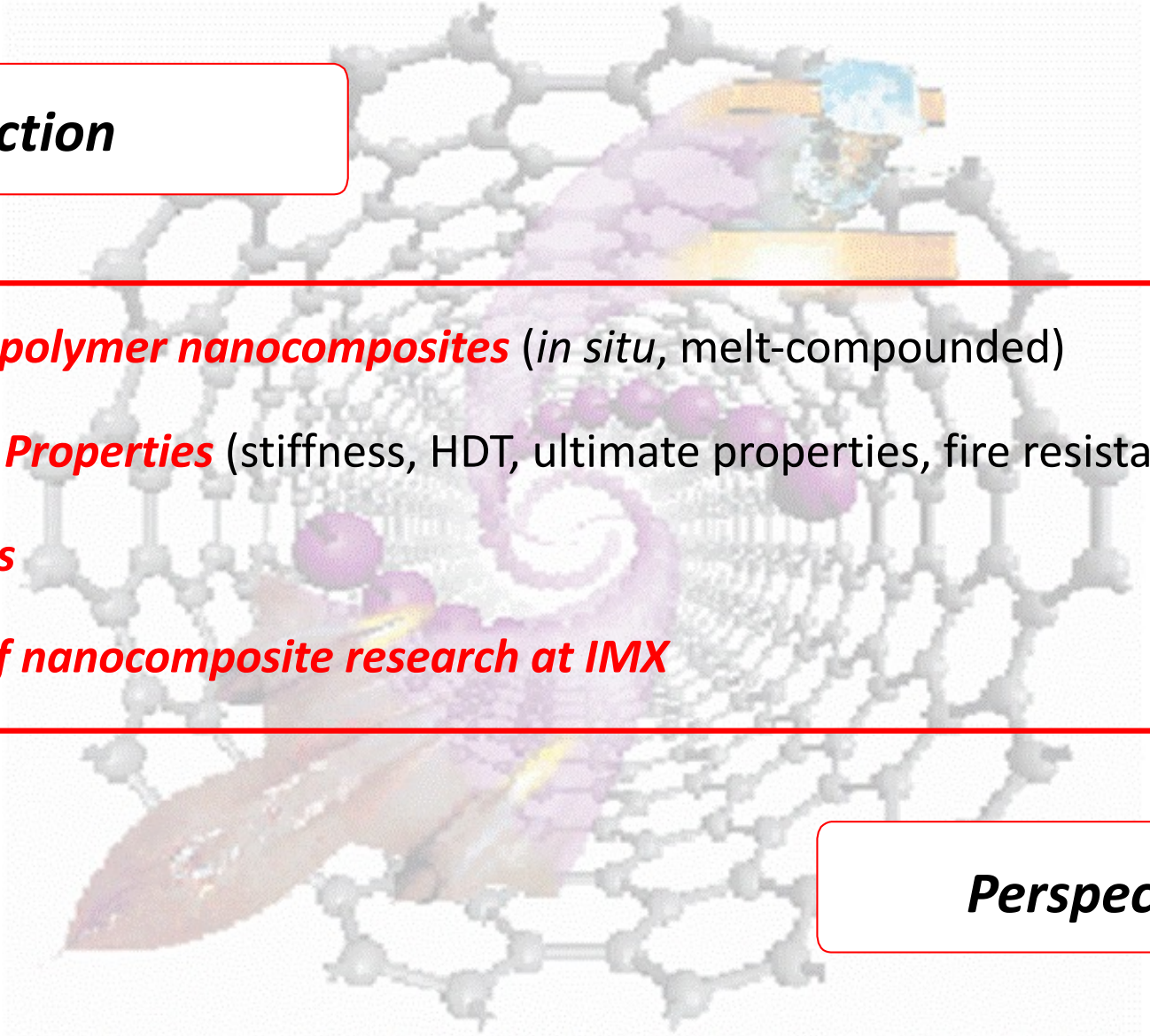
Polymer nanocomposites – Christopher Plummer (LMOM), December 2024



Introduction

- ***Clay-based polymer nanocomposites*** (*in situ*, melt-compounded)
- ***Some Basic Properties*** (stiffness, HDT, ultimate properties, fire resistance)
- ***Applications***
- ***Examples of nanocomposite research at IMX***

Perspectives

Why nanomaterials?

"There's plenty of room at the bottom!" Some examples …

- ***Better insulation*** (nanofoams, aerogels)
- ***Display technology*** (cheap "nanophosphors", better electrochromic displays)
- ***Tougher, harder, smaller cutting tools*** (nanocrystalline carbides)
- ***High energy density batteries*** (aerogels, nanocrystalline nickel, metal hydrides)
- ***High-power magnets*** (nanocrystalline yttrium-samarium-cobalt)
- ***High-sensitivity sensors, filters*** (nanocrystalline zirconia)
- ***Automobile fuel efficiency*** (light-weight structures, engine liners, spark plugs)
- ***Aerospace components*** (temperature, fatigue resistant materials, weight saving)
- ***Satellites*** (nanocrsytalline tungsten-titanium diboride-copper ignitors)
- ***Medical implants*** (wear resistant nanocrystalline carbides, zirconia)
- ***Ductile, machinable ceramics*** (nanocrystalline carbides, nitrides)

Why polymer nanocomposites?

Increased strength and stiffness: while maintaining the high elongation of the matrix.

Permeation Resistance: (plate-like fillers e.g. exfoliated clays) interest in nanocomposites barriers from packaging companies.

Transparency: low loadings and filler dispersion maintain inherent polymer transparency in thin sections (again interest for packaging)

Recyclability: nanofillers are not affected or degraded during processing → physical properties not seriously affected by recycling

Flame resistance: rapid char layer formation, excellent flame resistance

Transport properties: percolation at very low loadings in high aspect ratio systems, important for thermal, electrical conductivity (e.g. carbon nanotubes)

Functionality: bioactivity, hydrophilicity, magnetic and electrical properties etc. etc.

And all at loadings of a few wt% ***weight saving!!***

Are nanofillers worth it? Examples (2019)

- Natural clays (mined, refined, and treated)—$3–$15/lb.
- Synthetic clays—$10–$20/lb.
- Nanostructured silicas—$5–$200/lb.
- Nanoceramics—$100–$280/lb.
- Nanotubes (carbon based, MWNT)—$100–$200/lb.

Applications now include packaging, automotive, and wire and cable industries, and huge increase in demand for these fillers is projected
→ ***Lower prices in the future***

Clay-based polymer nanocomposites

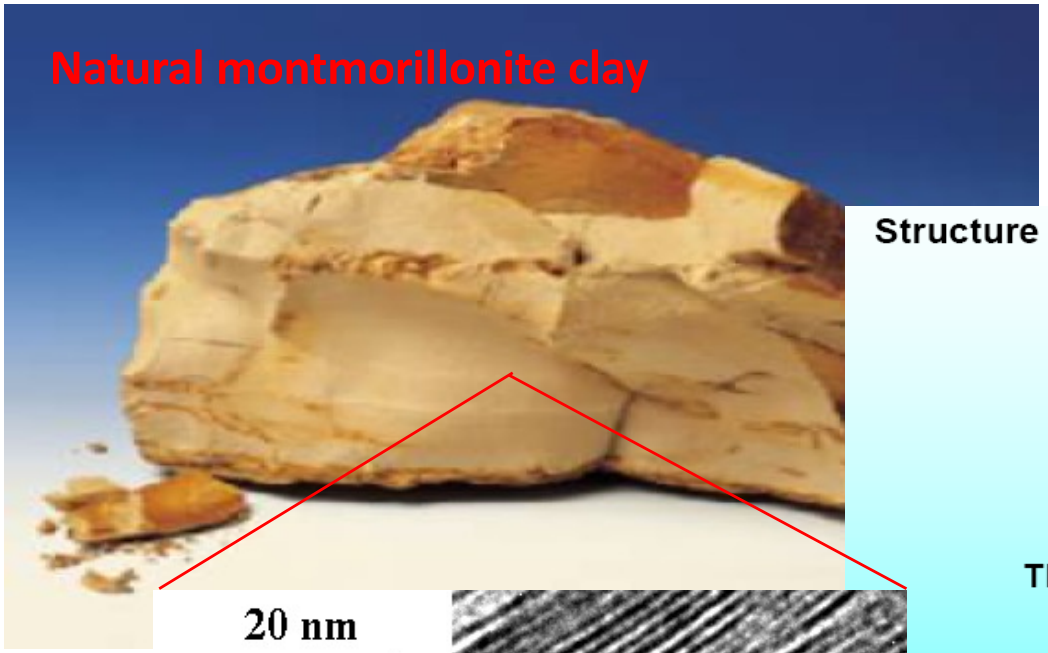
Some important dates in the history of polymer nanocomposites

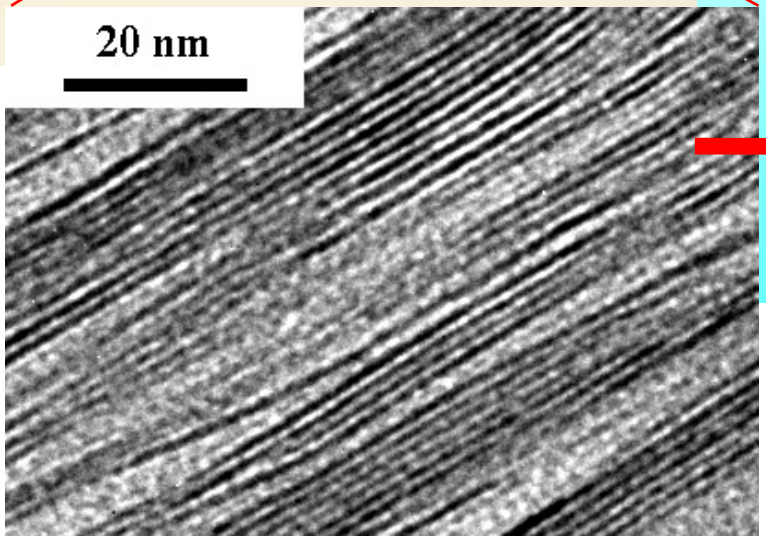
US 2,531,396	***1950***	***National Lead***	Onium ion treated clay to reinforce elastomers
US 3,084,117	***1963***	***Union Oil Company***	Organoclay-polyolefin composition masterbatch, melt blend, solvent, protonated amine
JP 10,998	***1976***	***Unitika***	***In situ* process** for layered silicate clay polyamide
US 4,739,007	***1988***	***Toyota***	Layered silicate clay polyamide composition
US 5,747,560	***1998***	***Allied Signal***	**Melt compounding** for nanocomposites; clay treated with protonated primary and secondary amines

Toyota, GM/Montel, GE, Dow/Magna, etc. currently active in nanocomposites

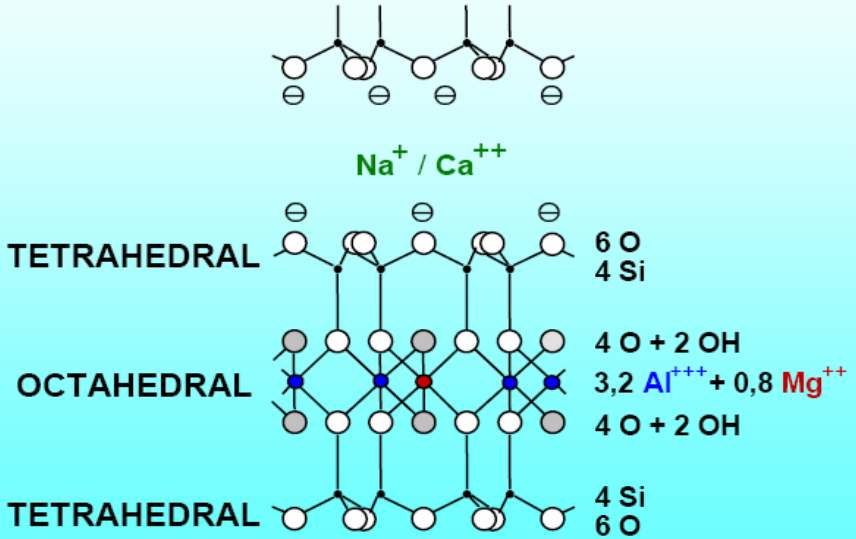
- Currently prefered nanoclay is **montmorillonite (MMT),** whose ***individual platelets are 1 nm thick*** and of the order of one micron in diameter, giving them an aspect ratio of about 1000:1.
- Main (US) suppliers of MMT and modified MMT: **Nanocore Inc.** and **Southern Clay Products.**

Montmorillonite clay: the most important current nanofiller





Structure of MONTMORILLONITE: $[(Al_{3,2}\ Mg_{0,8})\ (Si_8)O_{20}\ (OH)_4\ X_{0,8}]$

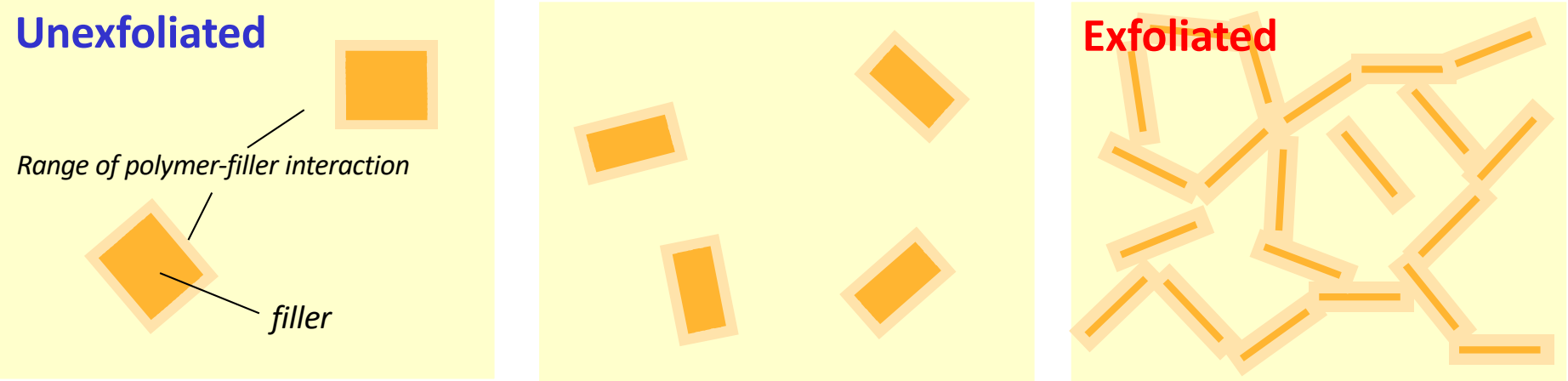


Regular stacks of 1 nm thick layers held together by ionic interactions

Clay-based thermoplastic nanocomposites

Exfoliation of layered silicates in a polymer matrix . . .

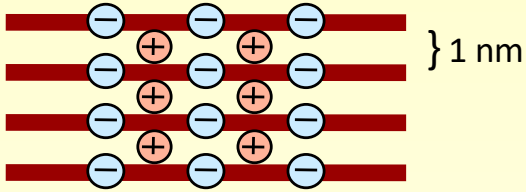
. . . high surface to volume ratios, large aspect ratios, ***percolation at low loadings***



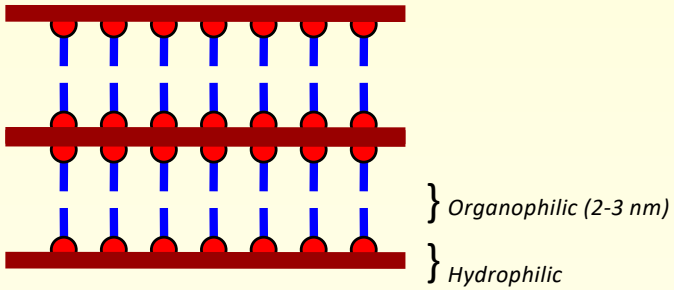
Goal: significantly modified physical properties

Manufacturing clay-based nanocomposites

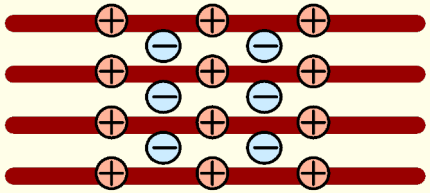
Natural clays (e.g. montmorillonite)



Ion exchange with organic modifiers



Synthetic silicates (e.g. hydrotalcite)



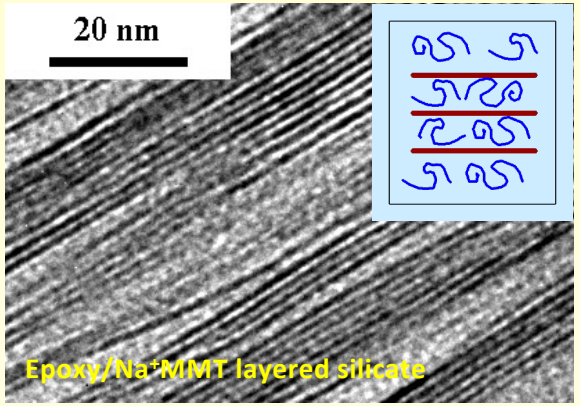
Clay/organo-clay
+
Polymer

- **Solution processing***
- **Melt mixing**
- ***In situ* polymerisation**

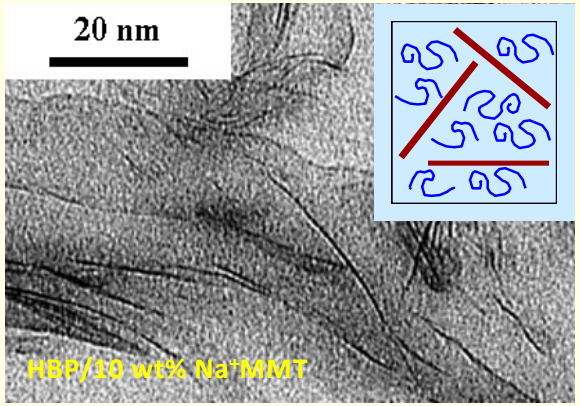
**Not used commercially for thermoplastics*

Nanocomposite

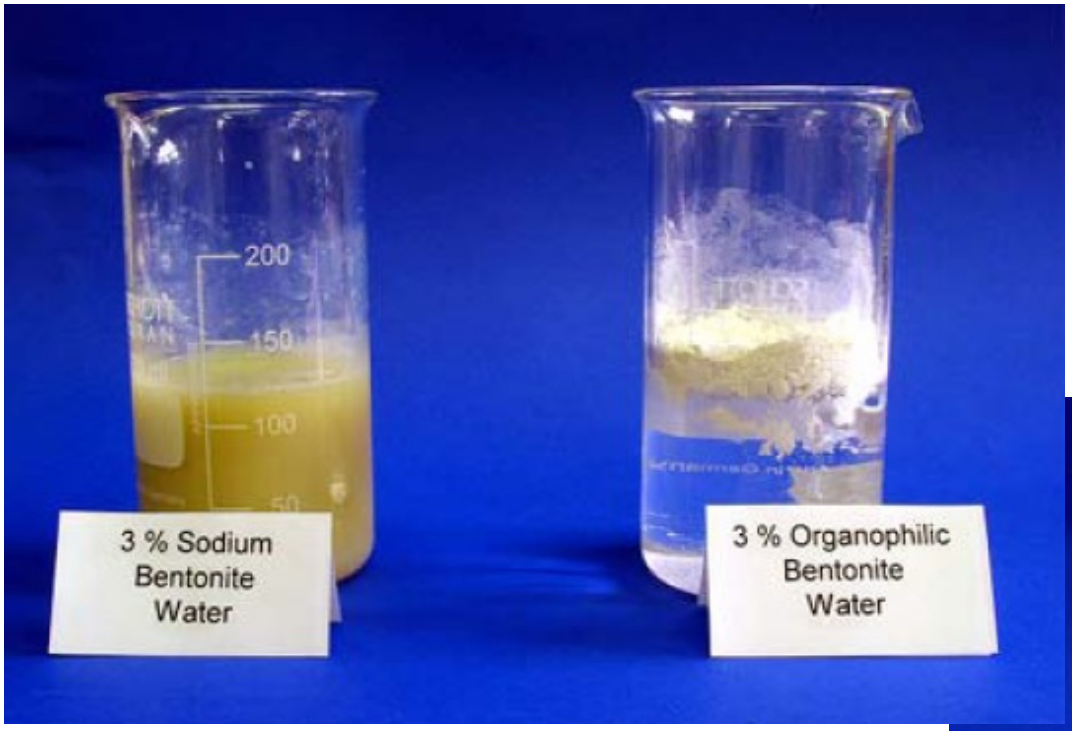
"Intercalated"

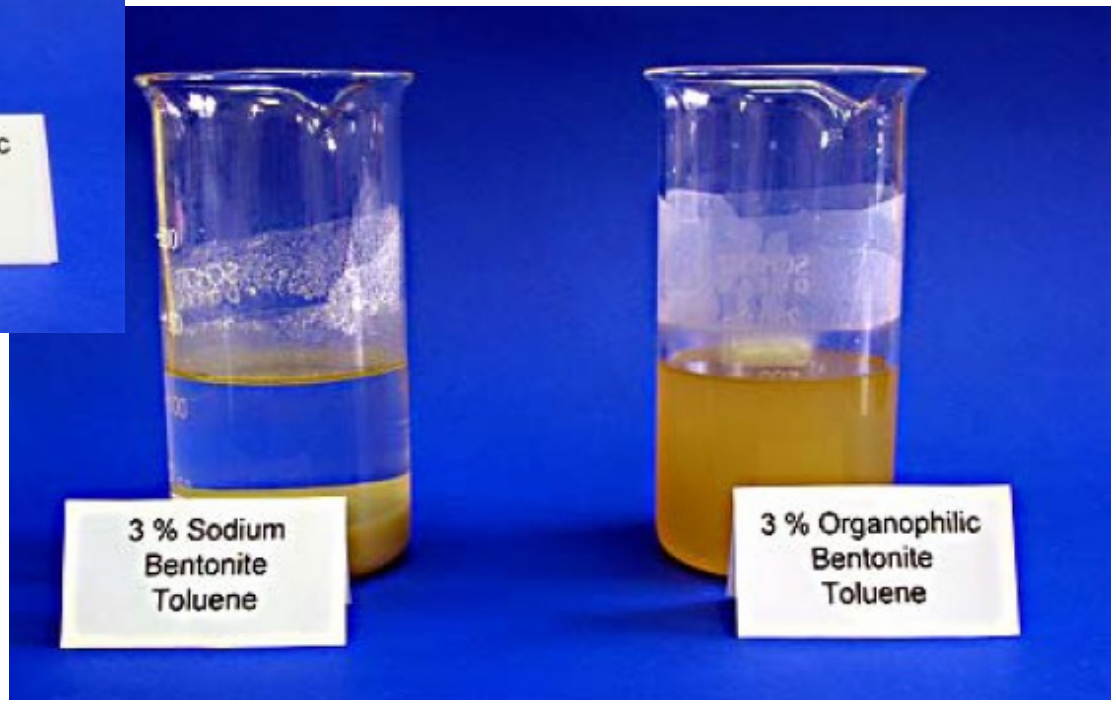


"Exfoliated"

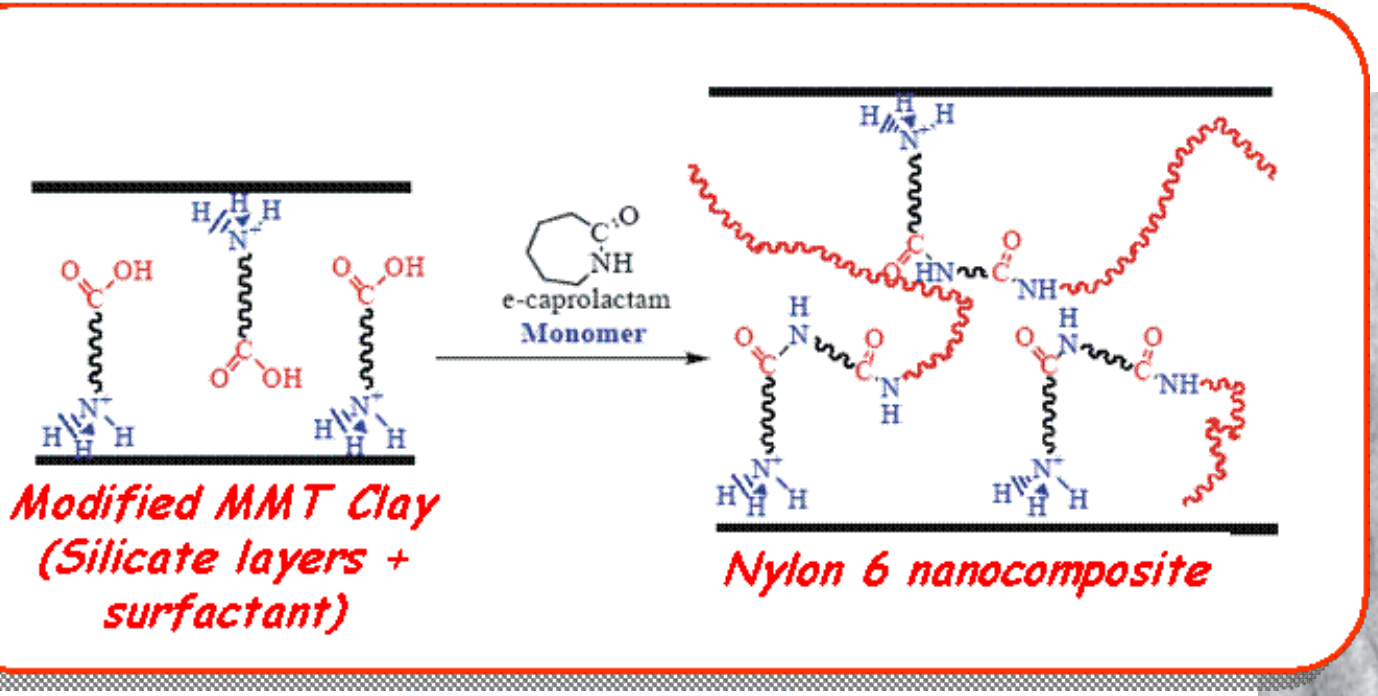


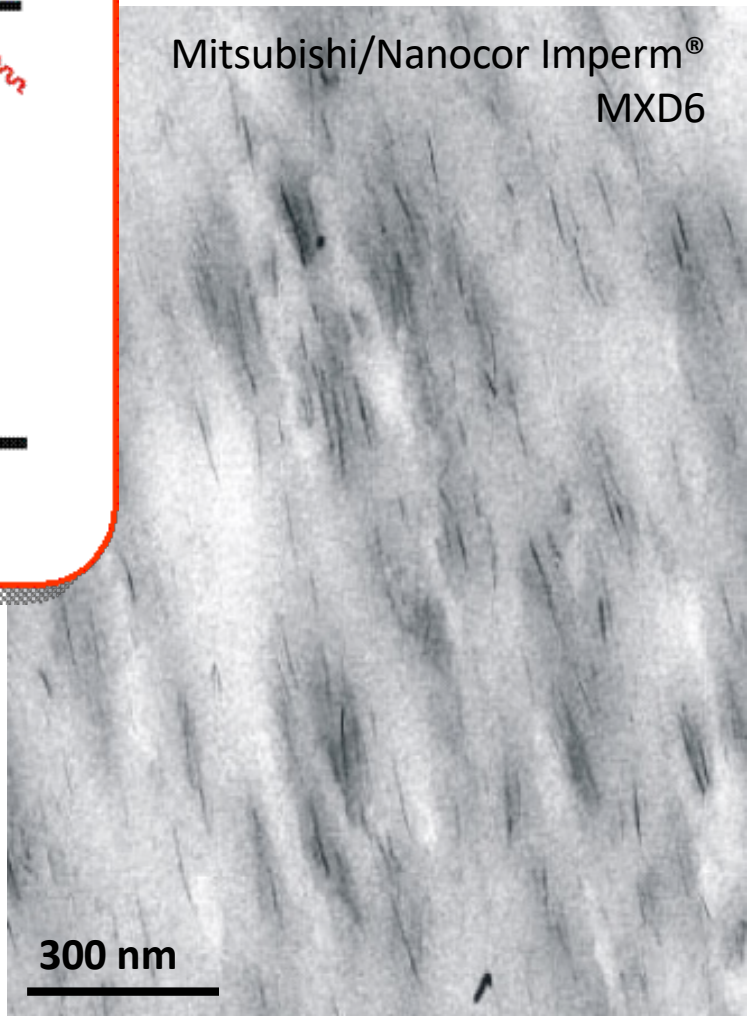
Practical demonstration of effect of organic modifiers





In situ Nanocomposites – Synthesis from monomer + clay



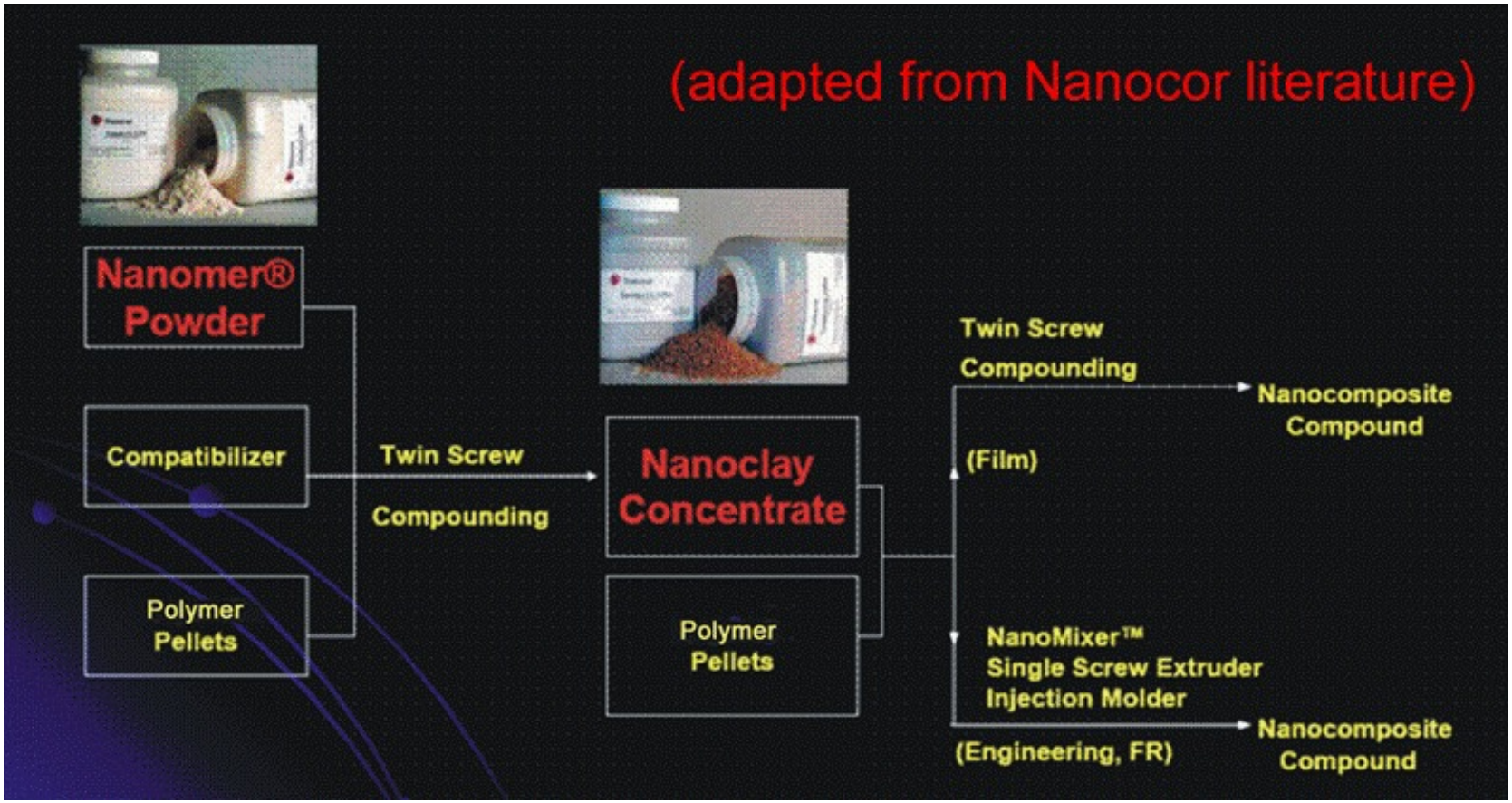


Toyota *technology licensed to* ***Nanocor***, ***Ube***,
sublicensed to other producers:

Ube ("NCH"), Unitika (Nylon M2350), Bayer (Durethan), Mitsubishi, Allied Signal etc.

Barrier films (packaging), structural mouldings (e.g. car parts, knife handles, light covers),

Melt compounding – mixing preformed polymer with clay



- Melt compounded PA6 nanocomposites now available as injection, film grades (**RTP Co**)
- "NPC" concentrate (**Nanocor**) allows compounders to produce a nylon 6 compound with about 90% of property levels achieved by the *in-situ* route

Polyolefin Nanocomposites (PP, TPO's, TPE's)

- Unlike nylon 6 nanocomposites, ***commercial polyolefin nanocomposites are not available through resin producers.*** Rather they are ***offered by independent compounders*** or produced at customer locations, using masterbatches supplied by masterbatch producers. ***Masterbatches available from Clariant Corporation and RTP Co., among others***.
- Masterbatches contain 40-50 wt% organically modified clay
- Nanocomposites contain up to 6 wt% clay
- Polyolefin-type materials have a wide range of hydrophobicity, so a specific grade of clay must be matched to a specific resin grade.

Mechanical and barrier improvements currently drive polyolefin nanocomposite use – *but* need for compatibiliser (usually MAH-grafted PP)

Basic properties of clay-based nanocomposites

Thermomechanical properties: *"in situ"* polyamides

The ***in situ*** material first developed by **Toyota** was claimed to have the following property improvements (RT/ambient humidity, about 5 wt% clay):

- 40 % higher tensile strength
- 68 % higher tensile modulus
- 60 % higher flexural strength
- 126 % higher flexural modulus
- Heat distortion temperature (HDT) increased from 65 °C (nylon-6) to 152 °C

Data given below are for a representative commercial system for diffferent clay contents (RT/ambient humidity, data from **Nanocor**):

Nanomer [wt %]	Flexural Modulus [MPa]	Tensile Modulus [MPa]	Heat distortion temperature [°C]
0	3404	3117	56
2	3474	4220	125
4	4578	4897	131
6	5388 (+90%)	5875	136

Thermomechanical properties: compounded polyamides

Supplier's data for a latest generation **melt compounded** PA6 nanocomposite from **RTP Co.**, *compared with conventional fillers:*

	Nylon 6	Nylon 6 5% Organo-Clay	Nylon 6 30% Mineral	Nylon 6 30% Glass
Tensile Strength [MPa]	60	92	65	96
Flex. Modulus [MPa]	2900	4300	4800	4100
HDT (at 1820 kPa)	65 °C	102 °C	92 °C	190 °C
Specific Gravity	1.13	1.14	1.36	1.35

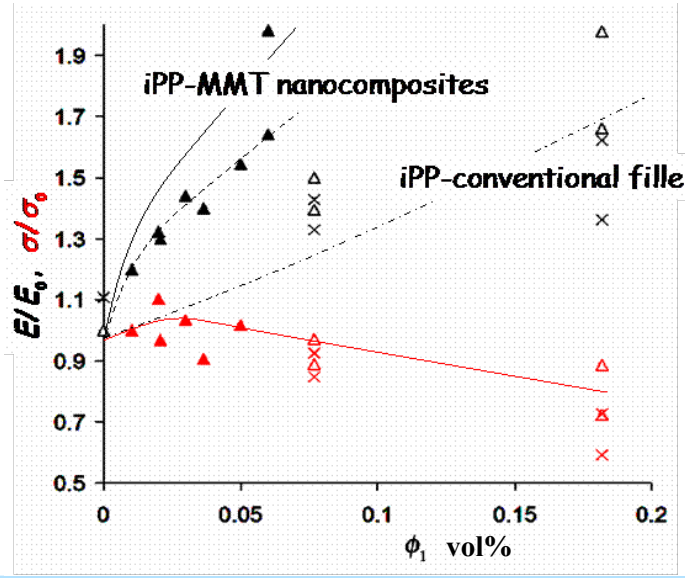
Representative values for different polyamides compounded with the **Nanocor** NPC concentrate:

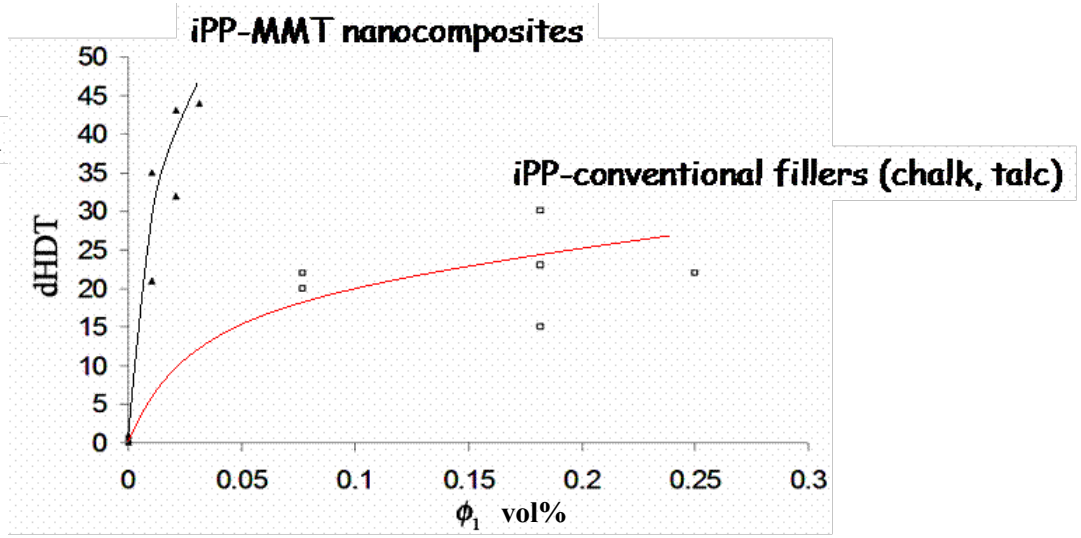
	NPC Content	Flexural Modulus [MPa]	HDT [°C]
Zytel 101 (PA66)	0	3413	68
	20%	5062	93
PA6	0	2480	53
	20%	3545	107

Thermomechanical properties: polypropylene mouldings

PP grade	Clay content [wt%]	Tensile Modulus [MPa]	HDT [°C]
Homopolymer	0	1412	87
(low melt flow)	6	2804 (+98%)	116
Homopolymer	0	1327	86
(medium melt flow)	6	2180 (+64%)	109

*(All melt compounded with NPC concentrate - source: **Nanocor**)*





Why such improvements? Micromechanical models for MMT dispersions

Basic Halpin-Tsai predictions for aligned discs with aspect ratio α

$$E \approx E_0\left(\frac{1+\zeta\eta\phi_1}{1-\eta\phi_1}\right) \qquad \eta = \frac{E_1/E_0 - 1}{E_1/E_0 + \zeta}$$

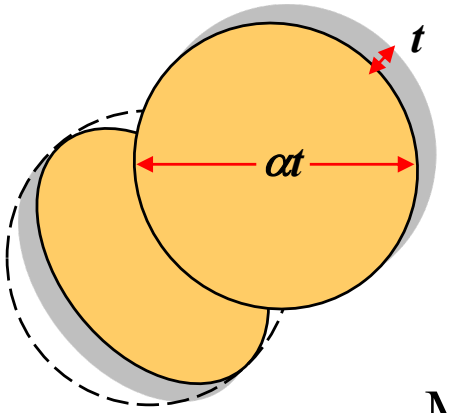
$\zeta = 2\alpha$ ⇨ *longitudinal modulus*
or
$\zeta = 2$ ⇨ *transverse modulus*

Modulus of an isotropic composite

$$E = 0.49E_l + 0.51E_t$$

For typical MMT particle aspect ratios, α, of up to 1'000, composite modulus, E, should increase as roughly $\alpha\phi_1$ ($E_1 \approx 120$ GPa >> $E_o \approx 2$ GPa (most thermoplastics)) – huge improvement at large ϕ_1 !?

Is this possible in practice for isotropic mouldings?



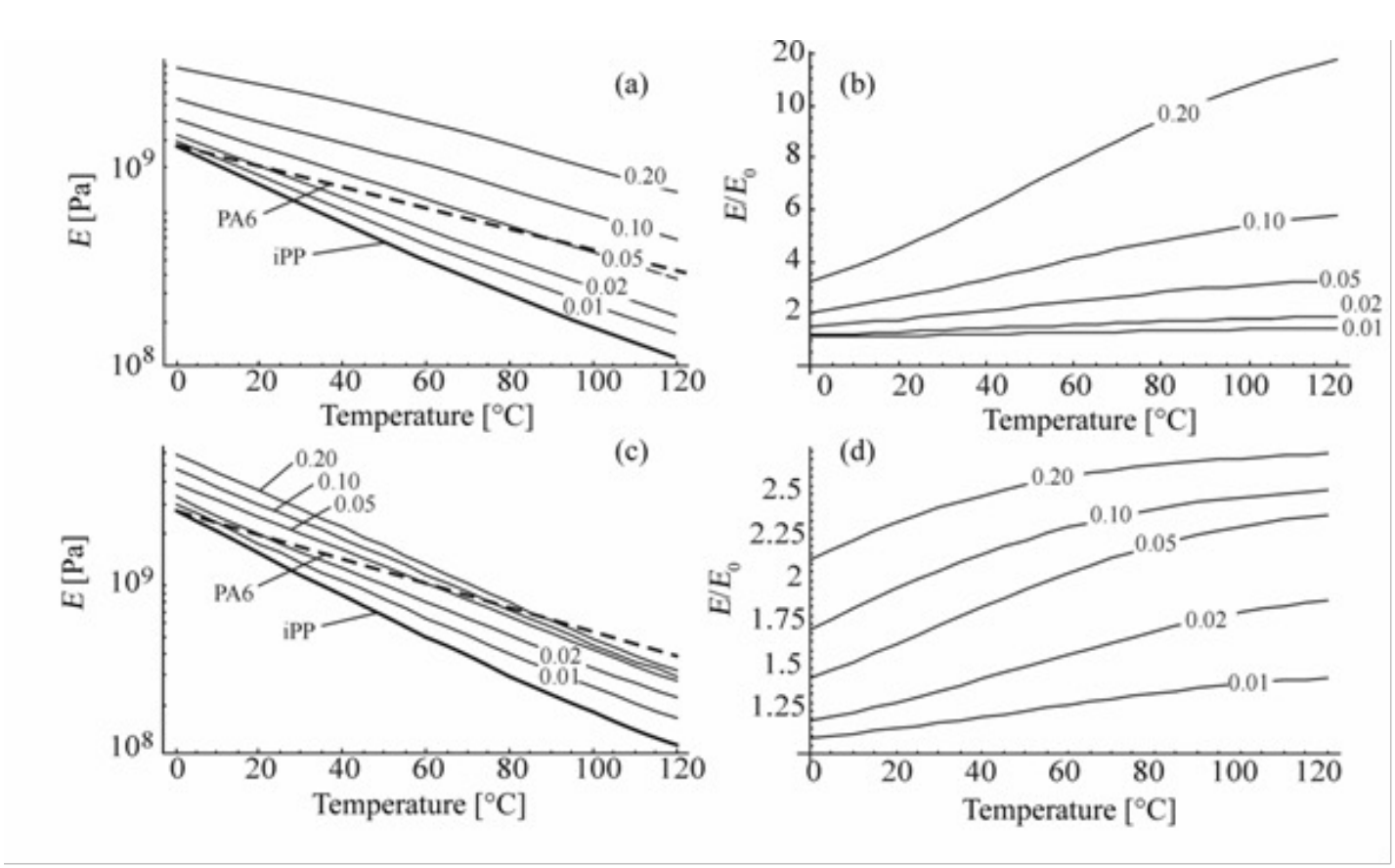
$$\text{Excluded volume} = \frac{\pi^2 (\alpha t)^3}{8}$$

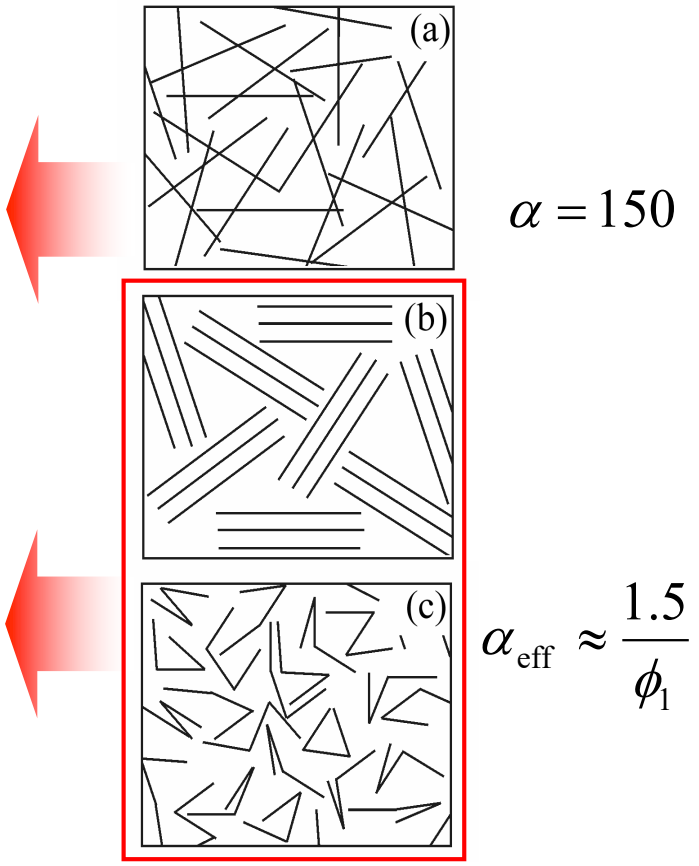
$$\text{Maximum packing fraction } \phi_{\max}^{\alpha} = \frac{1}{1.29 + 0.0598\alpha} \approx \frac{1.5}{\alpha}$$

For concentrations greater than ϕ_{max}, the platelets must either agglomerate or fold, and the effective aspect ratio will be limited to

$$\alpha_{\text{eff}} \approx \frac{1.5}{\phi_1}$$

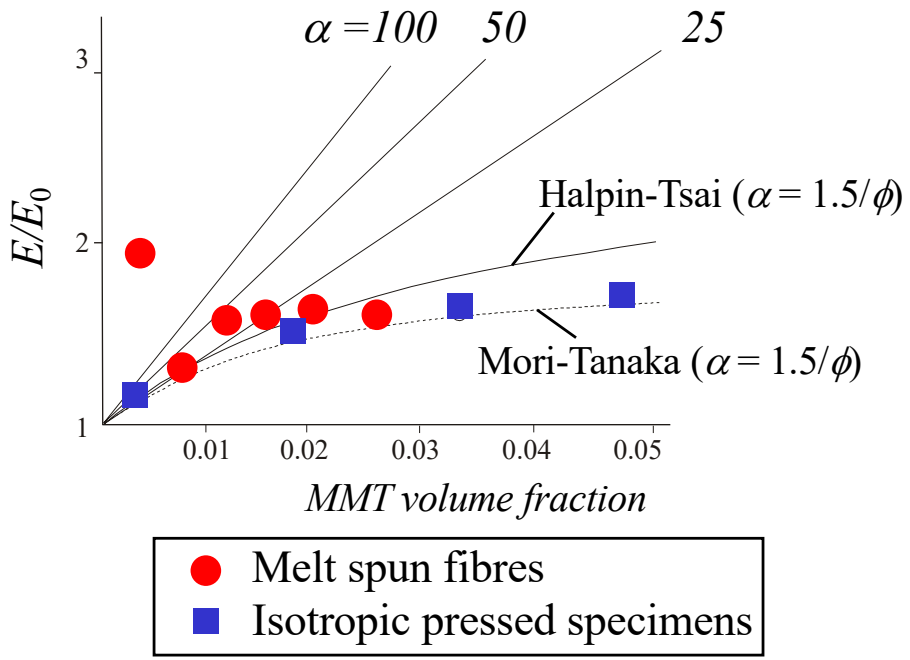
Predictions for iPP as a function of temperature





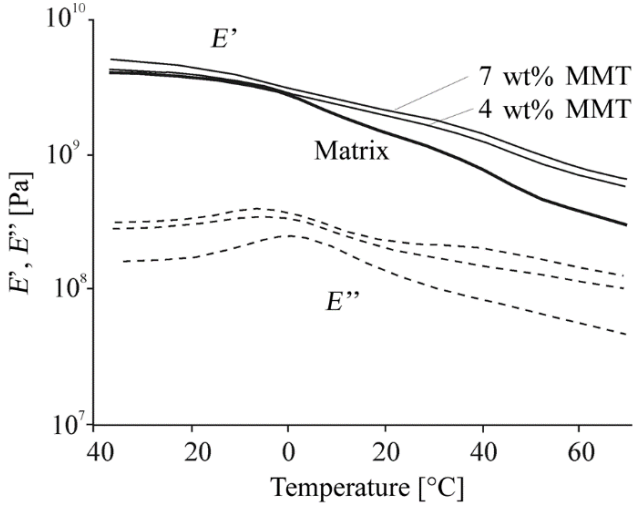
Estimates of (a) E and (b) E/E_0 in iPP as a function of T for different volume fractions of randomly oriented rigid exfoliated MMT platelets, taking $\alpha \approx 150$ and using experimental data for E_0; (c) and (d) show E and E/E_0 recalculated taking $\alpha = 1.5/\phi_1$. Data for dry polyamide 6 are also shown in (a) and (c) for comparison (dotted lines).

Comparison with data for iPP nanocomposites

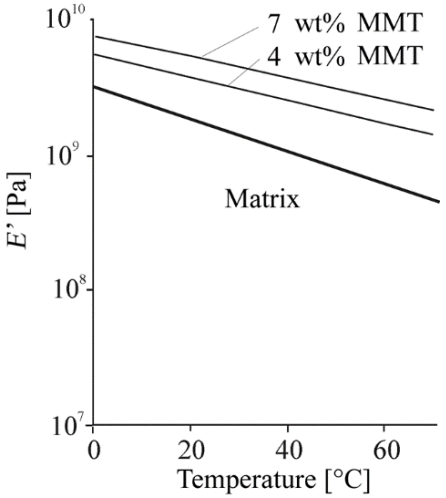


Room temperature response

Experimental data (DMS)

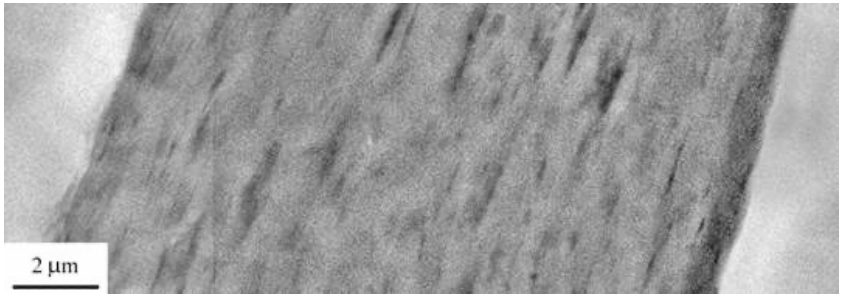


Halpin-Tsai ($\alpha = 100$)



Fibres at different *T*

- ***Reasonable agreement between Halpin-Tsai (with restrictions on α) & data for isotropic specimens***
- ***Qualitative prediction of* T *dependence of fibre modulus; quantitative agreement poor – incomplete exfoliation? Non-uniform fibre sections?***



Microstructure of a spun fibre with 7 wt% MMT

Some intermediate conclusions

- Highly exfoliated MMT (high aspect ratio, high stiffness) should lead to outstanding stiffness reinforcement
- In practice, reinforcement in mouldings is limited owing to local alignment, agglomeration and/or bending of the nanoparticles above a certain critical concentration
- Not much benefit from concentrations above about 5 vol% (or about 10 wt%) if random orientation – explains. the concentration range of commercial nanocomposites
- Could we align the nanoparticles? Possible, but difficult to achieve high degrees of alignment in mouldings

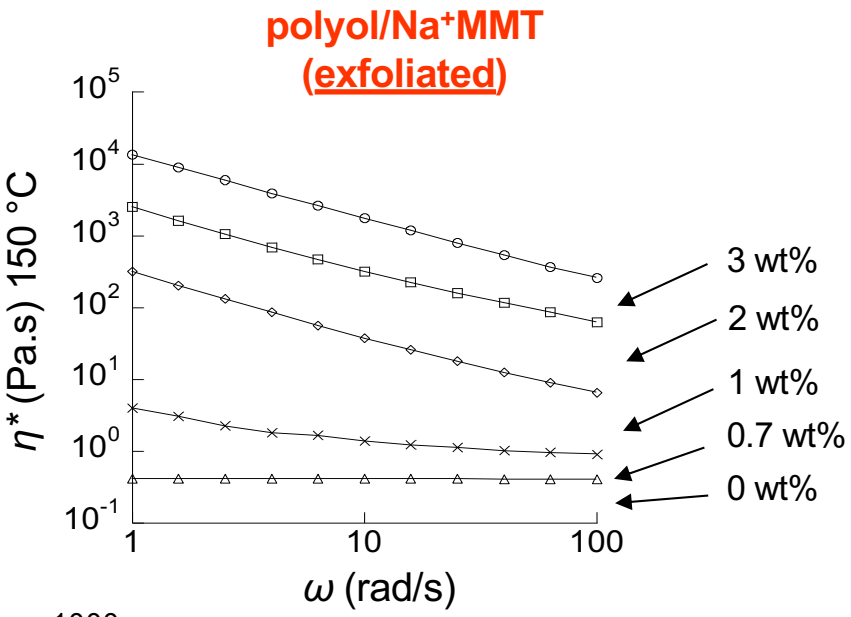
Other limitations: thermal stability during processing

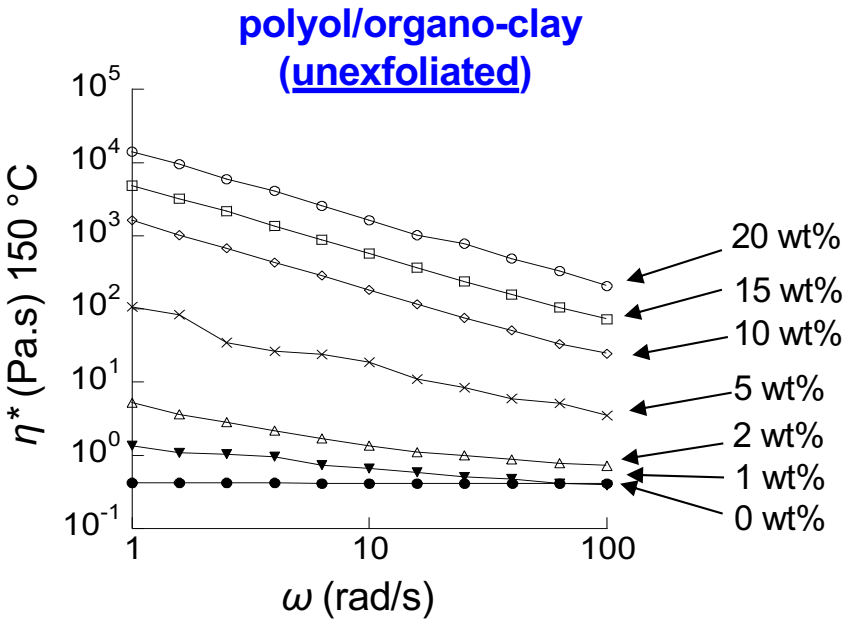
Limitations of current nanoclay formulations

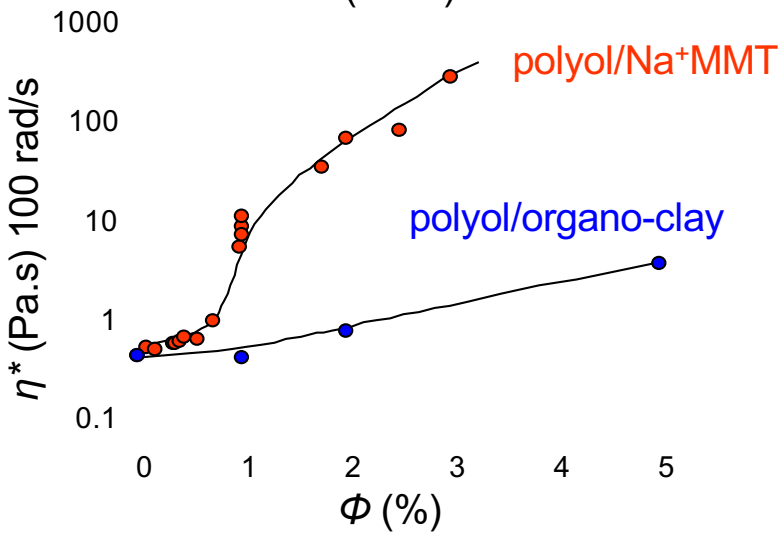
- ***Hoffman elimination***
- ***Alkyl chain scission***
- ***Processing temperatures < 250 °C***

Formulations with new heat-resistant chemistries under development

Rheological behaviour: MMT/low viscosity resins







Data here for a polyurethane precursor and two types of clay: shear thinning behavior and strong increase in viscosity at very low exfoliated clay contents

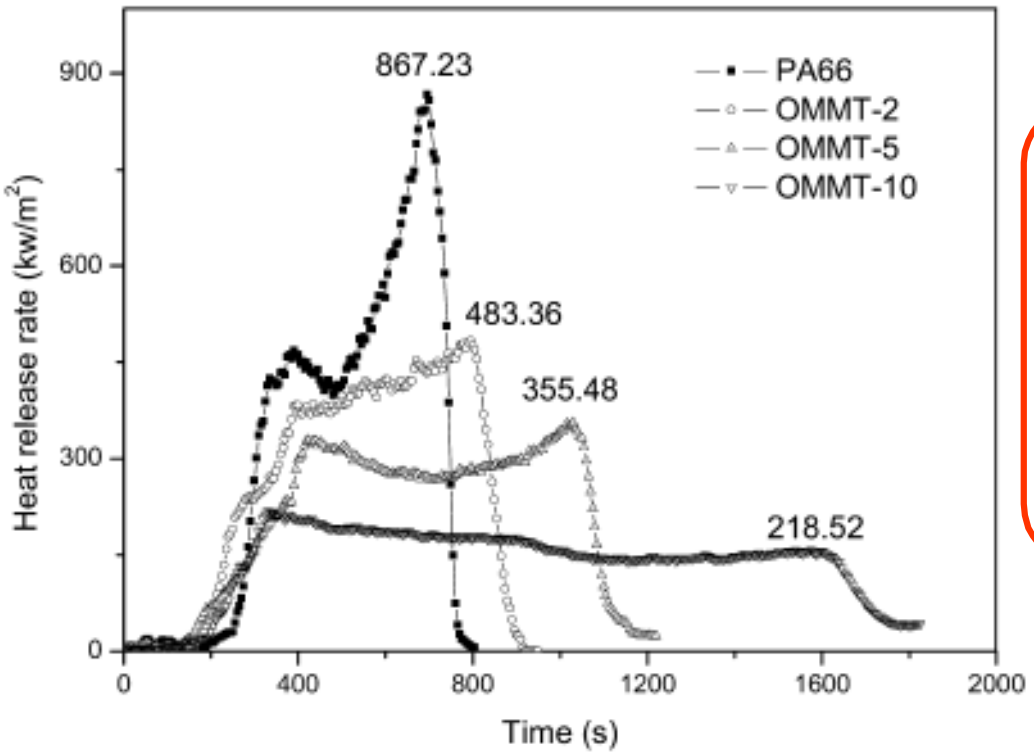
Potential processing problems for thermosets (we need low viscosity e.g. for mixing with hardener), less critical for thermoplastics (high initial viscosity)

Flame retardant (FR) properties

Clay as a "Nano fire extinguisher" (data from NIST)

- ***Rate of heat release*** (RHR) in cone calorimetry tests for nylon 6 nanocomposites containing 5% clay is ***about 60% lower*** than for pure nylon 6.
- ***No increase in carbon monoxide or soot*** generated during combustion.
- Mechanism of improved nanocomposite FR is not fully understood, but a ***durable carbon-silicate char*** is observed to form very rapidly in the burn tests.
- ***Similar results for other polymers***: RHR reduction of more than 75% with the PP-g-MA nanocomposite containing 4% silicate.
- Nano-clay in combination with reduced amounts of conventional FR fillers (e.g. MgOH) are likely to meet FR standards - ***cheaper, environmentally friendly solutions FR materials***

Typical Cone Calorimetry Results (PA66)



	PA66	2 wt% OMMT	5 wt% OMMT	10 wt% OMMT	5 wt% MMT
Peak HRR [kW/m²]	802.4	496.1	335.5	209.4	537.8
Total heat	249.2	245.0	247.5	247.8	235.3
Ignition time [s]	169	163	139	152	127

Heat release rates (HRR) for PA66 and different organically modified MMT (OMMT) contents (heat flux 35 kW/m²)

*Thermal stability and flammability of polyamide 66/montmorillonite nanocomposites, Huaili Qina, Quansheng Sub, Shimin Zhanga, Bin Zhaoa, Mingshu Yanga, Polymer **44** (2003) 7533–7538*

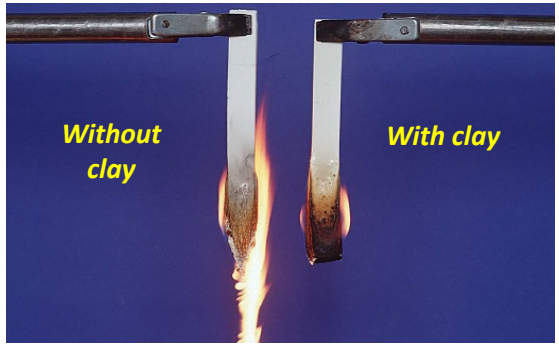
Comparison with PA6, PP nanocomposites

Material	*Residue [%]*	*Peak HRR [kW/m²]*
PA6	1	1010
PA6/2wt% OMMT	3	245
PA6/5wt% OMMT	6	378
PP	0	1525
PP/2 wt% OMMT	5	450
PP/5wt% OMMT	-	305

Peak heat release rates (HRR) for PP and PA6 and different organically modified MMT (OMMT) contents (heat flux 35 kW/m²)

In both cases, significant drop in HRR, but also decrease in ignition times on MMT addition

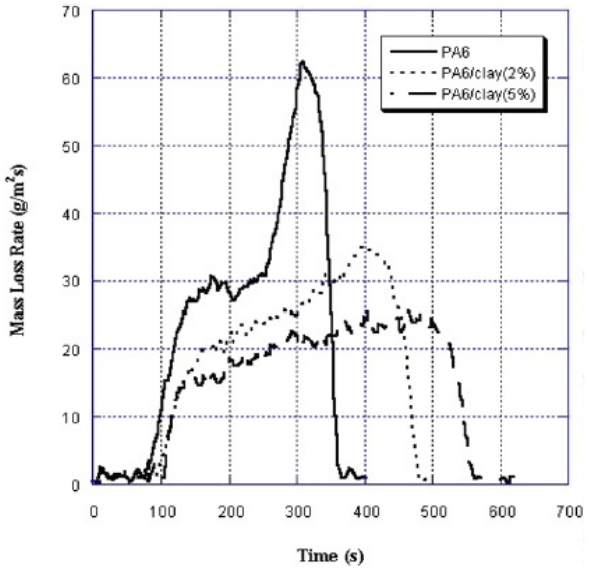
Also, antidrip effect, important for limiting spread of fires

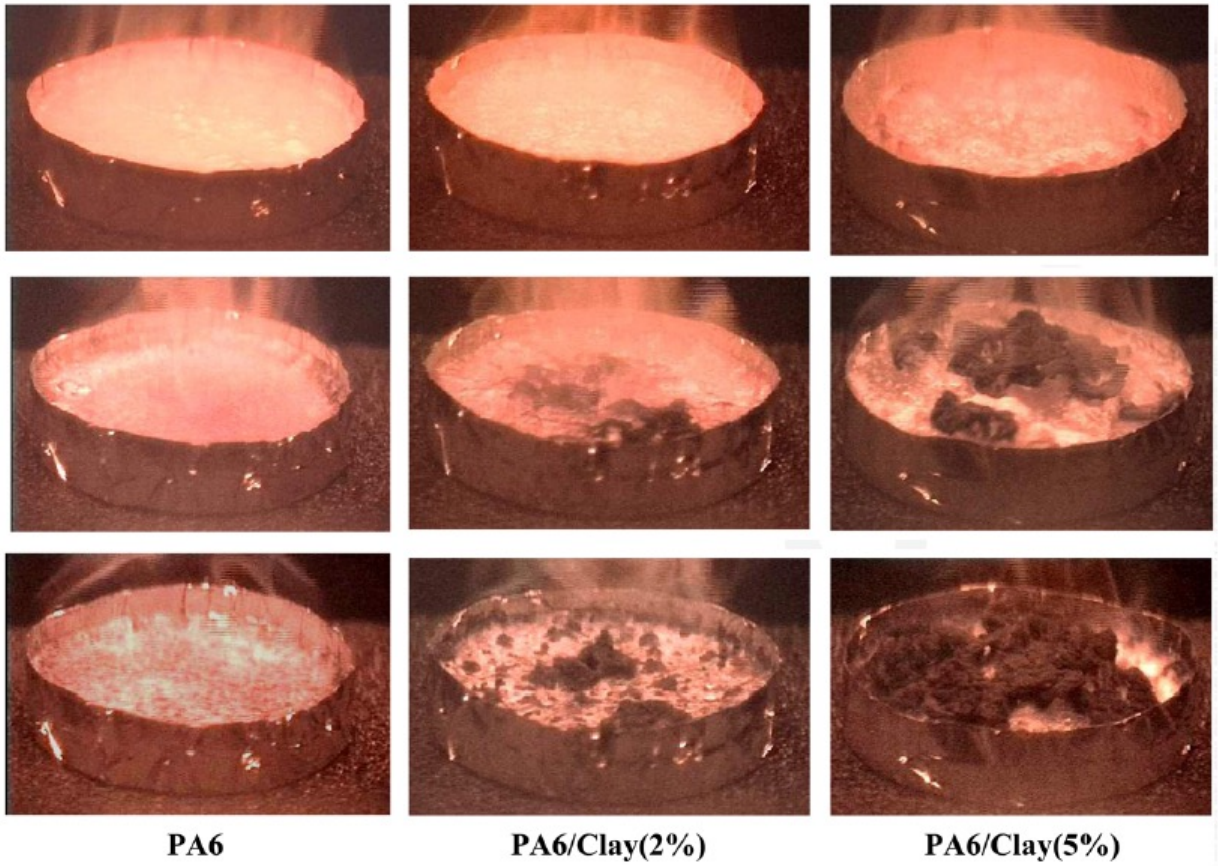


Possible Mechanisms?

Reduction in peak HRR is achieved by the ***formation of. protective flocs*** at the sample surface (80 % MMT)

Accumulation of MMT due to either ***degradation*** of resin or ***migration of MMT*** to the sample surface (convective flow)

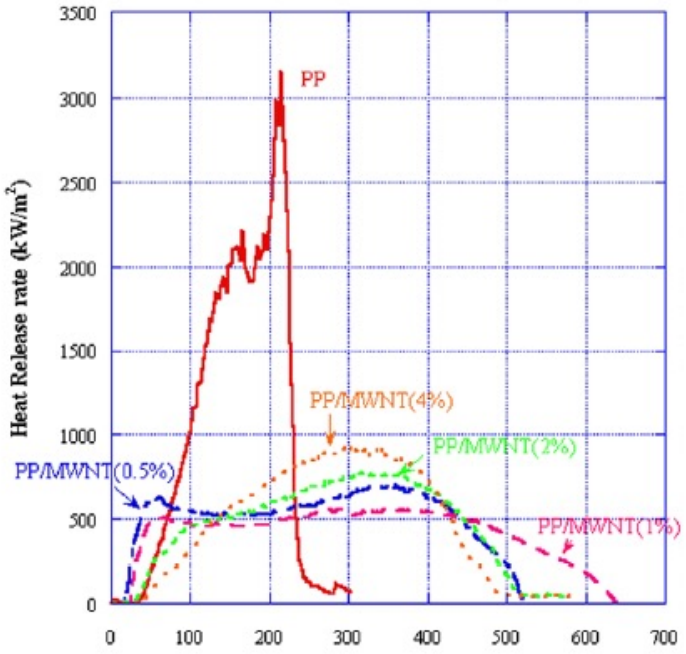




100, 200 and 400 s in nitrogen at 50 kW/m²

Flame retardant mechanism of polyamide 6–clay nanocomposites, Takashi Kashiwagia, Richard H. Harris Jra, Xin Zhangb, R.M. Briberb, Bani H. Ciprianoc, Srinivasa R. Raghavanc, Walid H. Awada, John R. Shields, Polymer 45 (2004) , 881-891

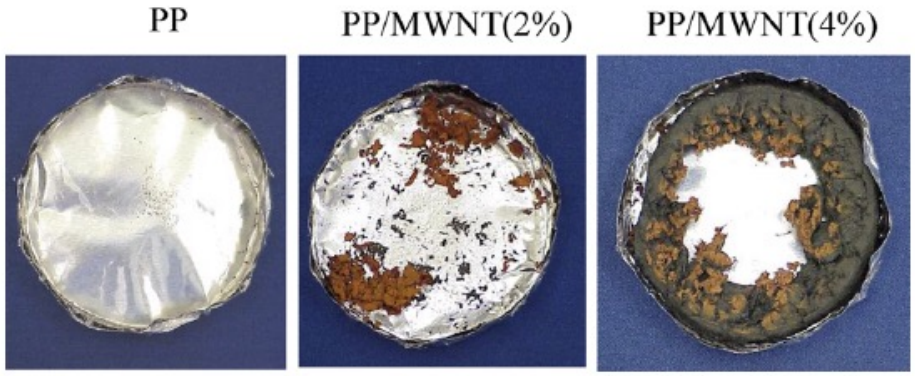
Similar effects with other (nano)fillers, e.g. Carbon nanotubes



Heat release rates (HRR) for PP with different CNT contents (heat flux 50 kW/m²)

Reduction in peak HRR again by ***formation of protective flocs***; ignition times decrease with CNT content as previously

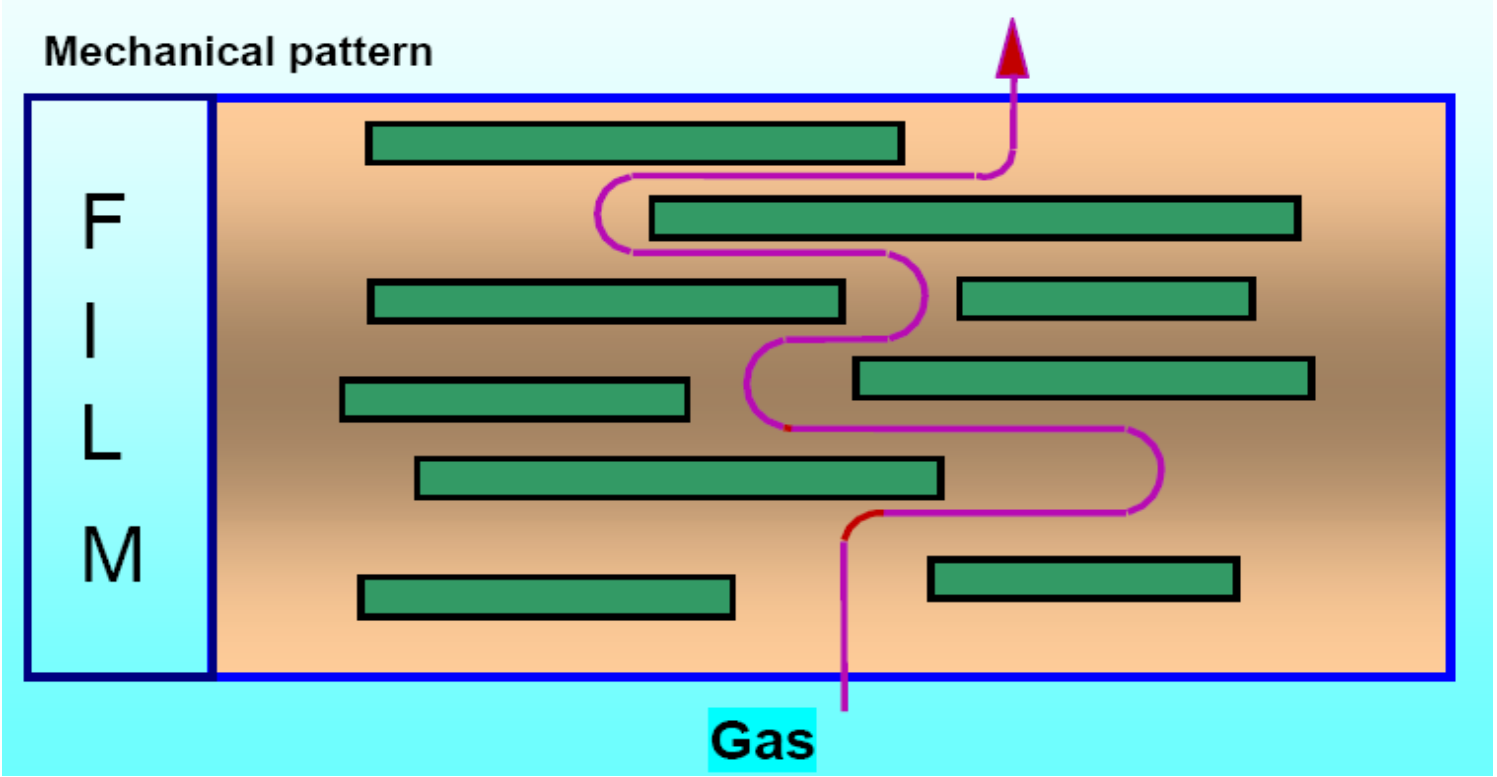
Thermal and flammability properties of polypropylene/carbon nanotube nanocomposites, Takashi Kashiwagia, Eric Grulke, Jenny Hilding, Kartrina Groth, Richard Harris, Kathryn Butler, John Shields, Semen Karchenko, Jack Douglas, Polymer 45 (2004) 4227-4239



Residues after flame-out and further 2 minutes heating (heat flux 50 kW/m²)

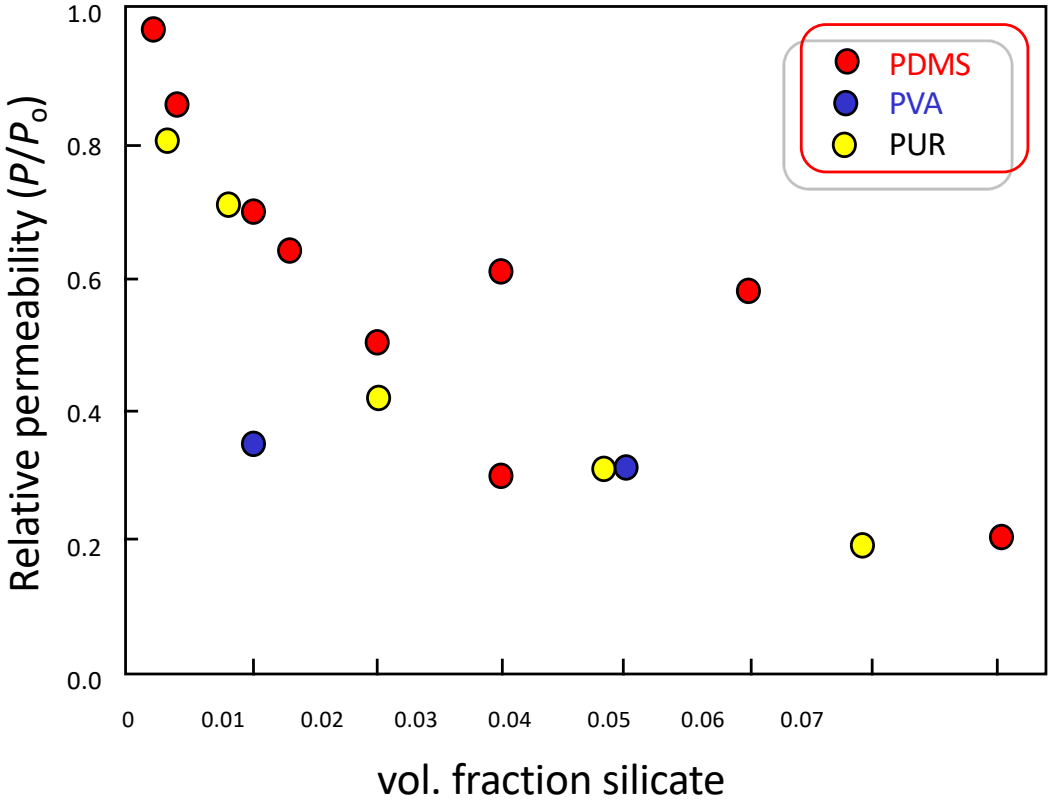
Barrier property improvements: theory

Improvement of barrier properties with montmorillonite layers oriented perpendicular to the diffusion path: "tortuosity effect"

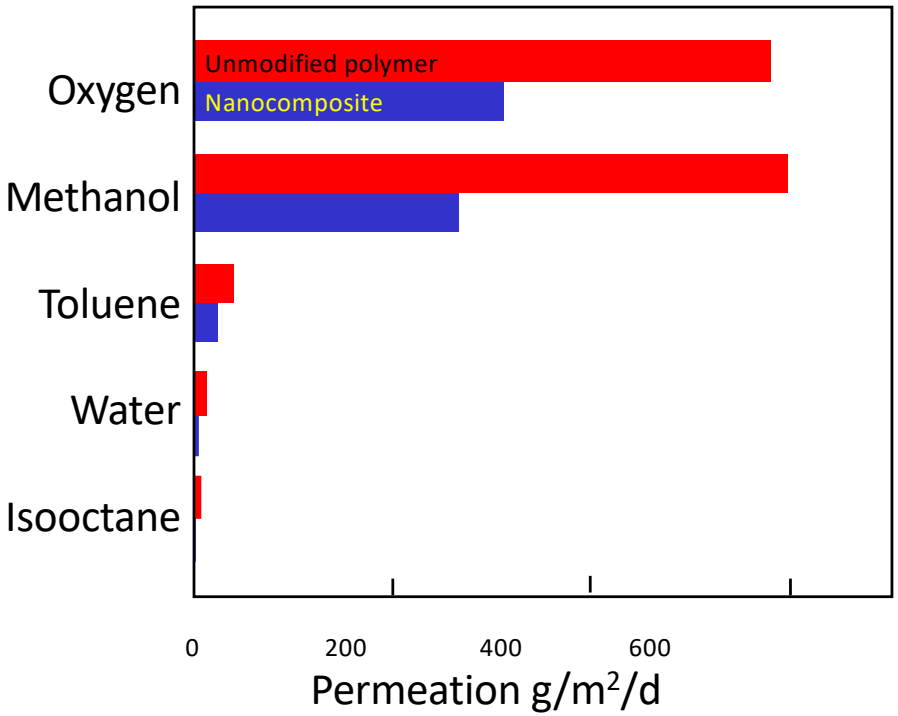


$$D = D_0 / \tau \quad \text{where} \quad \tau = 1 + \frac{\text{filler aspect ratio}}{2} \times \text{filler volume fraction}$$

Barrier property improvements: practice



Water vapour permeability through various polymer/MMT nanocomposites as a function of silicate volume fraction



Permeation of different gases in polyamide 12 and PA12/MMT nanocomposites (data from EMS-chemie)

Conclusions

A major advantage of thermoplastic nanocomposites is the ***increase in heat deflection temperatures (HDT)*** over the unfilled resin, comparable to that obtained with 20-30% load of a standard mineral-filled compound. Particularly for under-the-hood automotive applications, ***engineers can maintain the HDT while reducing the weight of the component (fuel and energy savings).***

Improved flame retardancy of current interest e.g. for the aeronautics industry, possibility of reducing use of conventional toxic flame retardants

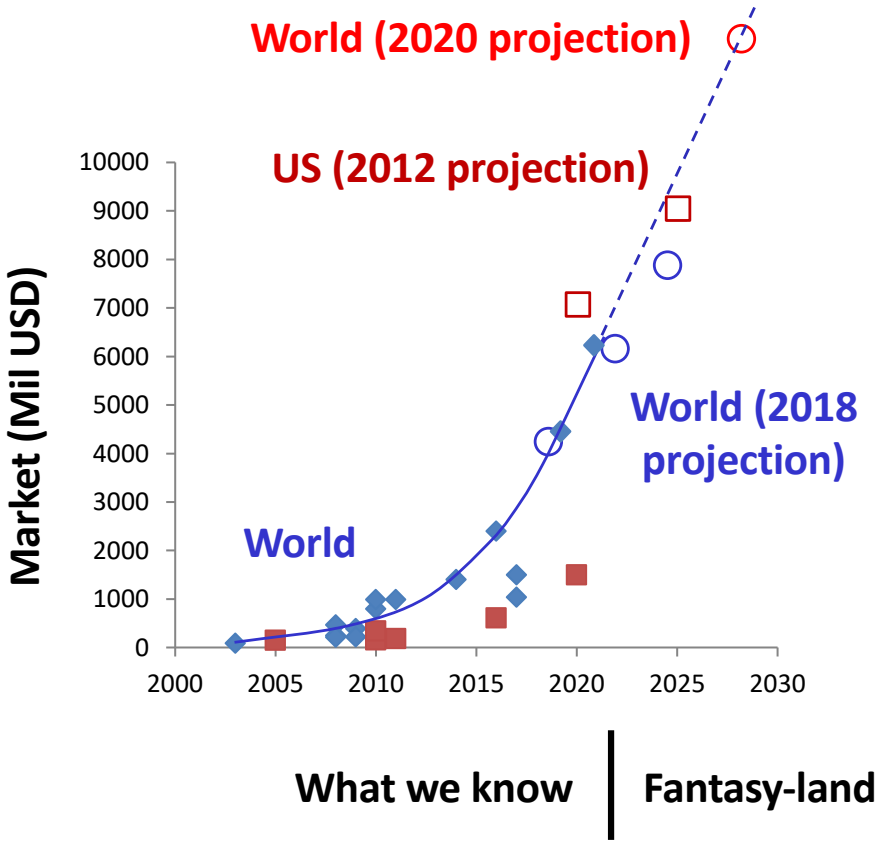
Improved barrier properties
Processing and recycling similar to virgin polymers, better transparency than conventional composites

. . . plus many other benefits specific to particular applications (paintability, surface finish etc.)

Applications

The nanocomposites market: some quotations …

The global nanocomposites market size was USD 4.32 Bn in 2019 and is projected to reach USD 14.34 Bn by 2027 (Fortune, 2020)



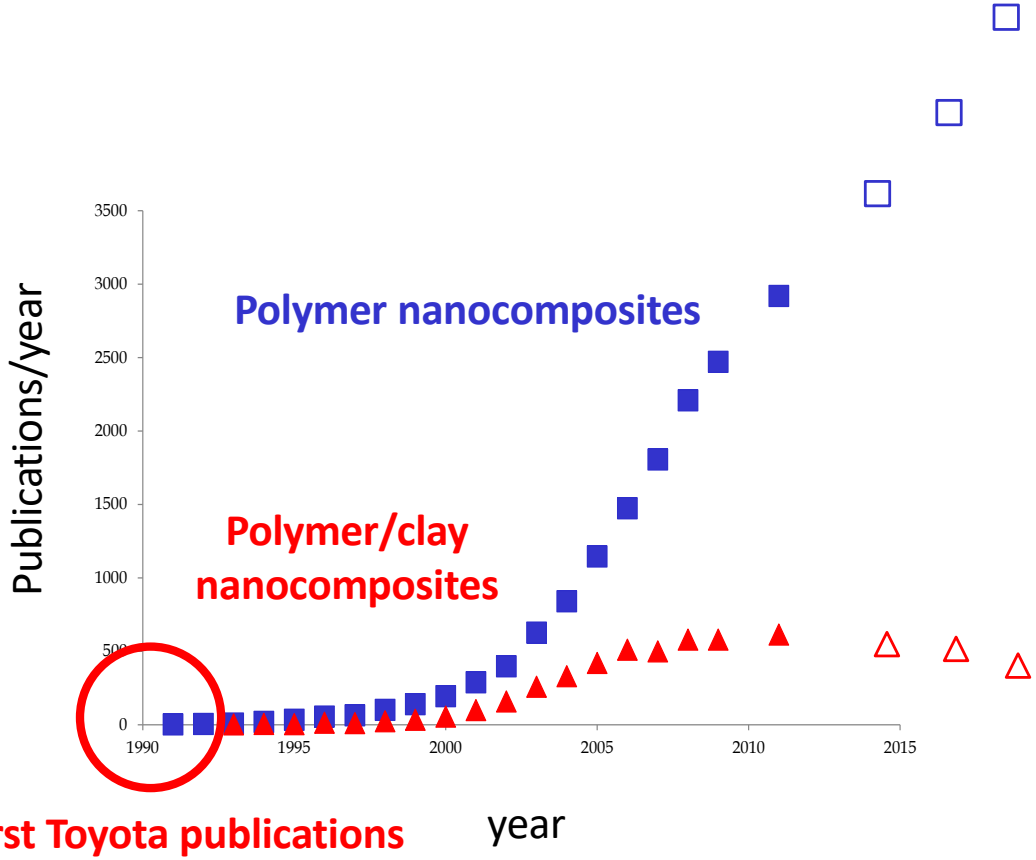
"It is estimated that widespread use of polymer nanocomposites could save over 1.5 billion liters of gasoline annually and reduce carbon dioxide emissions by nearly 10 billion pounds." (MRS Report, 2003)

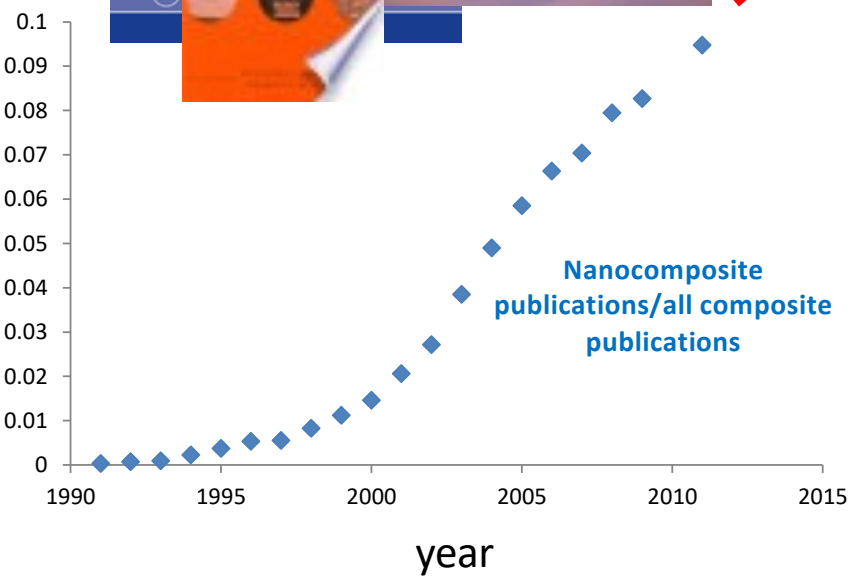
US NANOCOMPOSITES DEMAND (million pounds)				
plastemart.com your trusted business partner	2005	2010	2020	% Annual Growth 2005-2020
Nanocomposites Demand	154	344	7030	29
Thermoplastic	152	329	5600	27
Thermoset	2	15	1430	55

(2009 projection)

EPFL

Academic interest in polymer nanocomposites





Huge academic interest, and increasing industrial interest (although the word "nanocomposites" sometimes perceived to have negative connotations …)

Current applications: transportation (around 15 % of market)

HUMMER H_2 SUT: Nanocomposite TPO

Mass savings of 3 to 21%
- Specific Gravity of 0.92 vs. 0.96-1.13 g/cm3
- Lighter weight reduces cost, less adhesive for attachment

Improved Appearance
- Improved Knit Line Appearance
- Improved Colorability & Paintability
- Sharper Feature Lines & Grain Patterns
- Improved Scratch/Mar Performance

Large Processing Window
- Consistent Physical and Mechanical Properties
- Elimination/Reduction of Tiger Striping

Reduced Paint Delamination

Retains Low Temperature Ductility

Improved Recyclability

Lower Flammability

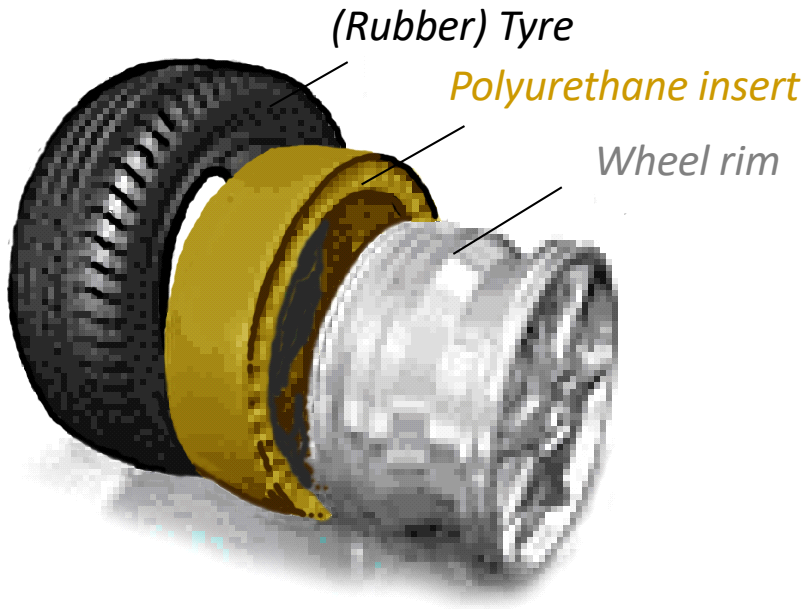
A long shot: polyurethane nanocomposites for tyres?

Fuel emissions: fuel efficiency may increase by more than 3%

Road noise: reduced volume of air, decreasing noise pollution

Weight: total weight of four tyres + insert. Less than five standard tyres (no spare needed)

(The first cars carried up to 6 spare tyres)!

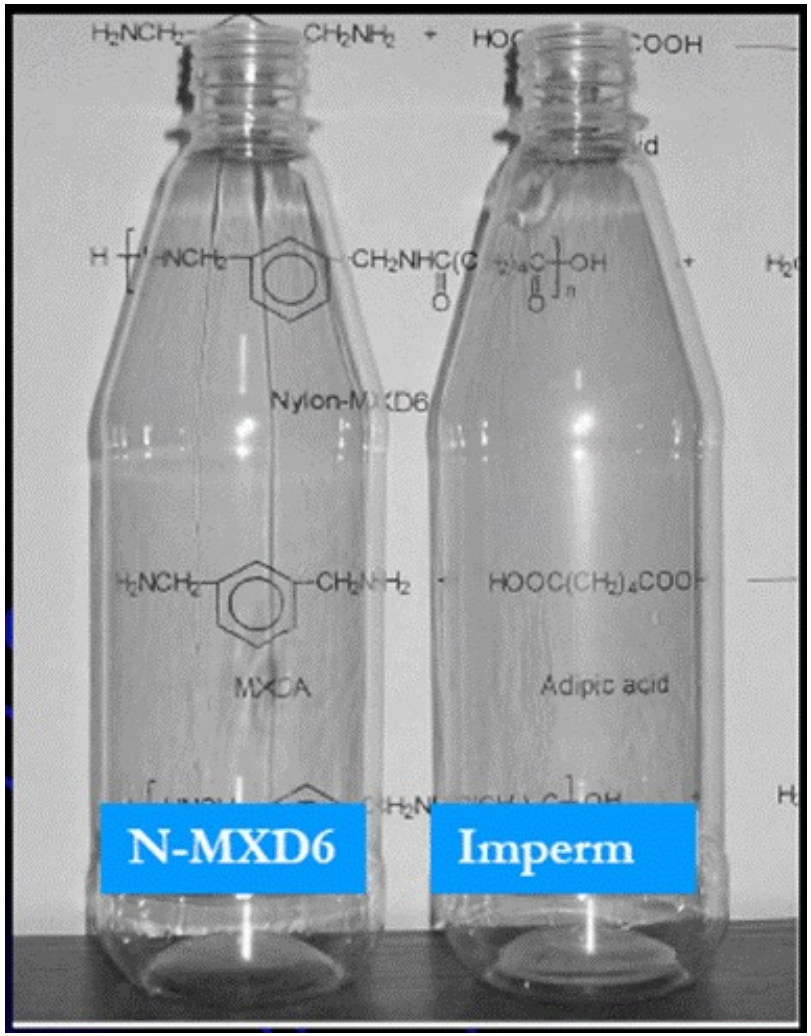


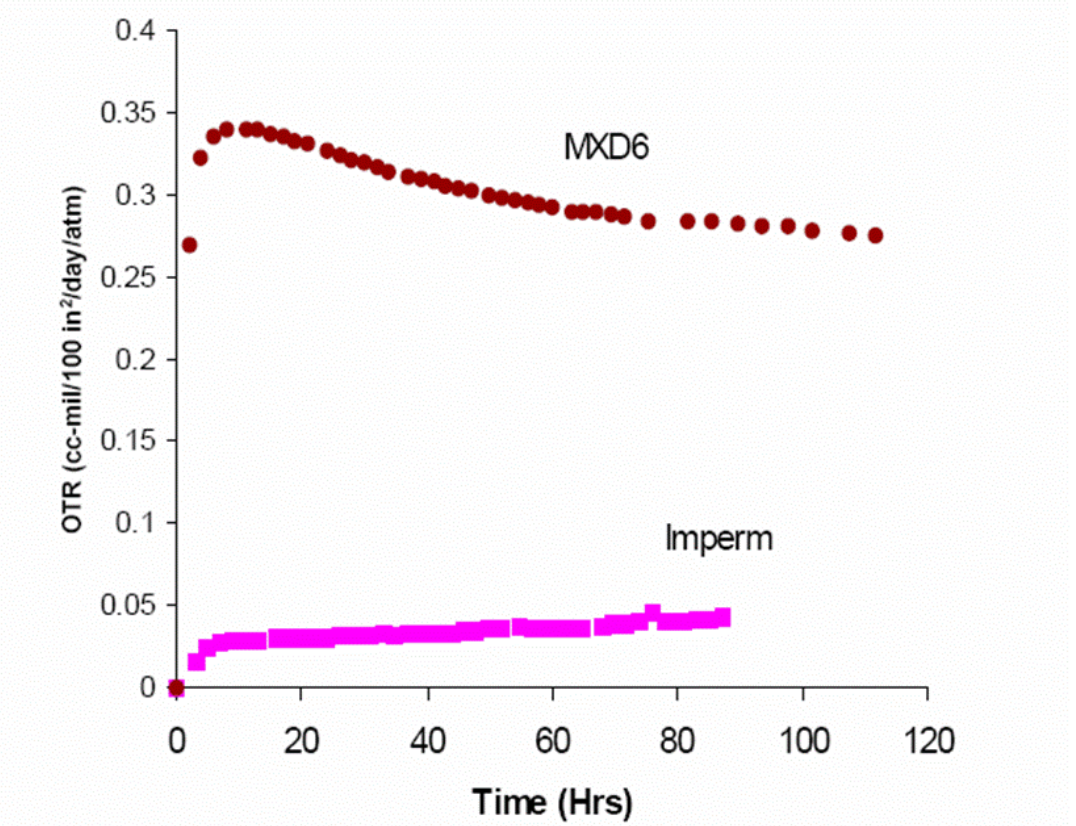
Lightweight nanoreinforced polyurethanes will provide the next generation materials - towards an all PU tyre? *(source Goodyear/Amerityre)*

Replacement of conventional technology by structural reactive injection moulding with reinforced PU

- *9' cycle time - 1/3 labour and **1/10 energy***
- *50% increase in tyre life*
- *Decrease in rolling resistance - **10% fuel efficiency***

Current applications: packaging (around 50 % of market!)

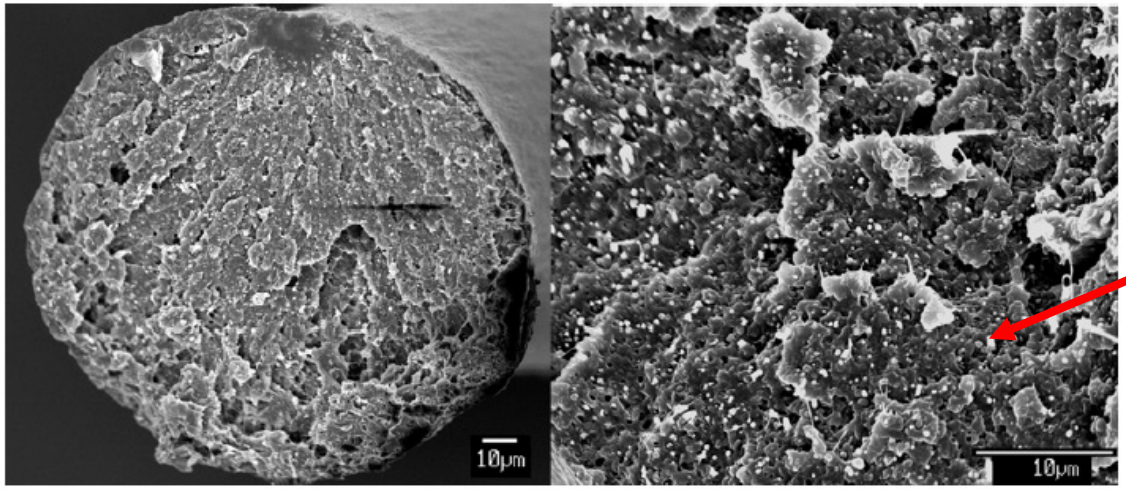


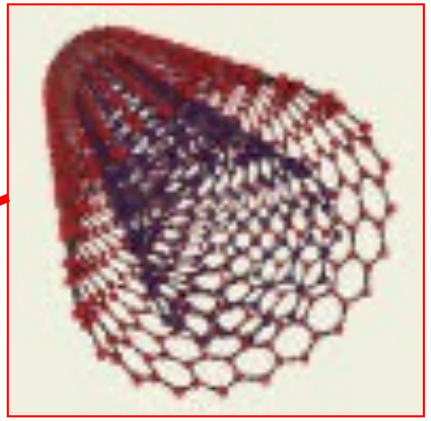


PA6 nanocomposite (Imperm®) compared with PA6 (MXD6) for blow moulded non-pasteurized beer bottle (tri-layer with PET)

Bottle haze 5% (OK for amber tinted bottles), Oxygen transmission > 100 times less than for monolayer PET, shelf-life about 30 weeks

Other polymer nanocomposites (i): PEEK/carbon *nanotubes*



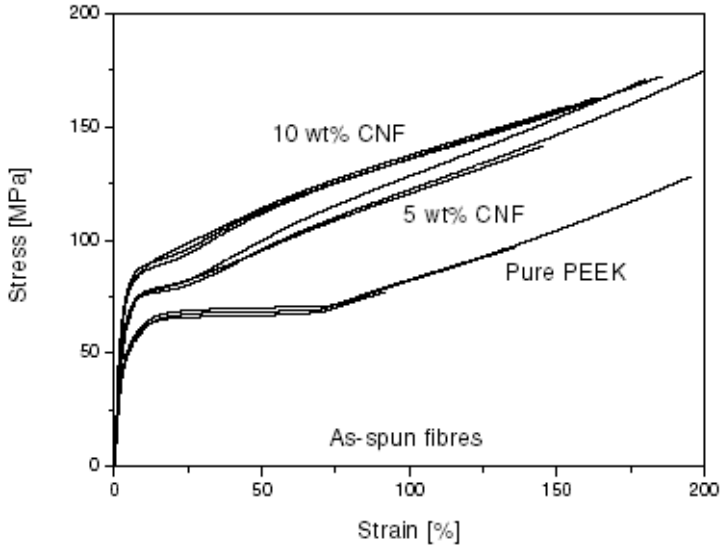


J. SANDLER, A. H. WINDLE JOURNAL OF MATERIALS SCIENCE 38 (2003) 2135–2141

An oriented carbon nanotube CNT has potentially a huge reinforcing effect as well as benefits for e.g. electrical properties (lower percolation threshold than standard carbon black?)

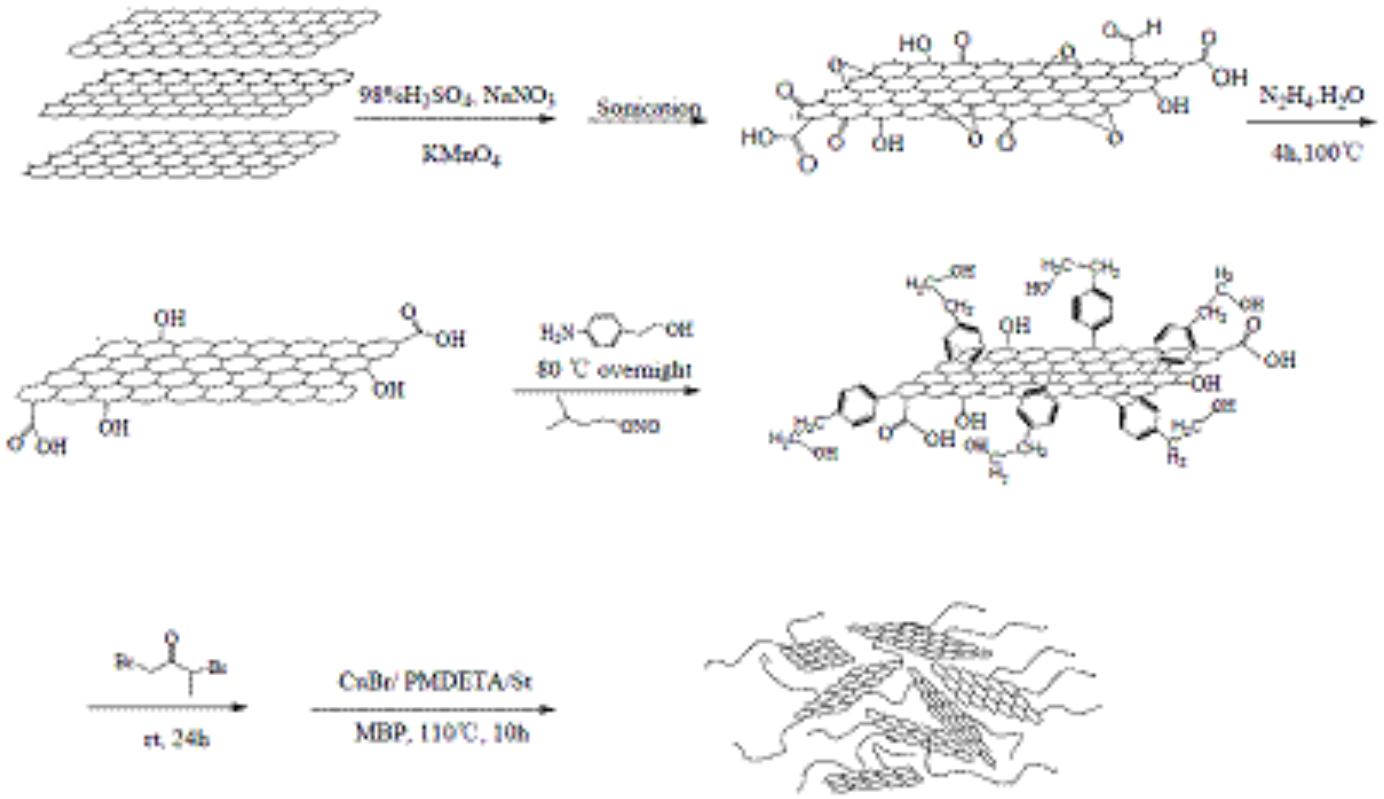
BUT …

How do we control dispersion and orientation in a polymer matrix? Here is an attempt to do so using fiber spinning.



Other nanocomposites (ii): *graphene nanocomposites*

Example of a chemical route to incorporating exfoliated graphene sheets in a polymer matrix
Lu H. et al., Journal of Materials Chemistry, 2009, 19, 7098–7105



Flat version of CNT
Similar goals and problems as for the dispersion of MMT clay and CNT in a polymer matrix

BUT …

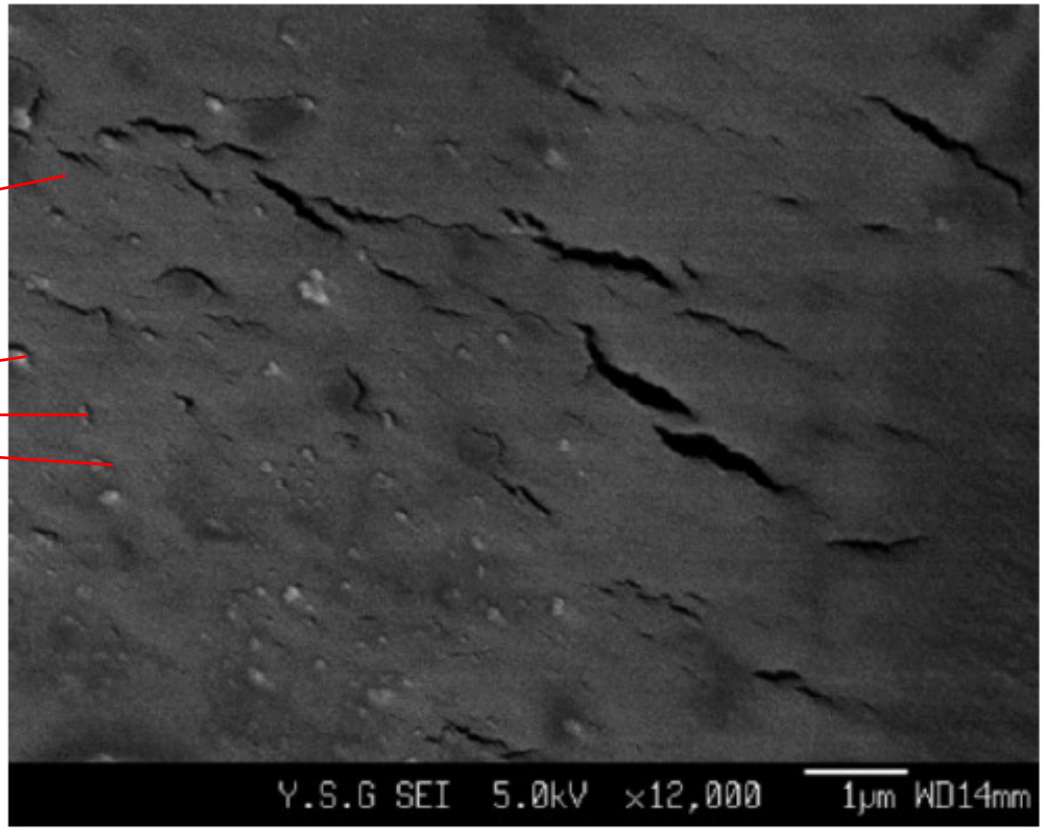
As with CNT, possibility of electrical conductivity for a percolating network

Other nanocomposites (iii): PP/Ag *nanoparticles*

Bactericidal function

Polypropylene matrix

Ag nanoparticles



SANG YOUNG YEO, HOON JOO LEE, SUNG HOON JEONG
JOURNAL OF MATERIALS SCIENCE 38 (2003) 2135–2141

	Ag content		Antibacterial evaluation (%)	
Sample	Weight (%)	Volume (%)	*Staphylococcus aureus*	*Klebsiella pneumoniae*
PPC-0	0	0	26.3	10.8
PPC-5	5.0	0.433	19.4	14.8
PPS-0.3	0.3	0.026	99.9	99.9
PPS-1.5	1.5	0.130	99.9	99.9

Electrospun polymer nanofibres

Electrospinning is the process of using electrostatic forces to distort a pendant droplet of polymer solution into a fine filament to be deposited onto a substrate.

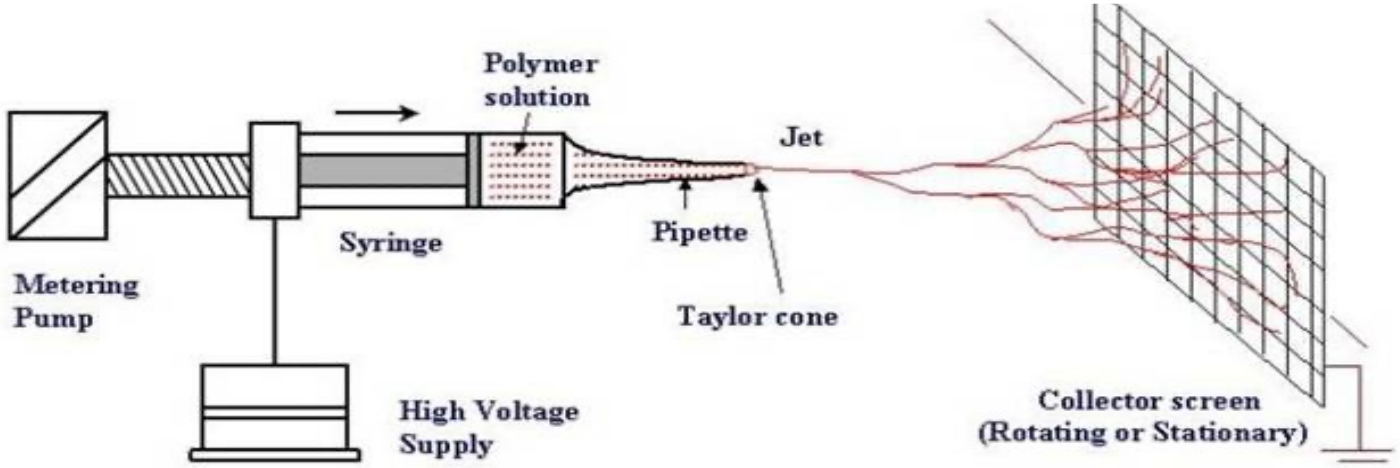


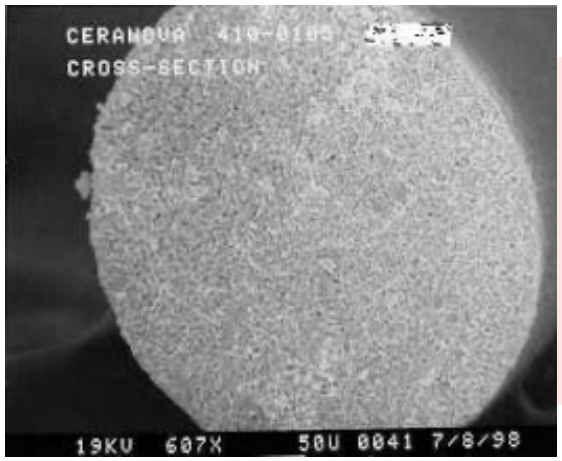
Figure 1. Schematic of the Electrospinning setup.

1-10 nm diameter continuous polymer fibres
(here PVDF electroactive fibers)
Can be used as precursors for ceramic e.g. carbon nanofibers

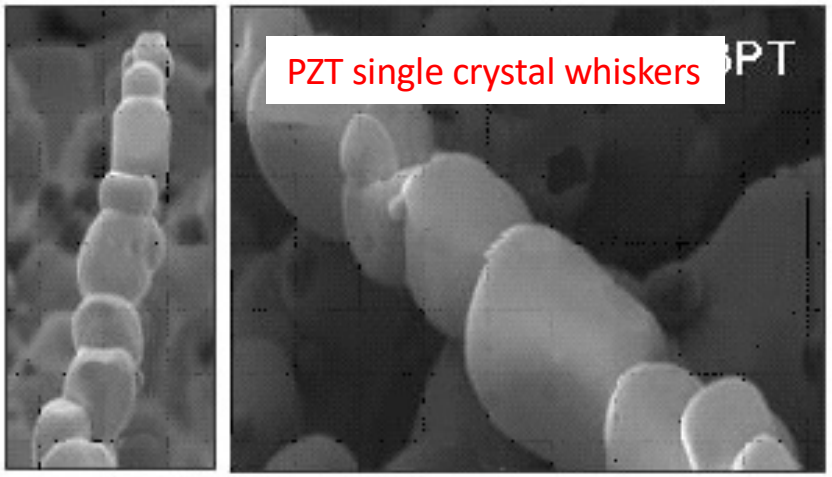
separation membranes, wound dressing materials, artificial organs, *nanocomposites*, and protective clothing.

Electroactive nanocomposites

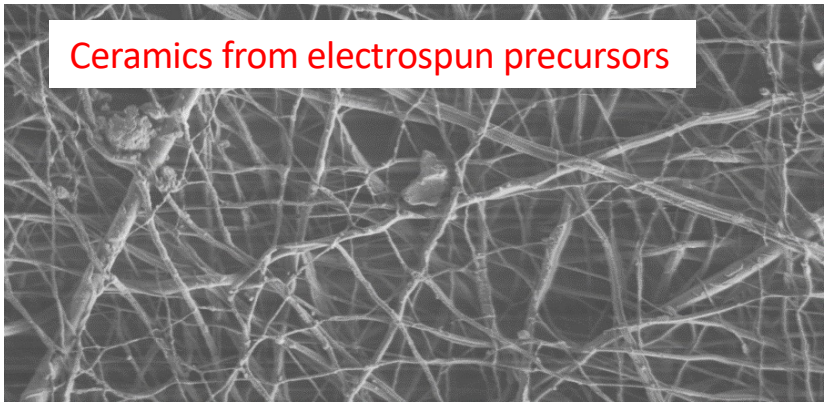
From conventional lay-up of macroscopic electroactive components (here a PZT fiber) ...



?



... to integrated processing of nanoscopic active elements



Low shrinkage nanocomposite resins

Resins for dental repair, devices, nanostructures …

We need – fast setting, resistant, low shrinkage, low viscosity resins that are biocompatible (non-toxic …)

Highly mineral filled UV-curable resins

- UV cure can be very rapid, and the filler reduces macroscopic shrinkage
- Very small (nano)fillers allow precision moulding e.g. for devices (feature sizes of the order of a micron), limited UV light scattering/abosrption during cure
- Mineral fillers may also contribute to hardness, thermal stability

The challenges

- At high nanofiller contents a liquid resin may show a solid-like response at low flow rates
- Avoiding development of excessive internal stresses during cure

A multiple approach to meeting the challenge

Intrinsically low shrinkage resins

Hyperbranched acrylate polymers – low viscosity, high molar mass

"pre-crosslinked" resins, delay stress build-up during cure

Nanofillers with controlled surface properties

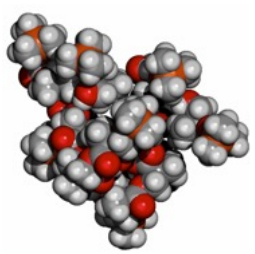
Tailoring particle-particle interactions in order to optimize dispersion and viscous response

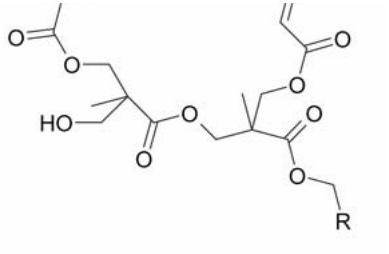
Sol-gel approach

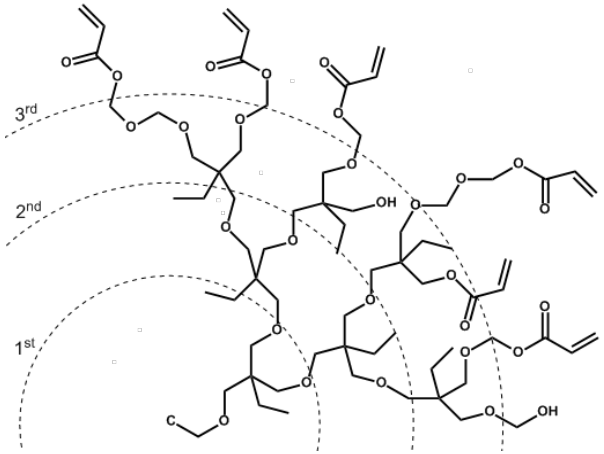
Inorganic particles precipitate during cure, high effective particle contents without the viscosity problem, but longer reaction times?

UV-curable acrylated hyperbranched polymers

Compact, nanometric spheres with high surface functionality







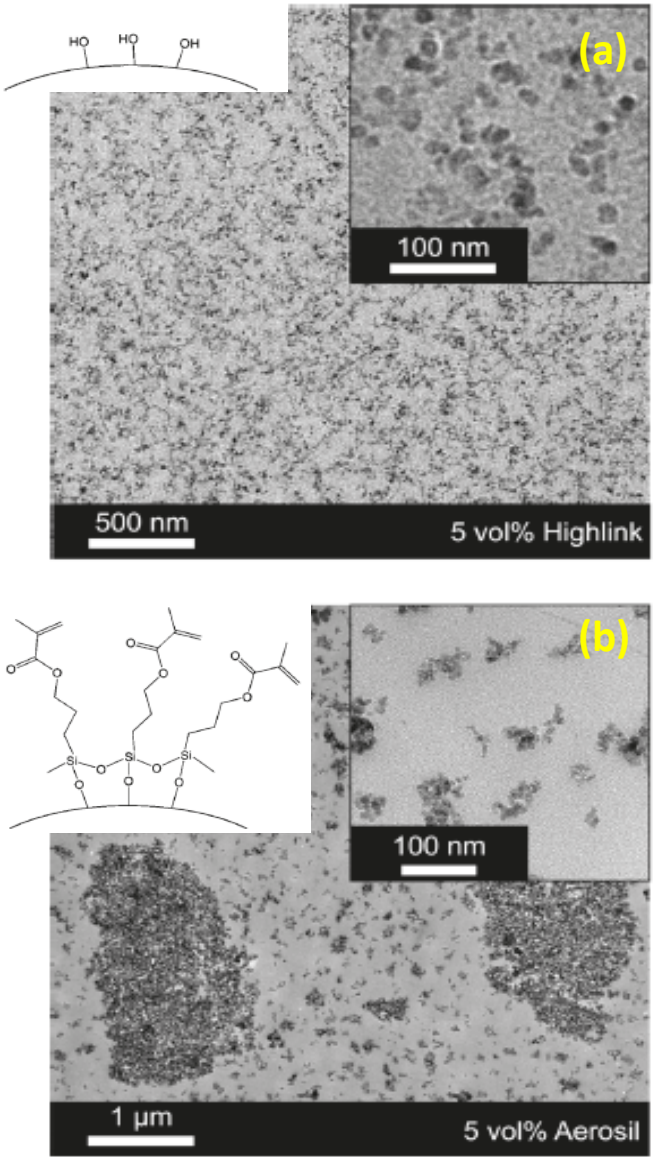
2nd & 3rd generation hyperbranched polyesters & polyethers (HBP)

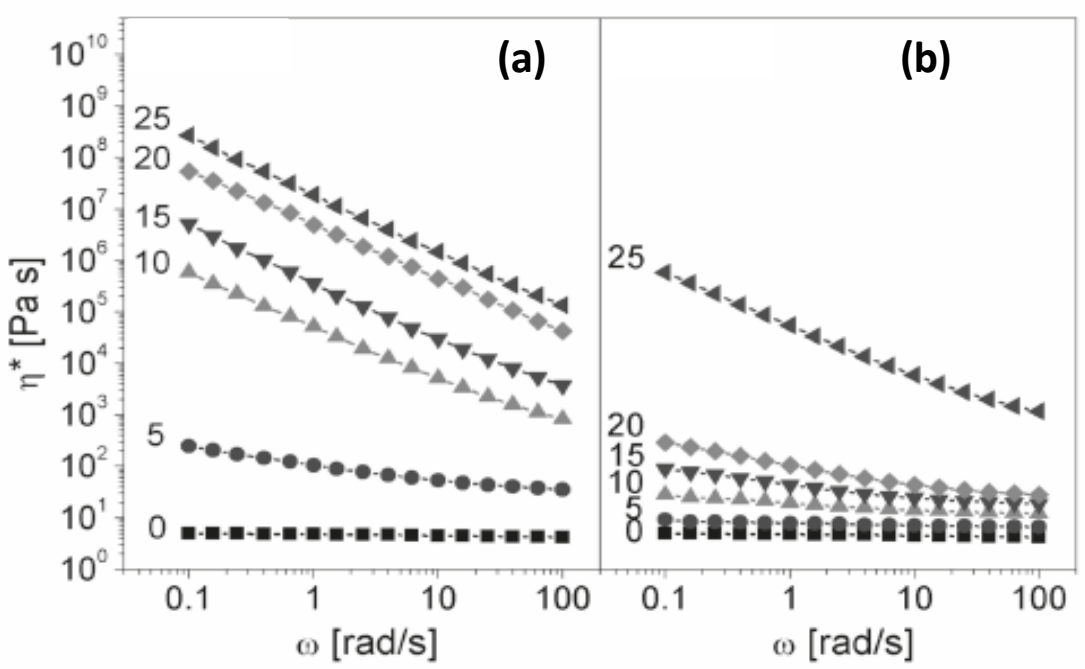
10 to 30 acrylate groups/molecule

M_w of 1'800 to 8'000 g/mol

- **High surface functionality → *rapid reaction***
- **Compact spherical morphology (little entanglement) → *low viscosity even for high M_w***
- **Delayed effective gelation → delayed modulus build-up … *low stress, low shrinkage***

Tailoring interfacial interactions in HPB-silica





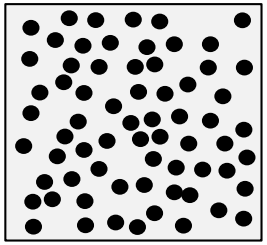
a) Good dispersion → ***solid-like behaviour***

b) Reduced interactions with matrix through surface treatment → ***poorer dispersion*** but ***viscous behaviour***

It is essential to optimize these interactions!

Ruggerone, Leterrier et al., Macromolecules, 43, 10490-10497 (2010)
Geiser, Leterrier et al., Macromolecules, 43, 7705-7712 (2010).

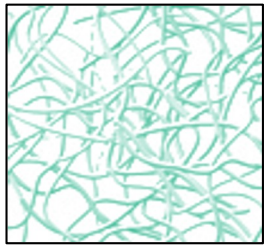
Integrated synthesis of hybrid nancomposites



Particulate composites

solvent assisted ultrasound mixing of resin and solid particles + UV cure

– dispersion of particles is challenging (surface treatment)
– thick paste difficult to process
+ fast cure
+ hard composite



Sol-gel composites

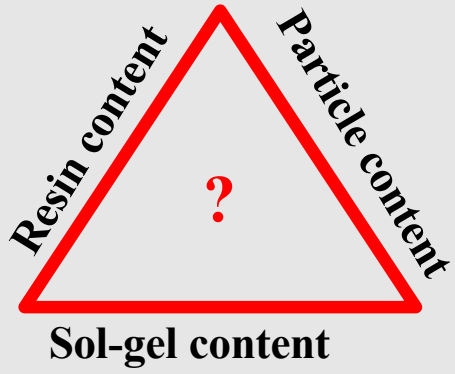
in-situ synthesis of liquid precursors in resin and dual-cure UV + thermal process

– long process time (condensation)
+ low viscosity
+ homogeneous nanostructure (transparency)

Hybrid composites based on hyperbranched polymers

combination of photo-polymerization and sol-gel processes

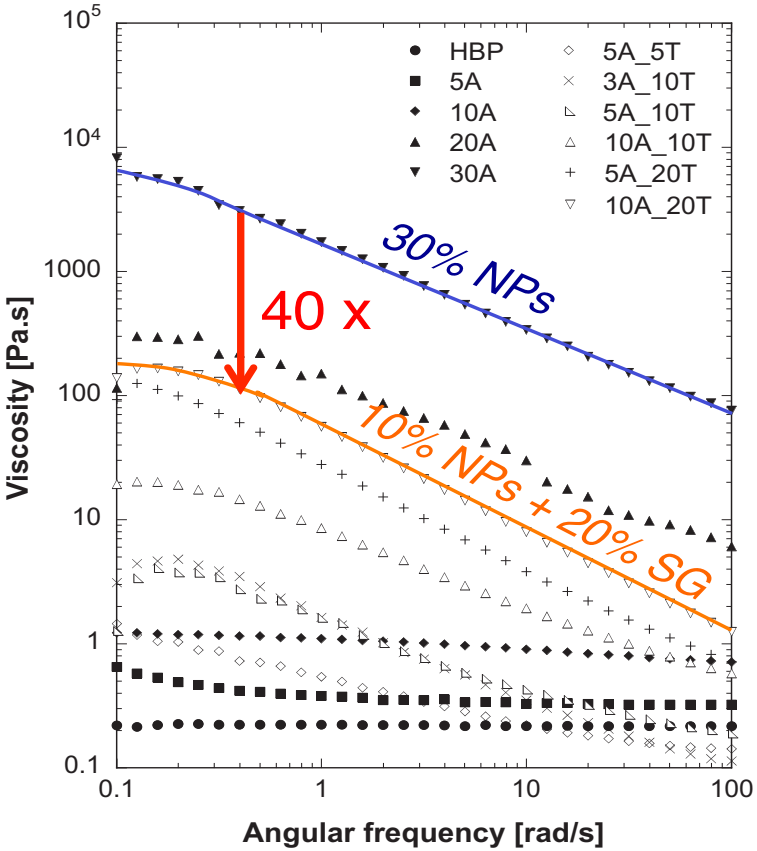
+ **hardness**
+ **low viscosity**
+ **low stress**
+ **transparency**
+ **rapid processing**



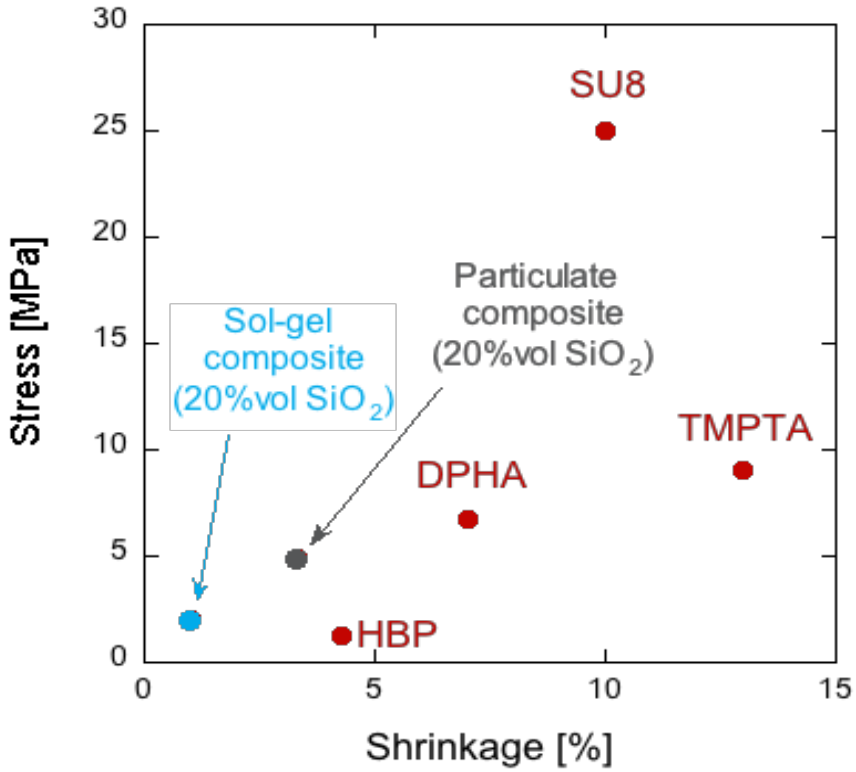
Geiser, Leterrier et al., Macromol. Mater. Eng., 297, 155-166 (2012)

Improved physical response

Low viscosity

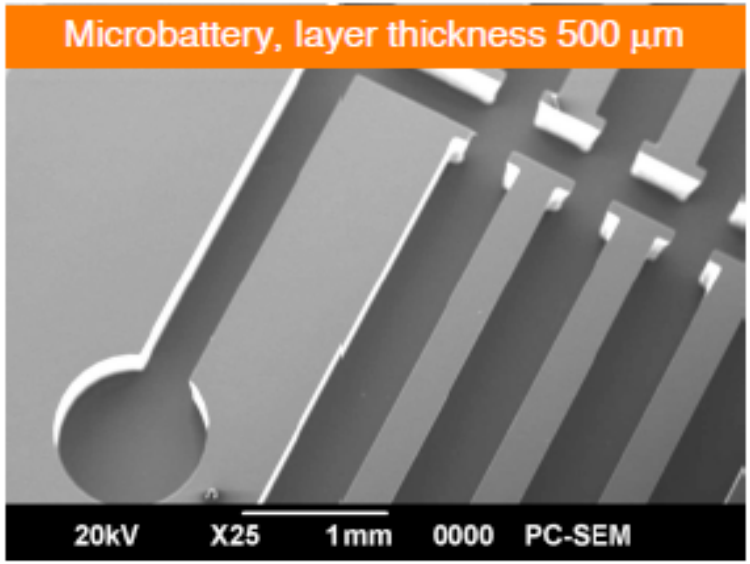


Shrinkage and Stress

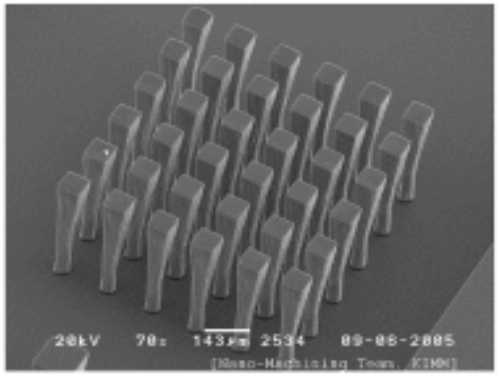


Geiser, Leterrier et al., Macromol. Sympos. 296, 144 (2010)
Gonzalez Lazo, Leterrier et al., Polymer 54, 6177 (2013)

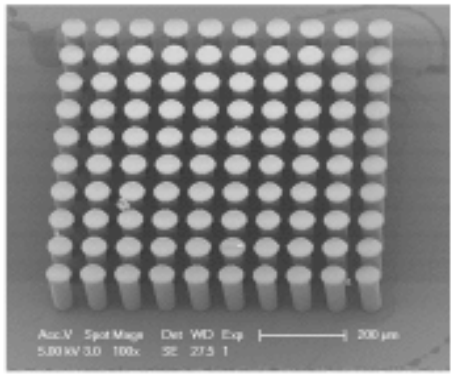
Improved applicative properties



Polyether HBP



SU8



FOM = (L x AR) / (Stress x Fab_Time)

Resist	Layer thickness, L (µm)	Aspect ratio, AR	Residual stress (MPa)	Fabrication time (h)	FOM
Polyether HBP	850	7.7	2.4	0.5	5454
Polyester HBP	500	3.3	4.5	0.5	733
SU-8	250	11	25	3	37

Jin Y.-H., J. Micromech. Microeng., 17, 1147-1153 (2007).
Schmidt et al., J. Micromech. Microeng. 18, 045022 (2008).

Structures by photolithography

Exercises