Flammability and Thermophysical Characterization of Thermoplastic Elastomer Nanocomposites

The 228th ACS National Meeting
Philadelphia, PA
August 22-26, 2004

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## Flammability and Thermophysical Characterization of Thermoplastic Elastomer Nanocomposites

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**Performing Organization Report Number:**
E04-082

**Distribution/Availability Statement:**
Approved for public release; distribution unlimited

**Security Classification:**
- Report: unclassified
- Abstract: unclassified
- This Page: unclassified

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18
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Financial Support:
Air Force Office of Scientific Research
Air Force Research Laboratory, Propulsion Directorate
OUTLINE

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- WHAT IS NANOTECHNOLOGY?
- SELECTION OF MATERIALS
- OVERVIEW OF NANOPARTICLES
- DISCUSSION OF RESULTS
  - Processing of Materials
  - Microstructure Analyses of Pre-Test Materials
  - Thermophysical Properties
  - Flammability Properties
  - Microstructure Analyses of Post-Test Materials
- SUMMARY AND CONCLUSIONS
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.
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?

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

- Human red blood cells: 10,000 nm
- Bacteria (E. coli): 1,000 nm
- Virus: 100 nm
- Polymer: 40 nm
- Q-rods: 30 nm, 10:1 aspect ratio
- QD: 7 nm

Courtesy of Vaia
Nanostructured Materials Uniqueness

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

Hierarchical Morphology Control
Nano, Meso, Micro

NanoPolymer Nanoinorganic

Macrocomposite $l = 1 \mu m$
- Reinforcement $l_i >> 1$
- Interfacial Region $0 < z < R_g$
- Bulk $z > R_g$

Nanocomposite $l = 1 \text{nm}$
- 10 nm

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Courtesy of Vaia
Novamet 60 and ASI Nanotubes (inset shows ~500 tubes)
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® (C₄₂H₃₈O₁₂Si₇) was used.
Montmorillonite Clays

Montmorillonite Clays

\[ \text{Na}_{1/3}(\text{Al}_{5/3}\text{Mg}_{1/3})\text{Si}_4\text{O}_{10}(\text{OH})_2 \]

Layer thickness is 0.96 nm

Na$^+$

Octahedral alumina layer

Tetrahedral silicate layer
Nanocomposite Classification

Unmixed

Intercalated

Exfoliated
Processing Challenge of Nanoclay

8µm Particle Platelets

>1 Million

Courtesy of Southern Clay Products
Dispersion Mechanism

8 µm Particle
~1MM Platelets

Chemistry

Chemistry/Processing

Processing

Tactoids/Intercalants

Partial Dispersion

Dispersion

Tactoids/Intercalants

Tactoids/Intercalants

Courtesy of Southern Clay Products

Dispersion Mechanism

Chemistry            Chemistry/Processing            Processing

Tactoids/Intercalants

Partial Dispersion

Dispersion

Tactoids/Intercalants

Tactoids/Intercalants

8 µm Particle
~1MM Platelets
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_{2}SiO); (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
- Nanoscopic in size with an Si-Si distance of 0.5 nm and a R-R distance of 1.5 nm
- May possess one or more functional groups suitable for polymerization or grafting
- 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.

POSS®-Molecular Silica Blends
Blended into 2 million MW Polystyrene

Domain formation
Partial compatibility
Phase inversion

R = cyclopentyl
Cp₈T₈

R = styrenyl
Styrenyl₈T₈

R = phenethyl
Phenethyl₈T₈

50 wt% loading and transparent!

Courtesy of A. Lee
Michigan State University
# Thermoplastic Elastomer Nanocomposites (TPUN)

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Pellethane™ TPU</th>
<th>Nanoparticles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2102-90A (100%)</td>
<td>None</td>
</tr>
<tr>
<td>2</td>
<td>2102-90A (95%)</td>
<td>5% Cloisite® 30B</td>
</tr>
<tr>
<td>3</td>
<td>2102-90A (95%)</td>
<td>5% Trisilanolphenyl-POSS®</td>
</tr>
<tr>
<td>4</td>
<td>2102-90A (95%)</td>
<td>5% PR-19-PS CNF</td>
</tr>
<tr>
<td>5</td>
<td>2102-90A (95%)</td>
<td>5% PR-24-PS CNF</td>
</tr>
<tr>
<td>6</td>
<td>2102-90A (85%)</td>
<td>15% PR-19-PS CNF</td>
</tr>
<tr>
<td>7</td>
<td>2102-90A (85%)</td>
<td>15% PR-24-PS CNF</td>
</tr>
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</table>
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)
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
WAXDs of 5 wt% Cloisite® 30B in 2102-90A TPU

File: AJ5160-B, ID: TPU-5 % 30B
Date: 10/21/03 08:42  Step : 0.030° Cnt Time: 1.800 Sec.
Range: 1.21 - 11.98 (Deg) Cont. Scan Rate : 1.00 Deg/min.
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

![Graph showing correlations of CTE of CNF and Nanoclay TPUNs](image)

- **CTE (microns/m K)**
- **Weight % nanofiller**

- **PR 19 PS**
- **PR 24 PS**
- **Cloisite 30B**
Heat Capacity of TPUN

5 wt% Nanofiller

<table>
<thead>
<tr>
<th>Nanofiller</th>
<th>0°C</th>
<th>55°C</th>
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<tr>
<td>none</td>
<td>0.5</td>
<td>2</td>
</tr>
<tr>
<td>30B</td>
<td>1.5</td>
<td>2.5</td>
</tr>
<tr>
<td>PR19PS</td>
<td>2.0</td>
<td>2.5</td>
</tr>
<tr>
<td>PR24PS</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>POSS</td>
<td>2.5</td>
<td>2.5</td>
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15 wt% Nanofiller

<table>
<thead>
<tr>
<th>Nanofiller</th>
<th>0°C</th>
<th>55°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td>PR19PS</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>PR24PS</td>
<td>1.5</td>
<td>1.5</td>
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Thermal Conductivities of Thermoplastic Polyurethane Nanocomposites

5 wt% Nanofiller

<table>
<thead>
<tr>
<th>Nanofiller</th>
<th>k @ 45 C (W/m-K)</th>
<th>k @ 55 C (W/m-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>0.15</td>
<td>0.2</td>
</tr>
<tr>
<td>30B</td>
<td>0.25</td>
<td>0.3</td>
</tr>
<tr>
<td>PR19PS</td>
<td>0.3</td>
<td>0.35</td>
</tr>
<tr>
<td>PR24PS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>POSS</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

15 wt% Nanofiller

<table>
<thead>
<tr>
<th>Nanofiller</th>
<th>k @ 45 C (W/m-K)</th>
<th>k @ 55 C (W/m-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>0.2</td>
<td>0.25</td>
</tr>
<tr>
<td>PR19PS</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>PR24PS</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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## Cone Calorimeter Data at Irradiance Heat Flux of 50 kW/m²

<table>
<thead>
<tr>
<th>Material</th>
<th>$t_{ig}$ (s)</th>
<th>PHRR (kW/m²)</th>
<th>Avg. HRR, 60s (kW/m²)</th>
<th>Avg. HRR, 180s (kW/m²)</th>
<th>Avg. Eff, $H_c$ (MJ/kg)</th>
<th>Avg. SEA (m²/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pellethane TPU</td>
<td>32</td>
<td>2,290</td>
<td>406</td>
<td>653</td>
<td>30</td>
<td>237</td>
</tr>
<tr>
<td>Pellethane-5% Cloisite 30B TPUN</td>
<td>34</td>
<td>664 (71% reduction)</td>
<td>560</td>
<td>562</td>
<td>25</td>
<td>303</td>
</tr>
<tr>
<td>Pellethane-5% PR-19-PS CNF TPUN</td>
<td>27</td>
<td>624 (73% reduction)</td>
<td>532</td>
<td>456</td>
<td>22</td>
<td>295</td>
</tr>
<tr>
<td>Pellethane-5% PR-24-PS CNF TPUN</td>
<td>30</td>
<td>911 (60% reduction)</td>
<td>407</td>
<td>554</td>
<td>25</td>
<td>283</td>
</tr>
<tr>
<td>Pellethane-5% Trisilanolphenyl-POSS TPUN</td>
<td>31</td>
<td>1,637 (29% reduction)</td>
<td>334</td>
<td>591</td>
<td>25</td>
<td>339</td>
</tr>
</tbody>
</table>

$t_{ig} = $ Time to sustained ignition  
PHRR = 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
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.
- Trisilanophenyl-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