# Sustainable Reformulation and Advanced Materials Research using HSP

Prof. Daniel F. Schmidt
Department of Plastics Engineering
and TURI-Affiliated Faculty Member
University of Massachusetts Lowell

# A Brief Introduction

- UML Plastics Engineering
  - Founded in 1954, ~40 km northwest of Boston
  - Only accredited Plastics Engineering program in the United States
  - 2,000 $m^2$ of state-of-the-art laboratory space
  - 3,000+ graduates in leadership positions in the plastics industry worldwide

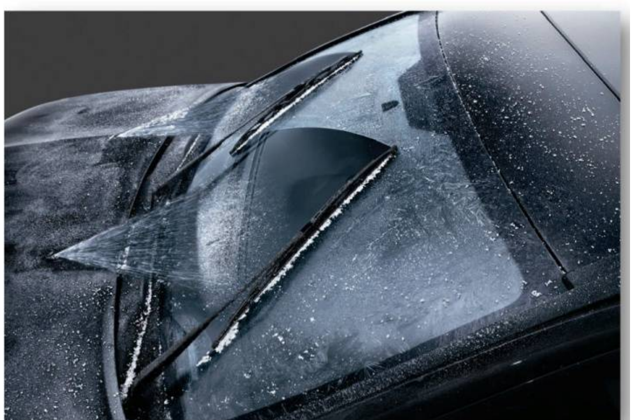
# A Brief Introduction

- Massachusetts Toxics Use Reduction Institute
  - State agency established with the Toxics Use Reduction Act of 1989
  - Works with businesses, community organizations and government agencies to reduce toxic chemical use, protect public health and the environment, and increase competitiveness

# Research Summary


Research Professor Gregory Morose
UML Public Health Department


*Expertise: safer solvents, alternatives assessment, life cycle assessment, Six Sigma, sustainable materials*



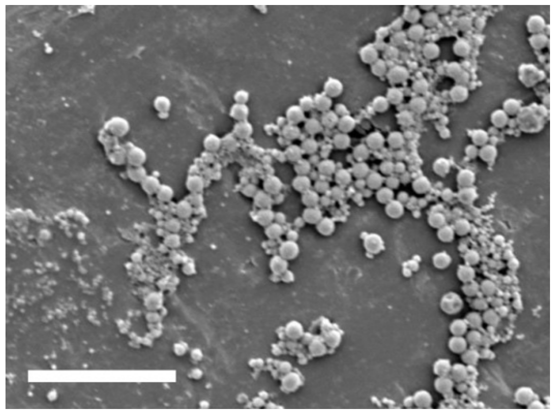
- ***Safer Solvents***
  - *Paint stripping formulations without methylene chloride or NMP*
  - *Contact adhesive formulations without toluene and hexane*
  - *Windshield wiper fluid formulations without methanol*
  - *Textile coating applications without dimethyl formamide*
- ***Alternatives Assessment***
  - *Lead-free solders, components, and circuit boards for electronics products*
  - *Phthalate-free wire and cables*
  - *Hexavalent chromium free anti-corrosion coatings for the aerospace and defense industry*

# Assistant Professor Christopher Hansen
## Department of Mechanical Engineering

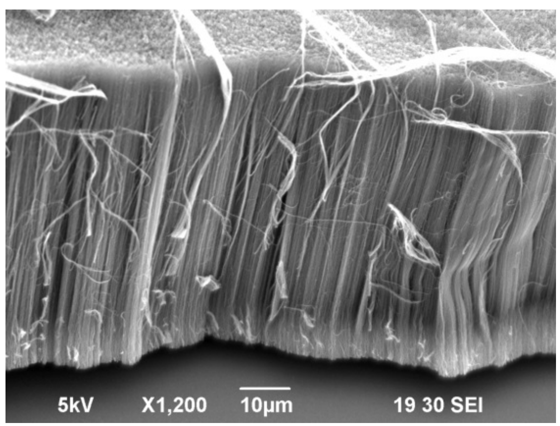
***Composites processing, multi-functional composites, self-healing materials, additive manufacturing, 3-D printing***
***Research Group: NASA, Army, SBIR/STTR, and Industrial Funding;***
***6 Ph.D. Students and 6 undergraduate students***

**3D print with composites**

**Self-healing nanocapsules**



**Automated manufacture of multi-functional composites**




**Vertically aligned carbon nanotubes for reinforcement, sensing**

- ***Composites processing***
  - *Resin transfer molding, VARTM*
  - *Automated fiber placement*
- ***Mechanical testing of composites***
  - *Tensile, compression, flexural, shear*
- ***Additive manufacturing and composites***
  - *Investigate 3D printing of composite molds or primary reinforced structures*
  - *Functional performance development in fiber-reinforced composites*
  - *Characterization of 3D composite materials*
- ***Self-healing materials***
  - *Self-repair of thermosets, thermoplastics, composites, and textiles*
  - *Heal microcracks, impact damage, fatigue damage, and cuts/tears in membranes*

# Research Summary

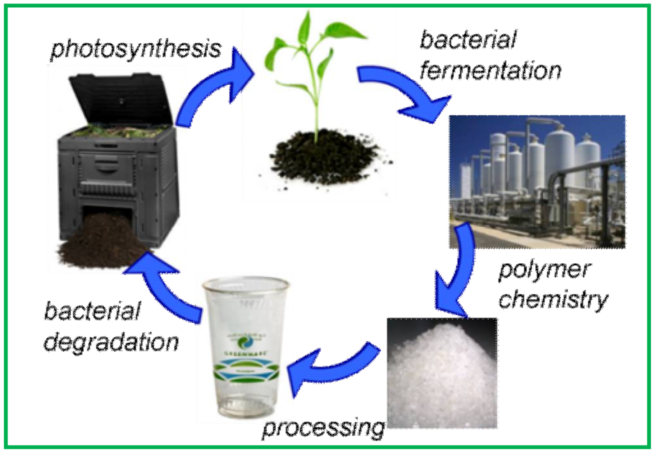

Assistant Professor Meg Sobkowicz-Kline

UML Plastics Engineering


***Expertise: Polymer blend and composite processing, Renewable polymers, Structure-property relationships, Recycling, Rheology, Polymer electronics***

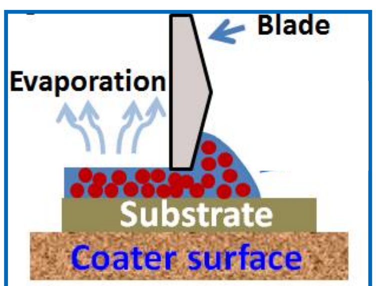
***Research Group: NSF and Industrial funding; 4 Ph.D., 1 M.S. and 3 Undergraduate***

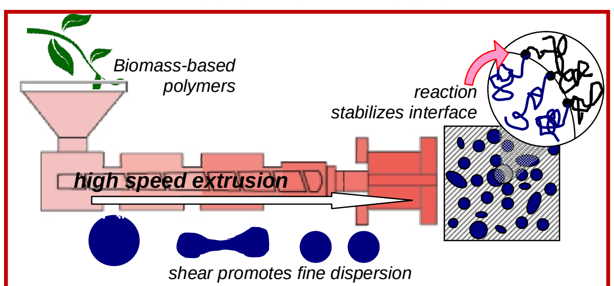
Renewable Materials




Rheology

Reactive Extrusion




## Current Projects:

### *Bio-based Polymer Blends*

Study effects of coupled high shear and chemical modification at the interface on structure-processing-property relationships

### *Aqueous Polymer Coating Systems*

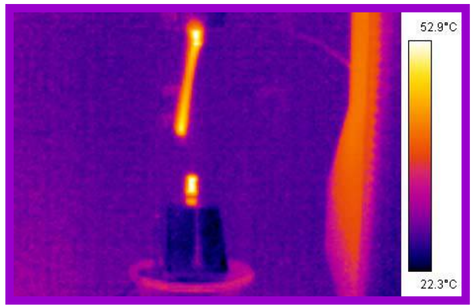
Investigate field-assisted assembly to produce hierarchical structures to enhance organic photovoltaics, flexible electronics and smart coatings

**Other Research Interests:** Recycling, Degradable Coatings, Membrane Production

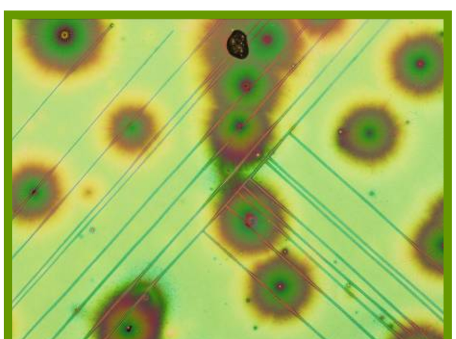
# Research Summary


## Associate Professor Daniel Schmidt
## UML Plastics Engineering


***Expertise: Nanocomposites, thermosets / polymer networks, materials chemistry, materials characterization, porous materials, sol-gel processing, sustainable materials***







- ***Polymer Networks***
  - *Flexible methodologies for the preparation of tissue engineering scaffolds*
  - *pH-responsive hydrogels for controlled transport and cell culture applications*
  - *Low toxicity thiol-ene adhesives and coatings*
  - *Green binders for engineered wood products*
  - *BPA-free epoxies for can coating applications*
  - *MEMS, microelectronics, functional and protective coatings from pre-ceramic polymers*
  - *Sustainable thermosets for wind energy*
- ***Hybrid Materials***
  - *Spray-deposition of polymer nanolaminates*
  - *Structure / properties relations in polymer / layered silicate nanocomposites*
  - *Industrial applications of polymer (nano)composites (packaging, HFFR, etc.)*
- ***Materials Analysis***
  - *Assessing deformation mechanisms via thermal tensile testing*
  - *Rapid screening of nanomaterial toxicity*

# HSP in Practice at UML

- Sustainable reformulation
  - Replacing methylene chloride in a gel-based paint stripper
  - Replacing styrene in vinyl ester resins
  - Replacing toluene, hexane in contact cement
- Advanced materials research
  - Finding solvents for conducting polymers, biodegradable polyesters
  - Finding solvents for high impact copolyesters
  - Predicting compatibility between biofilm inhibitors and medical plastics

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# Safe, Effective Alternatives to Methylene Chloride (MC) for Paint Stripping Products

*Greg Morose, Ph.D.*

*Toxics Use Reduction Institute*

*University of Massachusetts Lowell*

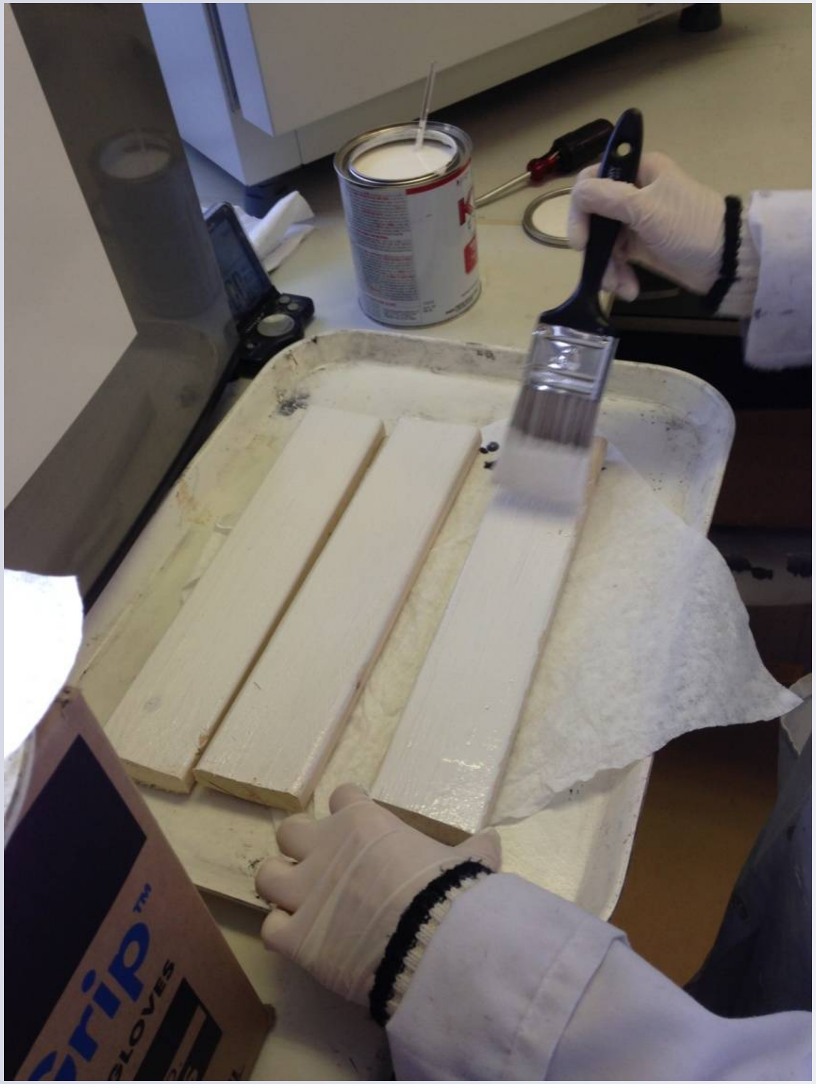
# Paint Strippers: Background

- Paint strippers are ~2-5% additives solvent
- MC is well-known, widely used in the US
  - Small molecular volume, low $\delta_H$ enable effective paint penetration
  - Toxic, carcinogenic; has lead to worker, consumer deaths
  - Marketing banned in the EU since 2012
- Non-MC paint strippers
  - HSP values far from optimal vs. common paints
  - Large molecular volume, high $\delta_H$ contribute to poor paint penetration
  - Longer, more numerous applications required

# Reformulation Requirements

- Safety: Safer than MC-based formulations
- Solvency: HSP values compatible with a wide range of paints and coatings
- Penetration: Similar molecular volume to MC (64.4), low $\delta_H$
- Substrates: Compatible with a wide range of substrates without altering appearance
- Cost: Less than ~£1.50/kg for raw materials
- Viscosity: Ability to cling to vertical surfaces (after addition of thickener)
- Volatile Organic Compounds (VOCs): <50%

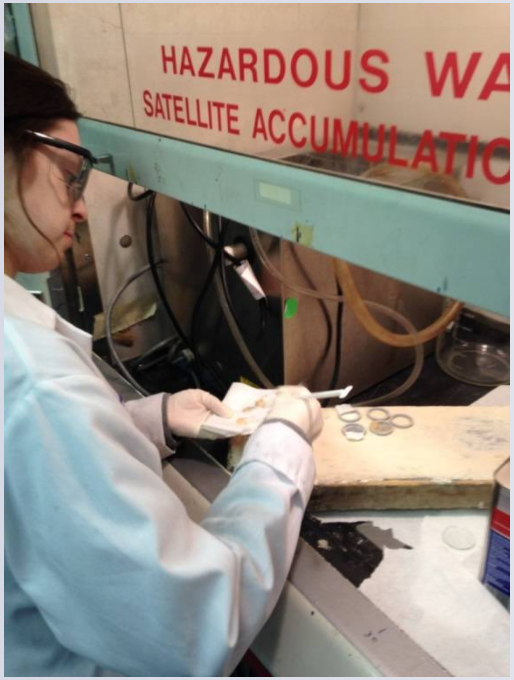
# Test Coupon Preparation




- Substrates
  - White pine
  - Masonry
  - Galvanized steel
- Coatings
  - 1 primer coat
  - 4 identical (typical)
  - 6 mixed finish coats (wood only)
  - Light sanding, isopropanol wipe before each coat
- Accelerated Aging
  - 3 weeks @ 60°C
  - Simulates 11 months

→ ***Exceeds ASTM D6189***

# Testing Procedure, Examples

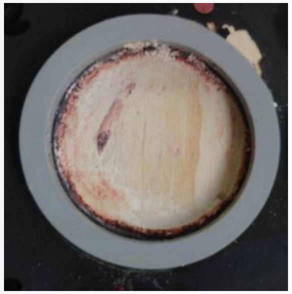



- Glue rubber gasket to test specimen
- Fill with 1.5 mL of paint stripper, cover and let sit
- Uncover, lightly scrape with plastic scraper
- Outputs:
  - Initial cracking time (min.)
  - Substrate exposure (%)

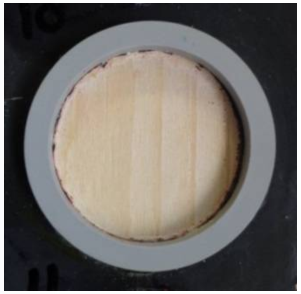
***Example Results:***


**0% exposure (no effect)**

0% exposure (partial attack)



60% exposure



100% exposure

# Alternative Formulations

- Using HSPiP and cross-referencing with cost data, four formulations identified:

| Formulation | Solvents | Approx. Cost (£ per kg) |
|---|---|---|
| Formulation 4 | Methyl acetate / DMSO / Thiophene | £1.65 |
| Formulation B | Methyl acetate / DMSO / Thiophene | £1.28 |
| Formulation F | Methyl acetate / DMSO | £1.04 |
| Formulation 9 | Acetone / DMSO / Thiophene | £1.65 |

*(Patent application filed August 2016)*

- Results vs. commercial paint strippers:

| | Average Exposure (%) | | |
|---|---|---|---|
| Substrate | MC | Non-MC | UML |
| Wood (7 coating types, 1 mixed) | 83-87 | **0**-0 | 60-78 |
| Masonry (2 coating types) | 90-97 | 0-20 | 70-78 |

(In contrast, all three classes were similarly effective on metal)

# HSP in Practice at UML

- Sustainable reformulation
  - Replacing methylene chloride in a gel-based paint stripper
  - **Replacing styrene in vinyl ester resins**
  - Replacing toluene, hexane in contact cement
- Advanced materials research
  - Finding solvents for conducting polymers, biodegradable polyesters
  - Finding solvents for high impact copolyesters
  - Predicting compatibility between biofilm inhibitors and medical plastics

# Identifying Replacements for Styrene in Polyester Resins

*Prof. Chris Hansen*
*Department of Mechanical Engineering*
*University of Massachusetts Lowell*

# Polyester Resins: Background

- Unsaturated polyester (UP) resins are inexpensive thermosets used in gel coats and fiberglass composites
- UP resins typically contain 40-50% styrene
  - Irritant, inhalation hazard, suspected carcinogen
  - No widely accepted alternative in spite of health concerns, regulatory pressure
- Clear exposure potential during UP resin processing (hand lay-up, spray application)

http://www.dehler.com/company/production.html

http://www.euromerespraycore.com/english/non-roll.html

# Needs, Approach and Results

- Reformulation requirements
  - Safety: Reduced volatility and toxicity
  - Solvency: HSP values compatible with various UP resins
  - Processing: Similar viscosity, handling, cure vs. conventional resins
  - Cost: Similar to styrene (£1.19/kg)
- Approach
  - Identified HSP space shared by multiple UP resins
  - Used MatLab to simultaneously optimize HSP match of two and three-component blends with multiple UP solubility spheres as well as cost and blend compatibility
  - Assessed safety using GHS classifications
- Conclusions
  - MatLab code works well, identifies multiple candidates
  - Difficult to match cost of styrene
  - Additional properties testing needed
  - Commercial partner is critical for success in this arena

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# Identifying and Evaluating Safer Solvents for Contact Adhesives

*Catherine Barry and Prof. Chris Hansen*
*Department of Mechanical Engineering*

*Greg Morose, Sc.D.*
*Toxics Use Reduction Institute*

*University of Massachusetts Lowell*

# Contact Adhesives: Background

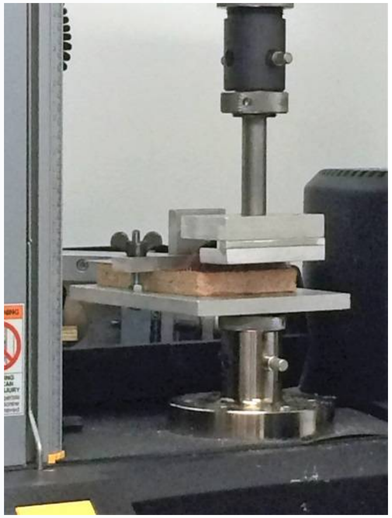
- Contact adhesives consist of rubbery, self-adherent polymers dissolved in a solvent
  - Applied to two surfaces, solvent allowed to evaporate
  - Surfaces then pressed together to give adhesive bond
- Commonly based on toluene and hexane
  - Toxic, regulated hazardous air pollutants (HAPs)
  - Volatile organic compounds (VOCs) as well
- Alternatives contain water, methylene chloride
  - Water-based systems have performance issues (evaporation time, bond strength, low and high T stability)
  - Methylene chloride is a toxic, regulated HAP
- Toxic solvents have consequences for human health and are under significant regulatory pressure

# Reformulation Requirements

- Safety: No hazardous air pollutants
- Solvency: HSP values compatible with polychloroprene, styrene-butadiene-styrene (SBS) & styrene-isoprene-styrene (SIS)
- Specific gravity: 0.7-1.0 (0.7-0.8 preferred)
- Appearance: Colorless (“water white”)
- Odor: Low to medium
- Handling: Stable, uniform, workable for brush, roller, & spray applications, compatible with aerosol propellants, liquid at 5°C
- Compatibility: Non-corrosive
- Dry time: 2-5 minutes at room temperature (RT)
- Open (bonding) time: Up to 60 minutes at RT
- Adhesion: Cleavage strength of 270-440 N (polychloroprene), 220-330 N (styrenics)
- Cost: Less than ~£1.15/kg for raw materials
- Volatile Organic Compounds (VOCs): <250 g/L for low-VOC markets

# Reformulation Approach

- HSP values of commercial solvent systems calculated
- HSP spheres of polymeric components determined using 27 different solvents, HSPiP analysis of results
- Alternatives identified using HSPiP with list of safer solvents
  - Matlab routine enabled consideration of greater numbers of components, other factors
  - Candidate blends down-selected based on cost, evaporation rate
- Testing carried out for solubility, evaporation rate, viscosity, application and bonding

# Alternative Formulations

- Using HSPiP and cross-referencing with cost and hazard data, seven formulations identified (with two controls for comparison):

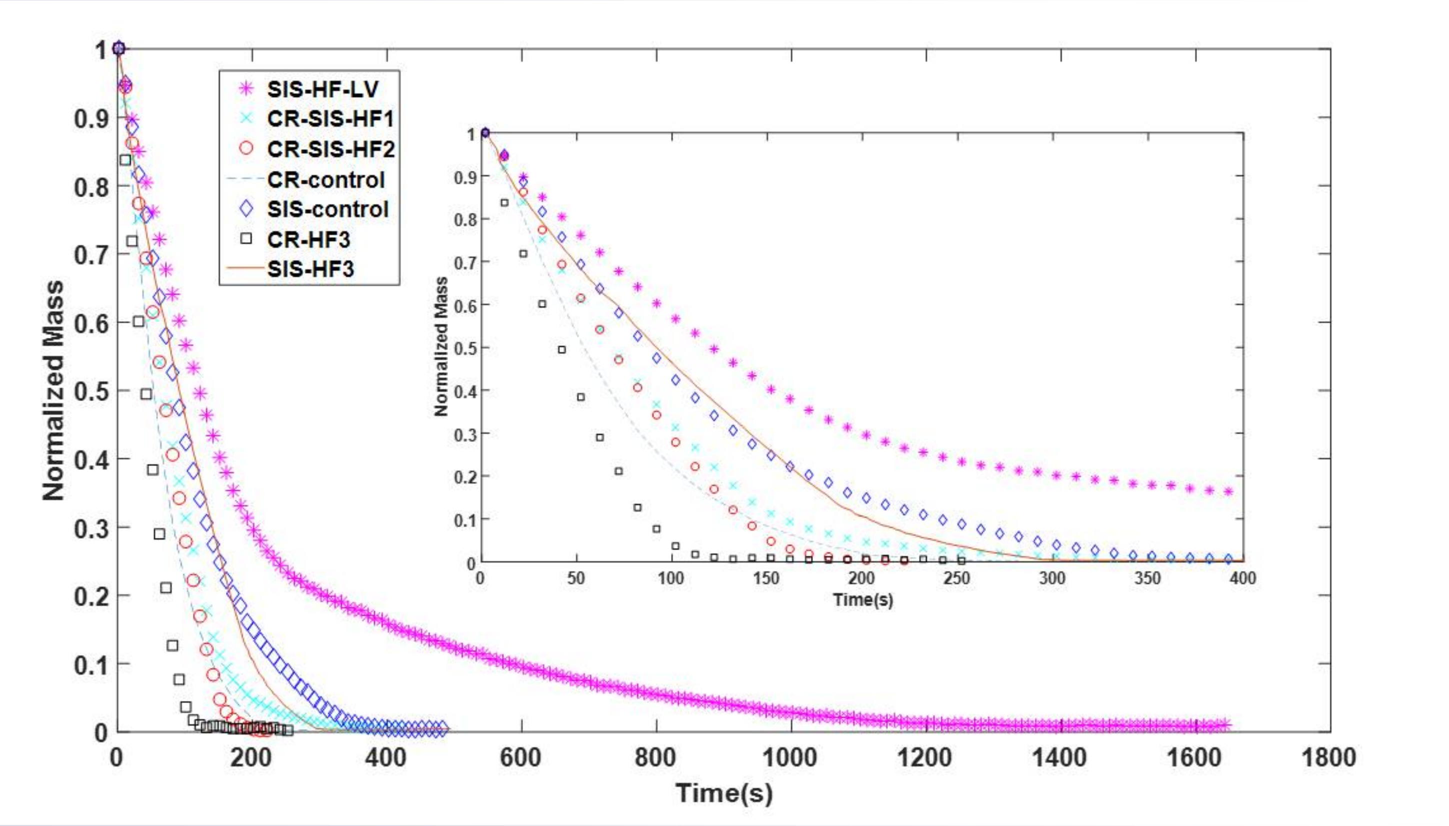
| Formulation | Solvents | Approx. Cost (£ per kg) |
|---|---|---|
| *SIS-control* | *Toluene / Hexane / Acetone* | *£1.59* |
| SIS-HF1 | Methyl acetate / Cyclohexene / Methylcyclohexane | £3.23 |
| SIS-HF2 | Methyl acetate / Cyclohexene | £3.47 |
| SIS-HF3 | Methyl acetate / Cyclohexane / Acetone | £2.30 |
| SIS-HF-LV | Methyl acetate / Cyclohexane / PCBTF | £2.80 |
| *CR Control* | *Toluene / Hexane / Acetone* | *£1.52* |
| CR-HF1 | Methyl acetate / Cyclohexene / Methylcyclohexane | £3.23 |
| CR-HF2 | Methyl acetate / Cyclohexene | £3.47 |
| CR-HF3 | Acetone / Cyclohexane | £2.18 |

*HF = HAP-free; LV = Low-VOC (<250 g/L); PCBTF = Parachlorobenzotrifluoride*

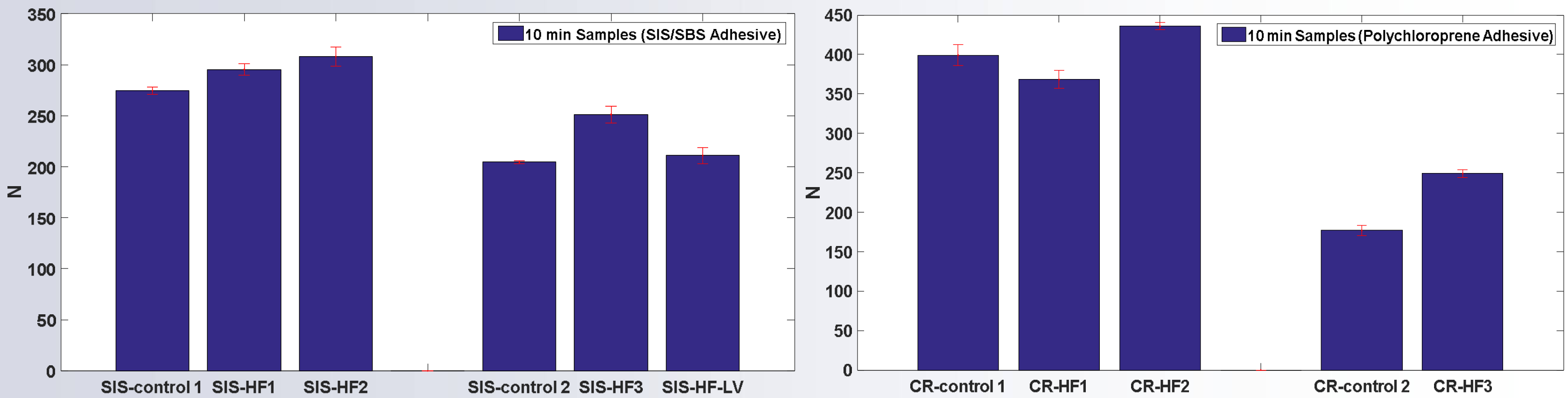
*(Patent pending, worldwide protection available)*

# Process Characteristics

- Similar dissolution times to controls in all cases
- Higher viscosities, but no problems spraying
- Promising evaporation behavior



# Adhesive Performance




- Adhesion strength compares is similar to or better than control systems in all cases
- Two blends (HF1, HF2) work well for both polymers
- Multiple HAP-free alternatives demonstrate functional equivalence vs. controls
- Low-VOC formulation (HF-LV) provides significantly better performance than water-based products

**C. Barry, G. Morose, K. Begin, M. Atwater, C. Hansen. "The Identification and Screening of Lower Toxicity Solvents for Contact Adhesives." *International Journal of Adhesion and Adhesives* (submitted)**

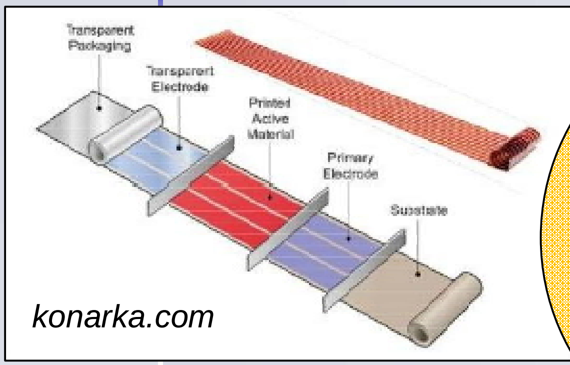
# HSP in Practice at UML

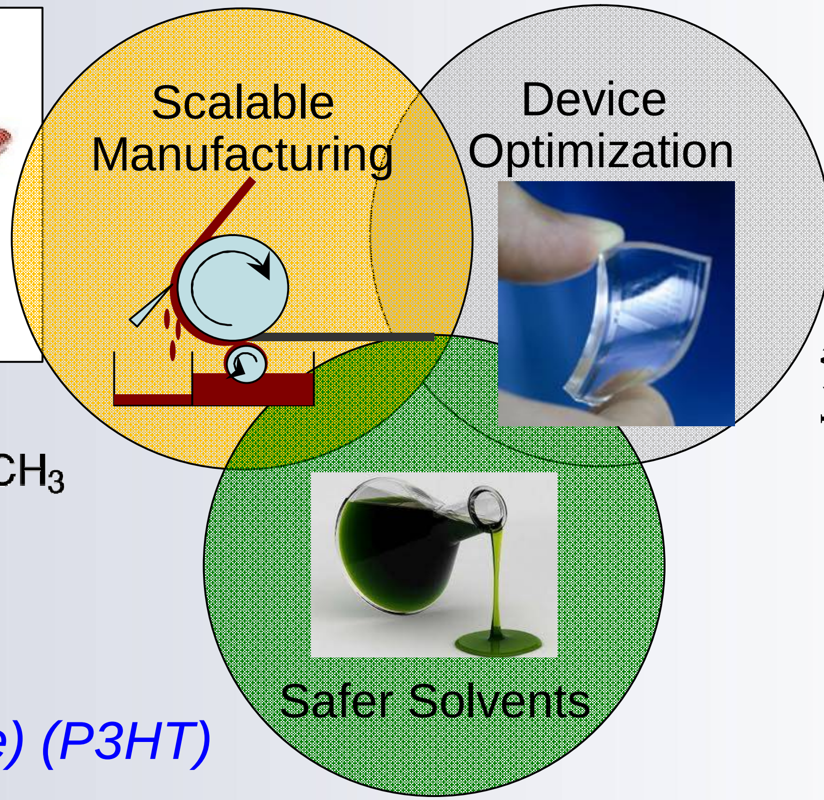
- Sustainable reformulation
  - Replacing methylene chloride in a gel-based paint stripper
  - Replacing styrene in vinyl ester resins
  - Replacing toluene, hexane in contact cement
- Advanced materials research
  - **Finding solvents for conducting polymers, biodegradable polyesters**
  - Finding solvents for high impact copolyesters
  - Predicting compatibility between biofilm inhibitors and medical plastics

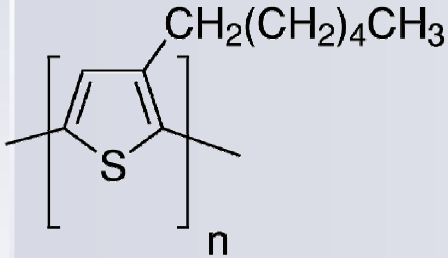
# Solvents for Flexible Electronics
# Solvents for Paper Coatings

*Prof. Margaret Sobkowicz-Kline*
*Department of Plastics Engineering*
*University of Massachusetts Lowell*

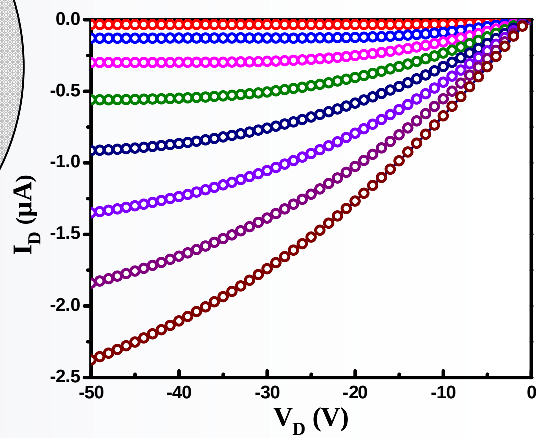
# Solvents for Flexible Electronics




*Poly(3-hexylthiophene) (P3HT)*

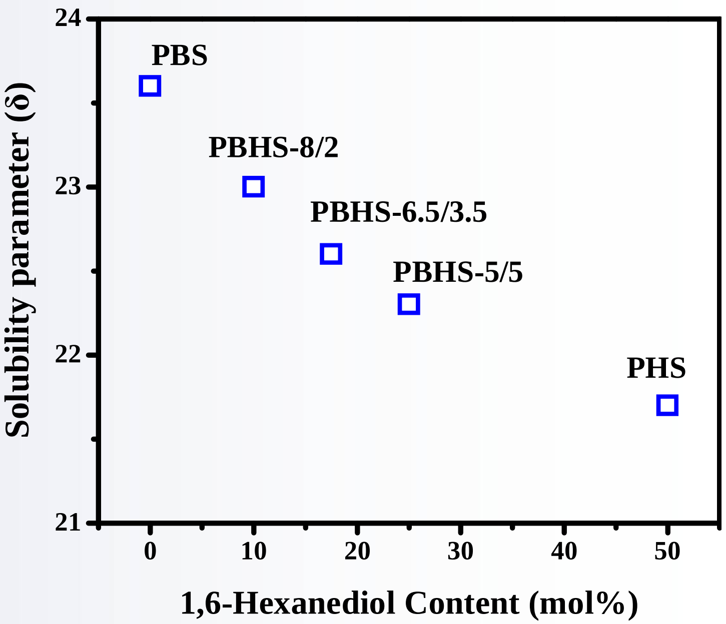



- Solution processing enables cheaper, faster, more versatile manufacturing
- Typically, conjugated polymers are coated from chlorinated aromatic solvents (high rigidity → challenging to solubilize)
- Seeking greener solvents; limited success using predictive methods
- Dispersion in aqueous media proved more feasible

# Solvents for Paper Coatings

- Solvent-borne biodegradable polyester paper coatings are of interest
- Chloroform is the only known solvent for poly(butylene succinate) (PBS), and is hazardous
- HSPiP used to identify alternative solvents for PBS, poly(hexamethylene succinate) (PHS) and their copolymers (PBHS)

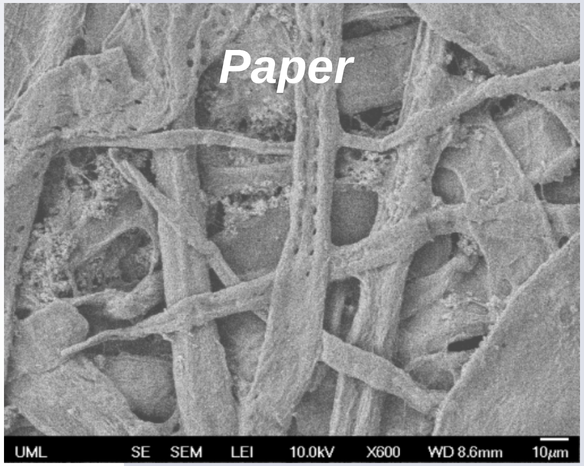
| Polymer | $\delta_D$ | $\delta_P$ | $\delta_H$ | $\delta$ |
|---|---|---|---|---|
| PBS | 17.1 | 10.7 | 12.2 | 23.6 |
| PBHS 8/2 | 17 | 10.2 | 11.5 | 23 |
| PBHS 6.5/3.5 | 17 | 10.1 | 11.2 | 22.6 |
| PBHS 5/5 | 17 | 9.7 | 10.8 | 22.3 |
| PHS | 16.9 | 9.1 | 10.2 | 21.7 |

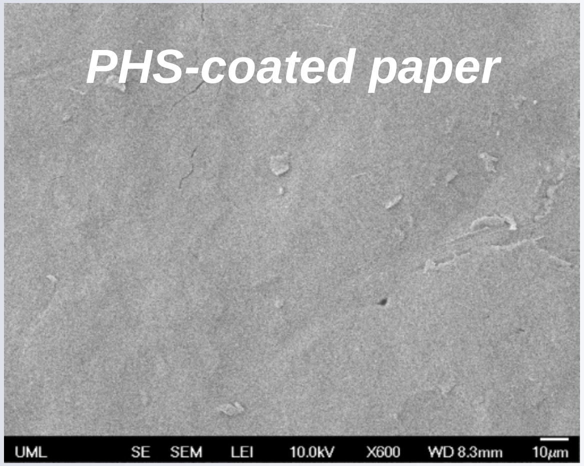


# Solubility Results and Paper Coating Appearance

| Solvent | PBS | PBHS 9/1 | PBHS 7/3 | PBHS 6/4 | PBHS 5/5 | PBHS 4/6 | PBHS 3/7 | PBHS 1/9 | PHS |
|---|---|---|---|---|---|---|---|---|---|
| Chloroform | + | + | + | + | + | + | + | + | + |
| Tetrahydrofuran | – | – | + | + | + | + | + | + | + |
| 1-Propanol | – | – | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| Acetone | – | – | – | ○ | ○ | ○ | ○ | ○ | ○ |
| Butanone | – | – | ○ | + | + | + | + | + | + |
| 1-Propanol / Butanone (54/46 v/v%) | – | ○ | + | + | + | + | + | + | + |

"+" indicates soluble at RT, "○" indicates soluble at 45°C, "–" indicates insoluble

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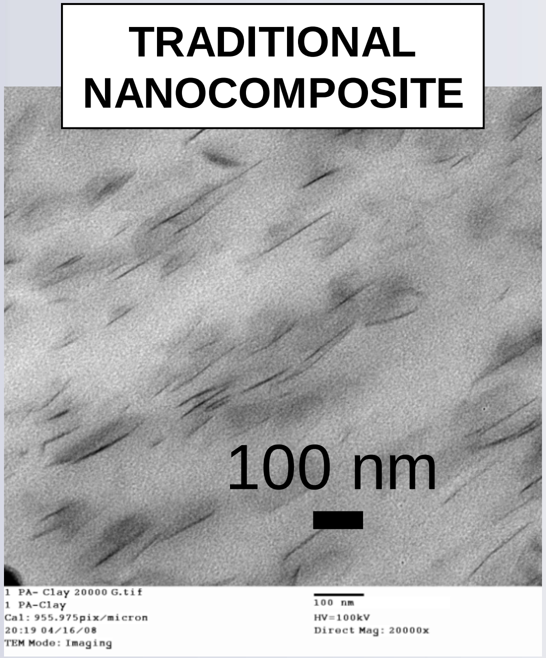
- Advanced materials research
  - Finding solvents for poly(3-hexylthiophene)
  - Finding solvents for poly(butylene succinate)
  - **Finding solvents for high impact copolyesters**
  - Predicting compatibility between biofilm inhibitors and medical plastics

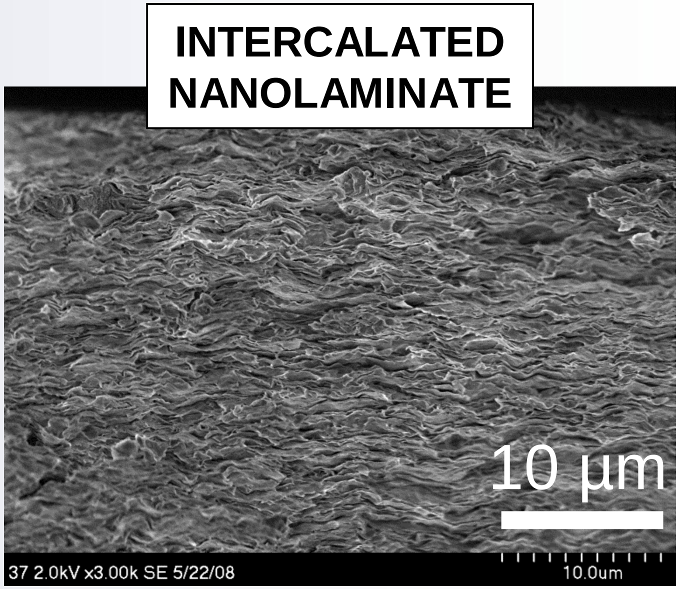
# Spray Deposition of Copolyester Nanolaminates

*Prof. Daniel F. Schmidt*
*Department of Plastics Engineering*
*University of Massachusetts Lowell*

# Solvents for High Impact Copolyesters

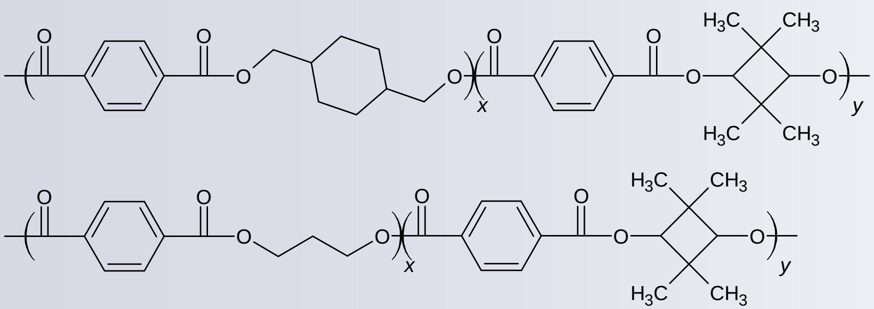
- Producing copolyester / clay nanolaminates
- Studying dynamic mechanical behavior



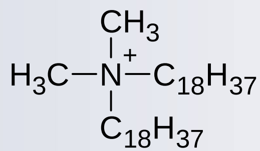



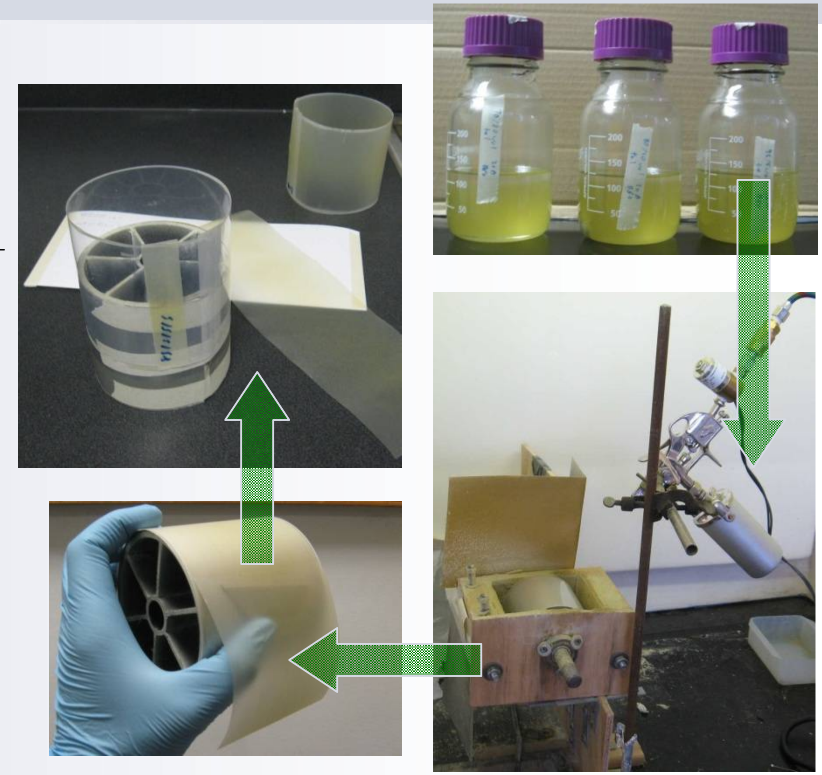
# Automated Spray Deposition

- Polymers:



- Nanoclay:
  - DMDT-MMT





- Polymer, nanoclay mixed in common solvent
- Automated spray deposition enables the formation of free-standing nanolaminates
- Ideal solvent should be safe, effective, inexpensive, non-corrosive, and have moderate evaporation rate

# Identifying Solvents with HSPiP

- 50+ solvents & blends tested
- 5 solvents dissolved copolyesters of interest; blends gave swelling only

| Solvent | $\delta_D$ | $\delta_P$ | $\delta_H$ | Notes |
|---|---|---|---|---|
| Chloroform | 17.8 | 3.1 | 5.7 | Too volatile |
| 1,1,1,3,3,3,Hexafluoro-2-propanol | 17.2 | 4.5 | 14.7 | Too volatile, too expensive |
| Trifluoroacetic Acid | 15.6 | 9.7 | 11.4 | Corrosive |
| m-Cresol | 18.5 | 6.5 | 13.7 | Corrosive, not volatile enough |
| 2-Chlorophenol | 19.0 | 5.5 | 13.9 | Corrosive, not volatile enough |

- Chloroform in use; search continues

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  - Finding solvents for high impact copolyesters
  - **Predicting compatibility between biofilm inhibitors and medical plastics**

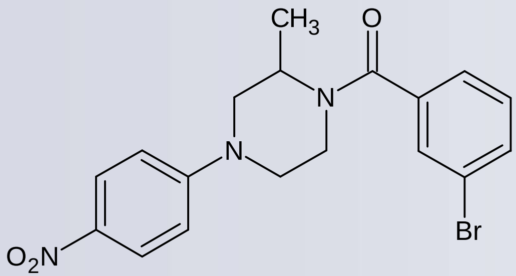
# Impregnation of Medical Plastics with Biofilm Inhibitors

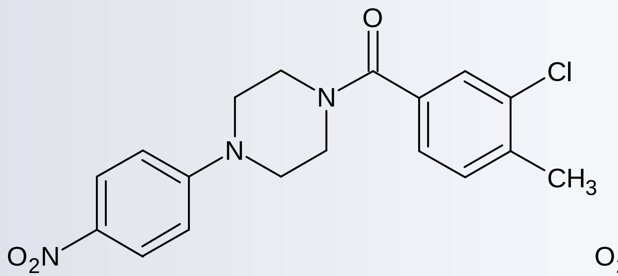
*Prof. Daniel F. Schmidt*
*Department of Plastics Engineering*
*University of Massachusetts Lowell*

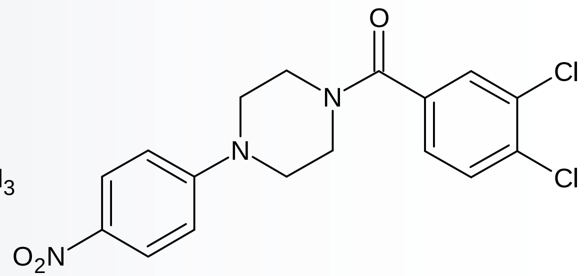
*Prof. Paul Kaufman*
*Department of Molecular, Cell and Cancer Biology*
*University of Massachusetts Medical School*

# Dissolving Biofilm Inhibitors

- Three fungal biofilm inhibitors identified via high throughput screening








  - No experimental data for compounds
  - Very little material to work with (tens of mg?)
- HSPiP used to identify minimally toxic, volatile solvents capable of dissolving biofilm inhibitors, swelling medical plastics

# Summary & Conclusions

- HSP approach works!
  - Not <u>all</u> of the time…
  - …but enough of the time that it's absolutely worth pursuing
- Successes have enabled sustainable reformulation, advanced materials research
  - Replacing methylene chloride in paint stripper
  - Replacing toluene, hexane in contact cement
  - Identifying solvents for poly(butylene succinate)
  - Predicting compatibility between biofilm inhibitors, solvents and medical plastics
- Application-oriented HSPiP wish list generated
  - Integrated structure drawing feature is of interest
  - Desire to optimize vs. other criteria on top of HSP
- Failures have inspired more fundamental questions
  - Intractable problems are trying to tell us something…

# Final Thoughts

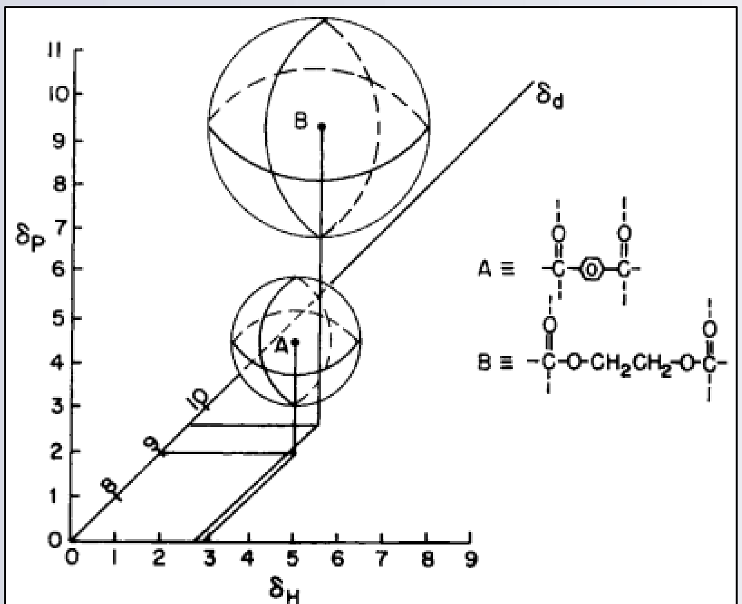
- Biggest issues were observed primarily when trying to completely dissolve (not just swell) stubbornly insoluble polymers
  – Polymers were generally semi-crystalline and / or high-$T_g$ (much harder to attack than amorphous rubbers)
  – Contained functional groups with a broad range of properties (as opposed to hydrocarbon-based polymers)
- How can we explain this?
  – The HSP approach is a “mean field” approach, with values representing averages over the entire molecule
    - OK when variations in cohesive energy density are small
    - Local variations could be a problem if our solvent notices them, however

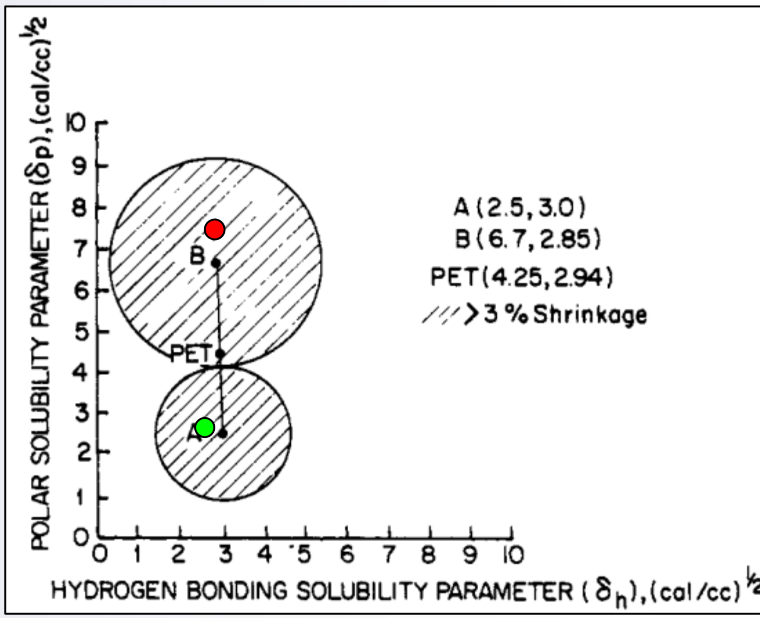
| Name | Structure | $\delta_D$ | $\delta_P$ | $\delta_H$ | Water soluble? |
|---|---|---|---|---|---|
| Poly(oxymethylene) | $–(–O–CH_2–)_n–$ | 16.8 | 9.8 | 6.4 | No |
| Poly(oxyethylene) | $–(–O–CH_2CH_2–)_n–$ | 16.5 | 6.9 | 4.8 | **YES** |
| Poly(oxytetramethylene) | $–(–O–CH_2CH_2CH_2CH_2–)_n–$ | 16.2 | 3.3 | 2.2 | No |

    - Perhaps here it’s the HSP *distribution* within the chain that matters?

# Final Thoughts

- The sole body of work found in this area, by a textile researcher on poly(ethylene terephthalate) fiber swelling / shrinkage in individual solvents, supports the idea that HSP distribution is important
- What about dissolution in solvent blends? (Recall copolyester results)
  – Need to identify not just any solvent blend but a *good* solvent blend
  – ASTM D4603 calls for intrinsic viscosity measurements of PET to be made with a 60/40 blend of phenol and 1,1,2,2-tetrachloroethane




→ **A new feature in the next HSPiP?**

B. H. Knox, *J. Appl. Polym. Sci.* **21** 225-247 (1977)