Determination of Mechanical and Surface Properties of Semicrystalline Polyhedral Oligomeric Silsesquioxane (POSS) Nanocomposites

Laura E. Moody¹, Darrell Marchant¹, Wade W. Grabow¹ Andre Y. Lee² and Joseph M. Mabry¹

¹Air Force Research Laboratory, Edwards AFB, CA 93534
²Michigan State University, East Lansing MI 48824

PREPRINT: Distribution A: Approved for public release; distribution unlimited
Overview

• Introduction
• Experimental
• Results and Discussion
• Conclusions
• Acknowledgements
Introduction

• Nanomodification of semicrystalline polymers
  – unequalled thermal, mechanical and surface properties at low volume fractions that cannot be obtained using conventional fillers

• Blending POSS molecules into polymers can increase the thermal and mechanical properties as well as the surface properties

• The objective of this study is to examine the effect of blending various POSS molecules into a variety of appropriate semicrystalline polymers.
Anatomy of a POSS Nanostructure

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.
Background

• Bruce Fu and coworkers
  – Methyl₈T₈ into ethylene-propylene copolymers yielded 70% increase in the Young’s Modulus.
  – POSS molecules crystallized and these nanocrystals formed weak bonds with the polymer chains.
• Unpublished results indicate that this reinforcement is not seen in polyethylene homopolymer blends.
  – Methyl pendant group on the polymer chain is influencing the reinforcing efficiency of the POSS molecules
• The primary reinforcing mechanism in the nanocomposites, POSS/POSS interactions, POSS/polymer interactions or a combination of the two, is a subject for future research.
Materials

POSS (polyhedral oligomeric silsesquioxane)

Fluoroctyl$_8$T$_8$
R = -CH$_2$CH$_2$(CF$_2$)$_5$CF$_3$

Fluorodecyl$_8$T$_8$
R = -CH$_2$CH$_2$(CF$_2$)$_7$CF$_3$

Methyl$_8$T$_8$
R = Methyl
Blend Preparation

Tetrafluoroethylene  
Hexafluoropropylene  
Polymerization  
FEP

Vinylidene fluoride  
Polymerization  
PVdF

Isotactic polypropylene
Blend Preparation

• Five and ten weight percent of methyl$_8$T$_8$, Fluoroctyl$_8$T$_8$ and fluorodecyl$_8$T$_8$ melt blended into FEP and PVDF using a DSM Microcompounder
  – Mixed under nitrogen at screw speed of 100 RPM
  – FEP blends compounded at 280 °C for three minutes
  – PVDF blends mixed at 180°C for three minutes
  – Injection molded directly from microcompounder
• Five and ten weight percent methyl$_8$T$_8$ blended into PP using a DSM Minicompounder.
  – PP blends processed at 220 °C for ten minutes
Results and Discussion

- **Methyl_8T_8** blended into FEP
  - 25% increase in modulus
  - No difference between 5 and 10 wt% of filler
- **Fluorodecyl_8T_8** or **fluoroctyl_8T_8**
  - No difference in modulus from unfilled FEP
  - Inconsistent results
Results and Discussion

• Blends with FEP and either fluorodecyl\textsubscript{18}T\textsubscript{8} or fluorooctyl\textsubscript{18}T\textsubscript{8}
  — Lower yield points, between 7-8 MPa, when compared to unfilled FEP, 10.5-12.5 MPa range.

• Blends with FEP and methyl\textsubscript{18}T\textsubscript{8}
  — No significant change in yield point compared to unfilled FEP
Results and Discussion

- Data gathered for FEP filled with fluorodecyl₈T₈ or fluorooctyl₈T₈ inconsistent
  - Outer layers of tensile bar flaked away as soon as tension was applied
  - Interior of the tensile bars frequently elongated to over 150% strain before breaking
  - Indirect evidence of surface migration of the nanoparticles with a core/shell morphology
  - Each region has different physical properties
Results and Discussion

• PVDF samples
  – Elongated until failure
    • 55% PVDF
    • Average of 80% nanofilled PVDF
  – All fillers lowered the modulus
    • On average 20% decrease
    – This may imply that there is a uniform concentration of the POSS throughout the sample
  – No significant difference was found among the various types of fillers or different loadings
• Unfilled PVDF samples had a slightly higher yield point (40.0 MPa) than did any of the POSS filled samples (36.0-37.5 MPa range)
Results and Discussion

Modulus of PVDF Blends (GPa)

- None
- 5% FO POSS
- 10% FO POSS
- 5% FD POSS
- 10% FD POSS
- 5% Me POSS
- 10% Me POSS
Methyl₈T₈/PP blends showed a minor increase (5-10%) in tensile strength compared to neat blends.

Contrasting results due to the different compatibilities of the methyl₈T₈ with FEP and PP.

Methyl₈T₈ has a higher affinity for the PP and thus has a stronger reinforcing capability.
Heat Distortion Temperature (°C)

- Addition of POSS to PP yielded a substantial increase (15 – 25%) in heat distortion temperature
- Increase is due to interactions between the POSS crystallites and polymer crystallites
• The addition of modulus increasing nanoparticles actually increases the impact properties (15 – 40% increase)

• Increase may be derived from the nanodispersion of the POSS crystallites, which are not large enough to create stress concentrations, and the reinforcing ability of the POSS crystallites.
Results and Discussion

- Addition of fluorodecyl\textsubscript{8}T\textsubscript{8} and fluoroctyl\textsubscript{8}T\textsubscript{8} greatly increased the hydrophobicity of PVDF blends
  - 5 wt % of either material increased contact angle from ~70° for unfilled PVDF to between 105-110°
- Addition of 10 wt % of FluoroPOSS yielded angles as high as 116°
- Addition of methyl\textsubscript{8}T\textsubscript{8} to PVDF showed a more modest increase in hydrophobicity, but still an improvement over the unfilled material
Results and Discussion

• Fluorodecyl$_8$T$_8$ and fluorooctyl$_8$T$_8$ increased the oleophobicity of PVDF
  — Unfilled PVDF samples yielded contact angles around 25°
  — Addition of fluorodecyl$_8$T$_8$ yielded contact angles greater than 70°
  — Addition of fluorooctyl$_8$T$_8$ yielded contact angles greater than 50°

• Addition of methyl$_8$T$_8$ decreased the oleophobicity of PVDF
Results and Discussion

- FEP filled with methyl₈T₈ yielded contact angles as high as 126°

- Surface of injection molded FEP samples was uneven
  - Contact angle measurements were inconsistent
  - Top layer polished off with very fine sandpaper
  - After polishing, contact angles were in the same range as those found for unfilled FEP samples
  - Either flow patterns during injection molding or surface migration may be pushing the fillers toward the surface
Conclusions

• FluoroPOSS blended into PVDF lowered the modulus
  – No significant difference was observed among different fillers
  – Slightly lower yield points were observed for the filled versus unfilled PVDF blends

• FEP blends showed indirect evidence of surface migration, as evident in core/shell morphology of injection molded tensile bars
  – Nanoparticles may not be evenly distributed
  – Methyl₈T₈ significantly increased the modulus of FEP blends
Conclusions

• POSS added to polypropylene/methyl\(_8\)T\(_8\)
  – Increased heat distortion temperature by about 25%
  – Increased impact energy by over 35%
  – Tensile strength increased with the addition of POSS

• Water and organic contact angles
  – FluoroPOSS blended into fluoropolymers increased the water and organic contact angles
  – Addition of methyl\(_8\)T\(_8\) to PVDF decreased the oleophobicity, but increased the hydrophobicity
Summary and Conclusions

- FEP w/POSS
- Core/Shell Morphology
  - Surface Migration – Functionally graded materials
  - Non-uniform dispersion – Poor processing
- Mechanical Properties
  - FluoroPOSS – no difference in modulus, lower yield stress
  - Methyl₈T₈ – increase in modulus, neutral yield stresses
  - CH₃ group on methyl₈T₈ interacting with CF₃ group on FEP
Summary and Conclusions

- **PVDF w/POSS**
- **Mechanical Properties**
  - POSS decreased modulus
  - POSS decreased yield stress
  - No POSS/polymer chain interactions
- **Contact angles**
  - Water contact angles increased
  - Organic contact angles
    - Increased with incorporation of FluoroPOSS
    - Decreased with incorporation of methyl POSS
Summary and Conclusions

• PP w/POSS

• Mechanical Properties
  – POSS increased Heat Distortion Temperature
  – POSS increased tensile strength
  – POSS increased IZOD impact strength

• Possible POSS/Polymer chain interactions