Flammability and Thermophysical Characterization of Thermoplastic Elastomer Nanocomposites

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  - Flammability Properties
  - Microstructure Analyses of Post-Test Materials
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INTRODUCTION

- **The introduction of inorganic nanomaterials as additives into polymer systems has resulted in polymer nanostructured materials exhibiting multifunctional, high performance polymer characteristics beyond what traditional polymer composites possess**
- **Selective thermoplastic elastomers have been used with montmorillonite organoclays, POSS®, carbon nanofibers to develop a flame resistant material**
- **Thermophysical and flammability properties of these polymer nanocomposites will be presented**

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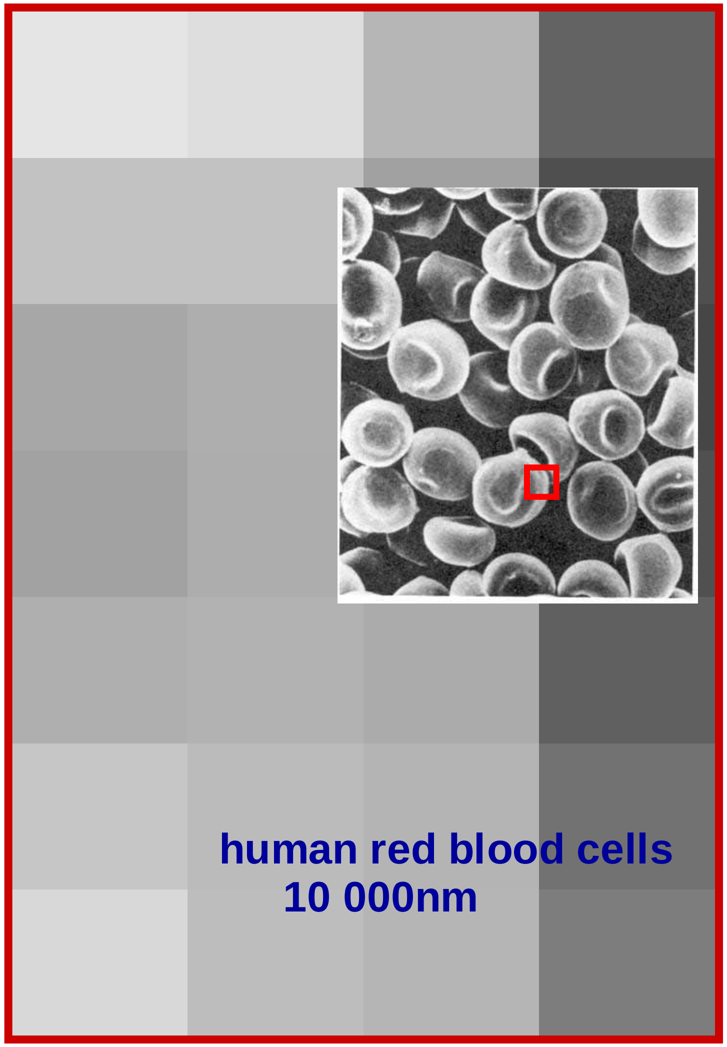
EXPERIMENTAL APPROACH

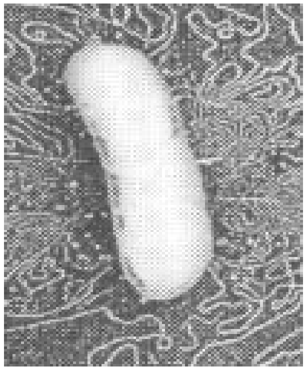
- A 30 mm Werner Pfleider co-rotating twin screw extruder was used and was configured for a wide variety of materials for polymer melt blending
- The extruder length/diameter (L/D) ratio can be varied from 21 to 48, with options of multiple feeds and vents
- The energy profile of the screw is optimized to meet the needs of the target product
- Long residence time screw designs are available for reactive products
- Varieties of feeders are available to accommodate the material handling characteristics of the raw materials
- Strand pelletization with low temperature chilled fluids allows processing of very soft or rubbery materials
- Approximately 5 lbs of each formulation were produced
- Specimens were injection molded in various configurations for measuring flammability and thermophysical properties

What “Nano” Really Means?



human red blood cells
10 000nm

- A nanometer (nm) is one billionth of a meter (10^{-9} m) about 4 times the diameter of an atom



bacteria *E.coli*
1 000nm

Q-rods 30nm
10:1 aspect ratio

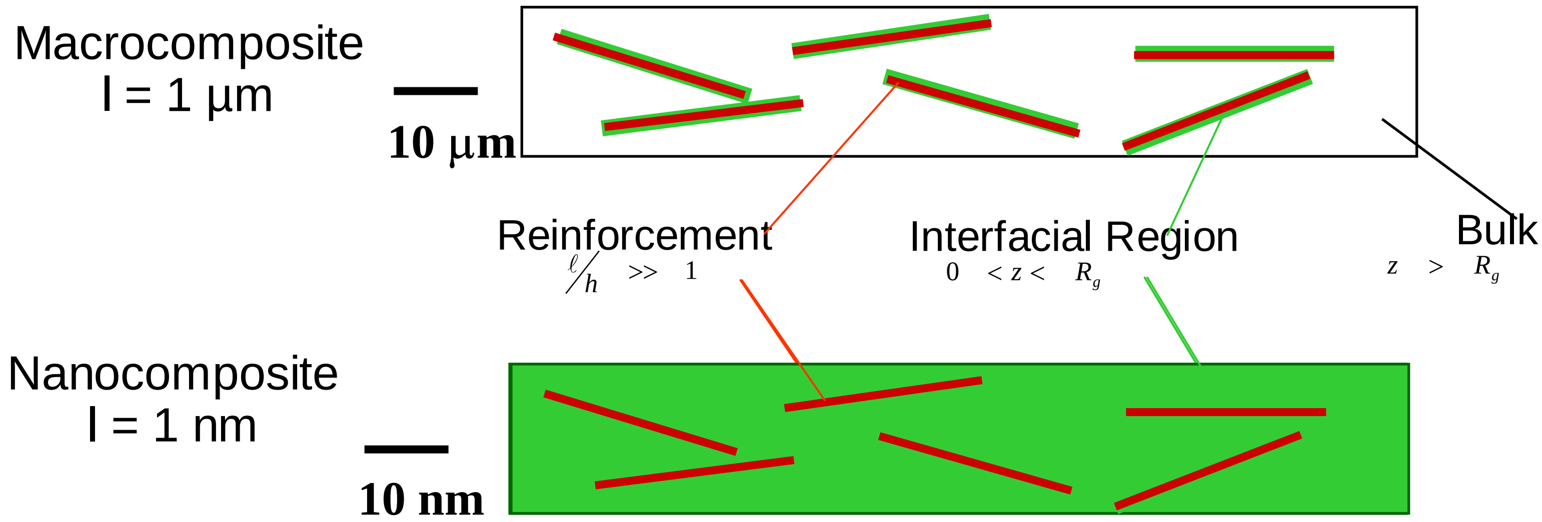
virus 100nm

QD 7nm

polymer 40nm

Courtesy of Vaia

Nanostructured Materials Uniqueness



<u>Characteristics</u>

Ultra-large interfacial area per volume
High fraction interfacial (interphase) material
Short distances between components

→ **Hierarchical Morphology Control**
Nano, Meso, Micro

NanoPolymer ***NanoInorganic***

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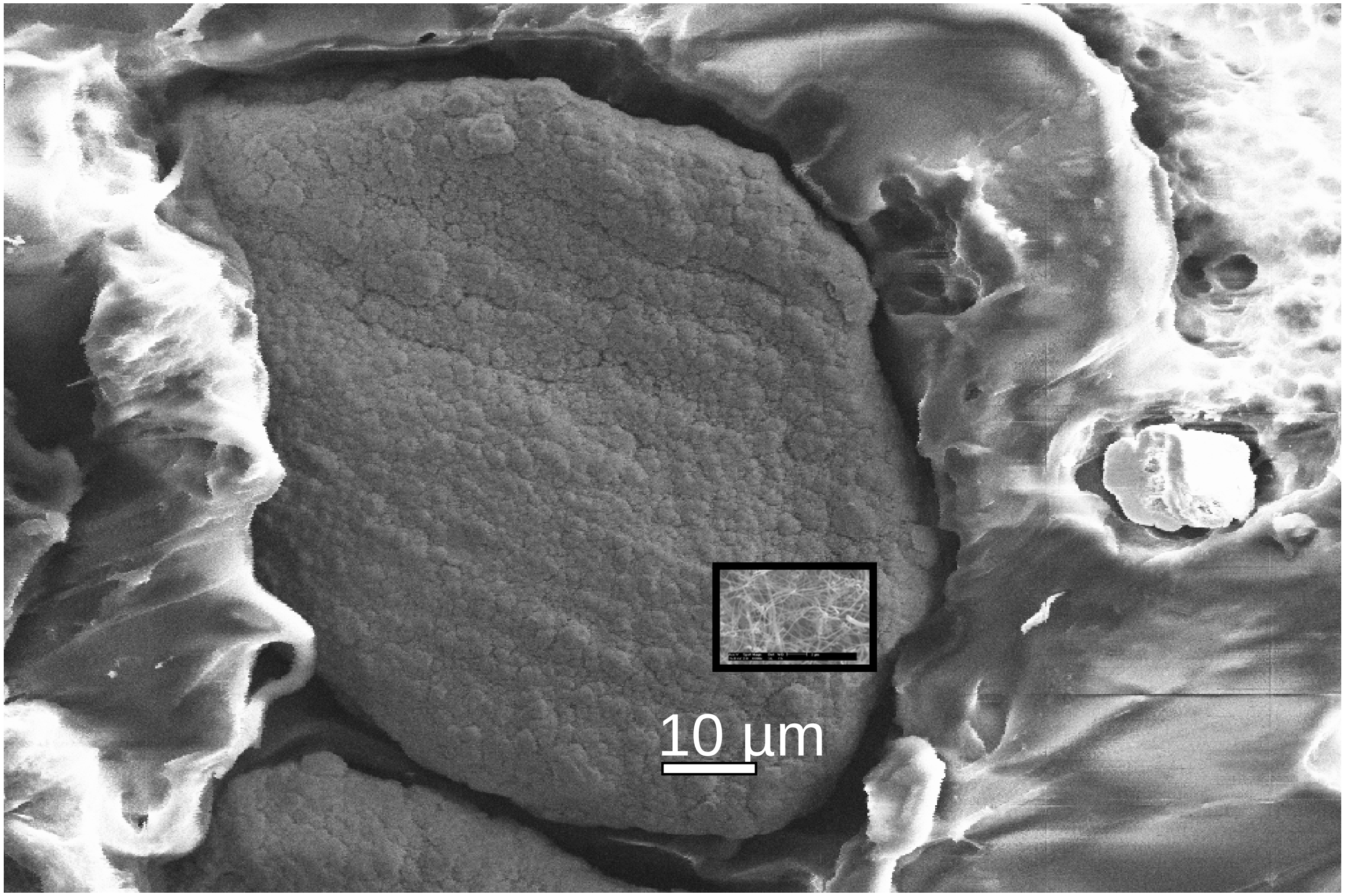
Courtesy of Vaia

Micro versus Nano

Novamet 60 and ASI Nanotubes (inset shows ~500 tubes)

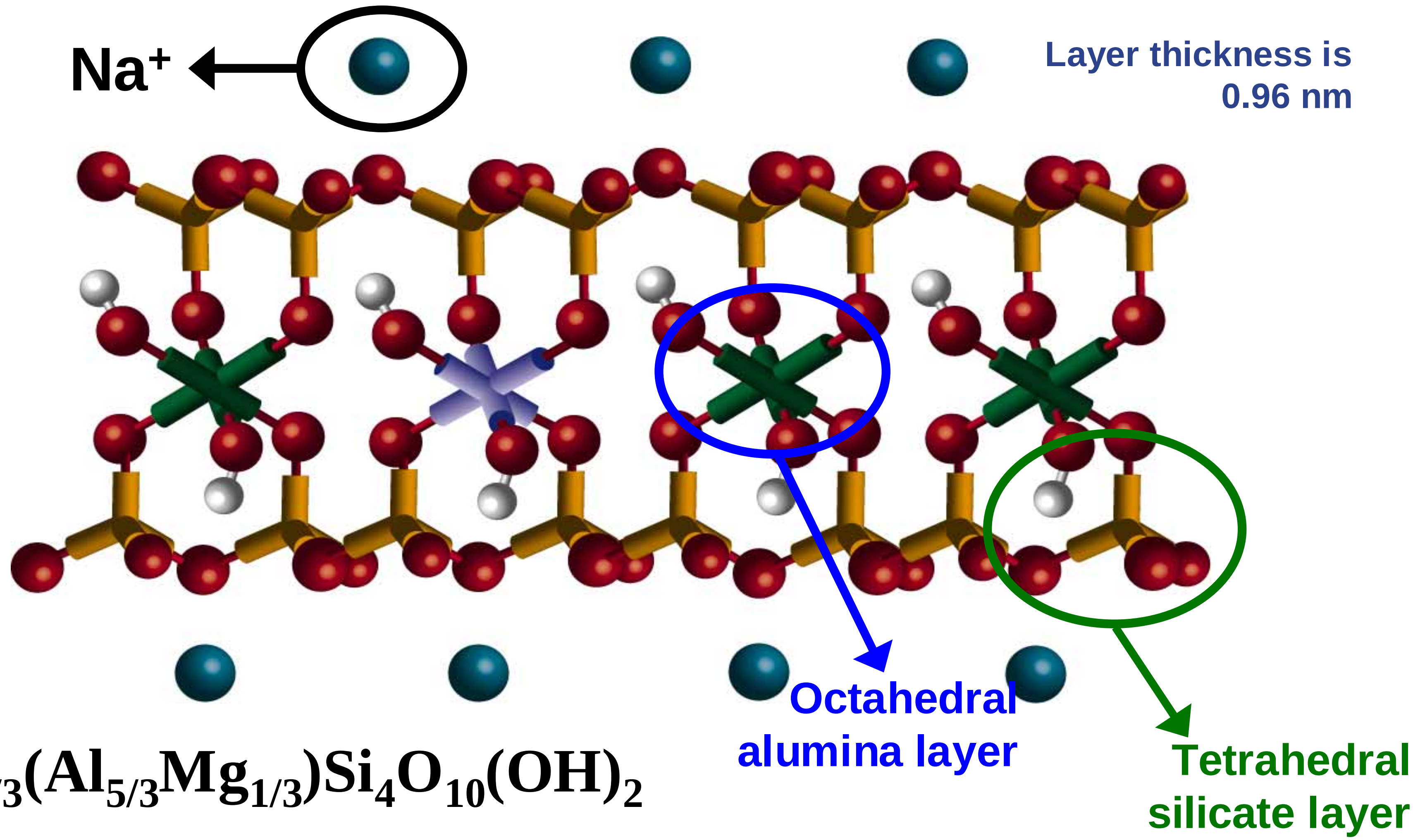


Alexander *et al.*

SELECTION OF MATERIALS

- **Thermoplastic Elastomers** – PELLETHANE™ 2102-90A thermoplastic polyurethane elastomer (TPU) is a polyester polycaprolactone elastomer manufactured by Dow Chemical. Its typical applications include seals, gaskets, belting, and others.
- **Montmorillonite Nanoclays** – Cloisite® 30B is a surface treated montmorillonite [Tallow bishydroxyethyl methyl, $T(EOH)_2M$] manufactured by Southern Clay Products
- **Carbon Nanofibers (CNFs)** – CNFs are a form of vapor-grown carbon fibers, which is a discontinuous graphitic filament produced in the gas phase from the pyrolysis hydrocarbons manufactured by Applied Sciences. PR-19-PS CNF and PR-24-PS CNF were used.
- **Polyhedral Oligomeric Silsesquioxane (POSS®)** – Representing a merger between chemical and filler technologies, POSS nanostructured materials can be used as multifunctional polymer additives, acting simultaneously as molecular level reinforcements, processing aids, and flame retardants. Hybrid Plastics' SO1458 Trisilanolphenyl-POSS® ($C_{42}H_{38}O_{12}Si_7$) was used.

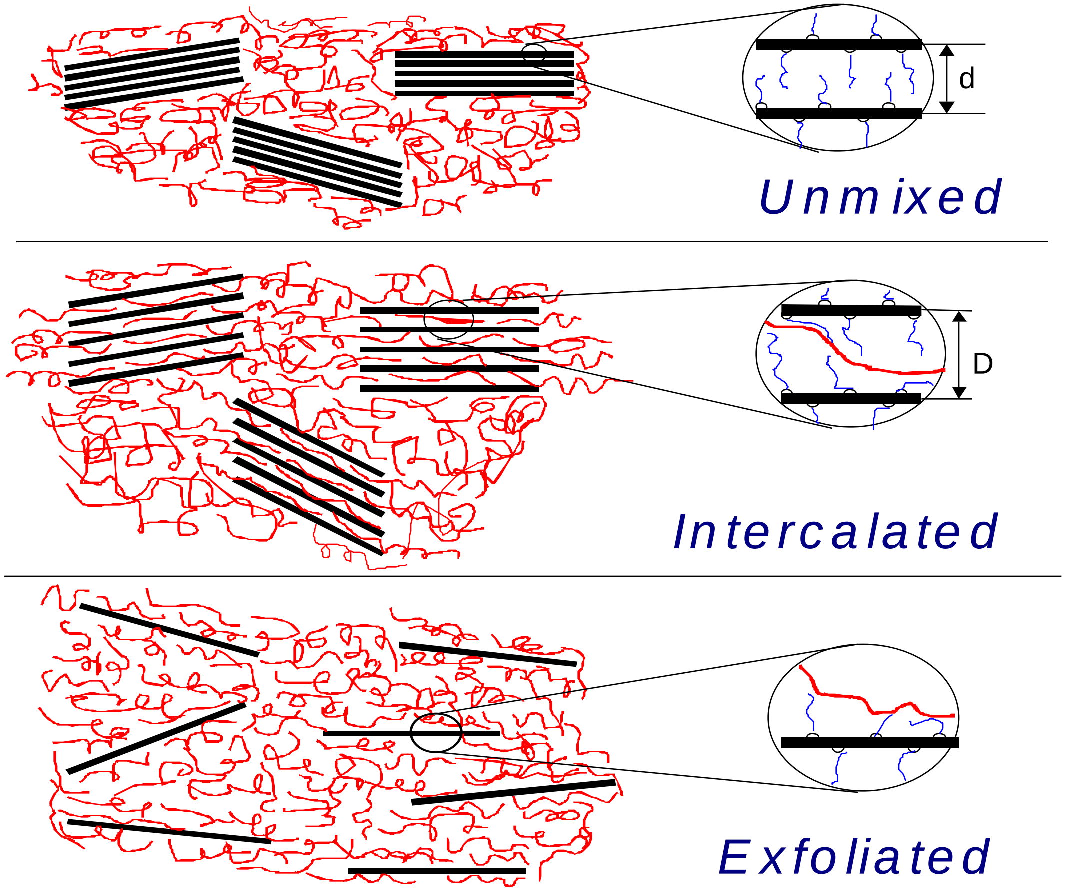
Montmorillonite Clays



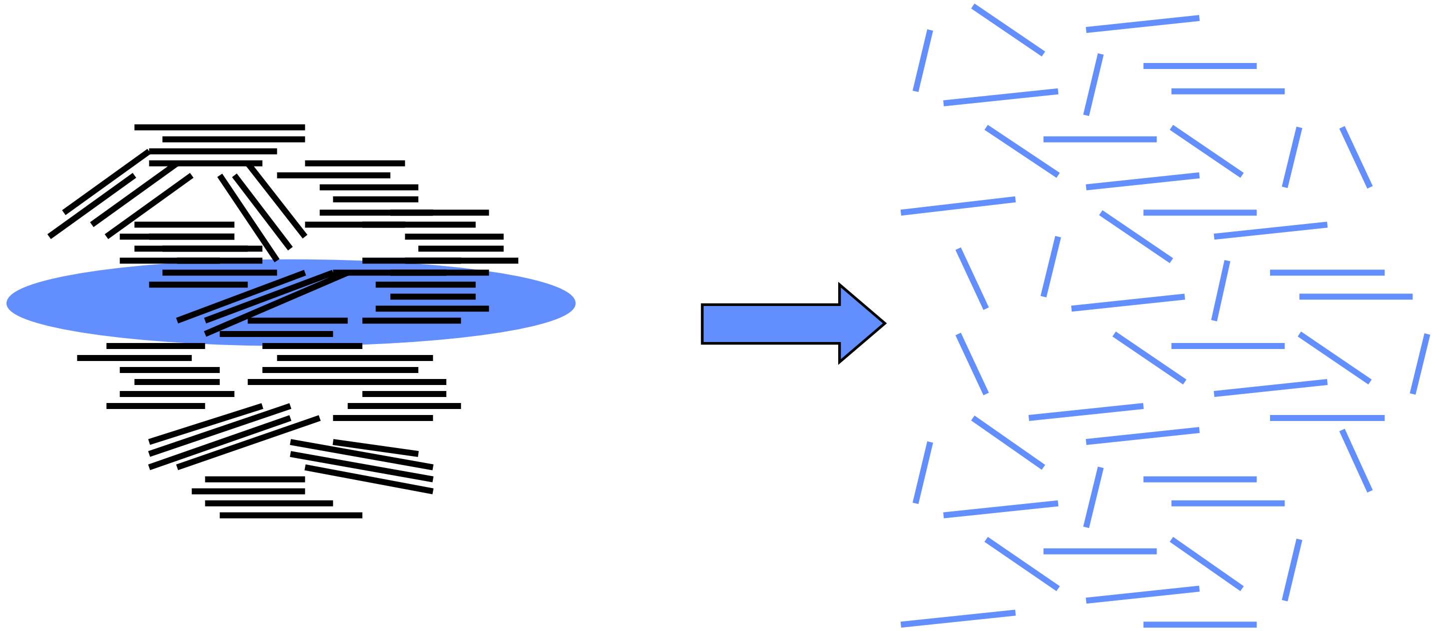
Layer thickness is 0.96 nm

$Na_{1/3}(Al_{5/3}Mg_{1/3})Si_4O_{10}(OH)_2$

Nanocomposite Classification



Processing Challenge of Nanoclay



8µm Particle >1 Million Platelets

Courtesy of Southern Clay Products

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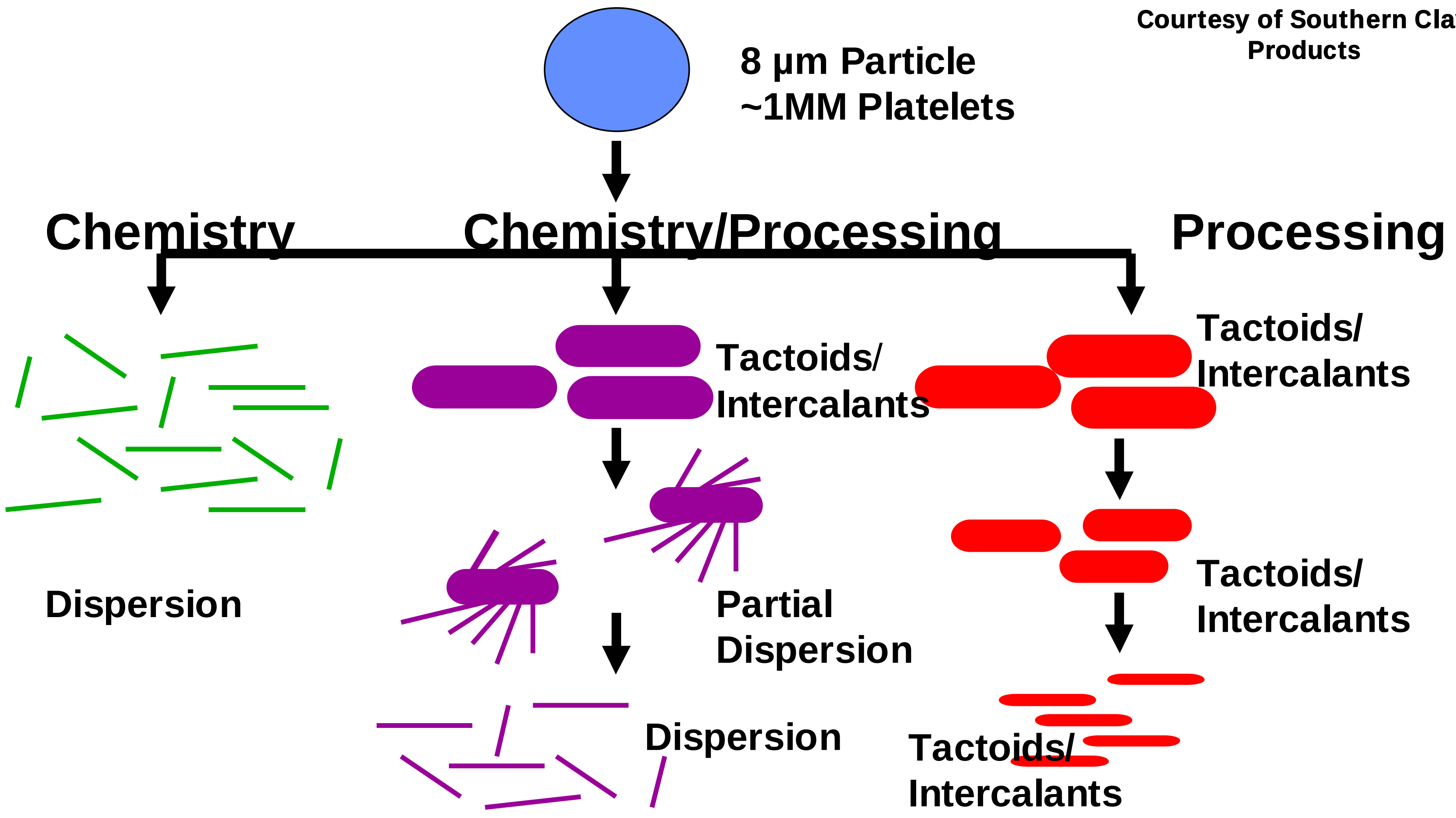
Dispersion Mechanism

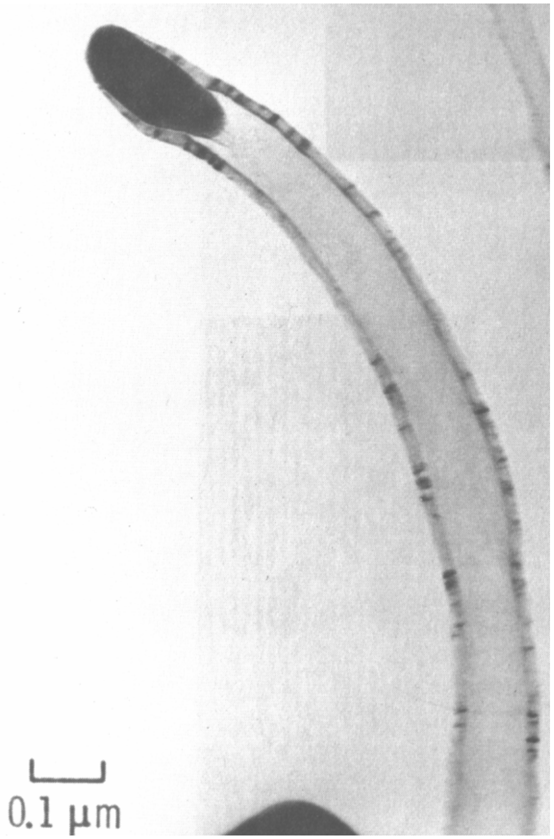
Courtesy of Southern Clay Products

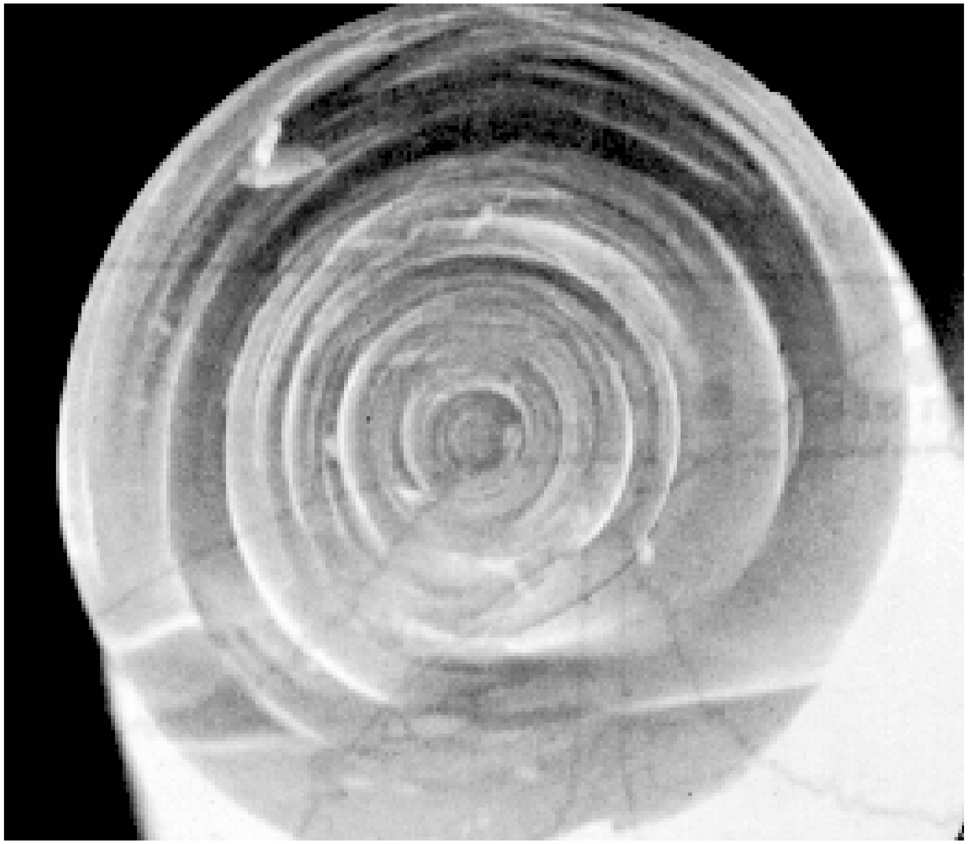


Carbon Nanofibers

- Carbon nanofibers **(CNFs)** **are a unique form of vapor-grown carbon fiber that bridges the gap in physical properties between larger, conventional PAN or pitch-based carbon fibers (5 to 10 μm in diameter) and smaller single-wall and multi-wall carbon nanotubes (1 to 10 nm in diameter)**
- Pyrograf®-III **is a very fine, highly graphitic carbon nanofiber manufactured by Applied Sciences Inc. that has an average diameter between 70 to 200 nm and a typical length of 50 to 100 μm**

Vapor-Grown Carbon Fiber





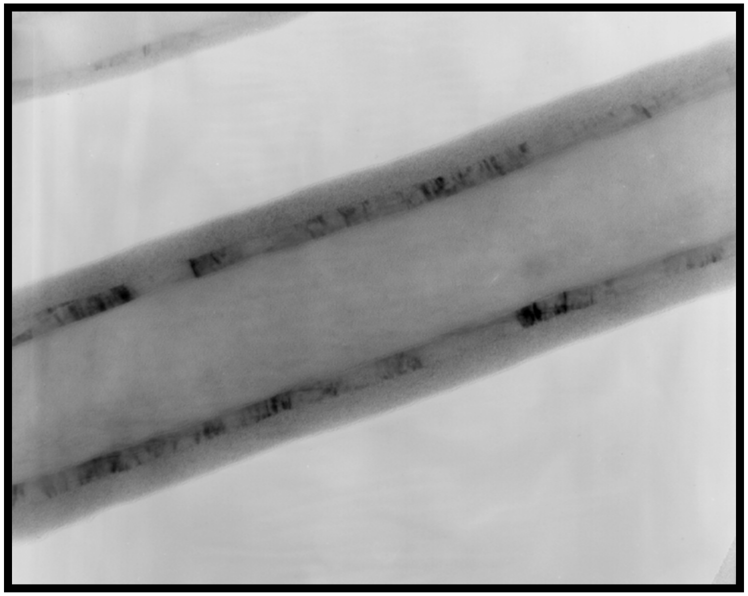
Pyrograf-III Carbon Nanofiber

Pyrograf-I VGCF

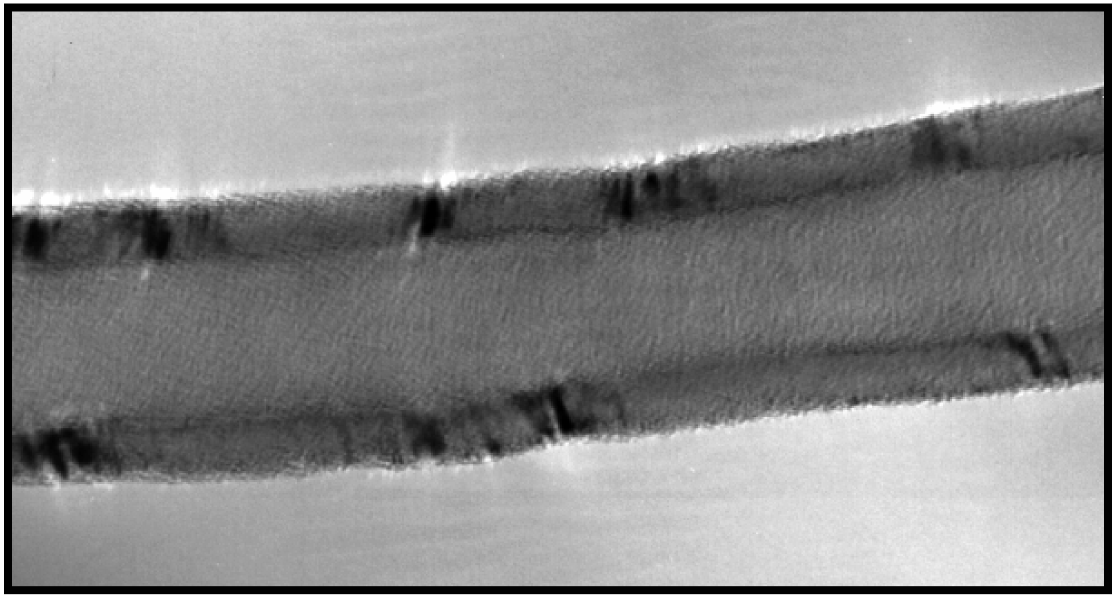
Courtesy of Applied Sciences

Pyrograf®-III TEMs

PR-19-PS with an average diameter of 128 nm



PR-24-PS with an average diameter of 65 nm



Courtesy of Applied Sciences

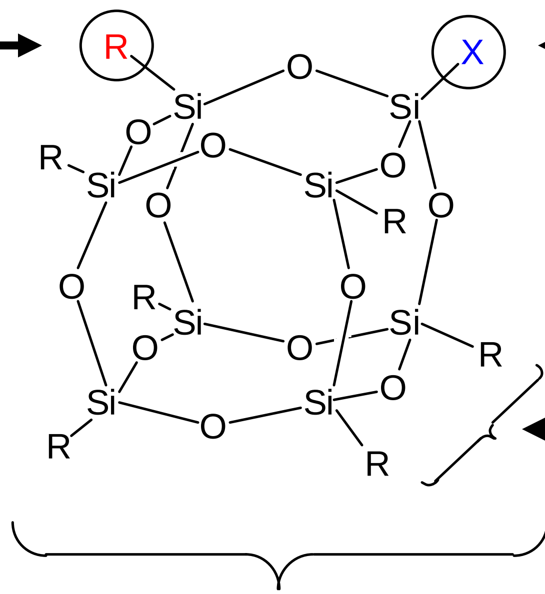
Polyhedral Oligomeric Silsesquioxane (POSS®)

- **Represents a merger between chemical and filler technologies, POSS® nanostructured materials can be used as multifunctional polymer additives, acting simultaneously as molecular level reinforcements, processing aids, and flame retardants**
- **They have two unique structural features: (1) the chemical composition is a hybrid, intermediate ($RSiO_{1.5}$) between that of silica (SiO_2) and silicones (R_2SiO); (2) POSS® molecules are nanoscopic in size, ranging from approximately 1 to 3 nm**

Anatomy of a POSS® Molecule

Nonreactive organic (R) groups for solubilization and compatibilization

May possess one or more functional groups suitable for polymerization or grafting



Nanoscopic in size with an Si-Si distance of 0.5 nm and a R-R distance of 1.5 nm

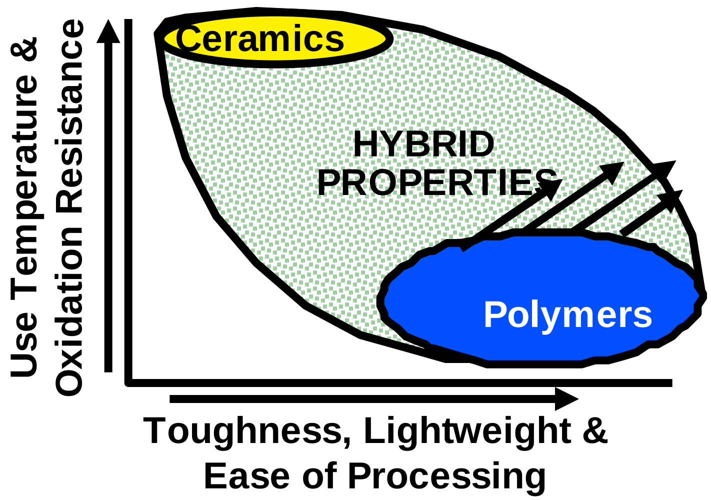
Thermally and chemically robust hybrid (organic-inorganic) framework

Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils

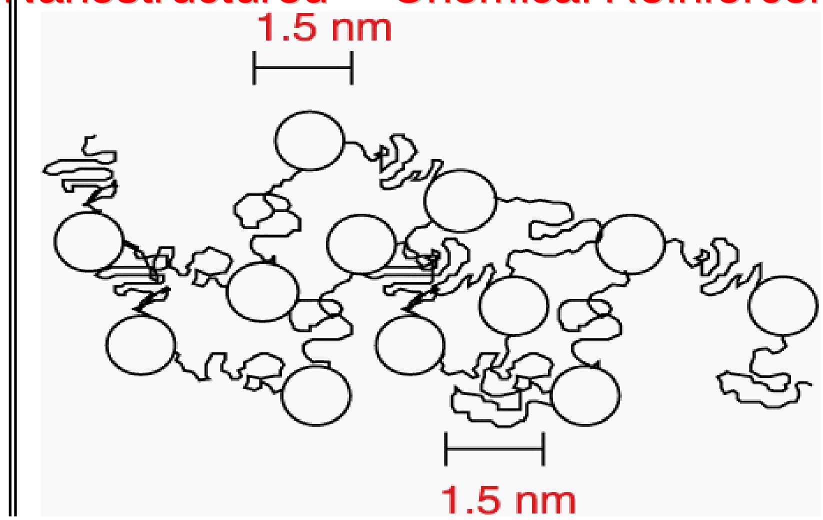
Courtesy of Hybrid Plastics

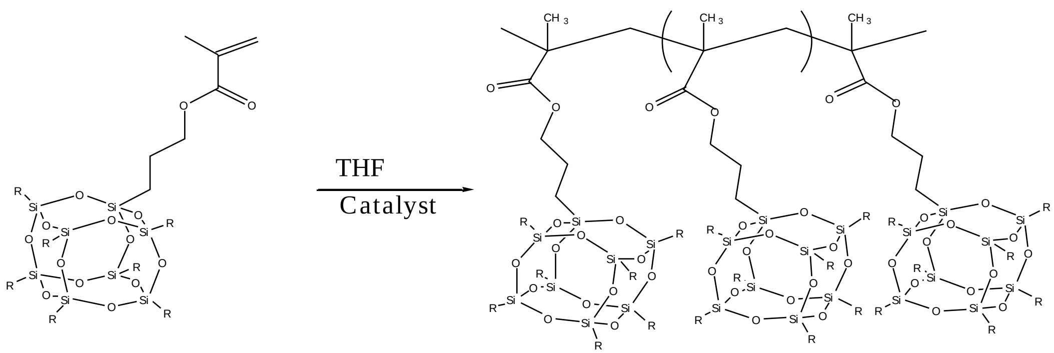
Key Aspects of POSS® Technology

Hybrid (inorganic/organic) Composition



Nanostructured™ Chemical Reinforcement





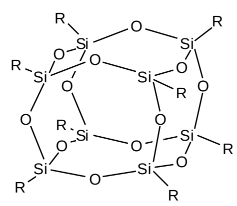
POSS® technology does not require manufacturers to retool or alter existing processes.

Lichtenhan et. al. *Macromolecules* **1993**, *26*, 2141.
Lichtenhan, *Polym. Mater. Encyclopedia* **1996**, *10*, 7768.

Courtesy of Hybrid Plastics

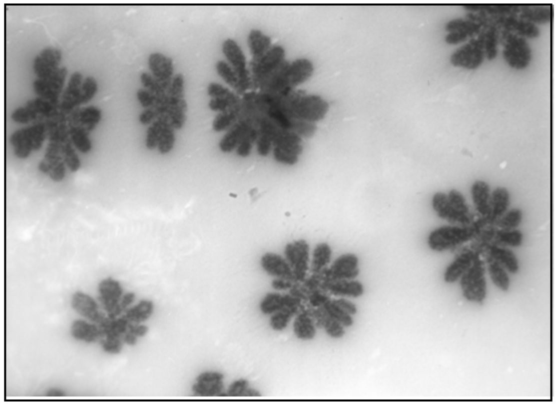
POSS®-Molecular Silica Blends

Blended into 2 million MW Polystyrene

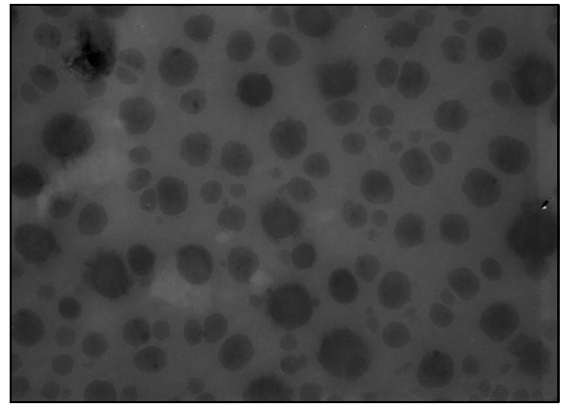


R = cyclopentyl

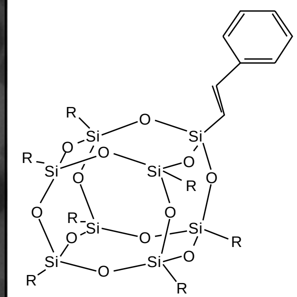
Cp_8T_8



Domain formation

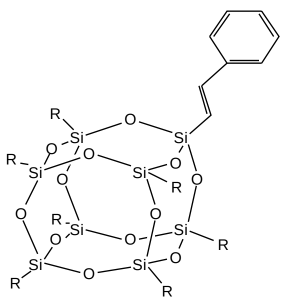


Partial compatibility



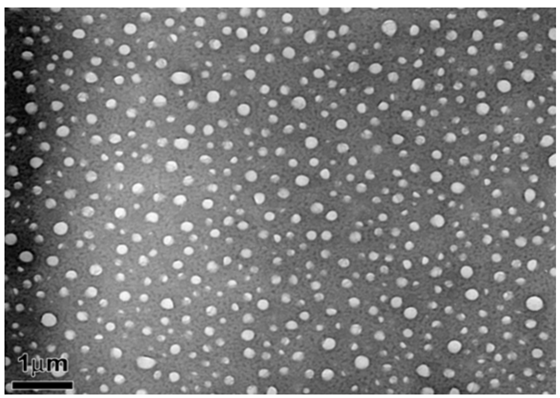
R = cyclopentyl

CP_7T_8Styrenyl

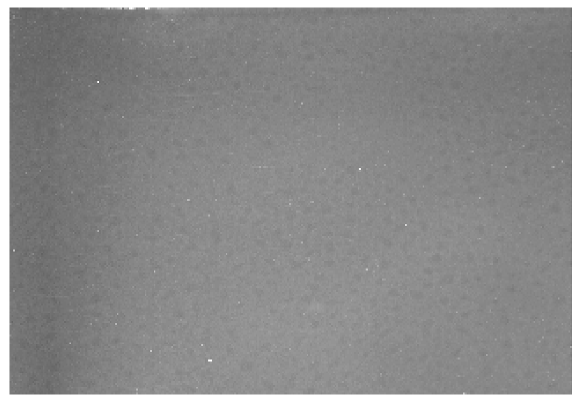


R = styrenyl

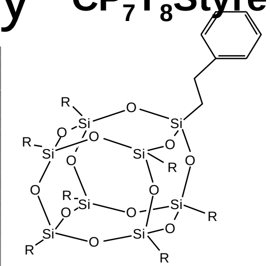
Styrenyl$_8$T$_8$



Phase inversion



50 wt% loading and transparent!



R = Phenethyl

Phenethyl$_8$T$_8$

Courtesy of A. Lee[20]
Michigan State University

Thermoplastic Elastomer Nanocomposites (TPUN)

Experiments	Pellethane™ TPU	Nanoparticles
1	2102-90A (100%)	None
2	2102-90A (95%)	5% Cloisite® 30B
3	2102-90A (95%)	5% Trisilanolphenyl-POSS®
4	2102-90A (95%)	5% PR-19-PS CNF
5	2102-90A (95%)	5% PR-24-PS CNF
6	2102-90A (85%)	15% PR-19-PS CNF
7	2102-90A (85%)	15% PR-24-PS CNF

Microstructures Analyses of Pre-Test Materials

- TEM analyses were conducted on all 7 blends to examine the degree of dispersion of each type of nanoparticles in 2102-90A TPU
  - PR-24-PS CNFs and PR-19-PS CNFs dispersed very well in 2102-90A TPU forming TPUNs
- In addition to TEM, the Cloisite® 30B modified materials were analyzed using WAXD
  - Tests showed that the Cloisite® 30B dispersed very well in 2102-90A TPU forming intercalated/exfoliated TPU nanocomposites (TPUNs)

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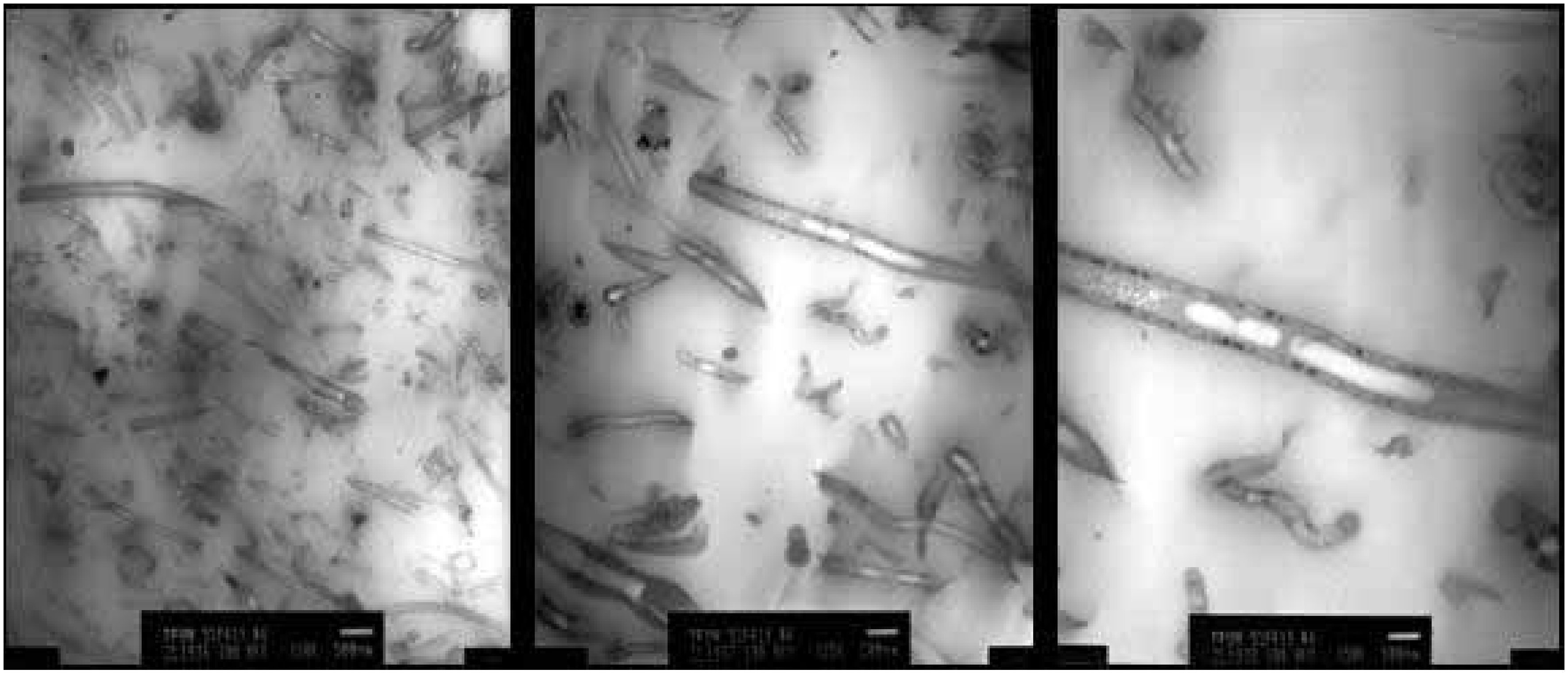
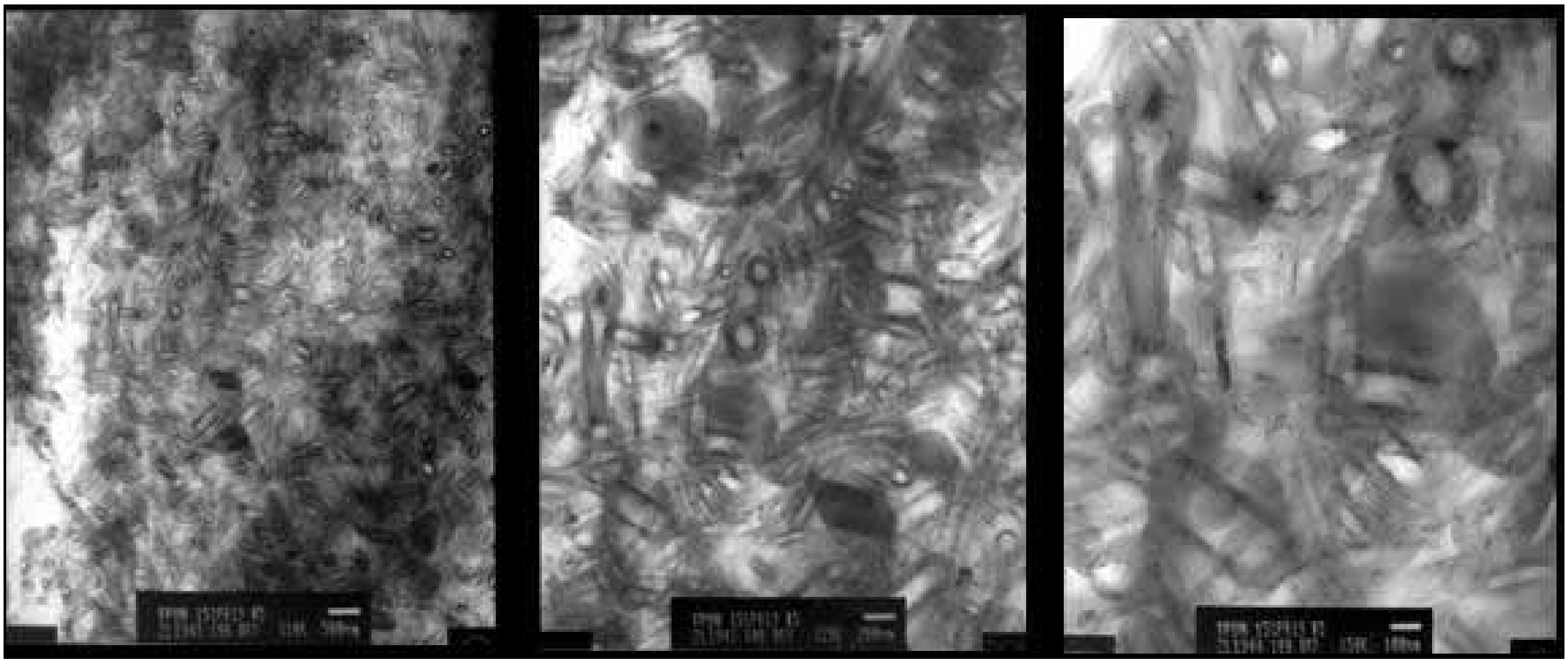
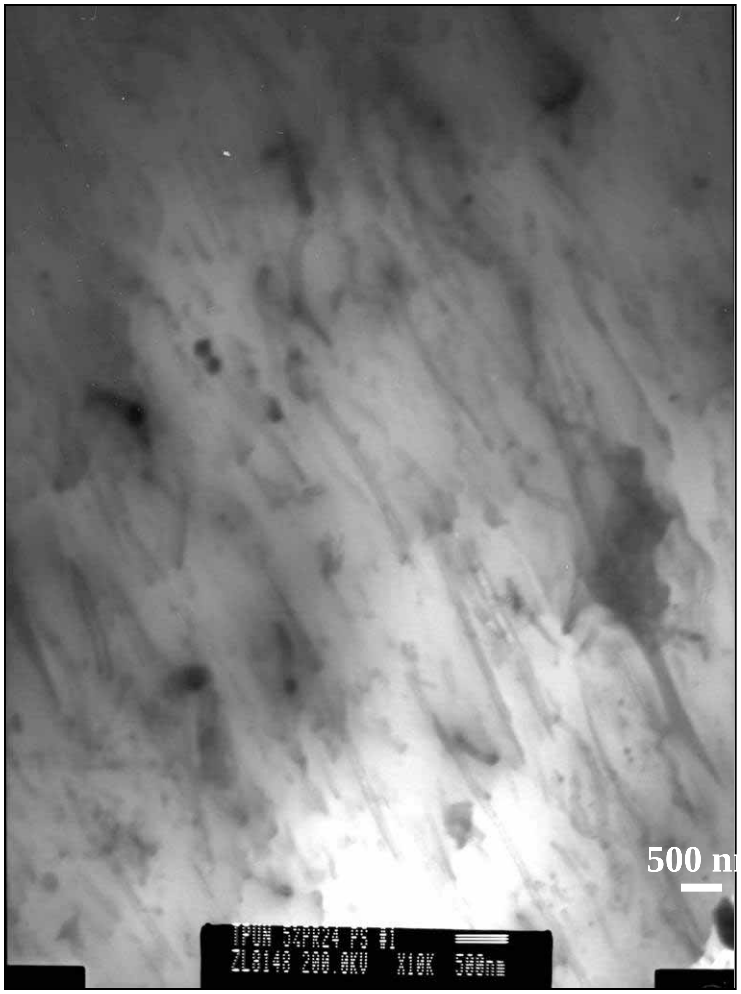
TEMs of TPUN:
5 wt% PR-19-PS CNF/95 wt% 2102-90A TPU

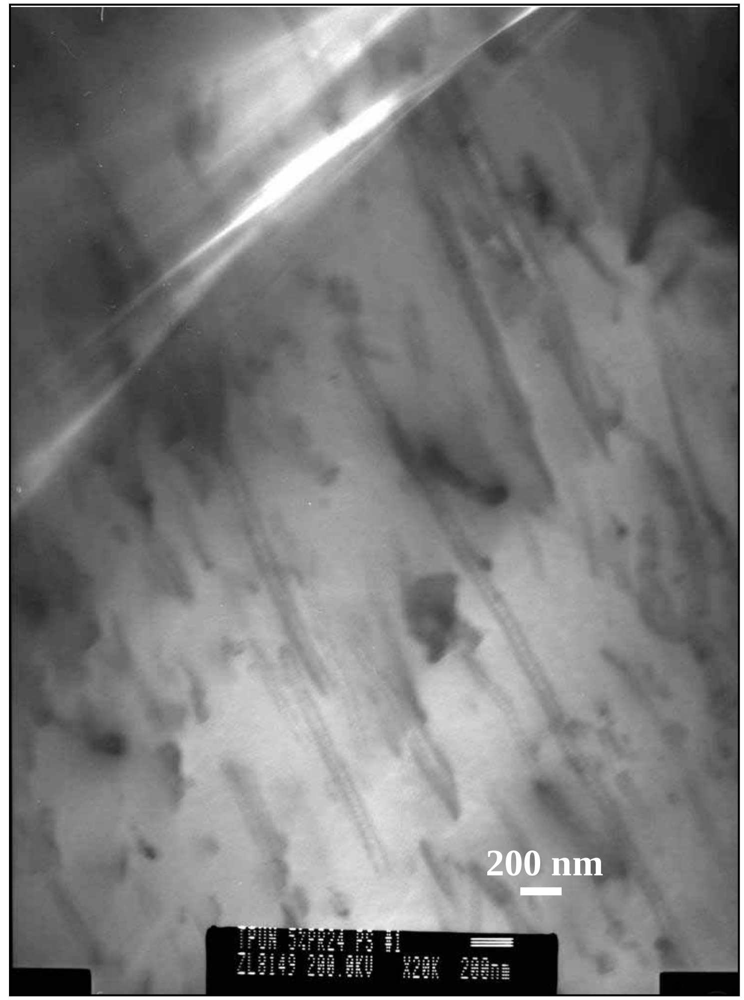


TEMs of TPUN:
15 wt% PR-19-PS CNF/85 wt% 2102-90A TPU

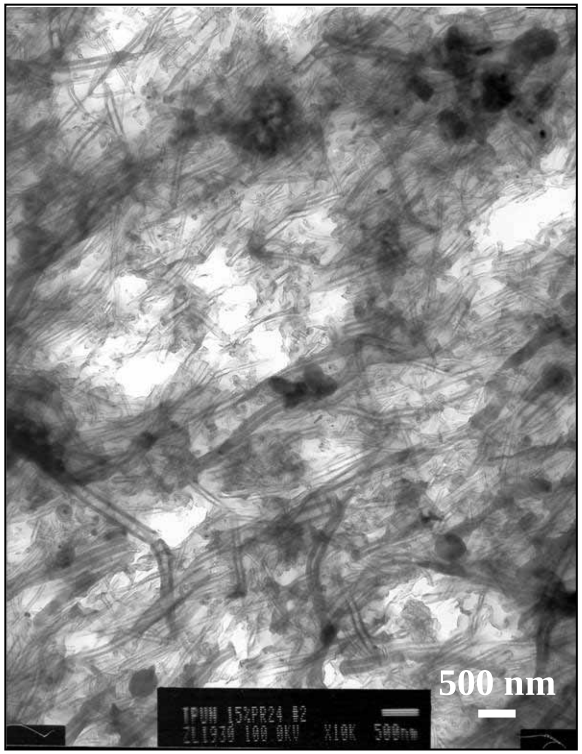


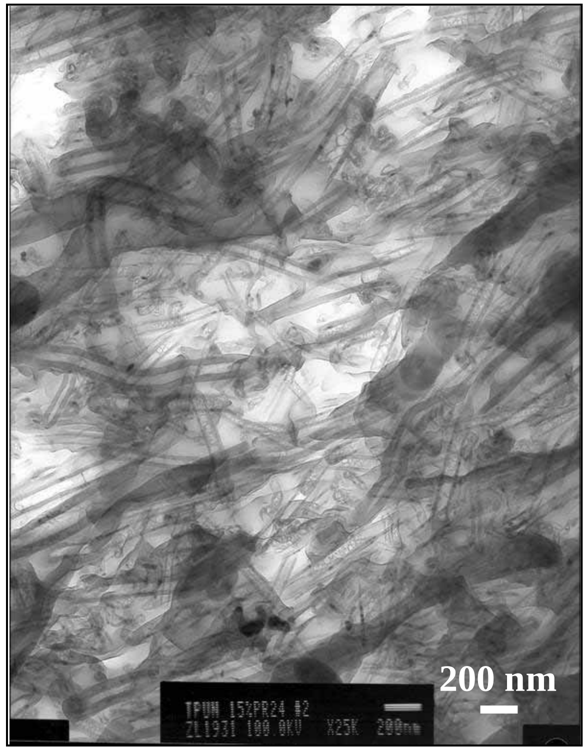
TEMs of TPUN:
5 wt% PR-24-PS CNF/95 wt% 2102-90A TPU





TEMs of TPUN:
15 wt% PR-24-PS CNF/95 wt% 2102-90A TPU





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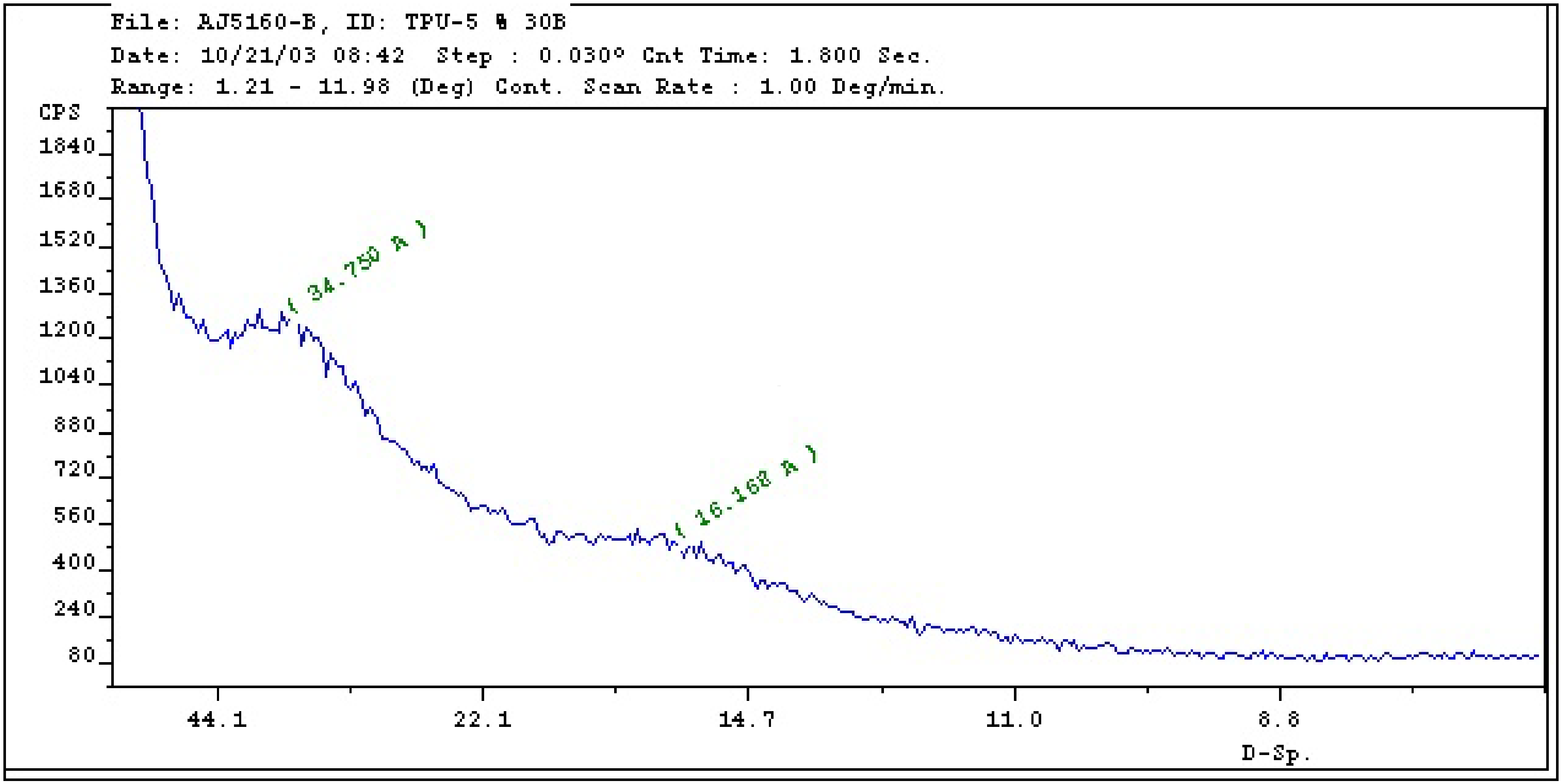
WAXDs of 5 wt% Cloisite® 30B in 2102-90A TPU



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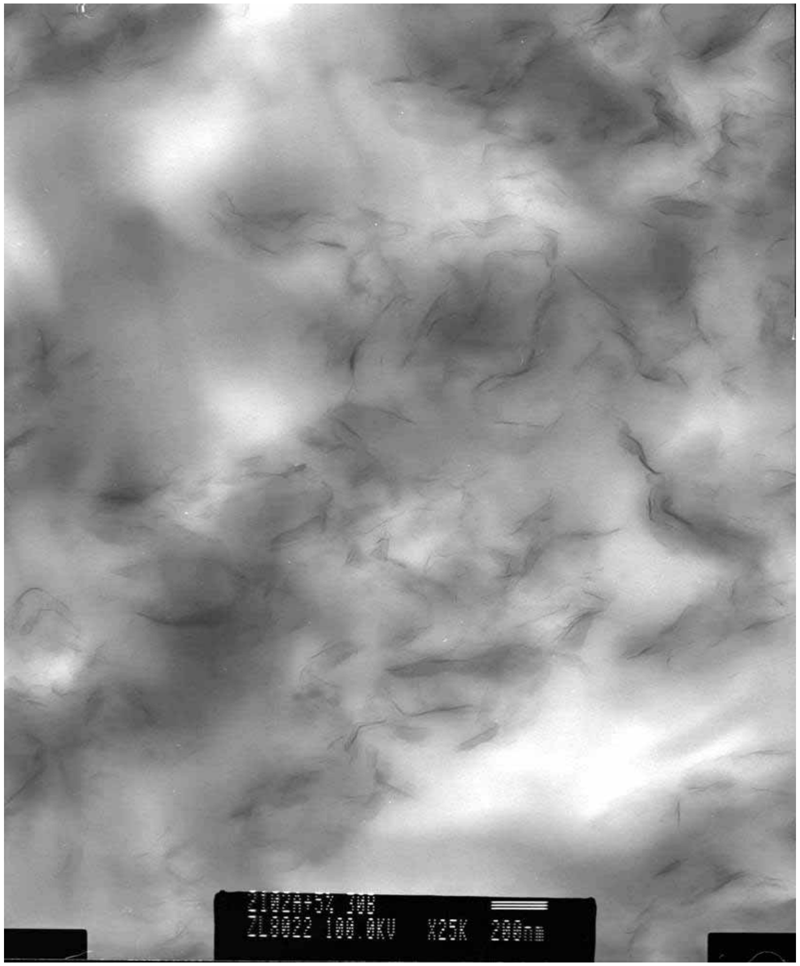
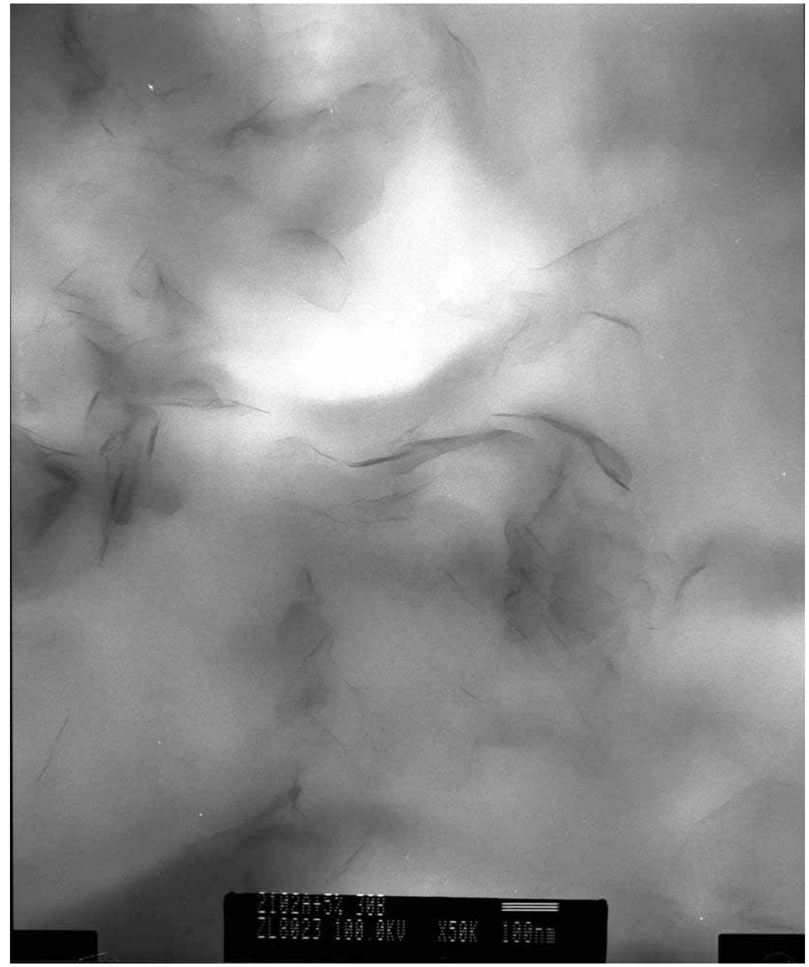
TEMs of TPUN:
5 wt% Cloisite® 30B/95 wt% 2102-90A TPU

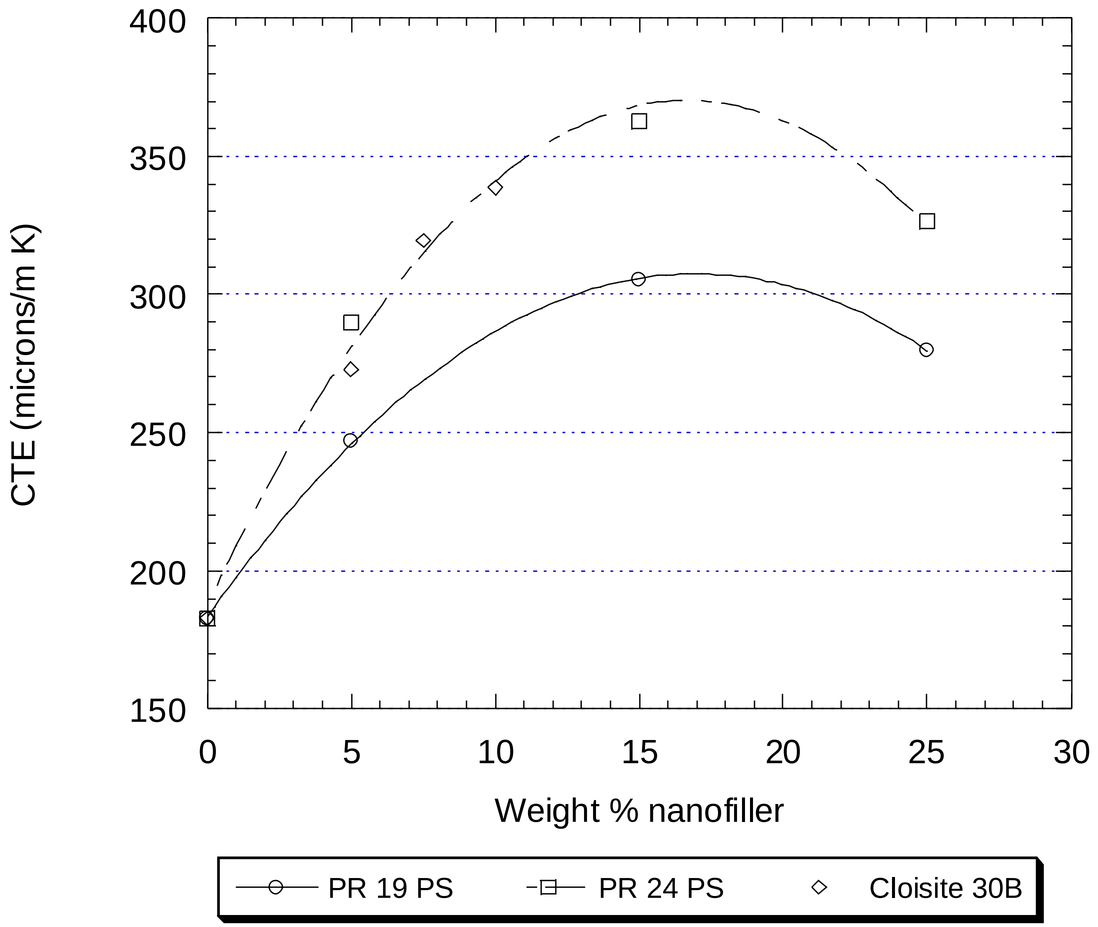




Properties for TPUNs

- **Thermophysical – coefficient of thermal expansion (CTE), heat capacity, thermal conductivity**
- **Flammability – Cone calorimeter data**

Correlations of CTE of CNF and Nanoclay TPUNs



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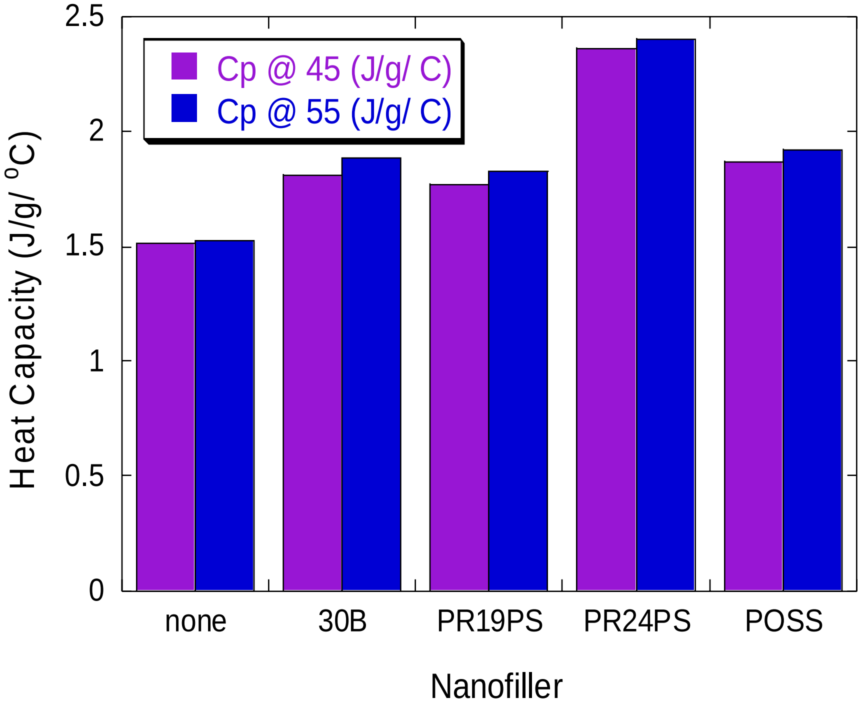
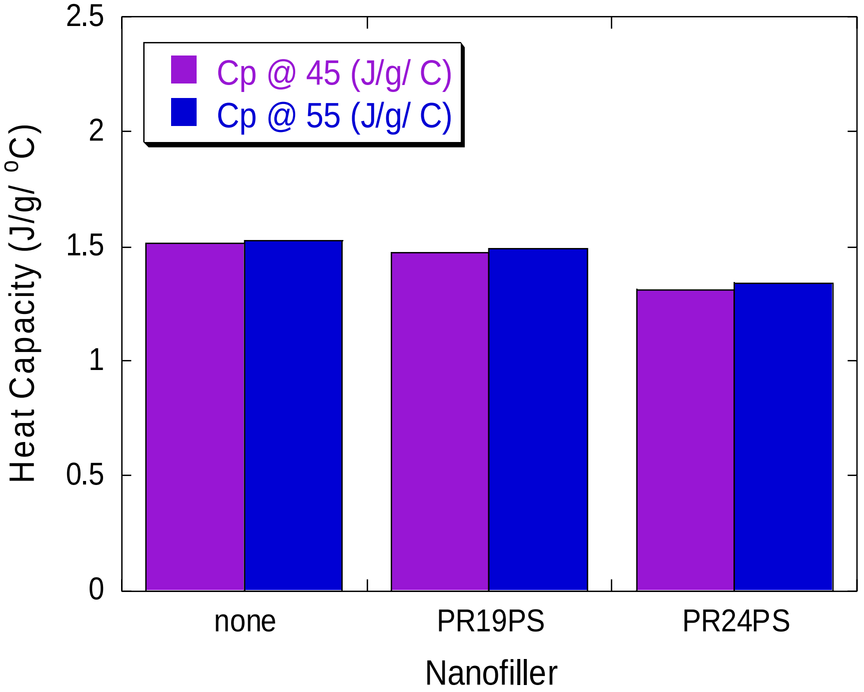
Heat Capacity of TPUN

5 wt% Nanofiller

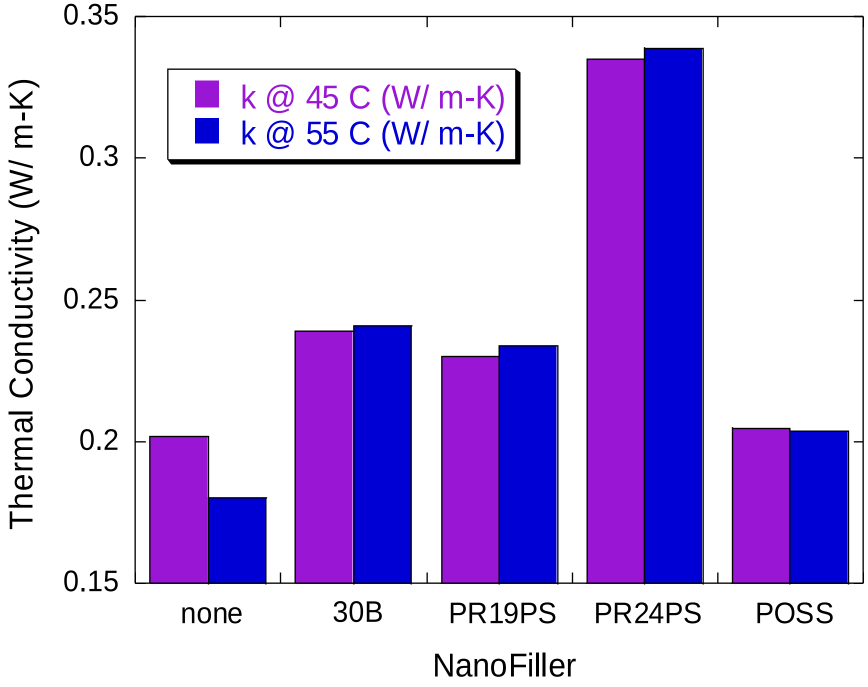


15 wt% Nanofiller

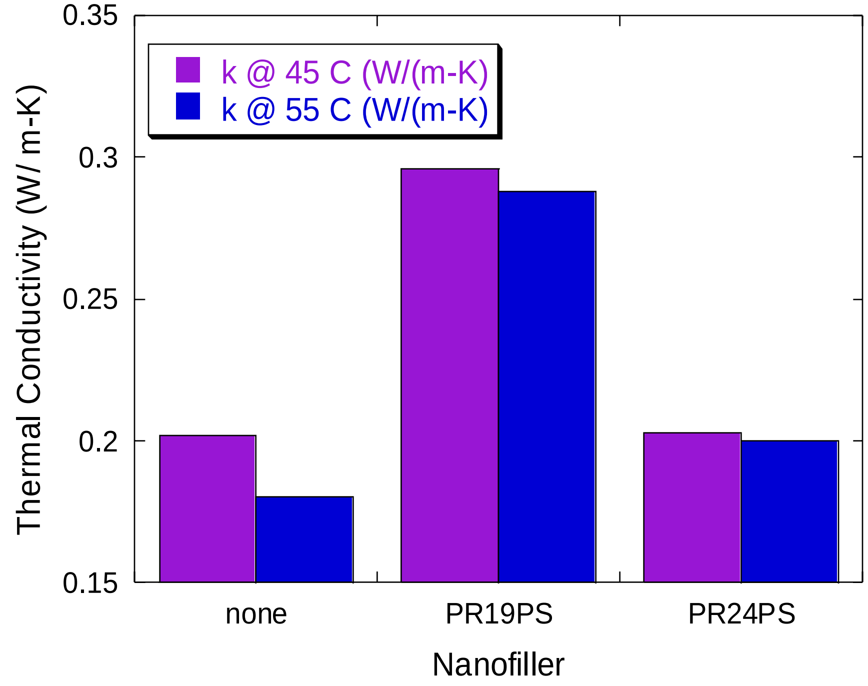


Thermal Conductivities of Thermoplastic Polyurethane Nanocomposites

5 wt% Nanofiller



15 wt% Nanofiller



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Cone Calorimeter Data at Irradiance Heat Flux of 50 kW/m^2

Material	t_{ig} (s)	PHRR (kW/m^2)	Avg. HRR, 60s (kW/m^2)	Avg. HRR, 180s (kW/m^2)	Avg. Eff, H_c (MJ/kg)	Avg. SEA (m^2/kg)
Pellethane TPU	32	2,290	406	653	30	237
Pellethane-5% Cloisite 30B TPUN	34	664 (71% reduction)	560	562	25	303
Pellethane-5% PR-19-PS CNF TPUN	27	624 (73% reduction)	532	456	22	295
Pellethane-5% PR-24-PS CNF TPUN	30	911(60% reduction)	407	554	25	283
Pellethane-5%-Trisilanolphenyl-POSS TPUN	31	1,637 (29% reduction)	334	591	25	339

t_{ig} = Time to sustained ignition
PHHR = Peak heat release rate
Avg. HRR = Average heat release rate after ignition
Avg. Eff, H_c = Effective heat of combustion
Avg. SEA = Average specific extinction area

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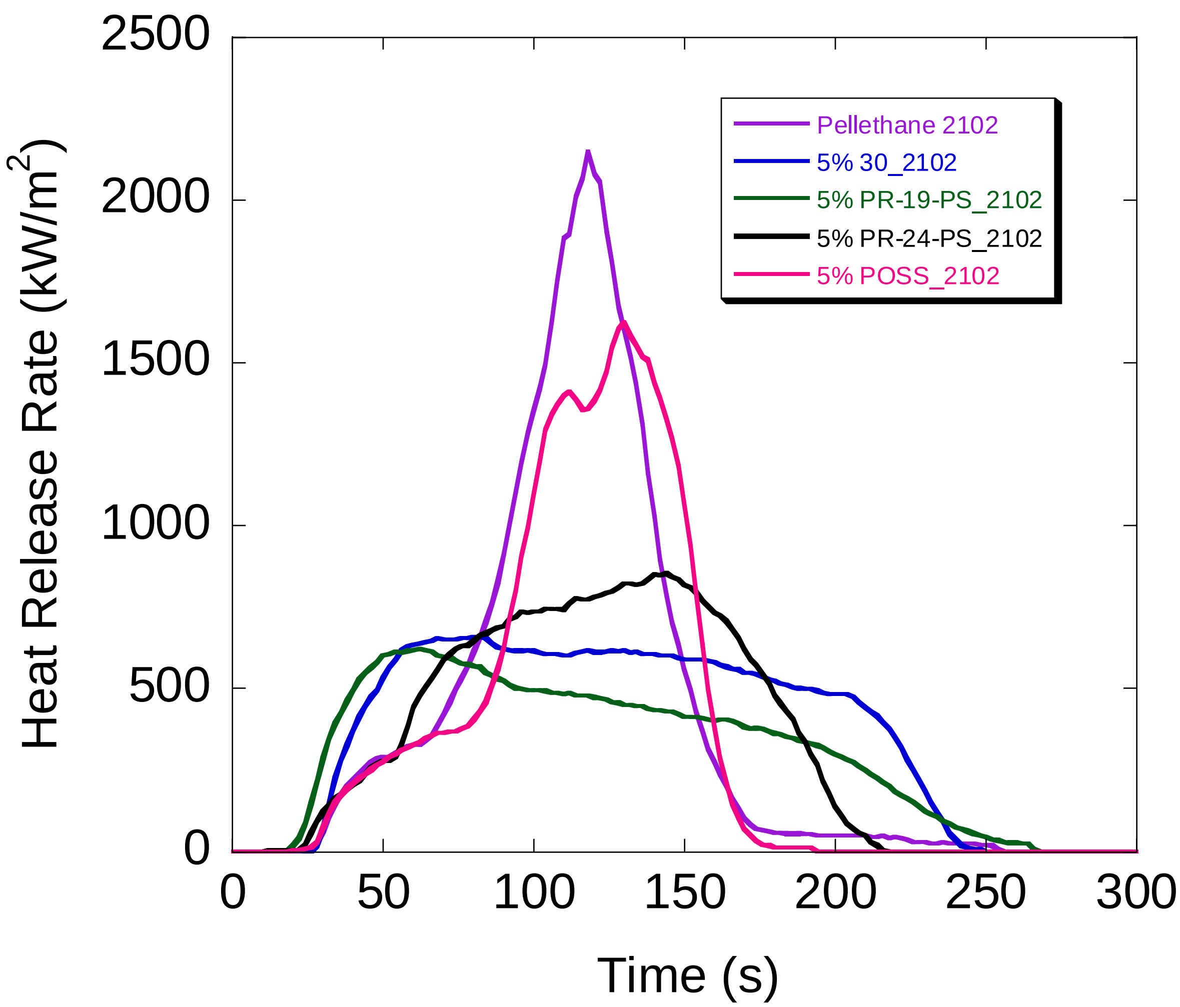
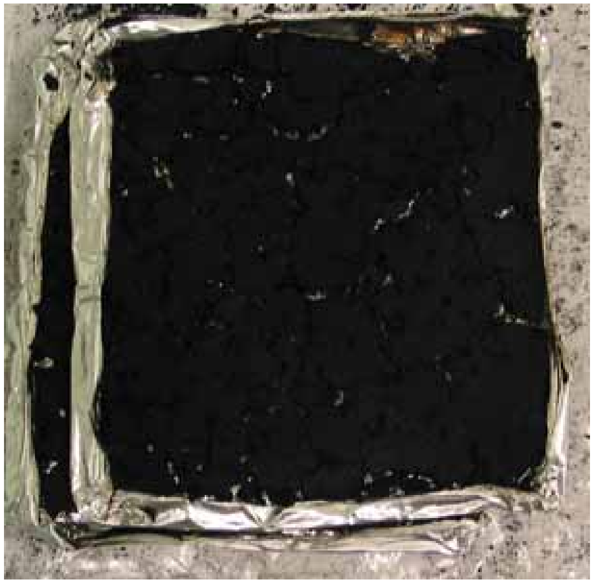
Heat Release Rate of TPUN



Cone Calorimeter samples after testing

Pellethane



Pellethane w/ 30B

Pellethane w/ PR19PS

SUMMARY AND CONCLUSIONS

- Blending of 5 wt% of nanoclay, CNF, and POSS® and 15 wt% of CNF in Dow's PELLETHANE™ 2102-90A TPU were conducted
- Thermophysical and flammability properties of these TPUNs were measured
- TEM analyses have demonstrated to be a very efficient way to study the degree of dispersion of nanoparticles in polymer matrix
- To obtain enhanced thermophysical and flammability properties, good dispersion of the nanoparticles in the polymer matrix is essential
- Dow's polyester polycaprolactone elastomer is very compatible with Cloisite® 30B nanoclay, PR-24-PS CNF, and PR-19-PS CNF as shown by TEMs
- Trisilanolphenyl-POSS® is not compatible with the PELLETHANE™ TPU and may actually degrade the material during process. Further investigation is underway.
- CTE of nanoclay TPUN increases with nanoclay to greater than 2x for 10 wt% nanoclay; and CTE of CNF TPUN goes through a maximum (~15 wt% loading)
- Correlations of CTE with Cloisite® 30B, PR-24-PS CNFs, and PR-19-PS CNFs were obtained as a function of nanofiller loading

SUMMARY AND CONCLUSIONS (cont'd)

- Thermal conductivity increases with the addition of nanoparticles
- Significant reduction of PHRR was shown by 5 wt% PR-19-PS CNF (73%), 5 wt% Cloisite® 30B (71%), and 5 wt% PR-24-PS CNF (60%) than baseline
- Time to sustained ignition of Pellethane was 32s with a slight increase of t_{ig} of 34s for 5% Cloisite® 30B, all other TPUNs have a slight decrease of t_{ig}
- Avg. HRR, 180s was lowered for all TPUNs
- Avg. effective heat of combustion was lowered for all TPUNs
- Avg. specific extinction area was slightly higher for all TPUNs