Polymer (nano)composites : key-role of chemistry

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

cuu duong than cong . com

CuuDuongThanCong.com https://fb.com/tailieudientucntt

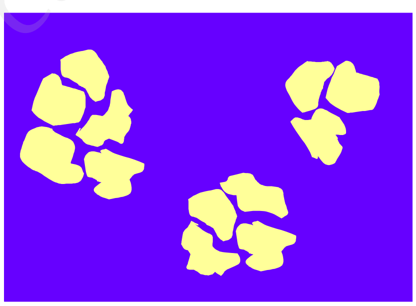
Chapter 1 :

Polymer microcomposites filled with microparticles

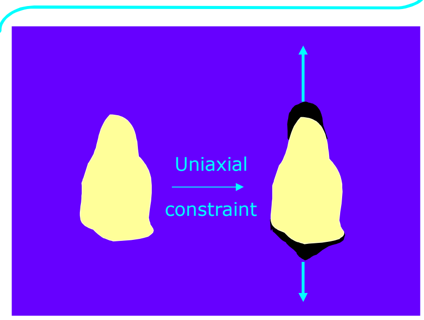
cuu duong than cong . com

Typical example : polyethylene filled with reinforcing inorganic particles

Hydrophobic polyethylene + Hydrophilic-surface Particulate fillers

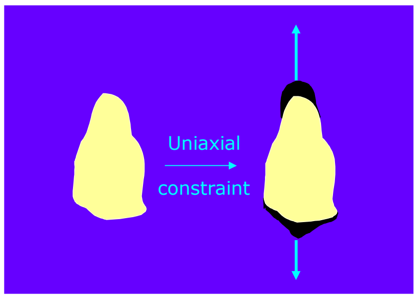


Fillers aggregation => mechanical brittleness

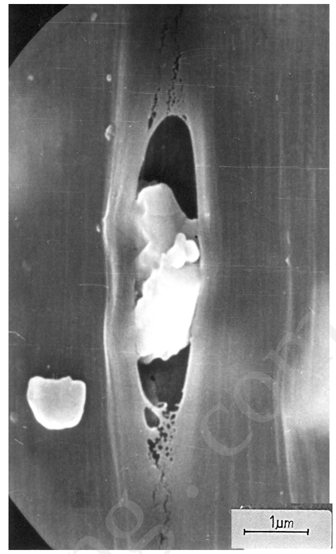


Generation of voids => propagation of the rupture

CuuDuongThanCong.com https://fb.com/tailieudientucntt



Generation of voids => propagation of the rupture



(From Prof. G. Marosi)

cuu duong than cong . com

Effect of particulate fillers on mechanical properties

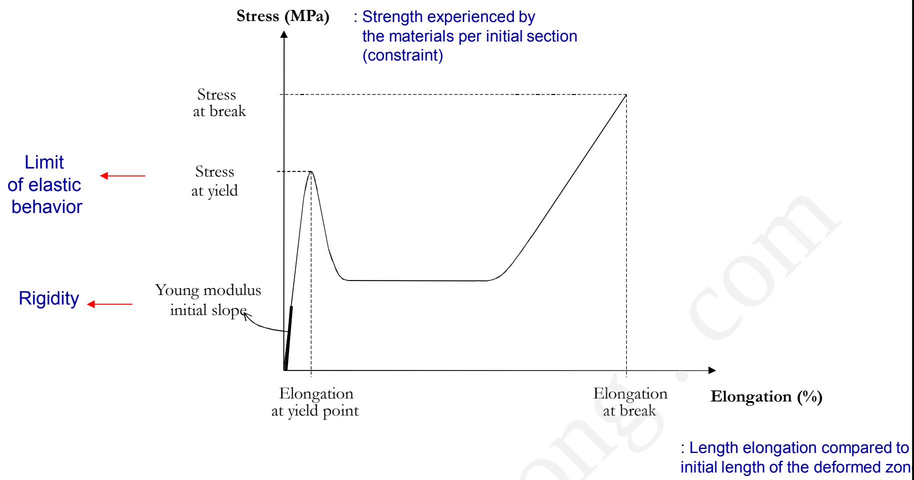
Materials	Stiffness	Brittleness (fast deformation)	Brittleness (slow deformation)
	Young's modulus (GPa)	Impact strength (IZOD test) (J/m)	Elongation at break (tensile test) (%)
HDPE*	0.7	80	900.0
HDPE + 40wt% kaolin	3.1	17	1.6
HDPE + 40wt% mica	6.5	20	0.3
HDPE + 40wt% $CaSO_4$	2.8	15	1.3
HDPE + 40wt% $CaCO_3$	2.7	21	3.0

BRITTLENESS → non-homogeneous mineral dispersion
BRITTLENESS → poor mineral-polymer interaction

* High density polyethylene (Mw ~ 90K)

CuuDuongThanCong.com https://fb.com/tailieudientucntt

NB : mechanical properties for a semi-crystalline thermoplastic like HDPE measured by tensile testing (in between T_g and T_m)

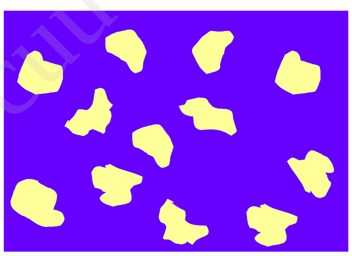


cuu duong than cong . com

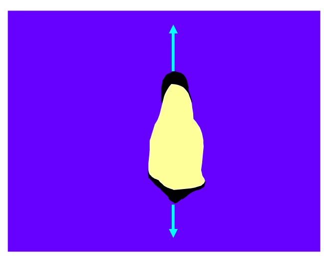
Solutions ?

1°) Decrease the hydrophilicity of the filler surface

Chemical treatment of the filler surface (alkoxysilane, alkylamine, Al carboxylates,…)



Improvement of the dispersion



Poor adhesion

Less brittle composite materials

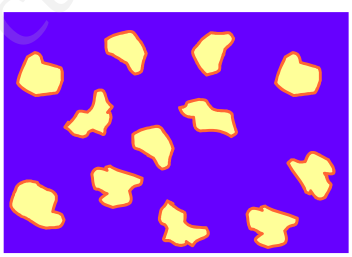
CuuDuongThanCong.com https://fb.com/tailieudientucntt

Filler or coating composition	Filler content (wt%)	Elongation at break (%)	Impact strength (kg m/m)
Reference materials			
Unfilled HDPE	0	1045	2.77
+ Kaolin	20	218	1.24
Kaolin + surface agents			
0.6 n-hexylamine	20	291	1.38
5.0 triethoxysilane	20	162	1.92
5.0 octadecyl triethoxysilane	20	668	1.38
2.5 oxylaluminum-2-ethylbutyrate	20	300	1.91

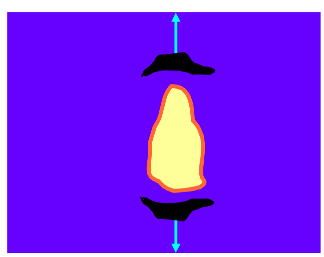
2°) (Polymer) grafting reaction onto filler surface

- via chemical treatment of filler surface with **coupling agents** *(vinylic or methacrylic alkoxysilanes, aluminum methacrylates,…)*

followed by polymer grafting all along melt blending/processing



Improved dispersion



Reinforced adhesion => Mechanical rupture within the matrix !

Rigidity and resistance to break significantly improved

cuu duong than cong . com

CuuDuongThanCong.com https://fb.com/tailieudientucntt

Filler or coating composition	Filler content (wt%)	Elongation at break (%)	Impact strength (kg m/m)
Reference materials			
Unfilled HDPE	0	1045	2.77
+ Kaolin	20	218	1.24
Kaolin + coupling agents			
2.0 3-(trimethoxysilyl)propyl methacrylate	20	277	1.96
2.0 vinyltriethoxysilane + 3.0 amyl-triethoxysilane	20	71	1.58
1.5 oxyaluminum methacrylate	20	420	2.79
1.5 oxyaluminum-methacrylate + 2.5-bis-(t-butylperoxy) -2,5-dimethylhexane [a]	20	430	3.04

(a) Peroxide content was 0.05 wt% kaolin.

Filler - Polymer Dispersion / Interaction

- **Surface modification of the filler**

  ☞**Surface agents** (monofunctional) :
  -silanes;
  -alkylamines;
  -Al carboxylates;
  -titanate esters; ...

  ☞**Coupling agents*** (difunctional/radical grafting):
  -vinyl silanes;
  -aluminum methacrylates; ...

  ➡ Better filler dispersion… with at best some improvement of adhesion*

- **Filler "pre-encapsulation"**

  ☞ **Surface coating by a crosslinked resin layer** (*Ceraplast* technology)
  (as diffuse « ca.12nm » interface of intermediate elastic modulus)
  -coupling agent (ω-unsaturated amines)
  …rylates)
  -thermally activated initiators (peroxydes)

  ➡ Combination of stiffness/toughness - costly

- **Polymerization from the filler surface**

  POLYMERIZATION-FILLED COMPOSITES : **PFC's**

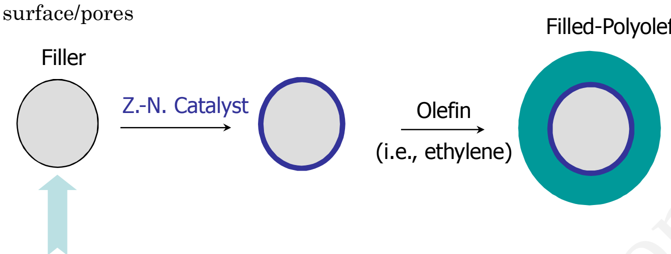
cuu duong than cong . com

CuuDuongThanCong.com https://fb.com/tailieudientucntt

Polymerization-Filling Technique

ENIKOLOPIAN N.S., USSR Pat. 763,379 (1976)
HOWARD E.G., US Pat. 4,104,243 and 4,097,447 (1978)

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



PFT on a wide range of fillers :

- acidic surface (kaolin, silica, glass beads,…)
- basic surface (magnesium hydroxide,…)
- organic fillers (graphite, carbon black,…)
- metallic fillers (nickel, zinc,…)

cuu duong than cong . com

Polymerization-Filling Technique

Mainly developed for ***Ziegler-Natta catalysts*** (transition metal complexes …)

Transition metal (M)

Physical adsorption → Sublimation, Impregnation or Deposition → Solid (M) phase on the filler surface

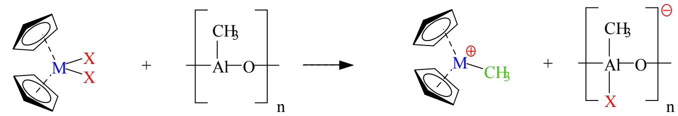
Chemical grafting → Support-OH + MR_n → Support-OMR_{n-1} + RH

Catalyst types :
- **Ti** : $TiCl_4/AlR_3$; $Ti(BH_4)_3$; $Ti(OR)_4/AlR_2Cl$
- **Zr** : $Zr(CH_2\text{-}C_6H_5)_4$; $Zr(BH_4)_4$
- **V** : VCl_4/AlR_3 ; $(VCl_3 + VO(OEt)_3)/AlEt_2Cl$
- **Cr** : $CrRCl_4$; $Cr(O_2CR)_3$
- **Hf** : $Hf(CH_2\text{-}C_6H_5)_4$; $Hf(BH_4)_4$

CuuDuongThanCong.com https://fb.com/tailieudientucntt

Metallocenes : Single Site Catalysts in Olefin Polymerization

☞ General structure – activation by methylaluminoxane MAO

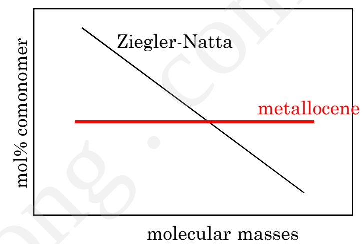


M = Ti, Zr, Hf
X = Cl, CH_3 ...

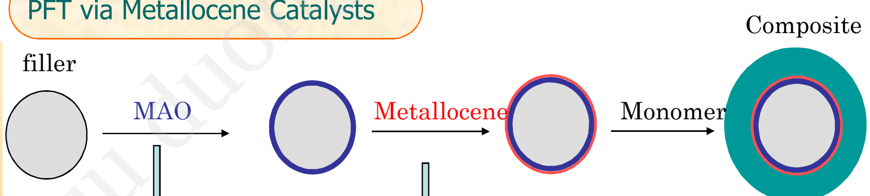
MAO for : - methylation
- cationization
- protic scavenger action

☞ Properties

-High catalyst activity
-Molecular weight control
(sensitivity to hydrogen)
-Copolymerization with α-olefins ➡
(thermoplastic to elastomer)



PFT via Metallocene Catalysts



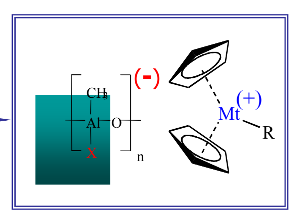
Deagglomeration of the filler

Fixation possible on basic, acidic, organic, metallic surfaces

Protection of ˙ve catalyst

Immobilization of the active species through ***electrostatic interactions***

Homogeneous dispersion of the filler



CuuDuongThanCong.com https://fb.com/tailieudientucntt

PFT with metallocene/MAO complexes : experimental procedure

- Filler treatment :

MAO fixation

* filler dispersion in heptane followed by contact with (TMA-depleted) MAO

* solvent evaporation and thermal treatment (150°C)

* (unreacted MAO washed out with toluene)

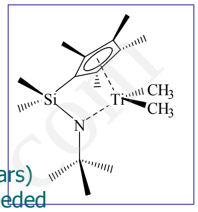
Metallocene activation

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

* transfer in the polymerization reactor and addition of ethylene (10 bars) and hydrogen when needed

* composite isolated by « precipitation » from acetone.

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



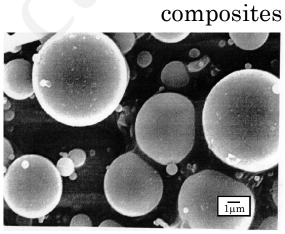
Polymerization from the filler surface

Advantages towards melt blending :

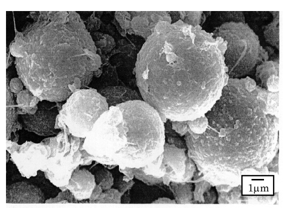
☞uniform distribution of the filler throughout the matrix

☞optimum polymer adsorption and wetting

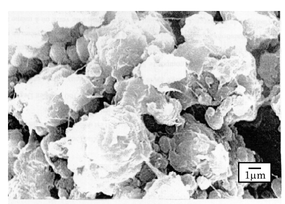
☞only process for the preparation of UHMWPE-based composites



uncovered glass beads



glass beads covered with 14.6 wt% PE



glass beads covered with 59.4 wt% PE

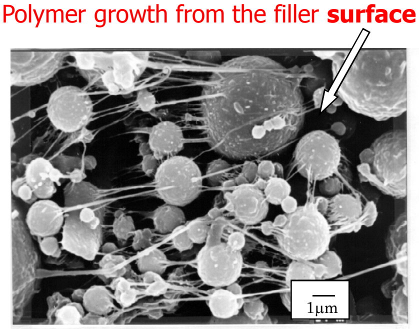
→ **Combination of HIGH STIFFNESS and HIGH IMPACT RESISTANCE**
(even at high filler content, > 60 wt%)

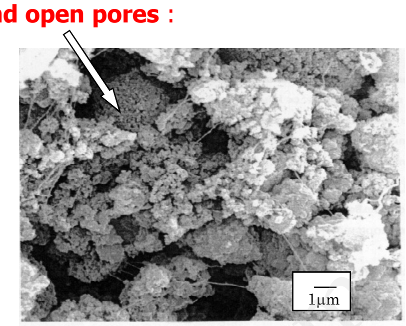
cuu duong than cong . com

CuuDuongThanCong.com https://fb.com/tailieudientucntt

Characteristic features of PFT via metallocene catalysis

- Polymer growth from the filler **surface and open pores** :





Glass beads coated by 7wt% of an ethylene-octene copolyHighly porous silica (160m²/g) with 38wt% of HDP

Filler and composite type		Content of filler (wt%)	Impact energy (kJ/m^2)
silica	melt blend	20	53.4
silica	PFC	22.4	576.4

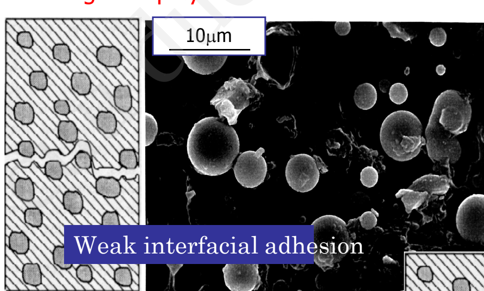
Improvement of impact properties

Silica specific area = $90m^2/g$

(Dubois, Jérôme et al., Chem. Mater., 13, 236 (2001))

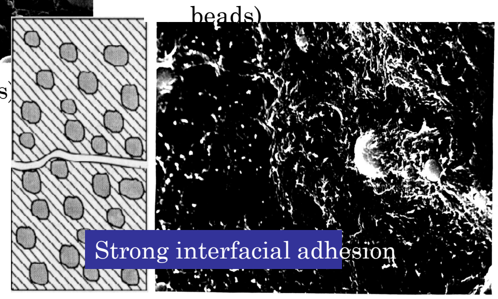
Characteristic features of PFT via metallocene catalysis

- Strong filler-polymer **adhesion** :



Melt blend (20wt% glass beads)

PFC(22wt% glass beads)



CuuDuongThanCong.com https://fb.com/tailieudientucntt

PFT via metallocene catalysis : some applications

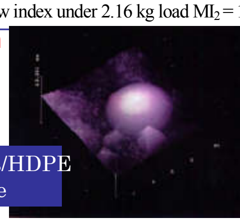
- Filler precoating : Dispersion of coated glass beads in HDPE

Precoating of glass beads by
either polyethylene (HDPE) or ethylene/1-octene copolymer (LLDPE)
and composites filled with 20 wt% glass beads

Composite: HDPE Matrix	Composite: Filler coating (wt %)	E (Gpa)	ε_r (%)	σ_r (MPa)	I.E. (kJ/m^2)
1[a)]	-	1.7	636	24.7	12.0
1[a)]	HDPE (14.5)	1.3	659	28.5	150.5
10[b)]	-	1.4	4.2	26.4	14.5
10[b)]	LLDPE (7.0)	1.5	6.9	28.9	41.0

a) Melt flow index under 2.16 kg load MI_2 = **1**g/10min.; b) MI_2 = **10**g/10min.

- AFM Phase detection



cuu duong than cong. com

Conclusions

PFC via metallocene-based catalysts

« Homogeneous » polyolefinic-based composites

Versatility of
- microsized fillers : - acidic (kaolin, silica, ...)
  - basic (magnesium hydroxide,...)
  - organic (graphite, cellulose,...)
  - metallic (nickel, iron,...)
- metallocene-based catalysts : Ti,Zr,(Hf),...

Allows for
- « control » over the molecular parameters
  - Mn (hydrogen as transfer agent)
  - composition (α-olefin copolymerization)
- high catalytic efficiency
- performant mechanical properties : stiffness and toughness (even at high filling)
  - filler deagglomeration
  - homogeneous filler dispersion (encapsulation)
  - enhanced interfacial adhesion

CuuDuongThanCong.com https://fb.com/tailieudientucntt

Chapter 2 :

Polymer nanocomposites filled with nanoparticles

Chapter 2 :

nanoparticles

Part I. Layered silicates as

cuu duong than cong . com

CuuDuongThanCong.com https://fb.com/tailieudientucntt

Layered Silicate Nanocomposites : Brief History

- 1950 First US Patent by Carter L.W. et al. (US 2,531,396) (assigned to National Lead Co.)
- 1976 Polyamide nanocomposites by S. Fujiwara S. et al. (Ja Appl. 109,998) (assigned to Unitika K.K.)
- 1993 Polyamide-6 organophilic clay nanocomposites by Okada A. et al. (Toyota Research) (Mater. Res. Soc. Proc., *171*, 45, 1993)

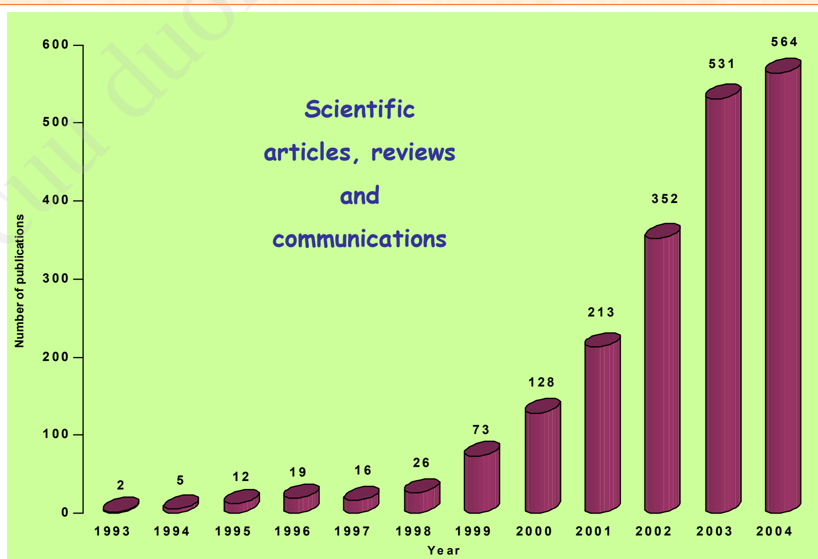
Claim : dramatic improvement of mechanical, barrier and thermal properties (at low clay content)

International academic and industrial research KICK OFF!!!

- Currently : huge interest for layered silicate nanocomposites based on thermoplastics, elastomers and thermosets…

cuu duong than cong . com

Polymer Layered Silicate Nanocomposites : Bibliographic Statistics



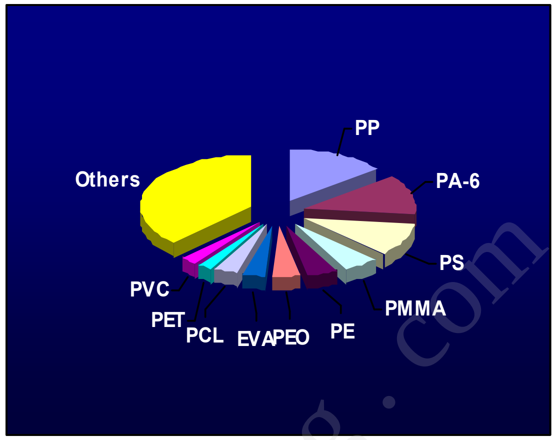
From CAS and Medline Databases – via Scifinder Scholar 2004 research tool

CuuDuongThanCong.com https://fb.com/tailieudientucntt

Polymer Layered Silicate Nanocomposites : the most cited matrices

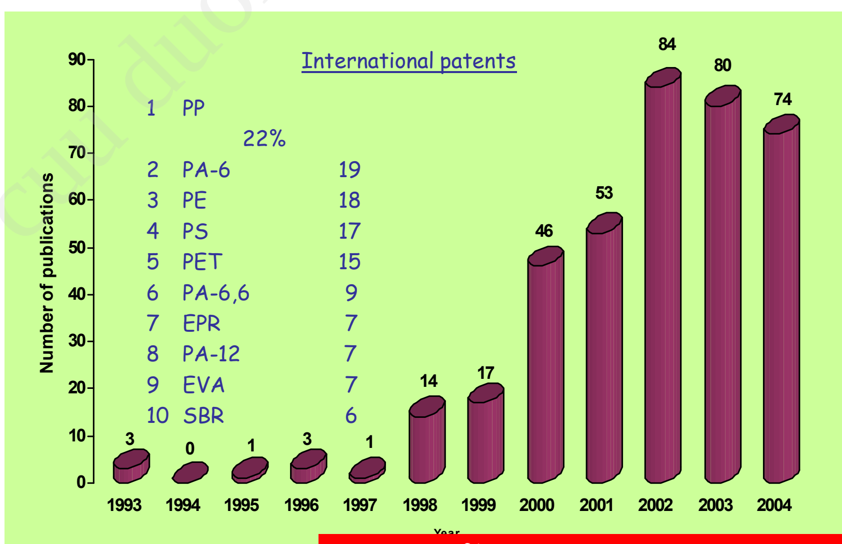
PP (13%)
PA-6 (12%)
PS (10%)
PMMA (5%)
PE (4%)
PEO (4%)
EVA (3%)
PCL (3%)
PET (2%)
PVC (2%)

Other polymers (42%)



NB : 1061 hits concern montmorillonite (~65%) !

Layered Silicate Nanocomposites : Bibliographic Statistics



NB : ~68% concern

From CAS Database – via Scifinder Scholar 2004 research tool

CuuDuongThanCong.com https://fb.com/tailieudientucntt

Nanocomposites : Definition and Generalities

Nanocomposite : heterophasic system where the dispersed phase (of a different nature than the continuous phase) has **at least one of its dimensions in the order of a few nanometers**

- Continuous phase : metal, ceramic, **polymer**,…
- Dispersed phase :

  3 nanodimensions : nanosized "isotropic" particles
  - metallic : Au, Pt, Ag, …
  - inorganic : CdS, SiO_2, ferrites,…
  - organic : carbon black,…

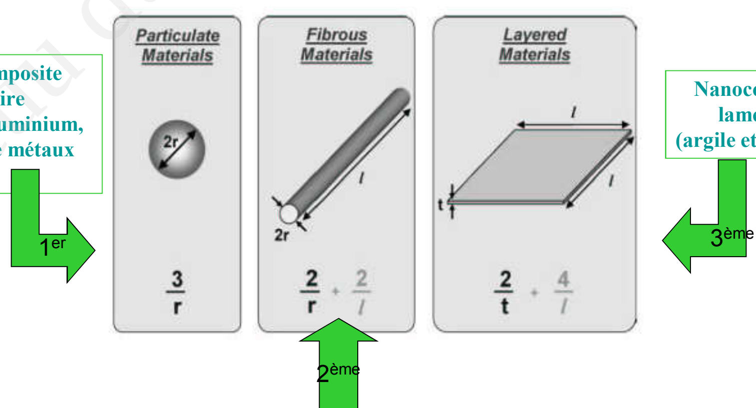
  } Nanopatterning, electromagnetic shielding, conductive materials,…

  2 nanodimensions : nanotubes and nanowhiskers
  - inorganic : palygorskite, sepiolite,…
  - organic : **carbon nanotubes**, cellulose and chitin nanowhiskers

  1 nanodimension : nanolayers
  - organic : exfoliated graphite, poly(muconic)acid crystals,…
  - inorganic : layered double hydroxides, **layered silicates or clays**,…

Classification :

Nanocomposite particulaire (SiO_2, Aluminium, Oxyde de métaux …)



Nanocomposite lamellaire (argile et graphite)

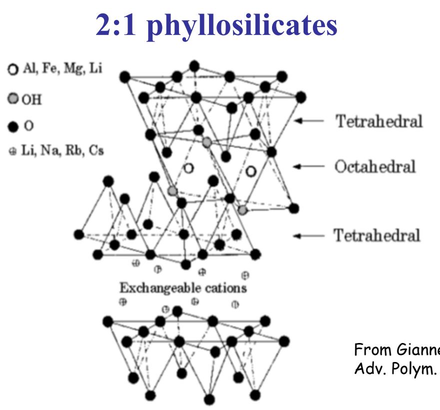
. Nanocomposite fibreux (nano fibre ou nano tube de carbone)

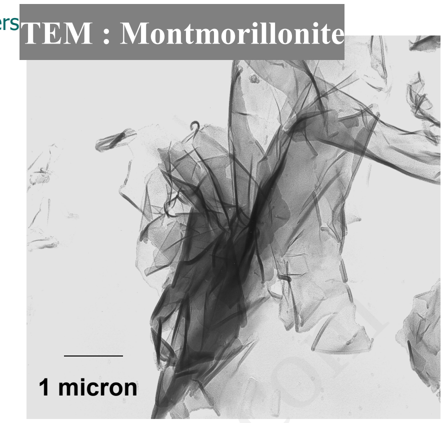
Erik T.Thostenson et al.; *Composite Sci. Technol. 65(2005)491-516.*

CuuDuongThanCong.com https://fb.com/tailieudientucntt

Polymer Layered Silicate Nanocomposites

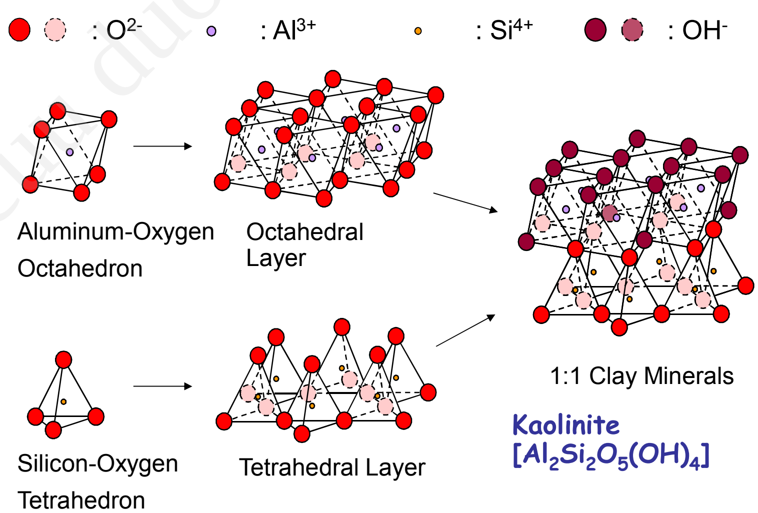
- "molecular" distribution of (alumino)silicate layers into a (polymer) matrix
- usually obtained starting from **smectite** clays (montmorillonite, saponite, hectorite,...)





From Giannelis et al., Adv. Polym. Sci. 118 (1999)

Building the Phyllosilicates

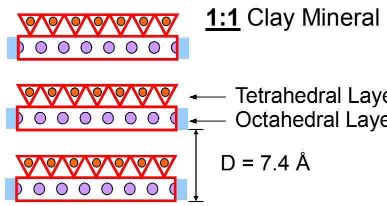


Kaolinite
[$Al_2Si_2O_5(OH)_4$]

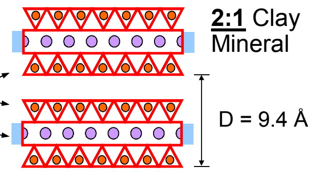
cuu duong than cong . com

CuuDuongThanCong.com https://fb.com/tailieudientucntt

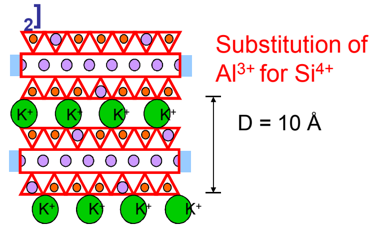
Kaolinite [$Al_2Si_2O_5(OH)_4$]



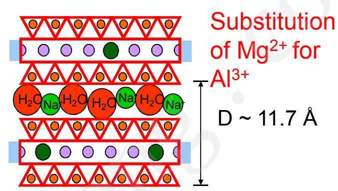
Pyrophyllite [$Al_2Si_4O_{10}(OH)_2$] *(ideal)*



Muscovite [$KAl_2Si_3AlO_{10}(OH)_2$]



Montmorillonite [$Na_xAl_{2-x}Mg_xSi_4O_{10}(OH)_2 . n H_2O$]



Crystal Systems

	Crystal systems	Axes system
	cubic	$a = b = c,\ \alpha = \beta = \gamma = 90^o$
	Tetragonal	$a = b \neq c,\ \alpha = \beta = \gamma = 90^o$
	Hexagonal	$a = b \neq c,\ \alpha = \beta = 90^o,\ \gamma = 120^o$
	Rhomboedric	$a = b = c,\ \alpha = \beta = \gamma \neq 90^o$
MMT →	Orthorhombic	$a \neq b \neq c,\ \alpha = \beta = \gamma = 90^o$
	Monoclinic	$a \neq b \neq c,\ \alpha = \gamma = 90^o,\ \beta \neq 90^o$
	Triclinic	$a \neq b \neq c,\ \alpha \neq \gamma \neq \beta^o$

cuu duong than cong. com

CuuDuongThanCong.com https://fb.com/tailieudientucntt

Montmorillonite : Origin and Resources

Tuffs / Volcanic ash

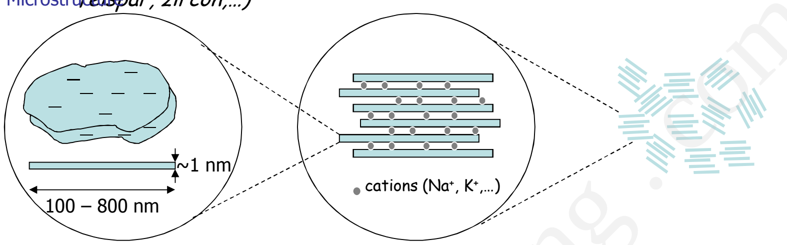
↓ Weathering

Bentonite *(numerous world-wide localities)*

↓ Purification *(- crystobalite, zeolite, quartz, biotite, felspar, zircon,...)*

Montmorillonite*

Microstructure



Lamella *(1 nm)*

primary particle *(8-10 nm)*

aggregate *(0.1-10µm)*

* $Na_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$

Montmorillonite : main characteristic features

- Surface area ~ 750 m²/g
- Density ~ 2.6

	Montmorillonite	(Fluoro) Mica	Synthetic Hectorite
Aspect ratio	~ 100-500	~ 200-600	~ 40-60
CEC [1]	~ 70 – 120 meq./100g	70-90 meq./100g	50-90 meq./100g
		(Talc/Na_2SiF_6)	
		$Na_{0.66}Mg_{2.68}(Si_{3.98}Al_{0.02})O_{10.02}F_{1.96}$	$Na_{0.46}(Mg_{5.42}Li_{0.46})Si_8O_{20}(OH)_4$

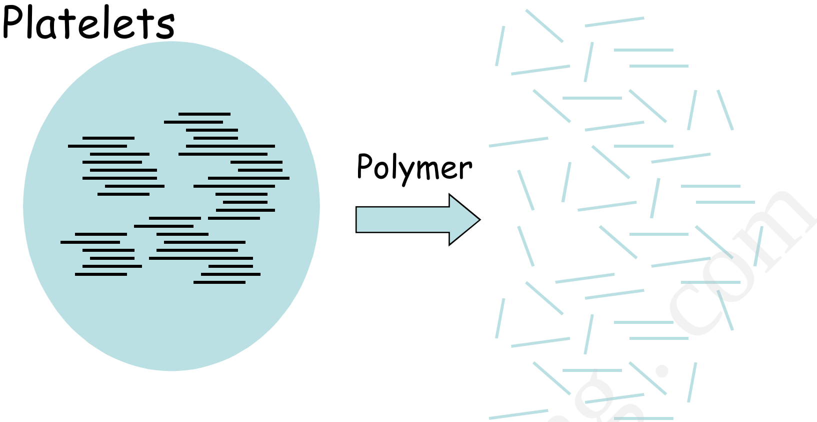
1) Cationic Exchange Capacity = maximum amount of cations, e.g. NH_4^+, that can be taken up per unit mass, in H_2O at pH 7 *(1meq/g is 96.5 Coulombs/g in SI units)*

CuuDuongThanCong.com https://fb.com/tailieudientucntt

The Processing Challenge

μm-size Particle Platelets

> thousands



☞ **Modification of CLAY, Why?**

Clay ♥ H_2O (hydrophilie)

Polymer ✕ H_2O (hydrophobie)

→ ??????

cuu duong than cong. com

CuuDuongThanCong.com https://fb.com/tailieudientucntt

MMT's modification methods :

- I/ Alkyl ammonium salts
  Alkyl phosphonium salts
  Alkyl sulfonium salts

2/ Polymers : PEO, PVA…

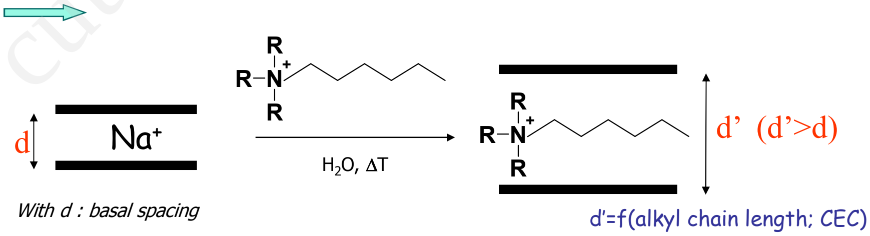
3/ Carboxylic Acids

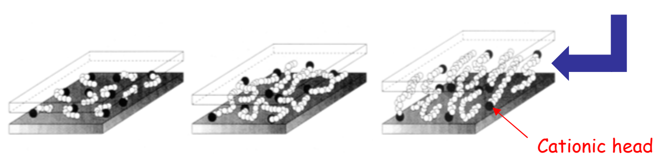
cuu duong than cong . com

Interlayer Organo-modification

- when using relatively **lipophilic** polymers, there is a need for rendering the interlayer less hydrophilic :

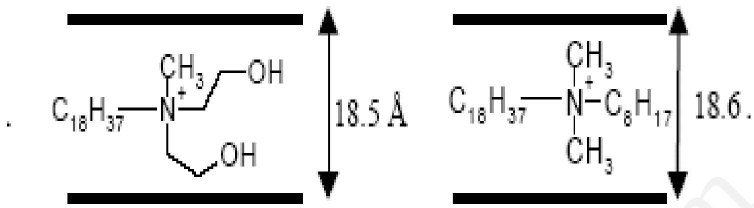
exchange of the inorganic cations with organic cations : *ammoniums bearing long alkyl chains*





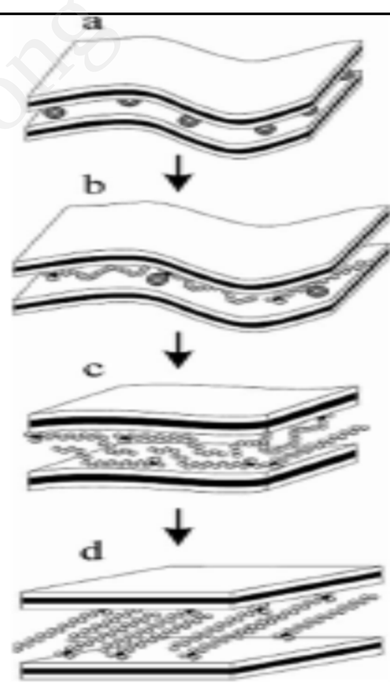
From Vaia et al., Chem. Mater. 6 (1994)

CuuDuongThanCong.com https://fb.com/tailieudientucntt



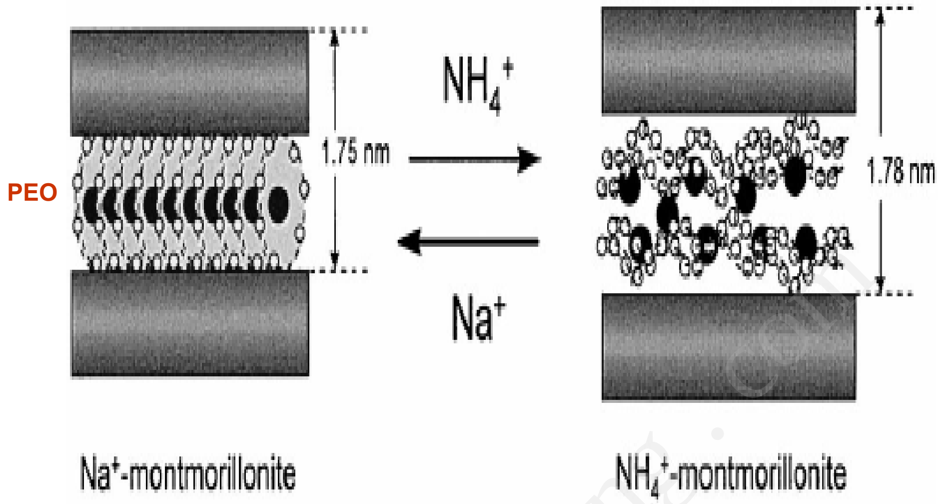
bis(2-hydroxyethyl)methyl hydrogenated tallow ammonium
MMT-$(OH)_2$

(2-ethylhexyl)dimethyl hydrogenated tallow ammoniu
MMT-Alk



CuuDuongThanCong.com https://fb.com/tailieudientucntt

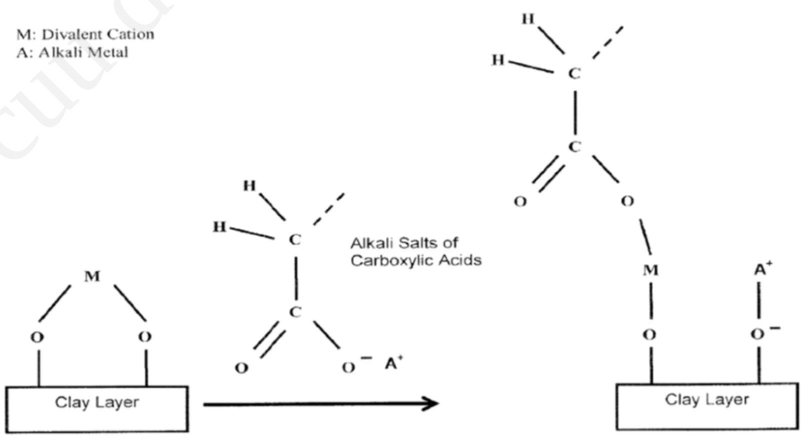
Modification of MMT by polymers



Process for preparing a nanocomposite rigid material ; *Ha Thuc Huy et al., US patent 2009 – No: US 20090209680A1*

Organic acid modified MMT

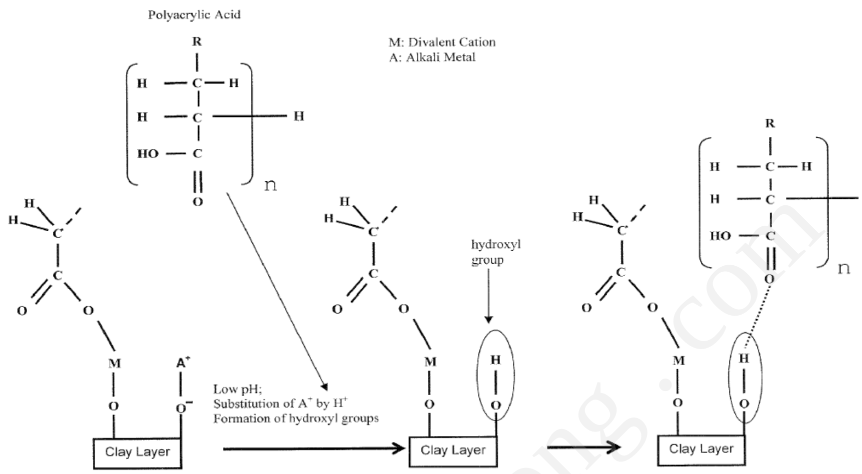
Step 1:



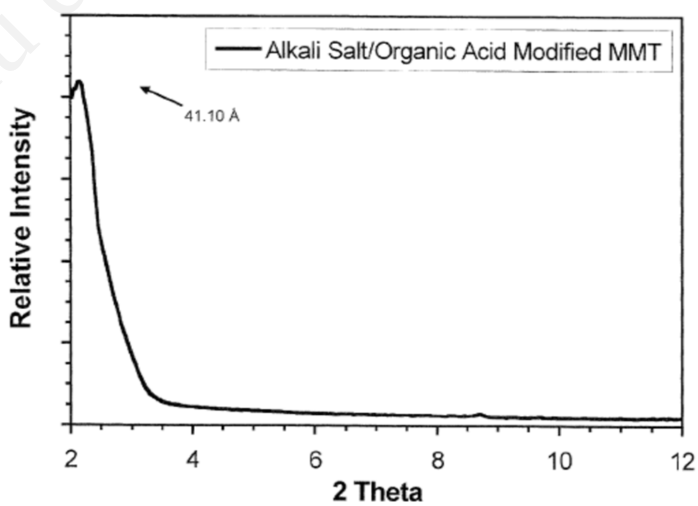
Kivanc Isik và Gokhan Andi *(US Patent 2008 - No : US 7,326,750 B1)*

CuuDuongThanCong.com https://fb.com/tailieudientucntt

Step 2 :



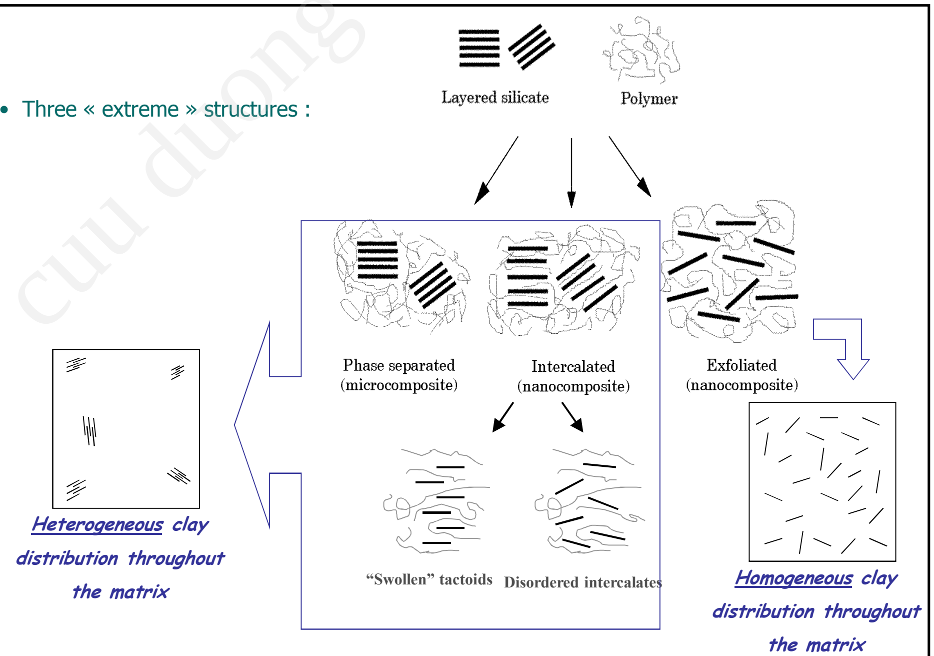
XRD diagramme of Organic acid modified MMT



CuuDuongThanCong.com https://fb.com/tailieudientucntt

Structures of NANOCOMPOSITES

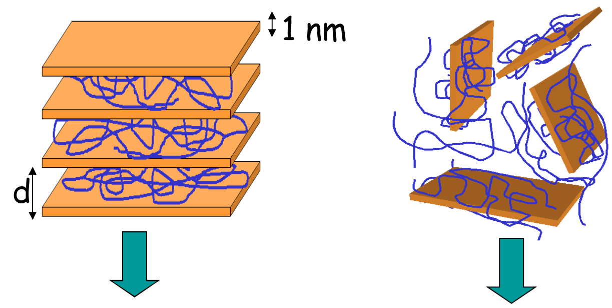
- Three « extreme » structures :



CuuDuongThanCong.com https://fb.com/tailieudientucntt

Characterization of Nanocomposite Morphology

- X-ray diffraction : XRD

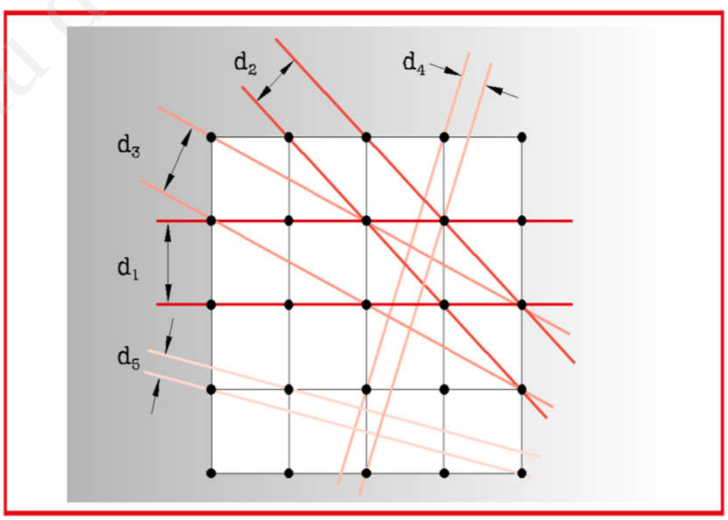


intercalated
increase of the basal spacing (d)

exfoliated
disappearance of the diffraction peak

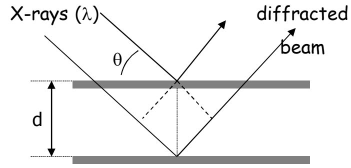
- Transmission Electron Microscopy : TEM

Reflection Planes in a Cubic Lattice



CuuDuongThanCong.com https://fb.com/tailieudientucntt

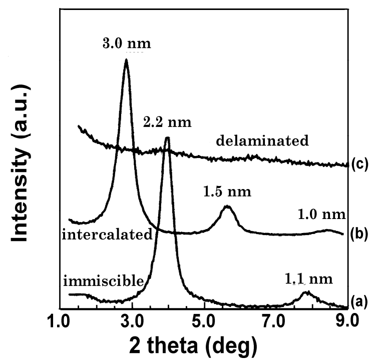
Layered Silicate Nanocomposites : Characterization by XRD



Via Braag law :

$n \, . \, \lambda = 2 \, . \, d \, . \, \sin \theta$

- e.g. :



Organo-modified hectorite in :

(c) Silicone rubber matrix → Exfoliation

(b) PS matrix → Intercalation

(a) HDPE matrix → Microcomposite

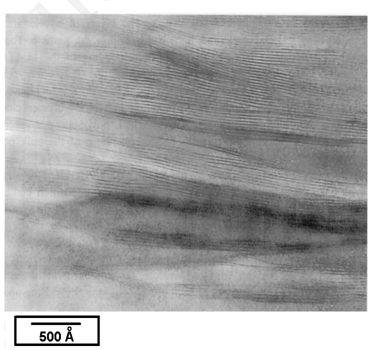
From Giannelis et al., Adv. Polym. Sci., 118 (1999)

Layered Silicate Nanocomposites : Characterization by TEM

- Recorded over (ultra-cryo)microtomed slides (50 to 80 nm thick) :

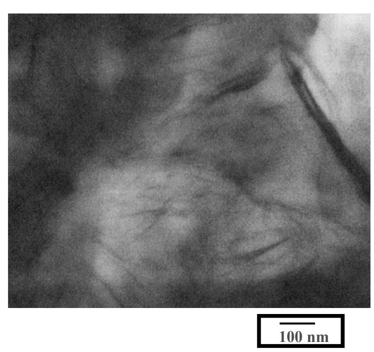
e.g., **PS-based nanocomposites** :

Intercalated



From Doh et al., Polym. Bull., 41 (1998) (1999)

Exfoliated



From Weimer et al., J. Amer. Chem. Soc., 121

cuu duong than cong . com

CuuDuongThanCong.com https://fb.com/tailieudientucntt

Polymer Layered Silicate Nanocomposites : General Properties

At low layered silicate content (as low as 3 to 5 wt%) :

- Improved material stiffness while maintaining good ultimate properties and impact strength
- Improved high temperature stability
- Enhanced/modified crystallinity (e.g., nylon-6)
- Improved gas barrier properties (e.g., to oxygen and water vapor permeability)
- Improved resistance against organic solvents
- Enhanced flame retardant behavior (lower heat release, no longer dripping, charring)
- Improved surface finish (gloss, smoothness)
- Good optical properties (transparency, haziness,…)
- Reduced linear thermal expansion
- Improved processability and rheology,…

From Alexandre and Dubois, Mater. Sci. Eng. R., 28 (2000)

Polymer Layered Silicate Nanocomposite Preparation

Three main techniques :

- *Exfoliation-adsorption in solution* : dispersion of the clay in a solutio of polymer, followed by solvent evaporation (or polymer precipitation)

-*Melt intercalation* : direct nanocomposite formation by clay intercalation by the preformed polymer chains in the molten state

- *In situ intercalative polymerization* : monomer intercalation within the clay galeries, followed by *in situ* (catalyzed) polymerization

CuuDuongThanCong.com https://fb.com/tailieudientucntt

I. Exfoliation-adsorption in solution

Organo-clay + Solvent → Swelling → (+ Polymer) Intercalation → Evaporation / Precipitation → Nanocomposites

- Water (widely used) — PVOH, PEO, PAA, poly(vinylpyrrolidone),...
- Organic solvents — HDPE (in xylene/benzonitrile)
  - PCL, PLA (in $CHCl_3$)
  - Nitrile copolymers (in DMF)...

Mainly intercalation (limited extent of delamination)

Exfoliation-adsorption in solution : nitrile copolymer-based nanocomposites

DMF (d = 1.65 nm) + Organo-MMT → Swelling → (+ Nitrile copolymer) Intercalation → Evaporation → Nanocomposites

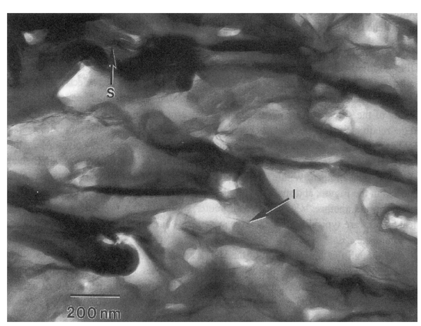
Vacuum at 80°C (24h) d = 2.15 nm

MMT (d = 1.18 nm) → Protonated dodecylamine → Organo-MMT

With 15 wt% MMT :

S = stacked silicates

I = individual layer



From Jeon et al., Polym. Bull., 41 (1998)

cuu duong than cong . com

CuuDuongThanCong.com https://fb.com/tailieudientucntt

II. Layered Silicate Nanocomposites by Melt Intercalation

Organo-clay + Polymer → Blending/shearing → Nanocomposites

Semi-crystalline Thermoplastics : Polyamides, PP, PE, PCL, PLA,…

Amorphous Thermoplastics : PS, PMMA,…

Rubber-like Matrices : EVA, SBS,…

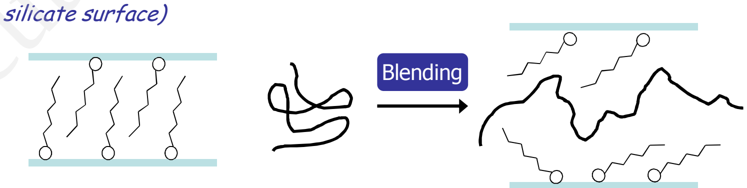
Elastomers : reactive PDMS, NBR (with a subsequent cross-linking step)

Outcome of molten polymer intercalation : interplay of entropic and enthalpic factors

From Alexandre and Dubois, Mater. Sci. Eng. R., 28 (2000)

Melt Intercalation : Driving Forces

Compensation of the ***loss of conformational entropy*** of polymer chains during intercalation by - ***gain of conformational entropy*** of ammonium alkyl chains and
- ***enthalpic interactions*** between the polymer and the organo-clay *(both apolar alkyl chains and polar silicate surface)*



- Key-parameters :
  - Polymer/organo-modifier compatibility (including external compatibilizers),
  - Layered silicate : CEC, aspect ratio, drying state,
  - Organic cations : length *(usually > C_{11})*, number and functionality of alkyl chains
  - But also… processing temperature and shearing, residence time vs. polymer MW.

From Vaia et al., Macromolecules, 30 (1997)

CuuDuongThanCong.com https://fb.com/tailieudientucntt

Melt Intercalation : effect of processing

- Degree of delamination and clay dispersion are dependent on :
  - Clay chemical treatment and polymer/organo-clay compatibility
  - Melt processing : shear extent, extruder and screw design, residence time, viscosity,…
- Four typical examples :

A) No compatibility : PP/Cloisite 15A

B) Tuned compatibility by external compatibilizer : PP/**MAGPP**/Cloisite 15A

C) Marginal inherent compatibility : Nylon-6/Cloisite 15A

D) High miscibility : Nylon-6/Cloisite 30B

Enhanced Polymer/Organo-clay Interaction

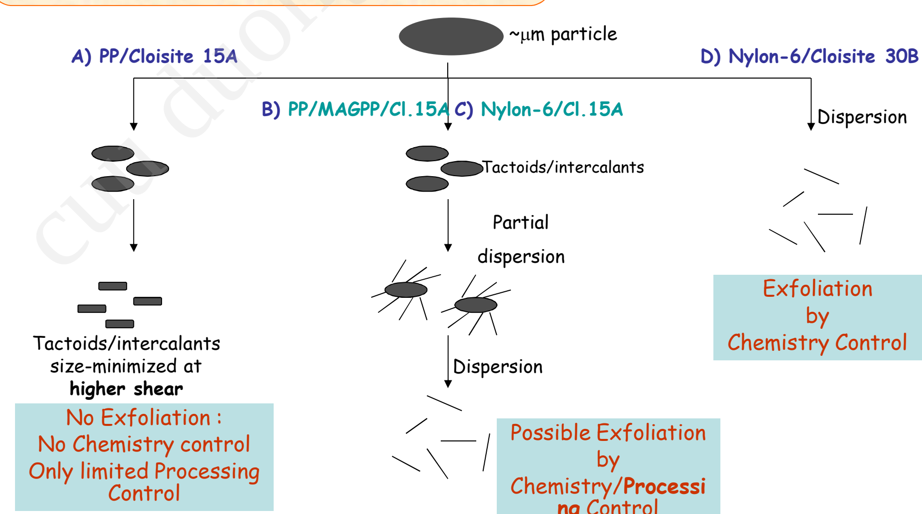
Effect of Processing Conditions on Nanostructure ?

- Cloisite 15A : MMT treated with $(C_{14\text{-}18}H_{29\text{-}37})_2N^+(CH_3)_2$
- Cloisite 30B : MMT treated with $(C_{14\text{-}18}H_{29\text{-}37})(CH_3)N^+(CH_2CH_2OH)_2$

From Paul et al., Polymer, 42 (2001)

cuu duong than cong . com

Melt Intercalation : effect of processing



A) No compatibility : PP/Cloisite 15A
B) Tuned compatibility by external compatibilizer : PP/**MAGPP**/Cloisite 15A
C) Marginal inherent compatibility : Nylon-6/Cloisite 15A
D) High miscibility : Nylon-6/Cloite 30B

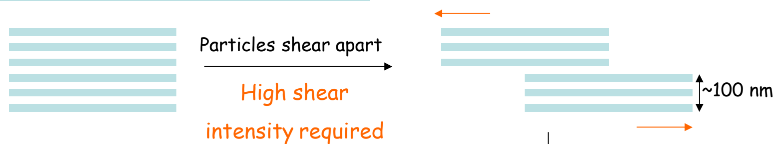
From Paul et al., Polymer, 42 (2001)

CuuDuongThanCong.com https://fb.com/tailieudientucntt

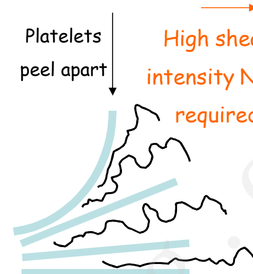
Melt Intercalation : effect of processing

- Cases B and C : Exfoliation by Chemistry/Processing Control : ***TWO STEPS***

1. Tactoids/intercalants formation



2. Platelets delamination



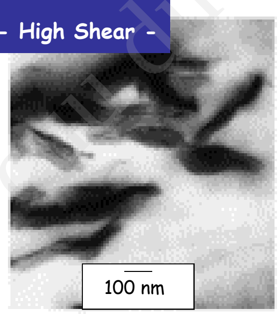
Via polymer chains diffusion into galleries
(facilitated by longer residence time)

B) Tuned compatibility by external compatibilizer : PP/MAGPP/Cloisite 15A
C) Marginal inherent compatibility : Nylon-6/Cloisite 15A

From Paul et al., Polymer, 42 (2001)

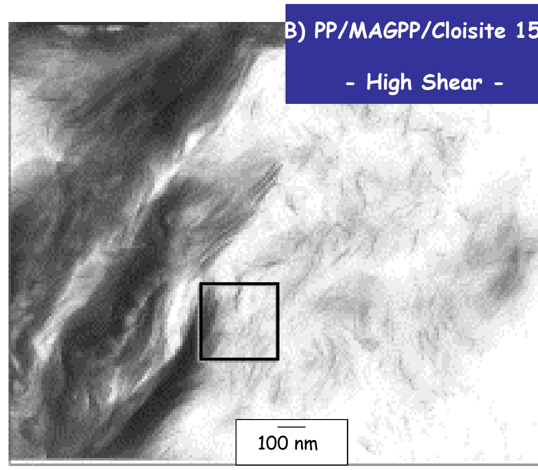
Melt Intercalation : effect of processing/chemistry

A) PP/Cloisite 15A – High Shear –



Particles Shear Apart

B) PP/MAGPP/Cloisite 15A – High Shear –



Platelets Peel Apart

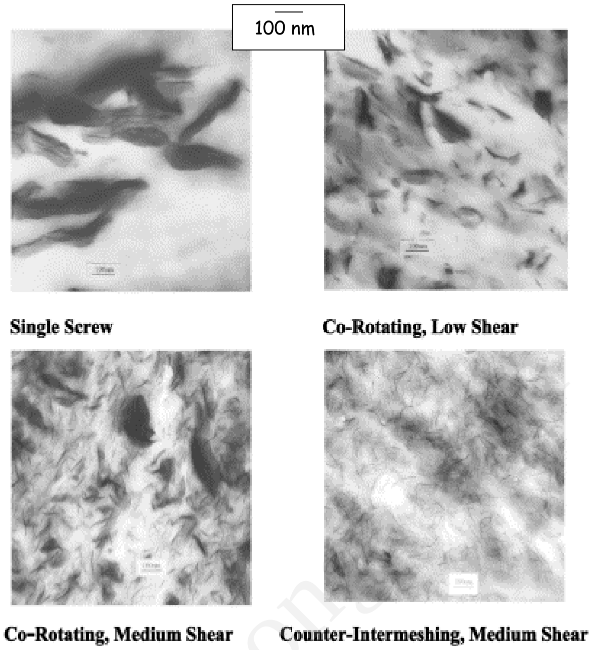
From Paul et al., Polymer, 42 (2001)

CuuDuongThanCong.com https://fb.com/tailieudientucntt

Effect of processing

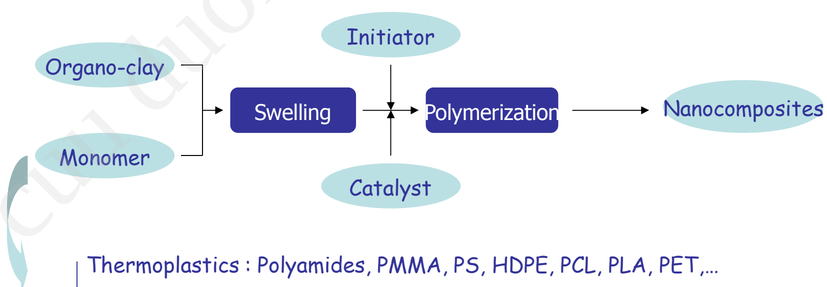
Type of extruder
and
screw configurations

C) Nylon-6/Cloisite 15A



From Paul et al., Polymer, 42 (2001)

III. Layered Silicate Nanocomposites by *In Situ* Polymerization



Thermoplastics : Polyamides, PMMA, PS, HDPE, PCL, PLA, PET,…

Thermosets : Epoxy (DGEBA/aromatic diamine-based), unsaturated polyesters, …

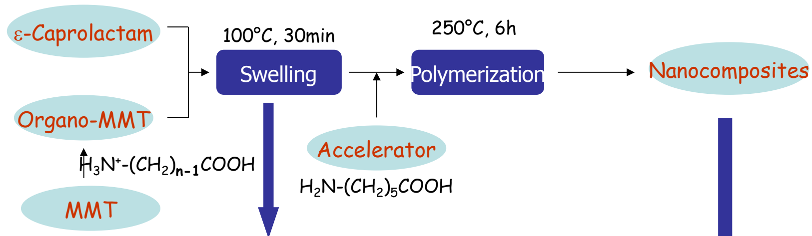
Driving forces :
1) Monomer attraction by the high surface energy of organo-clays
2) Monomer diffusion up to a swollen equilibrium is reached
3) Catalyzed/initiated intercalative polymerization, shifting the equilibrium
4) More monomer driven in the galleries → eventually, clay delamination possible

From Alexandre and Dubois, Mater. Sci. Eng. R., 28 (2000)

cuu duong than cong

CuuDuongThanCong.com https://fb.com/tailieudientucntt

In Situ Polymerization : Pioneer Works by Toyota Research Team



^+H_3N-$(CH_2)_{n-1}$-COOH n	d-spacing of modified clay (Å)	d-spacing when swollen by ε-CLa (Å)
2	12.7	14.4
3	13.1	19.7
4	13.2	19.9
5	13.2	20.4
6	13.2	23.4
8	13.4	26.4
11	17.4	35.7
12	17.2	38.7
18	28.2	71.2

Exfoliation (MMT<15wt%)

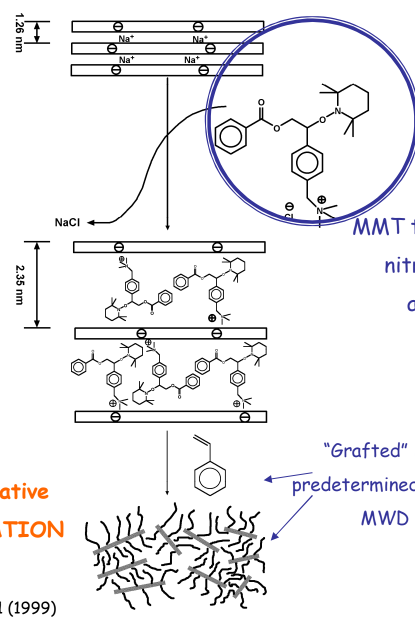
Intercalation (MMT>15wt%)

From Usuki et al., J. Mater. Res., 8 (1993)

cuu duong than cong . com

In Situ Polymerization

Controlled/"living"
intercalative
polymerization of
Styrene
(in bulk, 125°C)



MMT treatment with
nitroxyl-based
ammonium

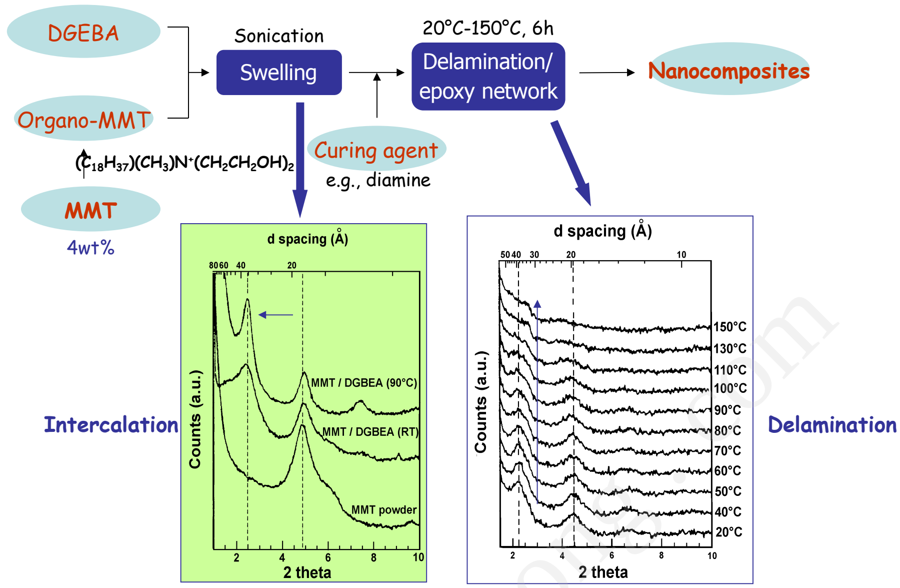
"Grafted" PS chains of
predetermined Mn and narrow
MWD (δ ~ 1.3)

Quantitative
EXFOLIATION

From Weimer et al., J. Amer. Chem. Soc., 121 (1999)

CuuDuongThanCong.com https://fb.com/tailieudientucntt

In Situ Polymerization : Thermoset (epoxy) Nanocomposites



From Messersmith et al., Chem. Mater., 6 (1994)

cuu duong than cong . com

Chapter 2, Part 1 : Intermediate Conclusions

Illustrated by Effective Industrial Applications :

- PE/EVA/organo-clay/$Al(OH)_3$: electrical cables — CableWerk Eupen (B)
- PET/PA/organo-clay : beer and juice bottles — Eastman-Nanocor (US)
- PA-6(-6,6)/organo-clay : fuel tank, engine cover — RTP, UBE (D)
- PA-6/organo-clay : « masterbatch » compounds — Aegis NC, Honeywell (US)
- PA-6/organo-clay : engine cover — Toyota (J)
  food packaging films — Bayer (D)
- PP/EPR/organo-clay : car part (step) — Montell-General Motors (US)

Promising future fo Selection of to relevant examples.

CuuDuongThanCong.com https://fb.com/tailieudientucntt

Applications of Nanocomposites in General Motors Vehicles

HUMMER H2 SU

Nanocomposite TPOs summary of tangible benefits

Mass savings of 3 to 21%
(Specific Gravity of 0.92 vs. 0.96-1.13 g/cm^3)
Improved Appearance, Colorability & Paintability
Improved Scratch/Mar Performance
Large Processing Window
Reduced Paint Delamination
Retains Low Temperature Ductility
Improved Recyclability
Lower Flammability

M-Van Step Assist: 1st Commercial Launch

Impala: 2nd Nanocomposite Application

From **Mark Verbrugge**, Materials Research Laboratories, General Motors (2004)

cuu duong than cong . com

CuuDuongThanCong.com https://fb.com/tailieudientucntt