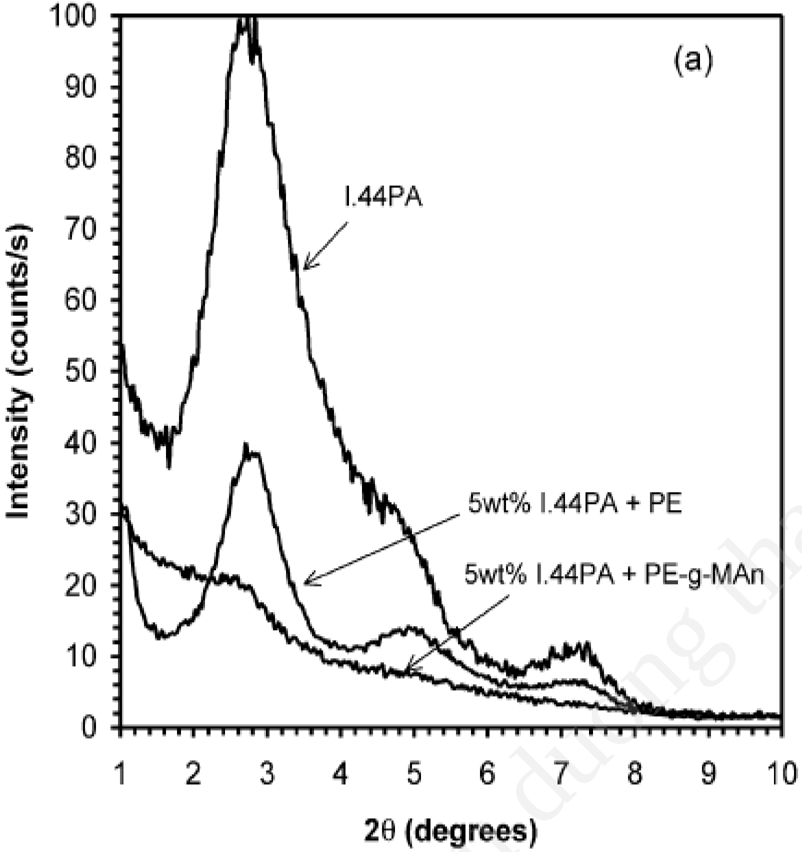
⇒ Necessary to use polar additives miscible or compatible with PP or PE to compatibilize the polyolefin with the organomodified clay

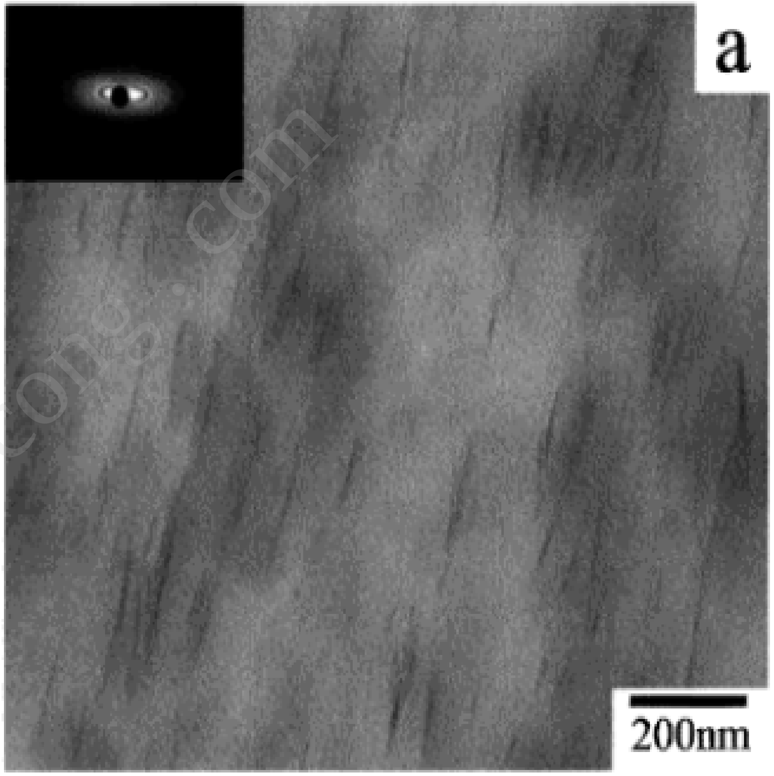
⇒ Extensive use of **polyolefins grafted with maleic anhydride**

Polyolefins bearing polar copolymers (**EVA**, chlorinated PE) are more compatible with organomodified clays

They readily form intercalated and even exfoliated nanocomposites

Polyethylene-g-maleic anhydride used as matrix : influence on morphology





I.44PA : MMT organomodified with 2HT2MN$^+$
PE-g-MAn : ~1wt% MAn

T.G. Gopakumar et al, Polymer, 43, p.5483 (2002)

Clay = Cloisite 20A (same ammonium cation)
PE-g-Man : ~3wt% MAn

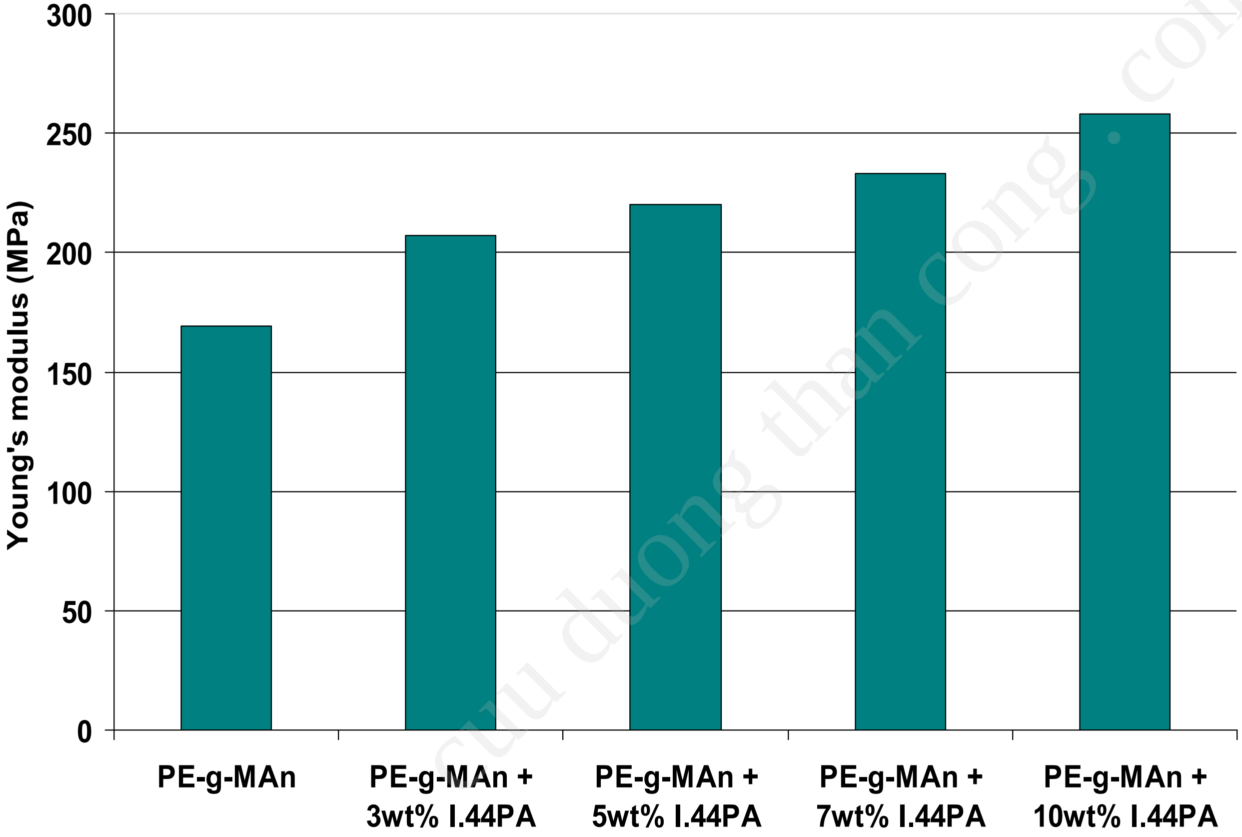
C.M. Koo et al, Macromolecules, 35, p.5116 (2002)

Intercalation (and even exfoliation) is observed

Polyethylene-g-maleic anhydride/clay nanocomposite : influence on properties

T.G. Gopakumar et al, Polymer, 43, p.5483 (2002)

Large increase in Young's modulus :



example: Ethylene-vinyl acetate copolymer based nanocomposites by melt-blend

EVA matrices tested

EVA	%wtVA	%molVA
UL112	12	4.2
UL119	19	7.1
UL328	27	10.8

VA = vinyl acetate

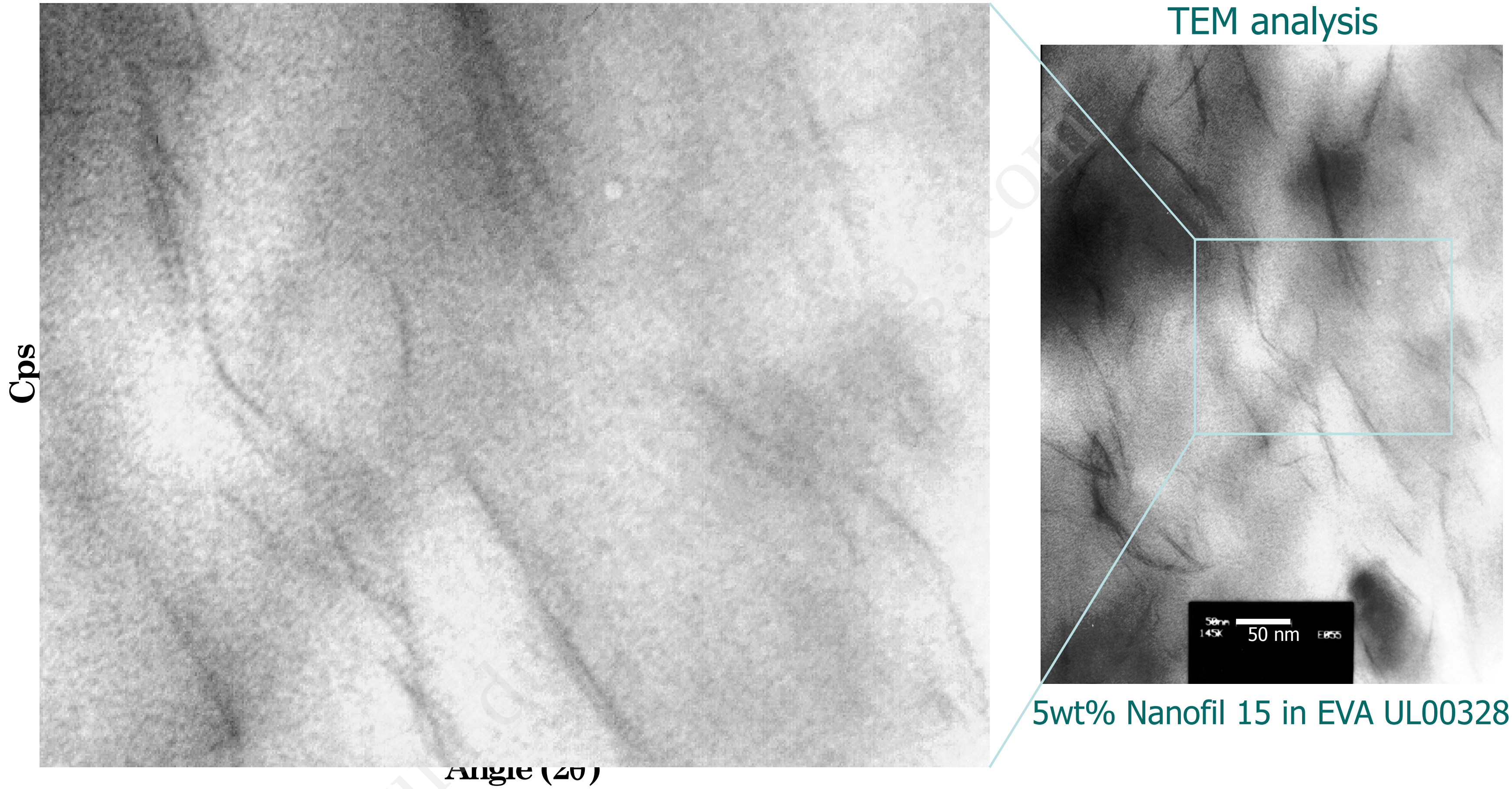
Montmorillonite modified with various alkylammoniums

Code	Ammonium cation
Nanofil 15	$(CH_3)_2N^+(C_{18}H_{37})_2$
Cloisite 25A	$(CH_3)_2N^{+}(C_{18}H_{37})$(2-ethylhexyl)
BHB	$(CH_3)_3N^+C_{21}H_{42}COOH$
11-AUDEA	$H_3N^+C_{10}H_{20}COOH$

Composite preparation by mechanical kneading of the organo-modified montmorillonite with the EVA matrix on a two-roll mill at 130°C for 10 min

Nanocomposite morphology

TEM analysis



5wt% Nanofil 15 in EVA UL00328

A **semi-exfoliated semi-intercalated structure** is obtained when using non-functionalized ammonium cations ($(CH_3)_2N^+(C_{18}H_{37})_2$ or $(CH_3)_2N^{+}(C_{18}H_{37})$(2-ethylhexyl) and phase-separated microcomposite with –COOH terminated ammoniums, whatever the vinyl acetate content

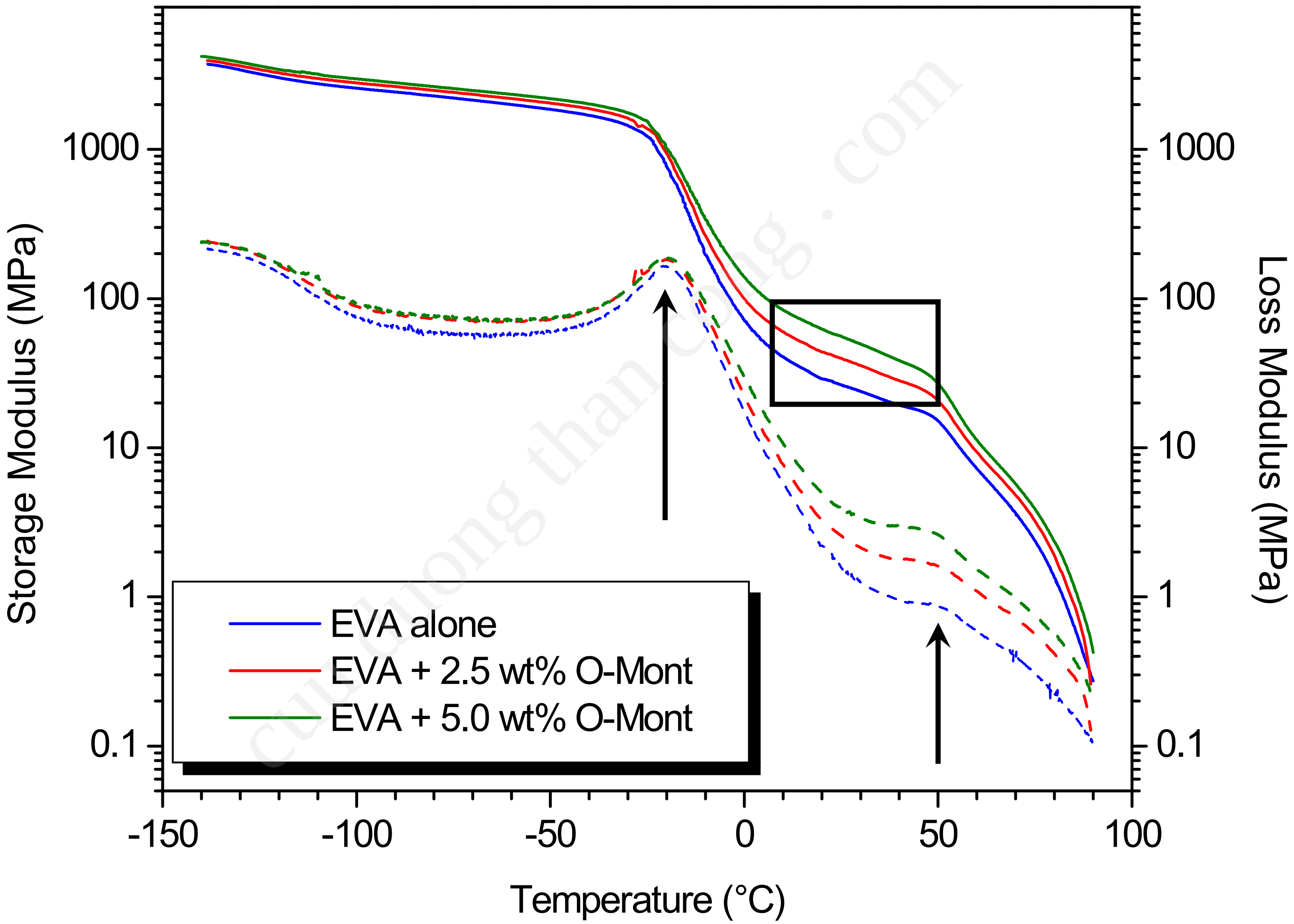
Mechanical properties

Tensile testing (ASTM D638 type 5)

Sample (5 wt% of clay)	Stress at break (MPa)	Strain at break (%)	Young's modulus (MPa)
EVA UL328 (no clay)	28.4+-0.7	1406+-28	12.1+-1.2
EVA UL328 + Mont-Na	25.0+-0.7	1333+-11	14.4+-0.2
EVA UL328 + Mont-DMDODA	26.2+-1.2	1264+-75	24.0+-0.5
EVA UL328 + Mont-DMODEHA	27.0+-0.8	1341+-16	23.1+-1.0
EVA UL328 + Mont-11-AUDEA	26.8+-1.5	1409+-13	12.0+-1.3

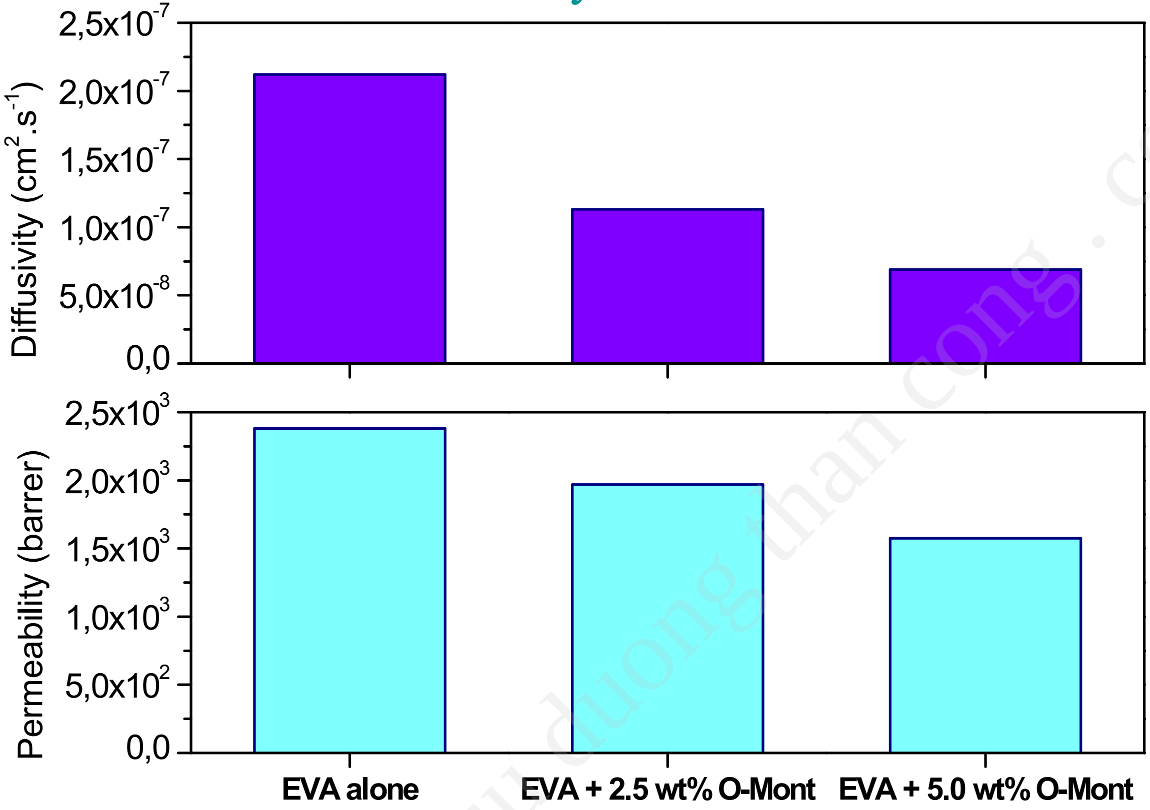
The nanocomposites exhibit a far higher Young's modulus (two-fold increase), while mainting acceptable ultimate properties

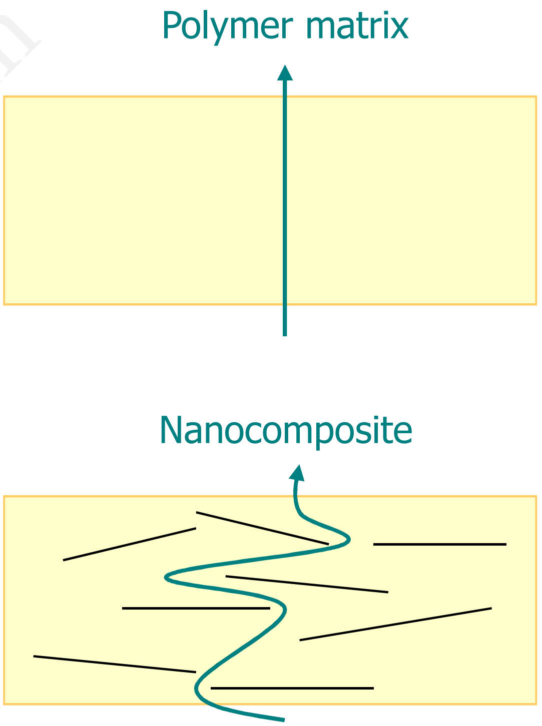
Dynamic mechanical analysis : film tension, 1Hz, 20µm deformation, 2°C/min



Water barrier properties

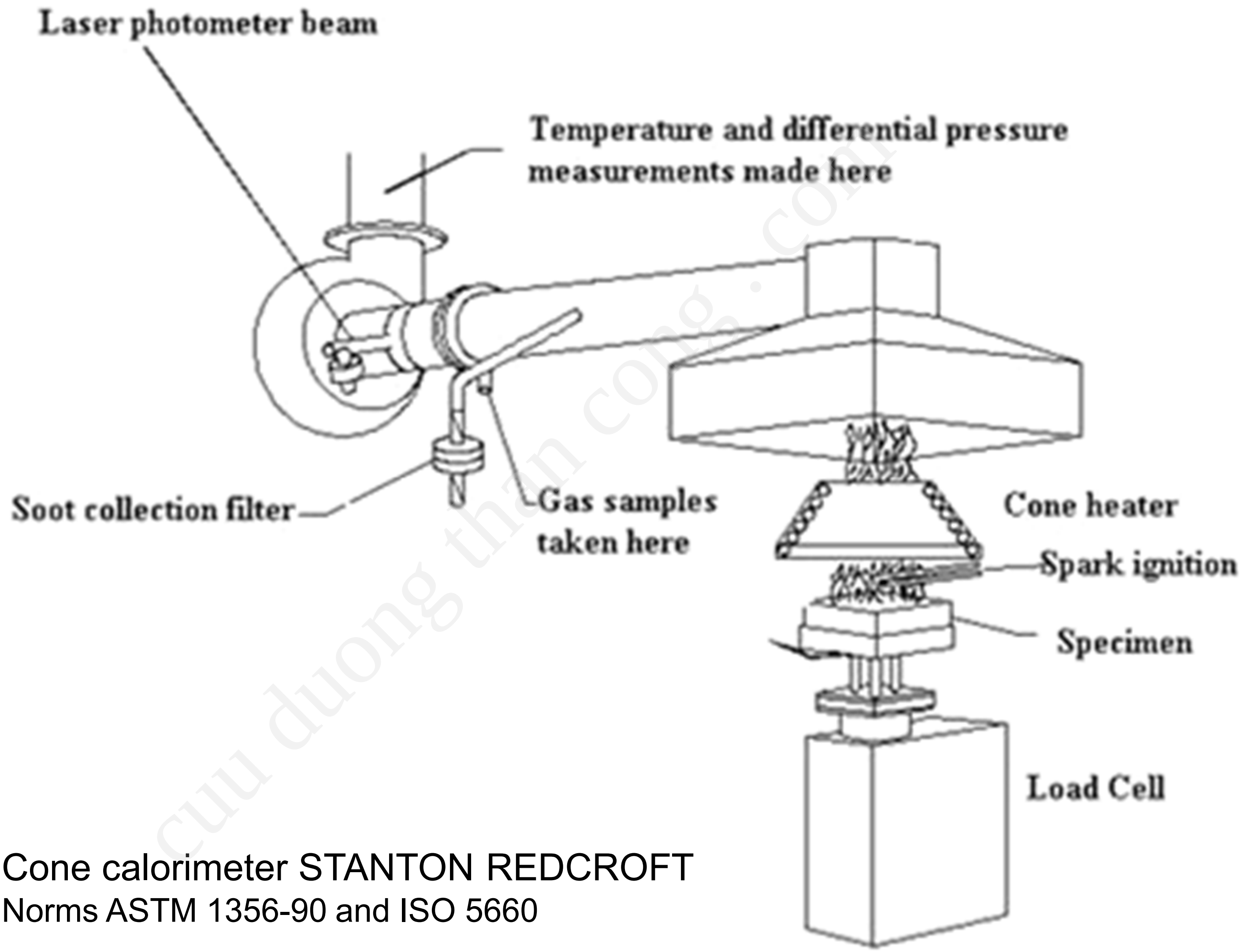
Permeability and diffusion coefficient of liquid water





Comparison of the values obtained for permeability P and diffusion coefficient D shows a more important relative decrease for the diffusion coefficient than for the permeability as the amount of O-Mont increases in the studied films

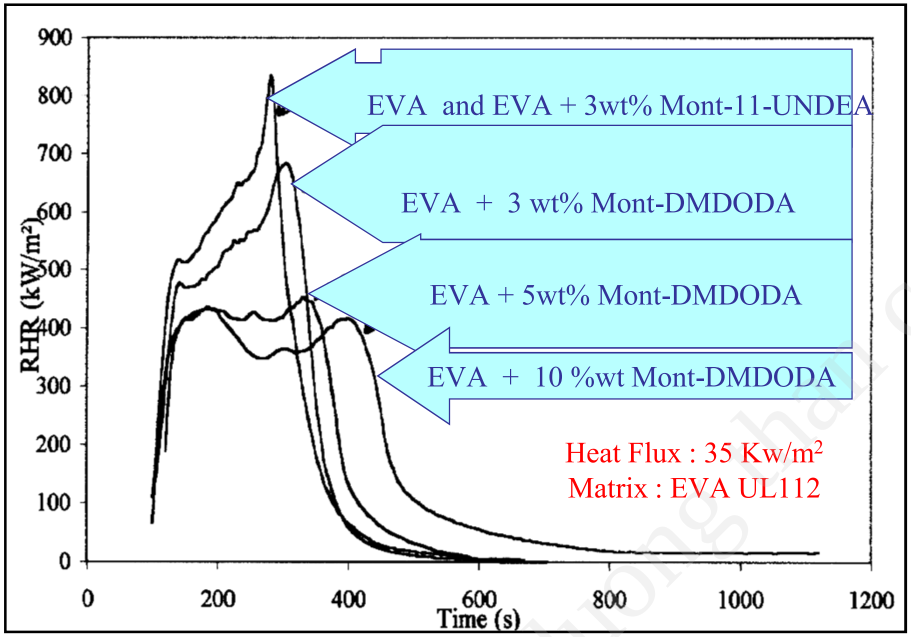
Flame retardant properties

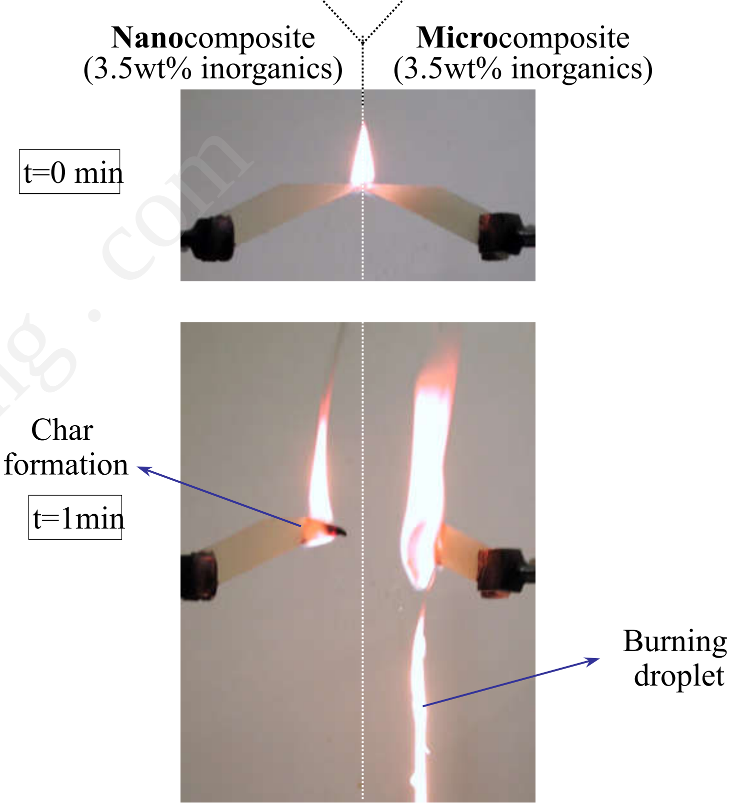


Cone calorimeter STANTON REDCROFT

Norms ASTM 1356-90 and ISO 5660

Cone calorimetry experiment burning behavior : flame retardant effect



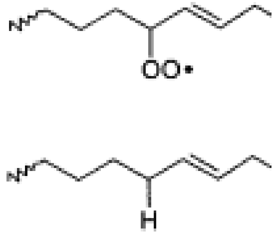


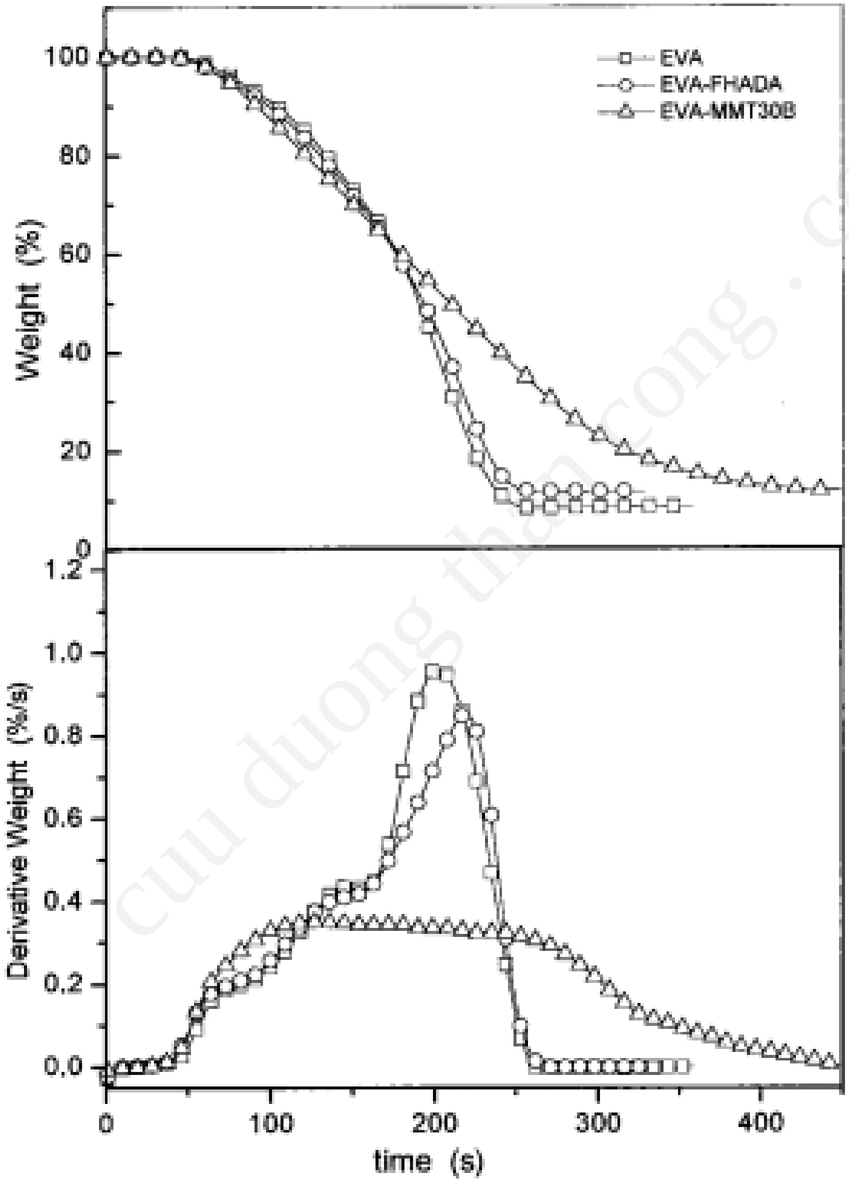
Char formation delays fire propagation and prevents burning droplets formation

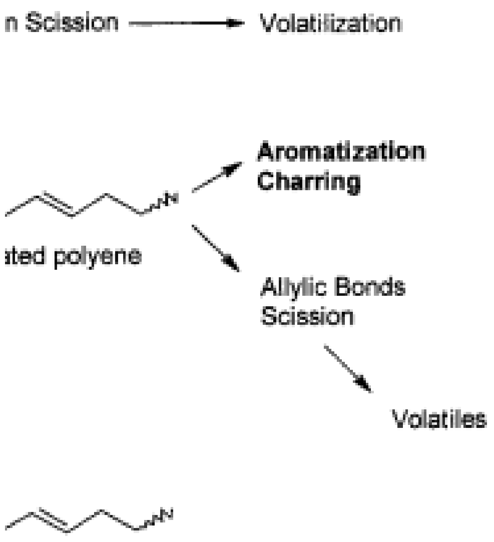
Decrease in the peak of heat release and shift towards longer time (char formation)

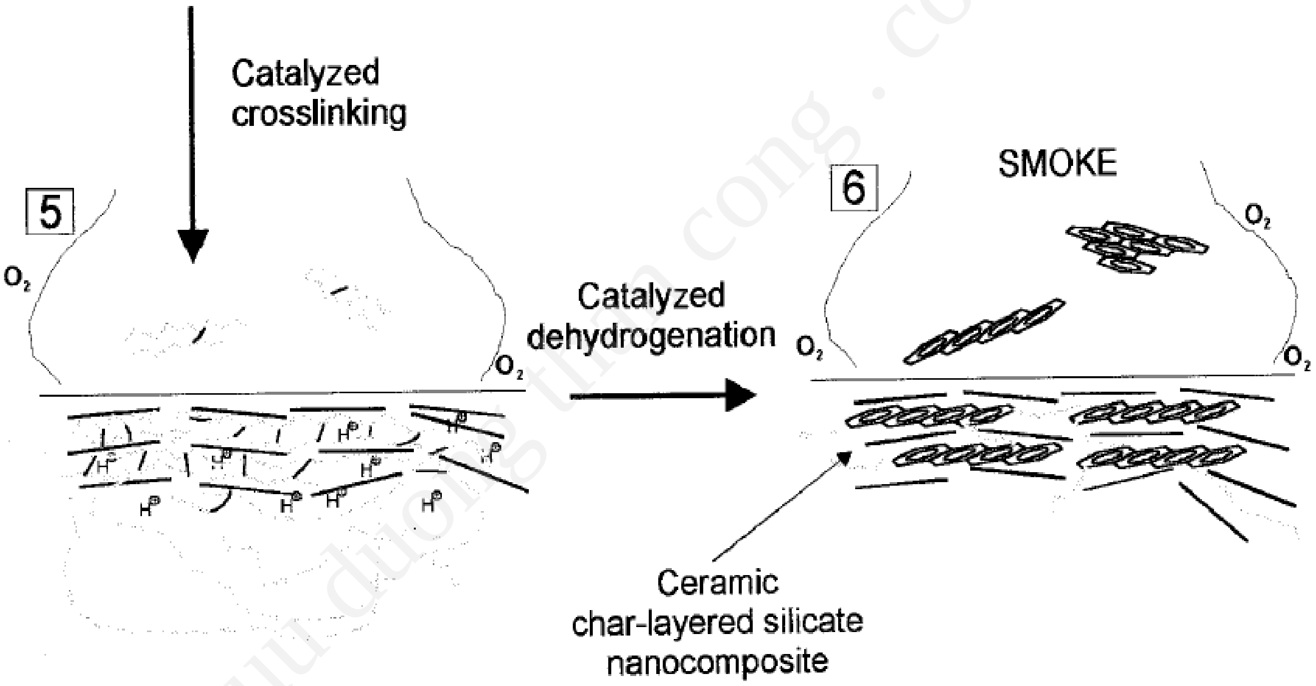
Effect reach a plateau between 5 and 10 wt% of DMDODA-modified montmorillonite

Proposed mechanism for char formation





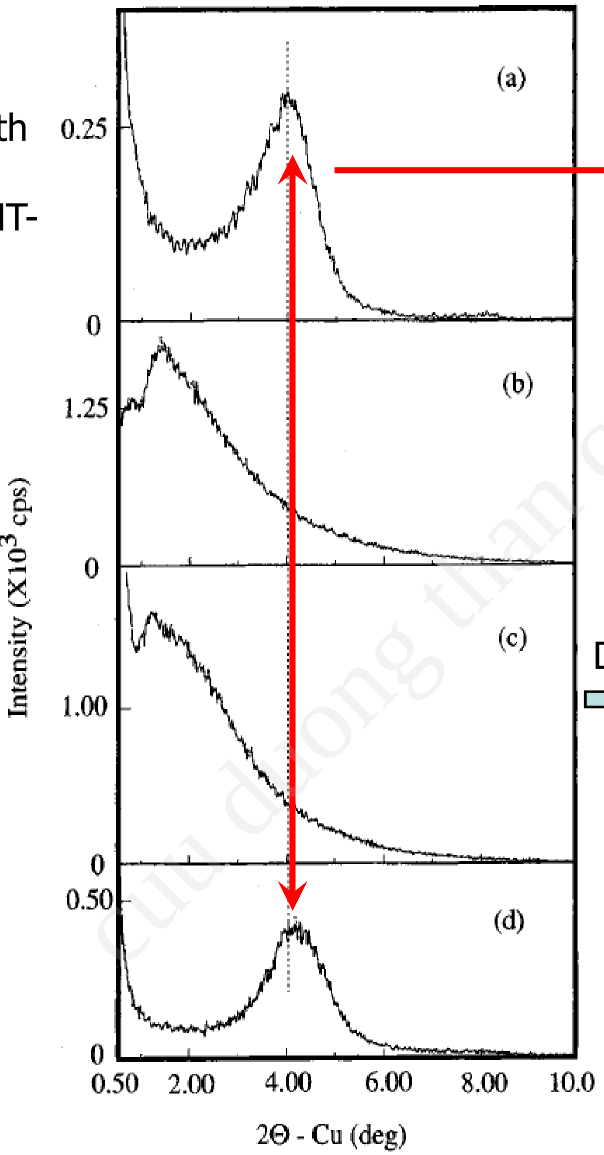




Zanetti M. et al, Chem. Mater. , 14, p.881 (2002)

PP/ clay nanocomposites : melt blending with an organoclay and addition of PP-g-MA

M. Kawasumi et al, Macromolecules, 30, p.6333 (1997)



MMT exchanged with protonated octadecylamine (MMT-C18)

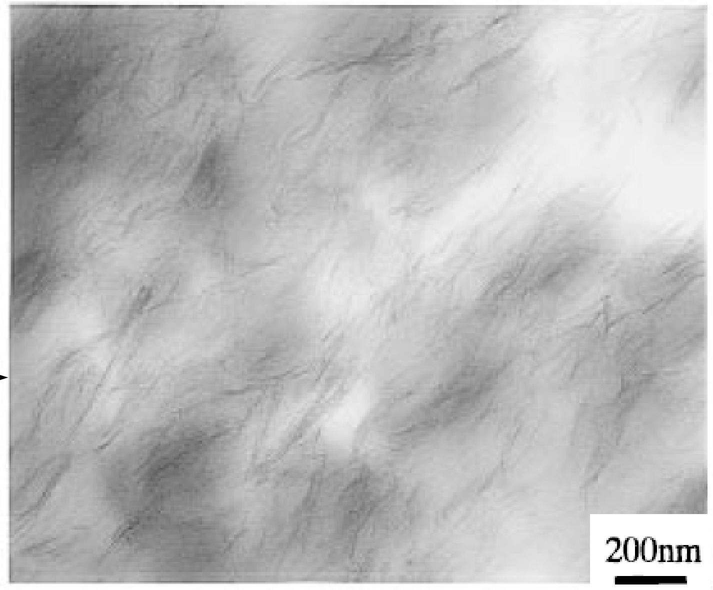
MMT-C18 melt-blended in PP-g-MA (52mgKOH/g) 1:3 in wt%

MMT-C18 melt-blended in PP-g-MA (26mgKOH/g) 1:3 in wt%

MMT-C18 melt-blended in PP (1:3 in wt%)

No dispersion of the clay in PP

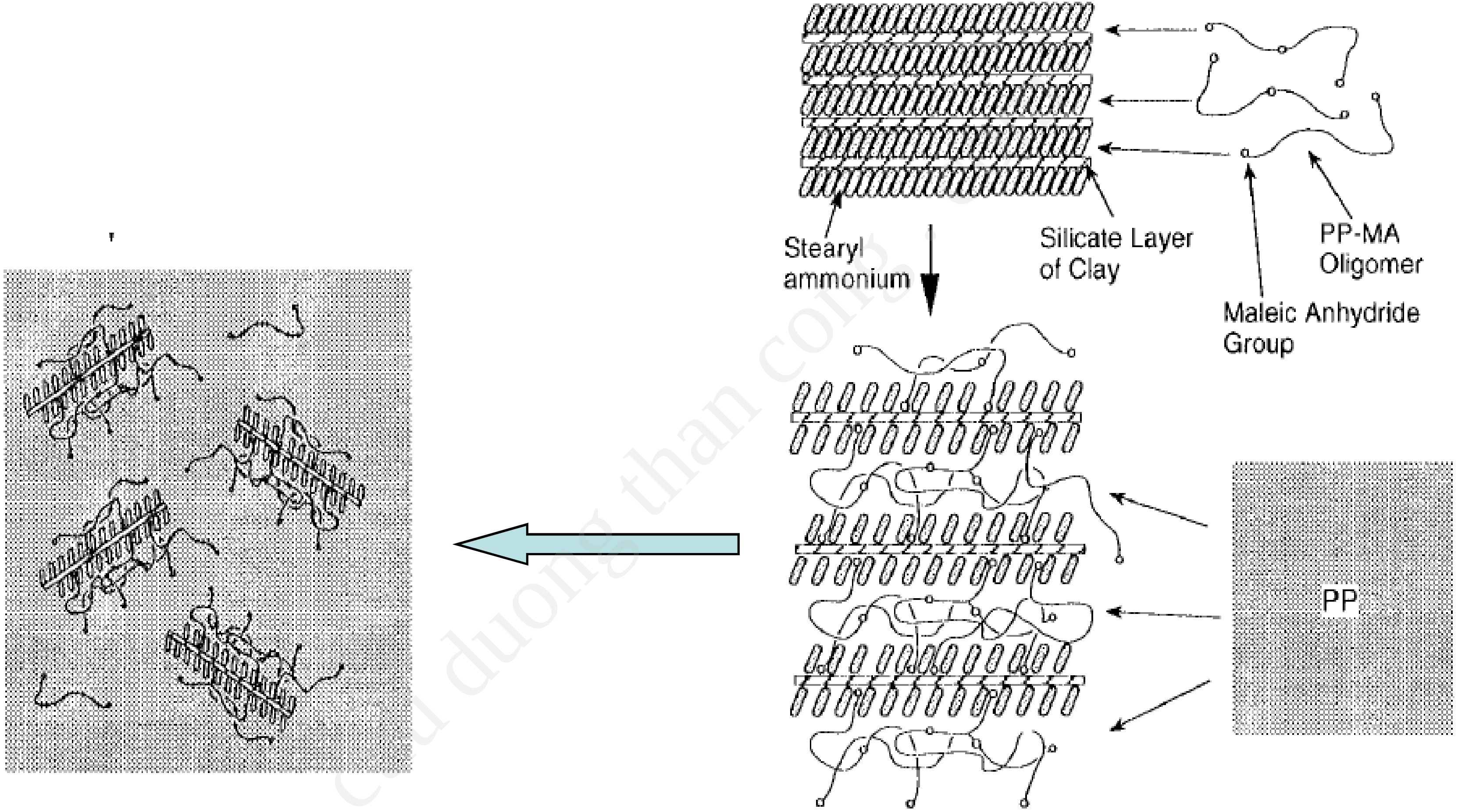
Dispersed in PP



(4,8wt% clay)

PP/clay nanocomposite compatibilized by PP-g-MA : proposed mechanism

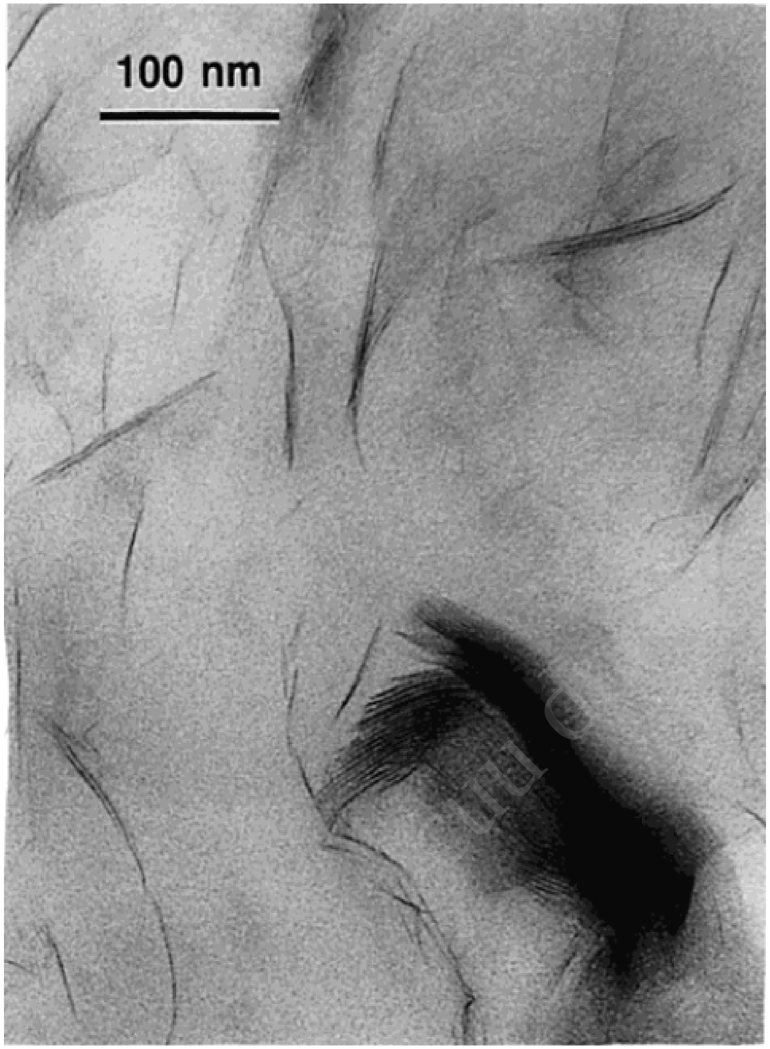
M. Kawasumi et al, Macromolecules, 30, p.6333 (1997)



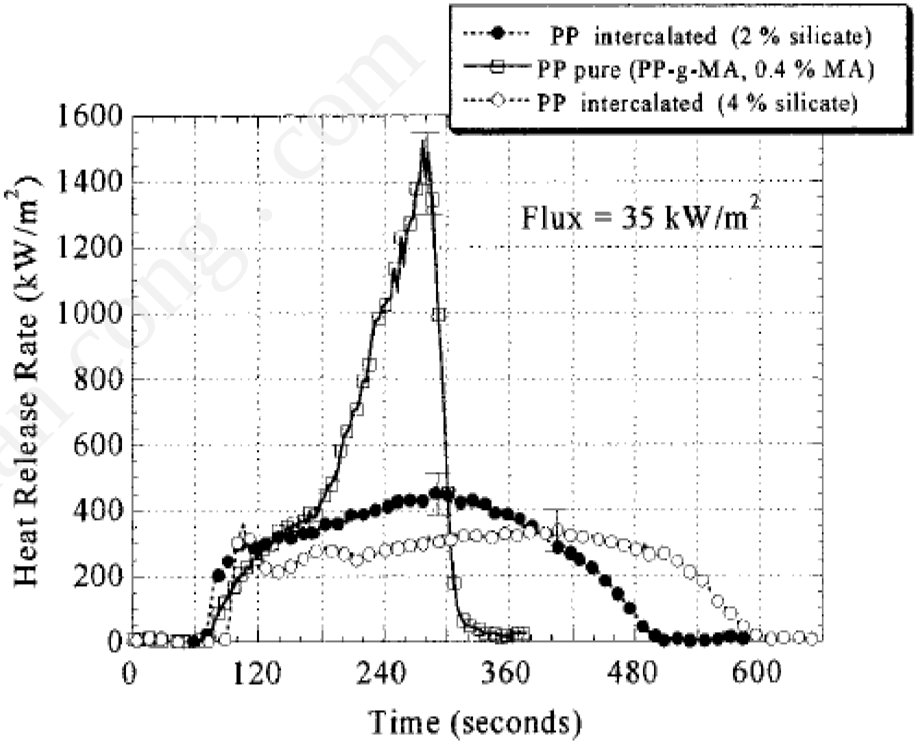
Based on this technique, lots of academic and industrial researches have been carried out

Morphology and flame retardant properties of MA-g-PP/ clay nanocomposites

TEM picture of a MA-g-PP/clay nanocomposite containing 4 wt% of clay



J.W. Gilman, Chem. Mater., 12, p.1866 (2004)

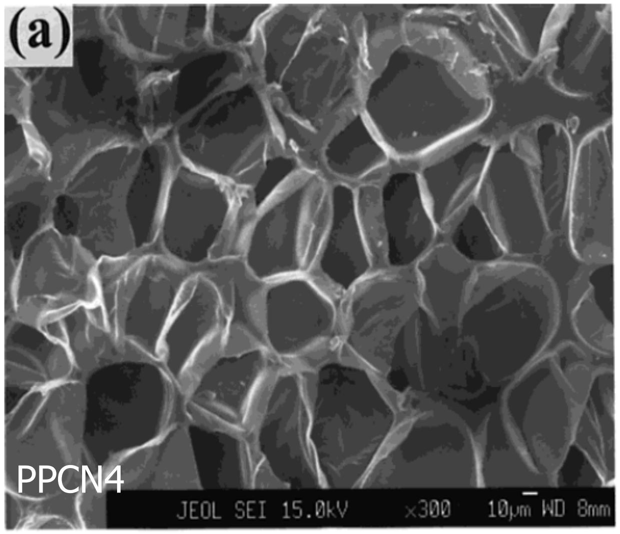


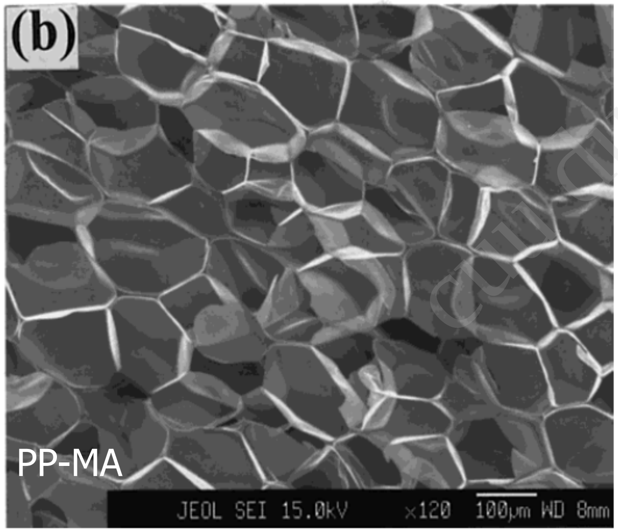
Nanocomposite formation strongly reduces the peak of heat release of PP-g-MA

Influence of organoclay on the foaming of PP-g-MA

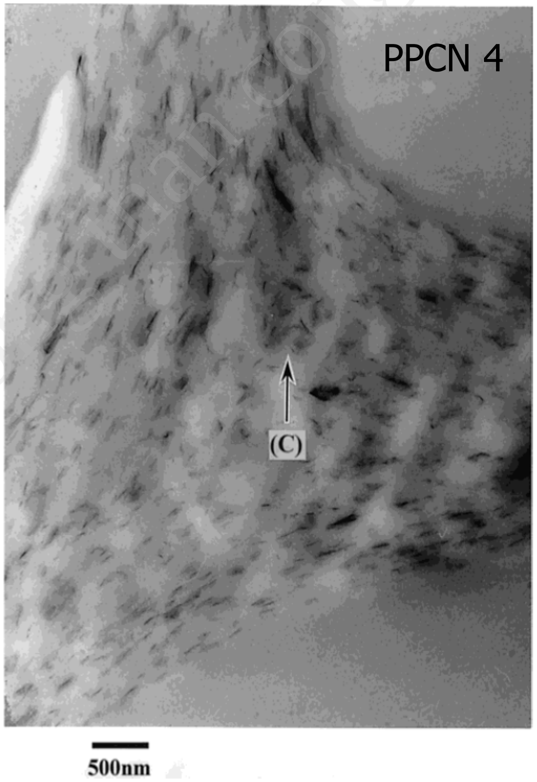
M Okamoto, Nanolett., 1, p.503 (2001)

Foams obtained by slow pressure release of supercritical CO_2 nanocomposite solution





foam	ρ_f/g·cm^{-3}	d/μm	$N_c \times 10^{-6}$/ cell·cm^{-3}	Compression modulus K'^a/MPa
PP-MA	0.06	155.3	2.49	0.44
PPCN2	0.06	133.0	3.94	1.72
PPCN4	0.12	93.4	9.64	1.95
PPCN7.5	0.13	33.9	220	2.80



Nanoclay acts as a nucleating agent
(increase of cell density and decrease of cell diameter)

Nanoclay organization in the cell wall participates to the increase in compression modulus

Partial conclusions :

Melt intercalation is the technique of choice to prepare clay/polyolefin nanocomposites on an industrial point of view

Obtaining and **maintaining** clay nanoplatelets exfoliation in PE and PP matrices remain the challenge !!!!

Indeed new techniques (power ultrasound, blending under electrical field, ultra-high shear compounding) are being tested but even if these techniques allow for exfoliation, it is still necessary to use polar additives to maintain this exfoliation upon molding.

To do so, more research must be done on adapting the properties, functionalization, organomodification of the clay, in order not to modify too much the properties of the polymer matrix (major component)

In the frame of polyolefins, three main properties may be interesting for clay-based nanocomposites:

- increase in **barrier** properties to fluids (gas and liquids)
- improve **flame retardant** behavior (especially for building oriented materials)
- keep the **transparency** of the materials while modifying others (mechanical, thermal, viscoelastic,…)

Polyolefin/clay nanocomposites

The three main preparative techniques have been used to tentatively prepare polyolefin/clay nanocomposites

Exfoliation adsorption :

PE + clay organomodified with protonated dodecylamine, dissolved in xylene/benzonitrile (80:20 wt%)
then precipitated in THF ⟹ Result : at best little intercalation H.G. Jeon et al, Polym. Bull., 41, p.107 (1998)

PE + clay organomodified with hexadecyltrimetylammonium , dissolved in toluene (autoclaved at 170°C)
then solvent evaporation ⟹ Result : claimed exfoliation (?) L. Song et al, J. Mater. Chem., 12, p.3152 (2002)

Processes involving organic solvents, no study of the nanocomposite stability if melt processed

Melt intercalation/exfoliation :

A large amount of research deals with this technique, easily implemented in industry (melt processing)

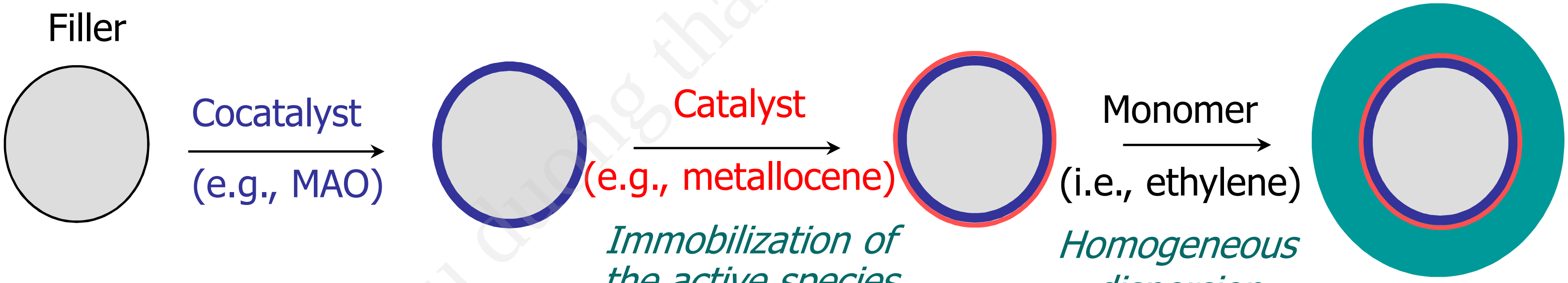
In situ intercalative polymerization :

Numerous studies mainly based on ethylene and ethylene/α-olefin (co)polymerization : Via CATALYSIS !

REMINDER : In Situ Polymerization via Coordination Catalysis

HDPE layered silicate nanocomposites → **Polymerization-Filling Technique (PFT)**

- fixation of a Ziegler-Natta type catalyst onto the filler
- olefin polymerization from the filler surface



Filler

Cocatalyst (e.g., MAO)

Catalyst (e.g., metallocene)

Immobilization of the active species through electrostatic interactions

Monomer (i.e., ethylene)

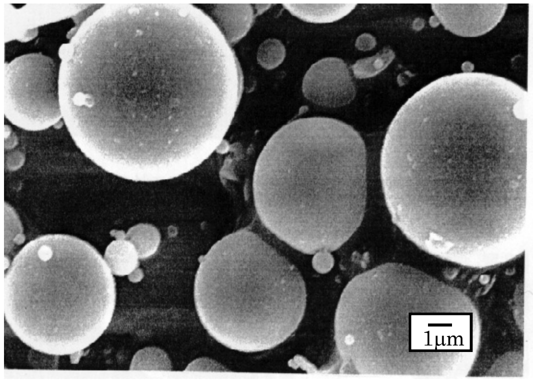
Homogeneous dispersion of the coated filler

Composite

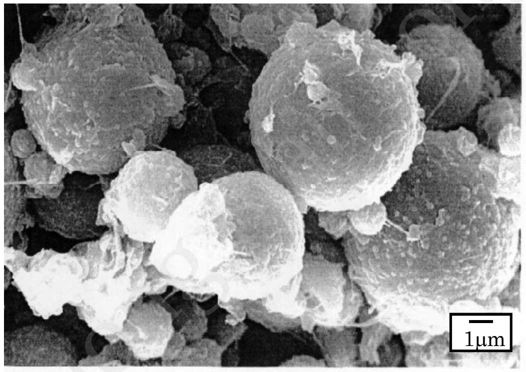
Dubois et al., J. Macromol. Sci.- Rev. Macromol. Chem. Phys., C38 (1998)

- **PFT with micro-fillers *(reminder)* :**

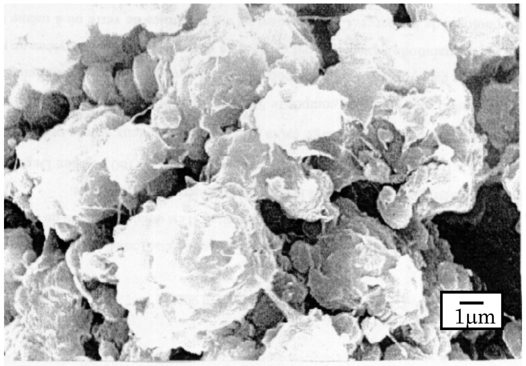
  - ☞uniform distribution of the filler throughout the matrix
  - ☞optimum polymer adsorption and wetting
  - ☞only process for the preparation of UHMWPE-based composites
  - ☞control of the molecular masses through transfer to molecular hydrogen
  - ☞possibility to synthesize copolymers with α-olefins (from thermoplastics to elastomers)



uncovered glass beads



glass beads covered with 14.6 wt% PE



glass beads covered with 59.4 wt% PE

→ Combination of HIGH STIFFNESS and HIGH IMPACT RESISTANCE
(even at high filler content, > 60 wt%)

(from Dubois, Jérôme et al., Chem. Mater., 13 (2001))

PFT in non-exchanged layered silicates

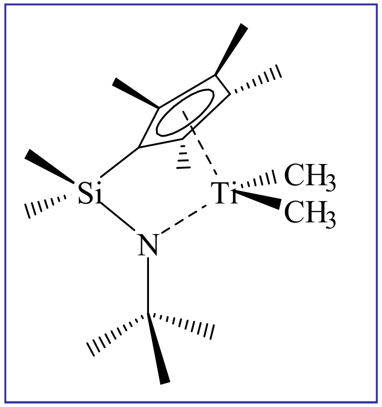
* (dried) clay dispersion in heptane followed by contact with MAO

* solvent evaporation and thermal treatment (150°C)

* *(unreacted MAO washed out with toluene)*

* treated filler suspended in heptane and contacted with the catalyst :

*(Tert-butylamido)dimethyL (tetramethyl-η^5-cyclopentadienyl) silane titanium dimethyl (**CGC1**)*



* in situ polymerization of ethylene (10 bars) (+ H_2 when needed)

* composite isolated by « precipitation » from acetone.

Polymerization-Filled (Nano)Composite

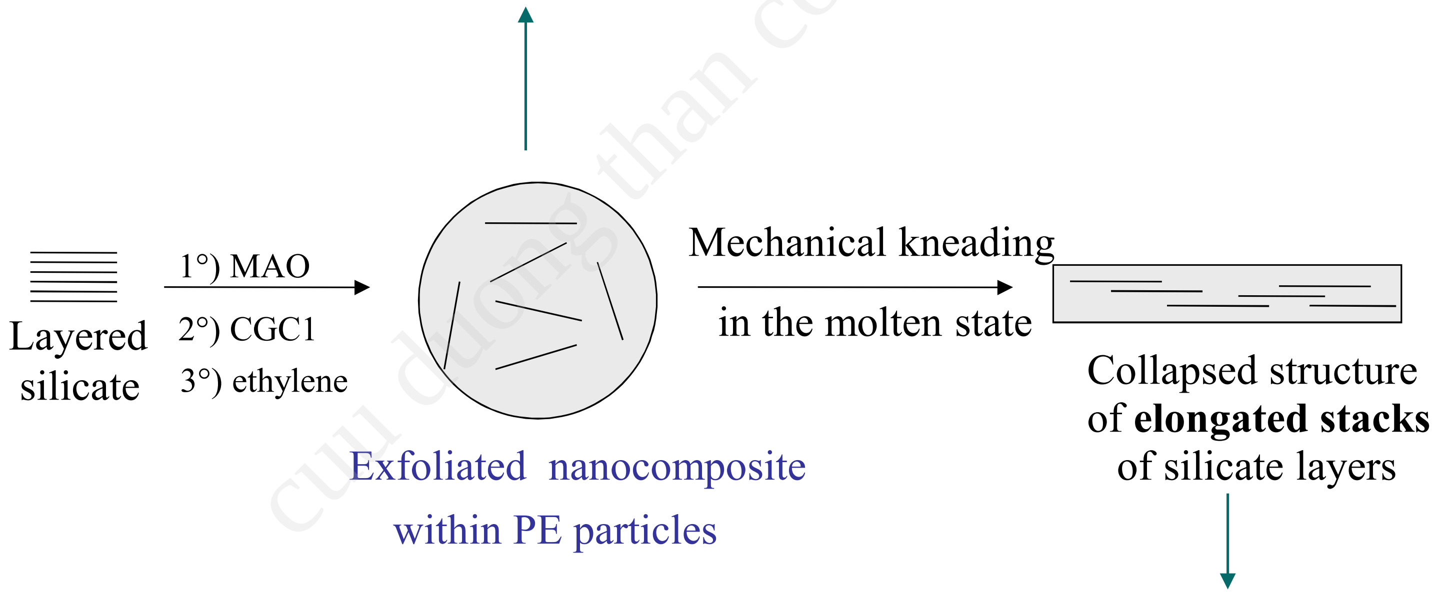
Alexandre and al., Polymer, 43 (2002)

Intermediate conclusions

PE- based nanocomposites can be readily prepared by
the so-called Polymerization-Filling Technique

UHMWPE-based nanocomposites display matrix-driven properties

HDPE-based nanocomposites show properties imparted by the presence of nanofill



Layered silicate

1°) MAO
2°) CGC1
3°) ethylene

Exfoliated nanocomposite within PE particles

Mechanical kneading in the molten state

Collapsed structure of **elongated stacks** of silicate layers

Thermodynamic in nature

PFT in organo-modified layered silicates

Overall Strategy

2) Necessity of functionalized (more polar) polyolefin

1) Need to destructurize the organo-clay

3) Use of HDPE matrix

A. Preparation of masterbatches

(nanofiller-enriched composites):

2 pathways

« physical » pathway

Spontaneous intercalation of « polar » copolymer

« chemical » pathway

ntercalative (*in situ*) synthesis of « polar » copolymer

B. Melt blending within HDPE

M. Mainil, Ph.D. thesis, UMH (2005)

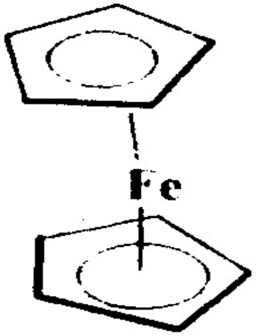


Schéma 1 ferrocene

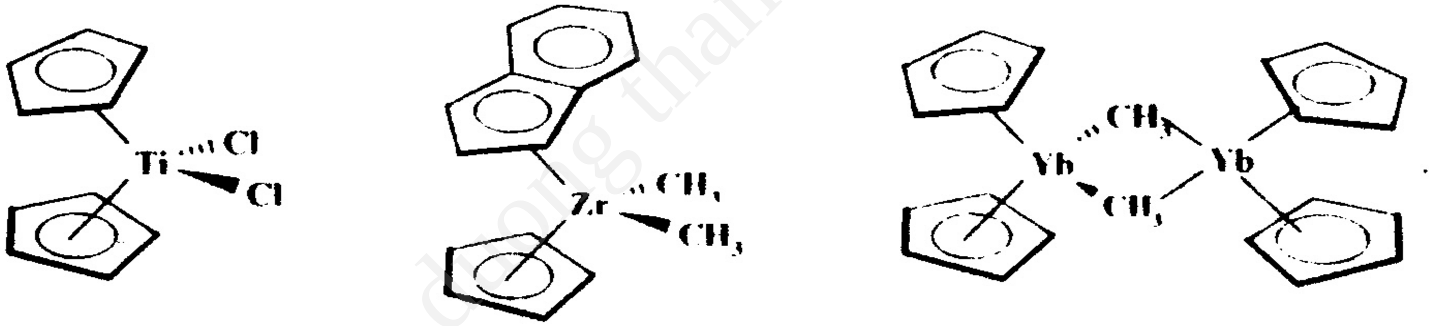
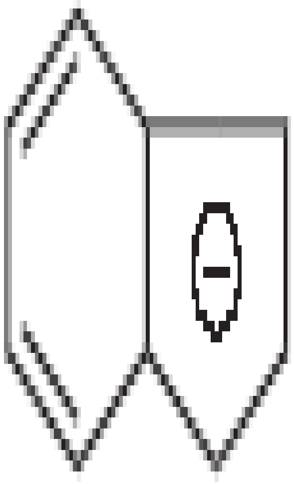
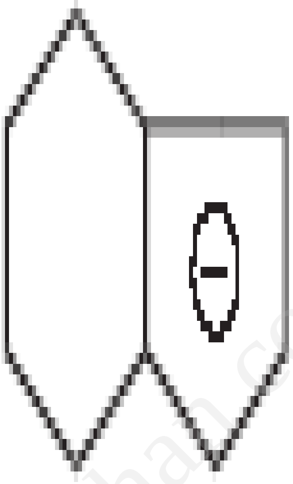


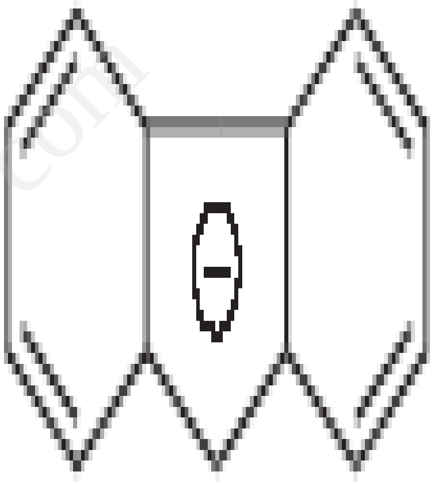
Schéma 2 exemples de metallocènes



Indenyl



Tetrahydroindenyl

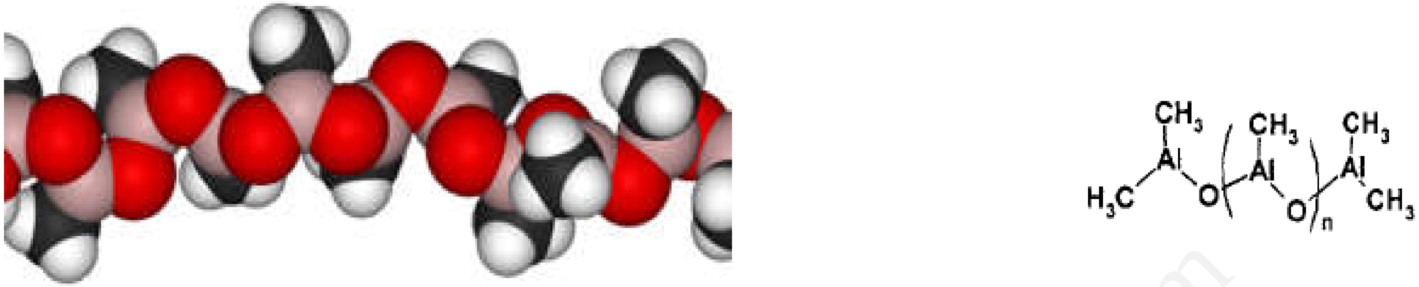


Fluorenyl

Métaux colonne IV
(Ti, Zr, Hf)
D.O +IV (modèle ionique)

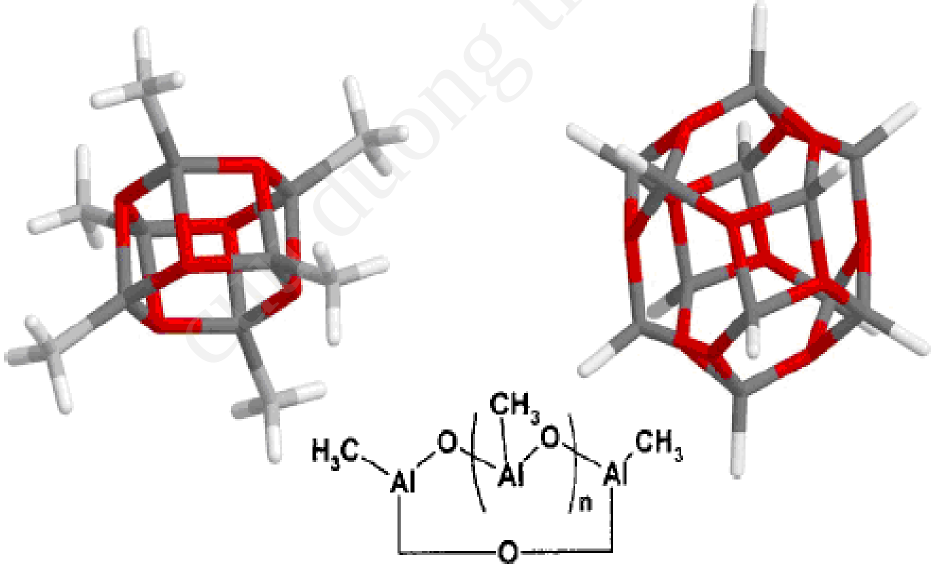
Métaux colonne III
+ Lanthanides
(Y, La, Sm, Yb, Lu)
D.O +III (modele ionique)

Schéma 3



Cấu trúc mạch dài của MAO

Cấu trúc lồng của MAO



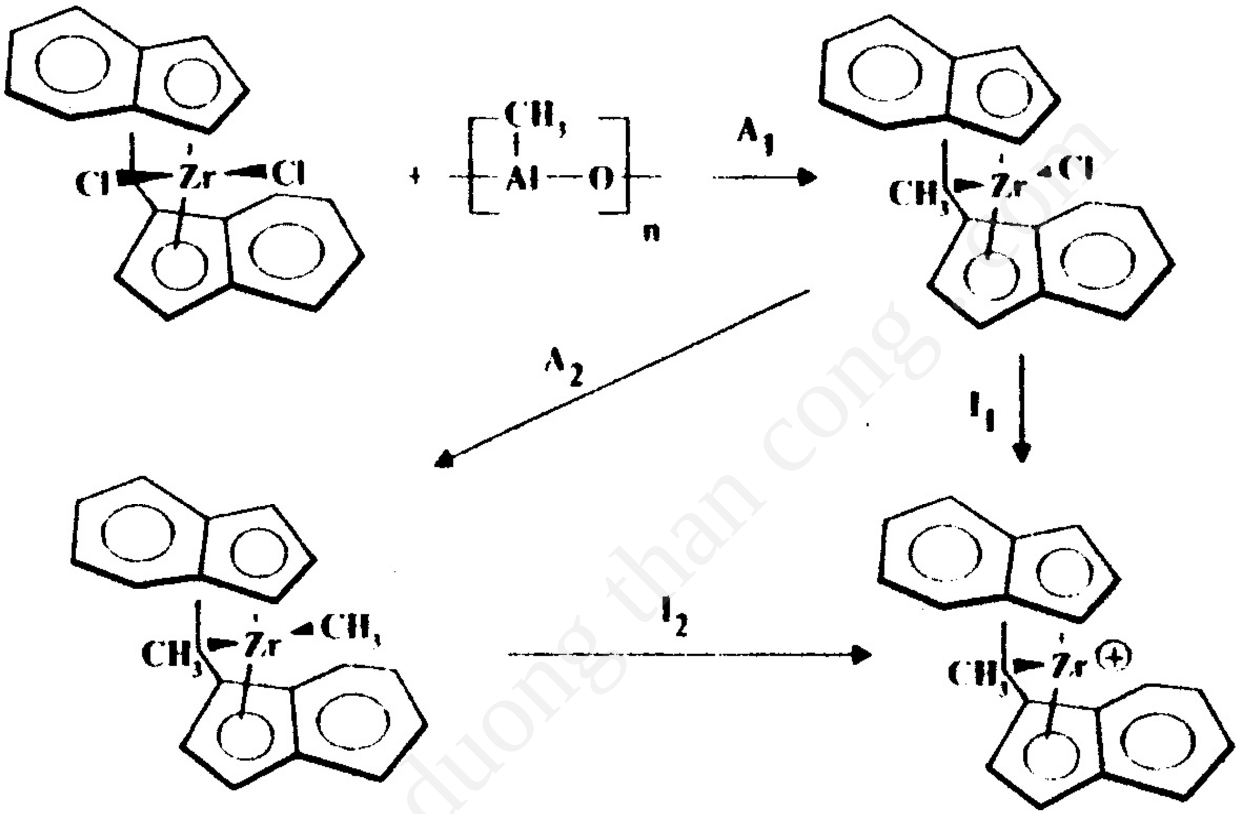
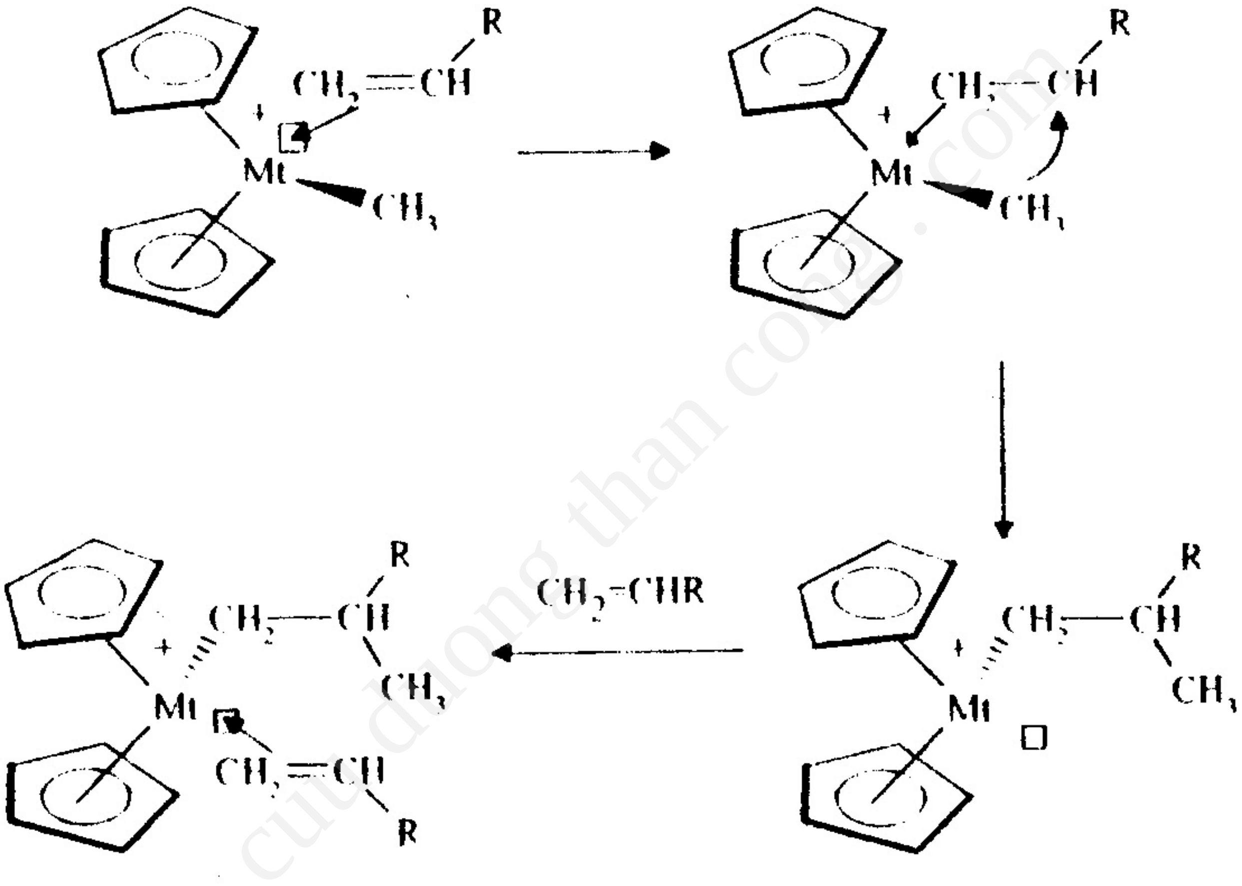
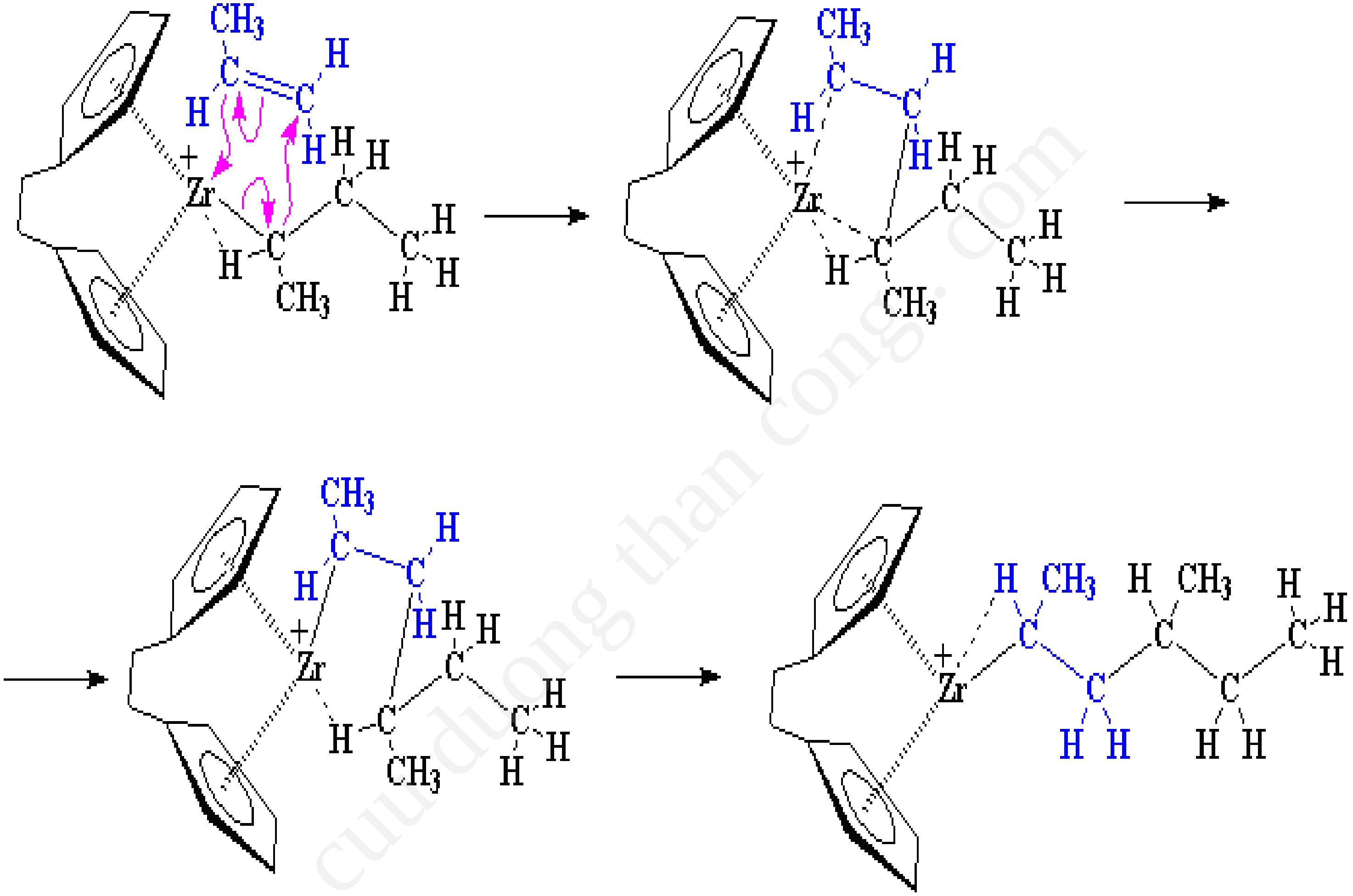
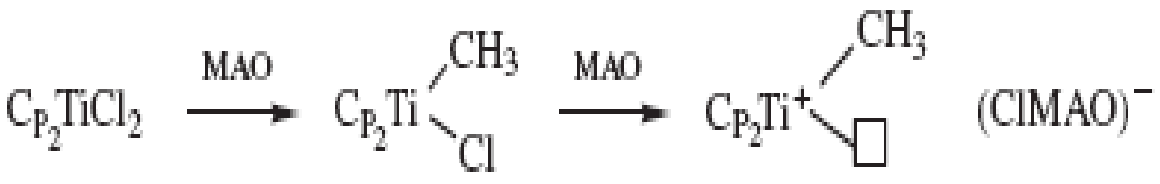


Schéma 6 : Formation des espèces actives dans le cas du système

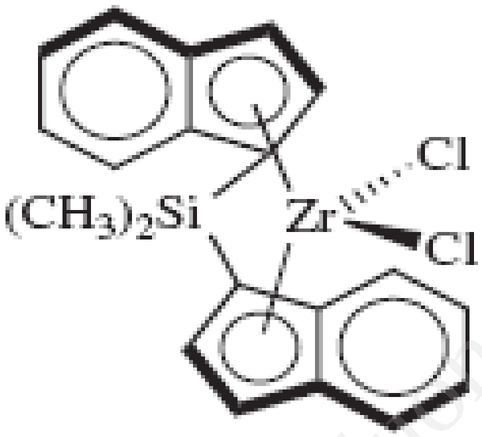
rac-éthylène bis (1-indenyl)$_2$ZrCl$_2$/MAO (19)


R
CH₂=CH
+
Mt
CH₃
R
CH₂–CH
+
Mt
CH₃
R
CH₂–CH
+
Mt
CH₃
CH₂=CHR
R
CH₂–CH
+
Mt
CH₃
CH₂=CH
R

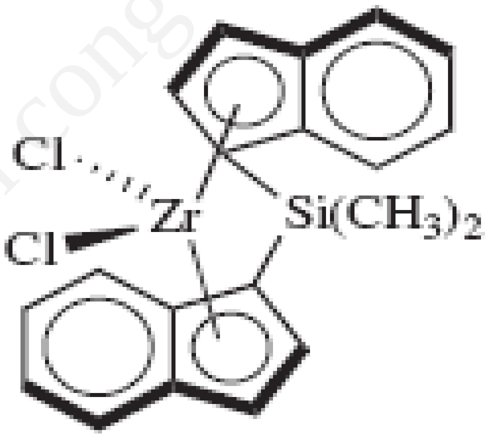

CH3
H
C
C
H
H
Zr
+
H
C
H
C
H
H
CH3
H
H



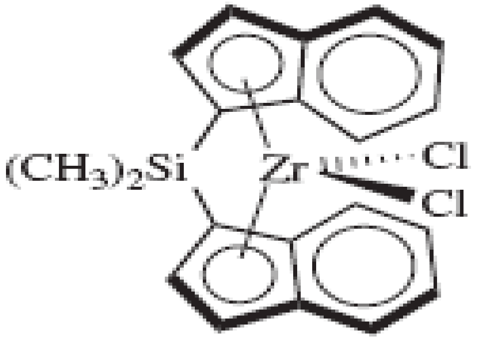
XXVII



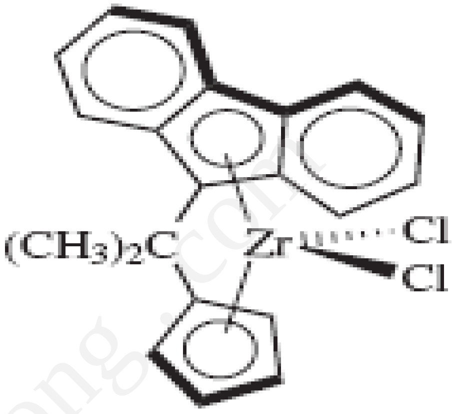
XXXIVa



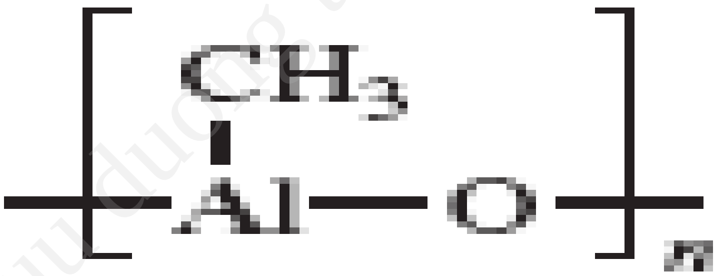
XXXIVb



meso-$Me_2Si(Ind)_2ZrCl_2$



$Me_2C(Cp)\ (Flu)\ ZrCl_2$



$$\left[\begin{array}{c}CH_3\\ |\\ \text{—Al—O—}\end{array}\right]_n$$

XXXVII

Ethylene (co)polymerisation

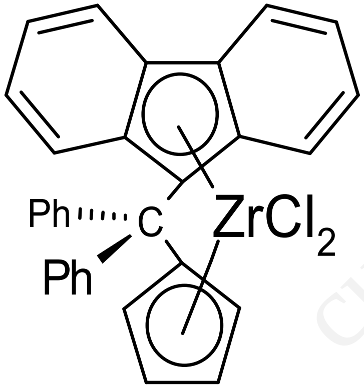
via coordination-insertion

Metallocene pre-catalyst

Zr(IV)-based complex

Activator/co-catalyst

Modified methylaluminoxane (MMAO)

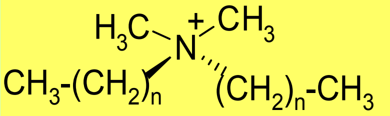


Ph$_2$CCpFluZrCl$_2$

Ethylene-**styrene** (ES) Copolymerization

Within the galleries of Cloisite® 20A

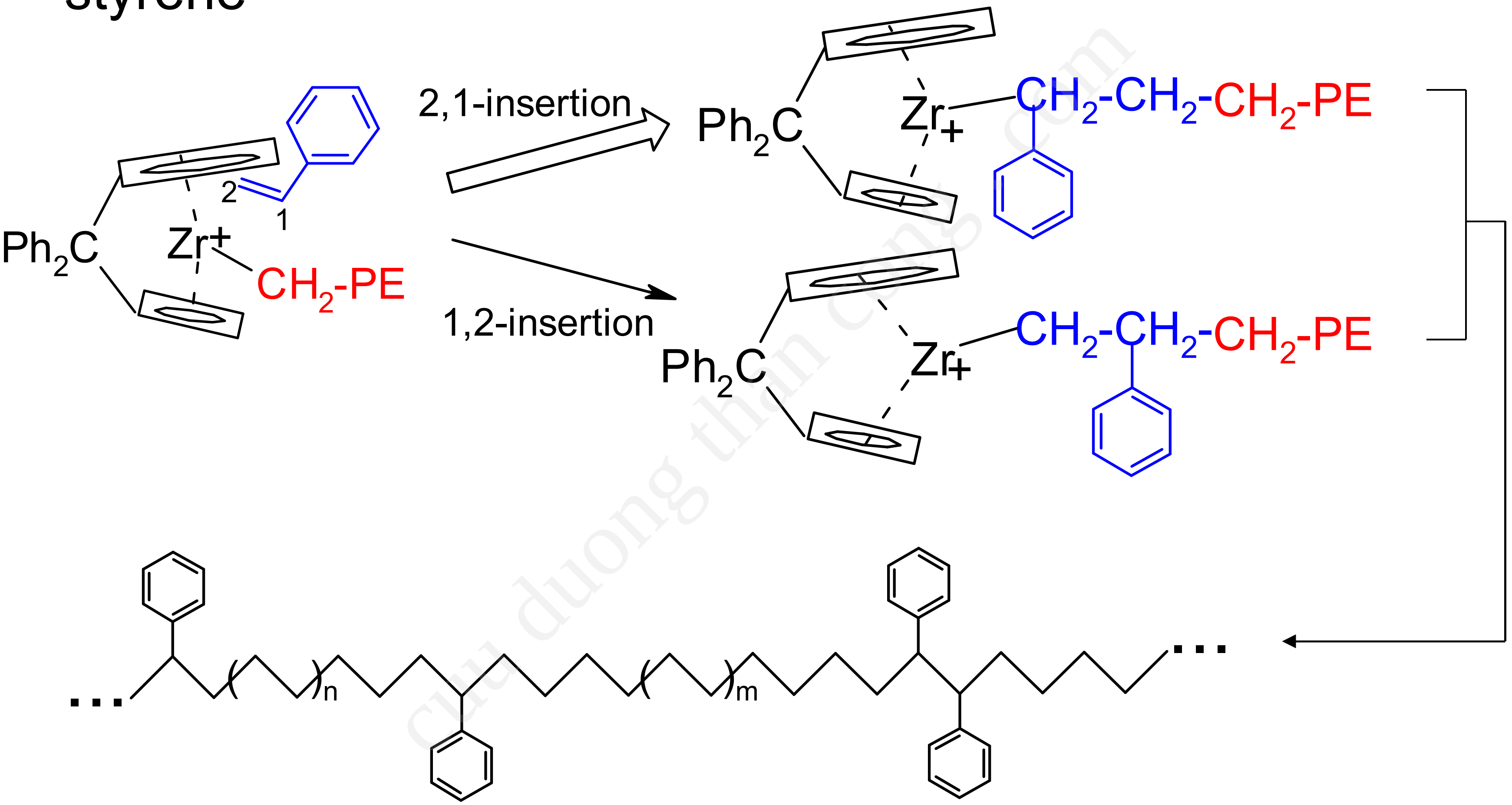
via



n = 13(5%), 15(30%), 17(65%)

previous intercalation by the MMAO/zirconocene catalytic system

Pseudo-random copolymerization of ethylene and styrene



Copolymère (E-co-S)

Conclusions

PE-based nanocomposites can be readily prepared by
the so-called **Polymerization-Filling Technique** applied to <u>organo-modified</u> montmorillonite

However, it is needed to enhance « polarity » of intercalated chains
for maintaining the nanoscale dispersion of silicate layers : compatibilization effect !

Styrene proved to be a good comonomer in ethylene copolymerization but
- if too low content in styrene : no stabilization of the intercalated nanostructure (for processing)
- if too high content in styrene : no longer miscibility with HDPE matrix !

Compromise in the range of **3 to 7 mol % in styrene** :
>>> semi-intercalated/semi-exfoliated nanocomposites

Future works :
New metallocene-based catalysts for copolymerization with MA and/or functionalized norbornenes