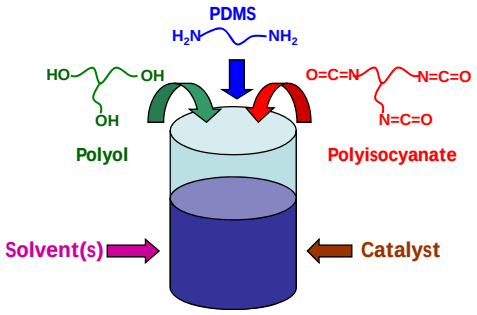
Toward Tough Fouling-Release Coatings: Self-Stratified Siloxane-Polyurethane Coatings

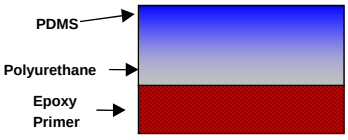
Dean C. Webster, Abdullah Ekin, Robert Pieper, Stacy Sommer, Rajan Bodhke, Shane Stafslien, Maureen Callow, Stephanie Thompson

Department of Coatings and Polymeric Materials
Center for Nanoscale Science and Engineering
North Dakota State University

Revolutionary Research . . . Relevant Results

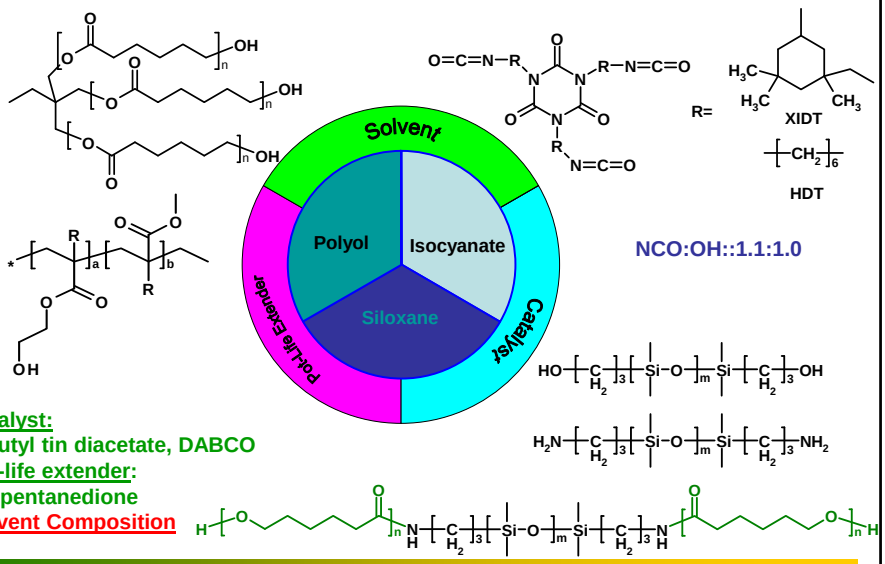
Siloxane-Polyurethane Coatings





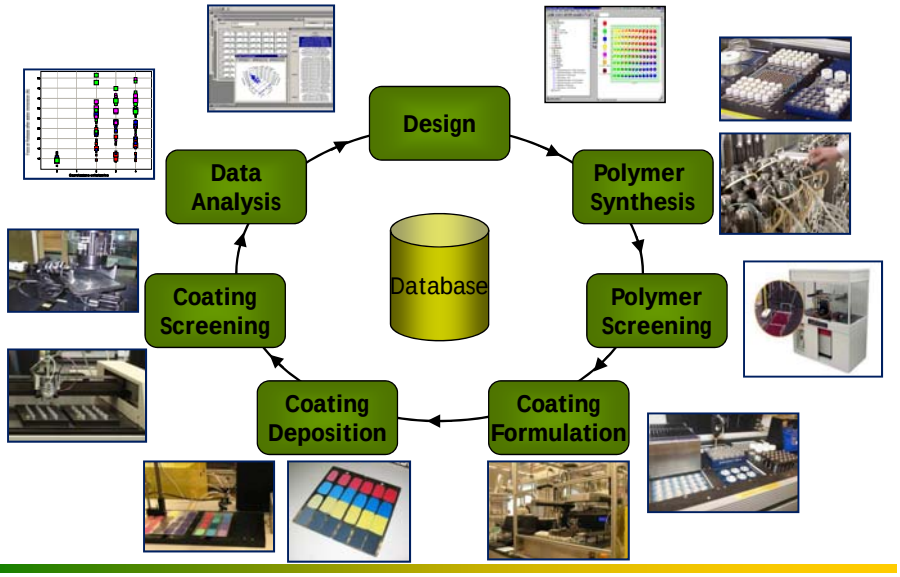
- PDMS → Low Surface Energy
- Polyurethane → Tough
- Polyurethane → Good Adhesion
- Crosslinking → Stable Under Immersion

Siloxane-Urethane Coatings



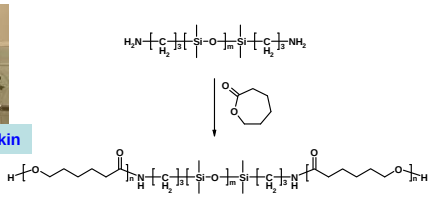
Catalyst:
Dibutyl tin diacetate, DABCO
Pot-life extender:
2,4-pentanedione
Solvent Composition

High Throughput Screening Workflow

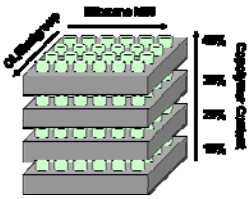


Siloxane - Caprolactone Tri-Block Copolymers

Abdullah Ekin

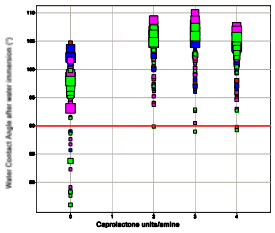


J. Polym. Sci. Part A: Polym. Chem., **2006**, *44*, 4880-4894

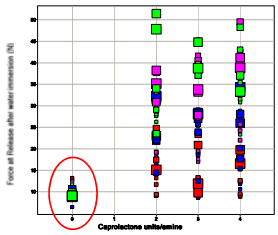


192 Coatings

Water CA After Immersion



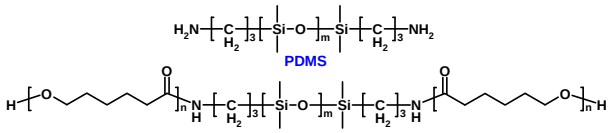
Pseudo-barnacle Adh. After Immersion



J. Combi. Chem., **2007**, *9*, 178-188.

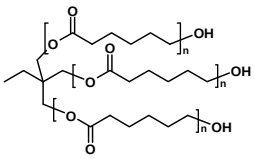
PDMS-Polyurethane Coatings

Downselected coatings from screening experiments

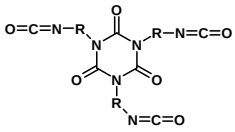


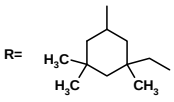
PDMS

PCL-PDMS-PCL, n=3



PCL Polyol





IDT Crosslinker

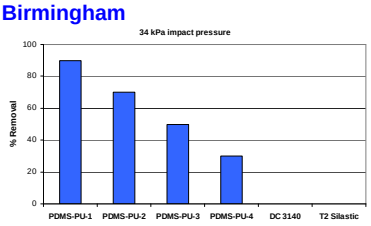
These are high modulus coatings with good adhesion.

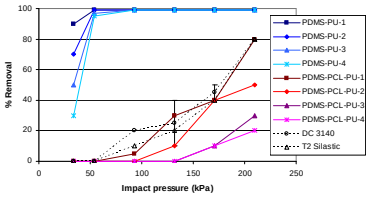
Ulva Assay PDMS-PU Coatings

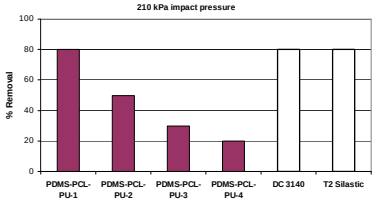
Callow Group - University of Birmingham

DC 3140	PDMS-PU-1 5k	PDMS-PU-2 10k
T2	PDMS-PU-3 20k	PDMS-PU-4 30k
DC 3140	PDMS-PCL-PU-1 5k	PDMS-PCL-PU-2 10k
T2	PDMS-PCL-PU-3 20k	PDMS-PCL-PU-4 30k

54 kPa







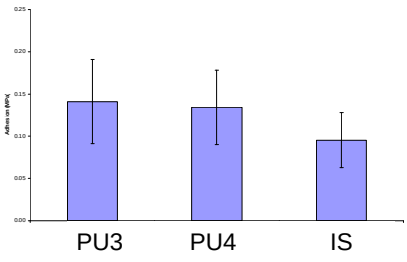
Confirms Pseudobarnacle adhesion results

Casse, et al., *Biofouling*, 2007, 23, 267-276

Field Testing - FIT

- Eight Experimental PSX-PU Coatings
- Intersleek Control
- AF control
- Four replicates of each coating
- Testing at:
  Florida Institute of Technology
  U. Hawaii
  Cal. Poly. - SLO

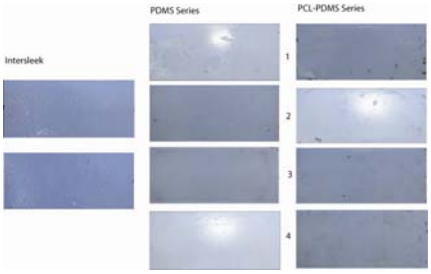
FIT Results:
- First 90 days – no barnacle fouling
- Panels cleaned, re-immersed
- Additional 12 weeks – barnacles
-Two PSX-PU showed fouling-release properties
-Coatings showing signs of degradation after cleaning; testing terminated



Cleaned Panels – Cal Poly

Panels were manually cleaned at 7 months

Relative ease of removal for each replicate cleaned back.		
Coating	**Replicate 2**	**Replicate 3**
Copper	Easy	Easy
Intersleek	Easy	Easy
PU-1	Moderate	Difficult
PU-2	Easy	Moderate
PU-3	Easy	Easy
PU-4	Easy	Moderate
PCL-PU-1	Moderate	Difficult
PCL-PU-2	Moderate	Difficult
PCL-PU-3	Difficult	Moderate
PCL-PU-4	Difficult	Difficult



Fouling can be removed with manual cleaning

Hawaii - Fouling Removal Force

Tubeworm removal force

6 months

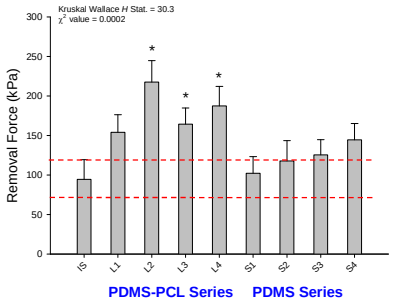


Figure 10. Mean force required to remove tubeworms (*Hydroides elegans*) from panels. Data were log transformed to meet the assumptions of normality and homogeneity of variance for parametric analysis. Asterisks above bars indicates coatings that performed significantly worse than the IS control coating (multiple contrasts with Bonferroni's correction, α=0.05). Bars = Mean of untransformed data. Error Bars = 1 Standard Error.

14 months

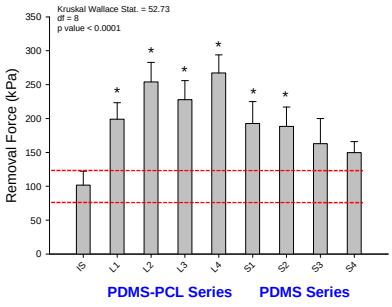


Figure 3. Mean force required to remove tubeworms (*Hydroides elegans*) from panels. Data were log transformed to meet the assumptions of normality and homogeneity of variance for parametric analysis. Asterisks above bars indicates coatings that performed significantly worse than the IS control coating (multiple contrasts with Bonferroni's correction, α=0.05). Bars = Mean of untransformed data. Error Bars = 1 Standard Error.

Hawaii - Fouling Removal Force

Barnacle removal force

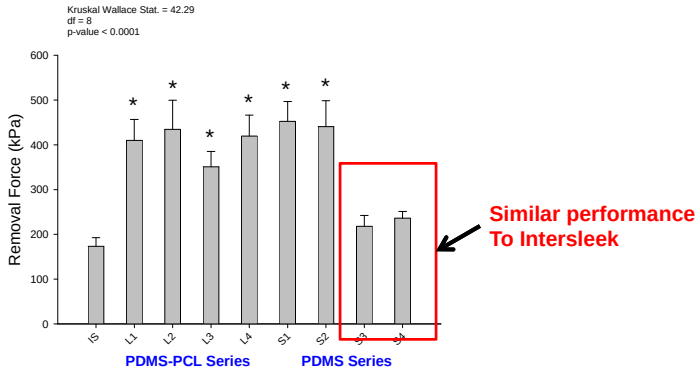
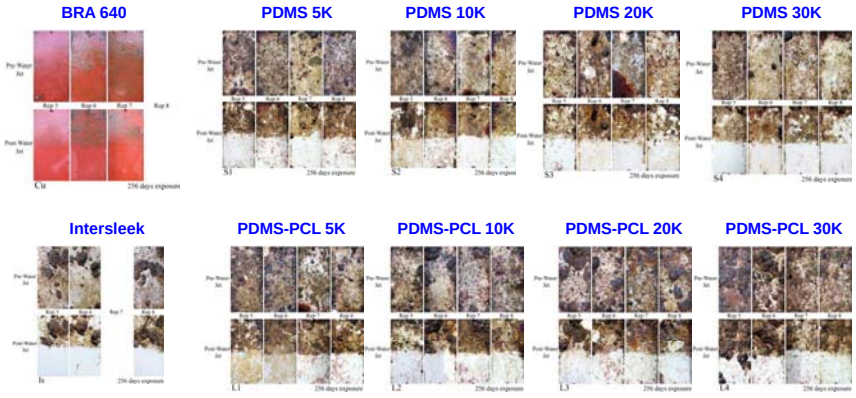


Figure 4. Mean force required to remove barnacles (*Balanus amphitrite*) from coatings. A non-parametric Kruskal-Wallace analysis of variance was performed on log-transformed data. Asterisks above bars indicates coatings that performed significantly worse than the IS control coating (multiple contrasts with Bonferroni's correction, a=0.05). Bars = Mean of untransformed data. Error Bars = 1 Standard Error.

Hawaii - Waterjetting

½ of each panel was cleaned with a waterjet at 256 days



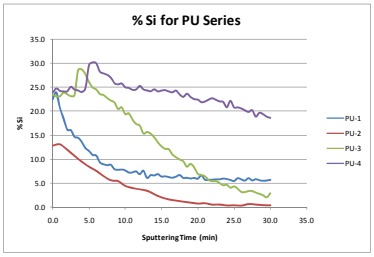
Fouling can be cleaned with waterjet.
PDMS series cleans better than PDMS-PCL series

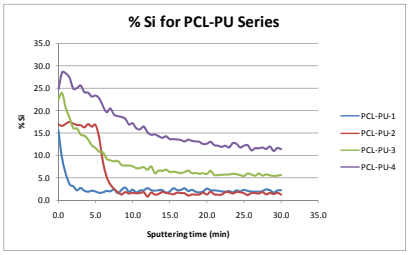
Further Testing of These Coatings

- Field tests are continuing at Hawaii and CalPoly
  - No signs of degradation yet…
- Key question: What is the difference in the surfaces of coatings from APTPDMS and PCL-PDMS block copolymers?
  - XPS analysis with ion milling – Carderock Lab (Azzam Mansour)

XPS Analysis of PDMS-PU Coatings

Ion Sputtering XPS Experiments





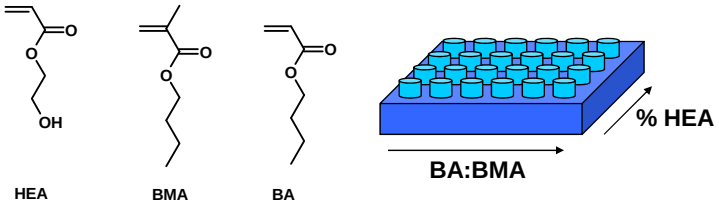
Stratified nature of coatings demonstrated
Currently calibrating sputtering rate

Data courtesy Azzam Mansour, NSWC Carderock Lab

Acrylic Polyols

Robert Pieper

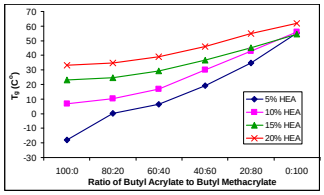
- Better hydrolytic stability than PCL polyols
- Control over coating properties
  - Resin T_g, MW, OH Functionality
  - → Coating T_g, Crosslink Density, Modulus
- Synthesized either in batch or semi-continuous processes



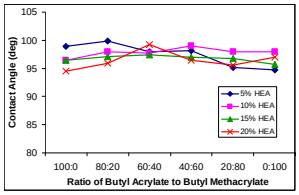
Siloxane-Acrylic-Polyurethanes

10% Aminopropyl PDMS
M_n = 10,000 g/mol

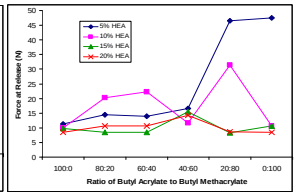
pDMTA T_g of PDMS-Urethanes



Water CA of PDMS-Urethanes

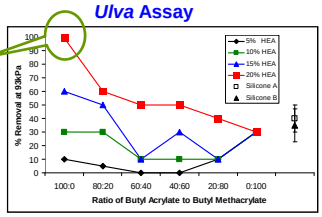


PB Adh. of PDMS-Urethanes

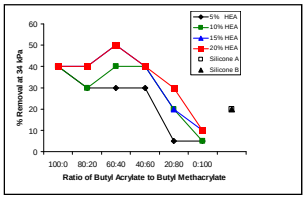


Best Performance

***Ulva* Assay**



***Navicula* Assay**

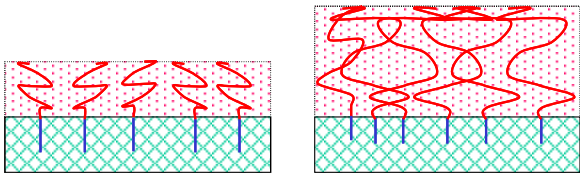


J. Coat. Tech & Res., 2007, 4(4), 453-461.

Monofunctional PDMS (mPDMS)

Stacy Sommer

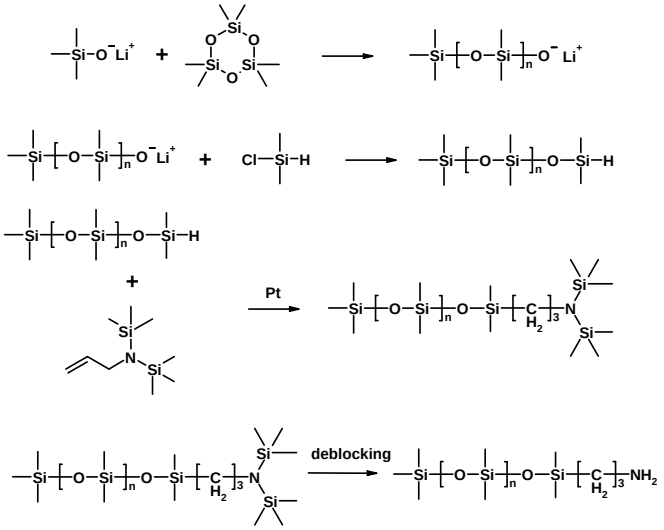
Objective: To synthesize PDMS with functional group on one chain end and incorporate into polyurethane coatings



Possible advantages:

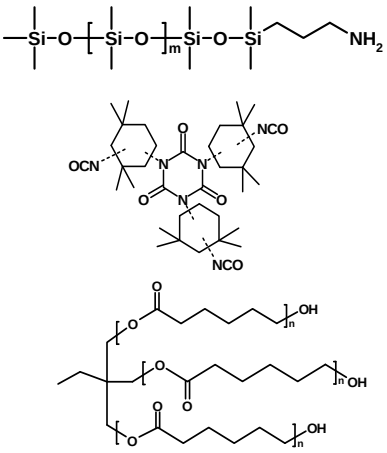
- **Prereact PDMS with polyisocyanate**
  - **2K Coating System**
- **PDMS has more surface mobility**
- **Use less PDMS: surface only**

Aminopropyl terminated PDMS



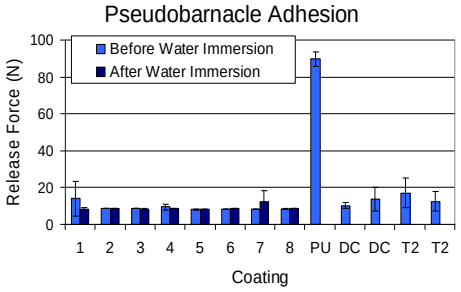
Siloxane-Polyurethane Coating Formulations

Coating ID	% PDMS	Theoretical MW PDMS (g/mol)
1	5.0	1000
2	10.0	1000
3	5.0	5000
4	10.0	5000
5	5.0	10,000
6	10.0	10,000
7	5.0	15,000
8	10.0	15,000
PU	0.0	NA



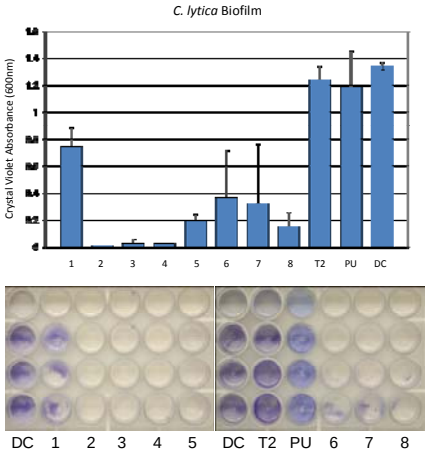
Surface Energy & Pseudobarnacle Adhesion Measurements

	Before Water Immersion	After Water Immersion
Coating	SE (mN/m)	SE (mN/m)
1	27.4	27.3
2	23.4	28.5
3	24.2	26.1
4	23.4	21.9
5	24.5	21.8
6	22.4	22.3
7	23.2	21.6
8	22.1	23.1
PU	37.6	36.9
DC	11.4	13.6
DC	11.3	16.5
T2	14.0	13.8
T2	12.0	16.0



- PDMS is at the surface
- Surface energy is stable upon water immersion
- Pseudobarnacle adhesion is very low for these coatings

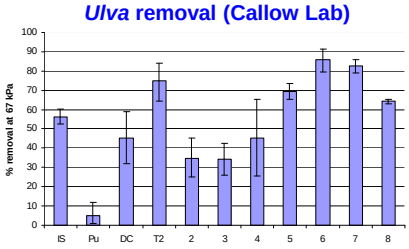
C. lytica Biofilm Retention



- Decreased biofilm retention was observed for the experimental coatings
- Biofilm could not form on most of the experimental coatings

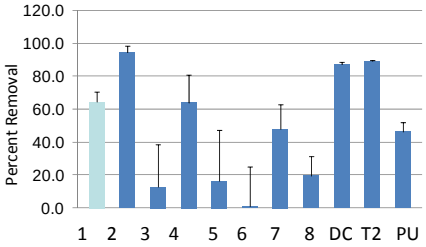
Algae Bioassays

***Ulva* removal (Callow Lab)**



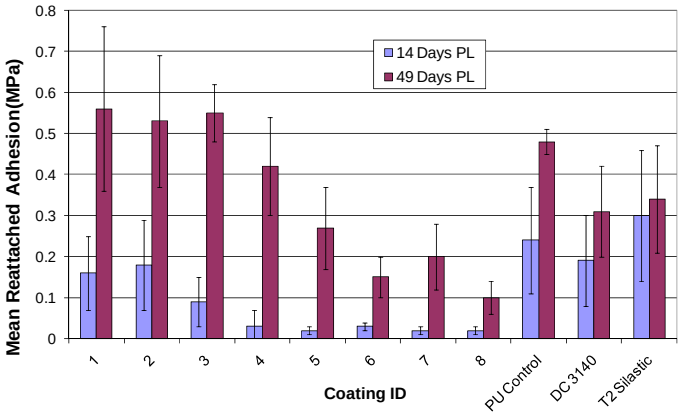
Good release of *Ulva* at higher MW

***N. Incerta* removal (NDSU)**



Navicula release is variable

Barnacle Reattachment Bioassay



- Consistently low release force for Coating #s 3,4,5,6,7,& 8
- Coatings with lowest release have surface energies in 22-24 mN/m range
- Barnacle adhesion higher after longer preleaching time

Summary

- PDMS-PU coating system continues to show promise
  - High modulus
  - Good adhesion
  - Easy-to-clean surfaces
- Future
  - Second Field Trial in water in June
  - Continued exploration of compositional space
  - Move toward a commercial coating system

Acknowledgements

- GRAs
  - Partha Majumdar
  - Abdullah Ekin
  - Robert Pieper
  - Chavanin Siripirom
  - Stacy Sommer
  - Rajan Bodkhe
- PDA: Mohammed Nasrullah
- CMRL
  - Bret Chisholm
  - David Christianson
  - James Bahr
  - Christy Gallagher-Lien
  - Plus many others…
- Collaborators
  - University of Birmingham
    - James Callow, Maureen Callow, Franck Cassé, Stephanie Thompson
  - Florida Institute of Technology
    - Geoff Swain, Emily Raslton
  - University of Hawaii – Mike Hadfield, Brian Nedved
  - CalPoly SLO – Dean Wendt, Lenora Brewer
  - University of Singapore – Serena Teo
- Office of Naval Research

ONR Revolutionary Research . . . Relevant Results

Questions?

NDSU Research and Technology Park

Combinatorial Materials Research Laboratory