



Background

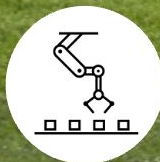


Approaches



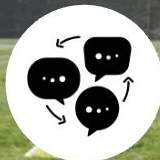
Drop-in Solvent

- Design criteria
- Recommended list
- Next steps



Process & Material
Change

- Process change
- Material Change
- Next steps



Discussion



The Nike Challenge: Alternatives to DMF-PU Synthetic Leather

Annie LaBine, Isaac Ramphal, Kimberly Hazard, Stephanie Ng & Surui Zhang
Greener Solutions: A Safer Design Partnership | Fall 2019



Background



Drop-in Solvent

- Design criteria
- Recommended list
- Next steps



Approaches



Process & Material
Change

- Process change
- Material Change
- Next steps



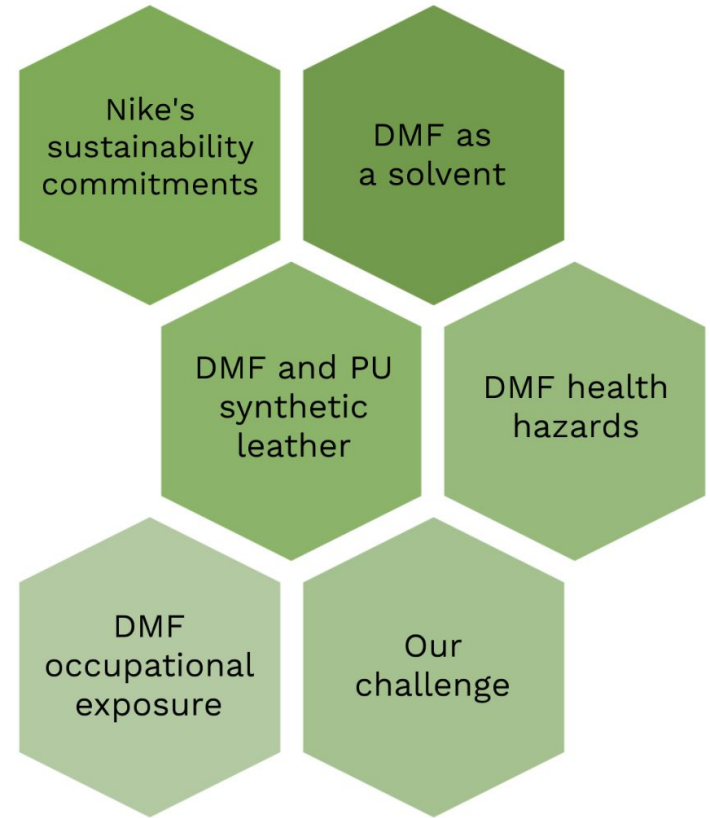
Discussion

The Nike Challenge: Alternatives to DMF-PU Synthetic Leather

Annie LaBine, Isaac Ramphal, Kimberly Hazard, Stephanie Ng & Surui Zhang
Greener Solutions: A Safer Design Partnership | Fall 2019

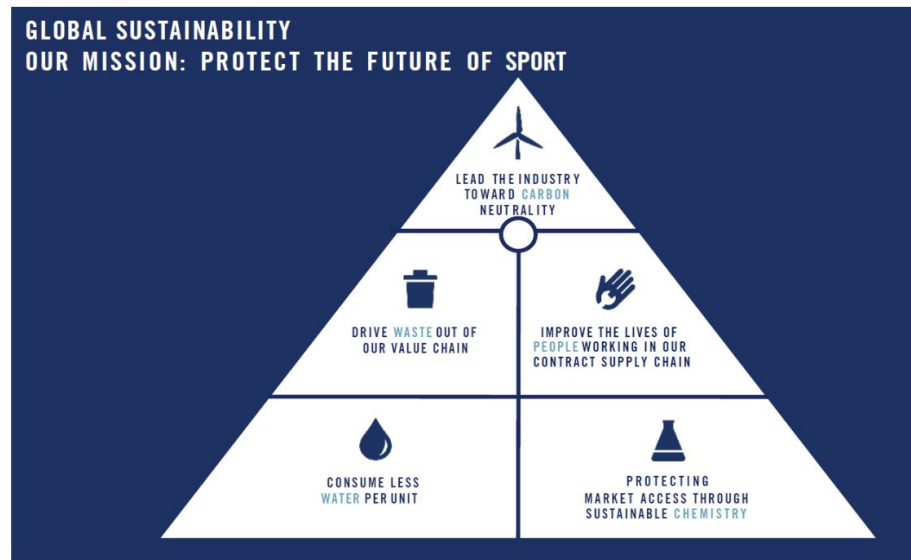
DMF: Good solvent, bad actor

- N,N-dimethylformamide (DMF) is used extensively in manufacturing of synthetic leather and throughout the textiles supply chain
- Many companies, including Nike, use DMF in polyurethane (PU) synthetic leather production for shoe wear
- DMF is easily absorbed through the skin and can cause liver damage and other adverse health outcomes



Nike is committed to greener chemistry

- DMF consists of 10% of total hazardous chemical usage
- Phase out DMF use for synthetic leather by 2025
- Zero Discharge of Hazardous Chemicals (ZDHC) coalition and industry-aligned manufacturing restricted substances list (MRSL)
- Moonshot challenge: double business with half the impact

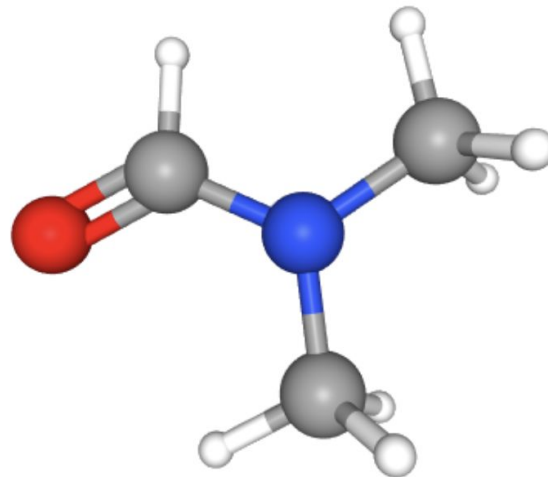


With permission from Nike



Why is DMF used?

- Solvent class: polar aprotic
- Miscible with water and many organic solvents
- Liquid: -60 to 150 C
- Dissolves PU and much more (glue, dyes, surfactants, etc.)
- Inexpensive and produced at scale

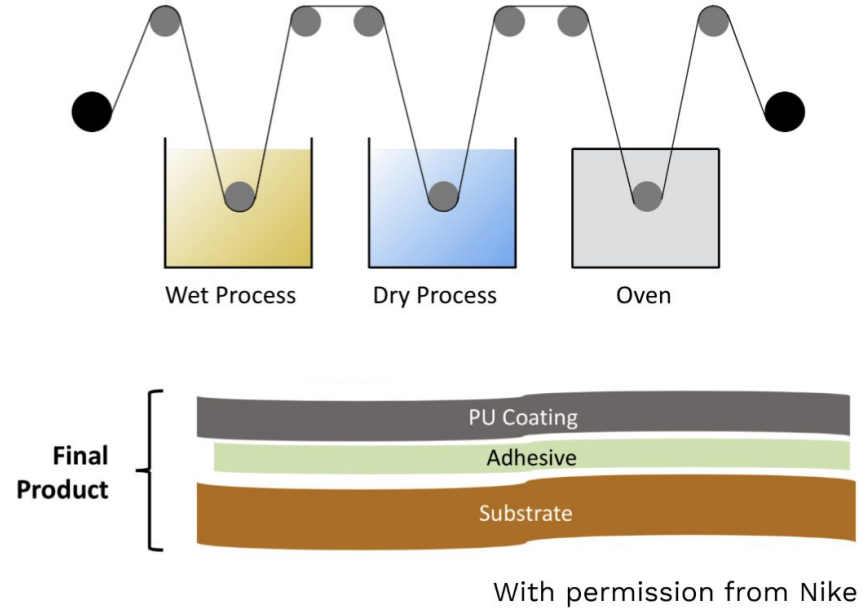


PubChem, 2019



DMF is used throughout manufacturing PU synthetic leather

- Multiple layers of PU on woven backing
- Dissolve PU components in DMF with and without water (wet/dry process)



DMF is inherently hazardous to human health

- IARC Group 2A - probable carcinogen for humans
- Easily absorbed and targets liver

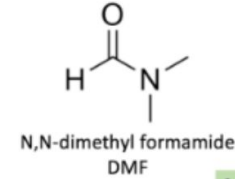
International Agency
Research on Cancer



World Health
Organization

High-Moderate hazards for:

- Carcinogenicity
- Mutagenicity
- Developmental & reproductive toxicity
- Endocrine activity
- Neurotoxicity
- Skin and eye irritation



Absorbed By:

1. Respiratory uptake
2. Dermal Exposure
3. Gastrointestinal intake

GSH depletion;
Oxidative stress

Apoptosis

Necrosis

Alteration of gut
microbiota
community

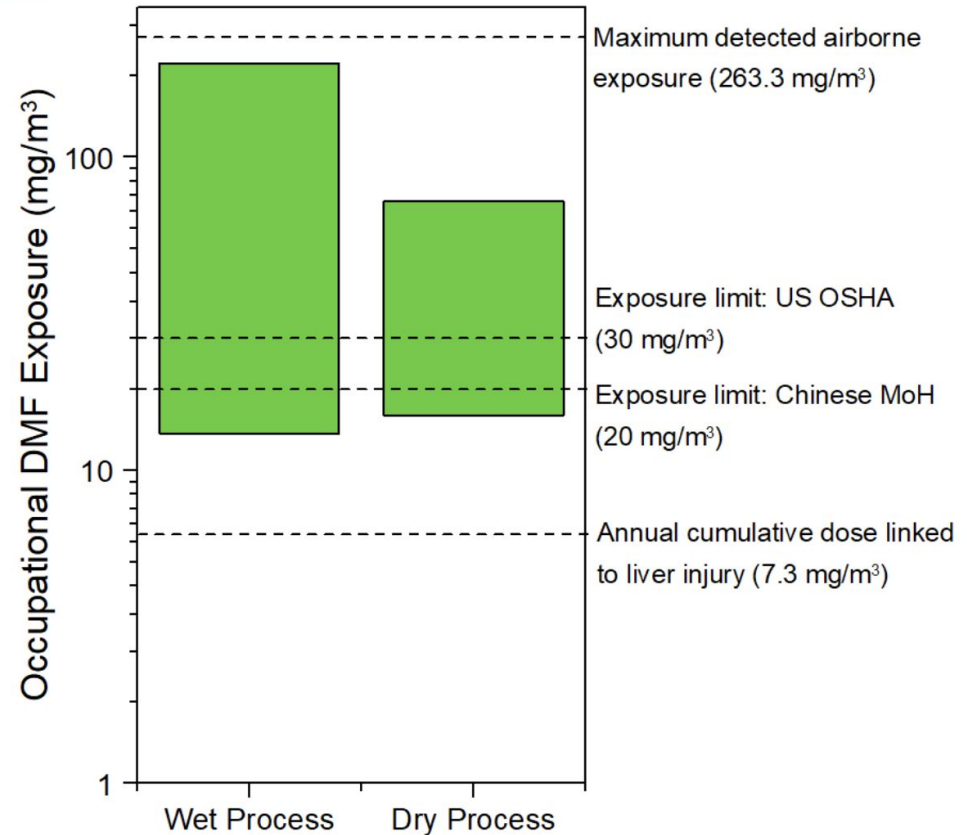
Liver is the primary target organ

Gescher, Chem. Res. Toxicol., 6, 1993, 245.



Workers are exposed to DMF

- Occupational exposure routes: respiratory and dermal
- Lower risk to consumers and environment



A low-angle, close-up shot of several people's arms and hands reaching up and clasping together in a huddle. The hands are of various skin tones, suggesting a diverse group. Some individuals are wearing athletic wristbands, including one with the Nike swoosh logo. The background is a blurred, outdoor setting with trees and a clear sky. A semi-transparent white rectangular box is overlaid on the lower half of the image, containing bold black text.

Our challenge:
Identify inherently safer alternatives to synthetic leather made with DMF to safeguard worker health and phase out the use of DMF within Nike



Background



Approaches



Drop-in Solvent

- Design criteria
- Recommended list
- Next steps



Discussion



Process & Material
Change

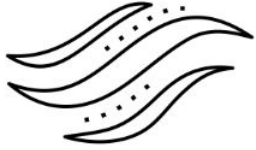
- Process change
- Material Change
- Next steps



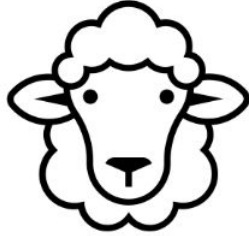
The Nike Challenge: Alternatives to DMF-PU Synthetic Leather

Annie LaBine, Isaac Ramphal, Kimberly Hazard, Stephanie Ng & Surui Zhang
Greener Solutions: A Safer Design Partnership | Fall 2019

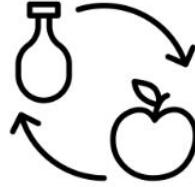
Places to intervene in the system



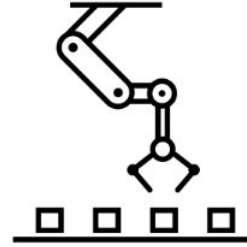
Created by Olena Panasovska
from Noun Project



Created by Symbolon
from Noun Project



Created by Path Lord
from Noun Project



Created by Laymik
from Noun Project



Created by achmad
from Noun Project

Radical Swoosh
Change

Radical Material
Change (Trino™)

Material Change -
Artificial Leather

Process Change

Drop-in
Replacement



A background image showing the lower legs and feet of several runners in motion on a paved track. The runners are wearing athletic gear like leggings and sneakers. The image is slightly blurred to convey a sense of speed. A semi-transparent dark box is overlaid on the center of the image, containing white text.

Design goals for any alternative

- Reduce or eliminate DMF from process to reduce risk
- Meet Nike's other sustainability goals
- Have same performance as existing solutions (strength, durability, aesthetic)
- Avoid toxic substitutions: DMAc

Performance metrics have changed over time

- Meet strength and aesthetic metrics required in shoes
- Quality metrics differ over time and between materials on the market




With permission from Nike



Framing the hazard assessment



Ranking tools:

- 
- Globally Harmonized System (GHS) categories
 - GreenScreen
 - Hodge-Sterner





Background



Approaches



Discussion



Process & Material
Change

- Process change
- Material Change
- Next steps

The Nike Challenge: Alternatives to DMF-PU Synthetic Leather

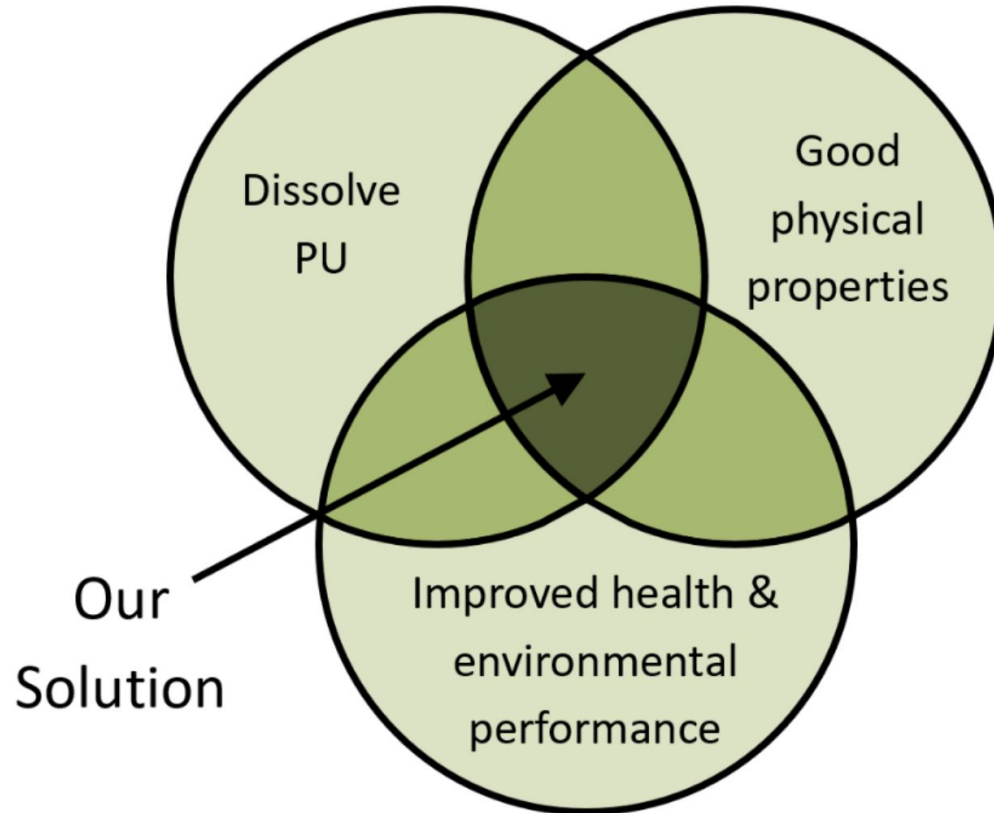
Annie LaBine, Isaac Ramphal, Kimberly Hazard, Stephanie Ng & Surui Zhang
Greener Solutions: A Safer Design Partnership | Fall 2019

Benefits of a drop-in solution

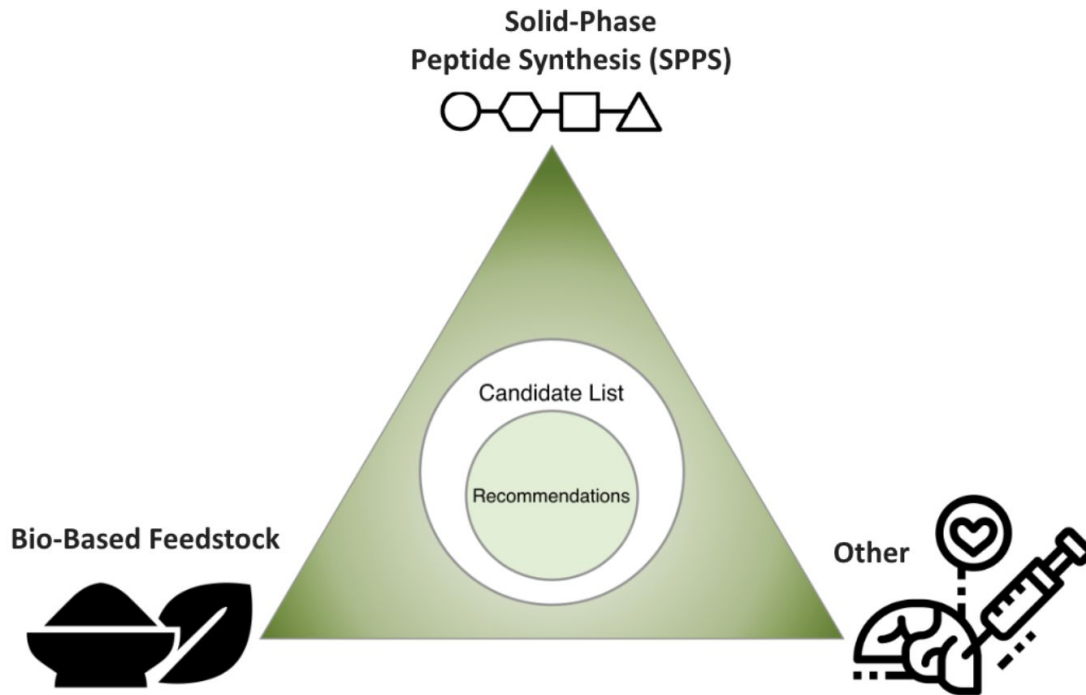
- Lower capital investment
- Broader cross-industry impacts
- Incremental, with wide impact on overall hazardous chemical usage
- Maintain current PU process



Design Criteria for Drop-in



Three categories of drop-in solvents

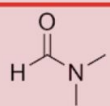


Supalerk laipawat, Tom Fricker,
Samy Menai from Noun Project

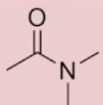


Drop-in candidate list

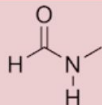
Traditional Polar Aprotics (for comparison)



N,N-dimethyl formamide
DMF



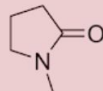
N,N-dimethyl acetamide
DMAc



N-methyl formamide
NMF

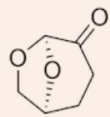


Dimethyl sulfoxide
DMSO

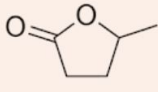


N-methyl pyrrolidone
NMP

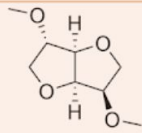
Bio-Based Renewables



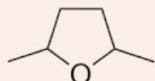
Dihydrolevoglucosenone
Cyrene



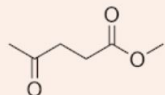
γ -valerolactone
GVL



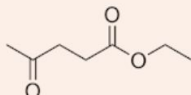
Dimethyl isosorbide
DMI



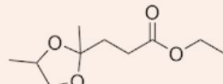
2,5-dimethyl tetrahydrofuran
DMTHF



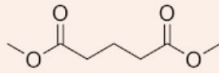
Methyl levulinate
ML



Ethyl levulinate
EL

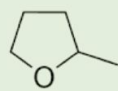


Ethyl levulinate propyleneglycol ketal
ELPK

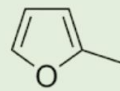


Dimethyl glutarate
DMG

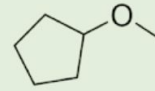
Solid-Phase Peptide Synthesis



2-methyl tetrahydrofuran
2MTHF



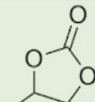
2-methyl furan
2MF



Cyclopentyl methyl ether
cPME

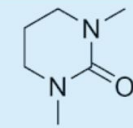


Ethylene carbonate
EC

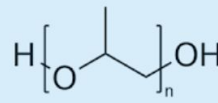


Propylene carbonate
PC

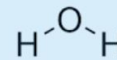
Other



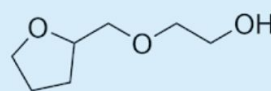
Dimethylpropylene urea
DMPU



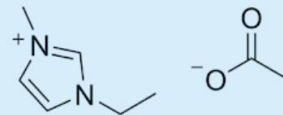
Poly(propyleneglycol)
PPG



Water







Glycofural
THFP



1-ethyl-3-methylimidazolium acetate
[emim][OAc]



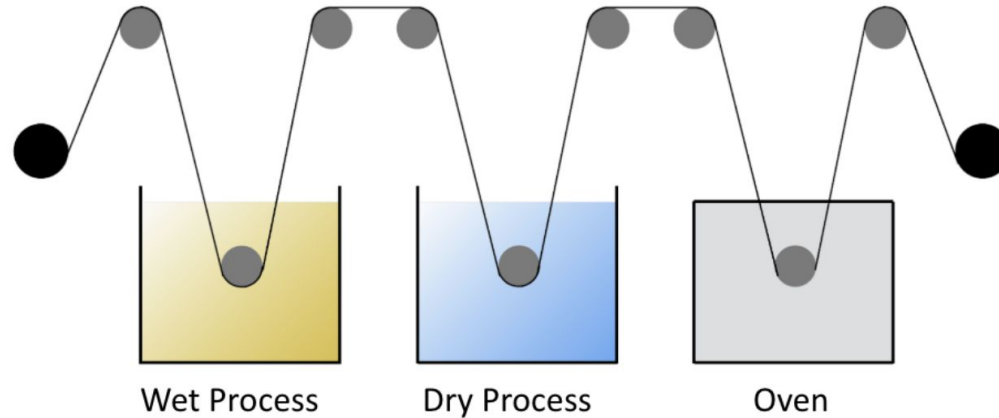
Narrowing our list using the design criteria

	Good physical properties	<ul style="list-style-type: none">• Water solubility• Low vapor pressure
	Dissolve PU	<ul style="list-style-type: none">• Hansen solubility parameters
	Health and environmental	<ul style="list-style-type: none">• Compile hazard data• Rank hazard data
	Literature	<ul style="list-style-type: none">• Relating to replacement of DMF



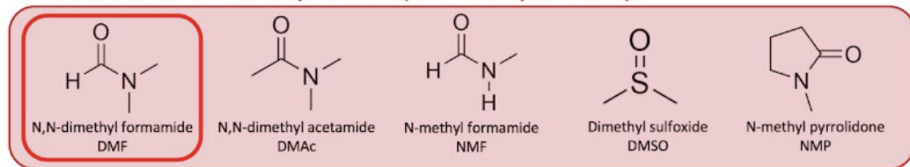
Narrowing through physical properties

- Low vapor pressure/high boiling point
- Water solubility (to wash out)

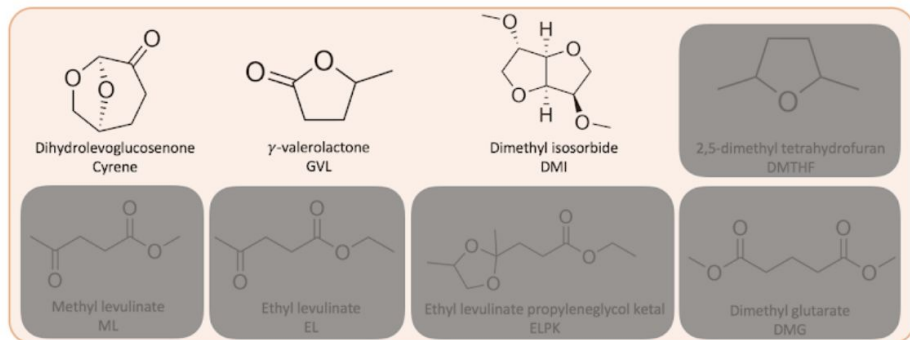


Narrowing through physical properties

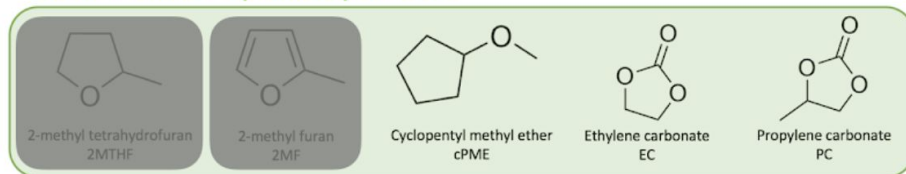
Traditional Polar Aprotics (for comparison)



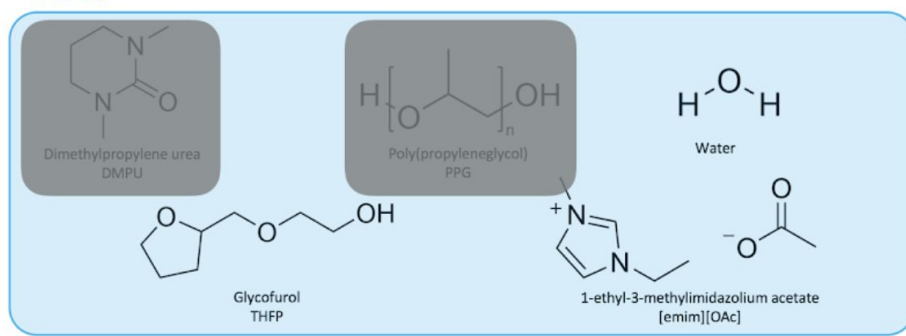
Bio-Based Renewables



Solid-Phase Peptide Synthesis

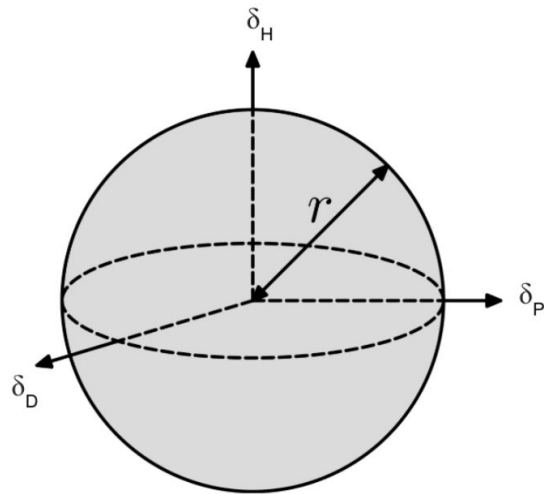


Other

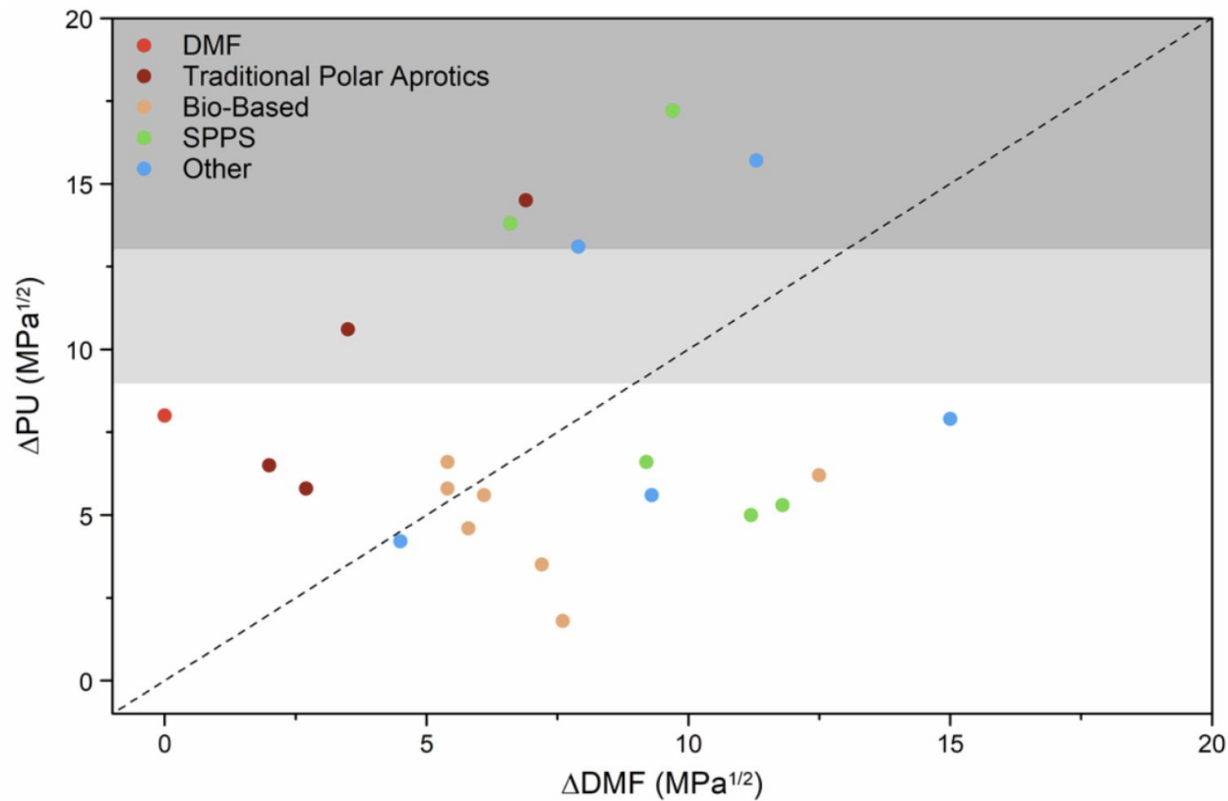


Predicting PU solvation using Hansen solubility parameters

- Hansen solubility parameters:
 - Dispersion forces
 - Polar interactions
 - Hydrogen bonding
- Match solubility parameters of PU (and DMF)
- PU solubility parameters found in literature



Hansen solubility results



Narrowing through PU solvation

Traditional Polar Aprotics (for comparison)



N,N-dimethyl formamide
DMF



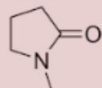
N,N-dimethyl acetamide
DMAc



N-methyl formamide
NMF

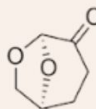


Dimethyl sulfoxide
DMSO

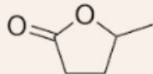


N-methyl pyrrolidone
NMP

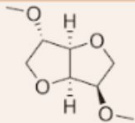
Bio-Based Renewables



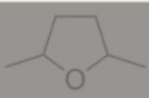
Dihydrolevoglucosenone
Cyrene



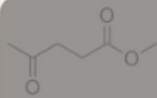
γ -valerolactone
GVL



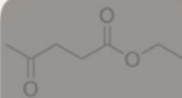
Dimethyl isosorbide
DMI



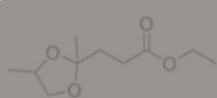
2,5-dimethyl tetrahydrofuran
DMTHF



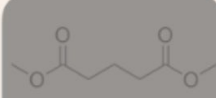
Methyl levulinate
ML



Ethyl levulinate
EL

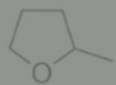


Ethyl levulinate propyleneglycol ketal
ELPK

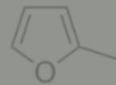


Dimethyl glutarate
DMG

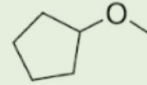
Solid-Phase Peptide Synthesis



2-methyl tetrahydrofuran
2MTHF



2-methyl furan
2MF



Cyclopentyl methyl ether
cPME

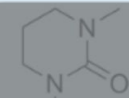


Ethylene carbonate
EC

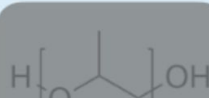


Propylene carbonate
PC

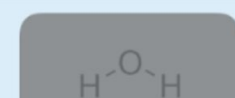
Other



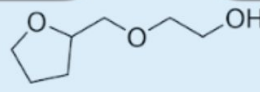
Dimethylpropylene urea
DMPU



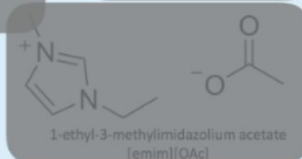
Poly(propyleneglycol)
PPG



Water



Glycofural
THFP

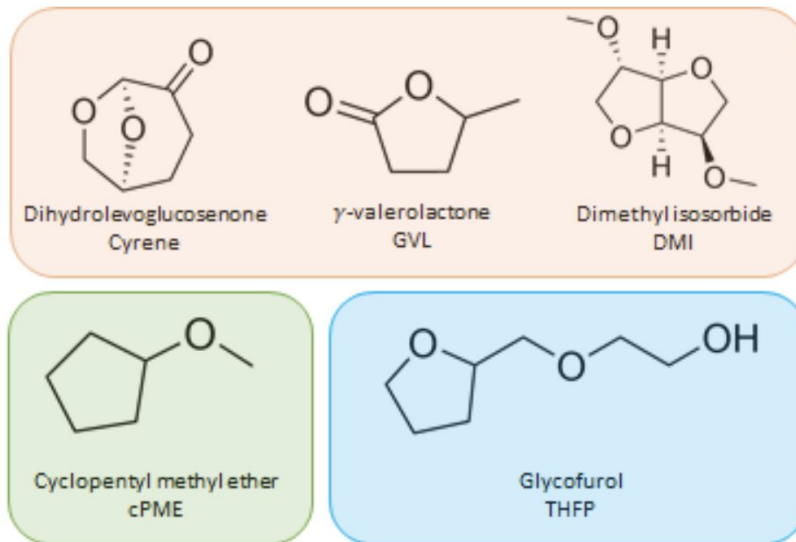


1-ethyl-3-methylimidazolium acetate
[emim][OAc]



Short list: our recommendations

- Bio-based
 - Cyrene
 - GVL
 - DMI
- SPPS
 - cPME
- Other
 - Glycofurool



Evaluation of health and environmental performance of short list

- GHS categories and REACH data
- Translated via GreenScreen
- Priority endpoints with sufficient data

Solvent	C/M/R	Systemic	Irritation	Acute	Aquatic	P/B
DMF	H	M	M	H	M	M

L: Low	M: Moderate	H: High	pC: potential concern	Data Gap
--------	-------------	---------	-----------------------	----------





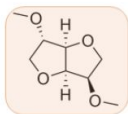
Cyrene™ (Dihydrolevoglucosenone)

- Biobased
- Commercial feasibility: feedstock is available, but not widely available by industrial/commercial production
- Emerged from green solvents literature (He, 2017)

Solvent	C/M/R	Systemic	Irritation	Acute	Aquatic	P/B
DMF	H	M	M	H	M	M
Cyrene™	L	L	L	M	L	L

L: Low	M: Moderate	H: High	pC: potential concern	Data Gap
--------	-------------	---------	-----------------------	----------





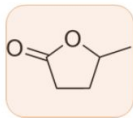
DMI (Dimethyisosorbide)

- Biobased
- Closest solubility parameters to PU
- Available for commercial production and at industrial scale
- Acceptable for pharmaceutical and cosmetic applications

Solvent	C/M/R	Systemic	Irritation	Acute	Aquatic	P/B
DMF	H	M	M	H	M	M
DMI	L		L	L	L	M

L: Low	M: Moderate	H: High	pC: potential concern	Data Gap
--------	-------------	---------	-----------------------	----------





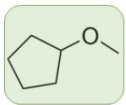
GVL (gamma-valerolactone)

- Bio-based
- Commercial feasibility: feedstock is available, but not widely available by industrial/commercial production
- One of the volatile flavor constituents in mango and honey
- Potential concern for carcinogenicity, mutagenicity, and developmental/reproductive toxicity via modeling
- Chalid, 2015

Solvent	C/M/R	Systemic	Irritation	Acute	Aquatic	P/B
DMF	H	M	M	H	M	M
GVL	pC		L	L	M	L

L: Low	M: Moderate	H: High	pC: potential concern	Data Gap
--------	-------------	---------	-----------------------	----------





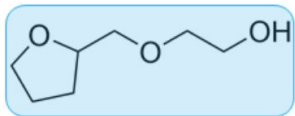
cPME (Cyclopentyl methyl ether)

- Successful example of solid-phase peptide synthesis (SPPS)
- Highlighted as green solvent in SPPS literature

Solvent	C/M/R	Systemic	Irritation	Acute	Aquatic	P/B
DMF	H	M	M	H	M	M
cPME	L	L	M	M	L	M

L: Low	M: Moderate	H: High	pC: potential concern	Data Gap
--------	-------------	---------	-----------------------	----------





Glycofurol (THFP)

- Used as a solvent in parenteral pharmaceutical formulations and is generally regarded as relatively nontoxic and nonirritant material at the levels used as a pharmaceutical excipient
- Potential to move into bio based category

Solvent	C/M/R	Systemic	Irritation	Acute	Aquatic	P/B
DMF	H	M	M	H	M	M
THFP				L		M

L: Low	M: Moderate	H: High	pC: potential concern	Data Gap
--------	-------------	---------	-----------------------	----------



Short list hazard table

Solvent	C/M/R	Systemic	Irritation	Acute	Aquatic	P/B
DMF	H	M	M	H	M	M
Cyrene™	L	L	L	M	L	L
DMI	L		L	L	L	M
GVL	pC		L	L	M	L
cPME	L	L	M	M	L	M
THFP				L		M

L: Low	M: Moderate	H: High	pC: potential concern	Data Gap
--------	-------------	---------	-----------------------	----------



FUTURE FORWARD



Next steps for drop-ins

- Make PU: test molecular weight and physical properties
- Neuro tox/ED health impacts



Background



Drop-in Solvent

- Design criteria
- Recommended list
- Next steps



Approaches



Discussion



Process & Material
Change

- Process change
- Material Change
- Next steps



The Nike Challenge: Alternatives to DMF-PU Synthetic Leather

Annie LaBine, Isaac Ramphal, Kimberly Hazard, Stephanie Ng & Surui Zhang
Greener Solutions: A Safer Design Partnership | Fall 2019



Process change

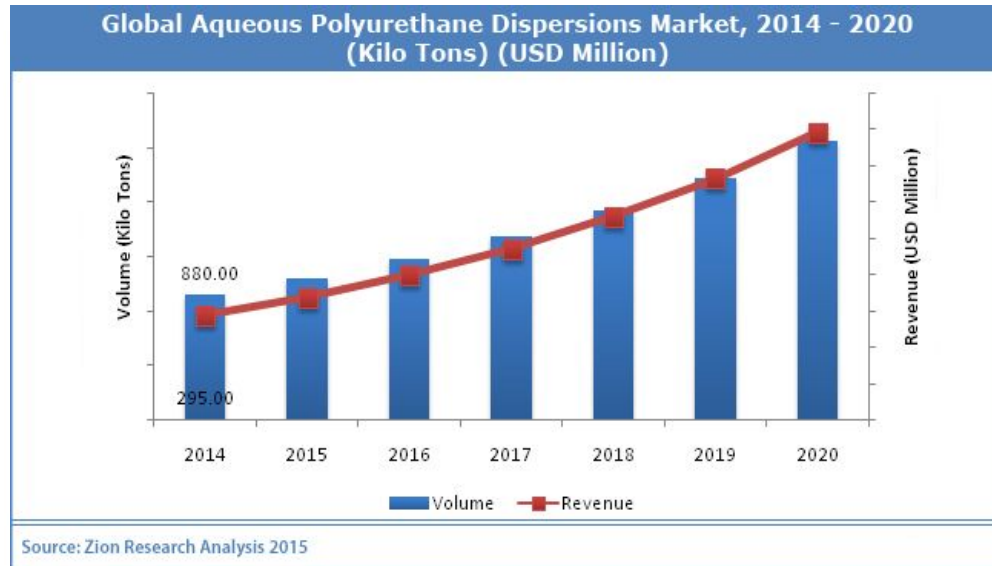
**PU
dispersion**

**Alternative
backbone
chemistry**



PU dispersion: a growing industry

- Aqueous polyurethane dispersion, waterborne polyurethane dispersion, solvent-free process
- Uses water as the primary solvent
- Polyols + isocyanate monomers + a water-dispersing monomer
- TFL, Bayer, and Evonik have promising PUD for artificial leathers



PU dispersion

Potential improvements

- Reduce or eliminate DMF
- Water and energy savings
- Abrasion resistance

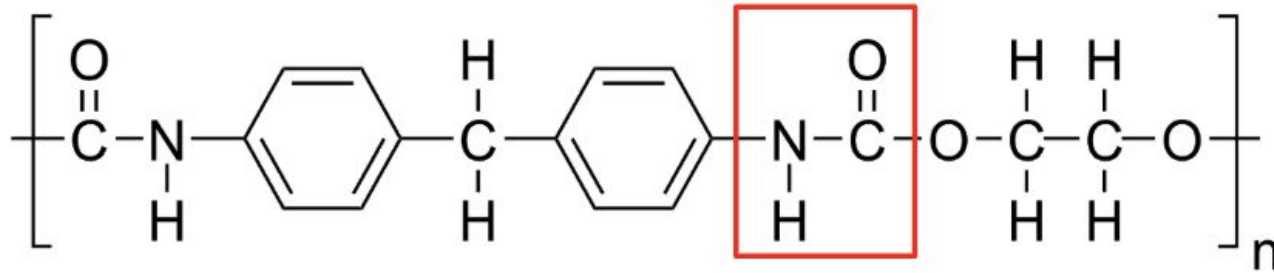
Potential concerns

- Cost
- Complete elimination of DMF?
- Color and quality
- Health and safety of additives



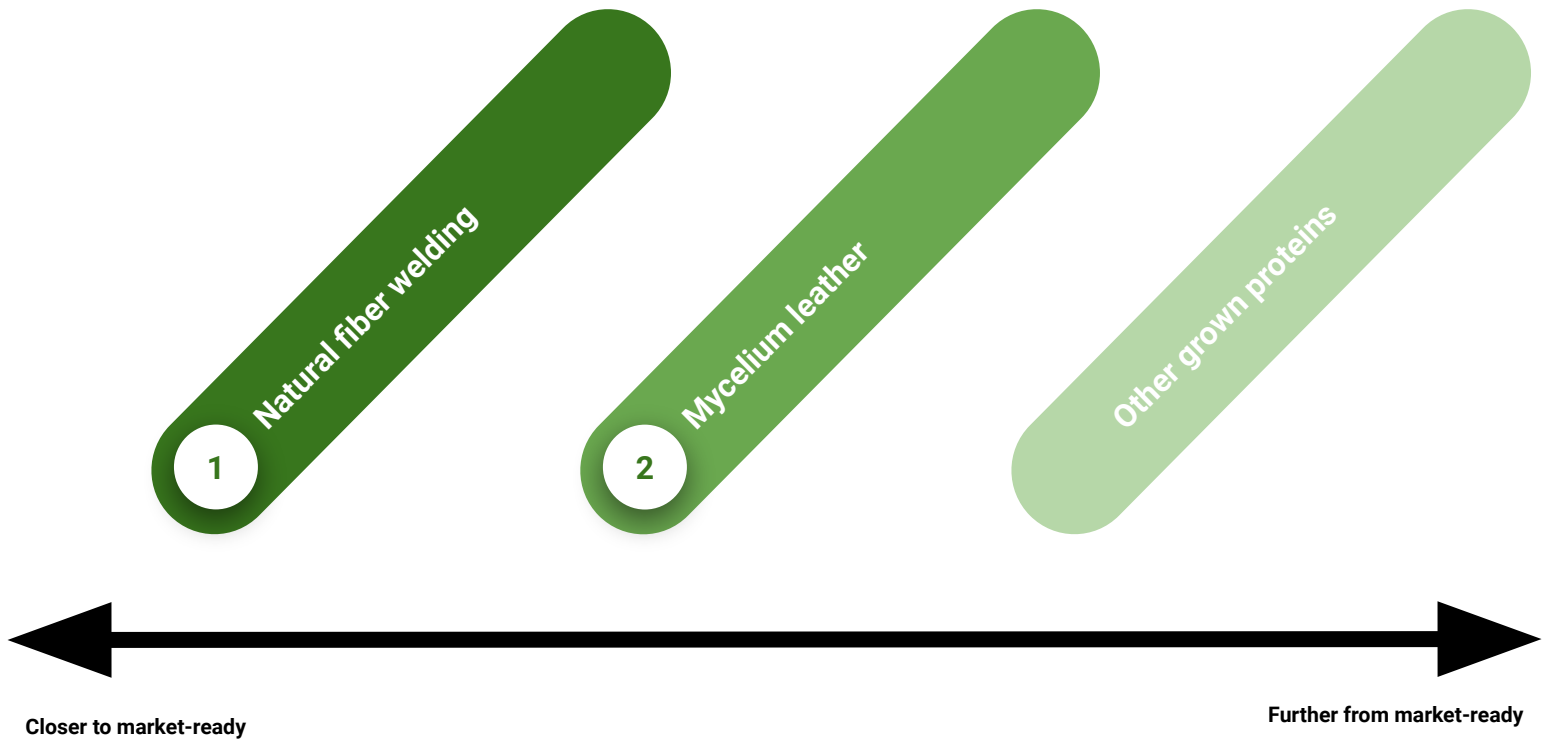
Alternative Backbone Chemistry

- Diisocyanates drive the need for aggressive solvent like DMF
- Replacing the isocyanates → No DMF
- Further investigation into PU chemistry and polymerization



Common PU used in textiles





Mushroom leather

- Mycelium: the vegetative tissue of fungi, grow into fibrous networks
- Feedstock: agricultural waste



Mycoworks, 2016

Potential improvements

- Eliminates harmful chemicals
- Carbon neutral
- 100% biodegradable
- As strong as conventional leather

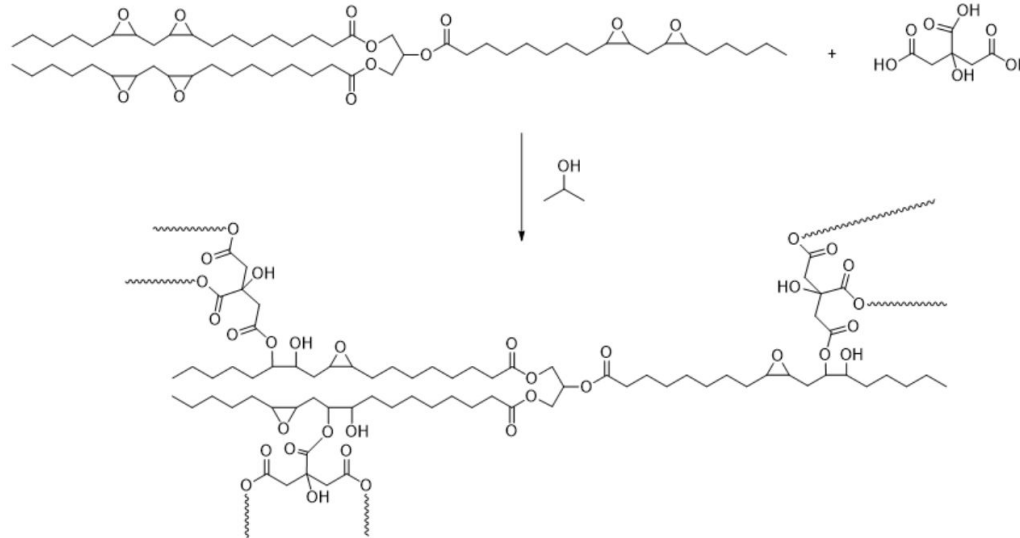
Potential concerns

- Cost
- Material grown in 2 weeks
- Other chemicals?



Natural Fiber Welding

- Crosslinking epoxidized natural oils with citric acid in alcohol solvent
- Short processing times (minutes)
- Appearance and physical properties similar to natural leather



Hazard Profile of NFW Leather

- Raw and epoxidized soybean oil expected to be safe
- Avoid acetone cosolvent and nitrogen-containing catalysts if possible

Name	C/M/R	Systemic	Irritation	Acute	Neurotoxicity	Aquatic	P/B
Soybean oil	L	L		L			L
Epoxidized soybean oil	L	L	L	L		L	L
Citric acid	L	L	L	L		L	L
Ethanol	L	L	L	L	L	L	L
n-Butanol	L	L	H	M	L	L	L
Isopropanol	L	L	H	L	M	L	L
Acetone	L	L	H	L	L	L	L
Quinoline	H	pC	H	M	L	M	L



FUTURE FORWARD



Next steps for process or material change

Confirm supplier claims

- Material Performance
- Hazard
- Feasibility

Pair with CO2 dying

Recommendations

- Many options presents as an improvement on hazards compared to current DMF-PU process
- Most appealing base on timeline:
 - PU Dispersion
 - Natural Fiber Welding
- Reframe marketing strategy
 - pilot limited edition series using new material (“Mushroom Air Max”)



Natural Fiber Welding, Inc., 2019





Background



Approaches



Drop-in Solvent

- Design criteria
- Recommended list
- Next steps



Process & Material
Change

- Process change
- Material Change
- Next steps



Discussion

The Nike Challenge: Alternatives to DMF-PU Synthetic Leather

Annie LaBine, Isaac Ramphal, Kimberly Hazard, Stephanie Ng & Surui Zhang
Greener Solutions: A Safer Design Partnership | Fall 2019

Overall, solutions are improvements over DMF-PU



**Recommended
drop-in
candidates**



**Natural
Fiber
Welding**



**PU
dispersion**

Broader impacts:

- Shift in the fashion and footwear industry
- Creates precedent for biodegradable synthetic fabrics
 - Impacts for global DMF use

FUTURE FORWARD

A photograph of a retail store window display. The background is a dark, perforated metal wall. Large, white, three-dimensional block letters spell out 'FUTURE FORWARD'. Below the text, several pairs of sneakers are arranged on a dark surface. The sneakers are in various colors, including white, brown, and blue. The lighting is dramatic, with bright spots and shadows.

Thank you for listening!

Special thanks to:
Meg Schwarzman
Thomas Mckeag
Billy Hart-Cooper
Renee Hackenmiller-Paradis
SLA Team
David Faulkner