GDR LIPS #3585
Groupement De Recherches Liquides Ioniques et PolymèreS

ICC2 International nano Composites Conference
March 14-15, 2018 • Bilbao (Spain)
2018 ImagineNano
NEW CONFERENCE

Ionic Liquids: versatility and potential as interfacial agents for designing physicochemical interactions and tailoring morphology and properties of nanofilled polymers

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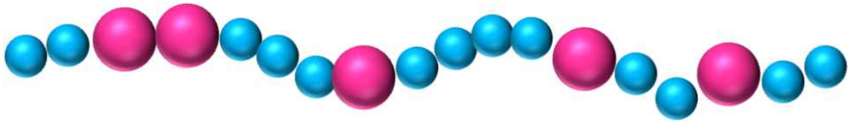
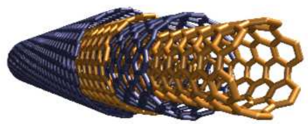
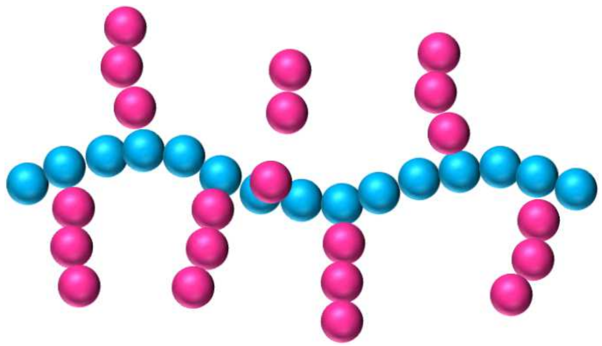
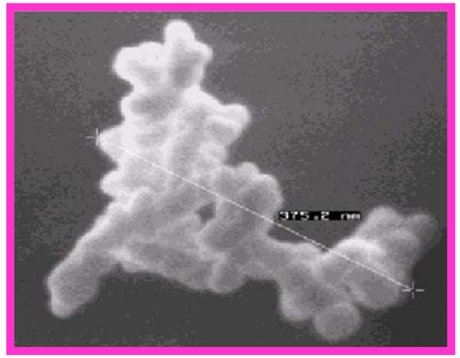
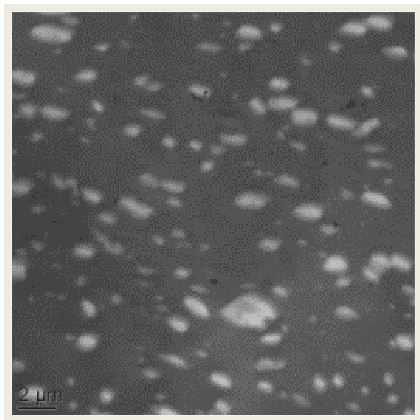
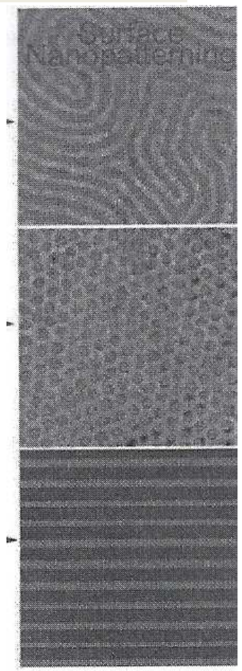
Université de Lyon · CNRS · Université Jean Monnet Saint-Étienne · INSA · UCBL · IMP Ingénierie des Matériaux Polymères

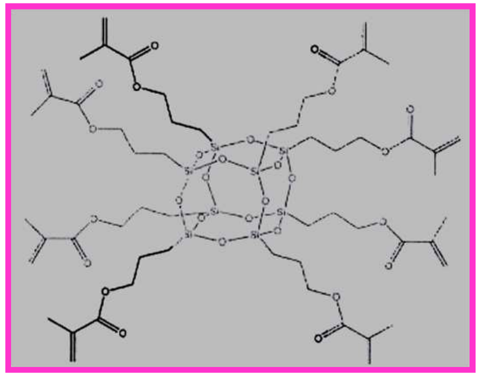
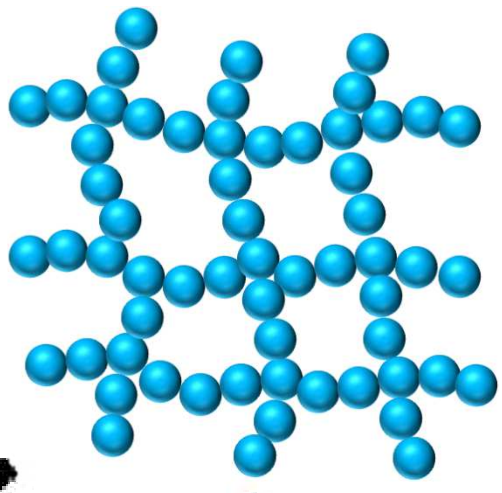
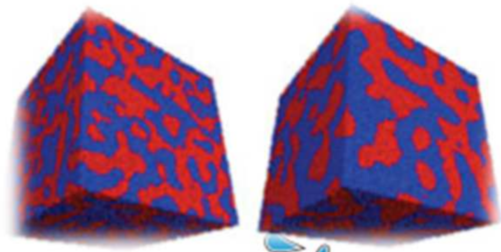
Introduction



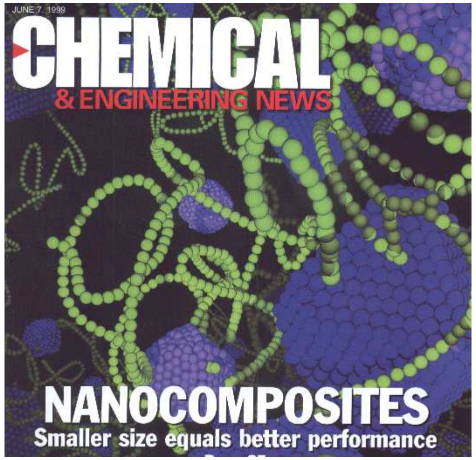






CONTENTS

Introduction – Nano Effect



Nanomaterials – Nanocomposites
What are fundamental mechanisms?

Introduction of organic or inorganic nanofillers in polymers

↓

Synergy due to the nanometric objects (particles, platelets,whiskers,…):

- Size of nano-objects compared to dimensions of polymer chains

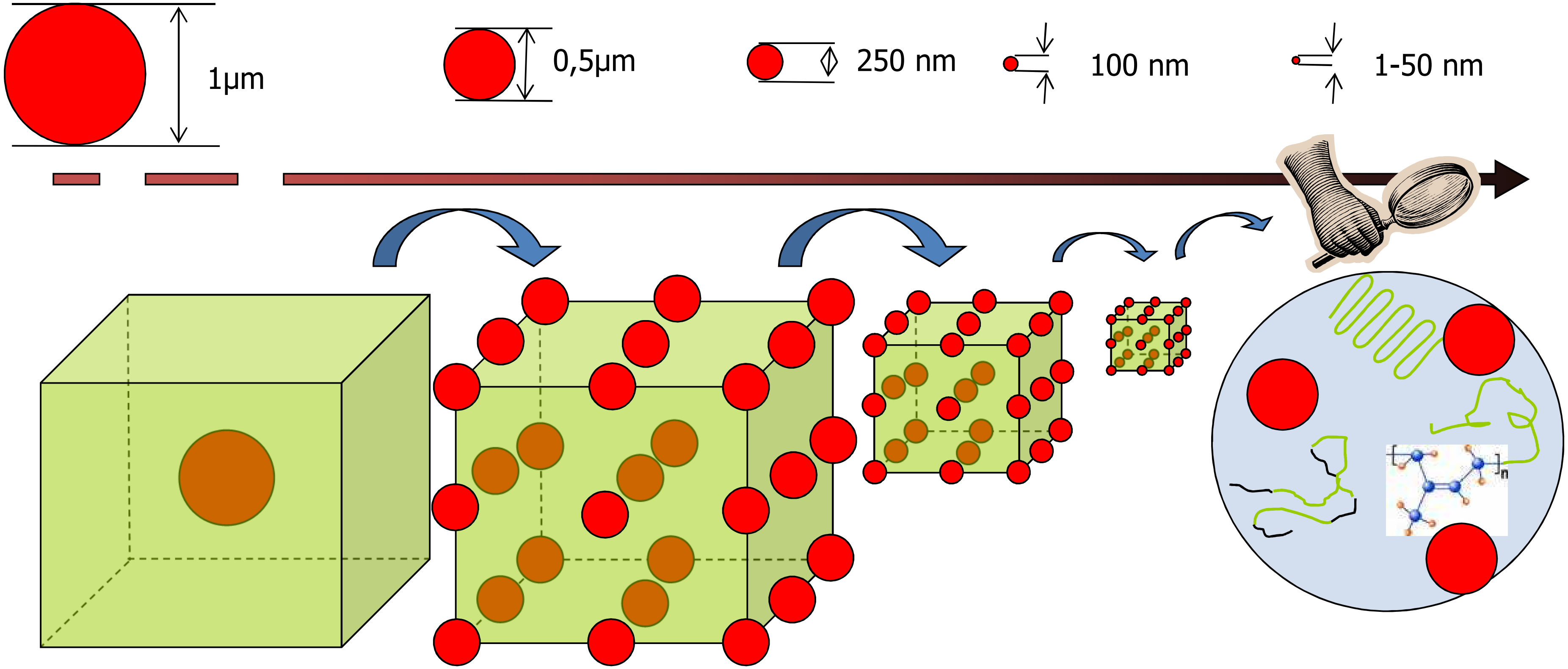
- High contact surface/ interfacial areas ('All is interface !')

Changes in polymer chain dynamics from interfacial interactions
That must be controlled by the surface treatment (chemistry of interface)

- Spatial Structuration of nano-objects

Introduction – Nano Effect

• Size of nanofillers compared to polymer chain dimensions



Large surface-to-volume ratio

→ sensitivity increased in respect to molecular parameters of matrix

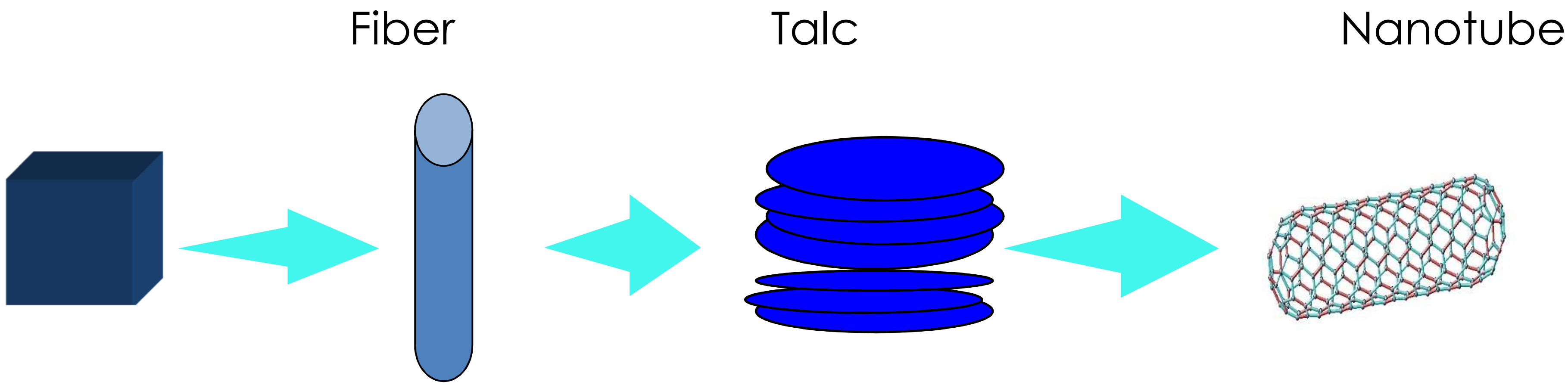
Decrease of particle-particle distance

→increasing of inter-particles interactions

Introduction – Nano Effect

- High contact surface / interfacial areas

Unexpected behaviours from increase of the interfacial areas

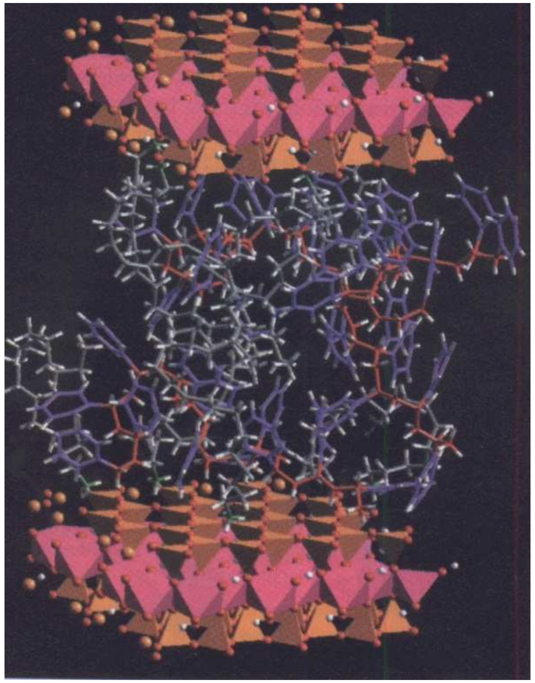


	Fiber	Talc	Nanotube
Size	10 µm	1 µm	10 nm
Vol. ratio :	30 %	30 %	3 %
Particles number	~ 10^6	~ 10^{10}	~ 10^{15}
Interface:	~ 0,1 m^2	~ 1 m^2	~ 100 m^2
Aspect ratio :	~ 20	~ 100	> 1000

Introduction –Nano Effect

- High contact surface / interfacial areas

Creation of a high quantity of interfacial areas
between polymer and inorganic surface of nanofillers



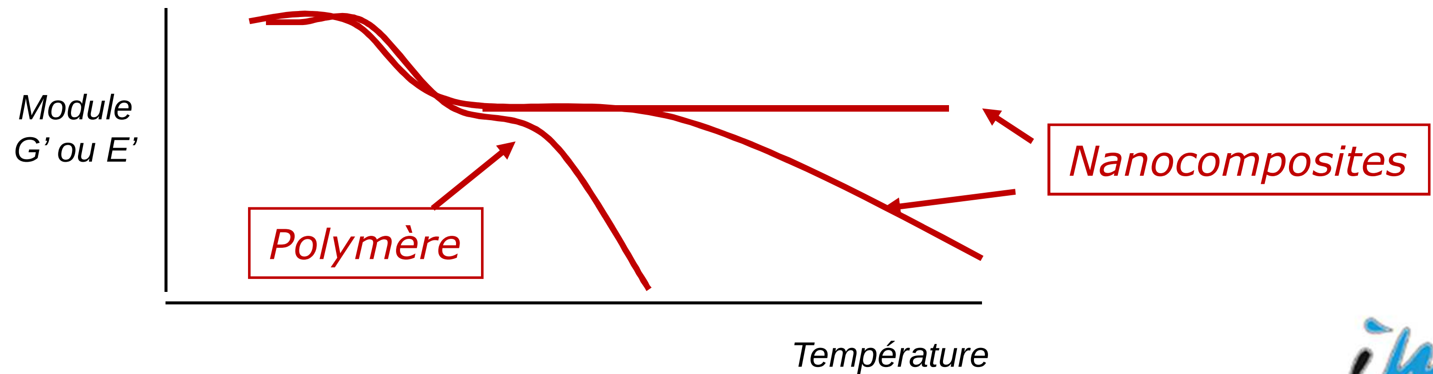
E. Giannelis (2000)

- *Modification of molecular mobility* (relaxation time)

Glass transition temperature, Tg
'Bound polymer'

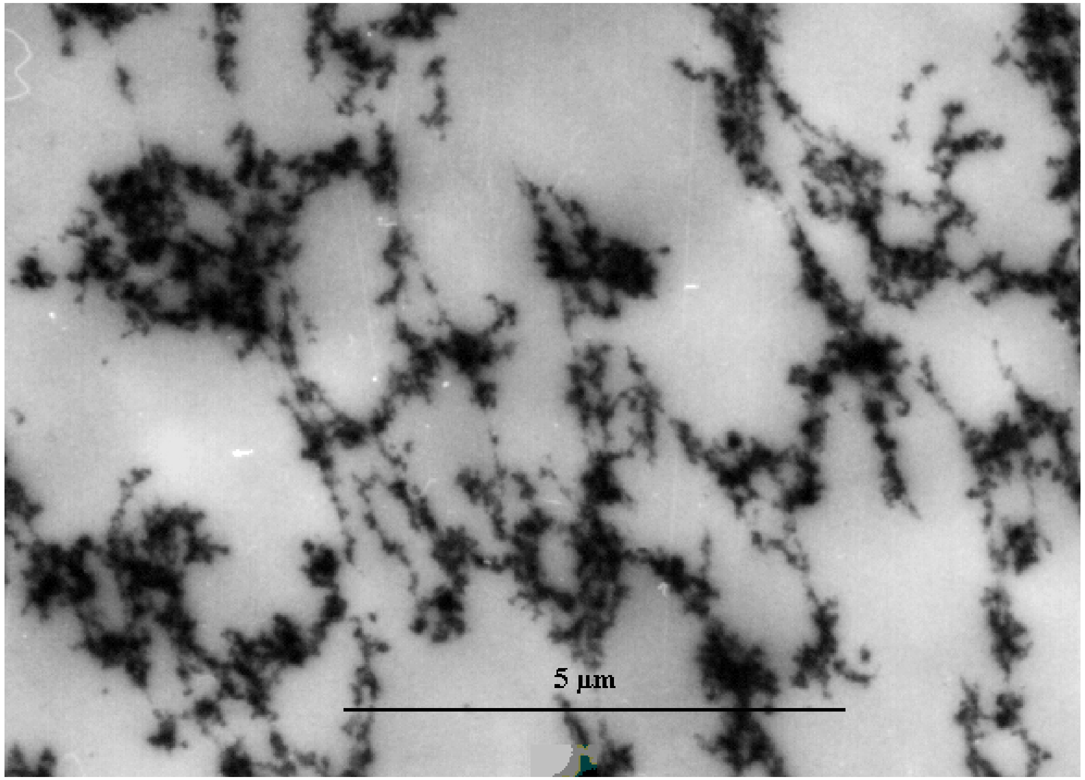
strong or weak interactions at interface

➔ Range of mechanical strength *résistance in temperature (HDT)*
➔ *TMS behaviour at high temperature*
flowing area beyong glass transition
(rubbery flow, liquid flow)



Introduction – Nano effect

• Spatial structuration of nano-objects



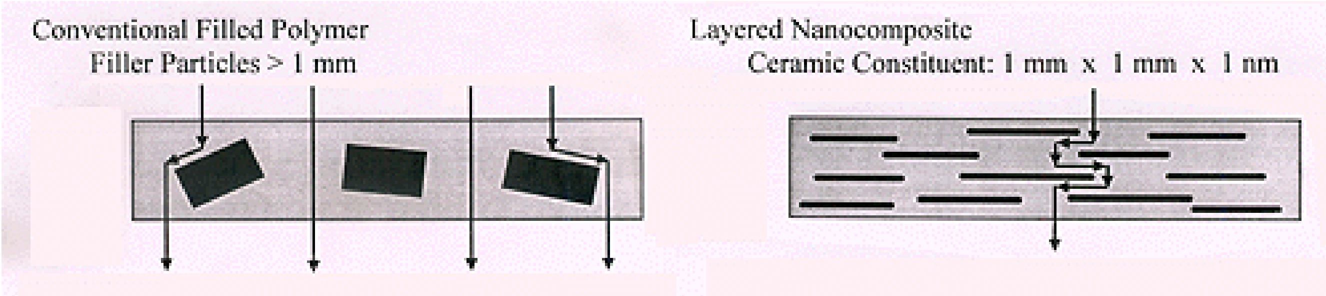
* Possibility of nanofillers network formation
interactions particule/particule (percolating network)

* Occlusive volume – apparent volume ratio higher than real introduced ratio

Introduction – Nano effect

- Spatial structuration of nano-objects

Structuration/assembling of 3D nanofillers



Tortuosity of medium in order to deviate nanofillers

➔Propagation of a crack

Surface Creation ⇨ K_{IC}, G_{IC}: Fracture Energy

Mechanical Properties

➔Diffusion of small organic molecules (gaz, solvents)

Permeability / membranes

➔Diffusion of electrical charges

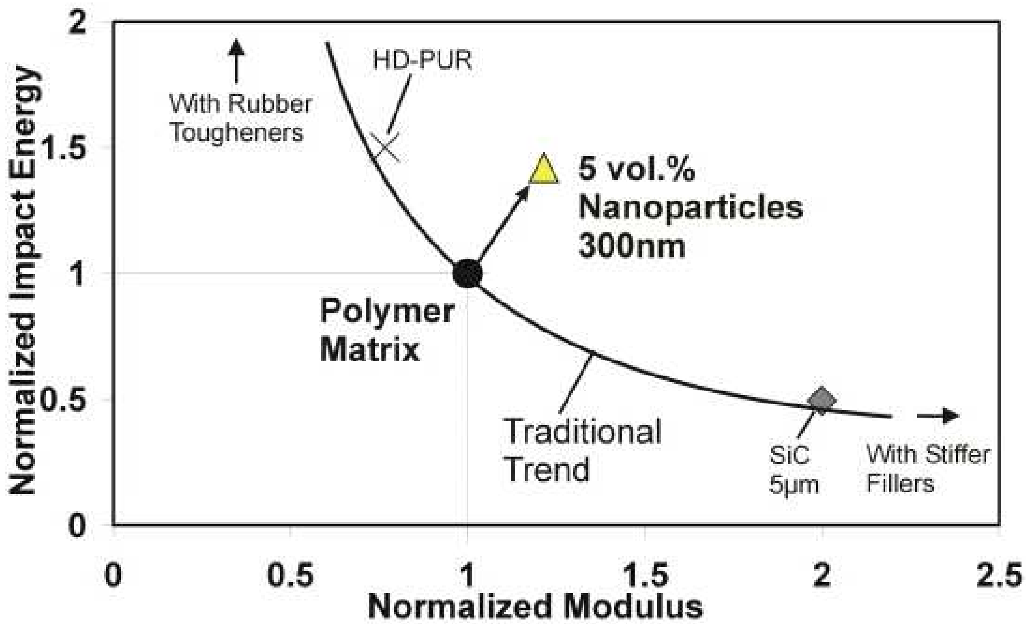
Conductivity / dielectrical properties

Introduction – Nano effect

- Spatial structuration of nano-objects

Compromise between paradoxical properties?
Example / mechanical properties
Compromise'Toughness-Stiffness' – An answer ?

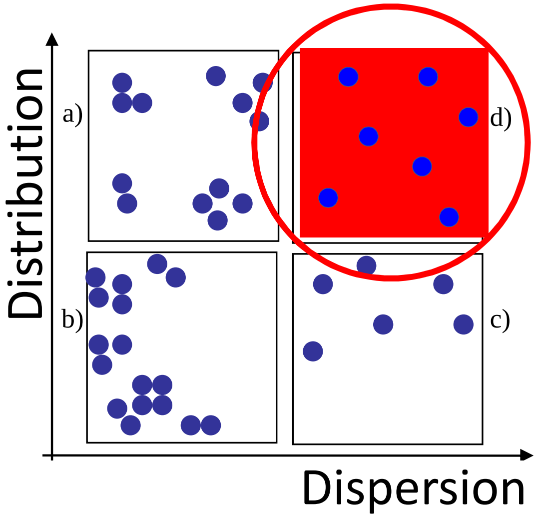
Exemple: Nanocomposites vs. Microcomposites



Michler (2002)

Polyurethane matrix

Introduction – IL : New Interfacial agents

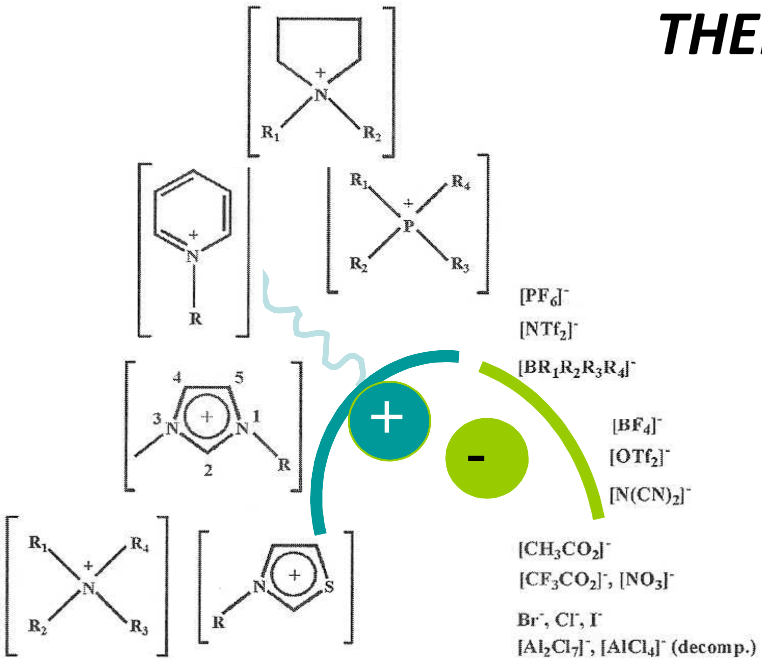


If dispersion is succeeded,
1 hectare of interface can be generated !

Tailoring of physicochemistry interactions at interfaces required

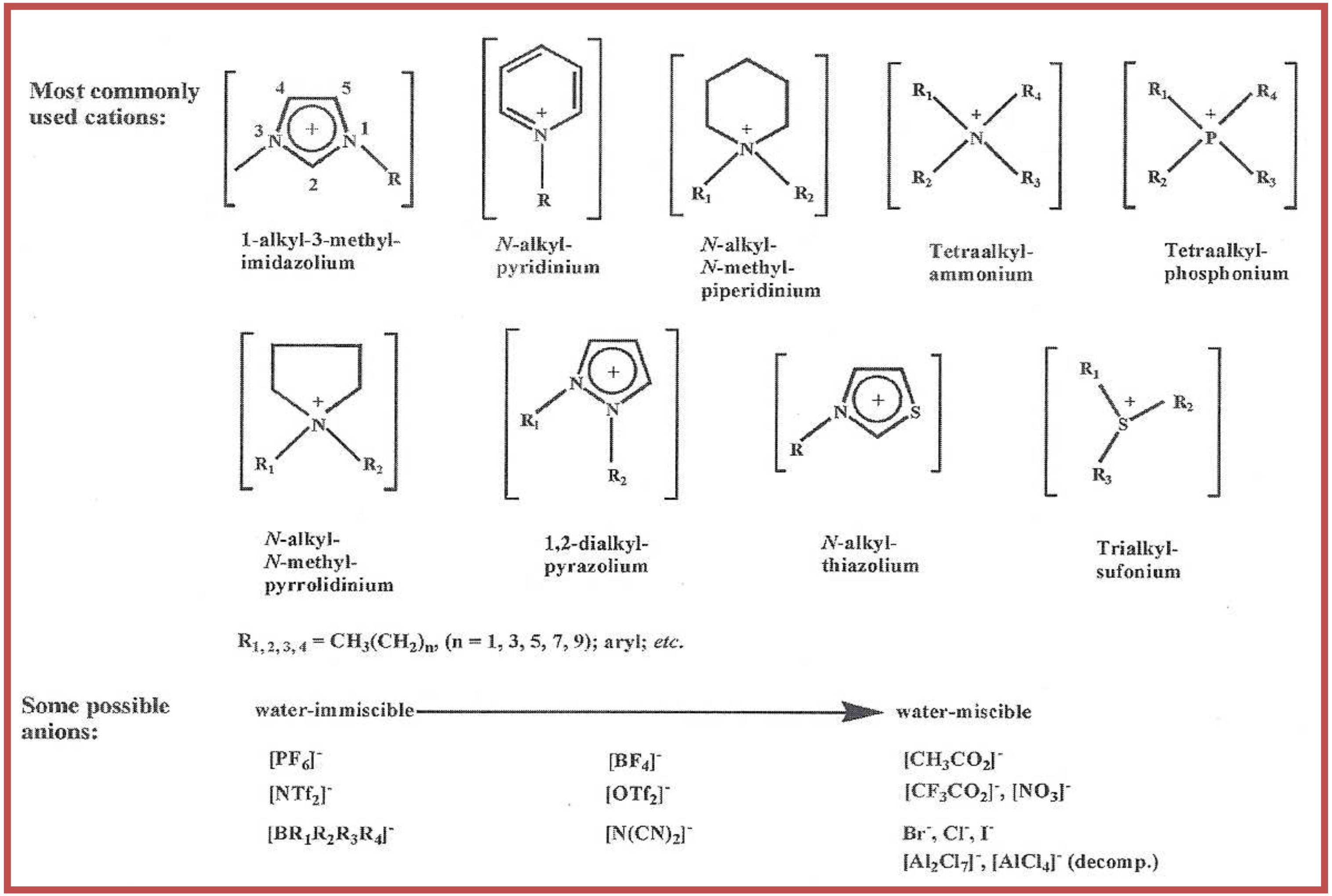
THERMOSTABLE IONIC LIQUIDS : NEW ALTERNATIVE

Organic Salts with $T_m < 100°C$



- Low vapor pressure
- Not explosive
- Great chemical stability
- Great thermal stability (up to 300°C)
- High ionic conductivity
- Large electrochemical range
- Liquid state on a large temperature range

Introduction – IL : New Interfacial agents

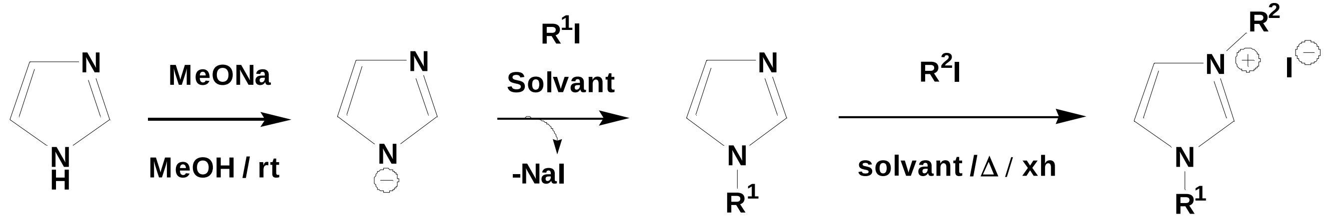


Adv. Mater. 2010, 22, 261-285

Combinaison Cation/Anion   Relevant synthesis   Specific Properties of ILs

Introduction – IL : New Interfacial agents

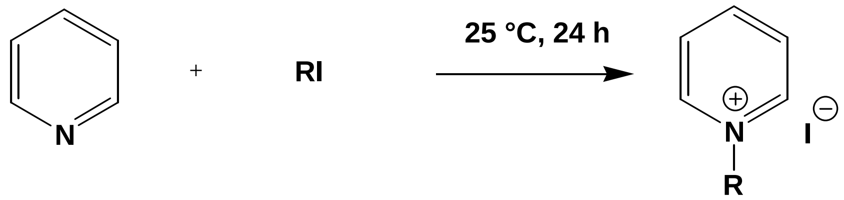
•Synthesis of N-octadecyl-N'-octadecylimidazolium iodide



$R^1 = CH_3\,(CH_2)_{17}$ $R^2 = CH_3\,(CH_2)_{17}$

$C_{18}C_{18}Im$

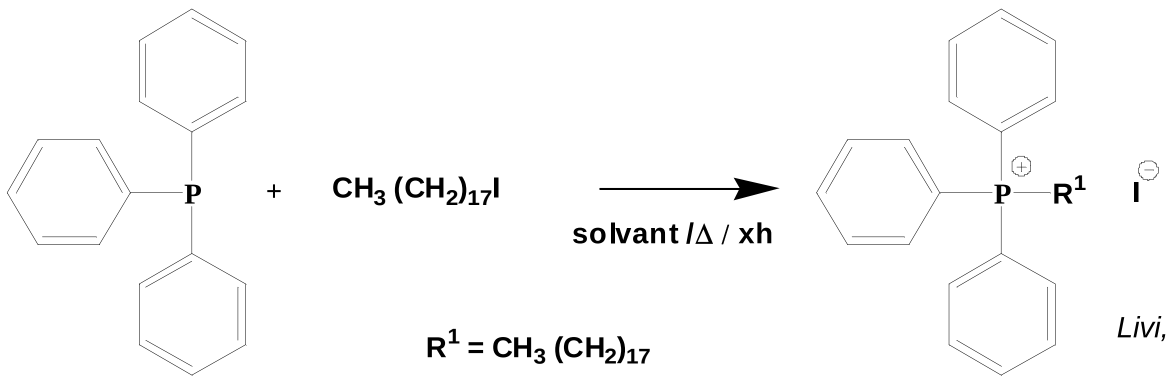
•Synthesis of octadecylpyridinium iodide



R = alkyl chain

$C_{18}Py$

•Synthesis of triphenyloctadecylphosphonium iodide



$C_{18}P$

Cation Chemical Nature

Livi, Gérard, Duchet. Chemical Communications, 47 3589 (2011).

Many cation/anion combinations make Ils tunable for specific applications

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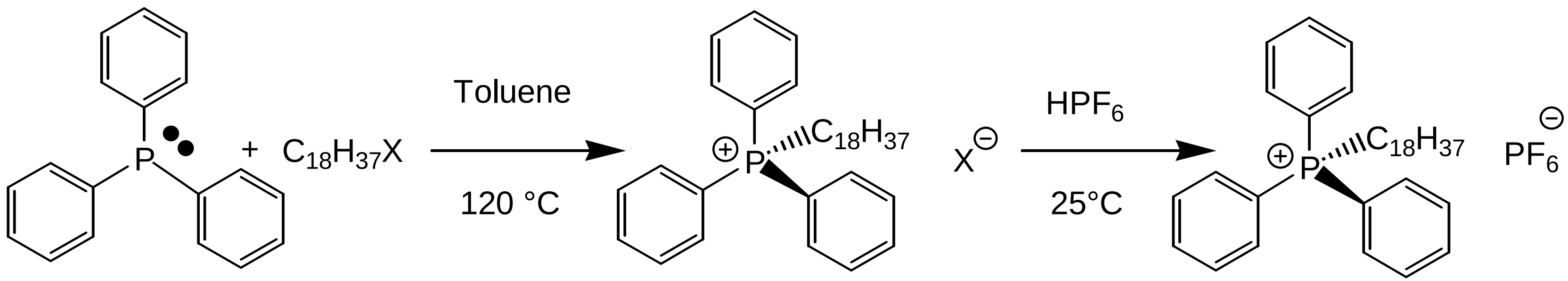
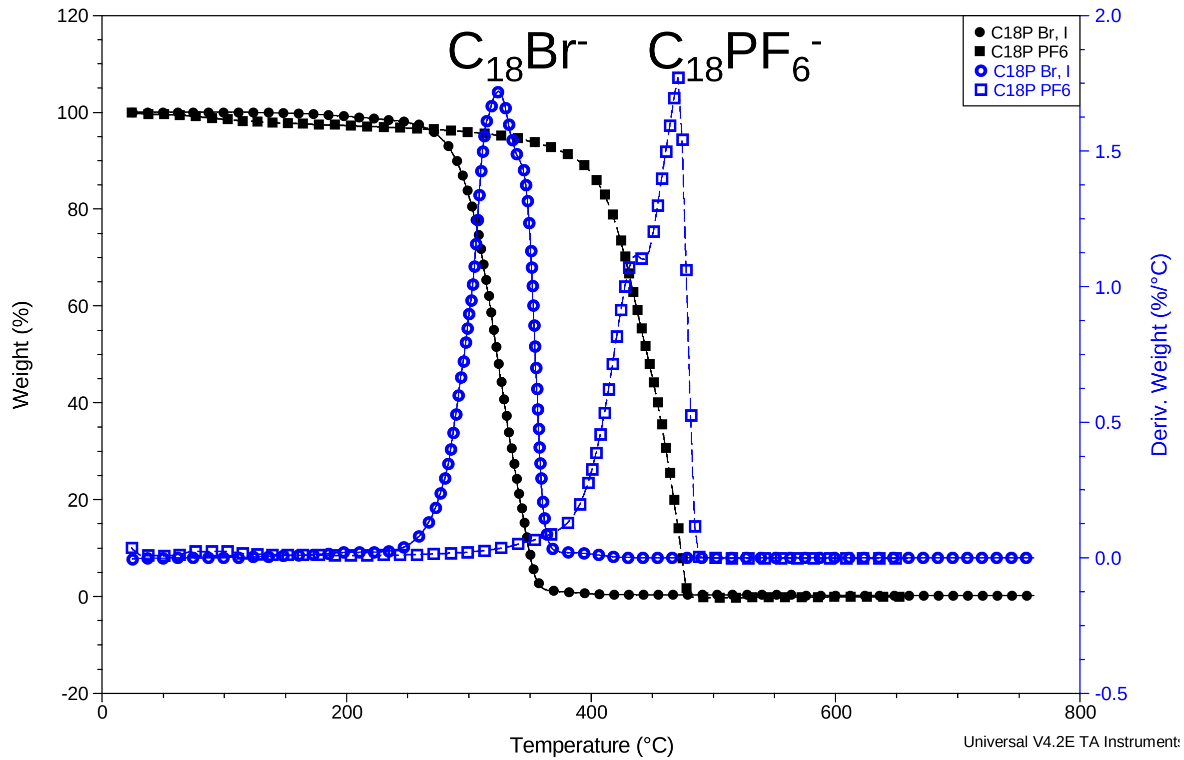
Introduction – IL : New Interfacial agents



X = I⁻ , Br⁻ → $X^- = PF_6^-$

Anion Chemical Nature



Fluoride Anion improves the thermal stability of phosphonium Ionic Liquid

+ 140°C between Br^- or I^- and PF_6^-

Livi, Duchet, Gérard. J.Coll. Interf. Sci. 354, 556-562 (2011).

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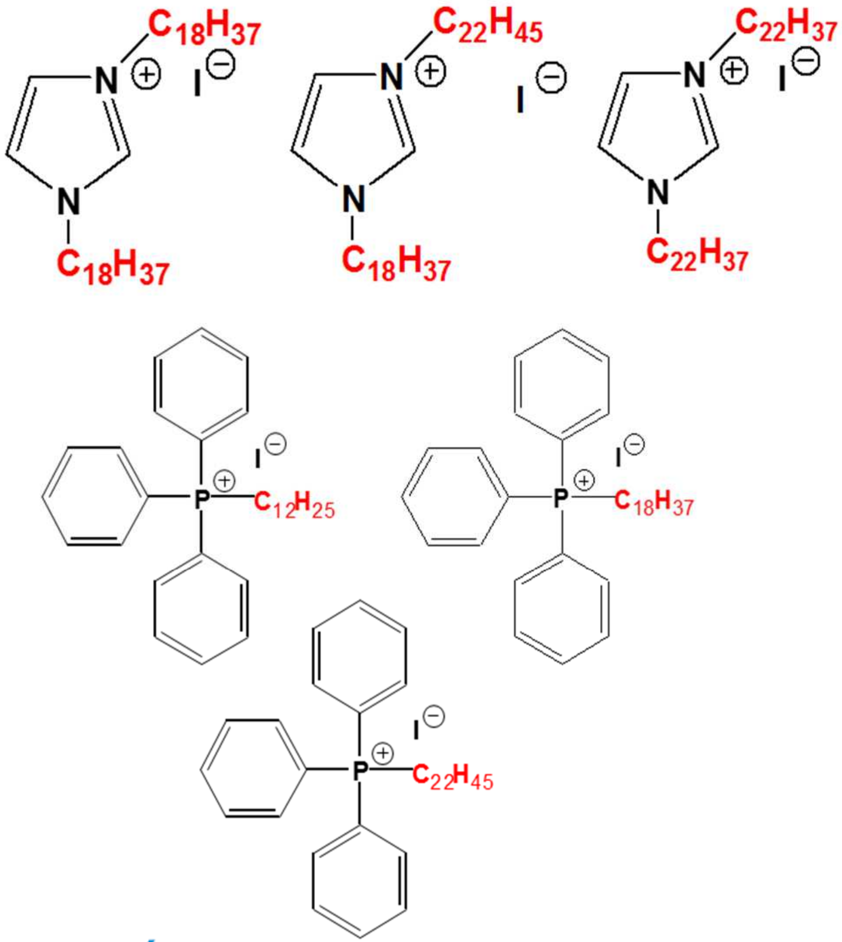
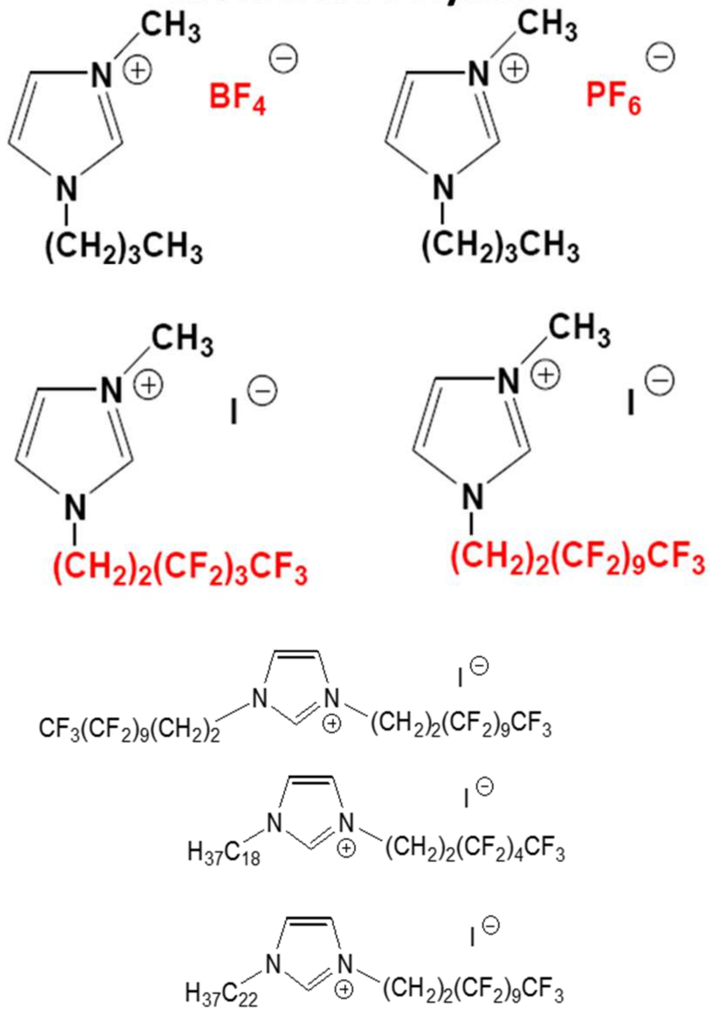
Introduction – IL : New Interfacial agents

Tunability of Ils towards the matrix

1. Polyolefin, Polystyrene, Epoxy, etc



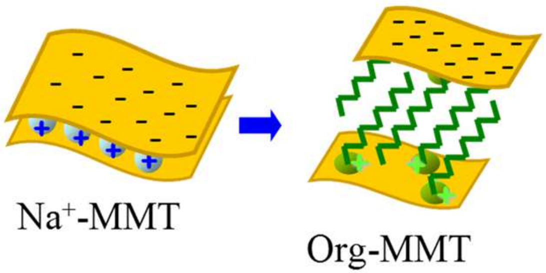
2. Fluoride Polymer



ILs : Interfacial agents

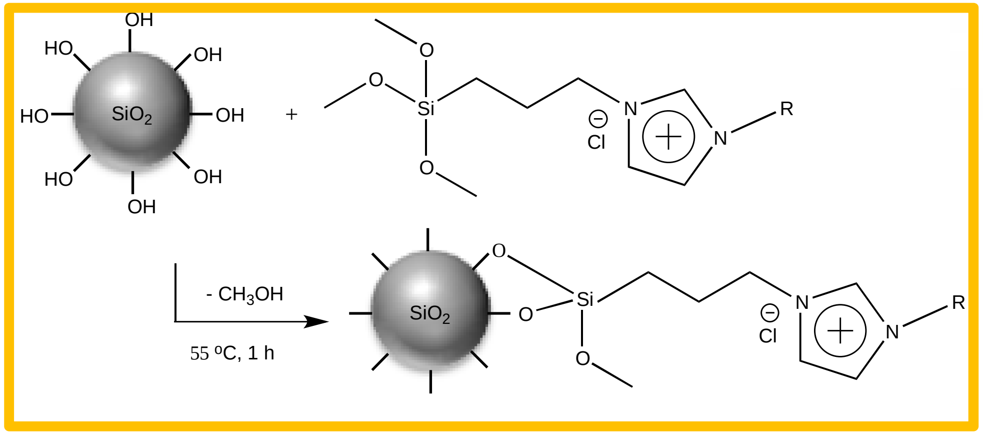
IONIC LIQUIDS as Interfacial agents able to establish different types of interactions

IONIC INTERACTIONS



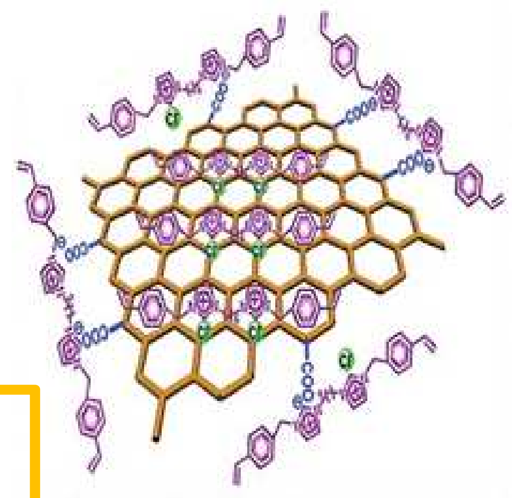
L. Le Pluart et al., Polymer (2005)
S. Livi et al., J. Coll. Interface Sci. (2011)
S. Livi et al., J. Coll. Interface Sci. (2010)

COVALENT INTERACTIONS



Kango, S.; Kalia, S.; Celli, A.; Njuguna, J.; Habibi, Y.; Kumar, R. *Prog. Polym. Sci.* **2013**. /Zou, H.; Wu, S.; Shen, J. *Chem. Rev.* **2008**, *108*, 3893–3957. // Xie, Y.; Hill, C. a S.; Xiao, Z.; Militz, H.; Mai, C. *Compos. Part A Appl. Sci. Manuf.* **2010**, *41* (7), 806–819.

Π–Π INTERACTIONS



Yang et al,
J. Mater. Chem. **2012**, *22*, 5666-5675

CONTENTS

1.- INTRODUCTION

- Effect 'Nanocomposite' : Why ?
- Why Ils for designing hybrid materials?

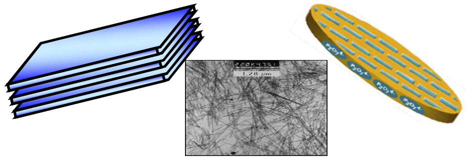
2.- IL MODIFIED LAYERED SILICATE-BASED NANOCOMPOSITES

3.- IL-MODIFIED GRAPHENE-BASED NANOCOMPOSITES

4.- IL-MODIFIED SILICA –BASED NANOCOMPOSITES

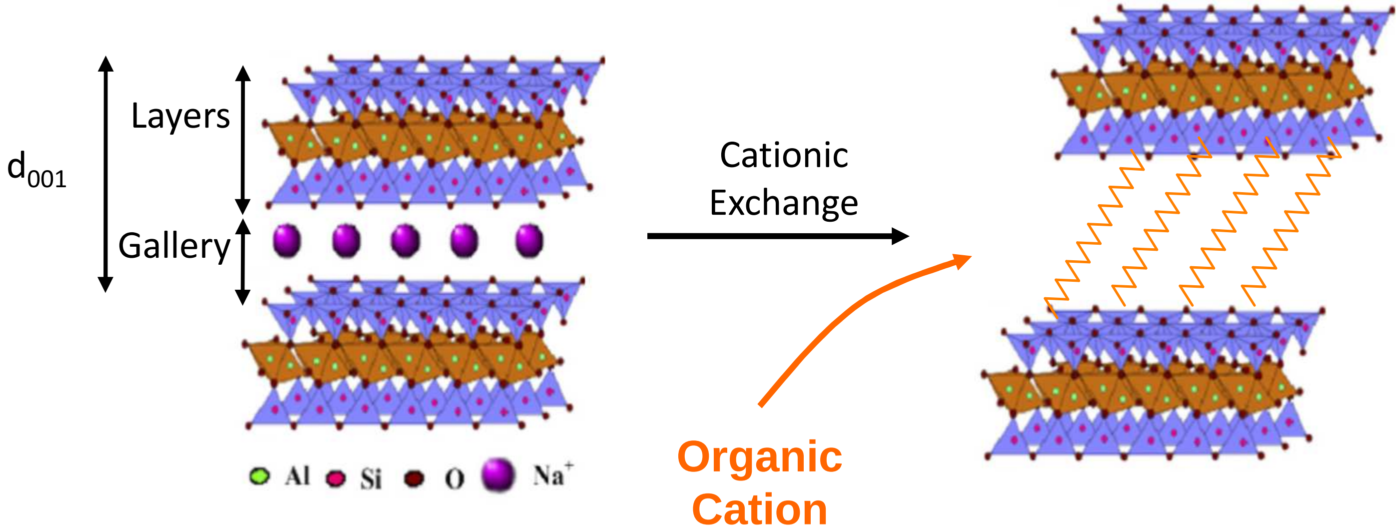
5.- CONCLUSION

ILs : Interfacial agents for layered silicates

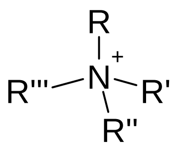


Layered Silicates
(montmorillonite, hectorite,laponite…)

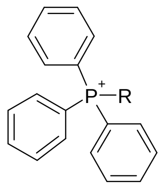
IONIC INTERACTIONS



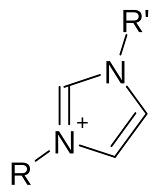
Alkyl-ammonium[1]



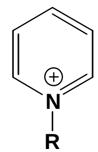
Phosphonium[2,3]



Imidazolium[2,3]

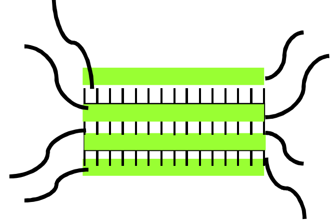


Pyridinium

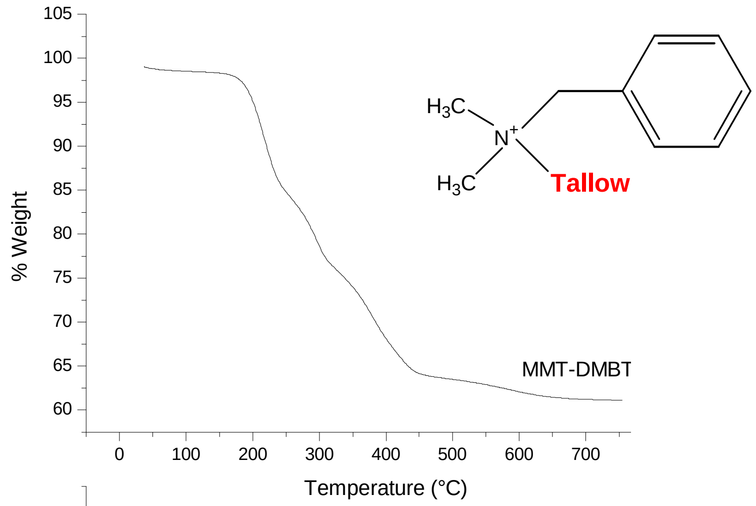


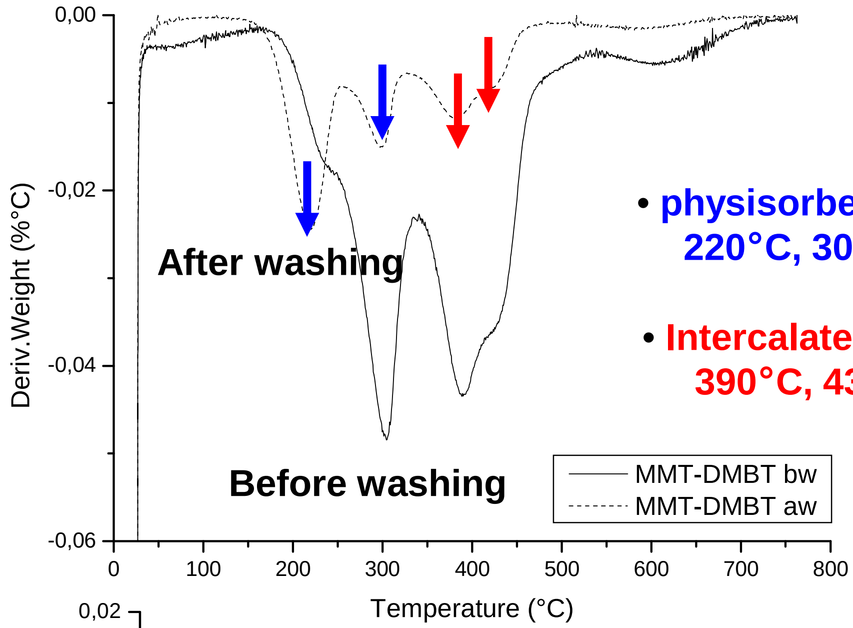
[1] L. Le Pluart , J. Duchet-Rumeau, H. Sautereau, Polymer 46, 2005, pp. 12267–12278
[2] S. Livi, J. Duchet-Rumeau, T.N. Pham, J.F. Gérard, Journal of Colloid and Interface Science 354, 2011, pp. 555–562
[3] S. Livi, J. Duchet-Rumeau, T.N. Pham, J.F. Gérard, Journal of Colloid and Interface Science, 2010, 349, pp. 424-433
[4] Z. M. Zhang, Macromolecules, 2003, 36, pp. 8919-8922

ILs : Interfacial agents for layered silicates



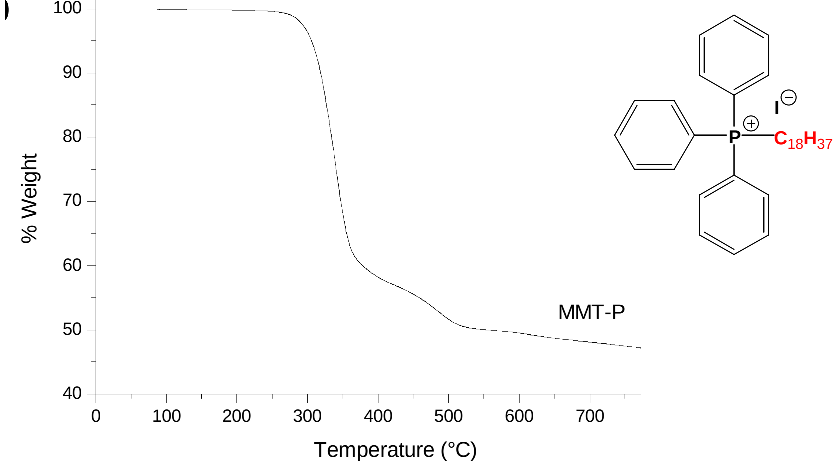
Thermal stability tuned by chemical nature of cation

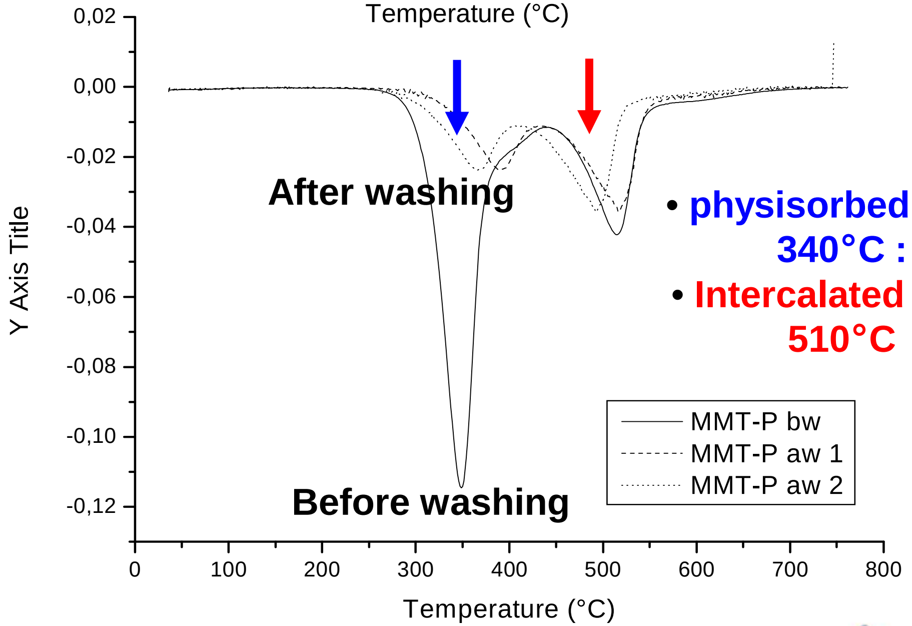




• **physisorbed ions** : **220°C, 300°C :**

• **Intercalated ions : 390°C, 430°C**





• **physisorbed ions** : **340°C :**

• **Intercalated ions : 510°C**

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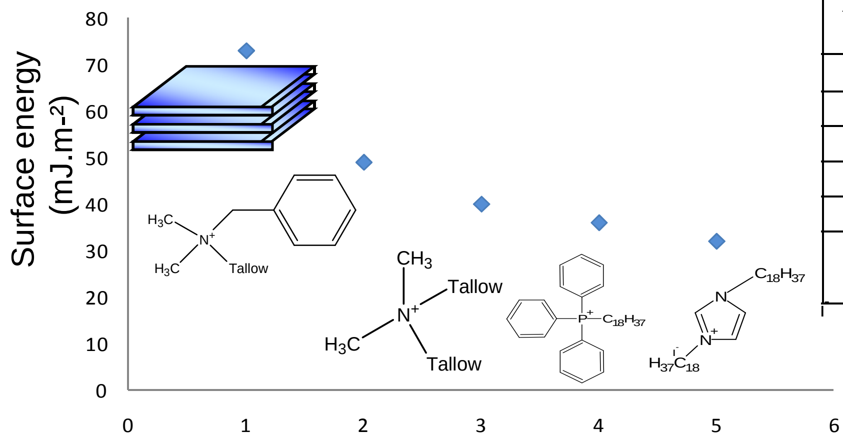
+ 120° C for physisorbed ions and + 90° C for intercalated ions

Ils : Interfacial agents for layered silicates

Rendering inorganic filler organophilic i.e. compatible with the matrix



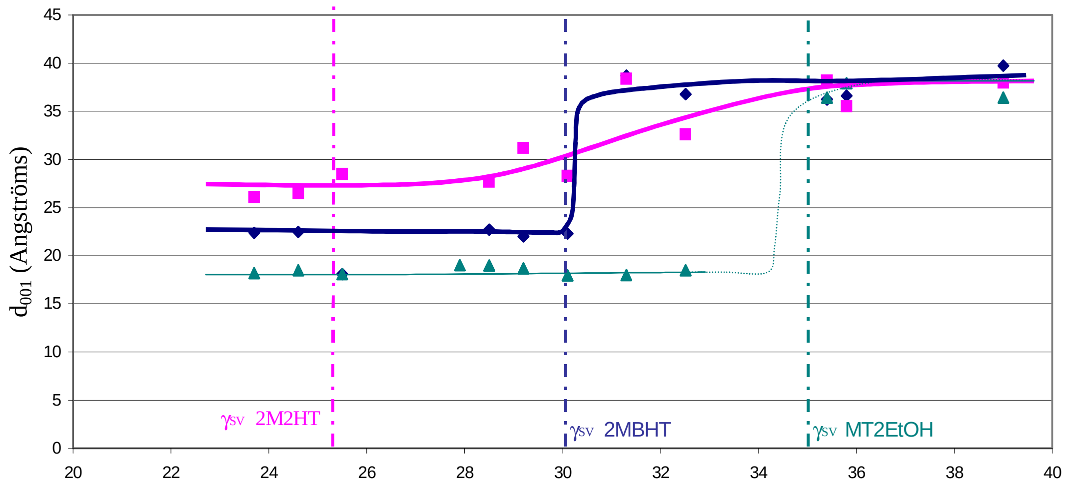
Montmorillonite	γ polar (mN.m^{-1})	γ total (mN.m^{-1})
MMT-Na^{+}	30	73
MMT-DMDT	9	40
MMT-DMBT	14	49
MMT-P	2	37
MMT-I	1	32
Polyethylene [28]	0	34

Modification of surface energy by LIs

- *Decrease of surface energy*
- *Very low non dispersive component*
- *Very hydrophobic lamellar fillers*

Surface energy similar to polyethylene one : better compatibility of IL-modified MMT ?

A key parameter : Surface Energy

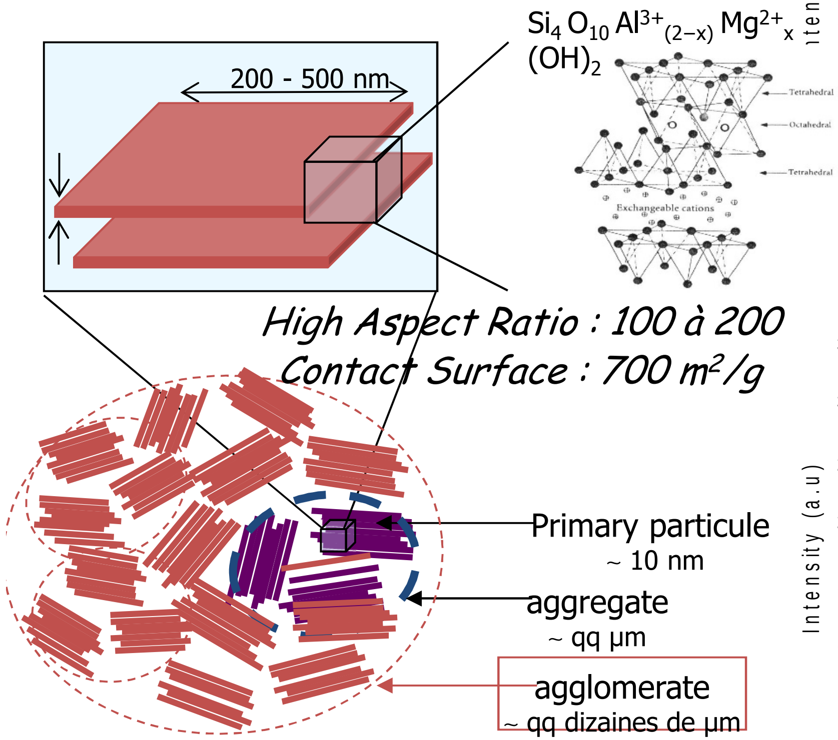


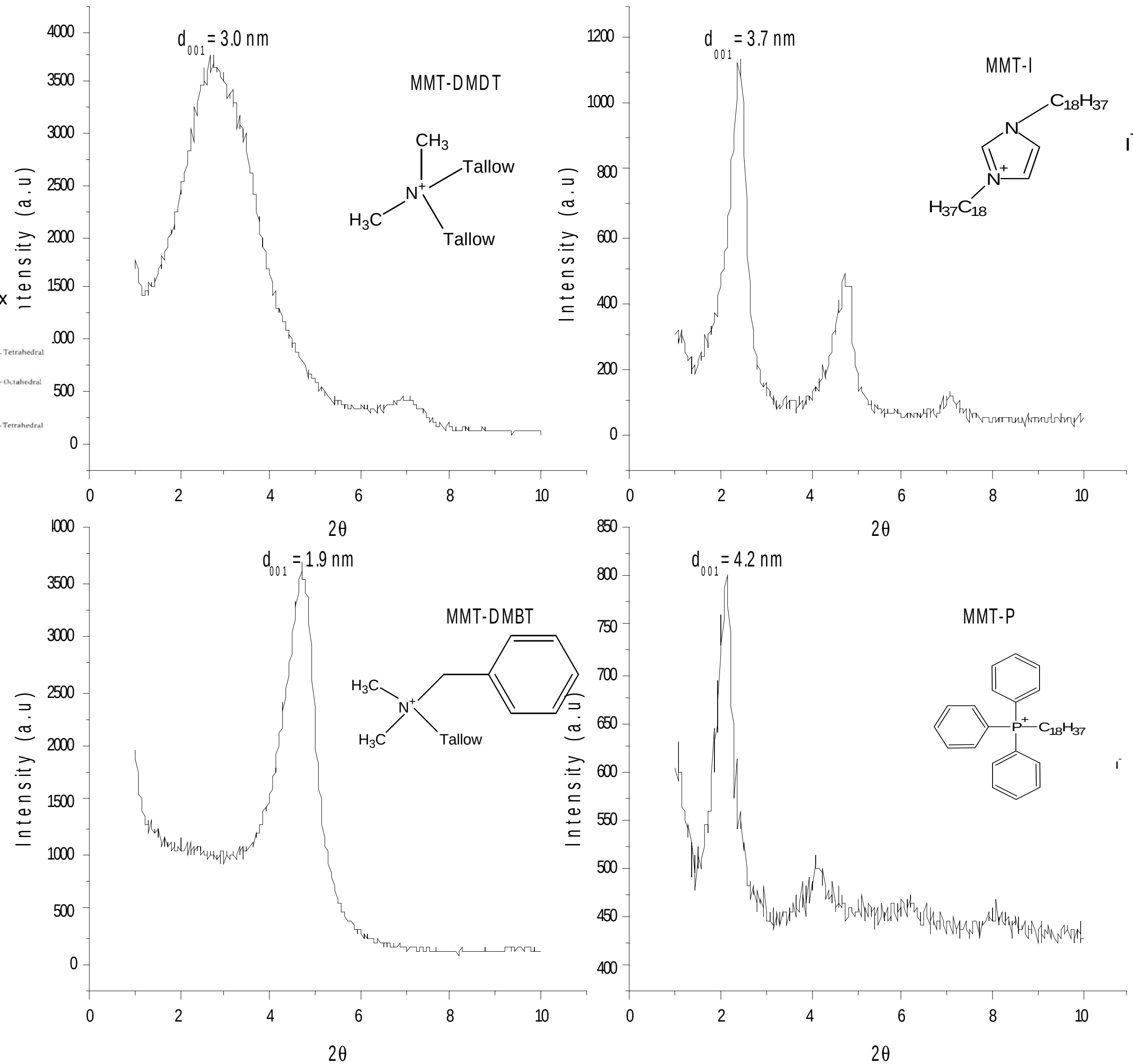
S. Livi, J. Duchet-Rumeau, J-F. Gérard,, **353** (1), 225-230 (2011).
S. Livi, J. Duchet-Rumeau, T. N. Pham and J-F. Gérard, *Journal of Colloid and Interface Science*, **354** (2), 555-562 (2011).
Burgentzlé et al. J. Coll Interf. Sci. 278, 26-39 (2004)

Δd_{001} = 40 Å for γ_{lv} (organic medium) > γ_s (clay)

Ils : Interfacial agents for layered silicates

MMT Na^+ : 1.2 nm





Significant increase of interlayers distances relevant to polymer chains intercalation

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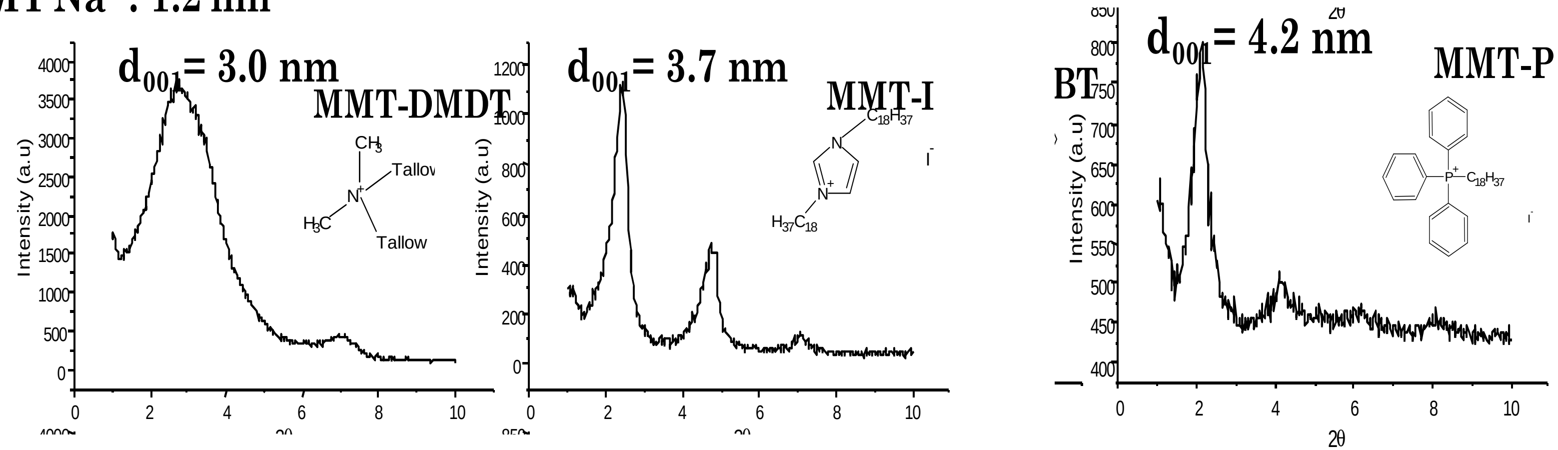
4-Ils as interfacial agents

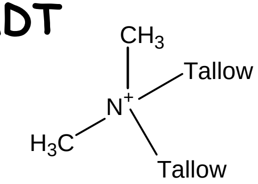
Melt Processing of IL- modified lamellar silicates within PE matrix

Montmorillonite	γ polar ($mN.m^{-1}$)	γ total ($mN.m^{-1}$)
MMT-Na^+	30	73
MMT-DMDT	9	40
MMT-DMBT	14	49
MMT-P	2	37
MMT-I	1	32
Polyethylene [28]	0	34

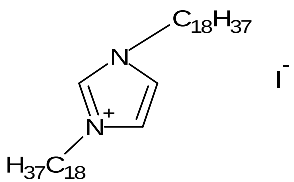
MMT Na^+ : 1.2 nm



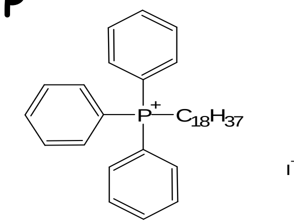
MMT-DMDT

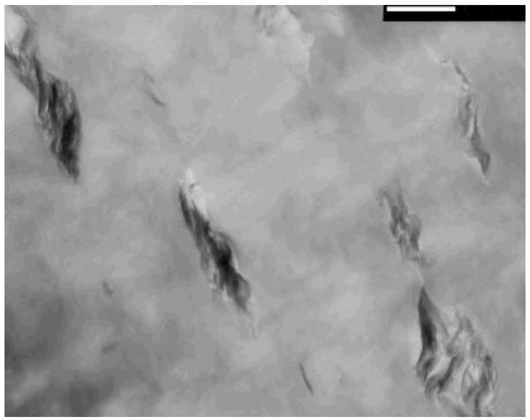


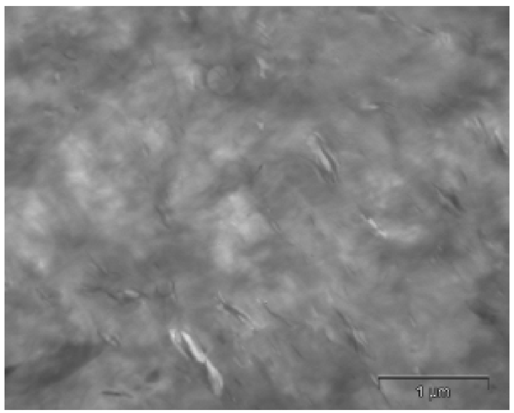
MMT-I

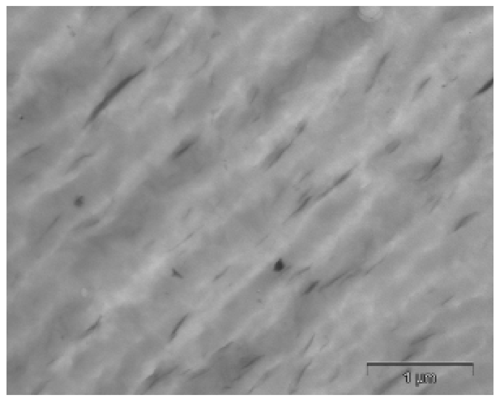


MMT-P









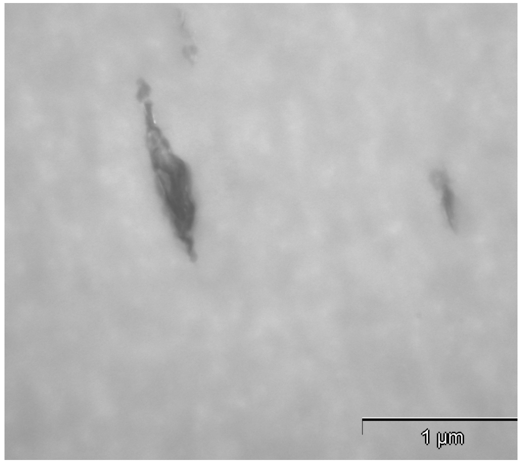
S. Livi, J. Duchet-Rumeau, T. N. Pham and J-F. Gérard, *JCIS*, **354** (2), 555-562 (2011).

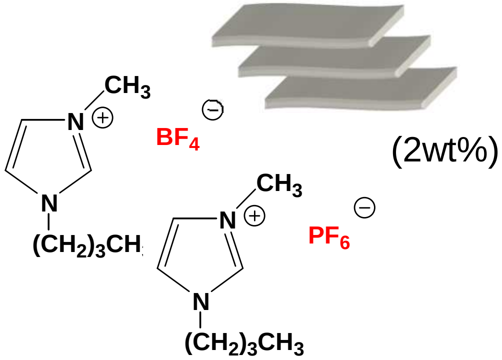
ILs : Interfacial agents for layered silicates

Melt Processing of Imidazolium modified lamellar silicates within PVDF matrix

$-(CF_2-CH_2)-$

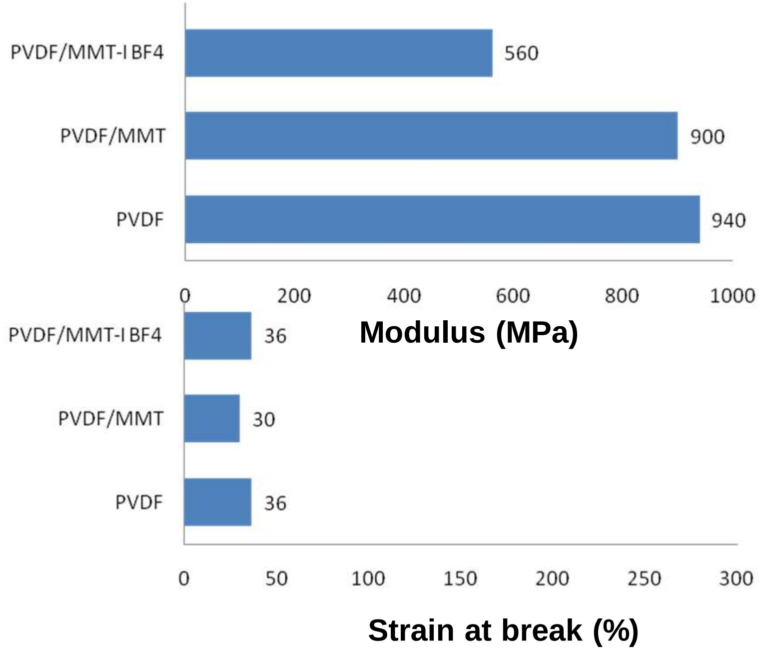
Polyvinylidene fluoride
-PVDF-

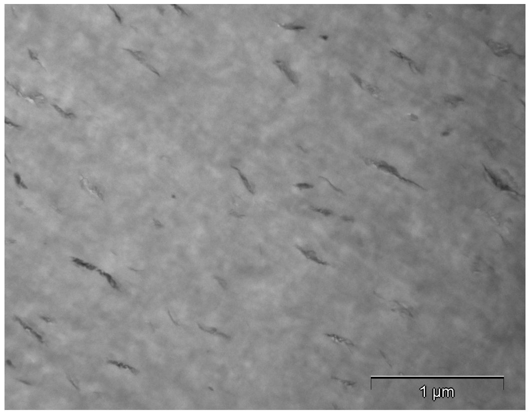


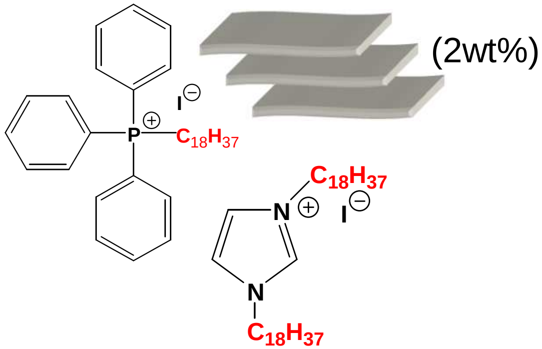


Decrease of modulus : - 40%
No change of Strain at Break : 0%

Microcomposite

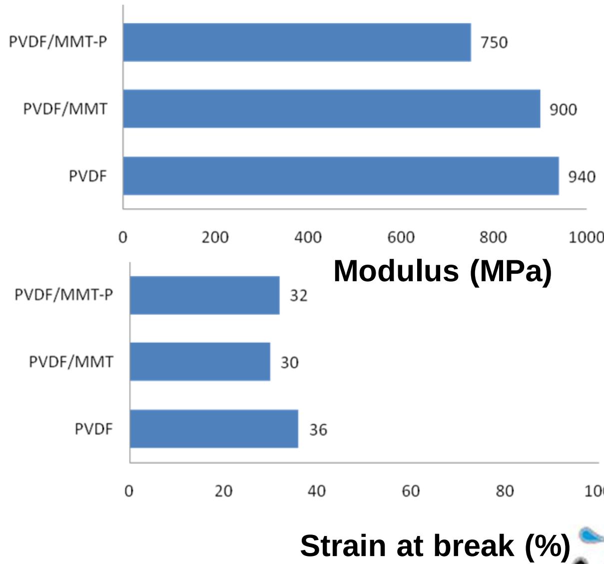






Decrease of modulus : - 20%
No change of Strain at Break : 0%

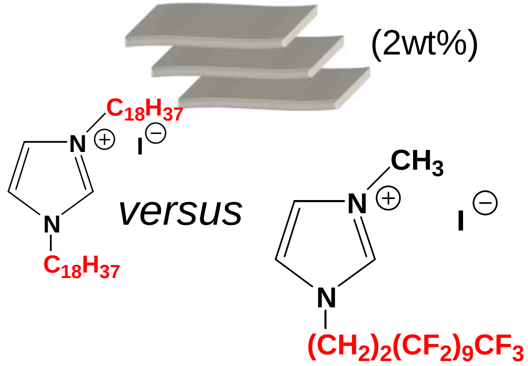
Intercalated Nanocomposite

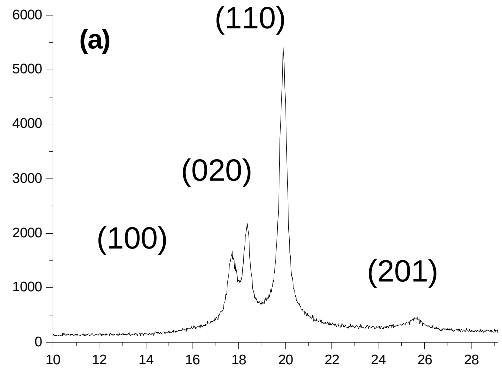


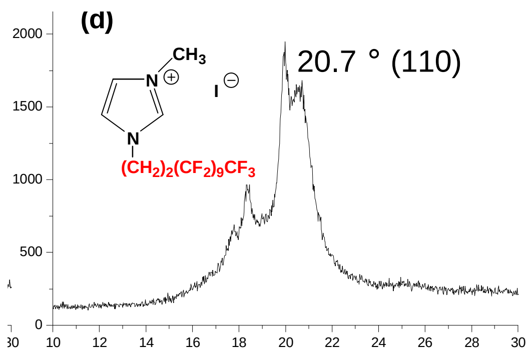
4-Ils as interfacial agents for layered silicates

$-(CF_2-CH_2)-$

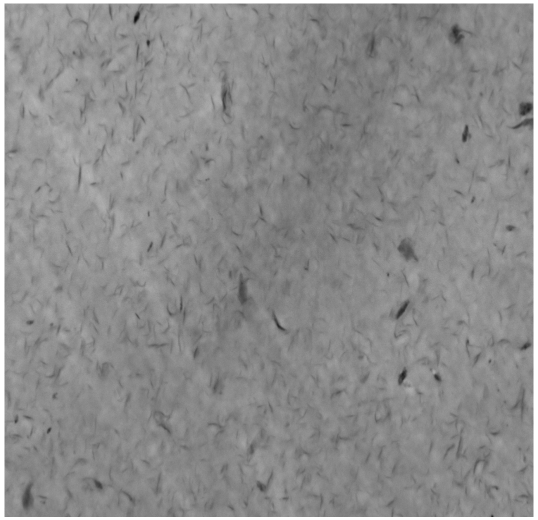
Polyvinylidene fluoride
-PVDF-



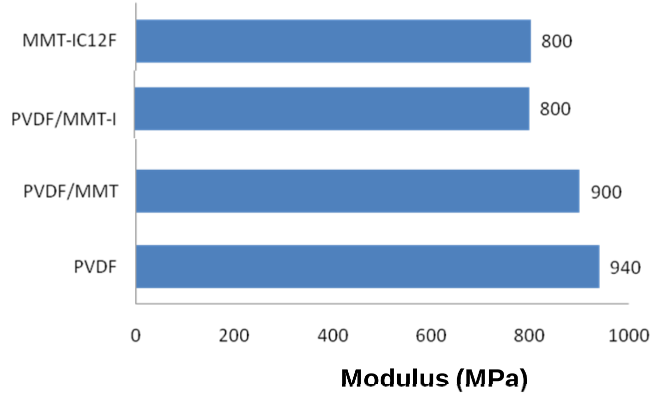


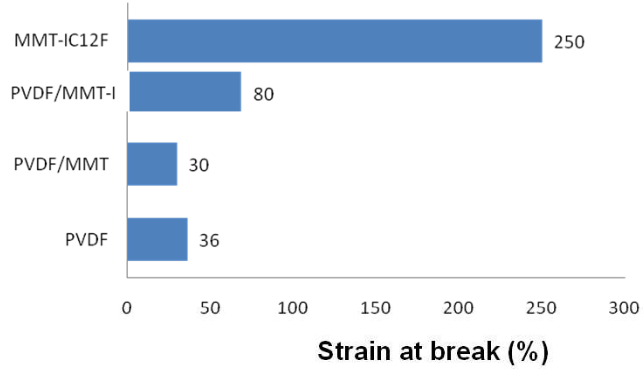


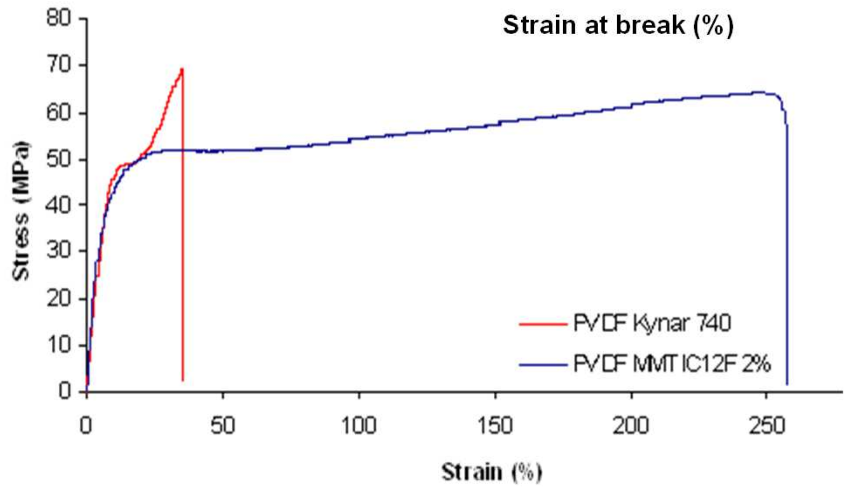
β crystalline form
Ideal for dielectrical properties



Exfoliated Nanocomposite







Plasticization of the PVDF matrix
upon addition of
treated MMT by perfluorinated imidazolium

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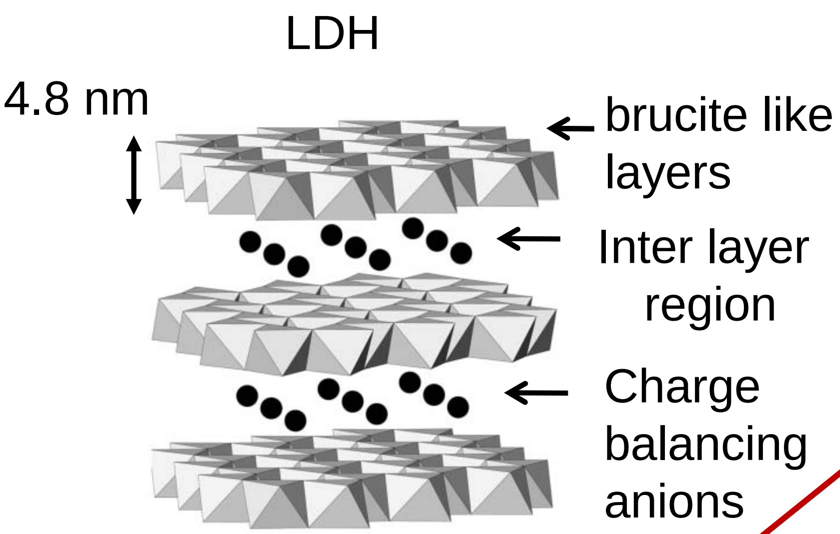
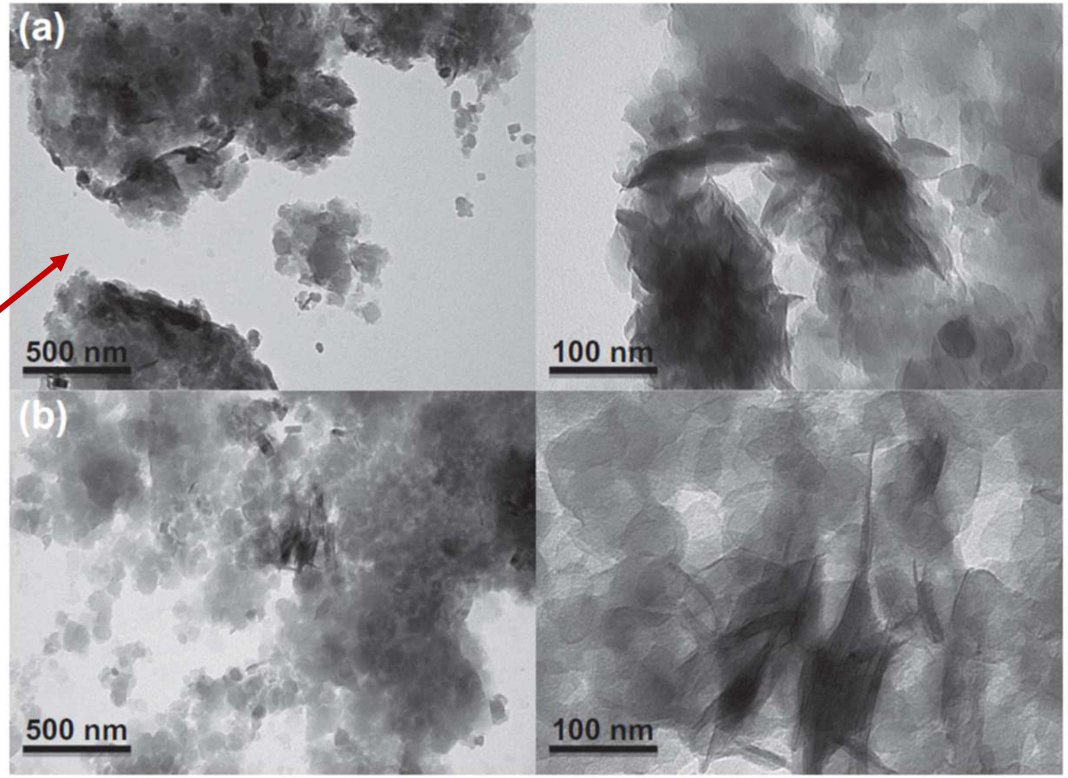
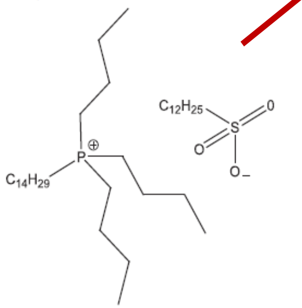
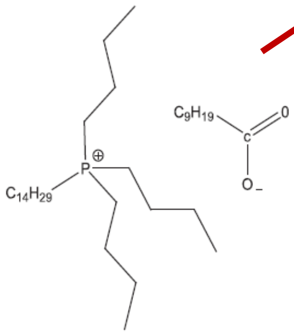
4-Ils as interfacial agents for layered silicates

Layered double hydroxides modified with ionic liquids in polylactic acid matrix





Trade name	Intercalant	Designation
	NO_3	LDH–NO_3
IL201		LDH–P1
IL103		LDH–P2

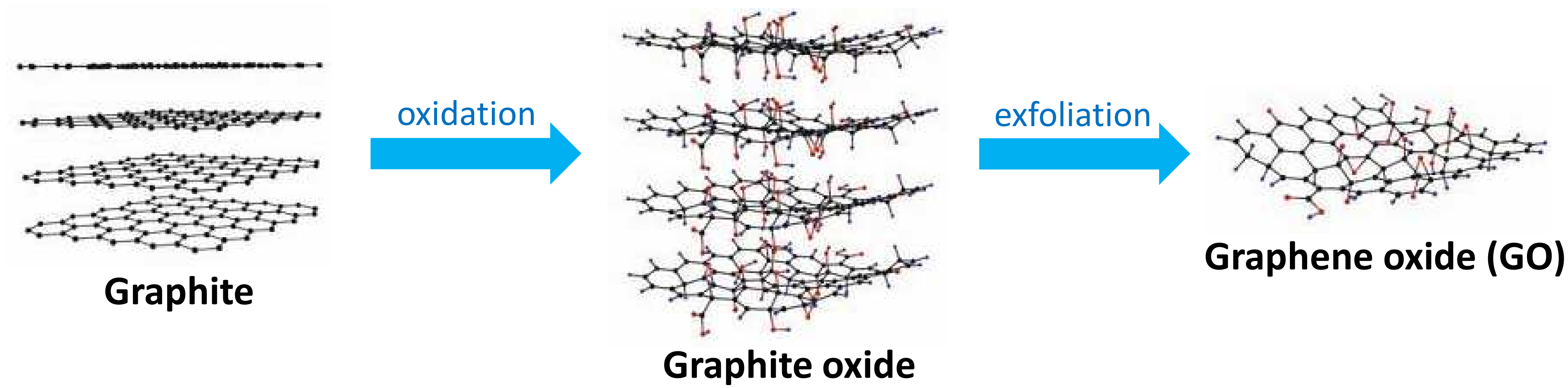
Sample	Tensile modulus (MPa)	Strain at break (%)	Glass transition (°C)	Xc
PLA	2215	3.7	62	53
PLA/LDH–NO_3	2200	2.8	61	53
PLA/LDH–P1	2116	3.6	59	52
PLA/LDH–P2	2147	9.5	53	48

S. Livi et al, J. Collloid Interface Sci. (2012)

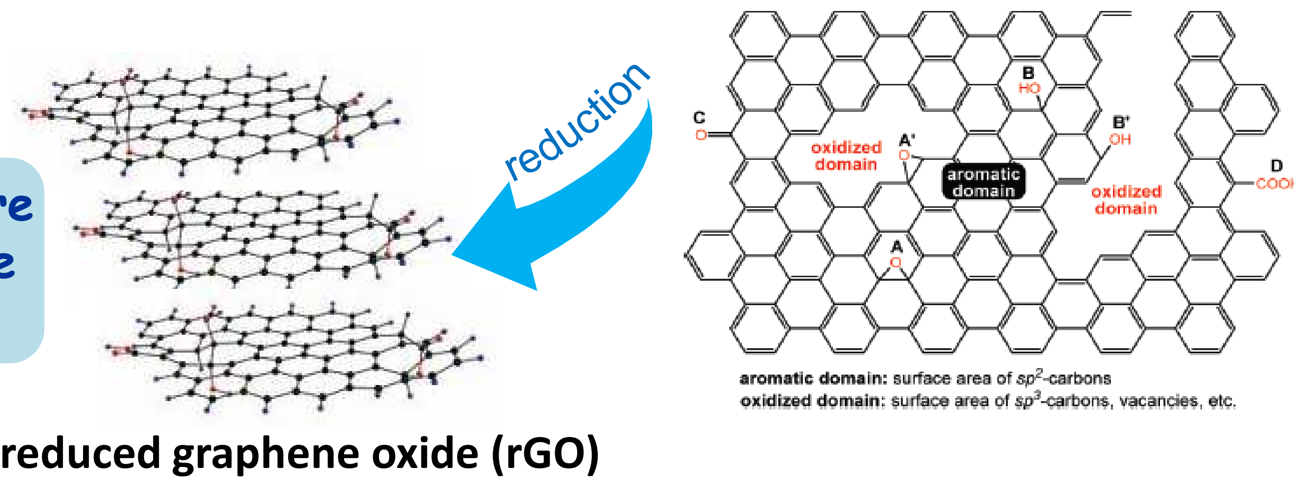
CONTENTS

4-Ils as interfacial agents for graphene

A routine way to prepare and utilize graphene as nanofillers



Aggregation to restore graphite-like one due to π-π stacking



Prog. Polym. Sci. **2010**, *35*, 1350-1375 *Adv. Mater.* **2011**, *23*, 1089-1115

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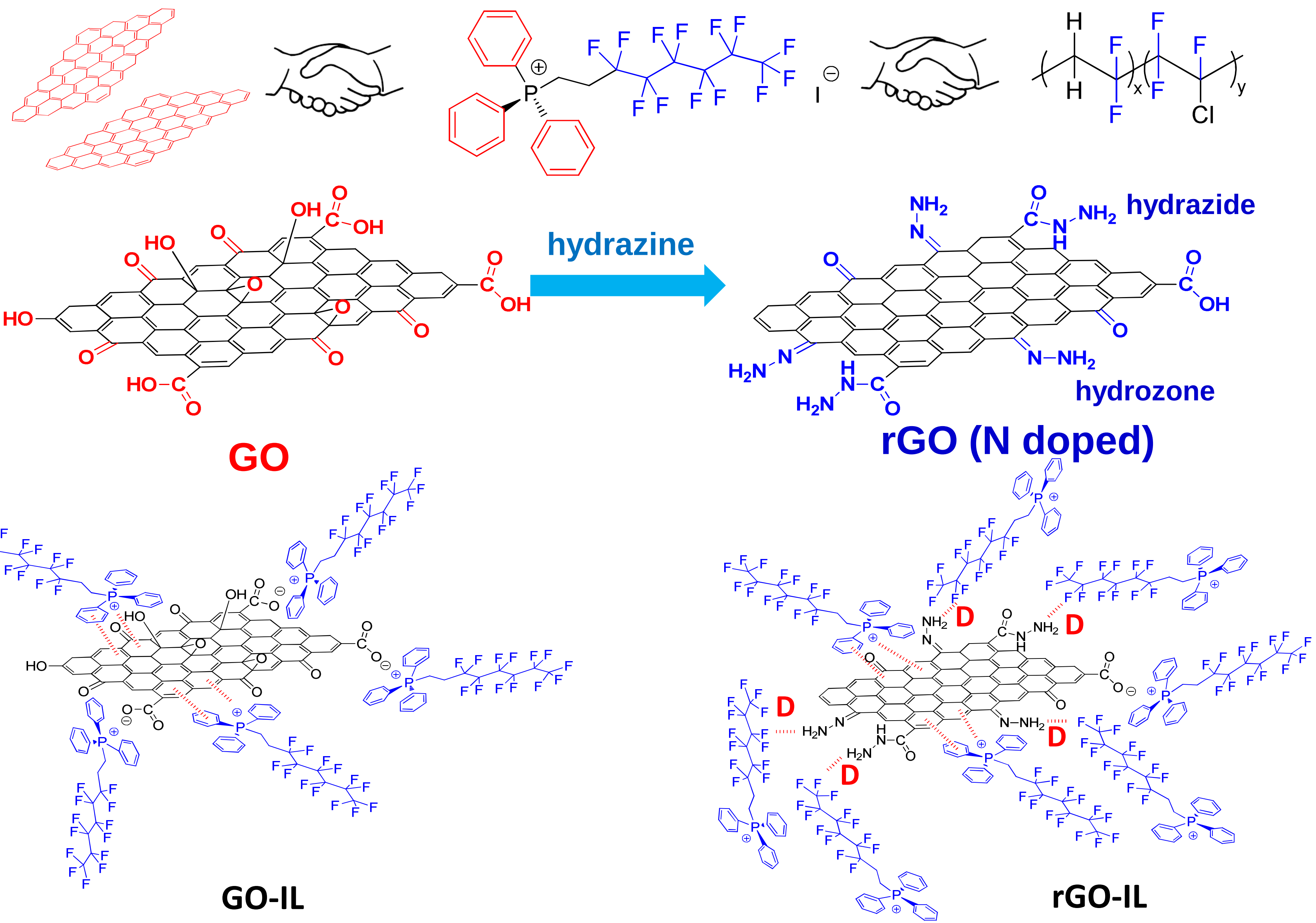
imp

3-Ils as interfacial agents

Solution Intercalation of Phosphonium modified graphene within PVDF-CTFE matrix

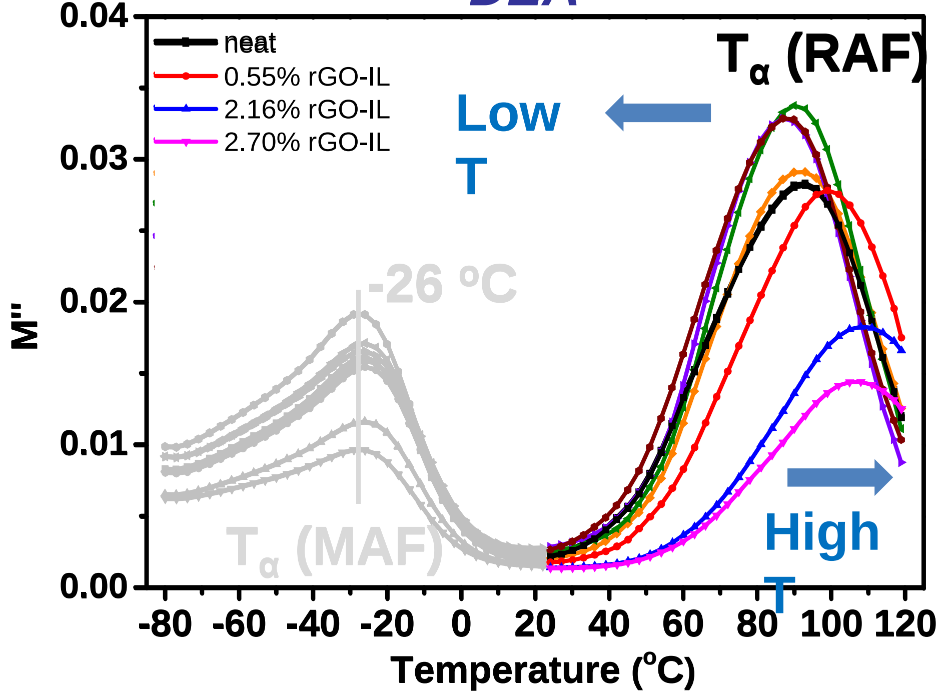


A: ionic interaction B: cation-π interaction C: π-π interaction **D: H-bond interaction**

3-Ils as interfacial agents

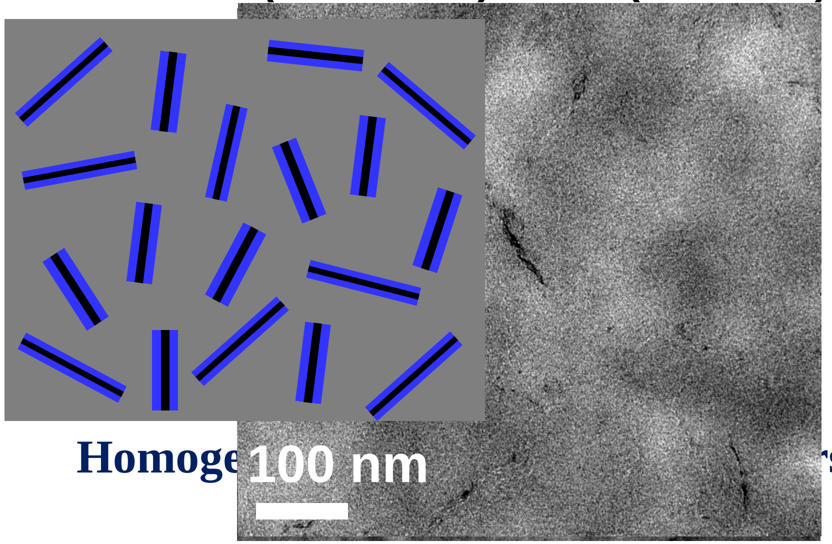
GDR LIPS #3585
Groupement De Recherches Liquides Ioniques et PolymèreS

DEA



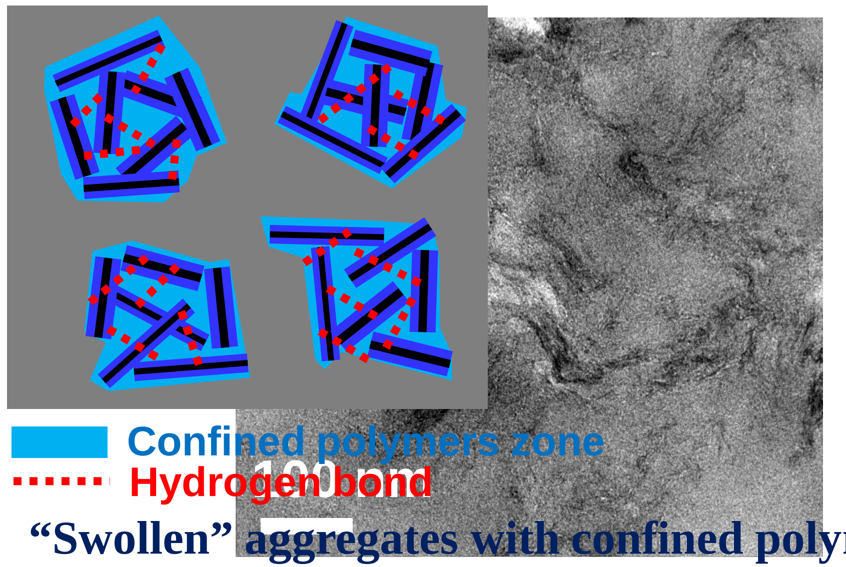
TEM

P(VDF-CTFE)/GO-IL (2.70 wt%)



Homoge … rsed

P(VDF-CTFE)/rGO-IL (2.70 wt%)



“Swollen” aggregates with confined polymer chains due to H-bonding interactions

- No changed T_α (MAF): no plasticization effect
- T_α (RAF):

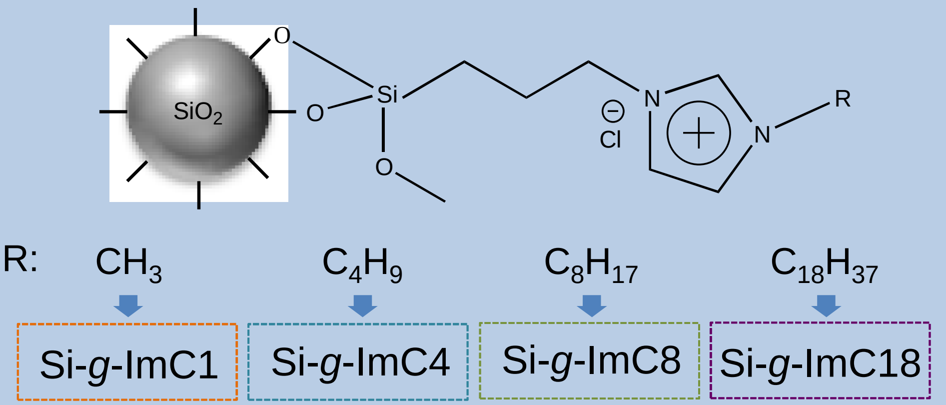
GO-IL ↘ : Interchain affinity was weakened

rGO-IL ↗ : Chain movement was constrained

CONTENTS

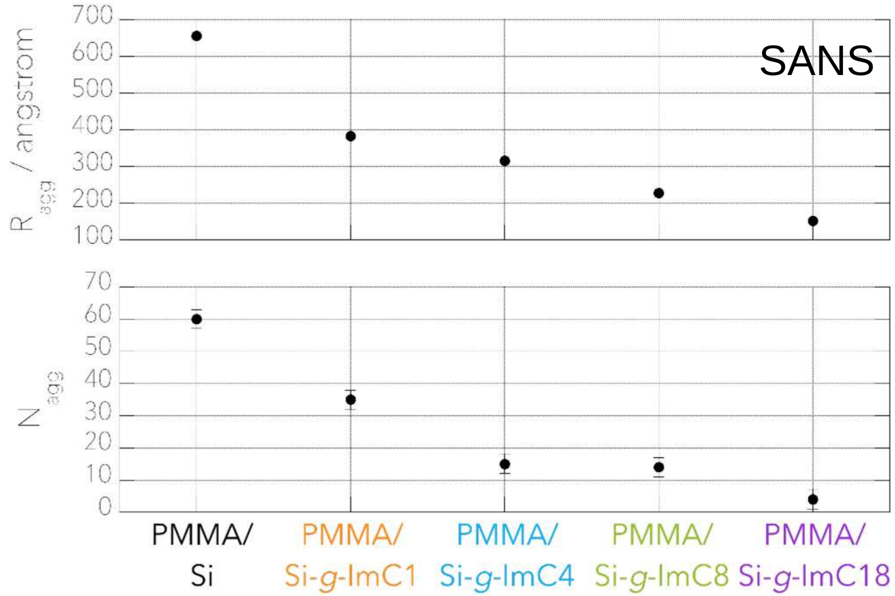
4-ILs as interfacial agents

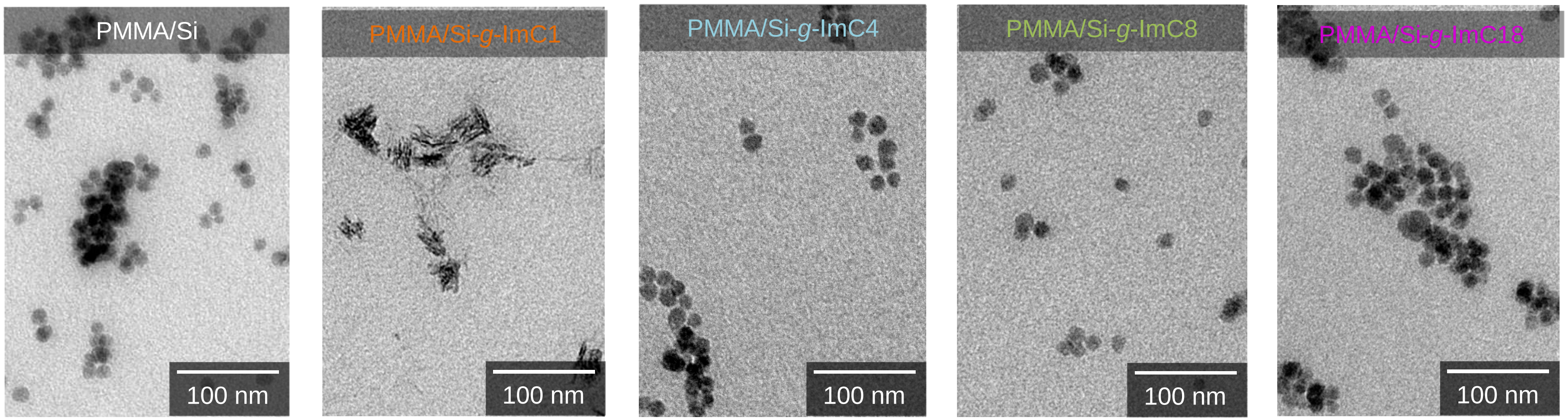
Surface modification of silica nanoparticles under $scCO_2$



Better state of dispersion

Better interfacial interactions between Si-g-ImCx and PMMA





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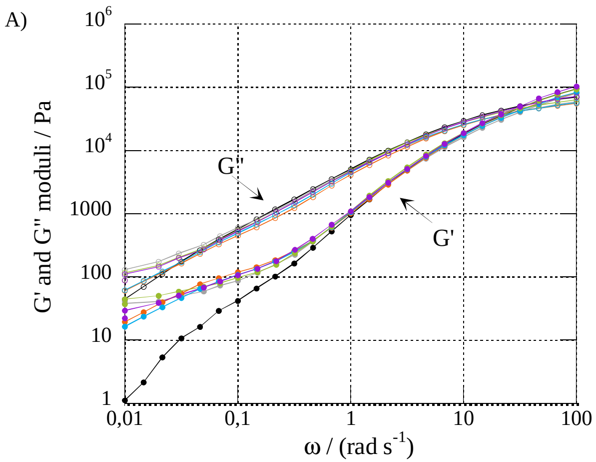
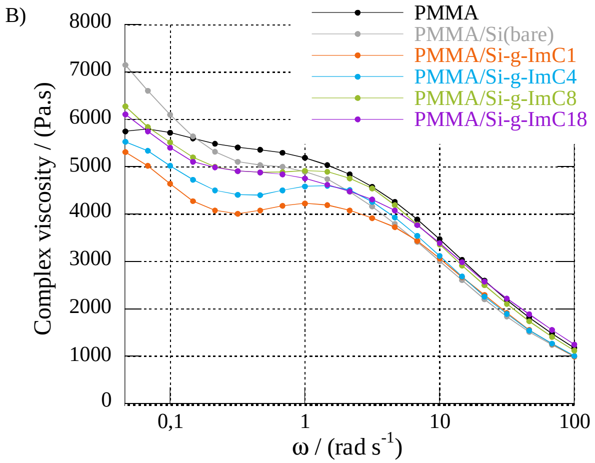
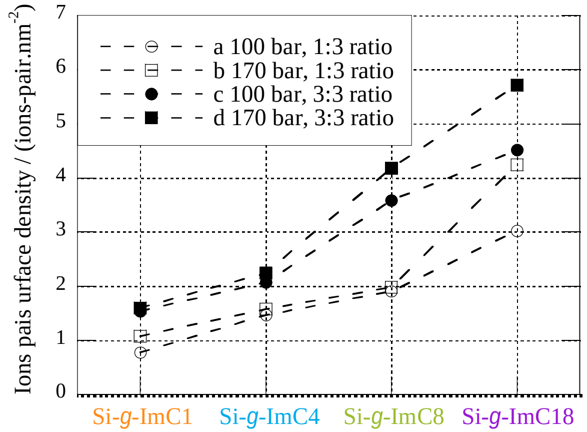
imp

4-Ils as interfacial agents

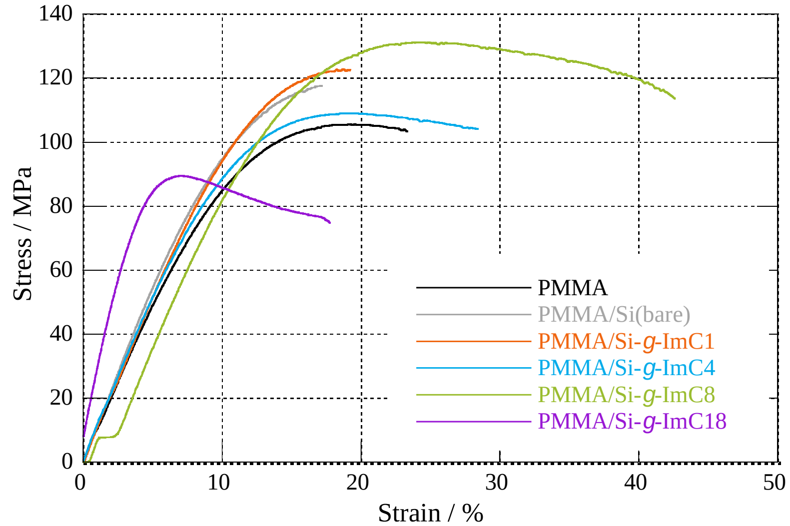




Higher G' moduli in the low w range : sign of a gel like behavior related to the formation of a percolated network of siica

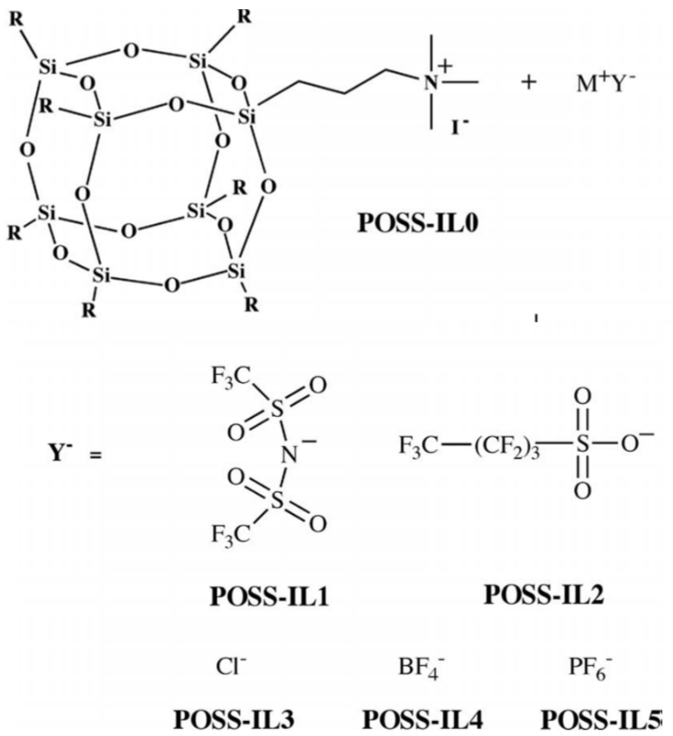


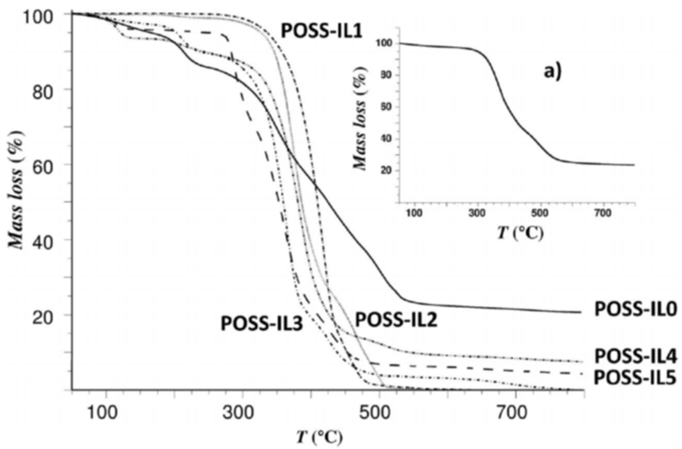
Longer the alkyl chain length, higher the surface density



interfacial reinforcement of long alkyl chains
Plasticizer effect of shorter chains

4-Ils as interfacial agents





Synthesis of POSS-ILs based on the trimethylpropylammonium hepta(isooctyl)octasilsesquioxane cation and a variety of anions

Table 3. Conductivity and dielectric constant of POSS-ILs at 1 MHz and 20 °C.

	ε_r	σ [Ω^{-1} m^{-1}]
POSS-IL0	2.13	1.65×10^{-6}
POSS-IL1	3.43	1.17×10^{-5}
POSS-IL2	2.59	3.65×10^{-6}
POSS-IL3	2.30	7.30×10^{-6}
POSS-IL4	2.75	3.36×10^{-6}
POSS-IL5	1.43	5.99×10^{-7}

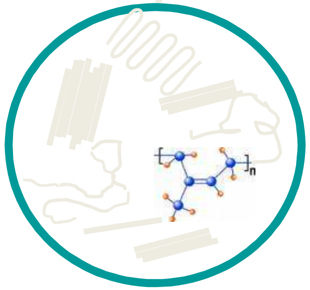
Presence of the POSS moiety :

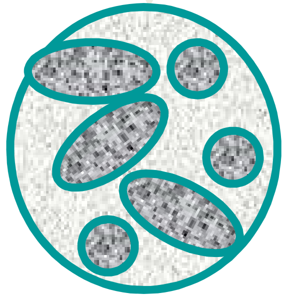
- **Improved thermal properties,**
- **Control of low room-temperature conductivity dielectric constants**
  (slight differences originating from the nature of the anions)
- **Long alkyl-chain substituents on the POSS core infer hydrophobic character and solution properties comparable to those of classic cationic surfactants**

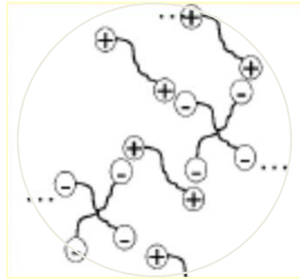
P. Cardiano et al., Eur. J. Inorg. Chem. (2012))

CONCLUSION

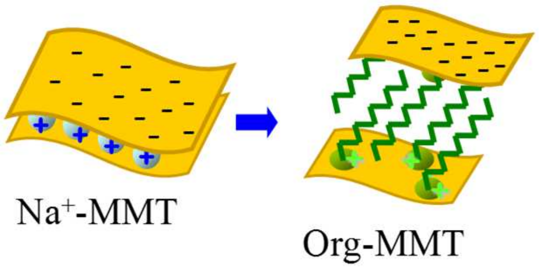
ILs : multifunctional additives for structured and functionalized materials



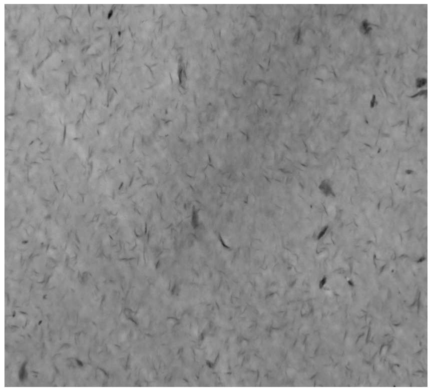




Nanocomposites

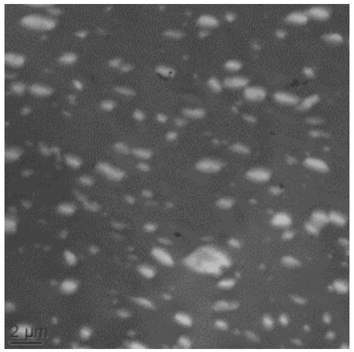


Livi, Duchet-Rumeau, Pham, Gérard JCIS 349, 424-433 (2010).

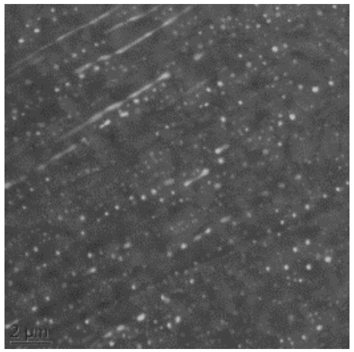


Polymer blends

PBAT/PLA



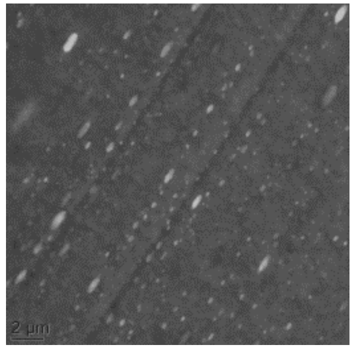
PBAT/PLA/IL (1%)



Livi, Bugatti, Marechal, Soares, Barra, Duchet-Rumeau, Gérard, RSC Advances, 5, 1989-1998 (2015)

Nanostructured Materials

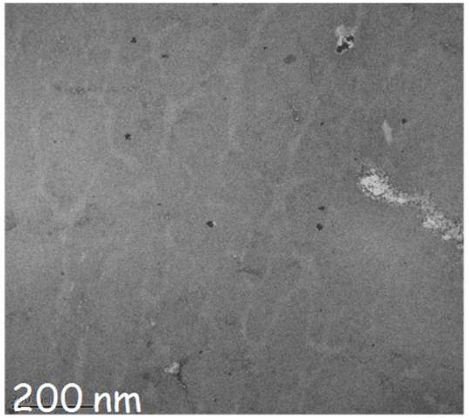
PBAT/IL-TFSI



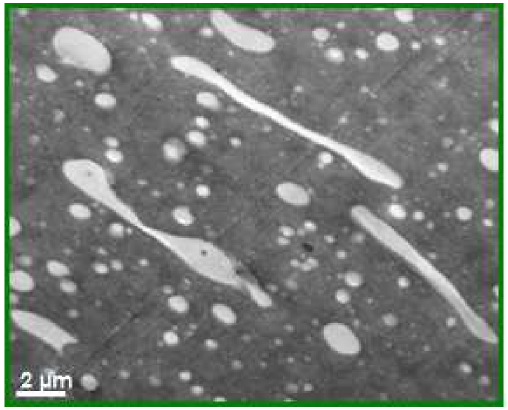
Livi, Bugatti, Soares, Duchet, Green Chemistry, 16, 3758-3762 (2014)

CONCLUSION

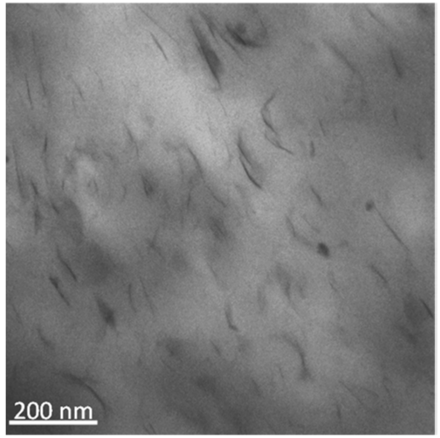
STRUCTURING AGENTS



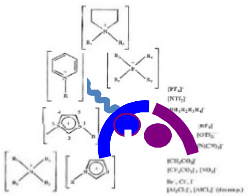
COMPATIBILIZING AGENTS

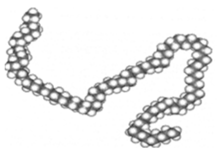


DISPERSION AIDS

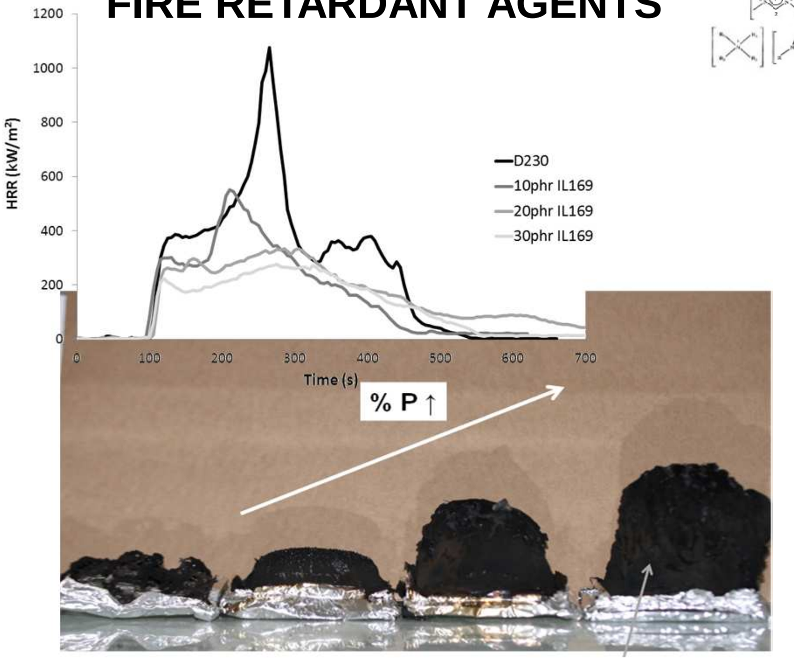


MULTIFUNCTIONAL AGENTS

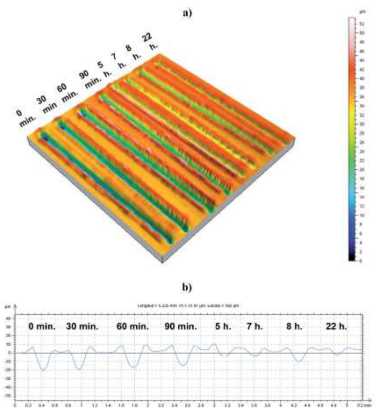




FIRE RETARDANT AGENTS

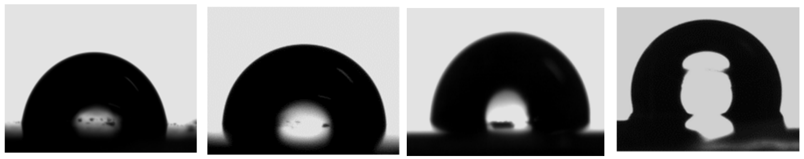


WEAR RESISTANCE



Sanes et al Wear 2010, 268
Saurin et al, RSC Advances 2016, 6, 37258

SURFACE MODIFING AGENT



MCDEA Water 80º	MCDEA/ PPE Water 89º	IL-TMP Water 91º	IL-TMP/PPE Water 101º

Nguyen et al, ACS Sustainable Chem. Eng., **2016**, *4* (2), 481–490

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for
your attention

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