PA-Based PNC Containing Synthetic Clay

Sepehr, M.; Utracki, L. A.; Simard, Y.

PA based PNC Containing Synthetic Clay

M. Sepehr, L. A. Utracki and Y. Simard

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Outline

- Introduction to synthetic clays
- Objectives
- Materials and method of compounding
- XRD measurements and TEM observations
- Mechanical properties
- Summary and conclusions
- Future work

Objectives

- Prepare PA-6 based nanocomposites with different synthetic and natural clay.
- Characterize the degree of clay dispersion and mechanical properties.
- Compare the behavior of PNC's with natural and synthetic clays.

Introduction 1

Comparison: mineral vs. synthetic clay

- 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)

- Fluoro mica (*Somasif* FM)
- ADVANTAGES
  - Aspect ratio: $p \leq 6{,}000$ (depends on p of talc)
  - Stable composition
  - Non-toxicity
  - Absence of color
- DISADVANTAGES
  - Limited and uncertain sourcing
  - Higher cost
  - Flame suppression

Introduction 2

Types of synthetic clays

1. ***Semi-synthetic***, prepared by modification of such minerals as, e.g., talc or obsidian. The resulting fluoro hectorite (or fluoro mica, FM) has variable aspect ratio and reactivity (modified by substituting F^- for –OH).
2. ***Fully synthetic***, prepared from metal oxides as, e.g., fluoro hectorite: $(Si_4O_{10})_2\,(Mg_{6-x}Li_x(OH)_{4-y}F_y$. Two sub-categories are known:
   a. The low temperature, hydrothermal slurry process that requires refluxing for 10 to 20 h to cause crystallization.
   b. The high temperature melt process that requires heating at 1300°C for 3 h and then purification by dissolution in water.
3. ***Templated synthetic***, based on organic templates (e.g., prepared by Carrado – non commercial).

Methods of preparation 1

- Semi-synthetic fluoro mica (FM), e.g., *Somasif from COOP – now CBC Co. Ltd.*
  - MMT chemical formula is: $[Al_{l.67}Mg_{0.33}(Na_{0.33})]Si_4O_{l0}(OH)_2$
  - Hectorite or fluoro hectorite: $[Mg_{2.67}Li_{0.33}(Na_{0.33})]Si_4O_{10}(OH, F)_2$ is obtained from talc: $Mg_3Si_4O_{10}(OH)_2$ by partially replacing Mg by Li or Na, and by substituting F for some (ca. 5-wt%) OH groups.
  - Non-exchangeable Na constitutes 30 to 40% of total Na, thus only ca. 75% of CEC may be used. Density = 2.806 g/mL.
  - Powdery mixture of talc with 10 to 35 wt% of $(Li, Na)_2CO_3$, $(Li, Na)_2SiF_6$ or LiF, is heated for 1 h at T = 700 to 900°C.
  - The composition for synthetic FM is, e.g.: talc/LiF/Na_2SiF_6 = 80:10:10, while for synthetic fluoro-MMT: talc/Na_2SiF_6/Al_2O_3 = 70:20:10.
  - The heating temperature greatly affects swellability and the interlayer spacing of FM, e.g.:
    - For T = 700 - 750°C, the XRD peak is at d_{001} = 0.91 nm
    - For T = 780 - 900°C, the XRD peak is at d_{001} = 1.61 nm.
  - Multiple peaks in Na^+FH are due to locally different level of hydration

Methods of preparation 2

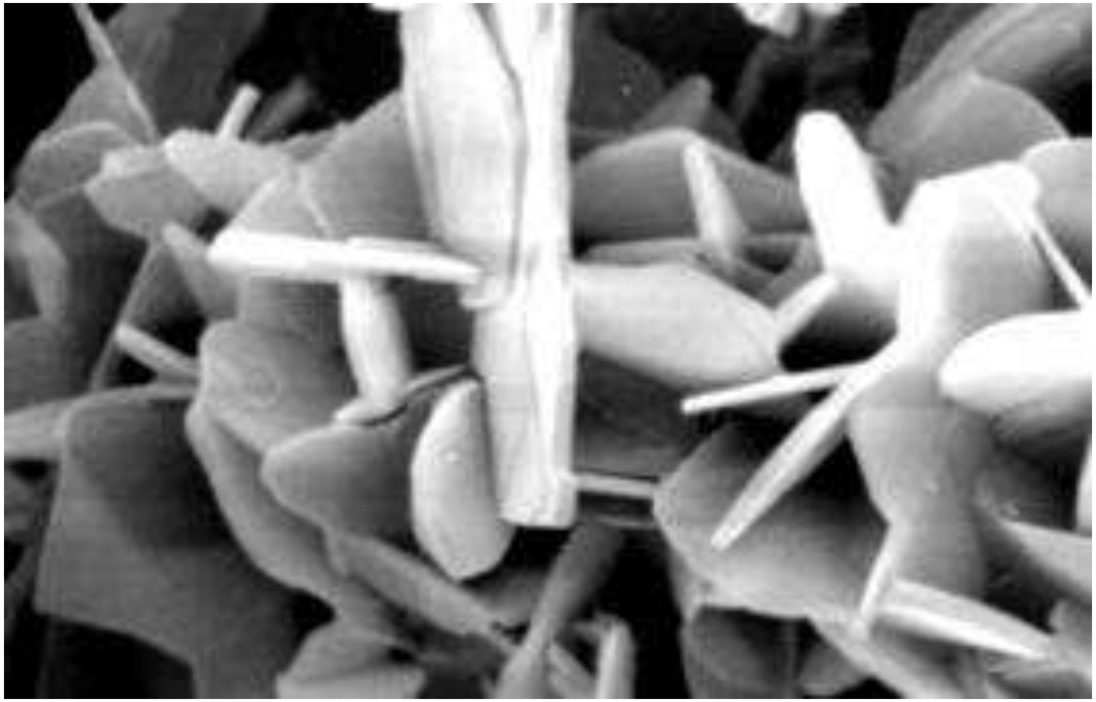
- **The fully-synthetic MMT or fluoro mica (FM), e.g., *Laponite, Sumecton-SA, Optigel SH***
- Several *hydrothermal* procedures have are used, viz.:
  - Centrifugation of aqueous slurry from: $MgCl_2$, Na_2SiO_3, Na_2CO_3, & LiF
  - Heating it under reflux 1 h at 100°C, and then for 10-20 h at 250 C
  - 24 hr cooling to RT, Washing, extruding wet cake, and drying at T $\leq$ 450 C
- The process controls the relative –OH to –F concentration, <u>thus reactivity</u>.
- The aspect ratio is low, p = 25 to 50, dependent on the crystallization.
- In Laponite, Lucentite, etc. the scattering domains are small – XRD peaks are weak & broad – constructive interference of X-rays is too small
- Laponite RDS: p = 20 – 30, CEC = 1.20 meq/g, specific surf. 370 m^2/g.
- Main use: surface coating, antistatic paper treatment, household cleaners, thickener for cosmetics, creams, toothpastes, low-fat sour cream, paints, adhesives, greases, etc.
- MMT was prepared at 220 C for 48 h, in the presence of HF-acid; d_{001} = 1.55 nm, $p \approx$ 200. Fluorine helps crystallization [Reinholdt *et al*., 2001; 2005].

Methods of preparation 3

- Fully-synthetic fluoro mica (FM), e.g., *Topy-4C*
  - The ***high-temperature*** **process** involves [*US Pat*., **3,936,383**]:
    - Powdering suitable salts, e.g., by ball-milling for 1 h: 3.7-wt% NaF, 2.3% LiF, 10.8 MgF_2, 20.9% MgO, and 62.3% silicic acid; or SiO_2, MgO, Na_2SiF_6 .
    - Placing the powder in a rotating horizontal crucible made from silicon carbide, and then heating in a combustion flame of fuel oil at 1350 to 1600 C for 2 h.
    - Steaming the slab on a wire net (40 mesh) for 2 h, and thus breaking it into particles of up to 5 mm diameter.
    - Dispersing the crystals in water under mild stirring at RT for 2 h.
    - Contamination by non-crystalline byproducts may be eliminated by repeated dissolutions and centrifugations.
    - The Na-hectorite particles dispersed in the sol state had thickness of 1-5 nm and diameter of p = 80 to 5,000.
  - There is a correlation between platelets and crystals orientation

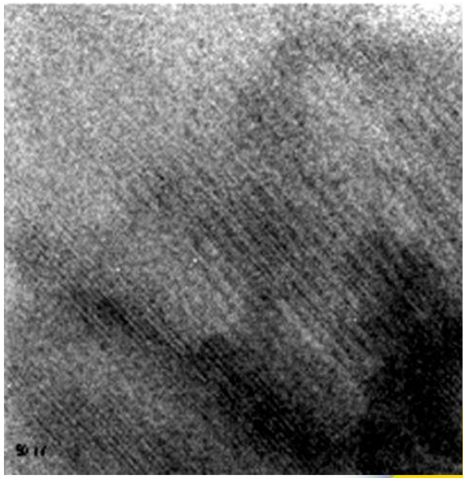
Properties of FH

- “House-of-cards“ structure of synthetic fluorohectorite from melt – absence of XRD (Klaus Beneke, 2005).
- The bond strength Si-F = 553 vs. 800 kJ/mol for Si-O.



Templated synthetic clays
non-commercial

- Kathleen Carrado-Gregar (2001); Example:
  1. Dissolve organic salts in water, add LiF with stirring.
  2. Dissolve $MgCl_2$ in water, add NH_4OH & crystallize $Mg(OH)_2$.
  3. Combine 1 & 2, stir for 15 min before adding silica sol.
  4. Clays grafted with organics were obtained using, e.g., phenyl-triethoxy silane (PTES) in the precursor composition.
  5. Stir and reflux for 40-48 h, then centrifuge crystals, wash & dry.
  6. Na-hectorite, had d_{001} = 1.48 nm, and platelets of L_a = 19.5 nm.
- Andreas Stein (2005); Example:
  - Hexadecyl trimethoxy silane (HDTMOS) & tetraethyl orthosilicate (TEOS) were combined and stirred to homogeneous solution.
  - The mixture was acidified and reacted for 1.5 h at RT & 1.5 h at 60°C with stirring. The products were filtered, rinsed and dried.
  - d_{001} = 4.8 nm; aggregates 0.9–1.3 μm; inorganics 23.3%



Properties 1

- Some synthetic clays used in polymers

No..	Company	Synthetic clay	Clay type
1	CBC Co., Ltd. (COOP) Japan wakisaka@cbc.co.jp	**Somasif™** ME100, large *p* fluoro hectorite (FH); intercalated grades available	Semi-synthetic with talc
2	CBC Co., Ltd. (COOP) Japan wakisaka@cbc.co.jp	**Lucentite** SWN; a *lithium-magnesium sodium silicate,* low *p*; intercalated grades available	Fully synthetic, Low-T hydrothermal
3	Topy Co. Ltd Japan s-oota@topy.co.jp	**Tetrasilicic mica**, FH, intercalated grades available for PP	Fully synthetic, High-T melt method
4	Kunimine Ind. Co. Ltd. Matsudo@kunimine.co.jp	**Sumecton** SA, sodium saponite (Al-Mg-silicate hydrate	Fully synthetic, T > 250°C hydrothermal
5	Laporte Ind. Ltd. (SCP) cevans@scprod.com	**Laponite** RD or B, respectively Na-Li-Mg silicate or fluorosilicate	Fully synthetic, Low-T hydrothermal
6	Süd Chemie AG www.sud-chemie.com	**Optigel** SH; Na-hectorite similar to Laponite RD	Fully synthetic, Low-T hydrothermal
7	Zhejiang Clay Chem. Co. Ltd. www.lin12.alibaba.com	**Suplite-MP** Na-Mg-silicate Na-hectorite similar to Laponite RD	Fully synthetic, Low-T hydrothermal
8	R.T. Vanderbilt Co. Inc. http://www.rtvanderbilt.com/	**Veegum** T or F; hydrated -Al-Mg-silicate	?

Properties 2

- Specifications of synthetic and (for comparison) mineral clays

- The highlighted clays are at IMI

Company	Organoclay	Intercalant	Wt. loss (%)	Aspect ratio	d_{001} (nm)	CEC (meq/g)
Synthetic clays						
CO-OP	Somasif ME-100	none		5000	0.95	1.1- 1.2
	Somasif MAE	2M2HT	30-40	5000	3.1	
	Somasif MTE	M3O	25-35	5000	2.4	
	Somasif MEE	M2EtOHC	20-30	5000	2.3	
	Somasif MPE	M2E-PPOH	60-70	5000	5..3	
	Lucentite SWN	none	< 10	~50	1.27	0.65
	Lucentite SAN	2M2HT	30-40	~50	1.79	1.2
	Lucentite SPN	M2E-PPOH	55-65	~50	4.37	
	Lucentite SEN	M2EtOHC	30-40	~50	2.39	
	Lucentite STN	M3O	22-32	~50	2.44	
Topy Ind.	Topy-4CTs	3MOD	~27	1000-5000	2.32	0.827
	Topy-4CDTs	2M2OD	~32	1000-5000	3.18	0.352
Kunimine	Sumecton SA	none	< 10	50	1.3	0.997 - 0.71
Laport Ind.	Laponite RD	none	~9.5	25 (mono)		0.48
Laport Ind.	Laponite B	none	< 10	~25		
Süd Chemie	Optigel SH	none	< 10	20 – 50		
FCC Inc.	Suplite-MP	none	< 10	~25		
Mineral Clays						
SCP	Na-MMT	none	7	~290	1.23	1.0
	10A	2MBHTA	39	~290	1.93	1.25
	20A	2M2HTA	38	~290	2.47	0.95
	30B	MT2EtOH	32	~290	1.86	0.90
Kunimine	Kunipia-F	none	< 10	320 (80-1120)	1.2	1.15
	Kunipia-T	3MOD	32.2	~320	2.07	
	Kunipia-D	2M2OD	43.8	~320	3.00	

Synthetic clay cost

- Comparative cost of 1kg natural and synthetic clay as cited in November 2005

Company	Quantity (kg)	Clay cost (US$/kg)	
		Natural	Synthetic
AIMPLAS June 2003 (general quote)	?	6 – 30	20 – 40
Cloisite 15A; SCP FOB Gonzales TX	1	15	
	>1000	6.94	
Somasif ME-100; CBC Co, FOB Narita.	1		18
	>1000		15
Lucentite SWN; CBC Co, FOB Narita	1		30
	>1000		25

Somasif™ ME-100

- CBC Co. JAPAN produces the semi-synthetic fluoro hectorite, SOMASIF, **in a solid-state reaction**, heating natural talc with 10 to 35-wt% Na_2SiF_6, and some LiF (to control –OH concentration).
- For example, a powdery mixture is heated for about 1 h at T = 700 to 900°C [Tateyama *et al.*, *US Pat.*, **5,204,078**,1993].
- Swellable fluoro hectorite (FM) is obtained starting with: talc/LiF/Na_2SiF_6 = 80:10:10.
- The FM produced at 700 - 750°C shows the XRD peak at: d_{001} = 0.91 nm (of talc) while that at 780 - 900°C shows d_{001} = 1.61 nm of swellable fluoro mica.
- Synthesis of MMT, or saponite-type synthetic clay requires addition of Al_2O_3 (e.g., talc/Na_2SiF_6/Al_2O_3 = 70:20:10), and higher heating temperature.

Lucentite™ SWN

- CBC Co. JAPAN also produces the fully synthetic hectorite, *Lucentite*™, **via a hydrothermal** process.
- The fully synthetic hectorite, $Na_{0.33}(Mg_{2.67}Li_{0.33})Si_4O_{10}(OH)_2$, *LUCENTITE*™ is prepared from:
  - Aqueous solutions of $MgCl_2$, Na_2SiO_3, Na_2CO_3, and Li_2CO_3
  - Combining the solution to form a slurry
  - Heating the slurry under reflux. This step is critical for crystallization, thus the conditions may vary depending on the desired level of crystal perfection and the aspect ratio; by increasing the salt concentration and pressure the reflux $T \leq 300^oC$ has been used
  - Washing away the non-crystalline contaminants
  - Drying at $T \leq 450$ C
- Organophilic Lucentite SPN, SEN, STN is available.

TOPY tetrasilicic mica

- TOPY Co., developed the high temperature process for the production of fully synthetic fluoro hectorite (FM):

$$NaMg_{2.5}Si_4O_{10}F_2$$

- The reaction of SiO_2, MgO, Na_2SiF_6 and possibly LiF takes place in the molten state at $T > 1500\,°C$.
- Crystallization of FM takes place during slow cooling (≤ 20 h).
- The crystalline product is purified by dissolution and centrifugation.
- The aspect ratio of FM is p = 1,000 to 5,000.
- TOPY has intercalated FM for PP-based CPNC:
  - 4C-Ts with tri-methyl octadecyl ammonium (3MODA), and
  - 4CD-Ts with di-methyl di-octadecyl ammonium (2M2ODA).

Sumecton®-SA

- Kunimine Ind. manufactures fully synthetic sodium-saponite, ***Sumecton***®-SA, a Al-Mg-silicate hydrate :
  $[(Si_{7.2}\,Al_{0.8})(Mg_{5.97}Al_{0.03})O_{20}\,(OH)_4]^{-0.77}\,(Na_{0.49}Mg_{0.14})^{+0.77}$
- The synthesis is hydrothermal, with the reflux temperature under high pressure of T > 250 °C. The product properties are:
  - Aspect ratio $p = 50$;
  - Specific surface area = 750 m^2/g;
  - CEC = 0.997 meq/g ($CEC_{measured}$ = 0.71 meq/g);
  - Average area per anionic site is 1.25 nm^2, thus the distance between ions (square array) is 1.12 nm
  - The interlayer spacing, d_{001} = 1.3 nm, increases upon intercalation to 2.6 nm.

PNC with PA-6 #1

- **Ube process**
  - MMT pre-intercalated with ω-amino dodecanoic acid in water; d_{001} = 1.8 nm.
  - Dispersed organoclay in molten ε-caprolactam and water at the ratio: 1:9:9.
  - Swelling the organoclay to d_{001} = 3.87 nm.
  - Polycondensation under N_2 at 250-270°C for 48 h was followed by pelletization.
  - The ε-caprolactam was extracted from the pellets immersed in a hot water, followed by vacuum drying [Deguchi *et al*., 1992].

- **Unitika process**
  - Several types of FM were prepared and tested at COOP.
  - **Mineral, non-intercalated FM** 20-wt% H_2O + ε-caprolactam.
  - The mixture was polymerized under N_2 at 250°C, stirring for 1 h at P = 4 to 15 atm.
  - The steam was reduced to 2 atm and polymerization continued at 260°C for 3 h.
  - The PNC pellets were washed with water at 95°C for 5 h, then dried at 100°C under vacuum for 8 h [Yasue *et al*., 1995].

PNC with PA-6 #2

- Properties of PNC prepared with ca. 1.6-wt% of mineral (Ube) and synthetic (Unitika) clay: (noteworthy are the relative values)

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	^oC	75	140	70	172
HTD (4.6 kg/cm^2)	D-648	^oC	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

PA-66 with Somasif^{TM}

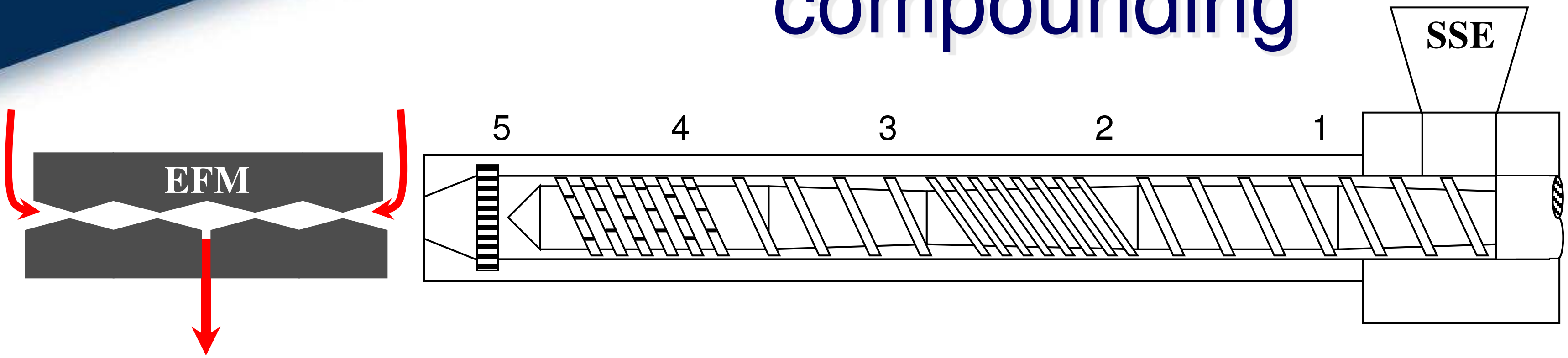
- Showa Denko melt-compounded in a TSE a rigid, flame-resistant PNC : (1) PA-66, (2) Somasif ME-100 intercalated with either triazine ($C_3H_3N_3$), melamine, cyanuric acid, or melamine cyanurate, (3) fibrous reinforcements, and (4) flame retardant
  [Inoue *et al., US Pat.*, **6,294,599**, 2002].

PNC of PA-66 with 1 phr of clay and 15 phr of GF. Data: [Inoue *et al.*, 2002].

No.	Organoclay or other filler	d_{001} (nm)	Flex modulus (MPa)	HDT (°C)	Deformation (mm)	Relative shrinkage (TD/MD)
1	***FM + m***	1.28	6.3	245	0.5	1.94
2	MMT + m	1.30	6.1	244	0.7	1.86
3	FM + mc	1.50	6.2	244	0.7	1.96
4	FM + 2xm	1.35	5.9	240	1.0	2.12
5	FM + 2M2ODA	3.5	5.8	230	1.2	1.88
6	Talc	0.96	6.0	243	1.0	2.13
7	nil	--	5.6	244	6.2	2.30

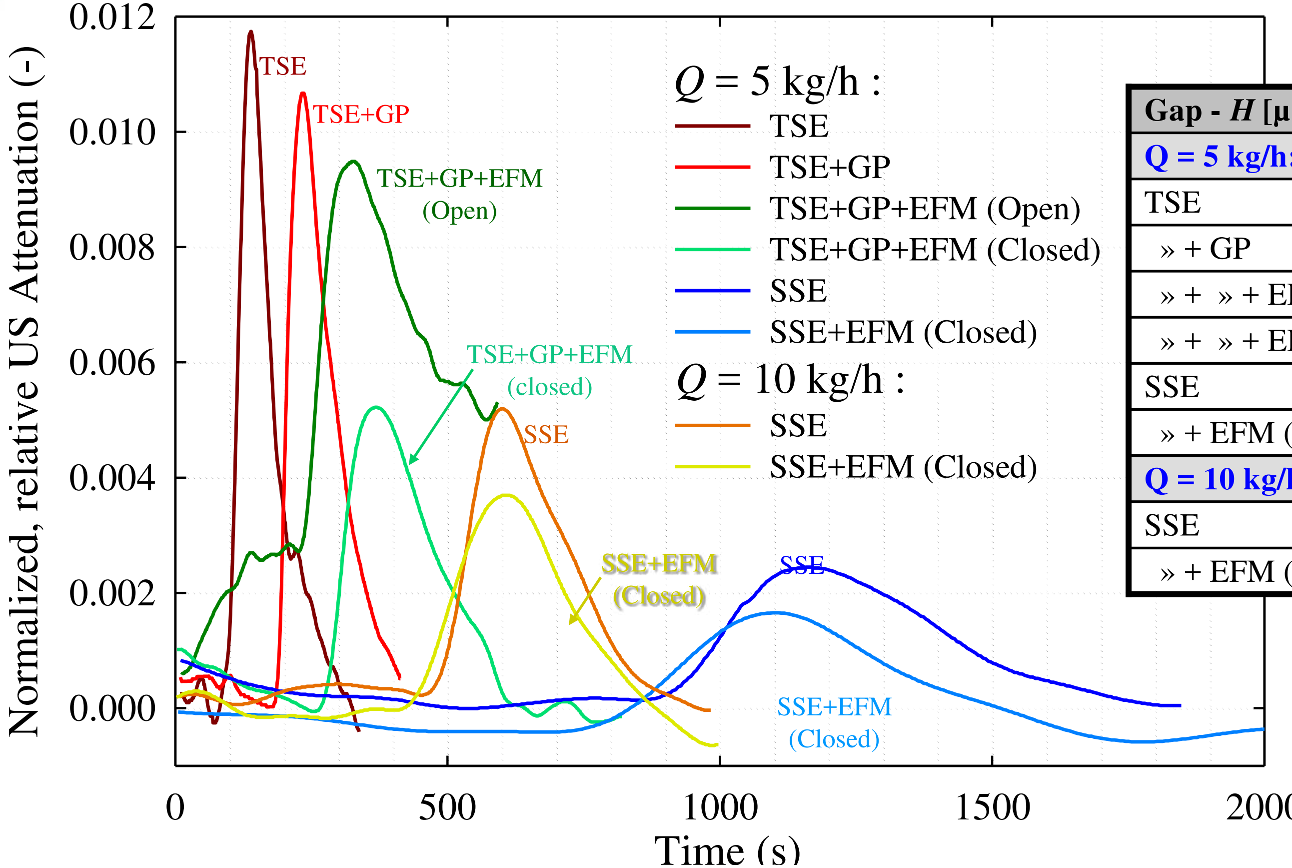
Notes: FM = synthetic clay, Somasif ME-100; MMT = Kunipia-F; m = melamine; mc = melamine cyanurate; 2M2ODA = di methyl -di-octadecyl ammonium chloride; 2x = twice stoichiometric.

Materials and method of compounding



- PA-6 (UBE1015B, M_w = 15 kg/mol) dried 48 h at 80 °C (no stabilizer).
- Clays and organoclays dried 24 h at 100 °C.
- PNC with 1.1-wt% inorganic part of clay was dry-blended before the extrusion in a SSE + EFM.
- EFM gap was adjusted at 30 µm.
- Dried PNC pellets were injection molded using Engel 150 T at 250°C with mold temperature at 55°C, the injection and holding pressure 65 and 6 MPa, respectively .

Residence time distribution



Gap - *H* [µm]	*t* (s)
Q = 5 kg/h:	
TSE	139
» + GP	236
» + » + EFM (2032)	320
» + » + EFM (5)	368
SSE	1163
» + EFM (15)	1103
Q = 10 kg/h:	
SSE	600
» + EFM (15)	608

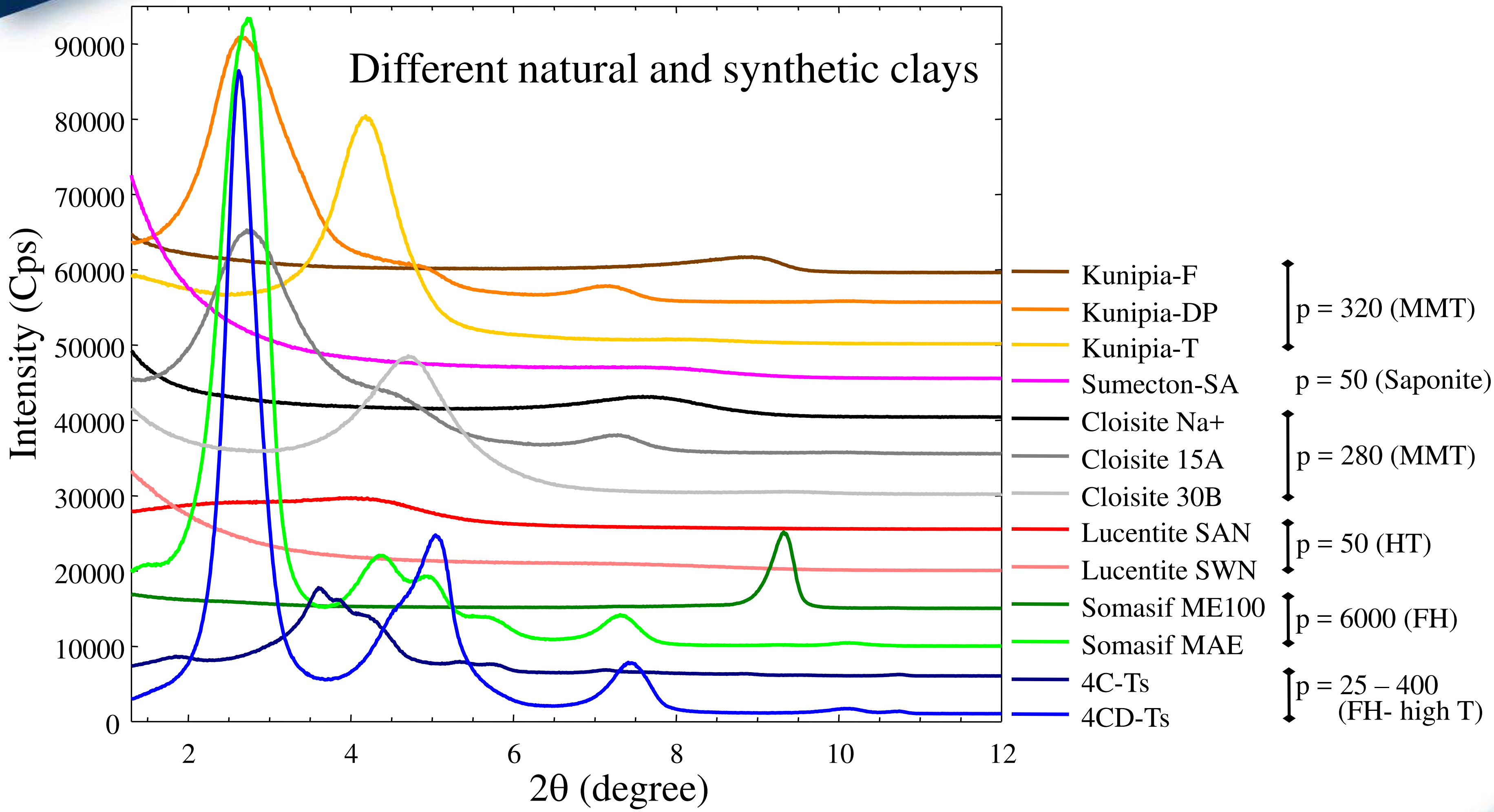
- RTD was measured by ultrasonics, extruding PP + $CaCO_3$ through:
  - TSE + GP + EFM at *Q* = 5 kg/h
  - SSE + EFM at *Q* = 5 and 10 kg/h.
- RTD peak position was unchanged for constant throughput in SSE even with the presence of EFM.

Characteristics of clays and organoclays

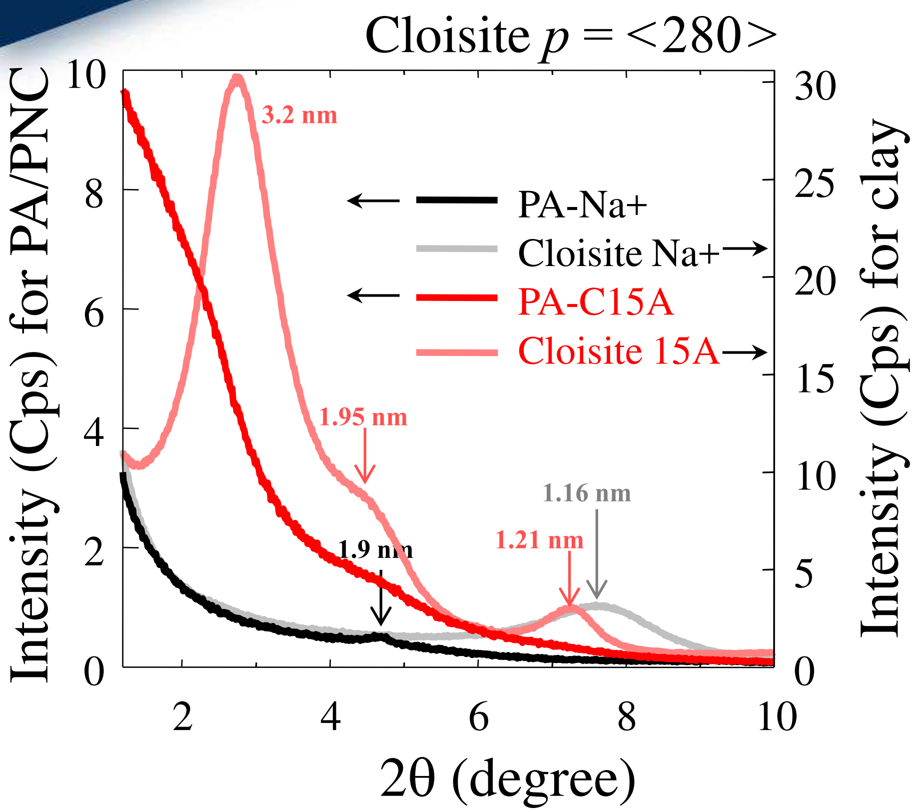
Company	Name	Nature	Aspect ratio	CEC (meq/g)	d_{001} (nm)		Organic part			Wt% in PA/PNC	
					Theo	Exp	wt % Theo	wt % Exp*	Intercal.	Org.	Mine.
Southern Clays	Cloisite Na+	Na-MMT	280	0.926	1.17	1.16	7	4.25	None	1.23	1.05
	Cloisite 15A				3.15	3.21	43	41.95	2M2HT	2	1.02
	Cloisite 30B				1.85	1.86	30	28.49	MT2Et	-	-
UNICOOP	Somasif ME100	Fluoromica	≤ 6000	1.2	0.95	0.95	-	1.03	None	1.16	1.00
	Somasif MAE				3.10	3.23	30 – 40	39.4	2M2HT	1.93	1.04
	Lucentite SWN	Hectorite	<50>	1.01	1.27	1.20	-	7.3	None	1.30	0.90
	Lucentite SAN				1.78	2.22	30 – 40	38.9	2M2HT	1.89	1.30
Topy	4C-Ts	Mica	25 – 400	?	2.32	2.40	?	23.1	3MOD	1.50	1.02
	4CD-Ts				3.18	3.38	?	37.6	2M2OD	1.86	0.89
Kunimine	Sumecton-SA	Saponite	<50>	0.997?	1.3	1.17	-	2.9	None	1.23	1.05
	Kunipia-F	Na-MMT	80 – 1120 <320>	1.2	?	0.995	-	3.5	None	1.22	0.93
	Kunipia-DP				3.00	3.32	43.7	43.8	2M2OD	2.02	1.10
	Kunipia-T				2.07	2.11	32.2	33.8	3MOD	1.68	1.07

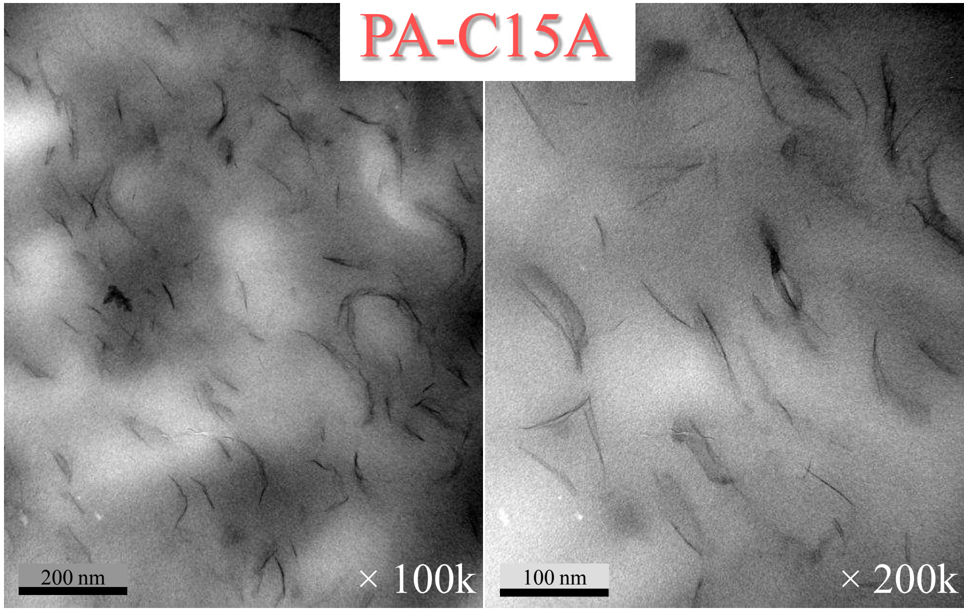
* Residue of dried clay at 700°C

XRD of clays and organoclays



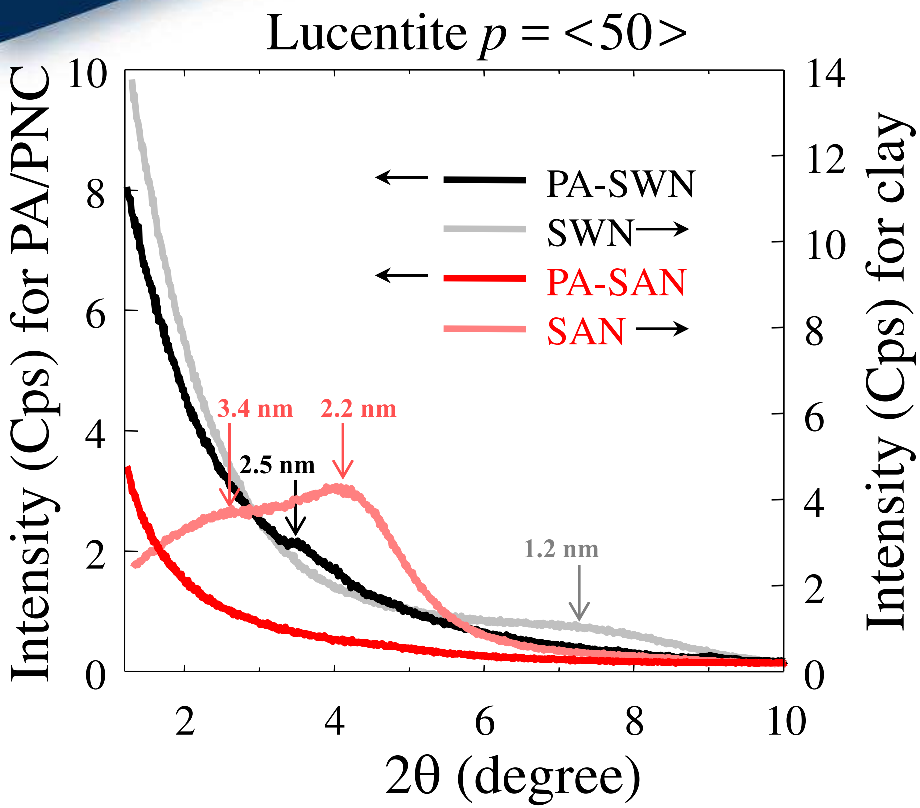
PA + Cloisite-Na & C15A

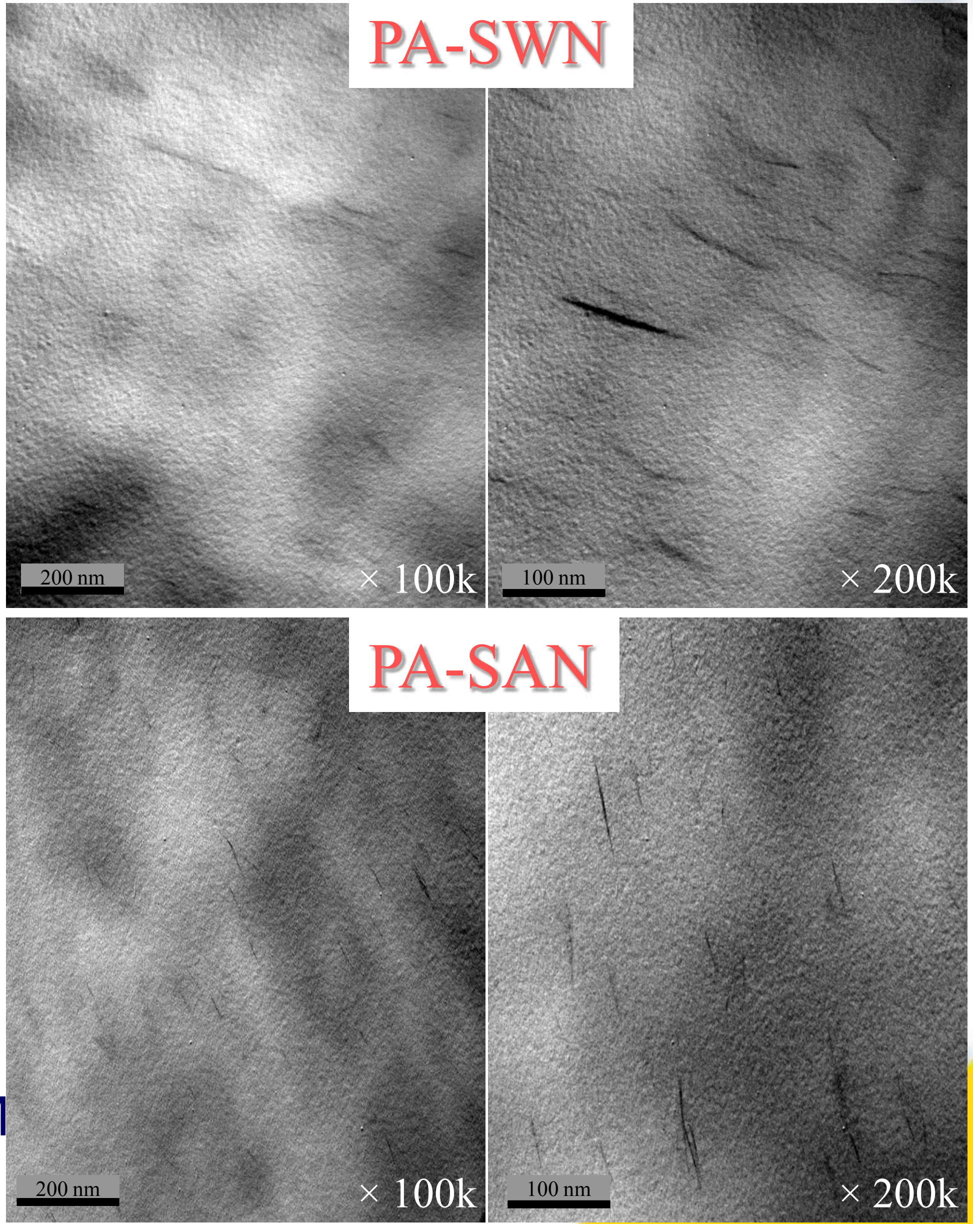




- A small peak can be seen for PA-Na^+ compound.
- By introducing 2-wt% C15A in PA-6, the peaks almost disappeared.
- TEM micrographs show twisted couple and triple layers stacks.

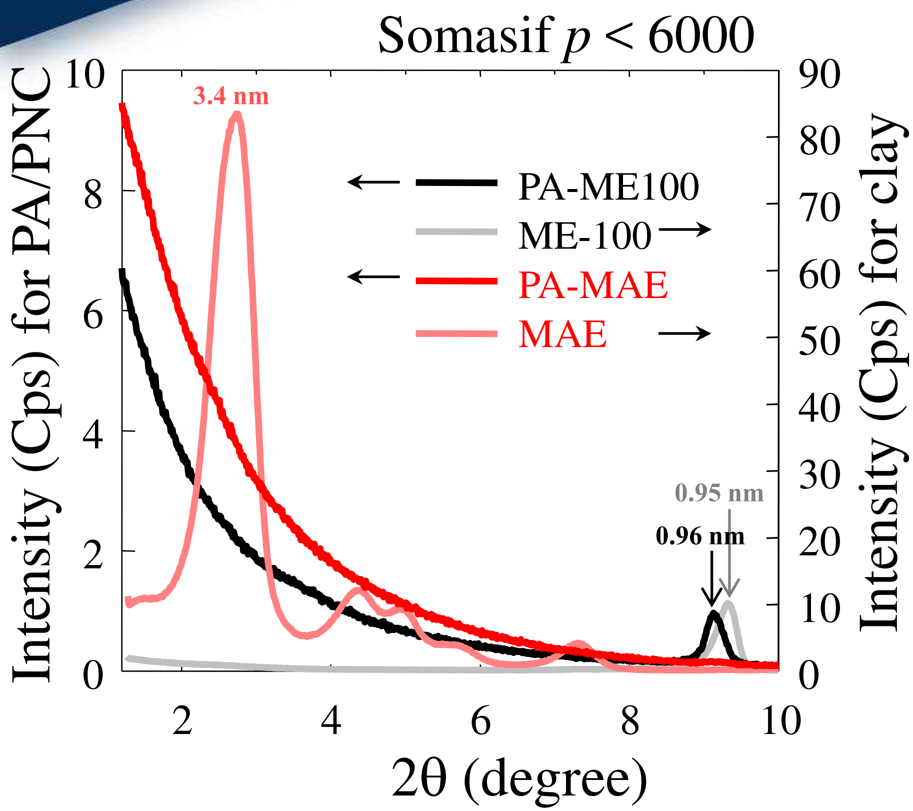
PA + Lucentite

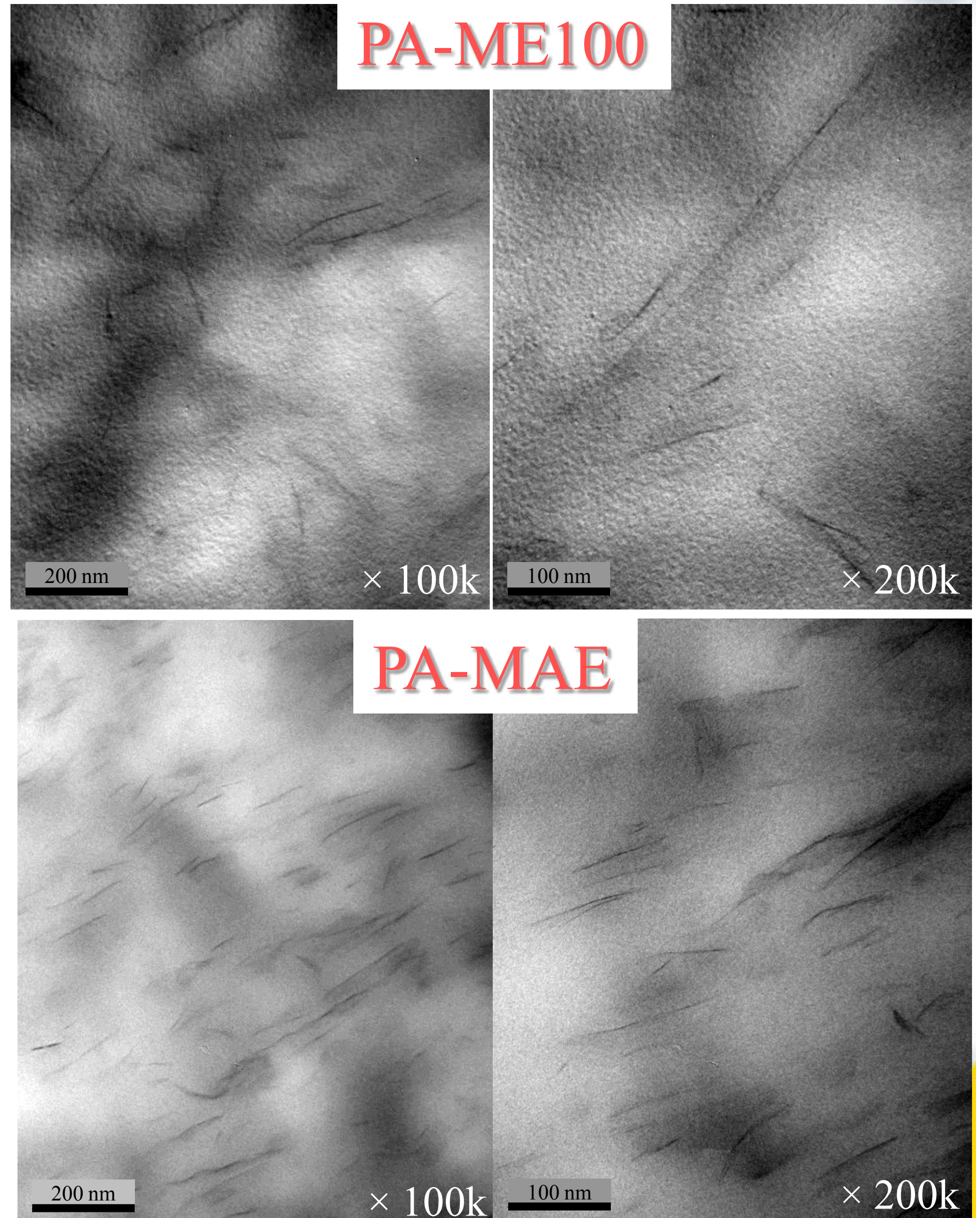




- No peak can be identified in PA-SAN sample however a small peak is present in PA-SWN compound.
- Particles are hardly detectable in TEM micrographs.

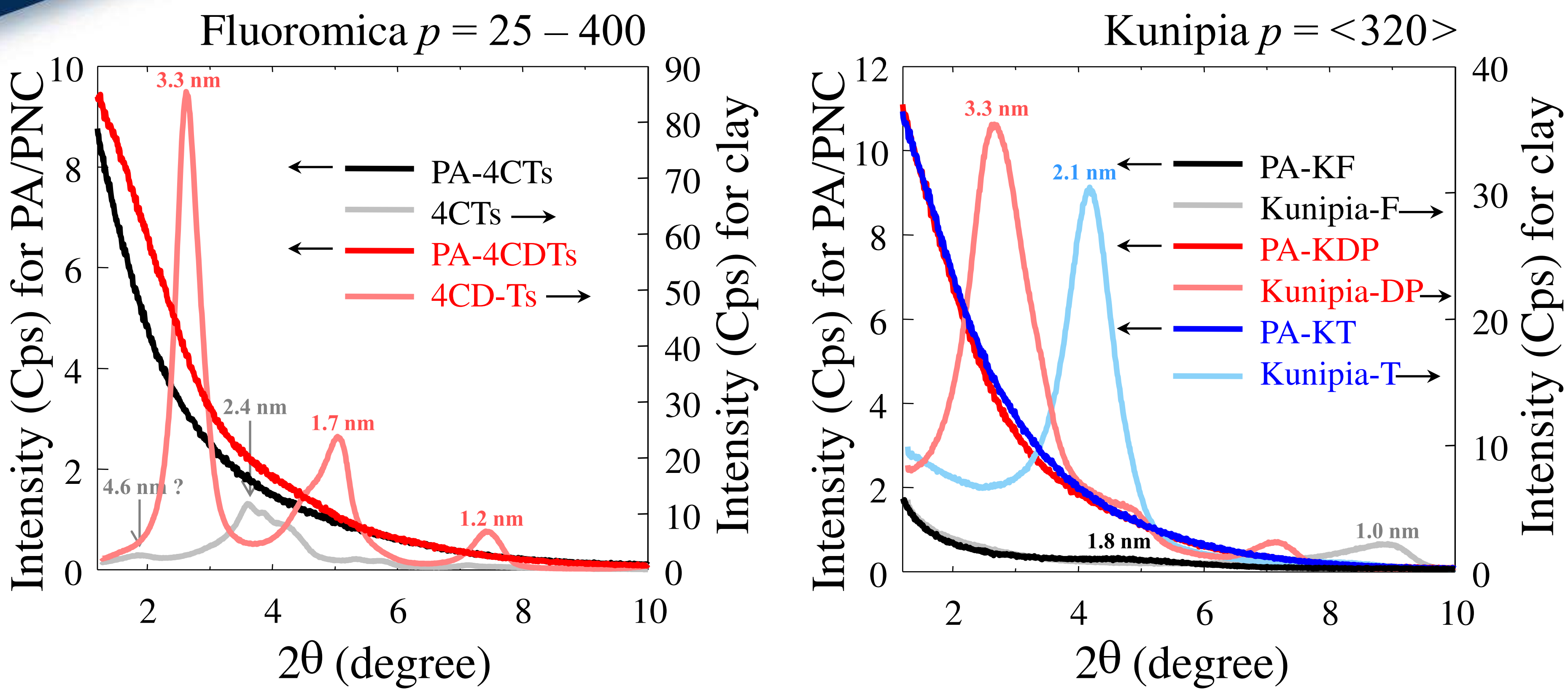
PA + Somasif





- No peak can be detected in PA-ME100 and PA-MAE compounds.
- No aggregates are seen in TEM micrographs; single and double platelets are observed.

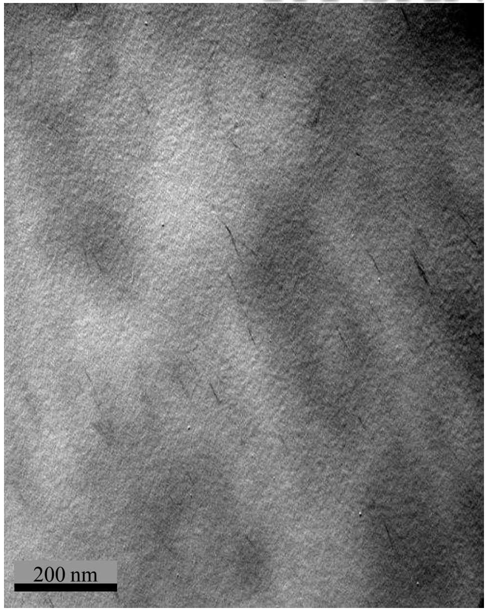
PA with fluoromica or MMT



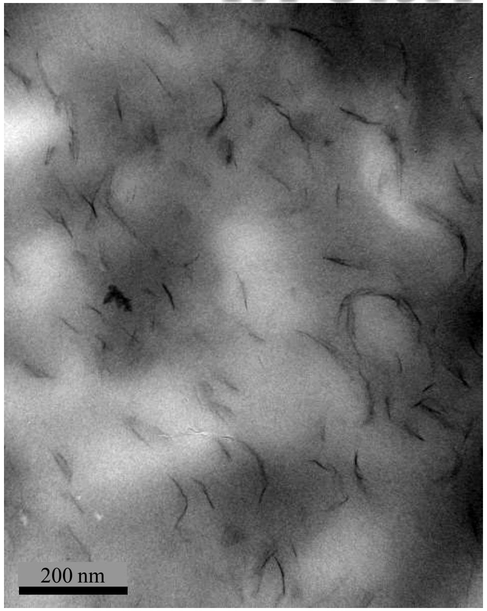
- No peak can be detected in PNC of PA-fluoromica.
- A small peak is detected in PA-KF but none in PA/PNC prepared with the Kunipia organoclays.

Comparison PNC with three 2M2HT organoclays (×100k)

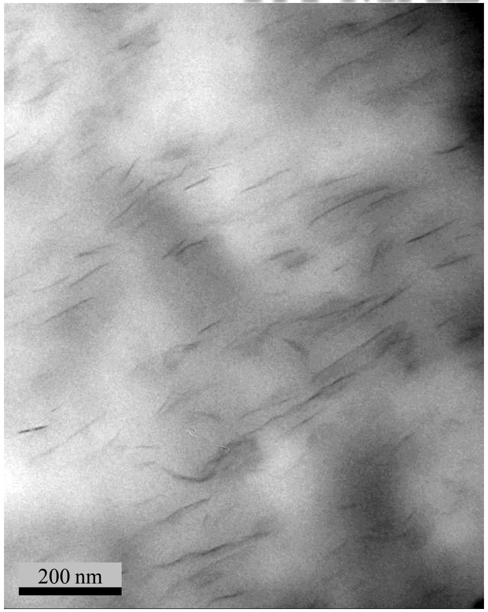
PA-SAN



PA-C15A

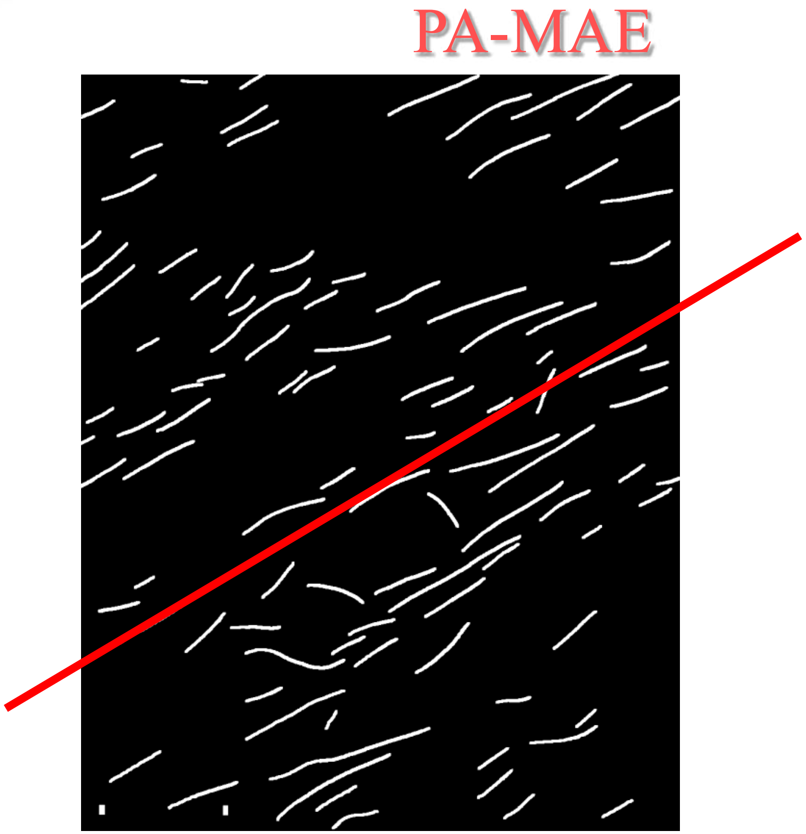


PA-MAE



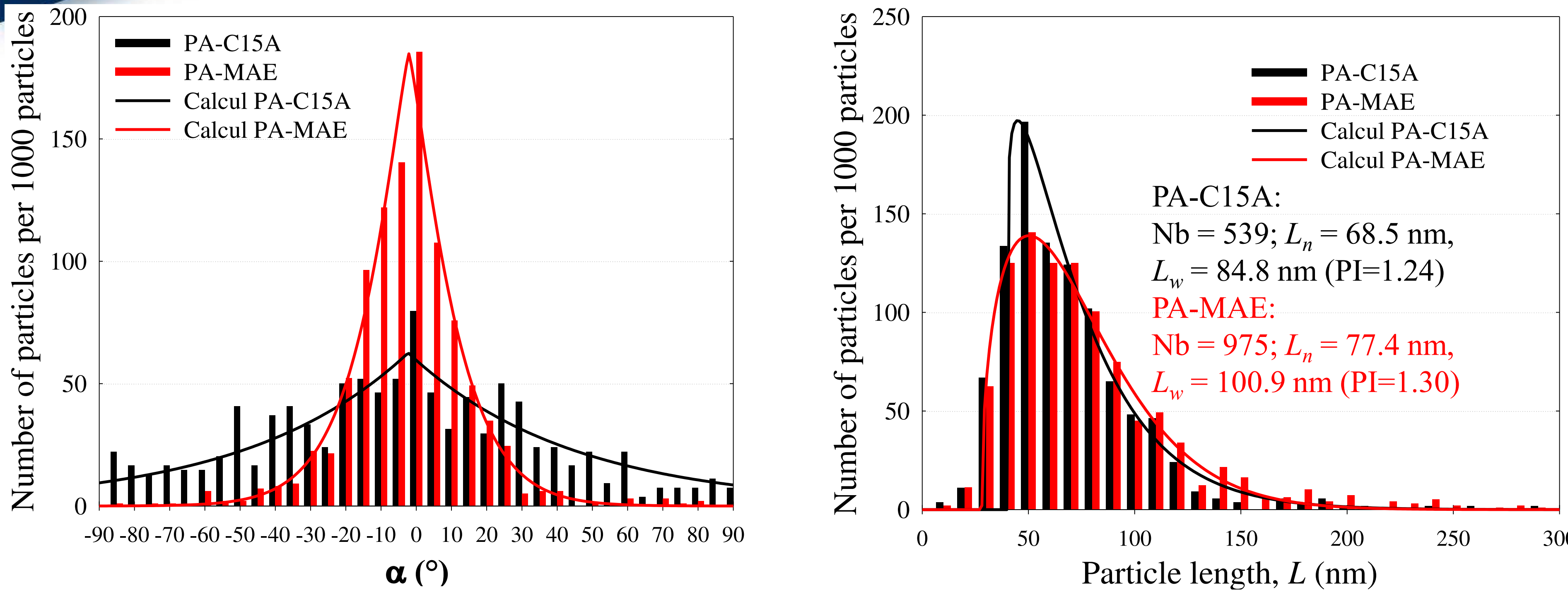
- Particles in PA-SAN are very small and hardly detectable.
- Particles in PA-C15A are more twisted. Most of stacks have two or three platelets.
- Most of the particles in PA-MAE are single layer and they seems to be more oriented and straight.

Image analysis



- To quantify the length and orientation of particles, a semi-automatic image analysis were used.
- Particles were drawn, their length and angle with the horizontal line were calculated.
- The main axis was assumed to be parallel to most of the particles and the disorientation was calculated by taking the assumed axis as reference.

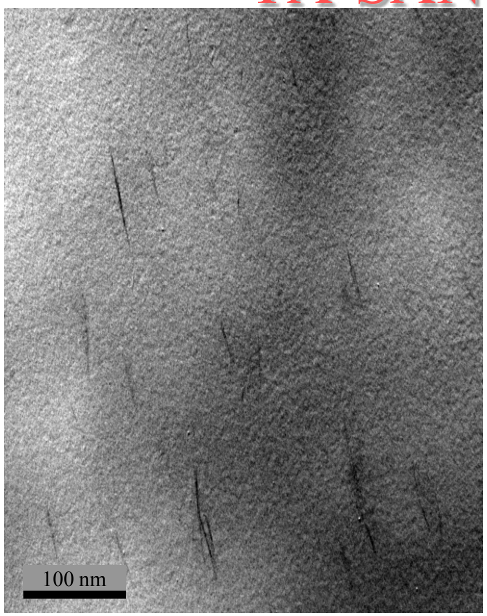
Disorientation and length of particles



- Particles are more oriented in PA-MAE than PA-C15A (effect of the aspect ratio, *p*, as well as the platelet modulus).
- Particles are longer in PA-MAE ($p < 6000$) than in PA-C15A ($p = 280$).

Comparison PNC with three 2M2HT organoclays (×200k)

PA-SAN

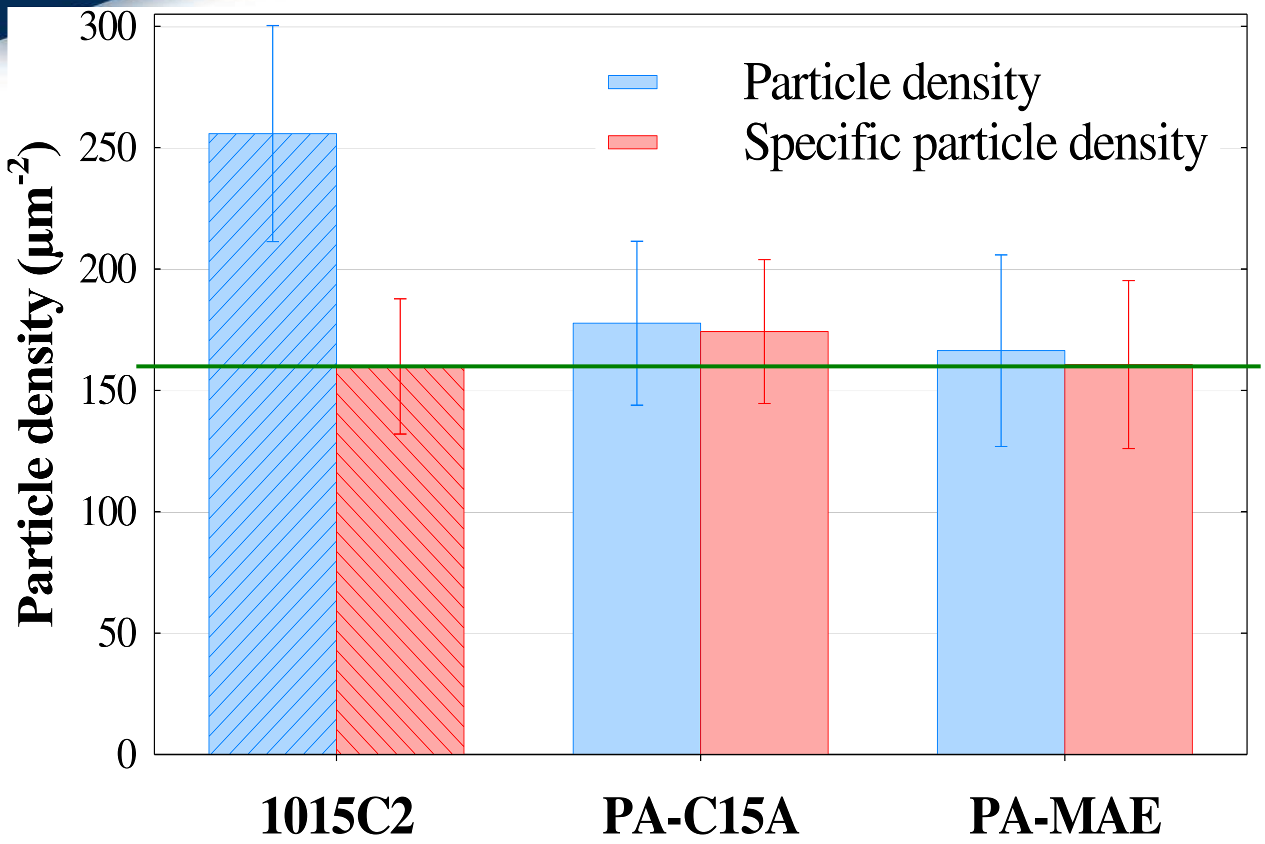


PA-C15A

PA-MAE

- Particles in PA-SAN are small and hardly detectable even at ×200k.
- Particles in PA-C15A are more twisted. Most of stacks have two or three platelets.
- Most of the particles in PA-MAE are single; they seems to be better oriented and straight.

Specific particle density



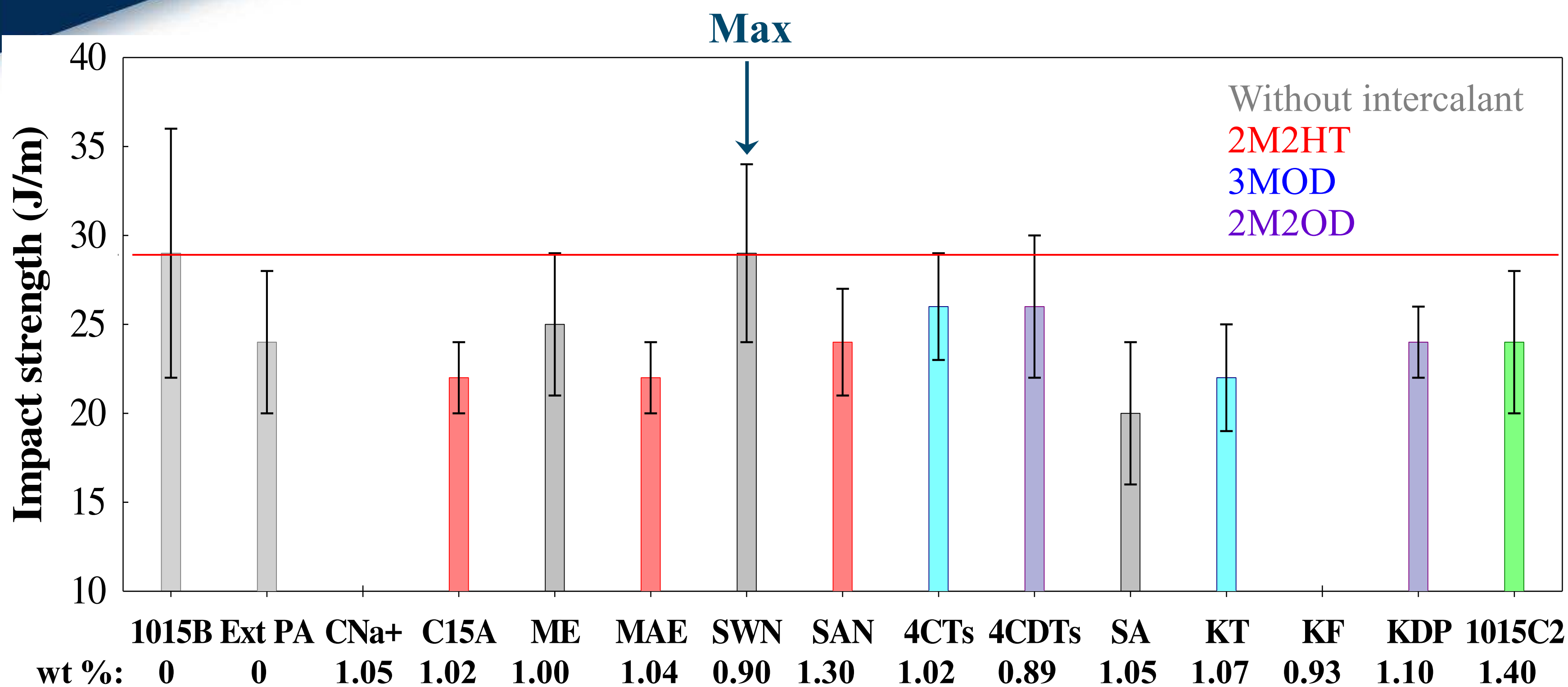
$$\text{Particle density} = \frac{nb}{A}$$

$$\text{Specific particle density} = \frac{nb}{A \cdot MMTwt\%}$$

- Specific particle densities measured from micrographs for PA-6 compounded with 2M2HT intercalated clays are as good as 1015C2: PA-C15A ≥ 1015C2 = PA-MAE

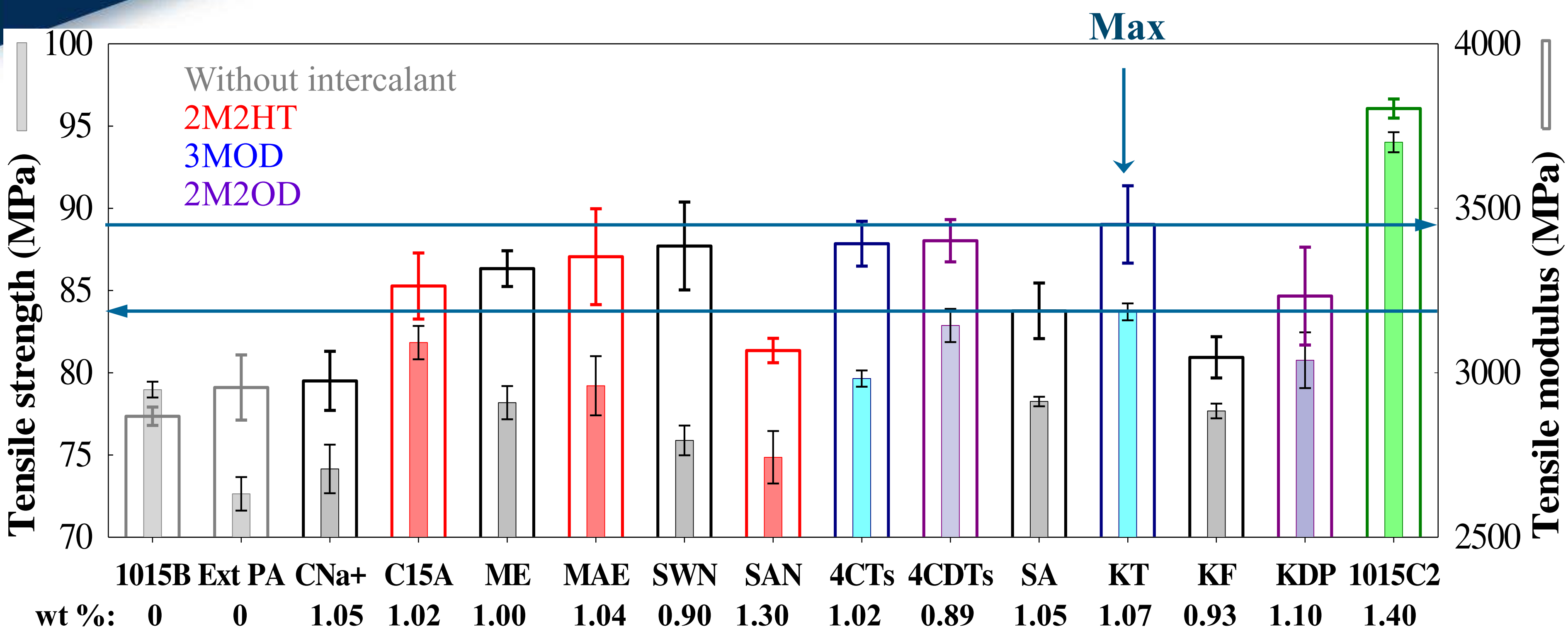
  $L_{MAE} > L_{C15A}$

Impact test results



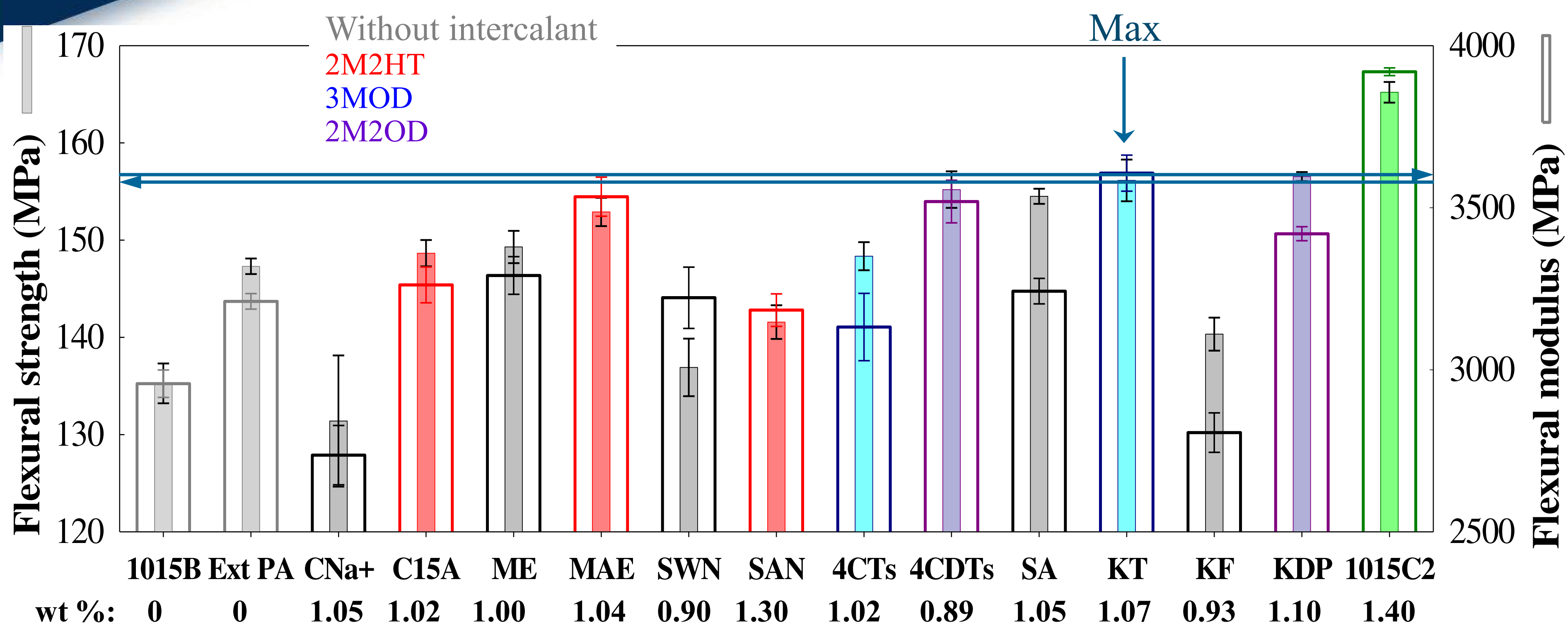
- Before testing the notched samples were dried at 50°C for 32 days under vacuum.
- Impact strength of specimen prepared with different clays were found independent of type of clay except for PA-SWN, which is comparable with the neat PA-6 (as received).

Tensile test results



- The tensile strength of the PNC specimens were higher by 2 to 15%, in comparison with that of extruded PA-6.
- The tensile modulus of the PNC specimens increased by 0.7 to 17% in comparison with that of extruded PA-6.
- Nb. 1015C2 with 2-wt% organoclay contains 1.6-wt% mineral clay.

Flexural test results



- Before testing the samples were dried at 50°C for 32 days under vacuum.
- The flexural properties of specimens prepared in SSE + EFM were found independent of the extrusion temperature, the gap size and throughput.

Summary and conclusions

- PNC with 1.1-wt% inorganic part of clay was dry-blended before the extruding in a SSE + EFM (gap = 30 µm).
- Most of the PA-6 based PNC's with different clays had featureless XRD indicating a high degree of clay dispersion.
- Similarly, TEM of PA-C15A, PA-Somasif-MAE and PA-Lucentite-SAN (organoclays with 2M2HT) showed high dispersion of clay in PA-6.
- The high aspect ratio clays, Somasif-MAE ($p < 6{,}000$), seems to break readily during compounding; in PNC its statistical length $L_w = 101$ nm.
- Impact strength of PA with Lucentite-SWN is comparable to that of neat PA. The impact strength of PA-fluoromica is the next highest after PA with Lucentite-SWN.
- The tensile performance of PA-fluoromica is the highest after PA-KT. The tensile modulus of PA with Lucentite-SWN is in between the two best PNC's – surprising considering the small aspect ratio of SWN.
- **PNC's with synthetic clays are colorless**

Future works

- Complete the study of:
  - Microstructure of PA and its PNC's.
  - Semi-quantitative studies of the TEM micrographs to compare the orientation, length and particle density.
  - Study of the interaction between PA and clays and their intercalant to be able to understand and predict properties.
- Extend the study to fully synthetic FM from TOPY mineral clay and organoclays.
- Considering the high aspect ratios of Somasif fluoro micas, mild processing conditions and long residence time should be examined.
- PNC's of low aspect ratio synthetic clays should be evaluated in a wide range of concentration in MD & TD.
- Compounding of non-intercalated (synthetic or natural) clays with ca. 20-wt% H_2O should be examined

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