Introduction to PNC Science and Technology

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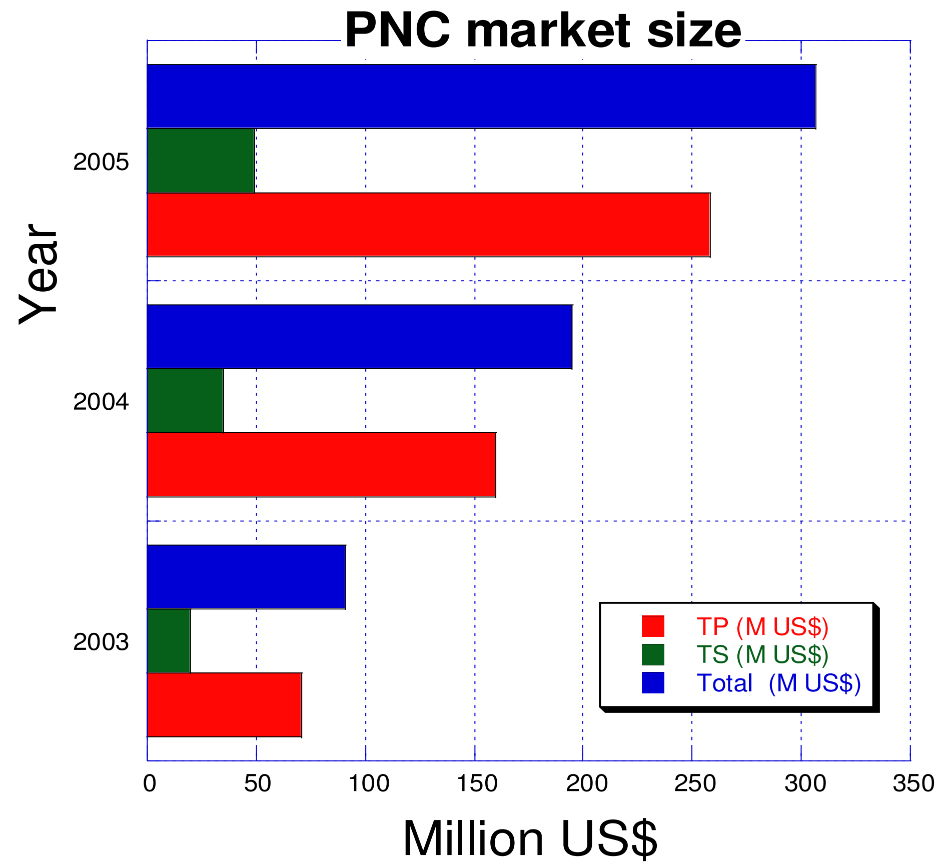
Outline

- **Introduction to polymeric nanocomposites (PNC)**
  - **Applications**
  - **Definitions**
  - **Clay intercalation & exfoliation methods**
  - **Compounding/dispersing PNC**
- **Elements of the science & technology**
  - **Mathematical modeling**
  - **Thermodynamics of PNC**
  - **Rheology of PNC**
  - **PNC performance** (*mechanical, barrier, flammability*)
- **Conclusions**

PNC market

- The PNC annual growth rate is AGR ≅ 18.4%/y.
- The growth rate for thermoplastics is 20%, and that of thermosets 10%.
- The thermoplastic matrices constitute ca. 77%, thus thermoplastic PNC market AGR ≅ 24%/y.



- According to BCC (2004), the global market for CPNC increased from US$90.8M in 2003, to 195 in 2004, and it is expected to increase to US$311M by 2008.

Use of CPNC in 2004

- GM has been using CPNC since 2002. In 2004, the company introduced body side molding in Chevrolet Impala. The latest application is the 2005 GM Hummer H2 using a TPO-clay formulation.
- PP-based CPNC are used in seat backs of the 2004 Acura TL. They are to be used for interior consoles of a 2006 light trucks.
- PolyOne has commercialized CPNC masterbatches with high impact strength and stiffness for consumer disposable applications. Its formulations combine chemical resistance and stiffness and dramatically reduce cycle time.
- Semi-aromatic PA-based CPNC (with PA-*m*XD6) have been used by Eastman as a barrier layer in multi-layer PET bottles and films for food packaging, e.g., in Europe for alcoholic beverage bottles, carbonated soft-drink bottles and thermoformed deli meat and cheese containers.
- Nanocomposite concentrates are being evaluated in films not only for enhancing barrier, but also to control the release and migration of additives such as biocides and dyes.

Other uses of CPNC's

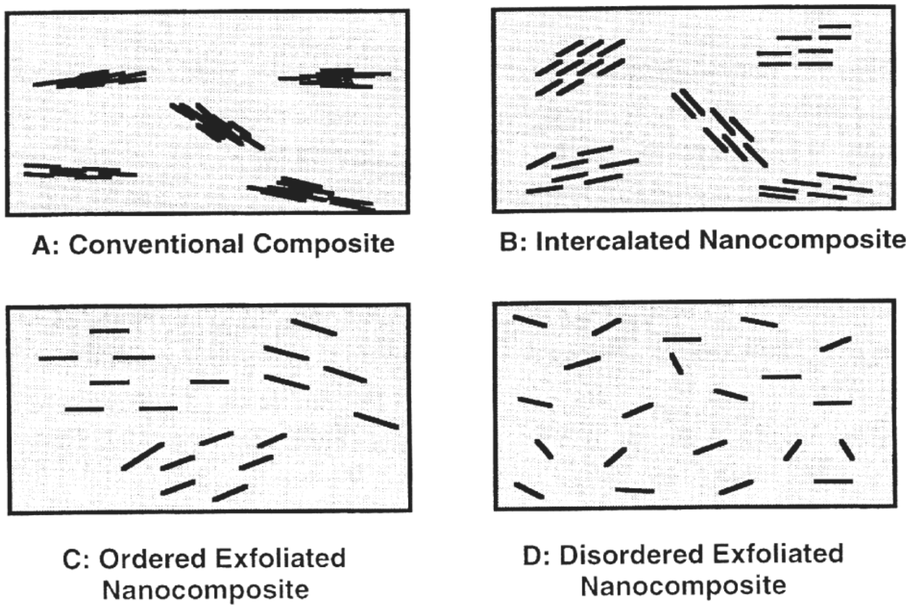
- **Unitica** produces injection-molding grades of PA-6 based PNC used for the production of car engine and converter covers for Mitsubishi & Toyota.
- The same grade is also used for injection molding of highly rigid bases for the electronic control tray & cover.
- Ube PNC is used for rear mirror housing and timing belt cover.
- Bayer manufactures PA-6 nanocomposites for transparent barrier film packaging.
- Kabelwerk Eupen uses EVAc/organoclay for wire & cable applications. Drastic reduction of heat release (flammability) at 3 to 5 wt% clay loading.
- Showa Denko produces PA-66 and POM nanocomposites for improved flame retardancy and rigidity at 0.4 mm thickness. The flex moduli are 30-80% higher, and HDT 30 to 80 C higher, than those of neat resins.

Definitions 1

- Nanocomposites (NC) = matrix + dispersed in it nanometer-sized (< 50 nm) particles.
  - The matrix may be single- or multi-phase.
  - It may comprise additives that complement functionalities of the system (reinforcement, electrical conductivity, toughness, *etc.*)
- Depending on the nature of matrix, NC is:
  - **Polymeric NC (PNC)**
  - Ceramic NC (CNC)
  - Metallic NC (MNC)
- To generate high enhancement of properties, the nano-particles ought to be anisometric, viz. Lamellar, Fibrillar, Tubular, etc.
- Spherical particles have been used to produce functional NC (*e.g.*, for electrical conductivity, optical or magnetic properties, *etc.*).

Definitions 2

- ***Exfoliated clay**:* − individual platelets dispersed in a matrix with spacing d_{001} > 8.8 nm. The platelets may form *Short stacks* randomly dispersed.
- ***Intercalated clay**:* − *having* organic or inorganic molecules inserted between *Platelets,* thus with d_{001} > 1.5 nm.



- ***Intercalant**:* − material sorbed between *Platelets* that binds with their surfaces to form an *Intercalate*.
- ***Interlayer**, basal spacing, or d-spacing*, $\boldsymbol{d_{001}}$ is the thickness of the repeating layers as seen by the XRD = mineral thickness (in MMT = 0.96 nm) + galley thickness, δ.

Crystalline clays

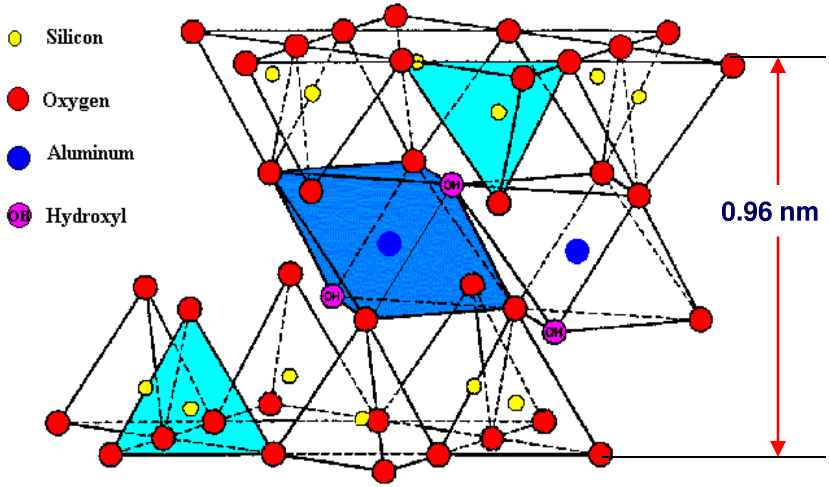
Mineral vs. synthetic clay

- Mainly montmorillonite (MMT)
- ADVANTAGES
  - Well-established technology
  - Availability
  - Lower cost
- DISADVANTAGES
  - Variability of composition
  - Platelets welded together by fault in crystal structure
  - Variable color
  - Contaminants (grit & amorphous clay)

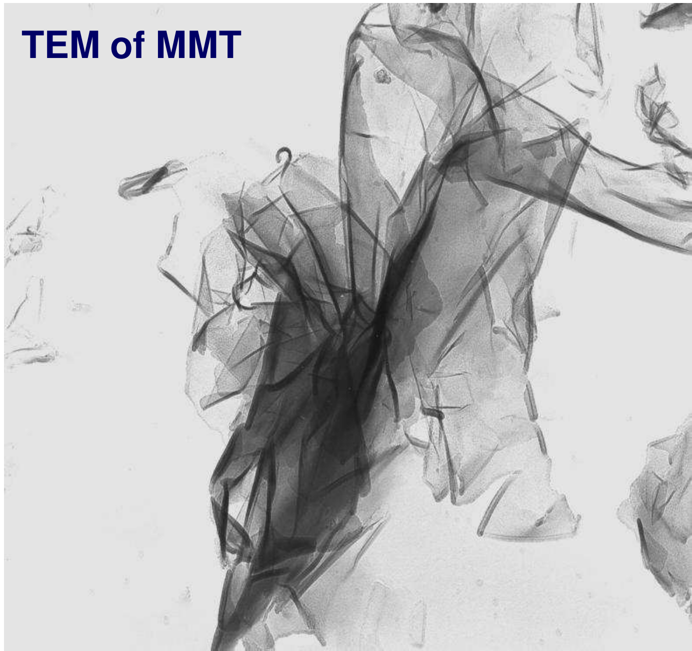
- Semi- or fully-synthetic MMT, hectorite or saponite
- Hydrothermal or molten glass
- Example: fluoro mica (FM, FH)
- ADVANTAGES
  - Aspect ratio: $p \leq 6,000$
  - Stable composition
  - Non-toxic
  - **Absence of color**
- DISADVANTAGES
  - Limited and uncertain sourcing
  - Evolving technology
  - Higher cost

Montmorillonite (MMT)

Cell unit MW (g/mol.)	540.46
Density (g/mL)	2.3 to 3.0
Mohs Hardness @20°C	1.5- 2.0
Cleavage	Perfect in one direction, lamellar
Characteristic	Expands up to 30 times in volume in H_2O
Appearance	Light yellow with dull luster
Field Indicators	Softness, and soapy feel



- At $T < 500$°C smectites have 4 layers:
  - Outer layer with H_2O and Na^+, K^+, Ca^{++}, Mg^{++} ions.
  - 3-layer sandwich: octahedral central between two tetrahedral: SiO_2-(Al/Mg)-SiO_2; 0.956 nm thick.
- Monoclinic, $(Na,Ca)(Al,Mg)_6(Si_40_{10})_3(OH)_6$-$nH_20]$, has: Al = 10, Si = 21, H = 4, and O = 65 (wt%); $p \cong 100$ to 300; $A_{sp} \cong 750\ m^2/g$ (*football stadium = 17 g MMT*); Cation exchange capacity: CEC $\cong 1.0 \pm 0.2$ meq/g.
- Reactive sites: anions and –OH groups on the surface and cations and –OH groups at the rim.


TEM of MMT

Intercalation 1

- *Intercalation* − diffusion of intercalant into clay galleries. *The intercalant* binds to the platelet surface.
- The aim of intercalation: to expand the interlayer space, facilitating diffusion of macromolecules (exfoliation).
- Intercalation depends on the balance of forces: positive that drives the molecules to bond with the solid surface and negative that requires breaking the solid-solid interaction and loss of entropy.
- Intercalation is a process of simultaneous expansion of ca. 200 clay platelets that form a tactoid. The layers are elastic, but there is a limit to the amount of bending they can undergo.
- The efficient strategy of intercalation involves reduction of the stack size and a progressive increase of the penetrant size, starting with H_2O, then an onium cation, ...

Intercalation 3

- Several routes have been used to intercalate clay particles:
  - Low-MW solvents and solutions, viz. water, alcohols, glycols, monomers.
  - Freeze-drying of expanded clay.
  - **Organic cations, viz. ammonium, phosphonium or sulfonium.**
  - Complexing of aromatic or cyclical (crown ether) compounds by Cu^{++} or Ag^{+}.
  - Compounding with organic liquids, viz. monomers, epoxies, PEG, PVAl, PDMS, PVP, and their solutions.
  - Inorganic compounds that form inter-layer pillars – stable porosity, **but no exfoliation**.
  - Mechanical or ultrasonic delaminations in aq. medium.
  - By cyclic compression/decompression.

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Intercalation 4

- For CPNC organoclay must be thermodynamically miscible with the matrix, hence great diversity of the intercalating agents have been described in the patent literature.
- They mainly comprise primary, secondary, tertiary or quarternary onium salts, viz. **ammonium, phosphonium, sulfonium** or their mixtures, with or without organosilane as a coupling agent.
- Process:
  1. Dispersion in aqueous medium at T = 60-77°C.
  2. Reaction with onium ions.
  3. Bond strength increases in order: $NH_4^+ < RNH_3^+ < R_2NH_2^+ < R_3NH^+ < R_4N^+$
  4. Secondary treatments, e.g., with a « sizing agent ».
  5. Addition of a monomer (then polymerization) or polymer (then melt compounding).

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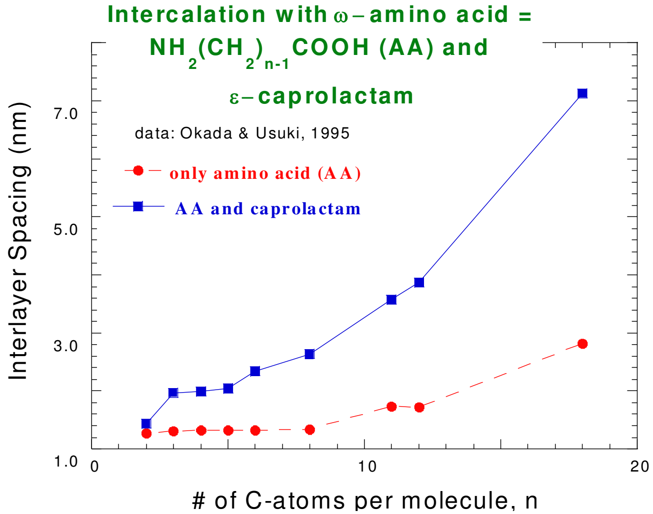
Intercalation 5



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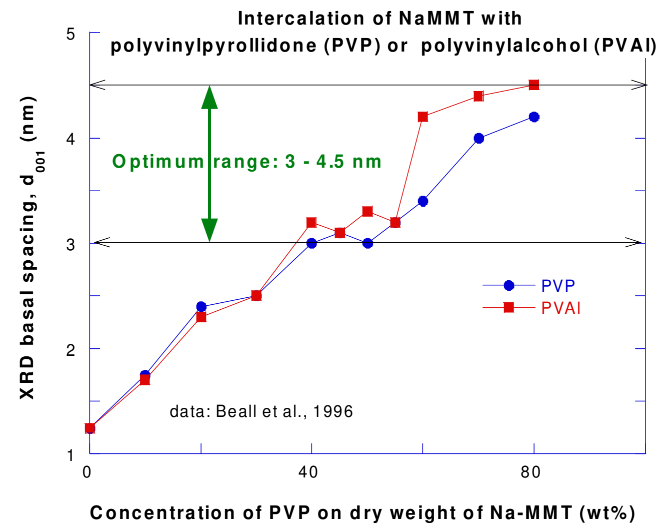

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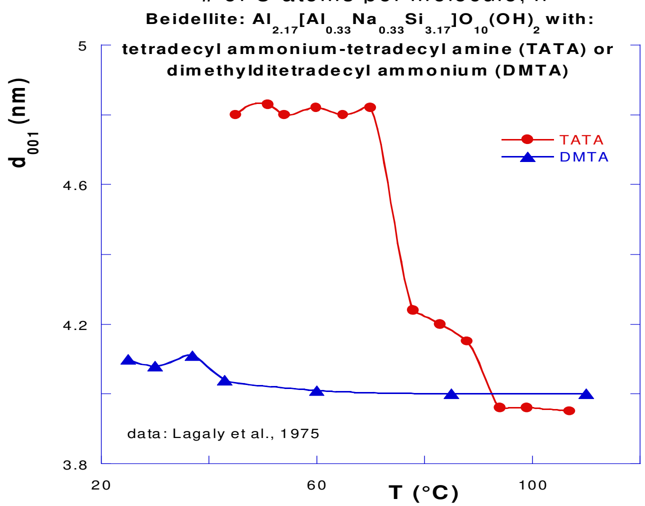

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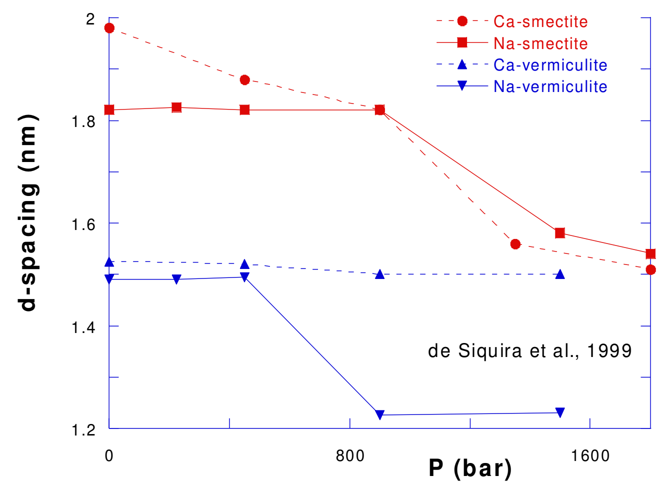

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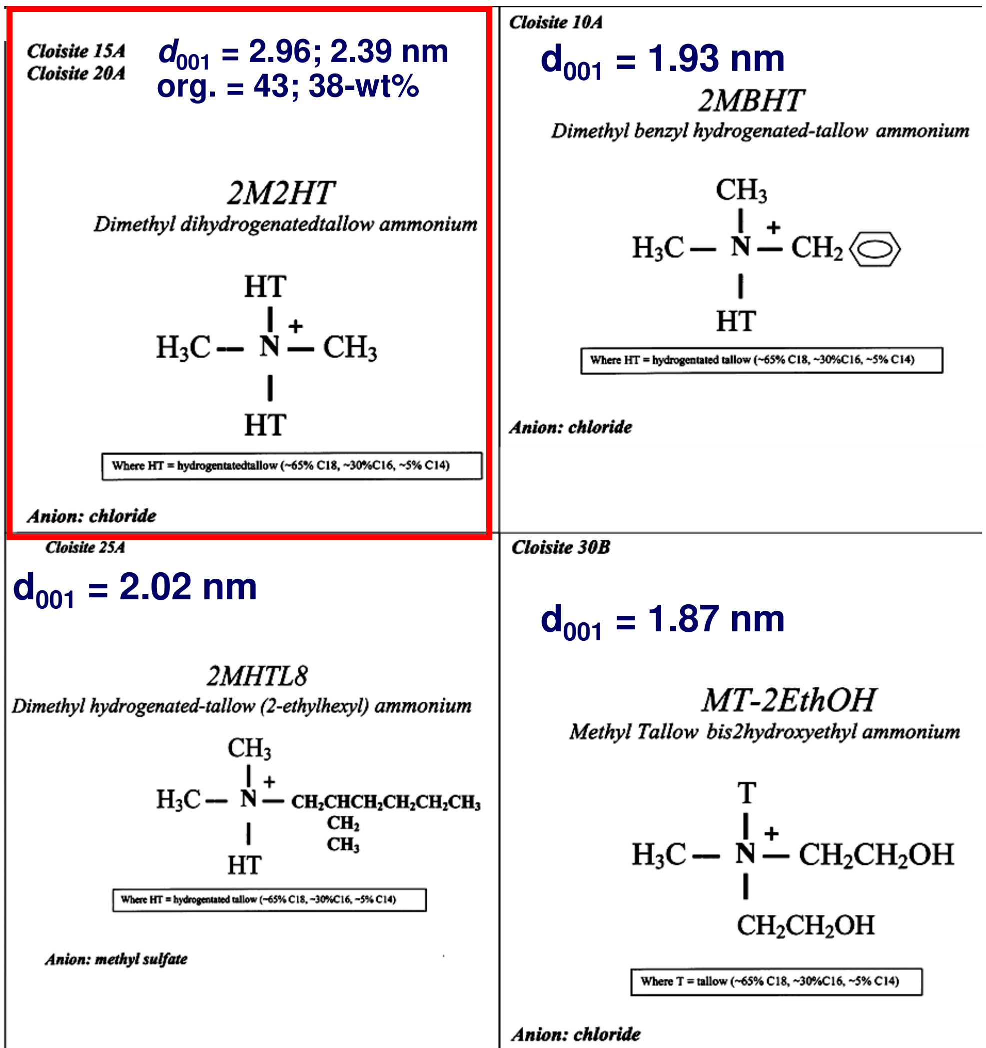
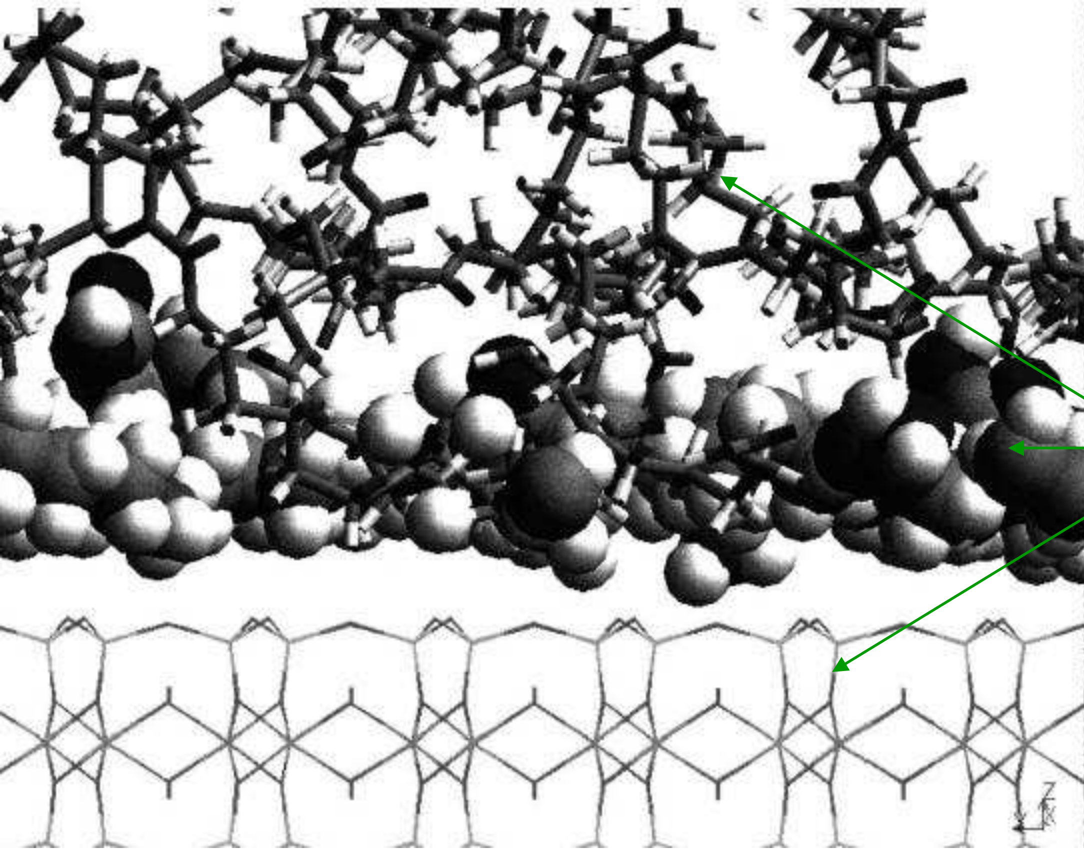
The d_{001}-spacing depends on: (1) Intercalant and its (2) concentration, (3) temperature and (4) pressure

Organoclays 1



- Commercial intercalated mineral or synthetic clays contain quarternary amines
- MMT cation exchange capacity: CEC = 100 ± 20 meq/100 g.
- Equilibrium of Na-MMT reaction with ammonium salt is shifted left, hence excess of onium salt is often used, *i.e.*, 0.9 to 1.4 meq/g or 23 to 40 % of the organic modifier.
- Intercalated clay contains 2 - 4 % water and up to 44 wt% of organic compounds (*Southern Clay Products, 2000*).

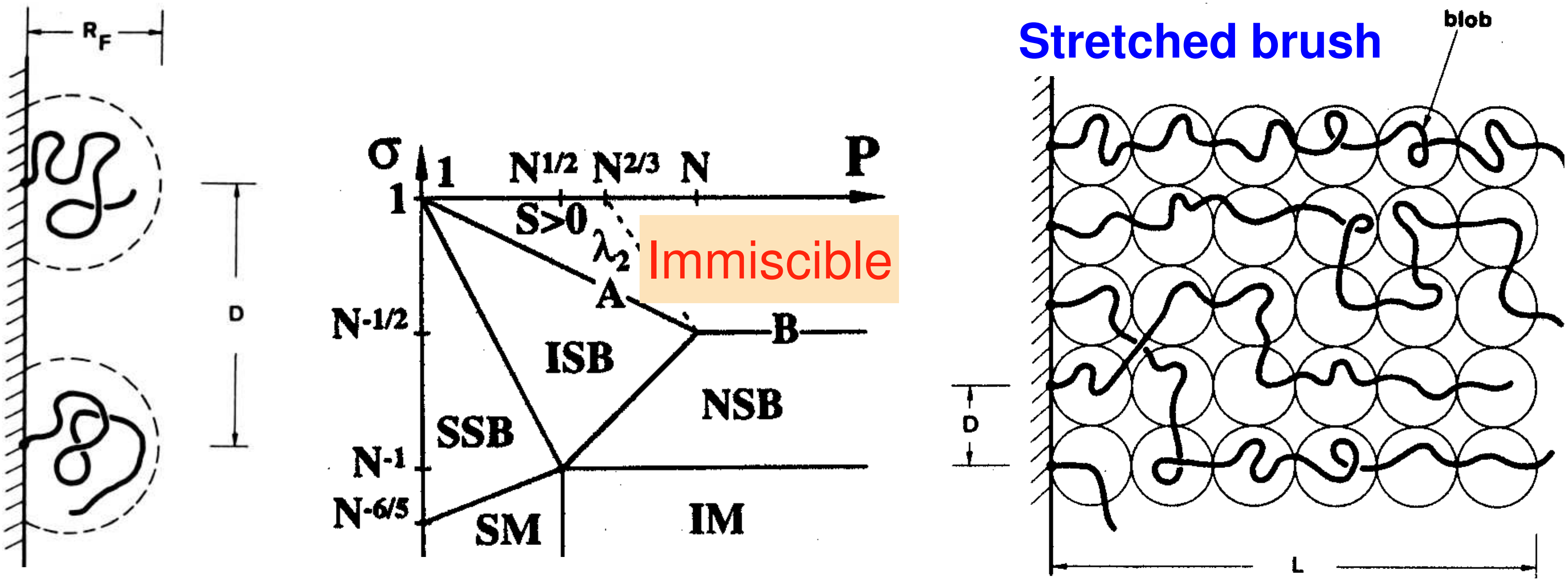


Organoclay structure

- Molecular dynamics (MD) of clay (*stick model*) intercalated with ω-amino acid (*space-filled model*), dispersed in PA-6 or -66 (*cylinder model*) [Tanaka & Goettler 2002; Brown D. *et al.*, 2003].
- The intercalant lays flat on the clay surface.
- MD indicates that the ammonium ion charge is dislocated and it spreads all over the molecule; the paraffin chains are straight.
- There is immiscibility between the non-polar intercalant chains and polar PA-66 molecules.
- The polymer has a limited access to the clay surface.
- **Best miscibility is between PA macromolecules and bare clay**.

Grafted clay platelets

Mushrooms



- Consider solid surface grafted with end-terminated polymers (MW = N), dispersed in chemically identical polymer (MW = P), where N ≤ P.
- The grafting density, σ (# of N per surface area), and MW control the shape.
- For low σ, the phase diagram show swollen (S) and ideal (I) **mushrooms** (M).
- At higher σ, S-, and I-**stretched brush**, as well as non-stretched brush (NSB).
- At high $\sigma > N^{-½}$, and high P > N the brush is non-penetrating – the grafted clay phase separates from the melt [Gay, 1997].

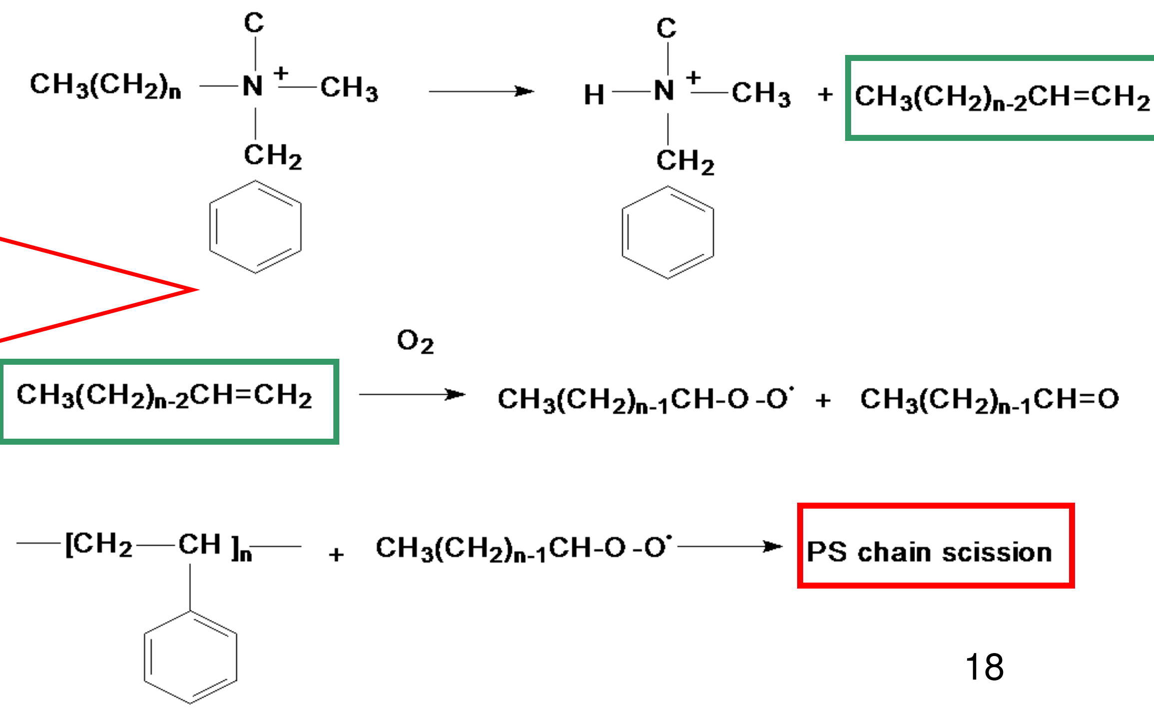
Organoclay drawbacks

- Organoclays are expensive, viz. Na-MMT \$1/kg; organoclay > \$14/kg.
- Organoclays are immiscible with most polymers of industrial interest.
- Organoclays are thermally instable – stability decreases with the degree of substitution.
- The decomposition occurs in steps, starting at 125 to 150^{o}C. Oxygen and shear accelerate the degradation.
- Stability may be improved by:
  - Using phosphonium instead of ammonium intercalants.
  - Using branched alkyl chains instead of linear.
  - Using aromatic substituents instead of paraffins.
  - Using metallo-organic complexes.
  - Other methods.
- Organoclays are expensive, and any attempt to improve thermal stability further increases the cost.

Hofmann elimination (1851)

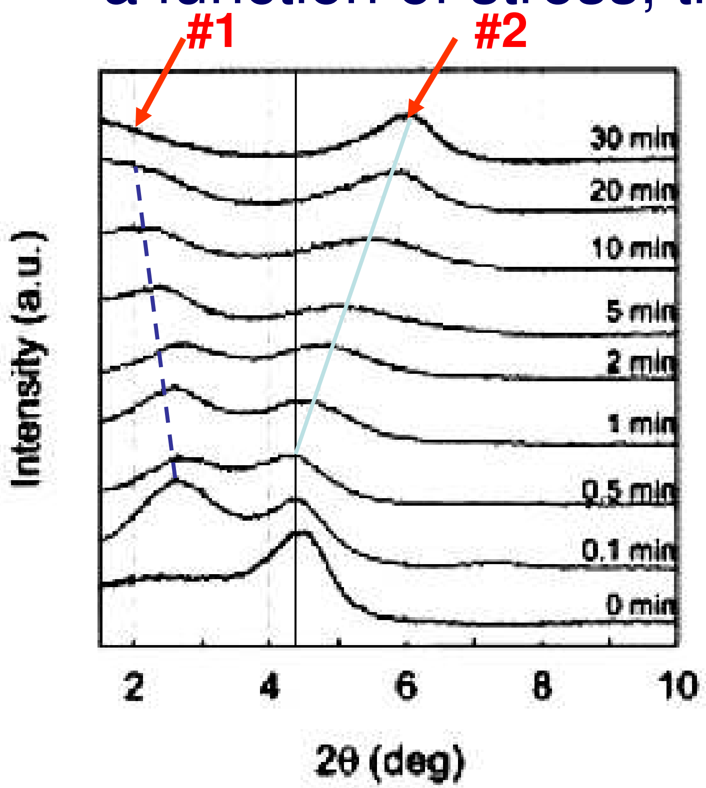
- Degradation of intercalants at $T > 150^{o}C$ is a major problem in CPNC technology
  - Phosphonium ions are more stable than ammonium.
  - Organo-metallic complexes show high stability.
  - Bulky, aromatic ammonium (e.g., dyes) form stable organoclays.

Thermal degradation in the presence of O_2 of ammonium intercalant in PS matrix resulted in formation of peroxy-radicals and subsequent degradation of the PS matrix.



Degradation effects

- Shear compounding results in two parallel processes:
  - Mechanical intercalation/exfoliation
  - Thermal degradation via Hofmann elimination reaction
- The result is a complex variation of the interlayer spacing as a function of stress, time, and temperature.



- The Figure illustrate these two processes: melt exfoliation (#1) and degradation (#2)
- The XRD data are for PS/Cloisite®10A mixed at *T* = 200 to 210°C, shear rate of 65 (1/s), for up to 30 min [Yoon *et al*., 2001; Tanoue *et al.*, 2004].

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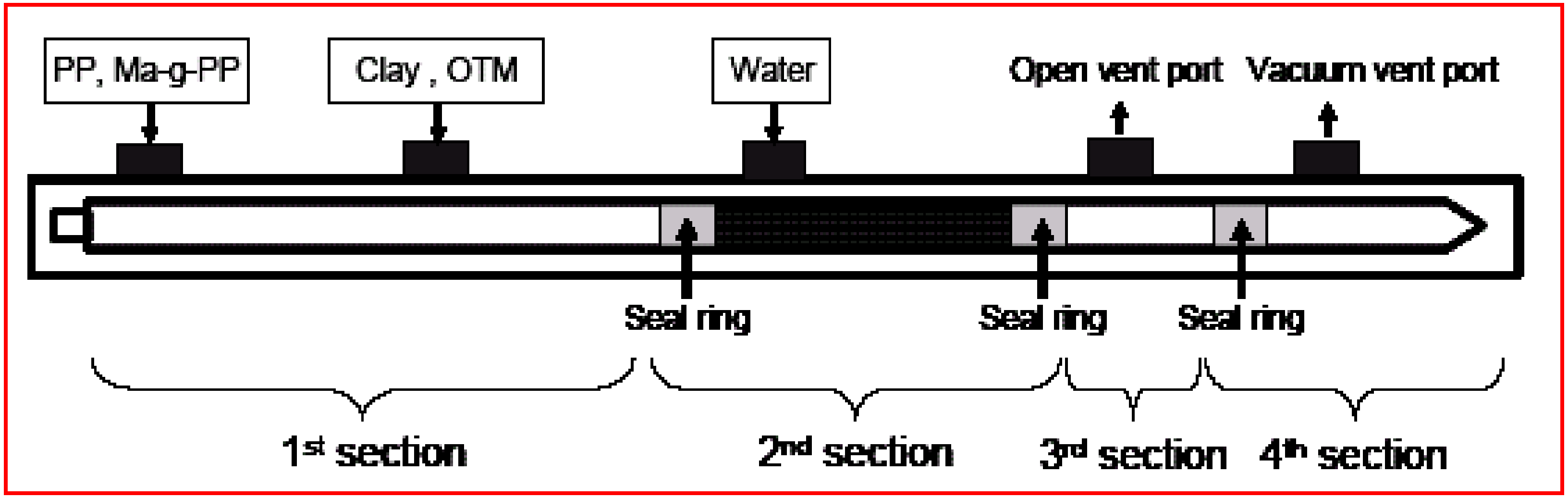
Compatibilization

- Compatibilization is a method of the interface control in PNC, especially these based on PO or PS resins.
- As in blends, the compatibilization must:
  1. Reduce interfacial tension coefficient, ν_{12}.
  2. Stabilize morphology against stress-destruction during forming.
  3. Provide adhesion between the phases in the solid state.
- Compatibilization is accomplished by:
  1. Addition of reactive macromolecular species that are miscible with the matrix polymer and have (preferably) a terminal group that reacts with the organoclay.
  2. For example, maleated-PO, acrylic acid grafted PO or PS, copolymers with glycidyl methacrylate serve as compatibilizers.
- Since compatibilizers' cost is higher than that of the matrix polymer, they must be used in small quantities.

Direct PNC compounding

- Hasegawa *et al.* [2003] described direct compounding of PA-6 with aqueous slurry of **Na-MMT** in JSW TSX-77.
- During the PNC-2003 symposium at NRCC/IMI, Kato *et al.* described a **New Production Method for a PP-Clay Nanocomposite**.
- Melt-compounding in TSX-77 of PP + PP-MA + **Na-MMT** (with or without octadecyl trimethyl ammonium chloride, OTM), than injecting H_2O to exfoliate.
- The performance of these new PNC's was reported comparable with that for the "classical" ones based on PA-6 or PP, respectively.



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Exfoliation – general

- The principal exfoliation methods for the production of CPNC are: (1) Reactive, (2) In solution, and (3) **Mechanical**.
- The **mechanical** exfoliation method is the most promising, as it potentially offers the capability to produce suitable CPNC to any compounder or manufacturer of plastics part.
- **It** starts with a polymeric matrix, suitably intercalated clay, and (often) a compatibilizer.
- The controlling factors are:
  - Interactions between organo-clay and polymer, e.g., in PA-6 *methyl tallow bis-hydroxy ammonium-MMT* is relatively easy to exfoliate, while *di-methyl di-hydrogenated tallow ammonium-MMT* is difficult.
  - Viscosity of the polymeric matrix.
  - Residence time in the processing equipment [*Dennis et al., 2000*].
  - Type and intensity of stress fields.
- **Thermodynamics controls the exfoliation – compounding only affects the kinetics!**

Usuki's classification

Exfoliation methods with increasing difficulties:

1. **Hydrophilic matrix with strong polar groups, e.g., P2VP:**

$$\text{clay} \xrightarrow{\text{water}} \text{swollen clay} \xrightarrow{\text{polar organic compound}} \text{CPNC}$$

2. **Hydrophobic matrix with strong polar groups, e.g., PA-6:**

$$\text{clay} \xrightarrow{\text{intercalant(s)}} \text{intercalated clay} \xrightarrow{\text{monomer}} \text{expanded clay} \xrightarrow{\text{polymerization}} \text{CPNC}$$

3. **Hydrophobic matrix with strong polar groups, e.g., PA-6:**

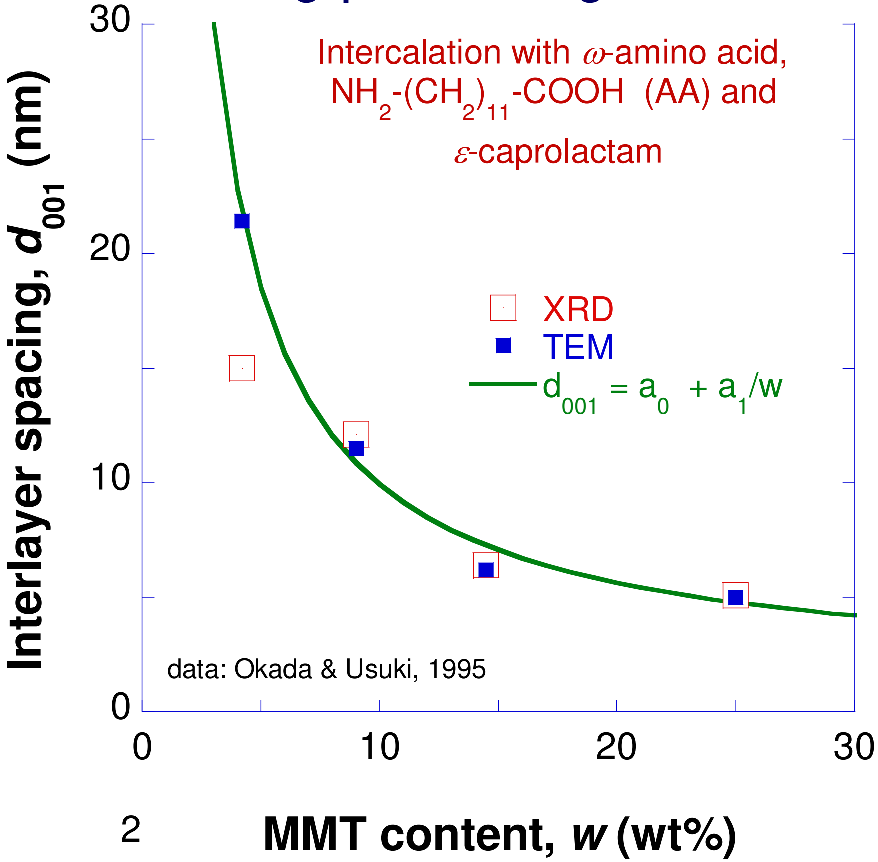
$$\text{clay} \xrightarrow{\text{intercalant(s)}} \text{intercalated clay} + \text{polar polymer} \xrightarrow{\text{compounding}} \text{CPNC}$$

4. **Hydrophobic non-polar matrix, e.g., PP:**

$$\text{clay} \xrightarrow{\text{intercalant(s)}} \text{intercalated clay} + \text{compatibilizer} + \text{non-polar polymer} \xrightarrow{\text{compounding}} \text{CPNC}$$

Concentration effects

- Assuming that clay platelets are circular discs with diameter, *d*, and thickness, *h* (aspect ratio $p = d/h$), **the geometry** of the freely rotating platelets gives:



- Ratio of the encompassed to actual volume = $2p/3$, and the maximum packing volume fraction $\phi_{max} = 0.93/p$.
- At $\phi > \phi_{max}$ platelets are not able to rotate freely, thus locally they form short stacks with :

$$d_{001} \cong 223 / w\,(wt\%)$$

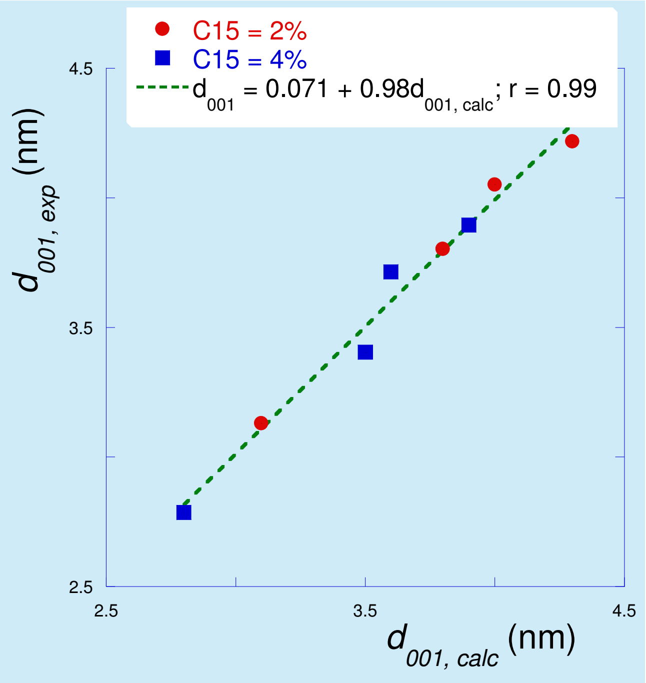
- For Ube PA1015C2 the factor is (ca. 100); hence twin platelets are to be expected.
- Exfoliation is feasible only for w(clay) ≤ 1.1 wt%.

Exfoliation in crystalline matrix

- Clay platelets are unable to exfoliate at higher concentration.
- As clay resides only in non-crystalline domain exfoliation in semi-crystalline polymers is more difficult:

$$d_{001} = d_{001}^{0} - a_1 C_{clay} - a_2 X \quad ; \quad d_{001}^{0} = 10.5 \pm 0.6, a_1 = 0.39 \pm 0.05, a_2 = 0.11 \pm 0.01$$

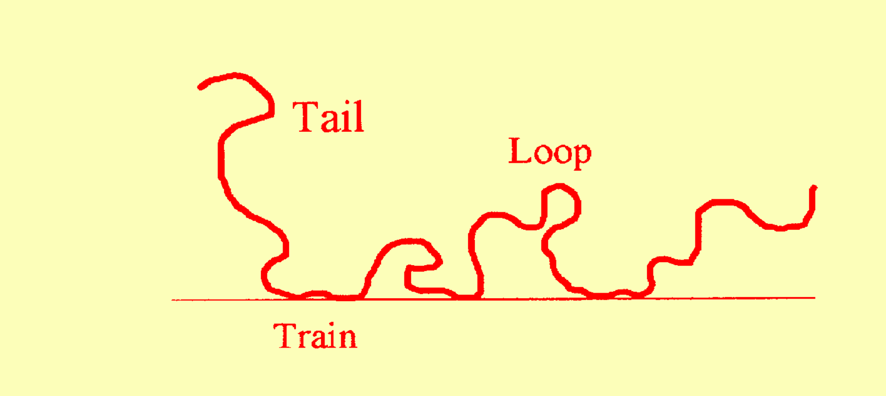
- Data for PP + PP-*co*-PE with 2 or 4-wt% Cloisite 15A (C15) followed the dependence with **σ = 0.115 & r^2 = 0.9994** (Ton-That, 2003).



- In the experiments, the crystallinity ranged from *X* = 46 to 60%.
- Since d_{001} of C15 is 2.96, no expansion of the interlamellar galleries is to be expected at: ***X* ≥ 60% crystallinity**.

Mixing – general 1

- **Mixing**— to combine ingredients into one mass, so that the constituent parts are indistinguishable, a synonym for homogenization.
- **Blending** — the processes that lead to formation of polymer blends.
- **Compounding** indicates preparation of “a compound”, frequently comprising fillers and reinforcements.
- Polymer mixing occurs only within the **laminar** flow region where the Reynolds number << 2000.
- Within the laminar region there are two mechanisms to be distinguished: distributive (or extensive) and the dispersive (or intensive).



Molecular adsorption 1

- ***Adsorption*** of polymer on solid surface has been predicted by numerical methods.
- Klein showed that from toluene solution PS is adsorbed on mica flakes to a layer of ca. 110 nm thick!
- **Luengo *et al.*** [1997] **observed a 3-layer structure of PBD on mica:**

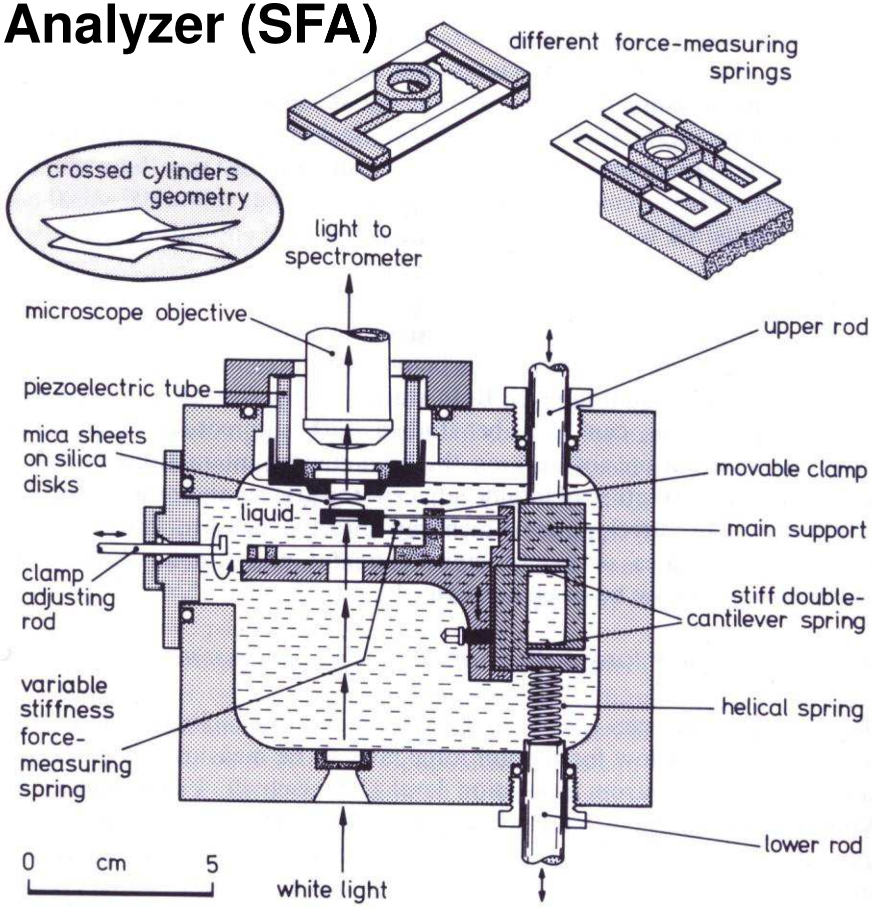
  $z_s < 6$ nm – solid-like

  $6 < z < 100$ – elastomeric

  $z_b > 100$ nm – bulk behavior

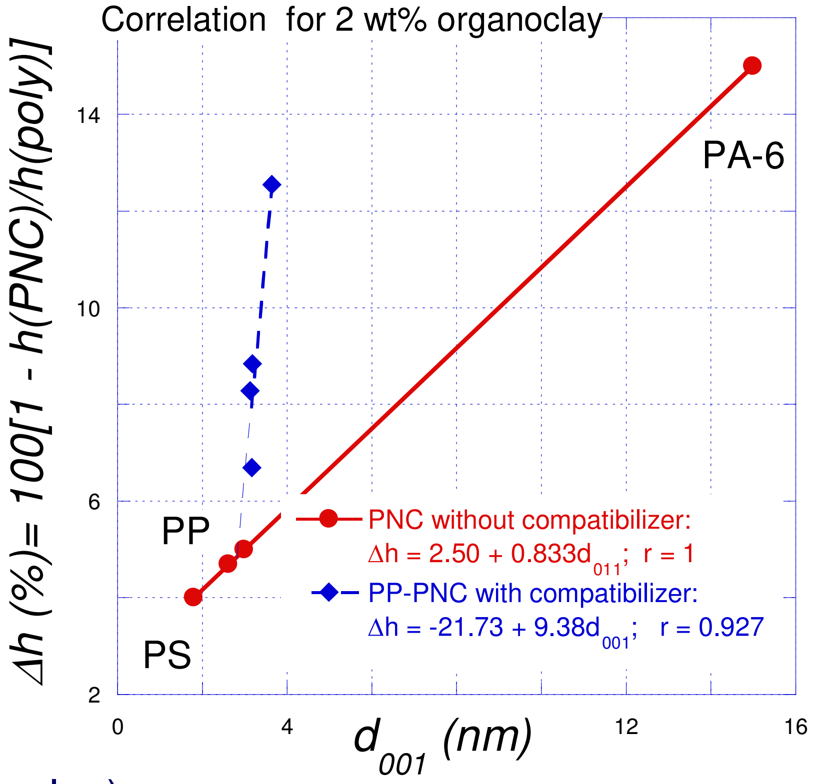
- **Thickness of the adsorbed solid-like layer, z_s, depends on M_w for $M_w > M_e$**

Surface Force Analyzer (SFA)



Free volume in CPNC

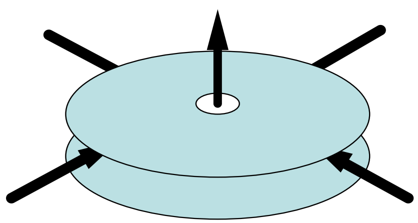
- The PVT data indicate that addition of clay results in reduction of free volume, Δh [Utracki & Simha, 2003; 2004].
- At constant clay content (2-wt% organoclay) Δh linearly depends on the interlayer spacing, d_{001} (standard deviation ± 0.15 nm).
- The Figure shows the correlation between d_{001}, and computed from PVT reduction of h (at 100 MPa & 500 K) for CPNC's based on PS, PP, and PA-6.

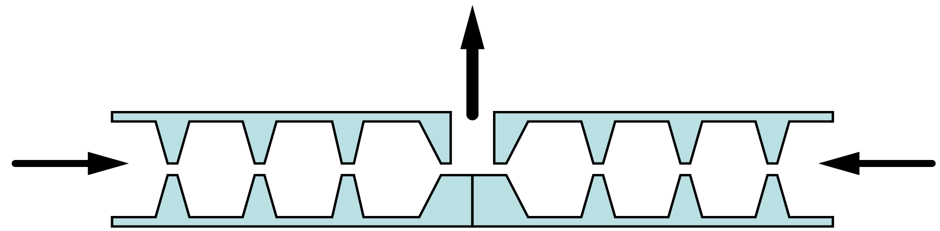


- Two dependencies are seen:
  - For a two component CPNC (polymer/organoclay)
  - For three component: PP/organoclay/compatibilizer systems.
- **The loss of free volume depends on the total clay surface capable to adsorb the macromolecules – equivalent to lowering *T* by ≥ 50°C!**

Generation of extensional flow

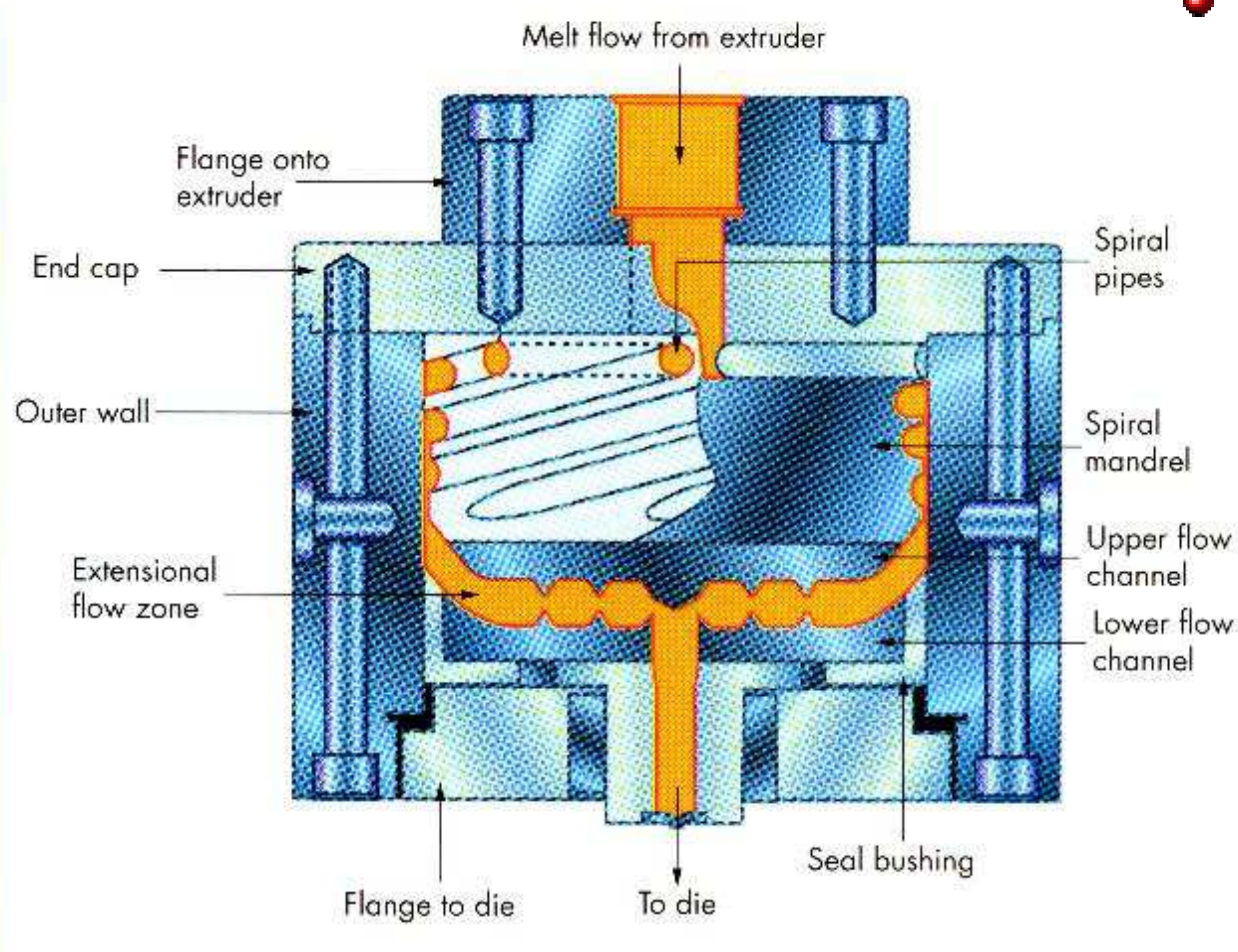
- The heart of EFM = two converging/diverging (C-D) plates separated by adjustable gap





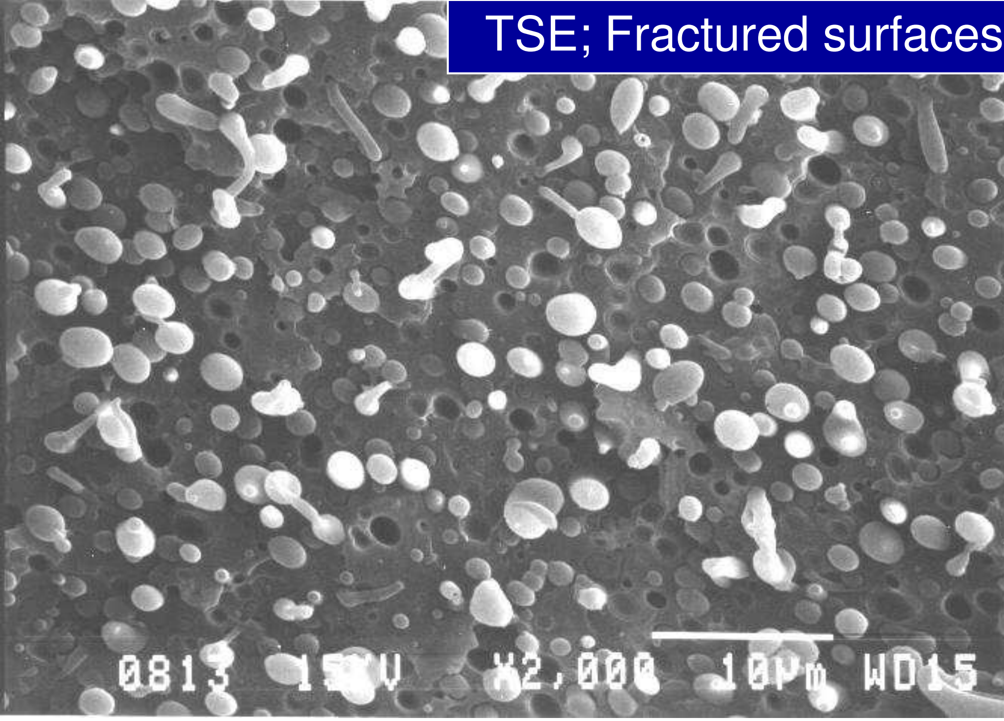
- The C-D plates of different geometries (number, position, and shape of the converging zones) have been used
- They generate radial flow of progressively increasing velocity and stress field.
- Since dispersion of clay stacks and liquid drops in flow are fundamentally different, new geometry of C-D plates was designed for the nanocomposites (EFM-N).

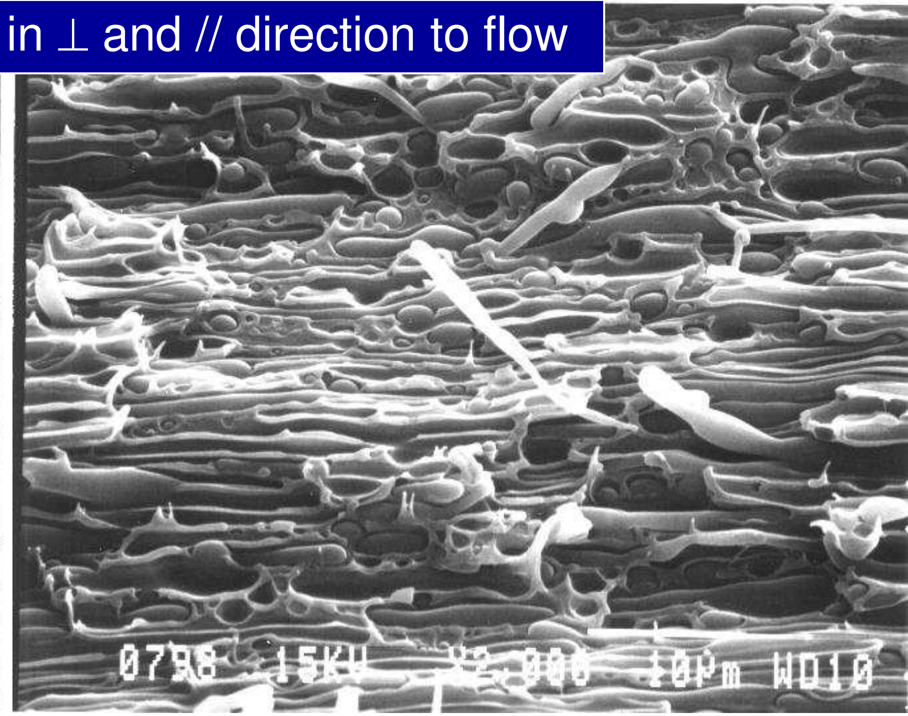
Extensional Flow Mixer, EFM-3



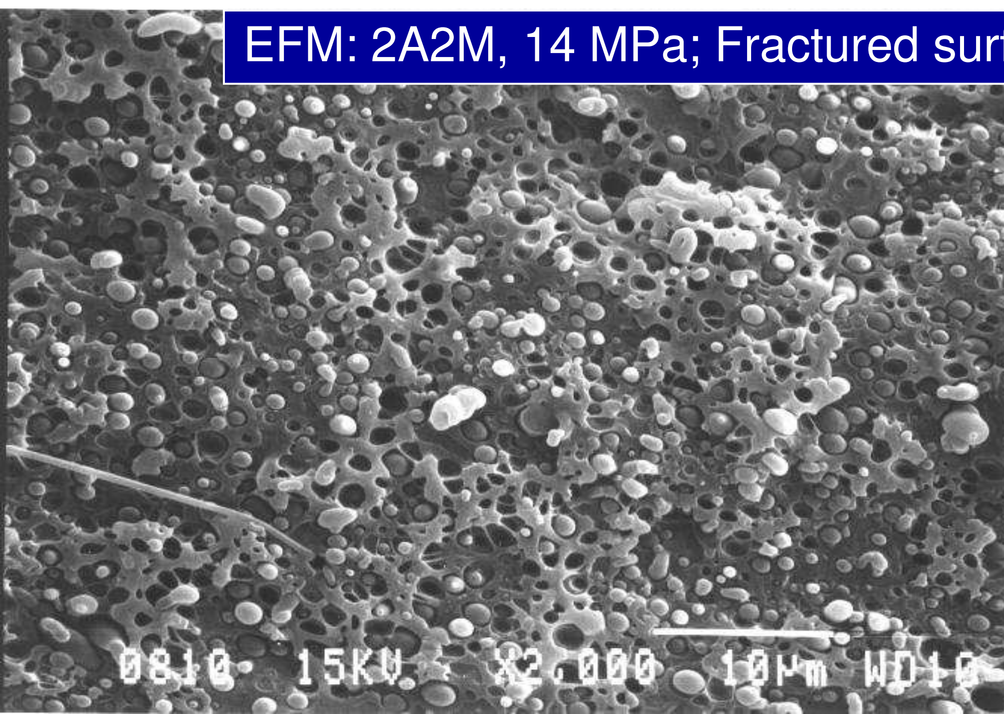
- Commercial mixers:
  1. Spiral feed for better *T*-control & rigidity.
  2. Redesigned C-D plates and mounting.
  4. Redesigned attachment to the die.

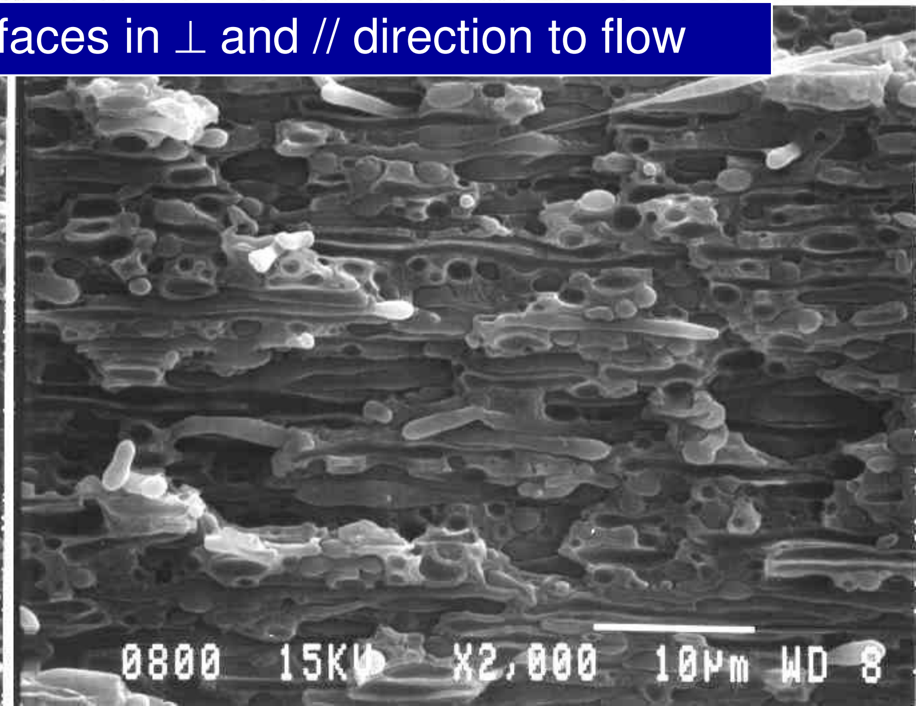
TSE; Fractured surfaces in ⊥ and // direction to flow





EFM: 2A2M, 14 MPa; Fractured surfaces in ⊥ and // direction to flow



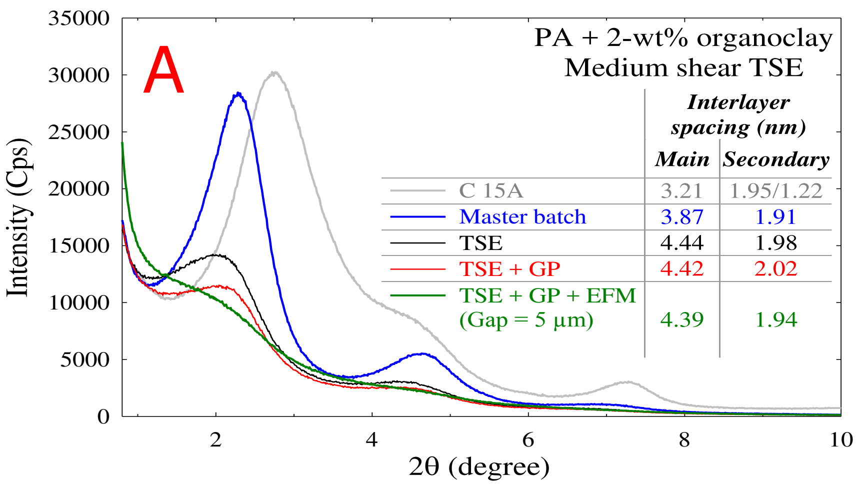


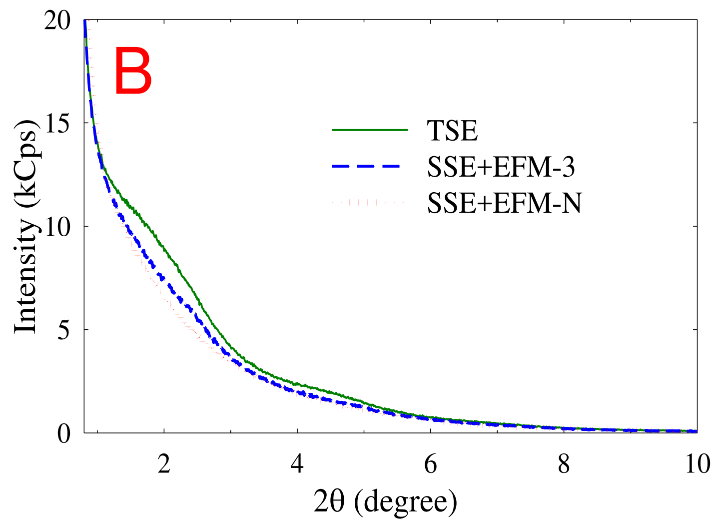
$$d_{00n} = n\lambda / (2 \sin\theta)$$

$$ex = 100(1 - A/A_0)$$

$$N = 1 + \frac{0.9 \cdot \lambda}{W_{\frac{1}{2} peak\ height} \cdot \cos\theta_{hkl} \cdot d_{001}}$$

XRD of PA-6/C15A





- Diluting 4-wt% C15A master-batch with PA-6 in a TSE+EFM (small gap) dramatically changed the degree of clay dispersion (Figure A).
- Dilution increased d_{001} and reduced *N* to a constant value, independent of the compounding method [Sepehr, 2004].
- As the EFM gap decreased the diffraction intensity diminished, indicating increased exfoliation (*ex*).
- Figure B shows that *the best* dispersion in TSE+GP+EFM (gap 5 μm) is worse than that obtained in SSE+EFM-3 or SSE+EFM-N (gap 30 μm).

Part 2

- **Elements of the science & technology**
  - **Mathematical modeling**
  - **Thermodynamics of PNC**
  - **Rheology of PNC**
  - **PNC performance** (*mechanical, barrier, flammability*)

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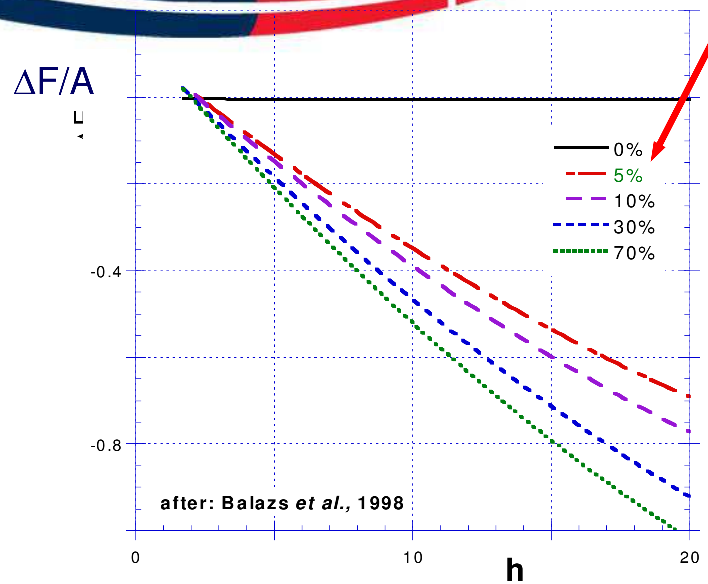
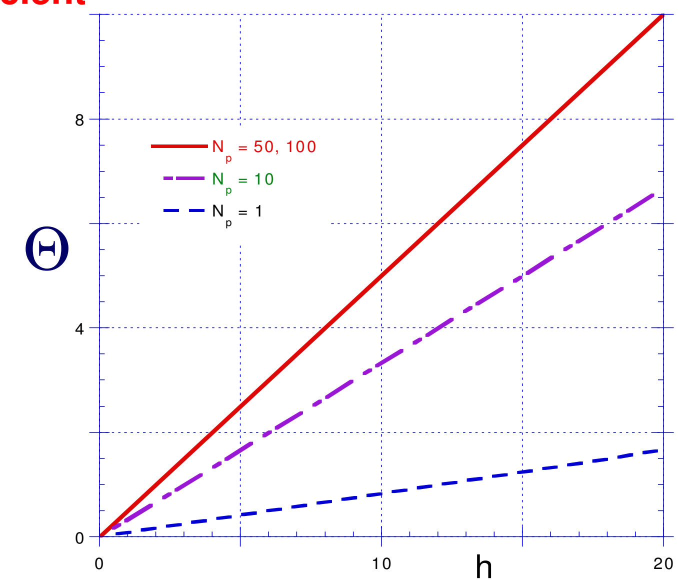
Balazs SCF model 1

- The **self-consistent field (SCF)** lattice model considers adsorption on a solid surface hence the properties change with the short range interactions, ε, and the distance from clay surface, $h_o < z < h$.
- The theory predicts that clay intercalation/exfoliation is reduced by high grafting density, ρ, the latter being related to:
  - Clay CEC (CEC = 0.02 for kaolin, 1 for MMT, 2.5 meq/g for hectorite),
  - Intercalant structure, viz. PA-6 with Cloisite-15A ($2xC_{18}$) or -30B ($1xC_{18}$).
- SCF shows that as the packing density increases it becomes harder for the macromolecules to diffuse into the gallery and mix with the intercalant chains – there is an optimum ρ for intercalation.
- **The SCF computations indicate that it is advantageous to use a macromolecular "sticker" compatibilizer with highly interactive end-group**.

Balazs SCF model 2

5% is sufficient



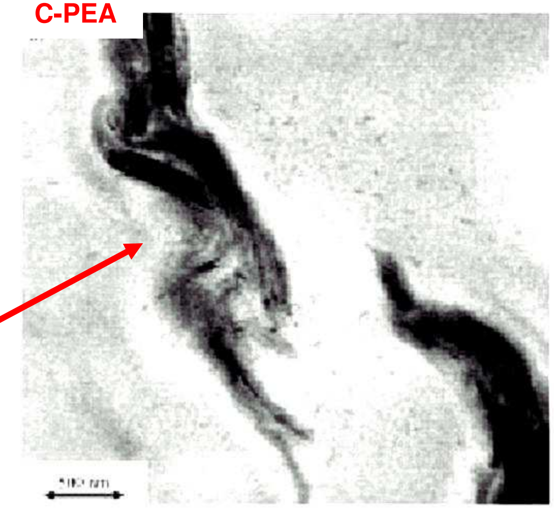


- Free energy vs. gallery height for clay-polymer-”sticker” system (its content is indicated). Thus, 5 wt% of “sticker” is sufficient for exfoliation.
- The amount of adsorbed functionalized “sticker” polymer with $N = 75$ and concentration $\phi = 0.05$ for four chain lengths of the non-functionalized polymer, $N_p = 1, 10, 50$ and 100

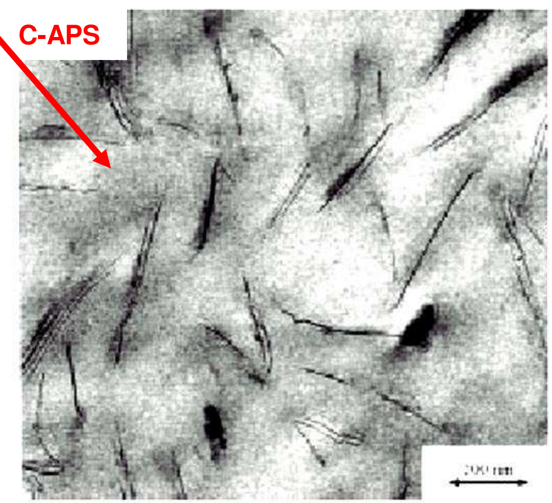
Confirmation of theory

1. **At least two US patents (AMCOL, Exxon) follow Anne Balazs theoretical predictions.**
2. **Hoffmann *et al.*** [2000] **intercalated synthetic fluoromica (Somasif) with:**
    1. 2-phenyl-ethyl amine (M_n = 121 g/mol) = C-PEA.
    2. amine-terminated PS (M_n = 5.8 kg/mol) = C-APS.
    - **Dried organoclays were compounded with the PS at 200°C**
    - **The intercalation expanded the interlayer spacing d_{001} to 1.4 nm with PEA and to > 4 nm with APS.**
    - **Compounding with PS produced large aggregates for C-PEA and full exfoliation for C-APS.**
    - **In C-APS clay platelets were ca. 600 nm long and 100 nm wide hence the aspect ratio: $p \cong 245$.**

C-PEA



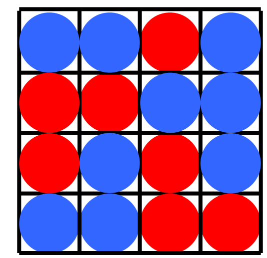
C-APS



4-component systems

$\Delta F = \Delta H - T\,\Delta S$

- System: 1. Clay platelet (s); 2. Host polymer (h); 3. Compatibilizer (g); 4. Organic modifier (o).



- Conformational Entropy, ΔS:

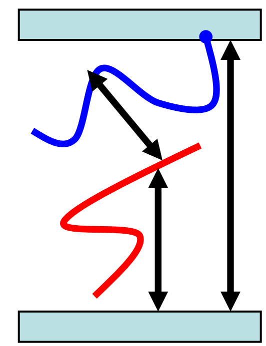
Number of ways to occupy free lattice site

- Mixing Enthalpy, ΔH:

Huggins-Flory short-range parameters

liquid-liquid : χ_{hg}, χ_{hg}, χ_{ho}

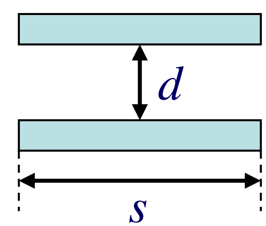
solid-liquid : χ_{hs}, χ_{hs} , χ_{os}



- Long-range interactions for solid-solid :

Van der Waals force between clay plates with Hamaker constant, *A:*

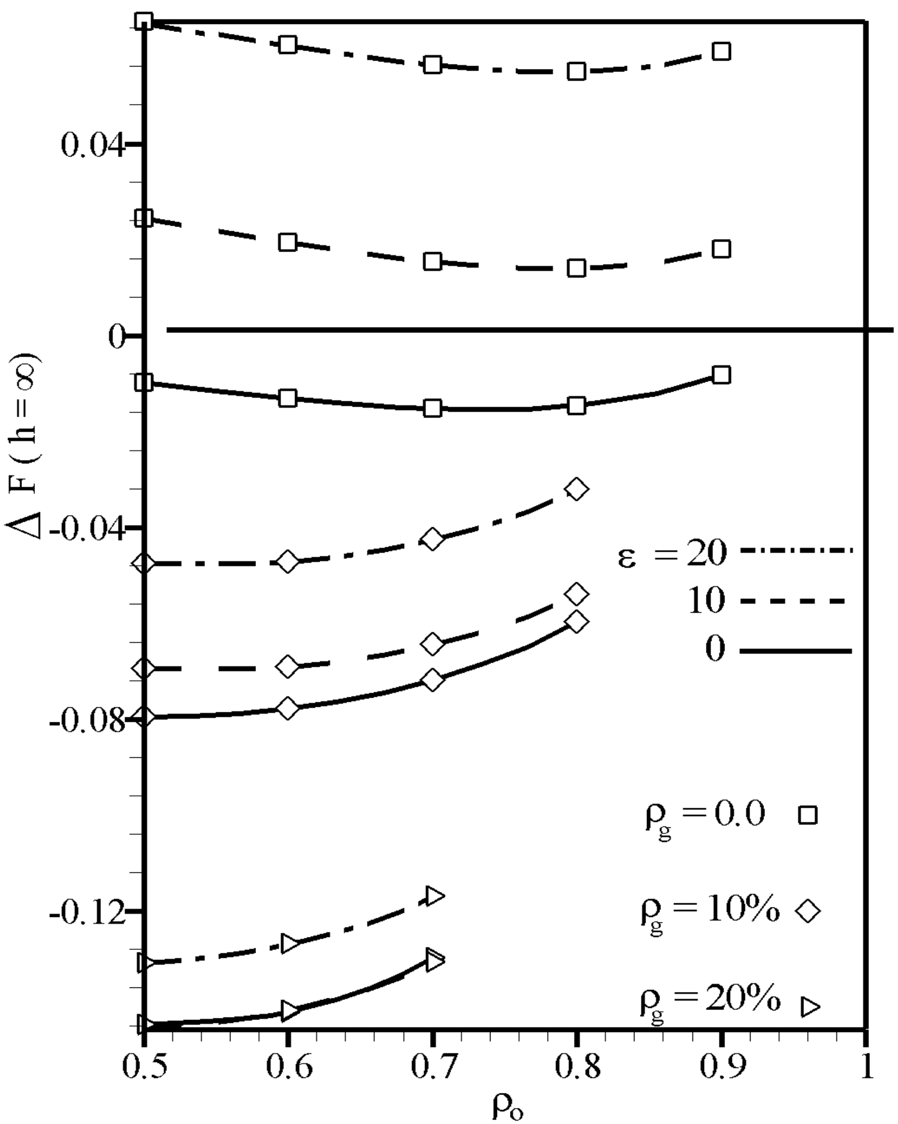
$$F = \frac{-A\,s}{12\pi\,d^2}$$



2

K. Kim, L. A. Utracki and M. R. Kamal, *J. Chem. Phys.*, ***121,*** *10766* (2004).

2D for 4-components



- The influence of the bare-solid area-lattice ratio (ε) and grafting density (ρ_g, ρ_o) on the excess free energy ($h = z \to \infty$).
- **Statistical chain length**

  $N_g = 200$, $N_h = 400$, $N_o = 10$
- **Surface properties**

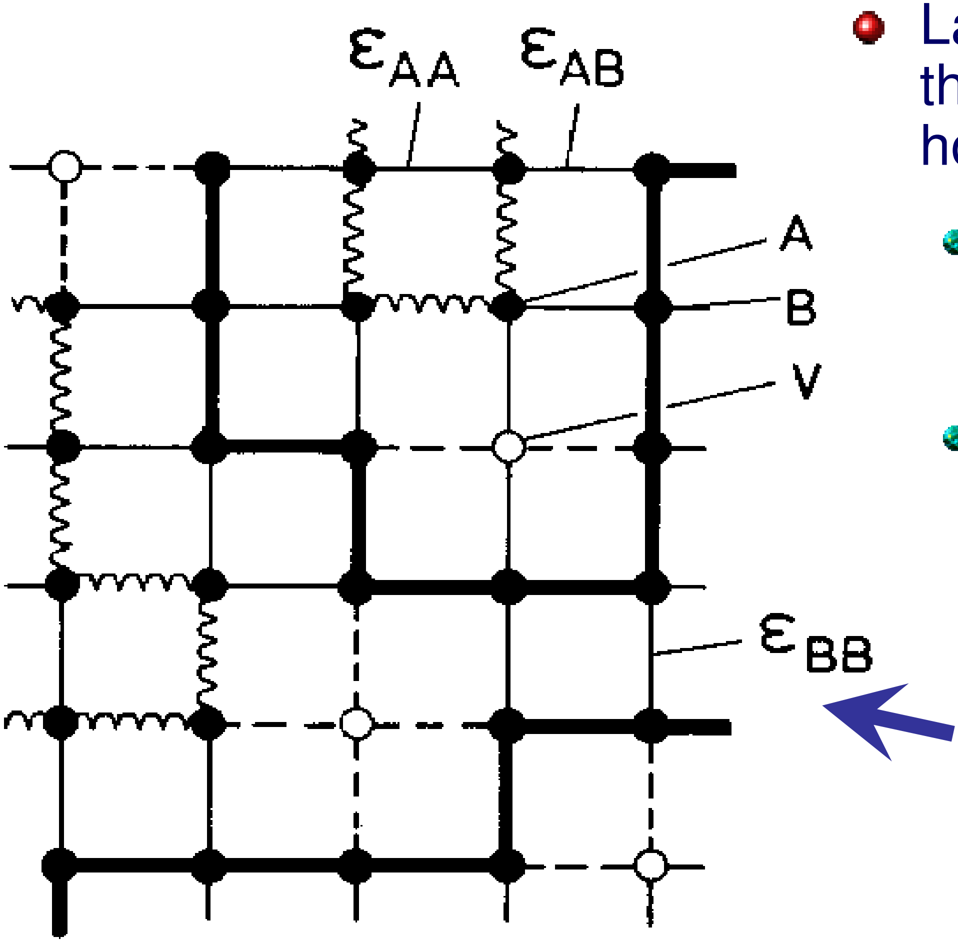
  $\rho_g \in [0, 0.2]$; $\rho_o \in [0.5, 0.9]$; and $\rho_v \in [0.02, 0.05]$
- **Influence of solid-solid interactions**

  $A = 20(k_B T)$, $\varepsilon \in [0, 20]$
- **Binary interaction parameters**

  $\chi_{hg} = 0$, $\chi_{ho} = 0$, $\chi_{go} = 0$,

  $\chi_{hs} = 0.01$, $\chi_{gs} = -0.01$, $\chi_{os} = -0.02$

S-S Lattice model



- Lattice model is a base for many theories, e.g., free volume, cell-hole, tunnel, etc. For example:
  - In 1941 Huggins & Flory calculated the configurational entropy of mixing.
  - **In 1969 Simha and Somcynsky (S-S) derived Helmholtz free energy, then PVT equation of state, etc.**

2D lattice containing two types of molecules and holes or vacancies (open circles). The binary interaction parameters, ε_{ij}, are also indicated.

S-S lattice-hole theory

- The S-S theory describes the thermodynamic properties of liquids, explicitly providing information how the hole fraction ($h = 1 - y$) changes with independent variables.
- From the Helmholtz free energy, *F*, using standard definition of P and thermodynamic equilibrium condition the coupled equation of states (eos) was derived:

$$\tilde{P} \equiv -\left(\partial \tilde{F} / \partial \tilde{V}\right)_T \quad \Rightarrow \tilde{P}\tilde{V} / \tilde{T} = \left(1-\eta\right)^{-1} + 2yG^2\left(AQ^2 - B\right) / \tilde{T}$$

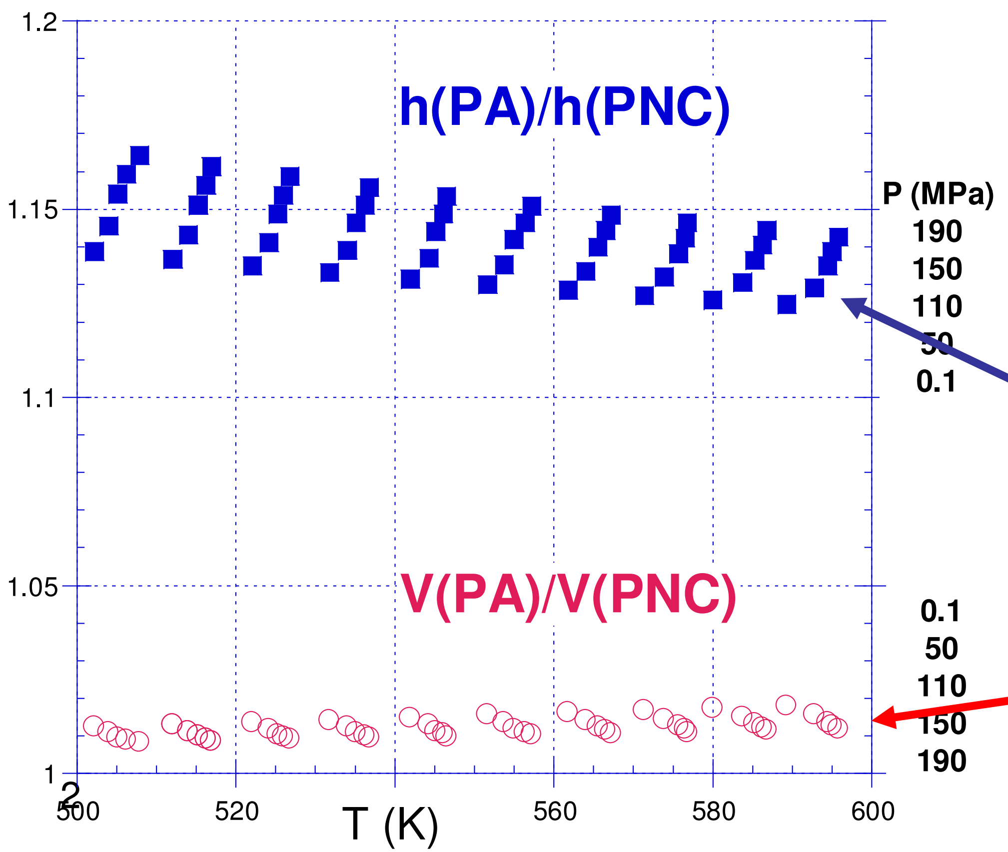
$$\left(\partial \tilde{F} / \partial y\right)_{\tilde{V},\tilde{T}} = 0 \quad \Rightarrow 3c\left[\left(\eta - 1/3\right)/\left(1-\eta\right) - yQ^2\left(3AQ^2 - 2B\right)/6\tilde{T}\right]$$

$$+\left(1-s\right) - s\,ln\left[\left(1-y\right)/y\right] = 0$$

$$where: \quad A = 1.011;\ B = 1.2045; \quad \eta = 2^{-1/6} yQ^{1/3}; \quad Q = \left(y\tilde{V}\right)^{-1}$$

PVT measurements 2

- To directly compare the specific volume and the hole fraction variations with T and P for PA and PNC, the ratios V(PA)/V(PNC) and h(PA)/h(PNC) at identical T and P for each point are shown.

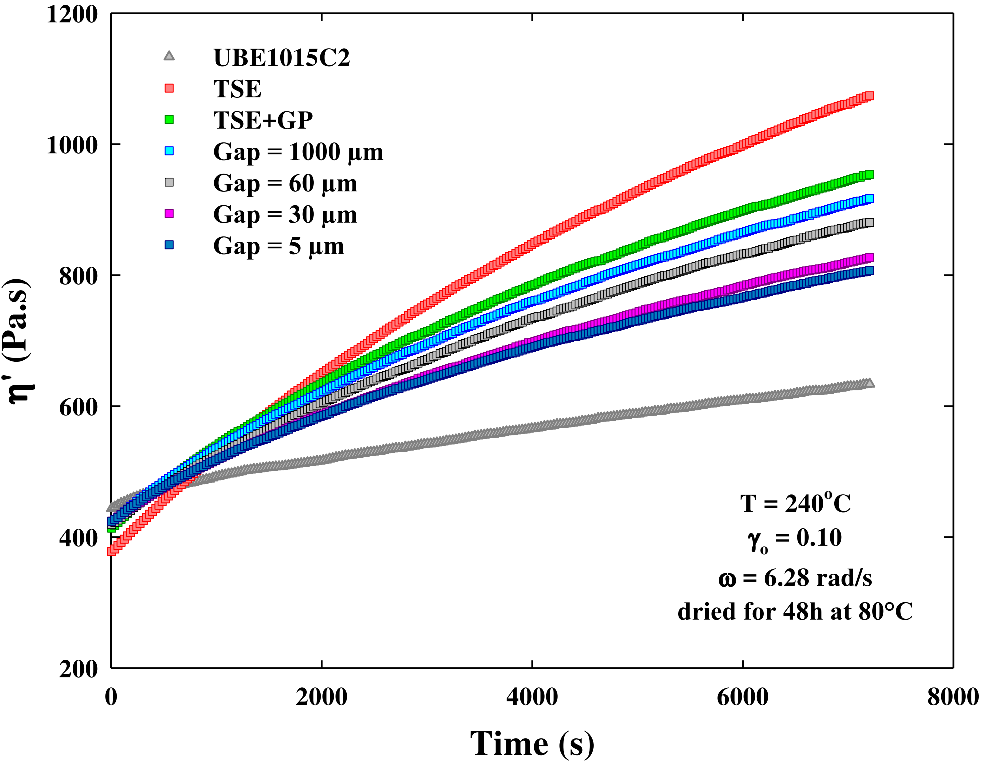


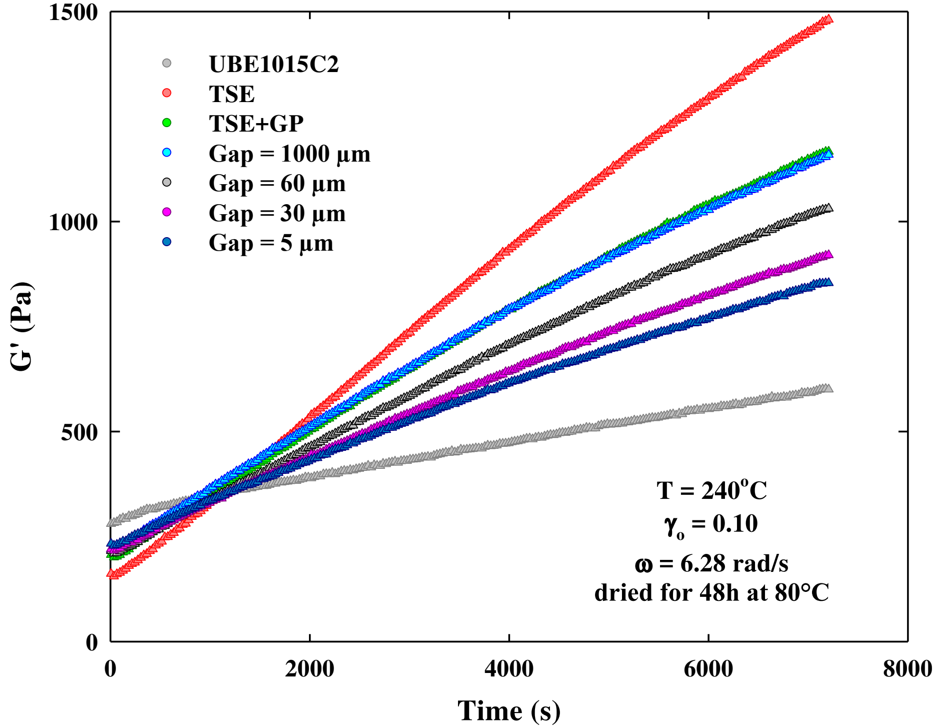
- Theoretical V-ratio for PNC with 0.64 vol% clay is: *V(PA)/V(PNC) = 1.0088*.
- The holes ratio: *h(PA)/h(PNC) = 1.125 to 1.159*.
- The experimental ratio *V(PA)/V(PNC) = 1.008 to 1.018*.

Rheology of PNC

- **Thermodynamics suggest the hairy-clay platelet (HCP) model for PNC.**
- **PA-6 and PA-6-based PNC from Ube** were dried and then compounded in a TSE with: 0; 25; 50; 75; and 100% of PNC.
- The rheological tests were carried out at 240°C under blanket of dry N_2 [Utracki & Lyngaae-Jørgensen, *Rheologica Acta,* **41,** 394 (2002)].
- During the time sweep the storage (*G*') and loss (*G*") shear moduli increased with time, due to polycondensation & exfoliation.
- The rates of these two processes differently depended on the intercalated clay content.
- All raw data were corrected for the polycondensation effects by extrapolating the measured signal to $t = 0$.

Time-effects



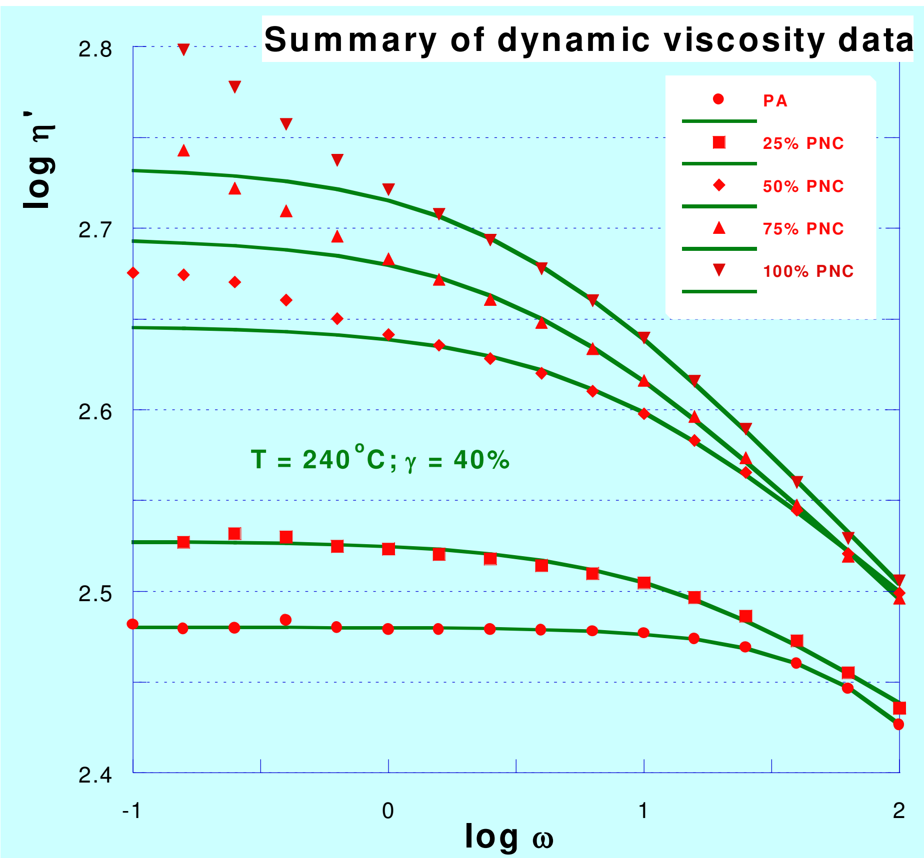


- The dynamic viscosity (left Figure) and the storage modulus (right Figure) for PA-6 with 2-wt% organoclay are presented [M. Sepehr, 2004].
- The polycondensation rate decreases with the increasing degree of clay dispersion.

Dynamic flow 1

Frequency sweeps at T = 240°C, γ = 10 & 40%

- G' and G" were corrected for the time effects using the rates determined in time sweep *(t < 600 sec).*



- The data were fitted to the relation:

$$G''/\omega = \eta_o\left[1+(\omega\tau)^{m_1}\right]^{-m_2}$$

where η_o is the zero-shear viscosity, τ is the prime relaxation time and the power-law exponent: $n = 1 - m_1m_2$.

- Thus, the shear viscosity data were separated into a pseudoplastic flow and yield-like contributions.

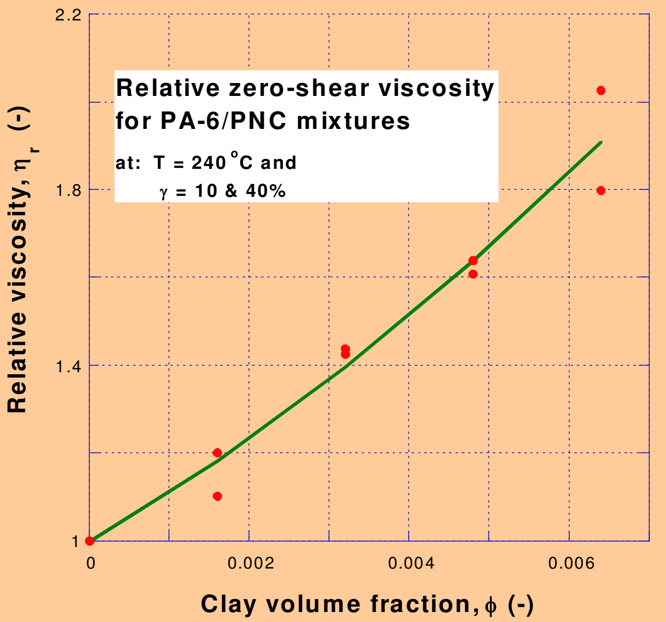
Dynamic flow 2

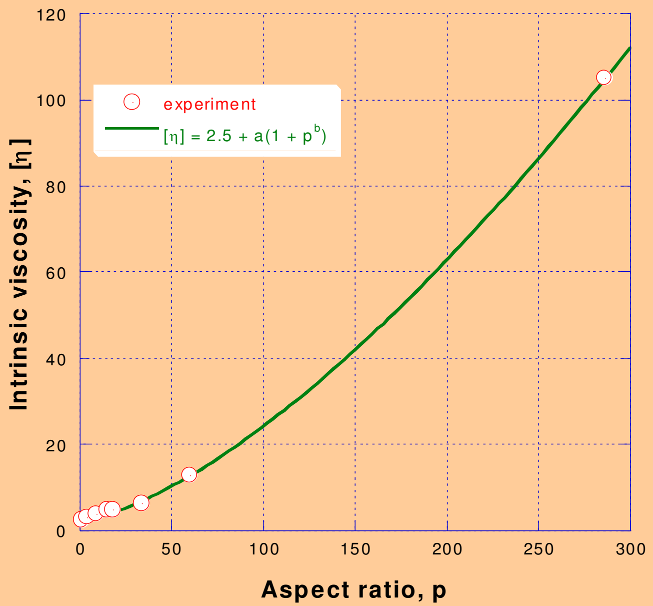
Zero-shear viscosity of PA-6/PNC mixtures

- The concentration dependence of η_o was described the relation derived for dilute suspensions:

$$\eta_r \equiv \eta_o^{'} / \eta_{o,PA}^{'} = 1 + [\eta]\phi + k\left([\eta]\phi\right)^2$$

where [η] is the intrinsic viscosity, k is a constant.

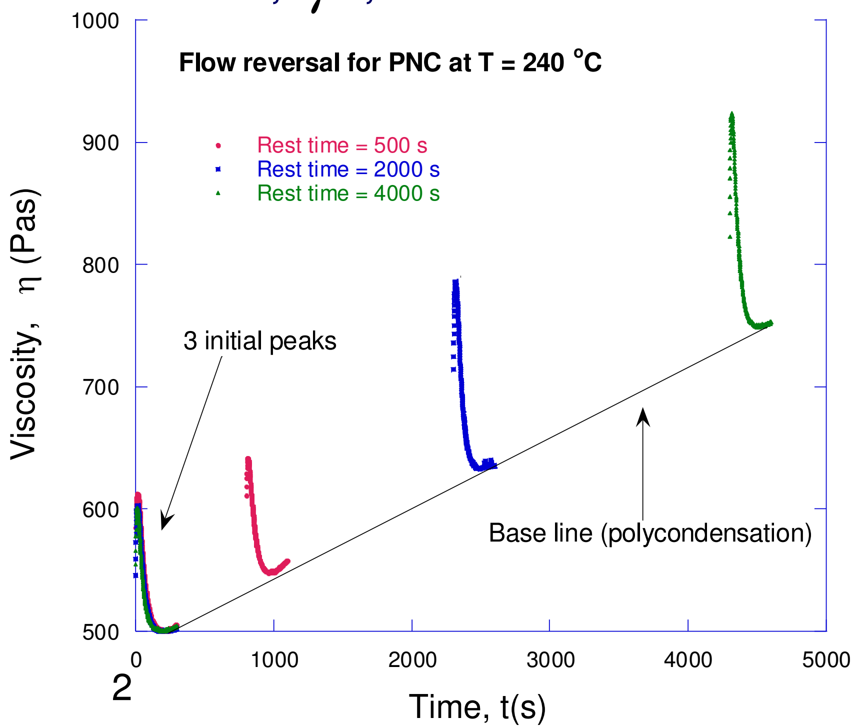




- For anisometric particles: $[\eta] = 2.5 - a(1-p^b)$, where p is the aspect ratio
- Computed from the flow data value of $p = 287 \pm 9$ agree with the nominal $p = 286$ determined from the barrier properties.

Stress overshoot 1

- The LCP model also predicts the stress overshoot:
  - PNC was pre-sheared at $\dot{\gamma}$ = 0.1 s^{-1} for 5 min; γ = 30.
  - The shearing stopped for the rest time, t_r < 4000 s.
  - Shearing re-started, but in opposite direction, at the same rate, $\dot{\gamma}$, and for the same time of 5 min.

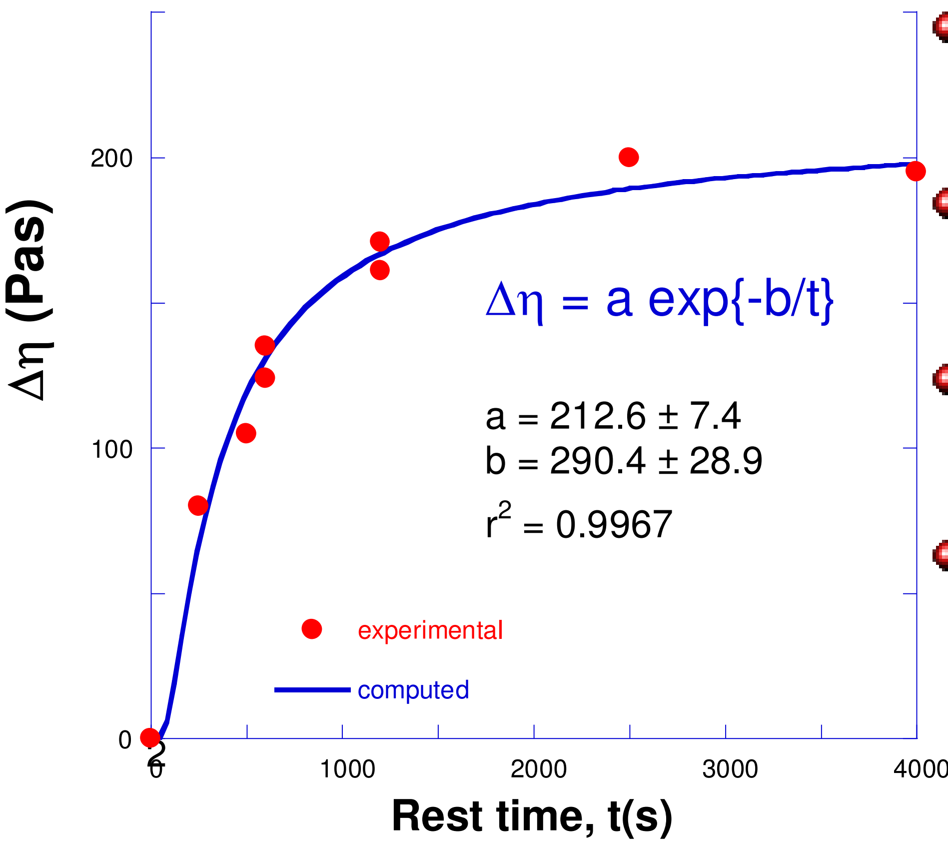


- In the Figure, stress overshoot vs. t_r is plotted:
  - First peak shows overlapping data for three separate specimens.
  - Other peaks were determined after rest time, t_r = 500, 2000 & 4000 s.
  - Due to polycondensation the base line is shifted.
- Stress overshoot is the peak height above base line.

2

Stress overshoot 2

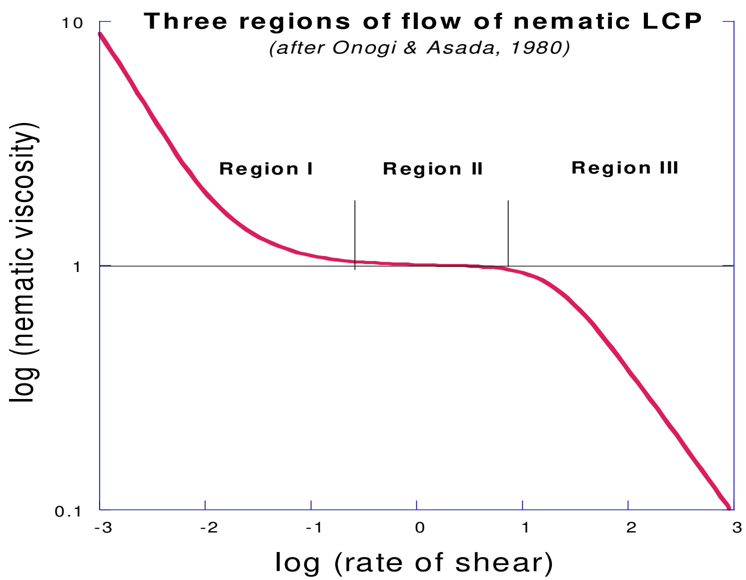
- The stress overshoot is related to orientation of anisometric elements during steady-state shear flow.
- Resuming shearing after rest time probes the extent of disorientation.

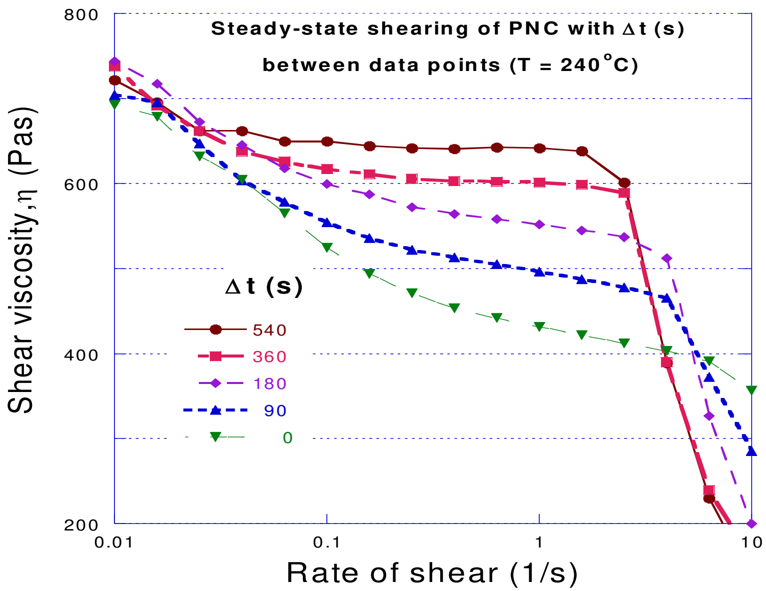


- The magnitude of the stress overshoot depends on the rest time at 240°C.
- There is but a small difference when shearing (after rest) is in the same or opposite direction.
- It takes about 1 hr for the platelets to return to the pre-shear random orientation.
- Experimental data follow a simple exponential relation hence one type of anisometry.

Steady-state flow

- **Flow of PA-6/PNC follows the LCP behavior:**





- The flow of LCP is characterized by the presence of three regions reflected by interactions between mesogenic groups:
  - I – the poly-domain structure gradually destroyed by shear.
  - II – rotation of nematic domains dispersed in a mono-domain continuous matrix,
  - III – flow by the tumbling motion, gradually replaced by flow alignment.

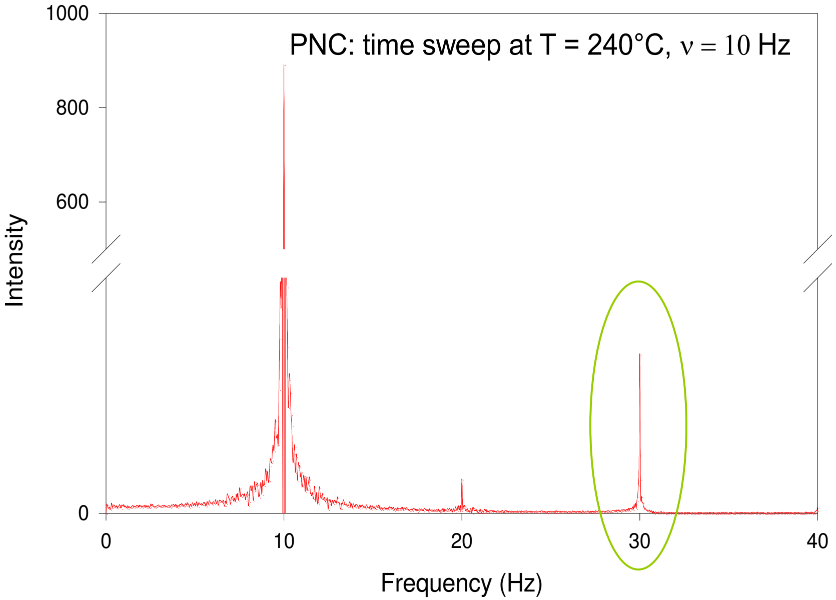
Fourier-transform rheology 1

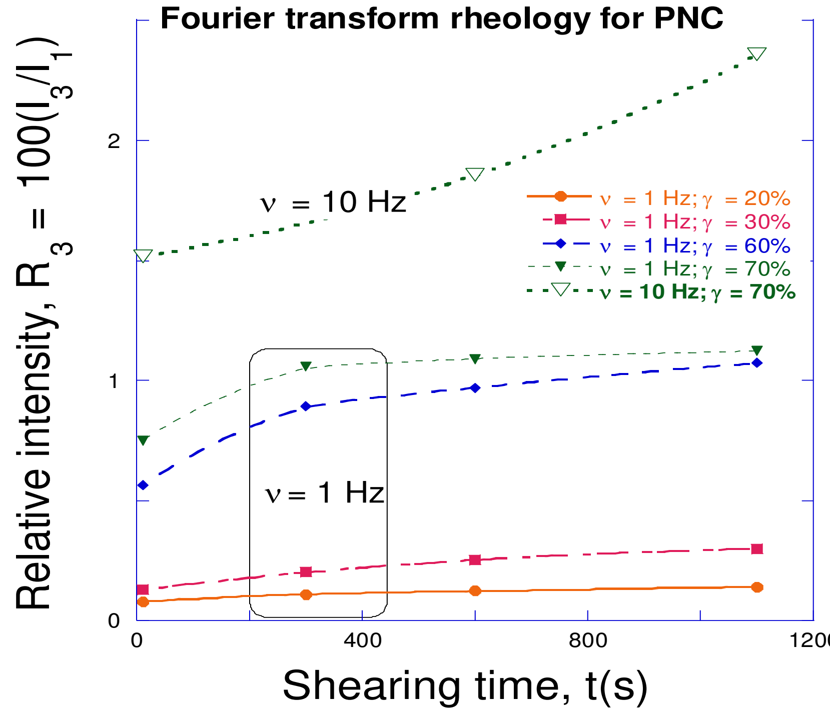
- The Fourier-transform rheology (FTR) has been used to analyze non-linear viscoelastic response in large amplitude oscillatory shear (LAOS) tests.
- The FTR measures higher harmonics that in the past were only qualitatively characterized by the Lissajou stress-strain loops [Wilhelm, 2002].
- Considering complex rheological behavior of molten PNC application of FTR may provide quantitative measure of the non-linear viscoelastic response caused by the time dependent ordering and orientation effects.
- According to FTR, the stress is a sum of odd harmonics:

$$\sigma \propto A_1 \cos 3\omega t + A_2 \cos 5\omega t + A_3 \cos 7\omega t + ...$$

- The simplest method for the analysis of FTR signal is to plot the relative magnitude of the odd harmonic peaks divided by the first one: $R_n(\omega) = I(n\omega)/I_1(\omega)$, with $n = 3, 5, 7, \ldots$
- For non-linear materials $R_i(\omega) = 1/n$, thus the strongest third harmonic, $R_3(\omega)$, contains all pertinent information.

Fourier-transform rheology 2

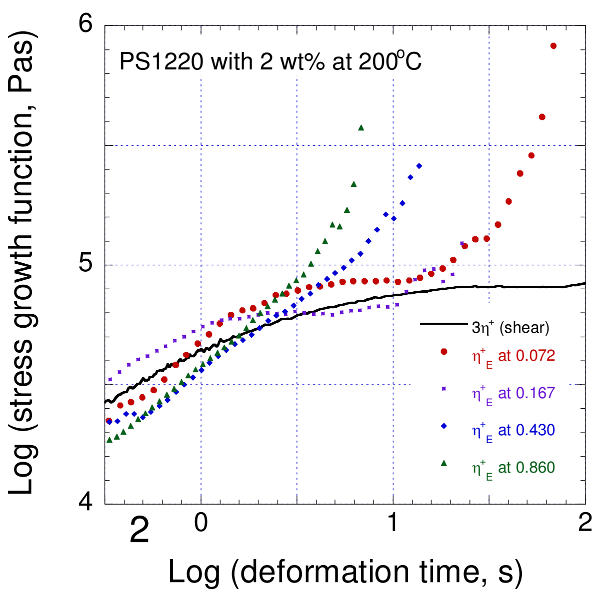


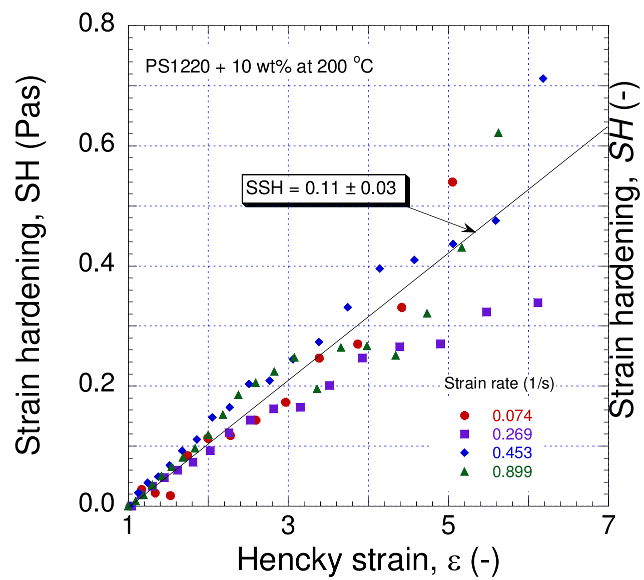


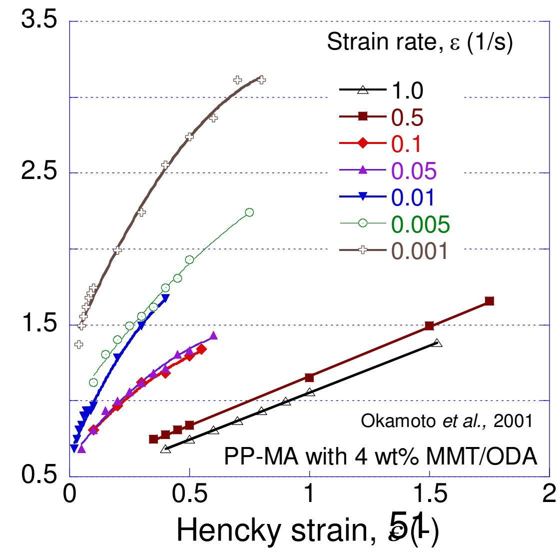
- **The Fourier-transform rheology (FTR) is a new method for quantifying the non-linear viscoelastic behavior of matter.**
  - Left Fig. shows the raw data: input peak and 3rd harmonic.
  - Right Fig. show the relative intensity of the 3rd harmonic – a measure of non-linearity as a function of frequency, strain and shearing time.

Extensional flow of PNC's

- PS-based PNC was measured in RER and in RME.
- Strain hardening (SH) was strain-rate ($\dot{\varepsilon}$) independent.
- Strong effects of ε were calculated from nanocomposites based on PP-MA, indicating strain and strain-rate dependent structure in this PNC.
- Since ***d_{001}* = 3.0 nm**, aggregation of MAH-groups is suspected.







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Summary of PNC Rheology

- The characteristic feature of the PNC flow is the presence an yield-like behavior at low deformation rates, *i.e.*, the viscoelastic non-linearity (VNL).
- The better dispersed is the system, the higher is the VNL.
- The flow of exfoliated PNC resembles that of lamellar LCP with very large mesogens (relaxation time of ca. 60 min).
- Fourier-transform rheology (FTR) is a useful tool for characterization of VNL hence the degree of dispersion.
- To interpret the PNC flow behavior the hairy-clay platelet (HCP) model was used:
  - The clay are enrobed in solidified organic phase, from which emanate long, able to entangle macromolecules
  - Consequently, for well dispersed PNC the VNL behavior is observed at concentration below that calculated from the encompassed volume principle.
  - Owing to large aspect ratio ($p \leq 300$) there is a strong orientational effect

PNC Performance

- Four main reasons for the development of PNC:
  - Enhanced rigidity (100% at 5 wt% clay)
  - Improved barrier properties (by a factor of 100 at 10 wt%)
  - Reduced flammability (PHRR reduced by 2/3 at 5 wt% clay)
  - Improved heat deflection temperature (HDT)
- Examples of published data for various systems are tabulated for PA-6 and its CPNC's with 2 wt% organoclay (mineral & synthetic):

Mechanical properties of PA-6 and based on it PNC.
Data from [Ube Industries, Ltd., 2002, and Unitika Plastics, 2004].

Property	ASTM	Units	Ube		Unitika	
			PA-6	PNC	PA-6	PNC
Tensile strength, σ	D-638	kg/cm^2	800	910	810	930
Tensile elongation, ε_b	D-638	%	100	75	100	4
Flexural strength, σ_f	D-790	kg/cm^2	1100	1390	1080	1580
Flexural modulus, E_f	D-790	kg/cm^2	28,500	35,900	29,000	45,000
Impact strength, *NIRT*	D-256	kg cm/cm	6.5	5	4.9	4.5
HTD (18.56 kg/cm^2)	D-648	°C	75	140	70	172
HTD (4.6 kg/cm^2)	D-648	°C	180	197	175	193
H_2O permeability, P_{H2O}	JIS Z208	G/m^2 24 h	203	106	--	--
Density, ρ	D-792	kg/m^3	1140	1150	1140	1150

Relative tensile modulus

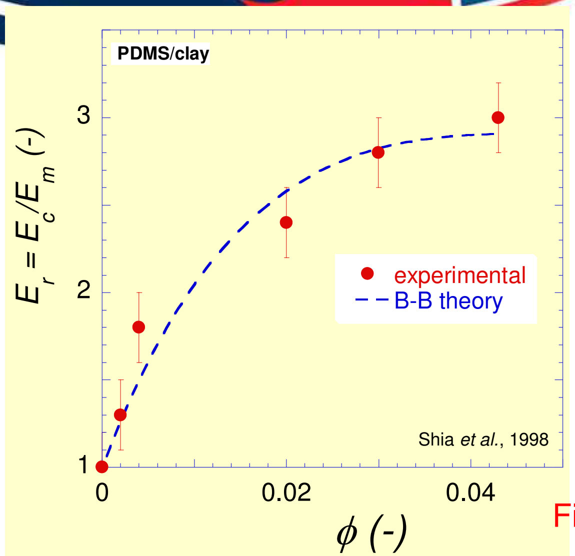


Fig. 1

$$p' = (p/N')/\left[1+(1-1/N')(s/t)\right]$$

$$\phi' = \phi\left[1+(1-1/N')(s/t)\right]$$

$$E_r' = \frac{E_r + (1-1/N')(s/t)}{1+(1-1/N')(s/t)}$$

$$N' = N + (1-N)(s/t)\frac{\phi}{1-\phi}$$

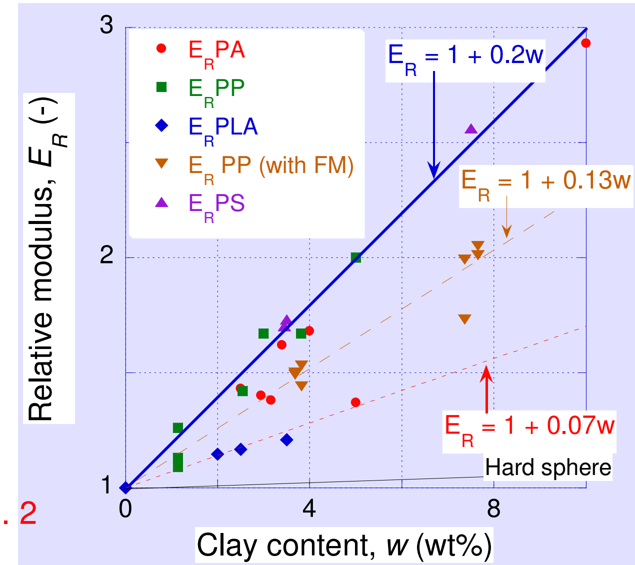
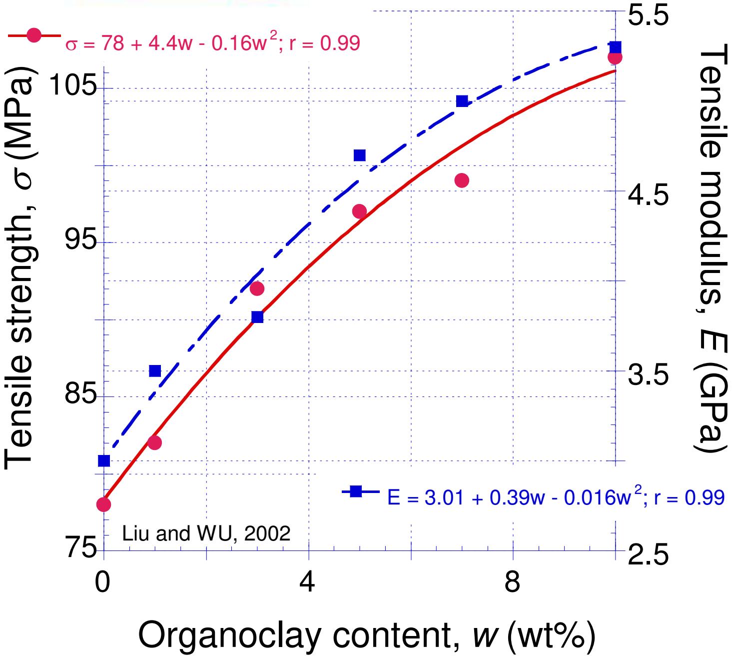
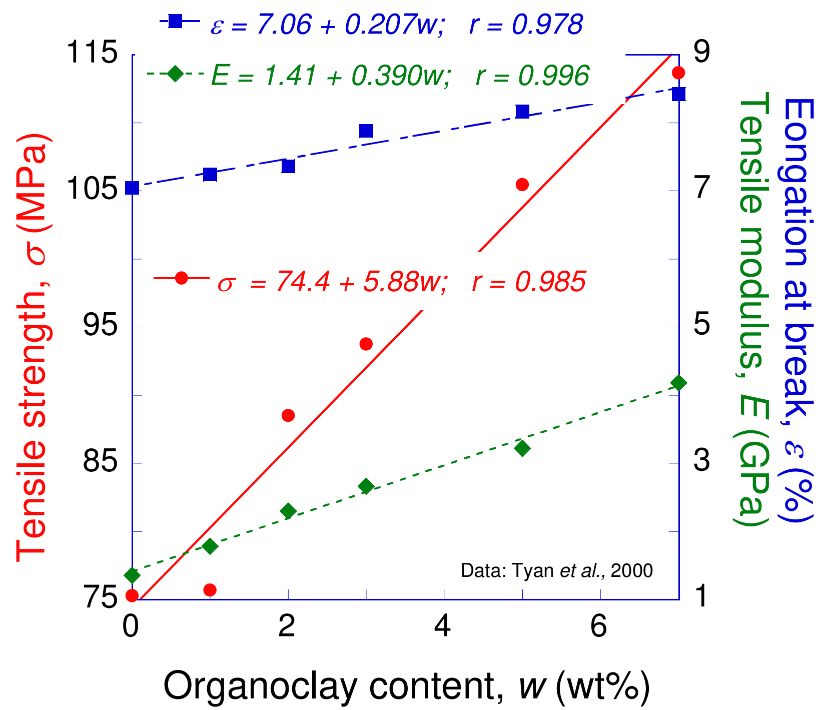


Fig. 2

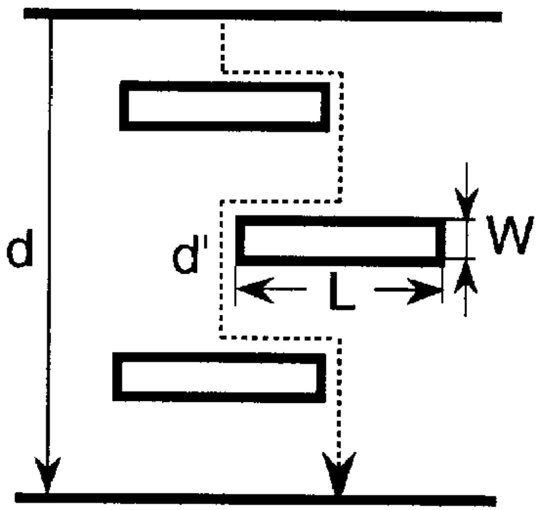
- Fig. 1: Relative modulus vs. clay content for CPNC with PDMS as the matrix. Experimental data [Shia et al., 1998] and theoretical prediction from Brune-Bicerano(B-B) relations (see center).
- B-B derived a relationship between tensile modulus & clay content for exfoliated and intercalated systems. In the Eqs. *p'* = the aspect ratio, ϕ' = clay volume fraction, and *E'* = the tensile modulus in platelet stack composed of *N*-clay layers, each with thickness *t* and the interlamellar gallery spacing, $s \cong d_{001} - 0.96\,nm$.
- Fig. 2: E_R vs. clay content for CPNC of PA-6, PP, PLA and PS with MMT, and PP with fluoromica (FM): $E_R \equiv E/E_m = 1+[\eta]\phi \cong 1+aw \Rightarrow a \simeq [\eta]/314$

Mechanical performance





- Tensile strength (σ), and modulus (E) of PA-66 vs. organoclay (MMT-3MHDA-DGEBA (*di*-glycidyl ether of *bis*-phenol-A). Points – experimental, lines – polynomials [Liu and Wu, 2002]. At 5-wt% loading: E and σ increased by 26%.
- Tensile modulus (E) tensile strength (σ), and elongation at break (ε) of polyimide (PI) with MMT-ODA [Tyan *et al.*, 2000]. The properties are well approximated by straight lines – their parameters are given. At 5-wt% loading: E, σ, and ε increased by ca. 139, 40, and 16%, respectively.



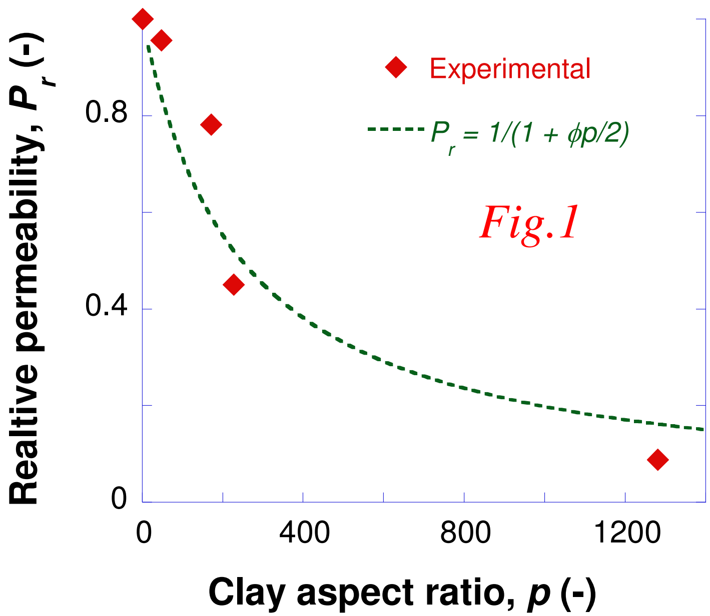
Permeability control 2

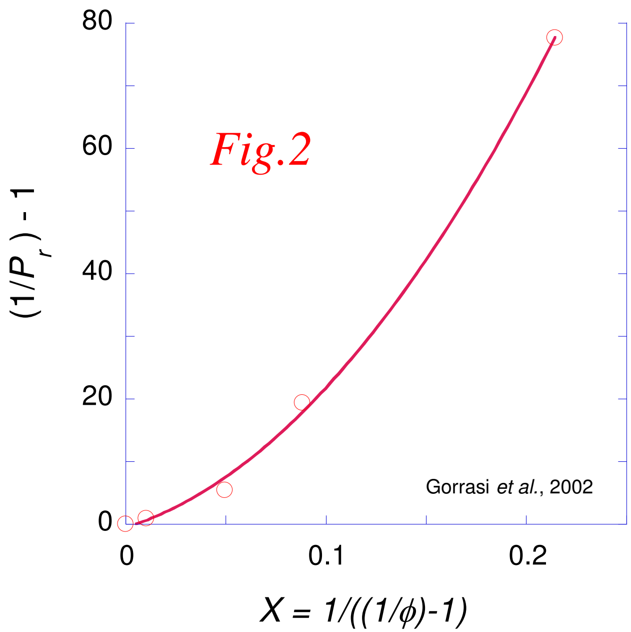
$$P_r \equiv \frac{P}{P_o} = \frac{1-\phi}{1+\phi p(S+1/2)/3}\,; \quad S = \left\langle 3\cos^2\theta - 1\right\rangle / 2$$

$$\therefore \left(1/P_r\right) - 1 = \left[1 + p(S+1/2)/3\right]\cdot\left[\phi/(1-\phi)\right]$$

- The relations specify, that the relative permeability, P_r, depends on the clay platelets aspect ratio, p, their volume fraction in the matrix, ϕ, and the orientation factor, S *[Bharadwaj, 2001]*.
- In the definition of S, θ is an angle between platelet and the wall surfaces; S = 1, -½, and ¼ for flux perpendicular to platelet ($\theta = 0$), in parallel ($\theta = \pi/2$; $P_r = 1$!), and random ($\theta = \pi/4$), respectively.
- Evidently, the degree of dispersion (exfoliation) enters into p.
- The second equation linearized the dependence (at low ϕ).

Permeability control 3

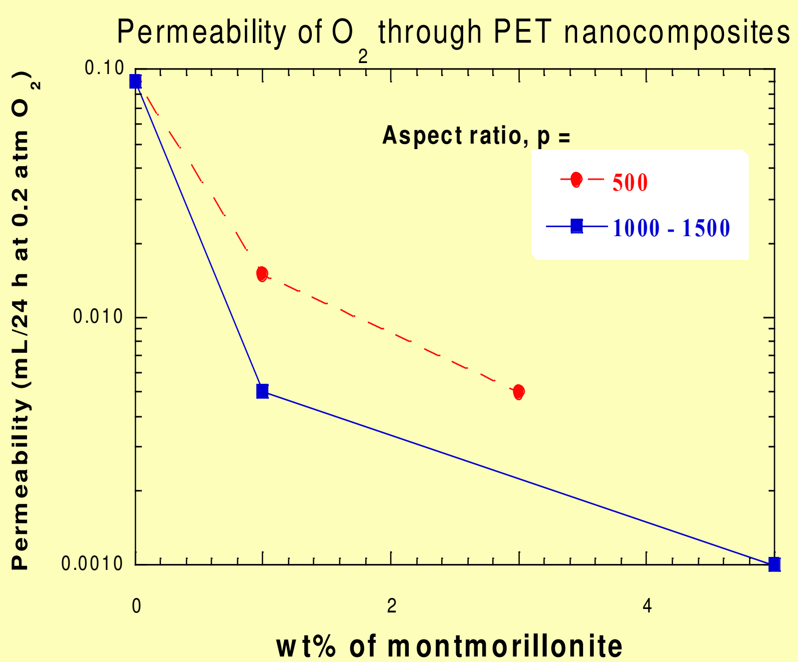




- *Fig.1:* Relative permeability of polyimide containing 2 wt% of clays vs. aspect ratio [Yano *et al.*, 1997]. Line was calculated from the presented relation.
- *Fig. 2:* Relative permeability of di-chloro methane through PCL-type CPNC, plotted as $Y = 1/P_r$ vs. $X = \phi/(1 - \phi)$. Data [Gorrasi *et al.*, 2002]. The line is the least square fit to the relation: $Y = 1 + (1 + \langle p\rangle/2)X + bX^2$, with the average aspect ratio: $\langle p\rangle = 197$ and the parameter $b = 1240$, indicating **enhanced barrier properties at higher clay loadings** (overlap?).

Permeability control 4

- Addition of 5 wt% of clay with *p* = 1000-1500 reduces the O_2 permeability by two orders of magnitude [Tetra Laval, 1999].
- Exfoliated clay increases container barrier properties and stiffness not affecting its transparency. Only 0.1-2 mm thick layer of a PNC is required.



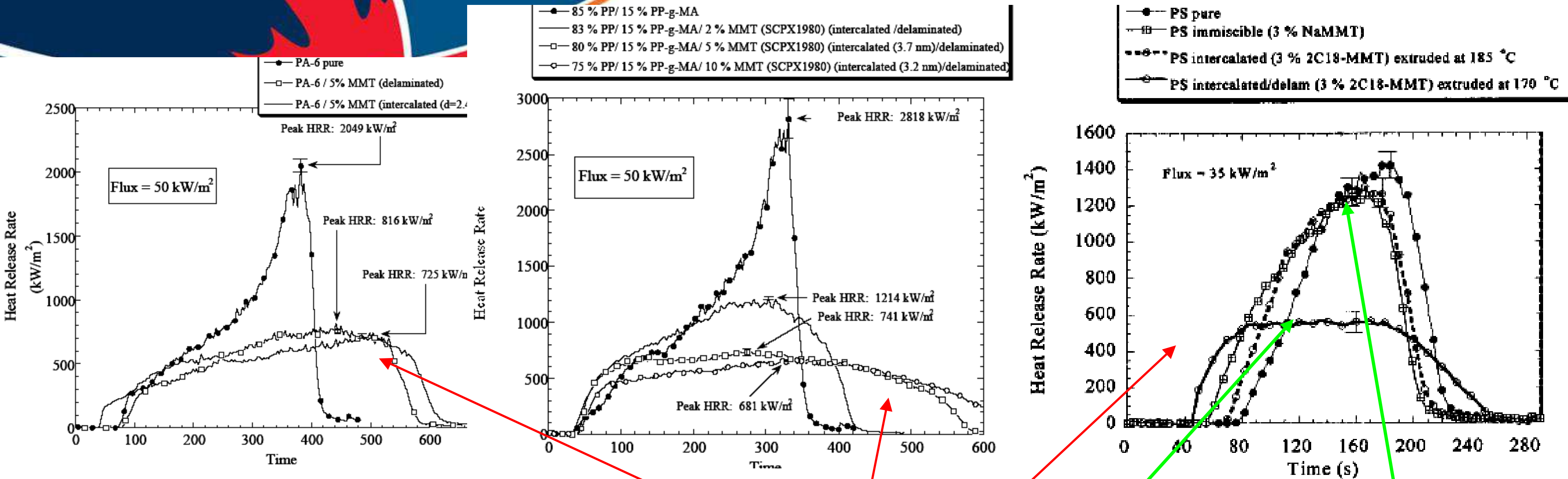
- The process involves polymerization in the presence of intercalated clay with a "swelling -&-compatibilizing" agent being present.
- Currently, the inner PNC layer in PEST containers is PA-based (MXD-6 = *meta*-xylene di-amine + adipic acid)!

Flammability 1

- In 1965 Blumstein reported that presence of MMT increased the thermal decomposition temperature of PMMA by 40-50°C.
- In 1997 Gilman labeled the PNC "*a revolutionary new flame retardant*":
  - 5 wt% clay reduced the peak heat release rate by 63% (but the kinetic and the total heat of combustion remained the same).
  - Clay enhances char formation. Owing to reinforcement by clay particles there is a significant reduction of the gas diffusion rate.
  - By contrast with the customary flame retardants that reduce the resin performance, in PNC the other physical properties are greatly improved.
- Incorporation of dispersed clay significantly increases the char (composed of clay + graphitized carbon) content:

PA6 PA6/Clay(2%) PA6/Clay(5%)

Flammability 2



- Flammability reduction of CPNC with PA-6, PP-*g*-MA or PS as the matrix, were measured in a cone calorimetry at NIST [Gilman *et al.,* 2000; Kashiwagi *et al.,* 2004].
- Peak heat release rate (PHRR) was reduced by 50%-75%.
- To affect flammability, MMT should be well dispersed, but not necessarily fully exfoliated.
- Synthetic fluorohectorite was *ineffective* at reducing the flammability of PS.
- Extrusion of PS with 3-wt% of 2M2ODA-MMT at 170°C reduced flammability, but at 185°C it did not (degradation of organoclay!).
- TEM and XRD were used to study the mechanism of flammability reduction.
- The type of clay, clay dispersion, and processing degradation influenced the flammability reduction.

Conclusions 1

- Na-MMT with CEC = 0.9 -1.2 meq/g and p = 200 - 500, is the most popular nano-filler.
- Success of PNC hinges on intercalation that involves, *e.g.*:
  - Reacting MMT^{-} anion with onium cation (ammonium, phosphonium or sulfonium).
  - Reacting acidified MMT with basic groups of a monomer.
  - Adsorbing a polar liquid (e.g., PVP, PVAl or PEG)
  - Inorganic structures by hydrolysis of metal-alcoholates
- Most common is intercalation with a quarternary ammonium ion –disadvantage: decomposition at $T > 180^{o}C$, and inherent immiscibility with most polymers.
- Performance depends on exfoliation and the clay-matrix interactions.
- The easiest to prepare PNC is via polymerization, but the intercalant may interfere with its kinetics, and catalyst with exfoliation!
- For PO's the MMT has been reacted with "sizing agents", e.g., organo silanes, titanates or zirconates and/or "compatibilizers" (PO-MAH).
- **Melt-compounding is the preferred method of PNC manufacture**.

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Conclusions 2

- Common strategy for melt-compounding is:
  - Compatibilization, sizing or intercalation (under N_2, then devolatilization)
  - DISPERSIVE mixing, based on microrheology
  - DISTRIBUTIVE mixing, based on the theories of laminar flows
- Theoretically, extensional mixing in is superior to shear mixing, viz.:
  - High strains, interface, aggregate deformability, specific energy of mixing
  - Low degradability of polymers, attrition of solid particles,
  - Strong orientation of anisometric particles, etc.
- PNC morphology depends on the thermodynamics, kinetics and flow.
- In PNC's the clay platelet might be treated as a large molecule, which first should be chemically modified to induce miscibility, and then mechanically dispersed.
- A precarious alternative is to use organoclay with partially bare surface (by partial intercalation or by degradation) and graft it either with a polar polymer (e.g., PA), or with functionalized macromolecules (e.g., PP).

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