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
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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
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)

With permission from Nike
DMF is inherently hazardous to human health

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

International Agency for Research on Cancer

World Health Organization

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

Workers are exposed to DMF

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

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He et al., 2010, CDC, 2014, IARC, 2018
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
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Places to intervene in the system

- Radical Swoosh
- Radical Material Change (Trino™)
- Material Change - Artificial Leather
- Process Change
- Drop-in Replacement
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
Framing the hazard assessment

- Authoritative lists (e.g. REACH)
- Broad literature searches
- Physical properties
- Modeling/metabolites

**Ranking tools:**
- Globally Harmonized System (GHS) categories
- GreenScreen
- Hodge-Sterner
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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

- Dissolve PU
- Good physical properties
- Improved health & environmental performance

Our Solution
Three categories of drop-in solvents

Solid-Phase Peptide Synthesis (SPPS)

Bio-Based Feedstock

Candidate List
  Recommendations

Other

Supalerk Iaipawat, 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)

Solid-Phase Peptide Synthesis
- 2-methyl tetrahydrofuran (2MTHF)
- 2-methyl furan (2MF)
- Cyclopentyl methyl ether (CPME)
- Ethylene carbonate (EC)
- Propylene carbonate (PC)

Bio-Based Renewables
- Dihydrolevoglucosenone (Cyrene)
- γ-valerolactone (GVL)
- Dimethyl isosorbide (DMI)
- 2,5-dimethyl tetrahydrofuran (DMTHF)
- Methyl levulinate (ML)
- Ethyl levulinate (EL)
- Ethyl levulinate propylene glycol ketal (ELPK)
- Dimethyl glutarate (DMG)

Other
- Dimethylpropylene urea (DMPU)
- Poly(propylene glycol) (PPG)
- Glycofurul (THFP)
- 1-ethyl-3-methylimidazolium acetate [emim][OAc]
- Water
<table>
<thead>
<tr>
<th>Category</th>
<th>Criteria</th>
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<tbody>
<tr>
<td>Good physical properties</td>
<td>Water solubility</td>
</tr>
<tr>
<td></td>
<td>Low vapor pressure</td>
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<tr>
<td>Dissolve PU</td>
<td>Hansen solubility parameters</td>
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<tr>
<td>Health and environmental</td>
<td>Compile hazard data</td>
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<td></td>
<td>Rank hazard data</td>
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<tr>
<td>Literature</td>
<td>Relating to replacement of DMF</td>
</tr>
</tbody>
</table>
Narrowing through physical properties

- Low vapor pressure/high boiling point
- Water solubility (to wash out)
Narrowing through physical properties

Traditional Polar Aprotics (for comparison)
- N,N-dimethyl formamide (DMF)
- N,N-dimethyl acetamide (DMAc)
- N-methyl formamide (NMF)
- Dimethyl sulfoxide (DMSO)
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- Dimethyl isosorbide (DMI)
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Other
- Dimethylpropylene urea (DMPU)
- Polypelargylic acid (PPG)
- Glycofurol (THF)
- 1-ethyl-3-methylimidazolium acetate ([emim][OAc])

Water
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

The graph shows the relationship between ∆PU (MPa^{1/2}) and ∆DMF (MPa^{1/2}). The graph includes different categories such as DMF, Traditional Polar Aprotics, Bio-Based, SPPS, and Other, each represented by different colored markers. The data points are scattered across the graph, indicating variability in solubility within each category.
Narrowing through PU solvation

Traditional Polar Aprotics (for comparison)
- N,N-dimethyl formamide (DMF)
- N,N-dimethyl acetamide (DMAc)
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- Water
- Glycofurol (THF)
- 1-ethyl-3-methylimidazolium acetate (emim)[OAc]
Short list: our recommendations

- Bio-based
  - Cyrene
  - GVL
  - DMI
- SPPS
  - cPME
- Other
  - Glycofurol
### Evaluation of health and environmental performance of short list

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

<table>
<thead>
<tr>
<th>Solvent</th>
<th>C/M/R</th>
<th>Systemic</th>
<th>Irritation</th>
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<th>Aquatic</th>
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<table>
<thead>
<tr>
<th>L: Low</th>
<th>M: Moderate</th>
<th>H: High</th>
<th>pC: potential concern</th>
<th>Data Gap</th>
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</table>

Legend:
- C/M/R: Combined/Modulated/Reversed
- L, M, H: Low, Moderate, High
- pC: Potential Concern
- Data Gap
Cyrene™ (Dihydrolevogluicosenone)

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

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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

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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

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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

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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

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# Short list hazard table

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- **Data Gap**
Next steps for drop-ins

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

![Graph: Global Aqueous Polyurethane Dispersions Market, 2014 - 2020 (Kilo Tons) (USD Million)]

Source: Zion Research Analysis 2015
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
1. Natural fiber welding
2. Mycellium leather
Other grown proteins

Closer to market-ready
Further from market-ready
Mushroom leather

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

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

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</table>
Next steps for process or material change

Confirm supplier claims
- Material Performance
- Hazard
- Feasibility

Pair with CO2 dying
Recommendations

- Many options present as an improvement on hazards compared to current DMF-PU process
- Most appealing based on timeline:
  - PU Dispersion
  - Natural Fiber Welding
- Reframe marketing strategy
  - Pilot limited edition series using new material ("Mushroom Air Max")
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Overall, solutions are improvements over DMF-PU

Broader impacts:
- Shift in the fashion and footwear industry
- Creates precedent for biodegradable synthetic fabrics
- Impacts for global DMF use
Thank you for listening!

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