2016 DOE Vehicle Technologies
Program Annual Merit Review

THE UNIVERSITY of TENNESSEE KNOXVILLE

Hybrid Ionic-Nano-Additives for Engine Lubrication to Improve Fuel Efficiency

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DOE HQ Program Manager: Kevin Stork
NETL Project Manager: Nicholas D'Amico

Project ID:
FT034

June 8, 2016

OAK RIDGE NATIONAL LABORATORY

UCMERCED UNIVERSITY OF CALIFORNIA

Overview

Timeline

- Project start date: Jan. 1, 2015
- Project end date: July 31, 2017
- Percent complete: 30%

Budget

- Total project funding: $1,135,274
  - DOE share: $898,013
  - Contractor share: $237,261
- Funding received in FY 2015: $466,373 (including cost share)
- Funding for FY 2016 $668,901 (including cost share)

Barriers

- For an internal combustion engine, 10-15% of the fuel energy is lost to parasitic friction.
- Using low viscosity oils improves fuel efficiency but poses challenges for wear protection.
- Nanoparticles have been demonstrated to be effective engine lubricant additives for reducing friction and wear, but the stability in base oil remains a great challenge.

Partners

- Oak Ridge National Laboratory
- University of California Merced

Relevance – Research Objectives

Overall Objectives:

- The project is aimed at developing a novel class of hybrid ionic-nano-additives that exhibit long-term stability in base oils for friction and wear reduction to improve engine energy efficiency via synergistic combination of **nanoparticles (NPs)** with oil-miscible **ionic liquids (ILs)/polymers**.
- Such hybrid NP lubricant additives allow the usage of lower viscosity engine oils to reduce >10% engine mechanical energy loss without impairing the engine durability.

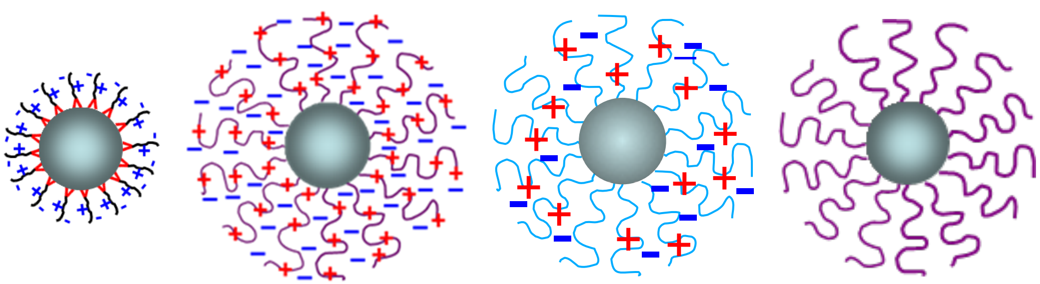
Objectives (01/2015 ~ 03/2016)

- Synthesizing oil-soluble IL- and polymer-modified NPs.
- Demonstrating the dispersibility and stability of hybrid NPs in lubricating base oils.
- Achieving significant reduction in both friction and wear compared with the lubricating base oil.
- Conducting modeling to investigate NP effects on friction.

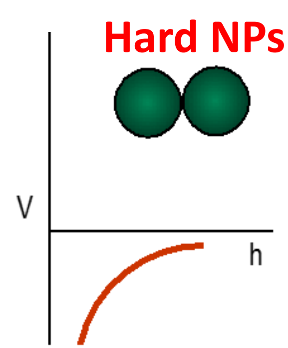
Milestone Title	Type	Milestone Description	Planned Completion Date	Milestone Status and Verification
Design of IL-functionalized NPs Completed	Technical	Design candidate IL molecular structures and NP geometries and identify approaches for stabilization of NPs in oils	March 31, 2015 (M3, Q1)	**Achieved and verified (Milestone report 04/29/2015)**
Synthesis of molecules and NPs Completed	Technical	Prepare candidate ILs, polymerization initiators, and NPs	June 30, 2015 (M6, Q2)	**Achieved and verified (Milestone report 07/29/2015)**
Characterization of IL-modified NPs' dispersion in lubricating oils Completed	Technical	Demonstrate stable dispersion of IL-functionalized NPs at 0.1 wt.% or higher in a base oil	April 30, 2016 (M9, Q3)	**Achieved (Milestone report will be submitted on time)**
Molecular-scale simulations of friction/wear reduction mechanisms Completed	Technical	Construct a molecular-scale simulation for the IL-modified NPs	July 31, 2016 (M12, Q4)	**On track**
Tribological bench evaluation Completed	Go/No-Go Point	Demonstrate >50% wear reduction for hybrid IL-NP additives when blended into a base oil in tribological bench tests	July 31, 2016 (M12, Q4)	**On track**

Approach

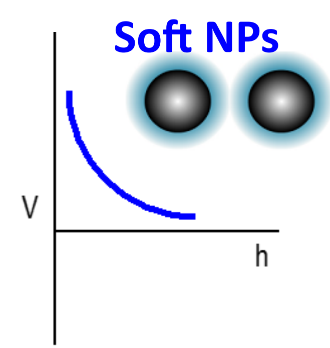
- **Our approach is to synthesize hybrid nanoparticles (NPs) via synergistic combination of NPs with ionic liquid (ILs)/polymers.**
- **ILs and NPs have complementary wear protection & friction reduction.**
- **Surface-tethered (polymeric) ILs help disperse and stabilize NPs in the lubricating oils.** The oil-miscible ILs are surfactants in nature.
- **Polymer-grafted NPs (hairy NPs) can be very stable in oils**. The brushes enable stability of NPs via steric interaction &/or electrostatic repulsion.
- **Polymer brushes likely introduce a new lubrication mechanism** due to osmotic pressure by counterions and the elasticity of polymer chains.



IL-NPs   Polymer Brush-Grafted NPs (Hairy NPs)



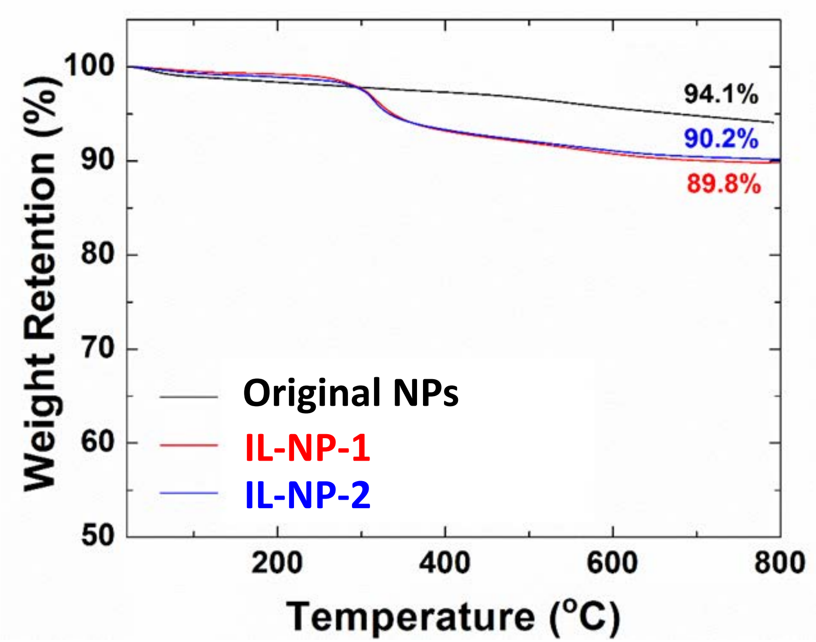
VDW forces
Depletion forces



Steric-stabilized
Charge-stabilized

Technical Accomplishment I: IL-NPs

Thermogravimetric Analysis (TGA)

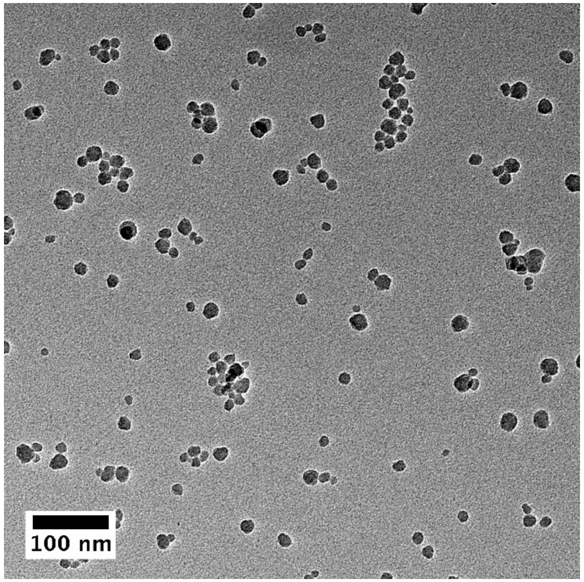


Original NPs: 94.1% weight retention at 800 °C.

IL-NP-1: 89.8% weight retention at 800 °C.

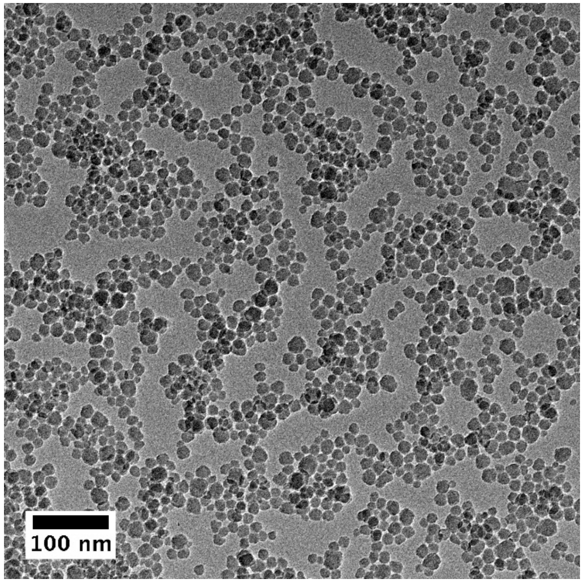
IL-NP-2: 90.2% weight retention at 800 °C

TEM



IL-NP-1

17.1 nm ± 3.0 nm
225 molecules/NP



IL-NP-2

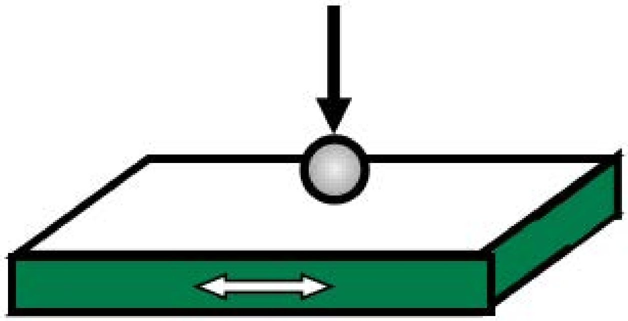
17.4 nm ± 3.6 nm
204 molecules/NP

Dispersion of IL-NPs in PAO 4 Base Oil

Freshly synthesized IL-NPs can be well-dispersed in PAO 4 base oil and form clear, stable dispersions.

Photo of two IL-NPs in solid forms (white) and dissolved in a PAO 4 cSt base oil at a concentration of 1.0 wt%

Tribological Testing



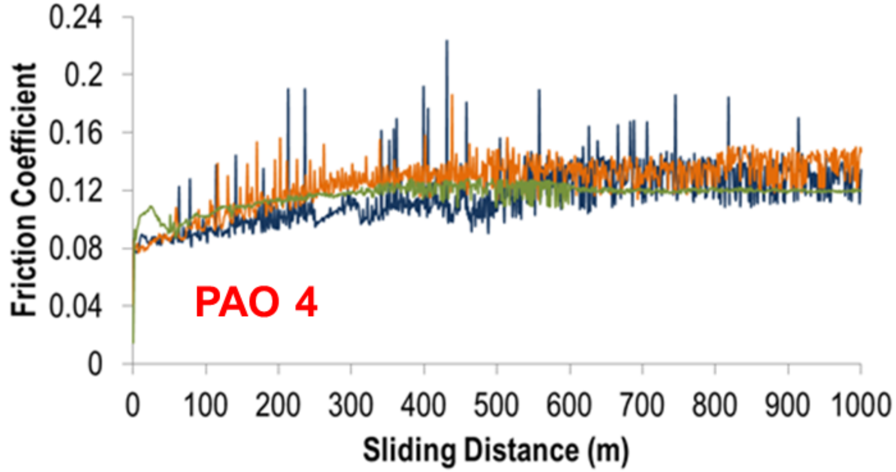
High Contact Stress Ball-on-Flat Reciprocating Tribological Testing

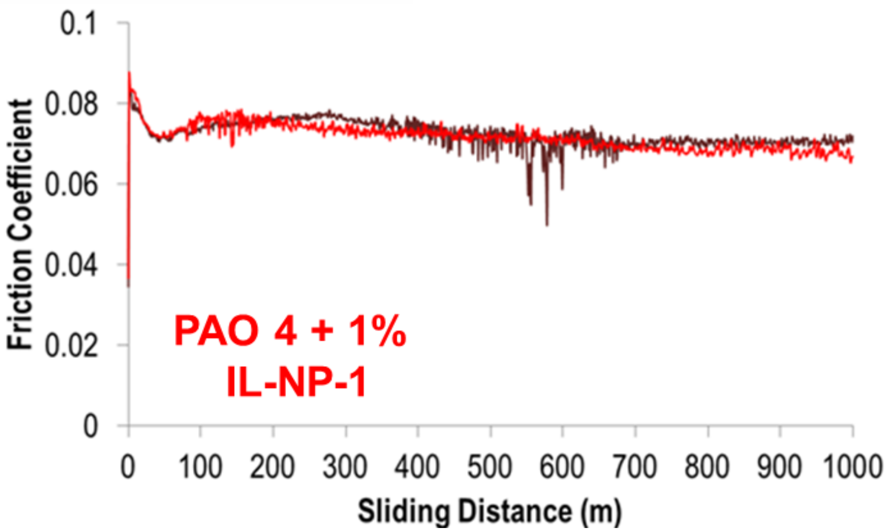
- Flat: CL35 cast iron
- Ball AISI 52100 Steel Balls (9.525 mm diameter)
- Point Contact Load: 100 N
- Temperature: r. t.
- Oscillation Frequency: 10 Hz
- Sliding Distance: 1000 m
- Submerged in Lubricant

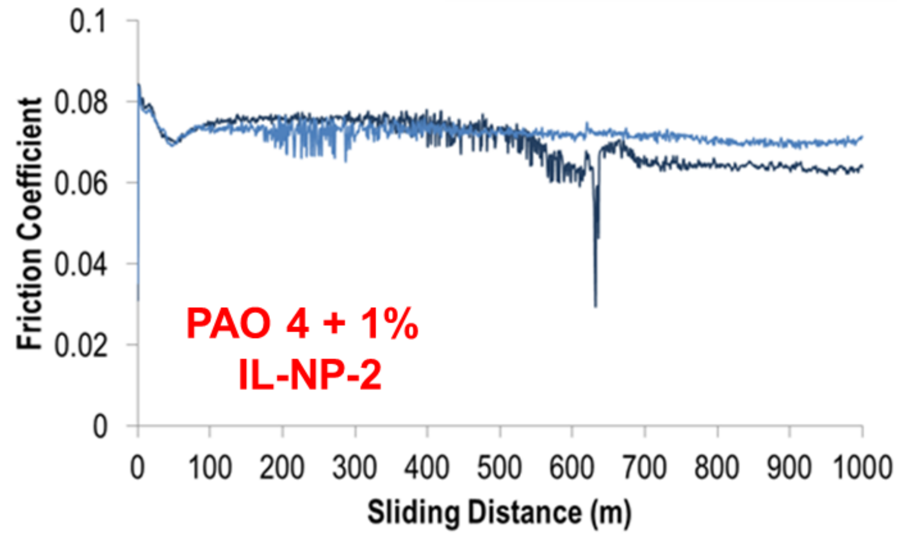
Lubricant: PAO 4 + 1 wt% IL-NPs with PAO 4 as Control

Tribological Properties of IL-NPs at R. T.

Ball-on-Flat at Room Temperature (R. T.)







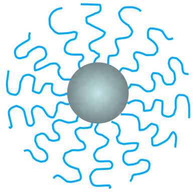
- **1% IL-NPs leads to ~ 50% friction reduction.**
- **However, scuffing is observed at 100 °C; further study is underway.**

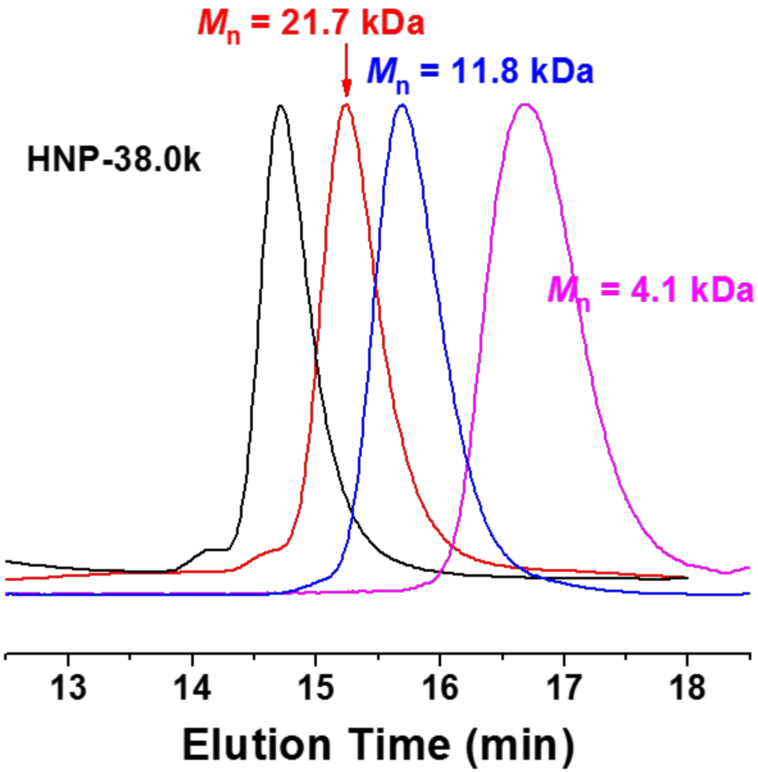
Technical Accomplishment II: Hairy NPs-1

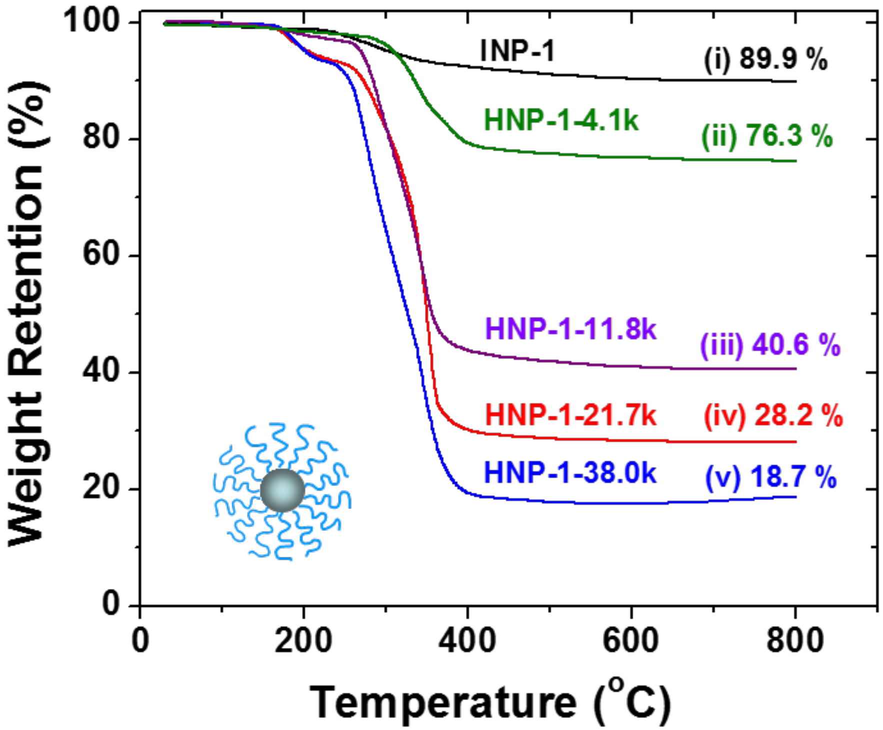
Four hairy NP samples with different molecular weights were made:

HNP-1-38.0k, HNP-1-21.7k

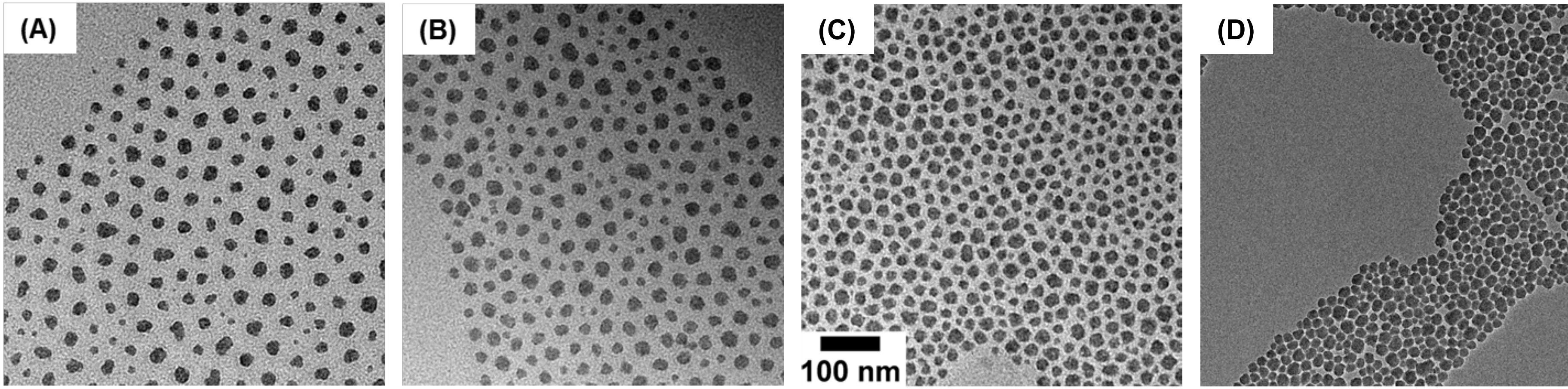
HNP-1-11.8k, HNP-1-4.1k





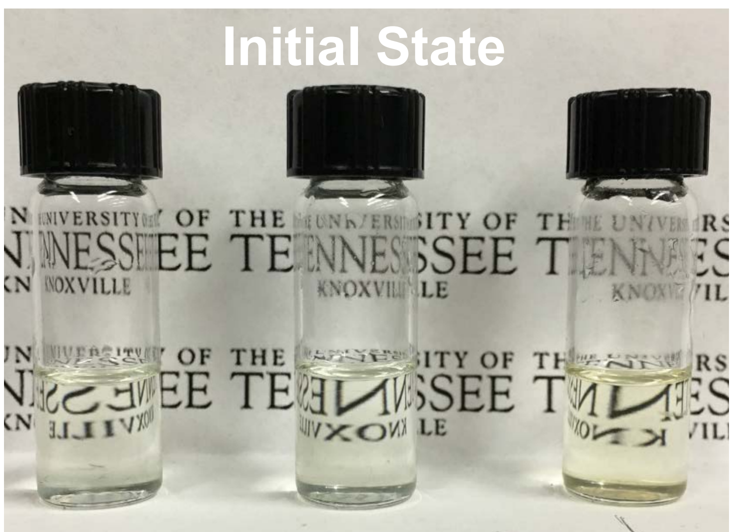


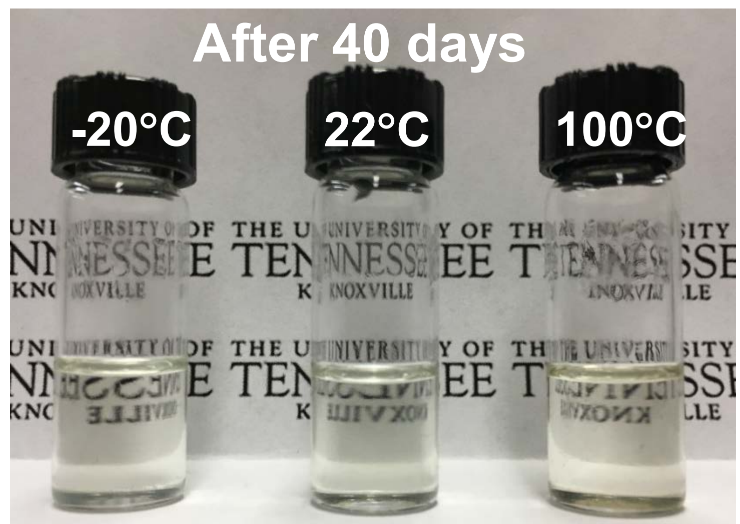
TEM of Hairy NPs and Stability of Hairy NPs in PAO



HNP-1-38.0k HNP-1-21.7k HNP-1-11.8k HNP-1-4.1k

Stability Study: 1 wt% HNP-1-4.1k in PAO 4





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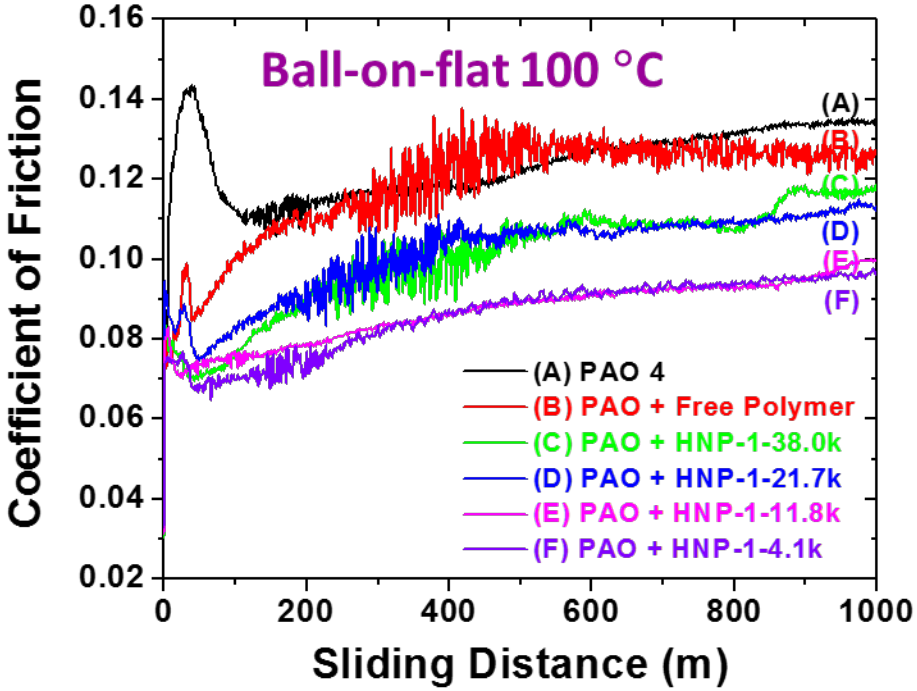
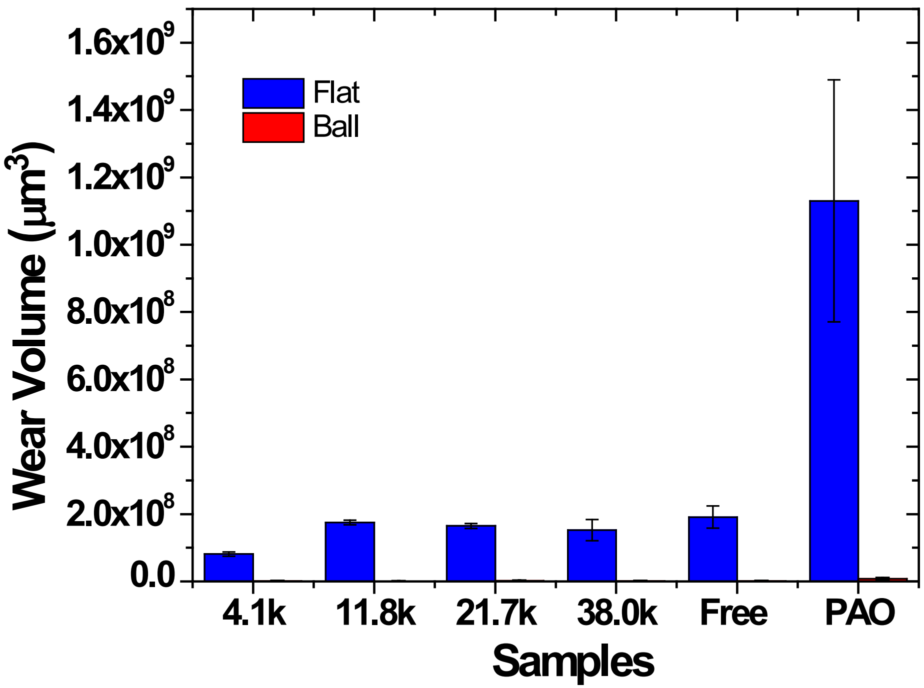
Tribological Properties of Hairy NPs-1 in PAO 4

Friction



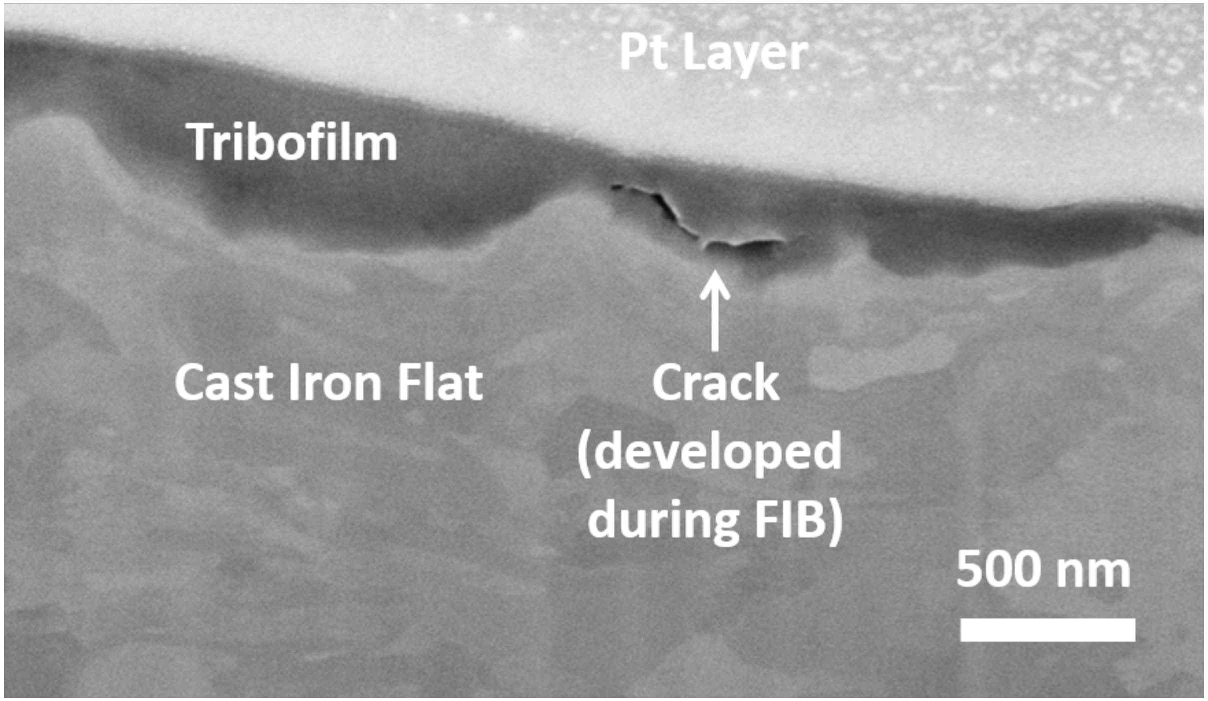
Wear



PAO 4 + 1 wt% Hairy NPs-1

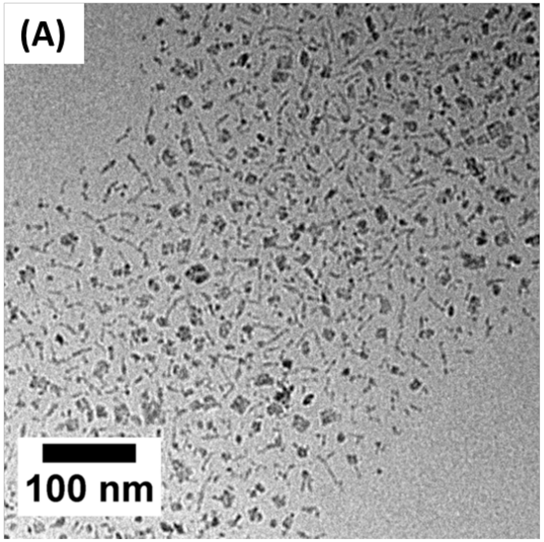
- **Adding 1 wt% hairy NPs results in about 16-30% friction reduction.**
- **Friction coefficient decreases with decreasing molecular weight.**
- **Adding 1 wt% hairy NPs leads to significant reduction in wear.**

SEM Characterization of Tribofilm after Tribological Testing of Hairy NPs-1

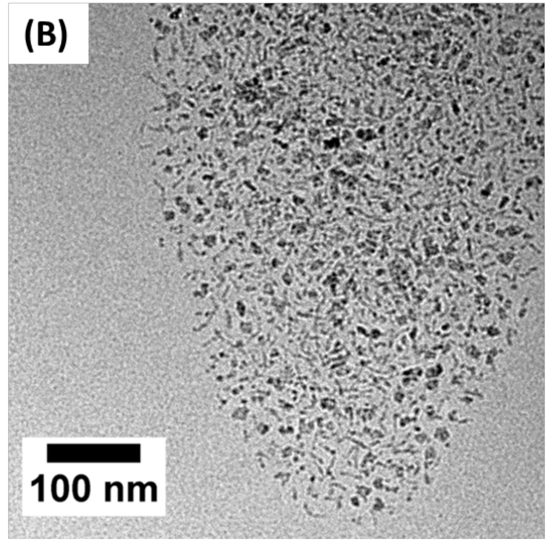


- The wear track, formed on the cast iron flat after tribological testing of 1 wt% HNP-1-4.1k-additized PAO 4, was characterized by SEM.
- The cross-sectional SEM sample of the wear track was prepared by focused ion beam (FIB) technique. A platinum layer was deposited on wear track.
- The tribofilm can be clearly seen.

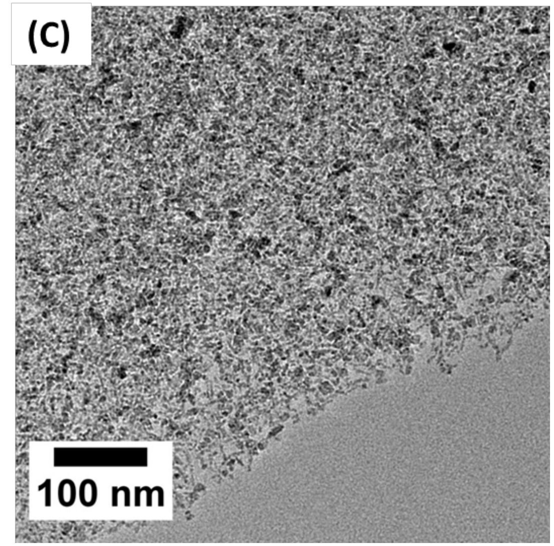
Technical Accomplishment II: Hairy NPs-2



HNP-2-21.5k

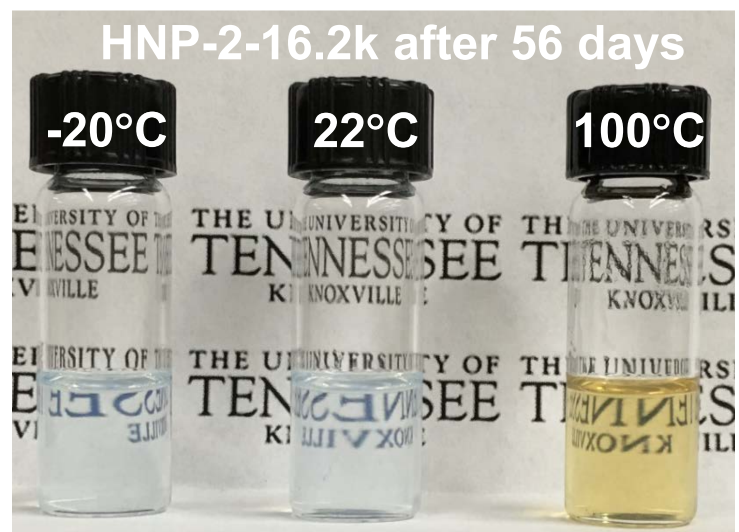


HNP-2-16.2k



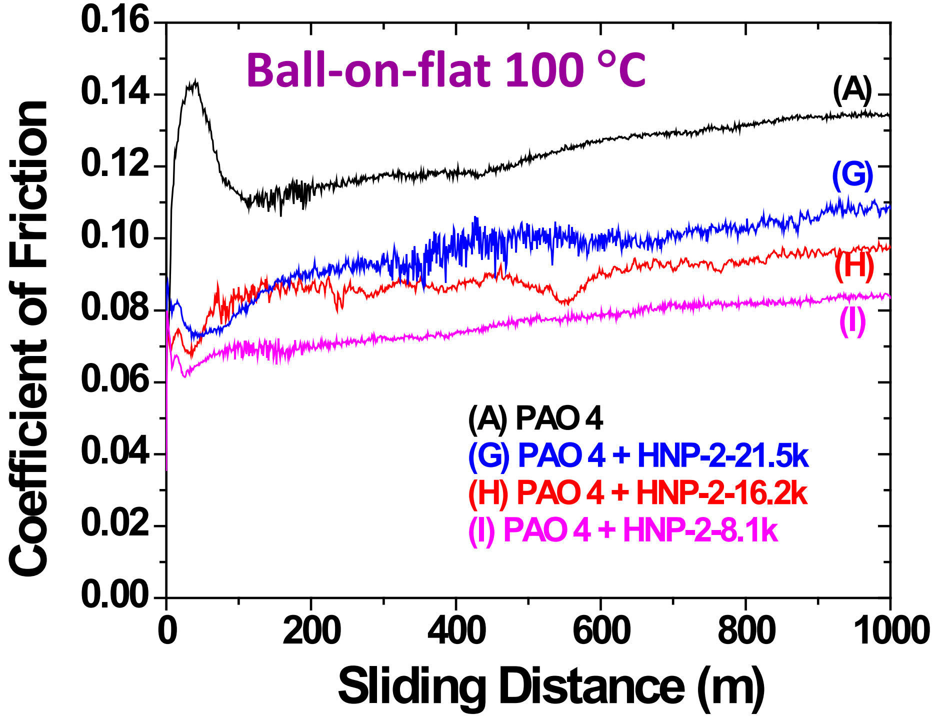
HNP-2-8.1k

Stability of 1 wt% HNP-2-16.2k in PAO 4

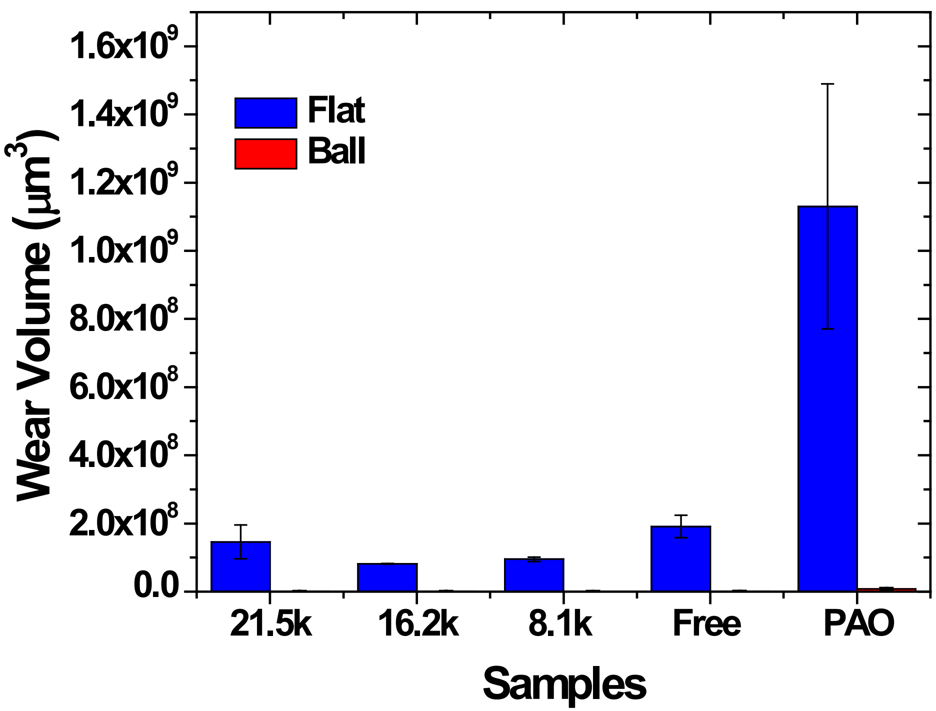


Tribological Properties of Hairy NPs-2

Friction



Wear



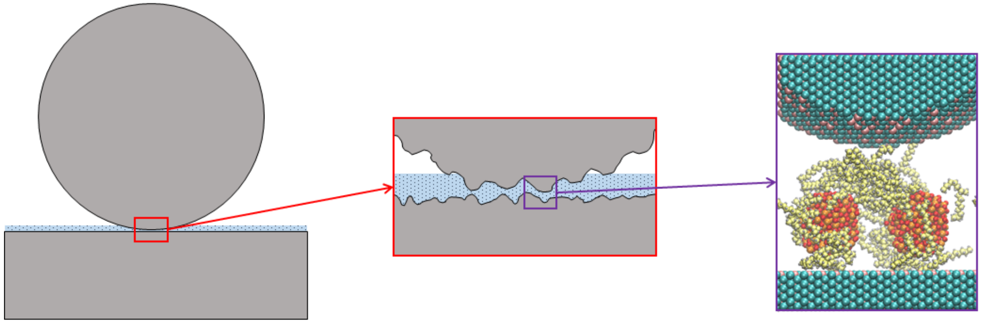
PAO 4 + 1 wt% Hairy NPs-2

- **Adding 1 wt% hairy NPs-2 into PAO 4 base oil results in friction reduction by about 20 – 40%.**
- **Adding 1 wt% hairy NPs-2 leads to significant wear reduction.**

Technical Accomplishment III: Modeling

Develop Boundary Friction Model for NP

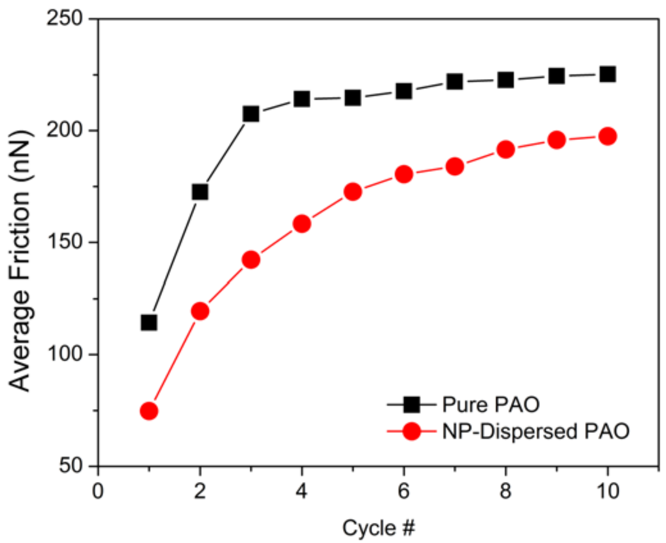
- **There are few precedents for modeling boundary lubricated sliding at the atomic scale in a physically-representative way.**
- **We developed a modeling approach based on the concept of capturing the sliding processes at a single asperity.**



- **Initial modeling carried out with simple NPs**
  - Model system consists of the NPs and a PAO fluid confined between two solid walls (one flat and one rounded).
  - Previous research showed that the effectiveness of NPs is dependent on the roughness of the substrate, so the lower counterface is grooved.
  - We apply a load and shear to the upper counterface and calculate the frictional resistance to sliding.

Investigate NP Effects on Friction

- In this example result, we see that **the friction increases with number of cycles due to wear of both the upper and lower counterface** and that **the friction is lower with the NPs.**



- We analyzed this behavior qualitatively and observed that **the NPs move into the groove and round its edges**, thereby leading to lower friction; however, in other cases, the NPs are not found to be beneficial.

- We are now trying to understand which conditions lead to the NPs reducing friction and wear by varying the size and number of the NPs, and changing the depth of the surface groove.

Responses to Previous Year Reviewers' Comments

Not Applicable

– This project is new and was not reviewed last year.

Collaboration & Coordination with Other Institutions

Lead: UTK
PI: Bin Zhao, co-PI: Sheng Dai
Design and synthesis of oil-miscible hybrid IL-/polymer-Nanoparticle Additives

Postdoc: Dr. Kewei Wang
Graduate Student: Roger Wright

Partner: ORNL
PI: Jun Qu, co-PIs: Huimin Luo and Beth Armstrong
Synthesis of ILs, stability study in oils; tribological bench evaluation

Postdoc: Dr. Yu Xie (left)
Postdoc: Dr. Chanaka Kumara (starts on 04/15/2016)

Partner: UCM
PI: Ashlie Martini
Molecular scale simulation of friction/wear reduction mechanisms

Graduate Student: Larry Gao

Vendor by Contract (Responsible: Jun Qu and Bin Zhao)
Engine dynamometer testing at vendor

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Remaining Challenges and Barriers

- **The first two batches of IL-NPs performed very well at r.t., but not at 100 °C. In addition, the synthesis of IL-NPs needs to be further improved upon.**

- **There is a challenge in incorporating functional groups into hairy NPs by current method. Incorporation of functional groups may cause a decrease in dispersibility/stability of hairy NPs in PAO 4.**

- **The current approach for the synthesis of hairy NPs works well, but the process is complicated – scale-up is a challenge.**

- **Lubrication mechanisms of IL-NPs and hairy NPs are unclear.**

- **Extend the simulation methods developed for modeling bare NPs to IL-NPs and hairy NPs.**

Proposed Future Work

- **Develop new synthetic routes for the synthesis of oil-soluble IL-NPs with new molecular structures.**
- **Develop new polymerization methods that allow facile incorporation of functional groups into hairy NPs to further reduce friction and wear, and study the effect of incorporating functional groups on dispersibility and stability of hairy NPs in PAO 4.**
- **Develop alternative methods for synthesizing hairy NPs, which should allow facile scale-up synthesis of hybrid NPs.**
- **Investigate the effect of NP's chemical composition on tribological properties of hybrid NPs.**
- **Investigate lubrication mechanisms of IL-NPs and hairy NPs by both experiments and modeling.**

Summary

Relevance/Objectives: To develop hybrid (polymeric) ionic-nano-additives for engine lubrication to improve energy efficiency via synergistic combination of NPs with ILs/polymers, allowing the use of lower viscosity engine oils to reduce >10% engine mechanical energy loss.

Approach: – Synergistic combination of NPs with ILs and polymers

Accomplishments:

– Synthesized IL-NPs that showed promising tribological properties at r.t.
– Synthesized hairy NPs that exhibited long-term stability at both low and high temperatures and significant reduction in friction and wear.
– Developed boundary friction model for NP and studied NP effect on friction.

Collaboration:

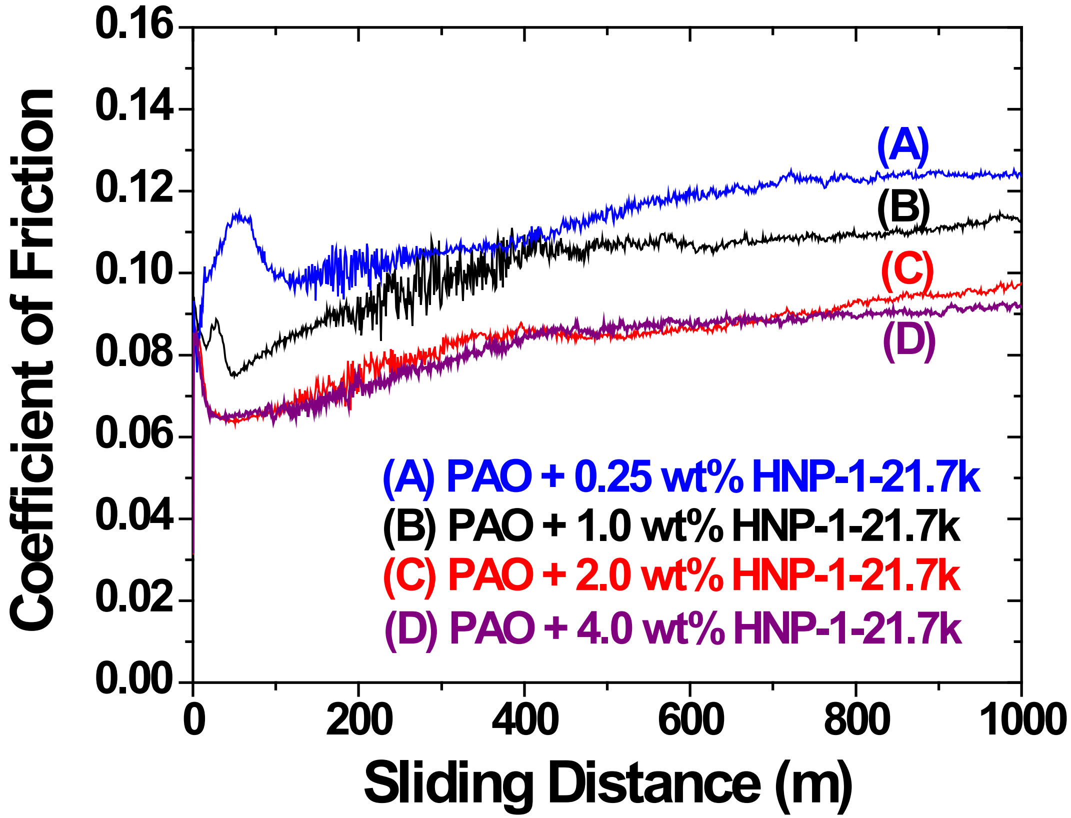
– University of Tennessee Knoxville (Bin Zhao and Sheng Dai)
– Oak Ridge National Lab (Jun Qu, Huimin Luo, and Beth Armstrong)
– University of California Merced (Ashlie Martini)

Future Work:

– New synthetic routes for IL-NPs and (functional) hairy NPs
– Investigate lubrication mechanisms by both experiments and modeling

Technical Back-Up Slides

Concentration Effect of Hairy NPs-1 in PAO 4 on Tribological Properties



Friction curves for PAO 4 dispersion containing (A) 0.25 wt%, (B) 1.0 wt%, (C) 2.0 wt%, and (D) 4.0 wt% of HNP-1-21.7k performed at 100 °C under a point contact load of 100 N for a sliding distance of 1000 m.