Greener Solutions:

SLA 3D Printing Resin for Autodesk

December 8th, 2015

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CONTEXT

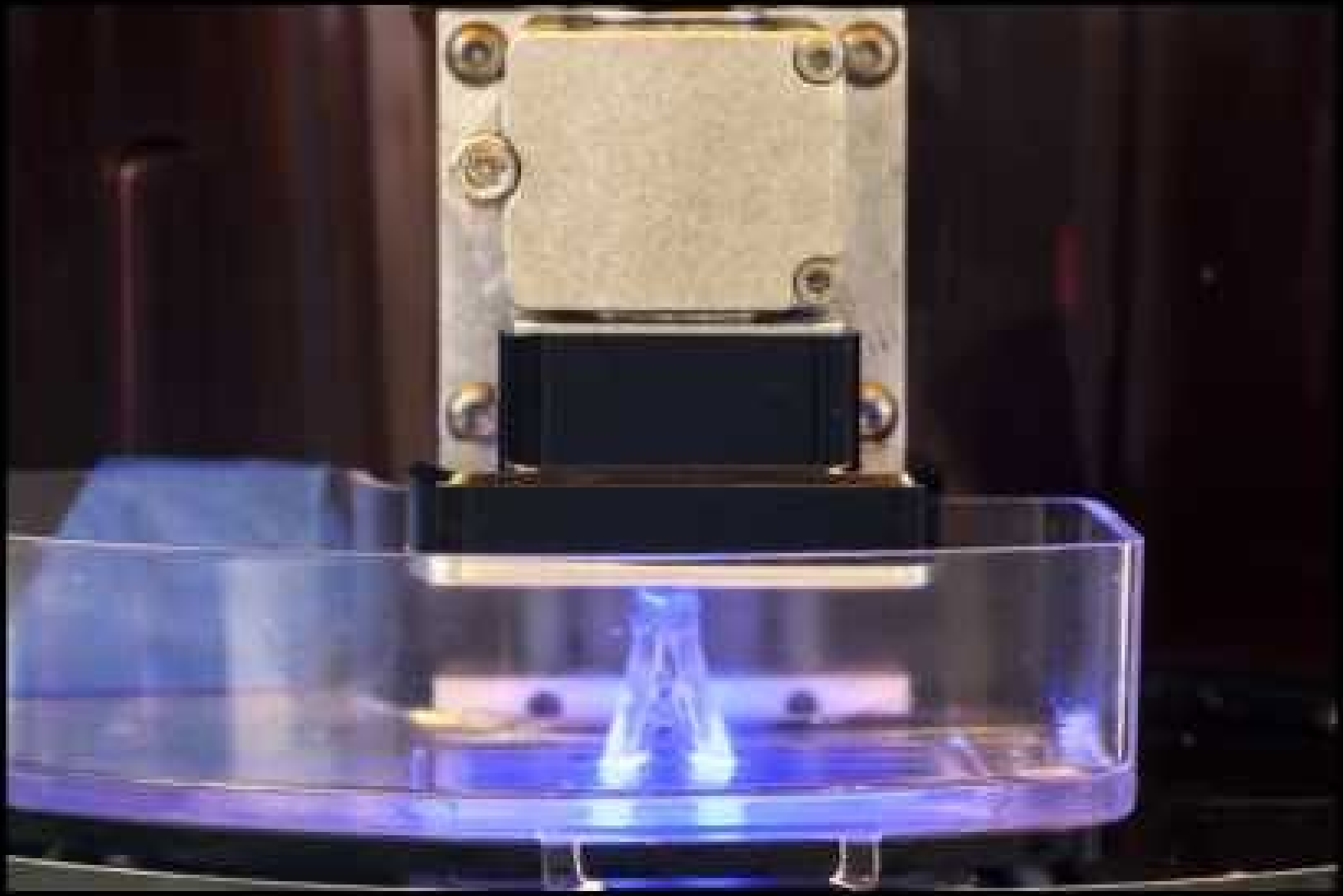
METHODS

ALTERNATIVES

EVALUATION

CONCLUSIONS

CONTEXT



Photoinitiator

(0.4%)

Reactive Oligomers

(79.55%)

Reactive Monomer

(19.88%)

UV-blocker

(0.16%)

Reproductive toxicant

Eye irritant

Skin irritant

Aquatic toxicant

Skin sensitizer

Explore and evaluate biomimetic, green chemistry, and life-cycle solutions for less hazardous stereolithography (SLA) resins

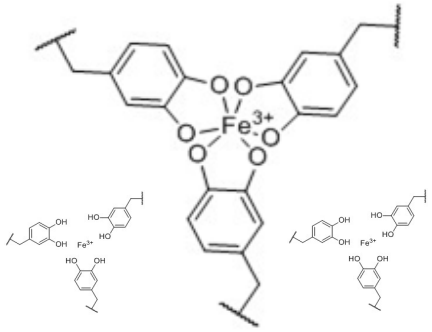
METHODS

Explore

Bio-inspired Approaches

Identify

Alternative Resin Materials



Evaluate

New Resin Materials

How Does Nature Inspire Design?


Unity within Diversity


Multitasking Monomers


The Optimal Activator


Shape is Strength


Taking Advantage of Gradients


Bottom-Up Construction


Hierarchy Across Linear Scales


Self Organization


Composite Construction


Functionally Graded Materials


Water is the Universal Medium

Martin Mulvihill, Justin Bours, Berkeley Center for Green Chemistry, and Tom McKeag, BioWerks (April 2015)

Evaluation Criteria

Technical Feasibility

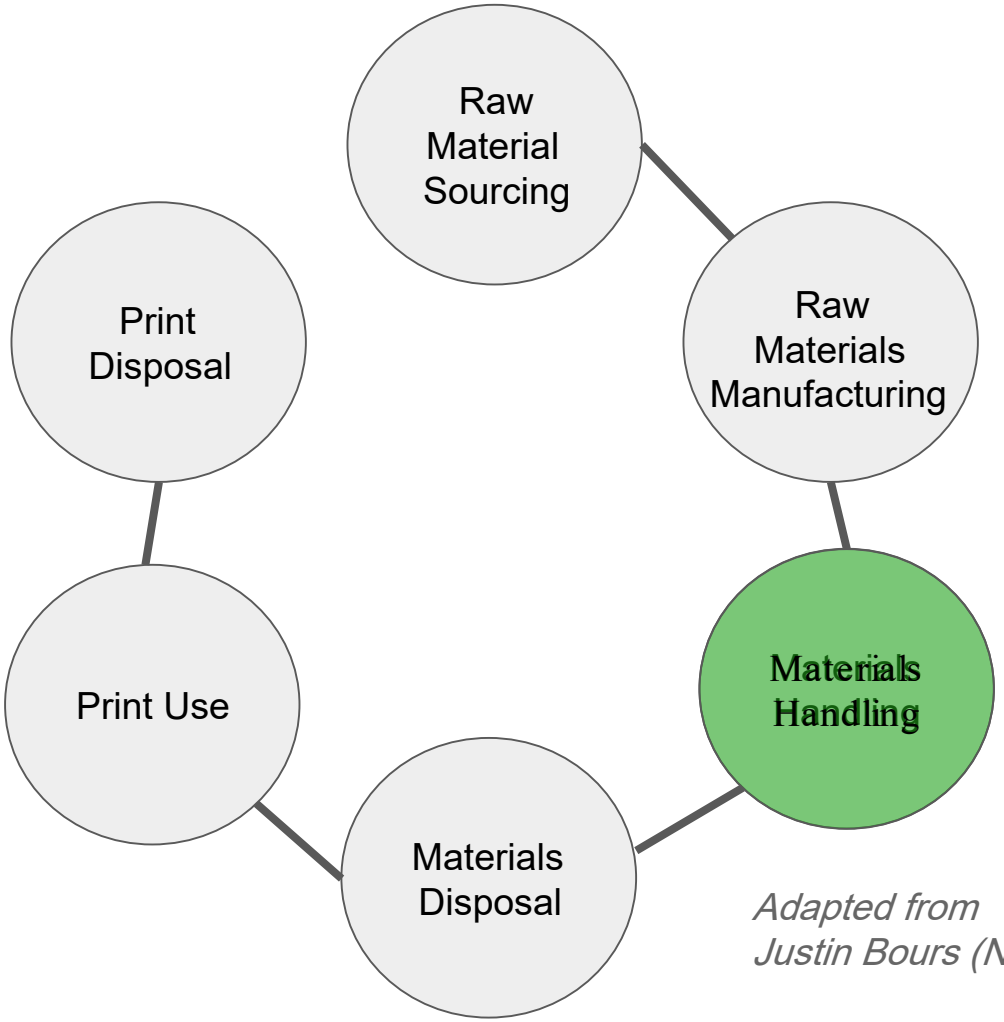
Hazard Potential

Use Cases

Technical Feasibility

	PR48 Resin
Strength	
Polymerizable	
Time	
Commercially available	
Price	

Hazard Potential



Adapted from Justin Bours (Nov 2015)

- Skin Sensitization
- Eye Irritation
- Skin Irritation
- Aquatic Toxicity
- Reproductive Toxicity

Use Cases

Current Use Cases

Experimental Use Cases

Biocompatibility

ALTERNATIVES

I. REPLACING THE PHOTOINITIATOR

Strategy A: Curcumin & Riboflavin

II. MODIFYING ACRYLATE-BASED RESINS

Strategy B: Triglycerides
Strategy C: Chitosan

III. pH PHOTOINITIATED RESINS

Strategy D: Calcite
Strategy E: Metal Ligand Complexes

1 Replacing the Photoinitiator

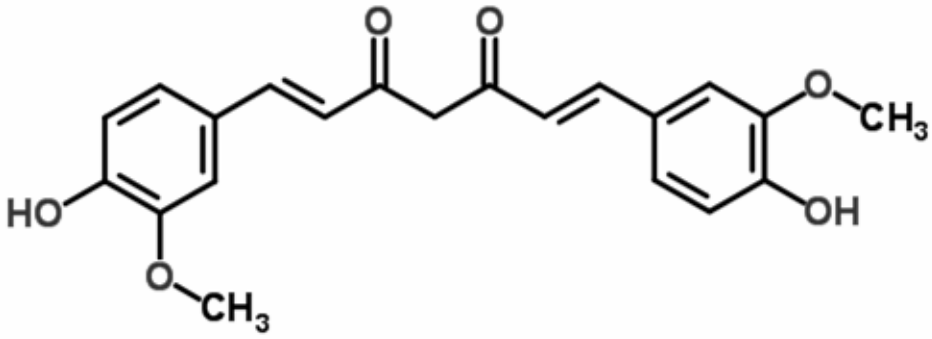
STRATEGY A: CURCUMIN & RIBOFLAVIN

STRATEGY A:
CURCUMIN & RIBOFLAVIN

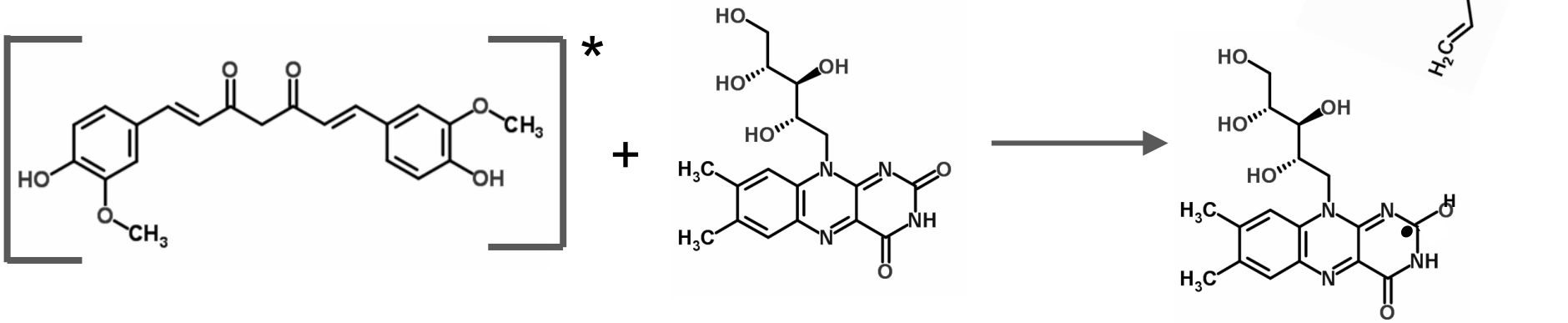
The Optimal Activator

BIOLOGICAL INSPIRATION

STRATEGY A:
CURCUMIN & RIBOFLAVIN



405 nm



STRATEGY A:
CURCUMIN & RIBOFLAVIN

Hazard Endpoints	Current Photoinitiator	Curcumin	Riboflavin (B2)
Skin Irritation	●	●	●
Eye Irritation	●	●	●
Aquatic Toxicity	●	●	●
Reproductive Toxicity	●	●	●

KEY: ● *Significant Data Gap* ● *Identified Hazard* ● *Decreased Hazard*

STRATEGY A:
CURCUMIN & RIBOFLAVIN

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Modifying Acrylate-based Resins

STRATEGY B: TRIGLYCERIDES

STRATEGY C: CHITOSAN

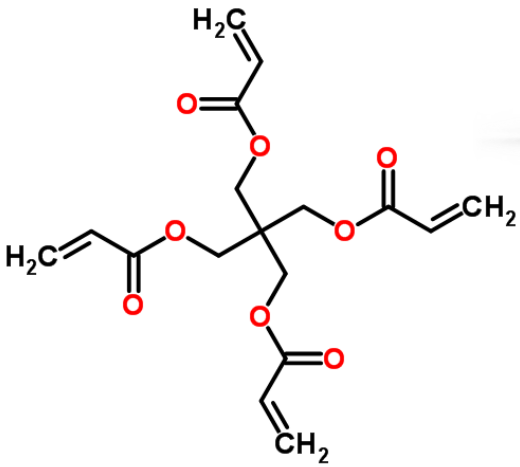
STRATEGY B: TRIGLYCERIDES

Unity within diversity

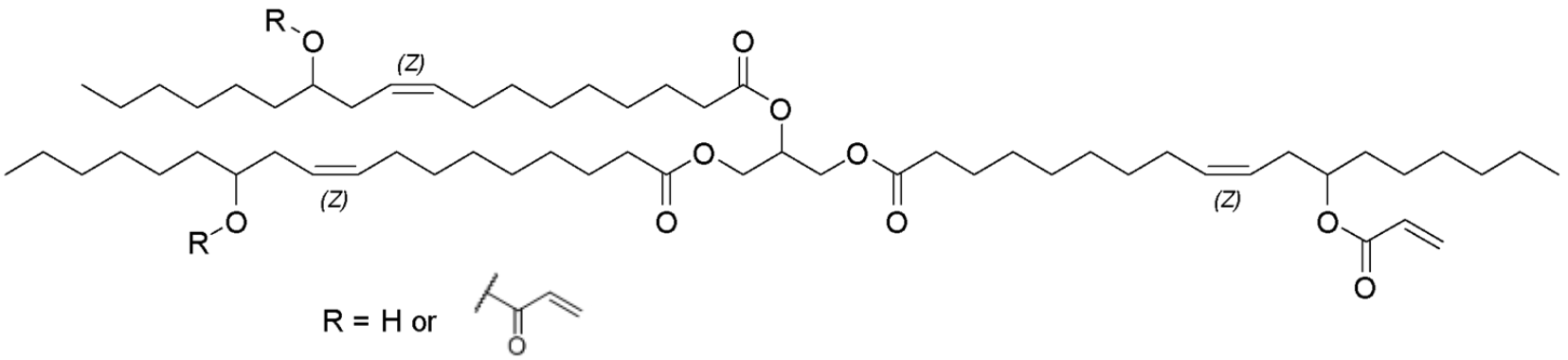
BIOLOGICAL INSPIRATION

STRATEGY B:
TRIGLYCERIDES

- Similar mechanism of polymerization
- Potentially reduced bioavailability and hazard due to the increase in the molecular weight

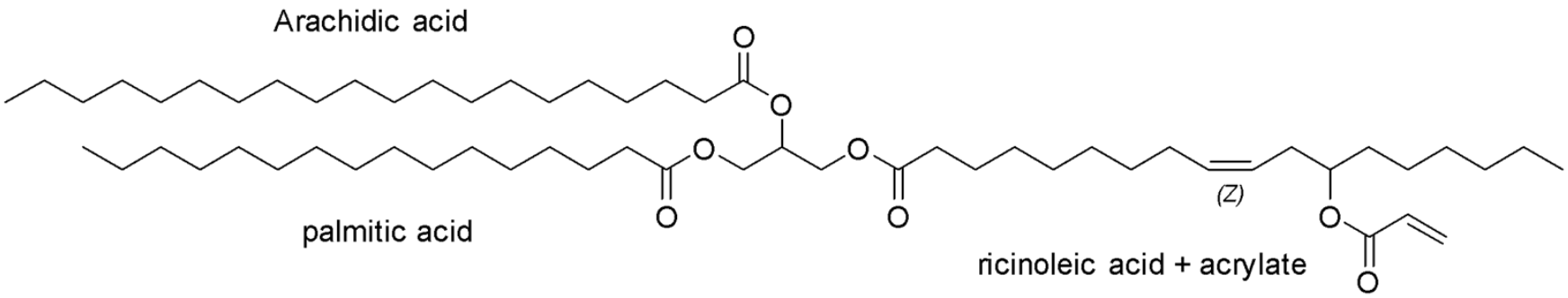


Sartomer SR 494



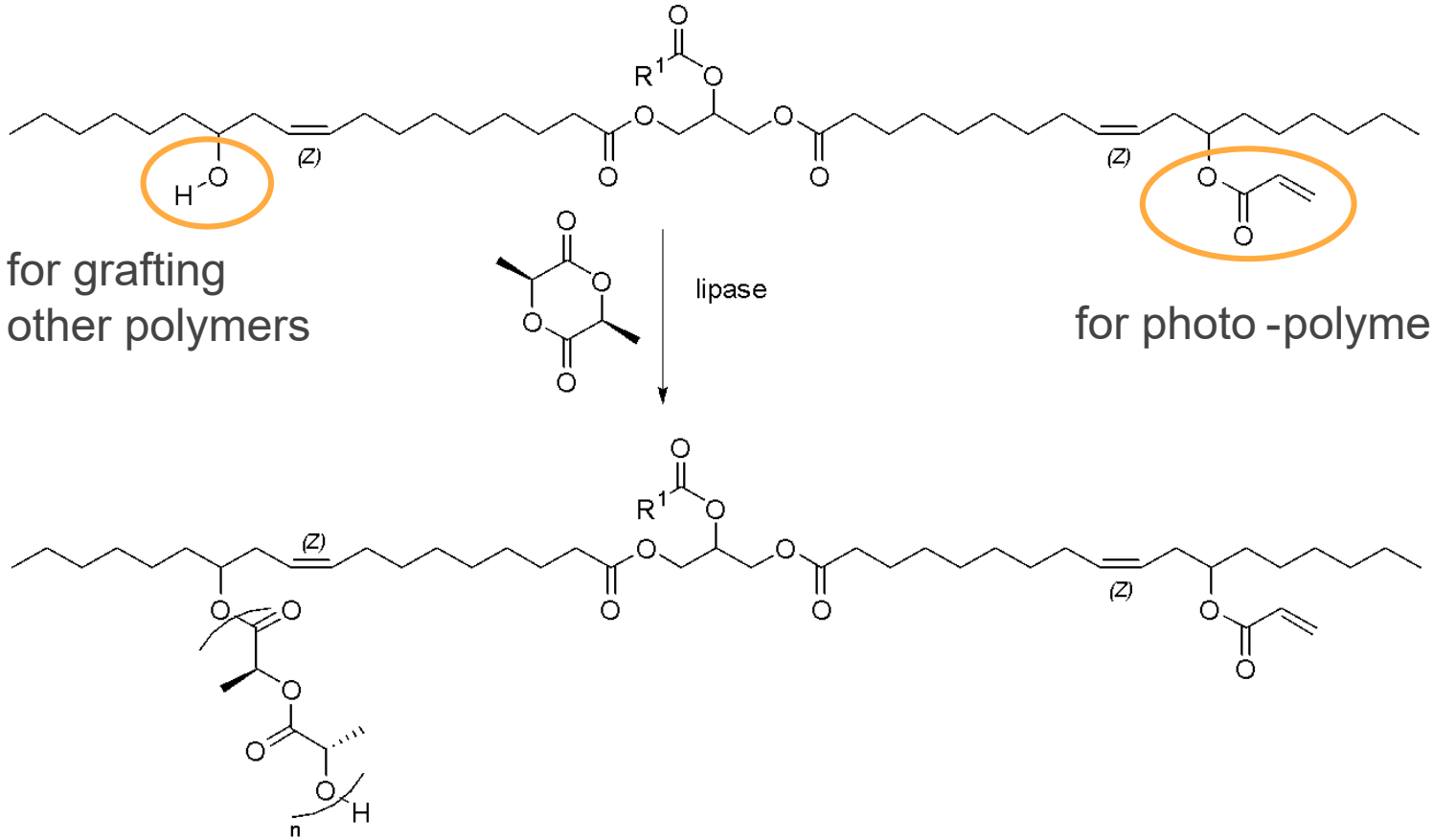
STRATEGY B:
TRIGLYCERIDES

- Tuning physical properties of the monomers by varying the fatty acid chains



STRATEGY B:
TRIGLYCERIDES

- Diversifying polymer architecture by grafting polymers from the fatty acid chains



STRATEGY B:
TRIGLYCERIDES

Hazard Endpoints	PR48 Resin	Triglyceride Acrylate
Eye Irritation	●	●
Skin Irritation	●	●
Aquatic Toxicity	●	●
Reproductive Toxicity	●	●

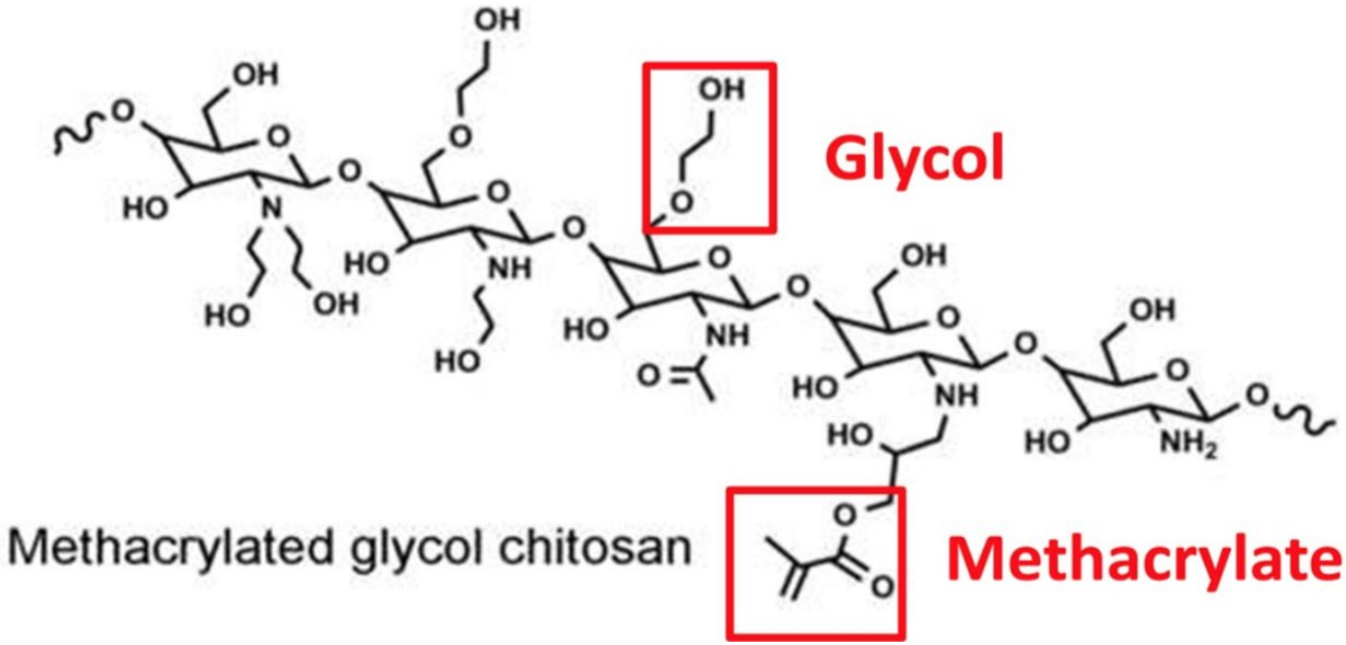
KEY: ● *Significant Data Gap* ● *Identified Hazard* ● *Decreased Hazard*

STRATEGY B: TRIGLYCERIDES

STRATEGY C: CHITOSAN

Self Organization

STRATEGY C:
CHITOSAN



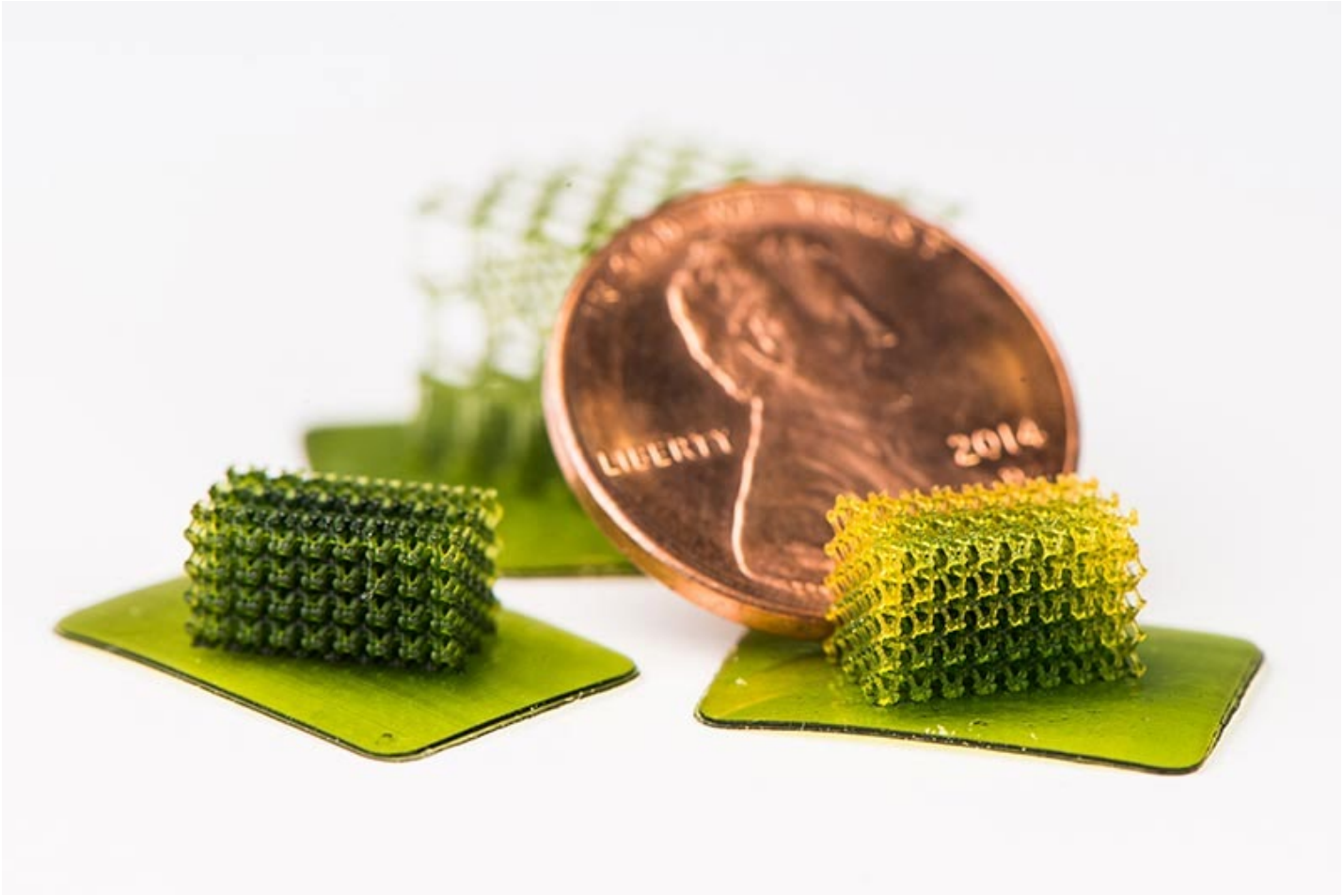
Arakawa et al. 2014

STRATEGY C: CHITOSAN

Hazard Endpoints	PR48 Resin	Methacrylate Glycol Chitosan
Eye irritation	●	●
Skin Irritation	●	●
Aquatic Toxicity	●	●
Reproductive Toxicity	●	●

KEY: ● *Decreased Data Gap* ● *Significant Hazard* ● *Identified Hazard*

STRATEGY C: CHITOSAN



Arakawa et al. 2014

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pH-Photoinitiated Resins

Strategy D: Calcite

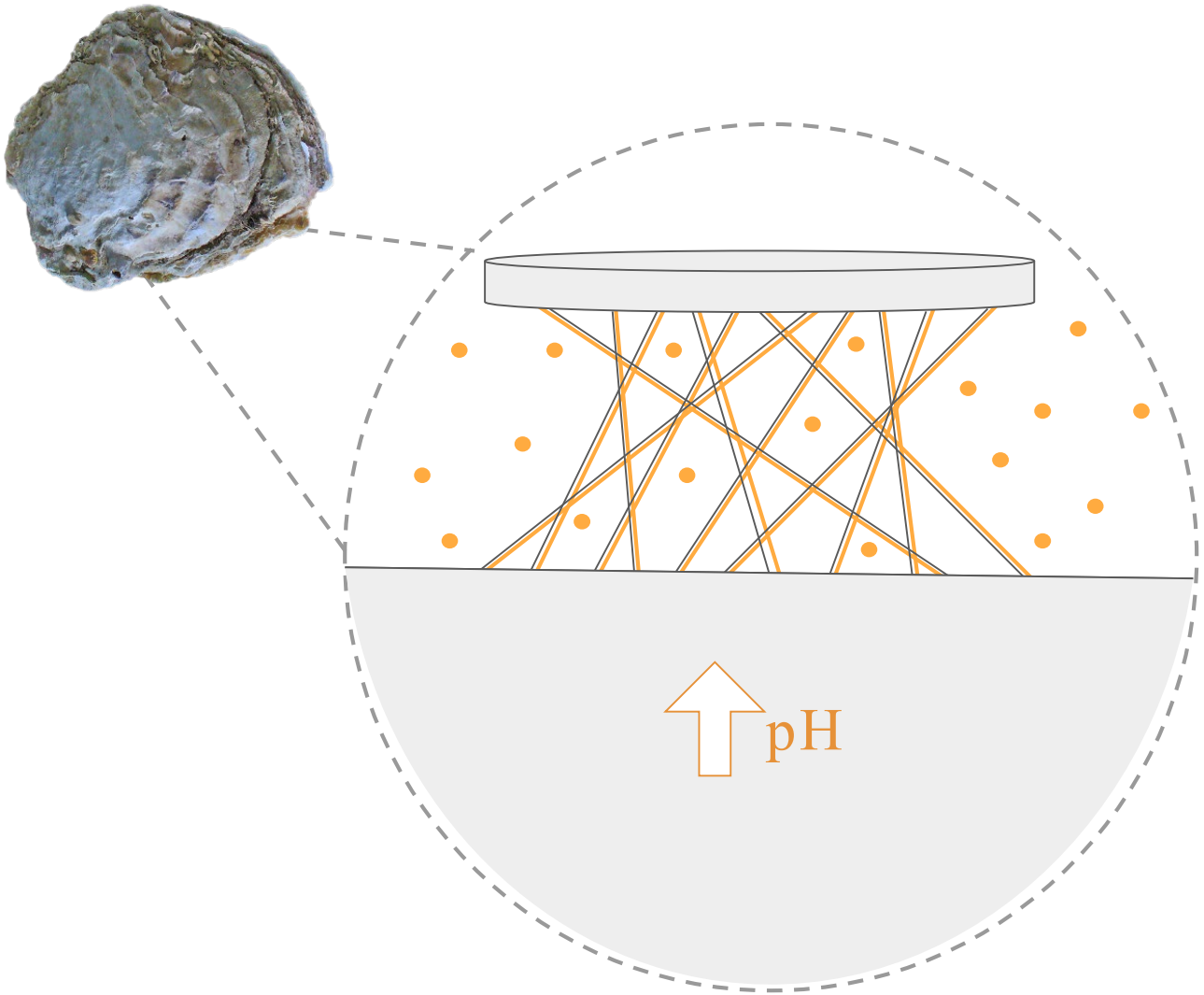
Strategy E: Metal-catechol complexes

Strategy D:
Calcite

Taking Advantage of Gradients

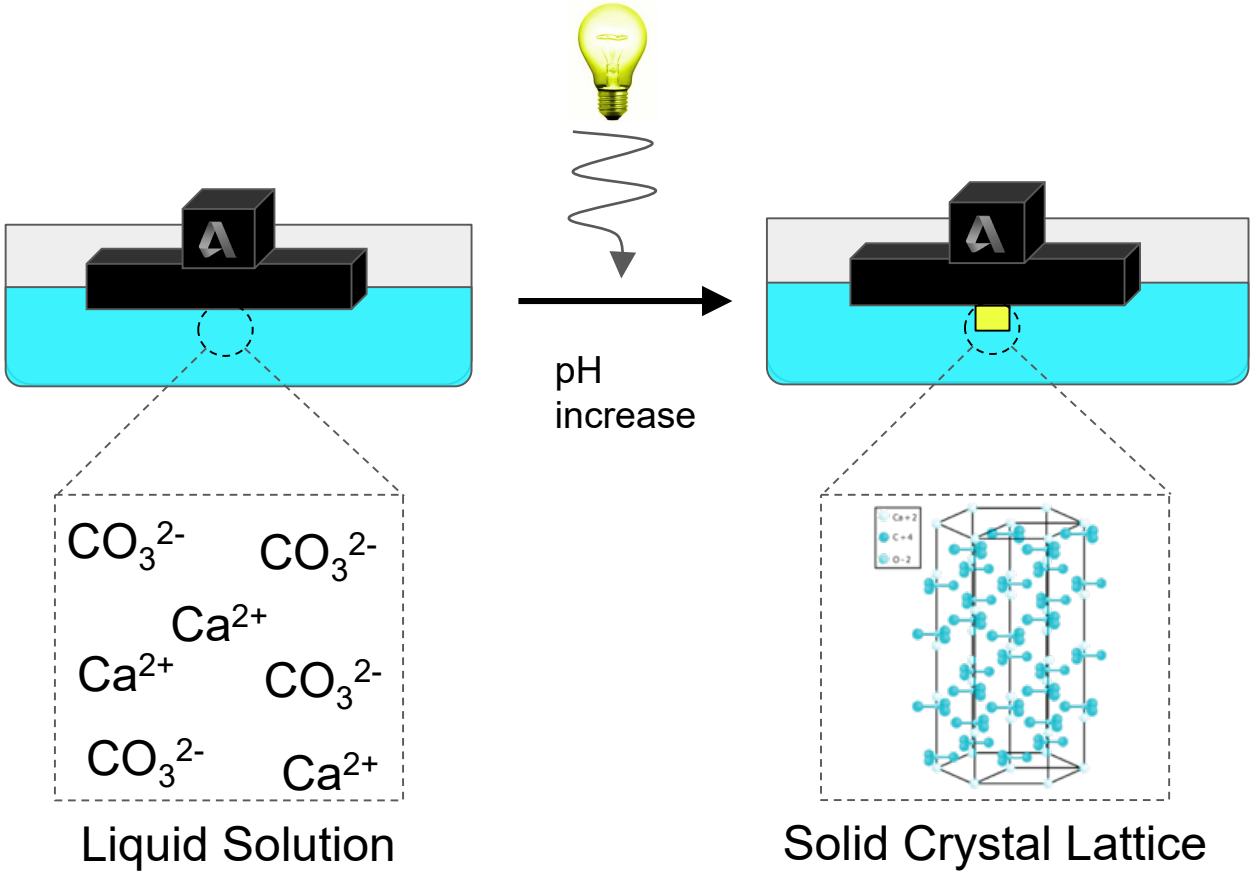
BIOLOGICAL INSPIRATION

Strategy D:
Calcite



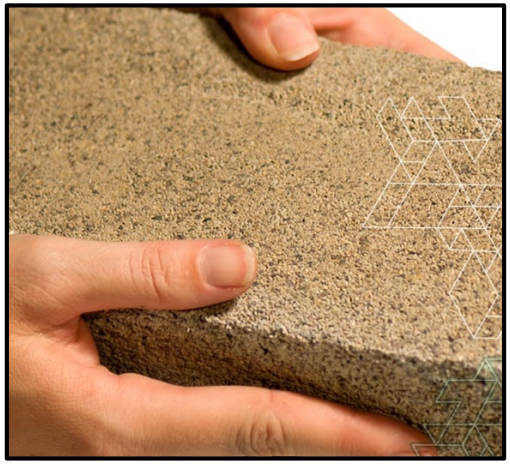
Strategy D:
Calcite

Can we pattern a liquid to solid using pH?



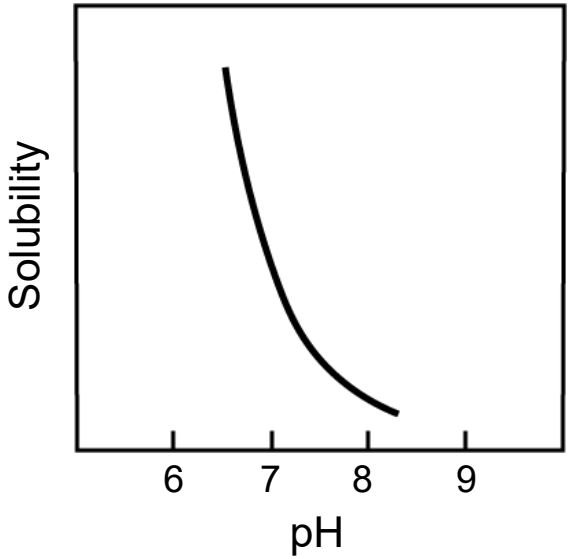
Strategy D:
Calcite

INITIATION

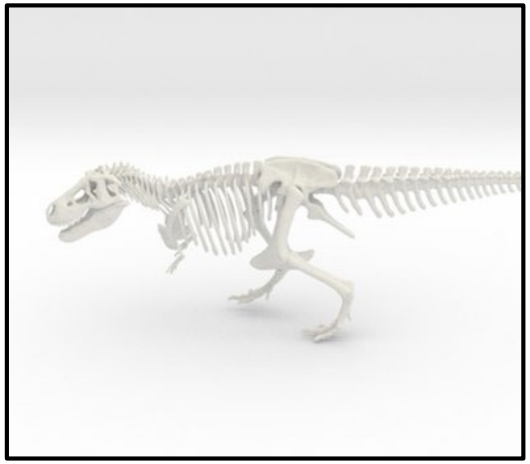


BIOMason Brick

PROPAGATION



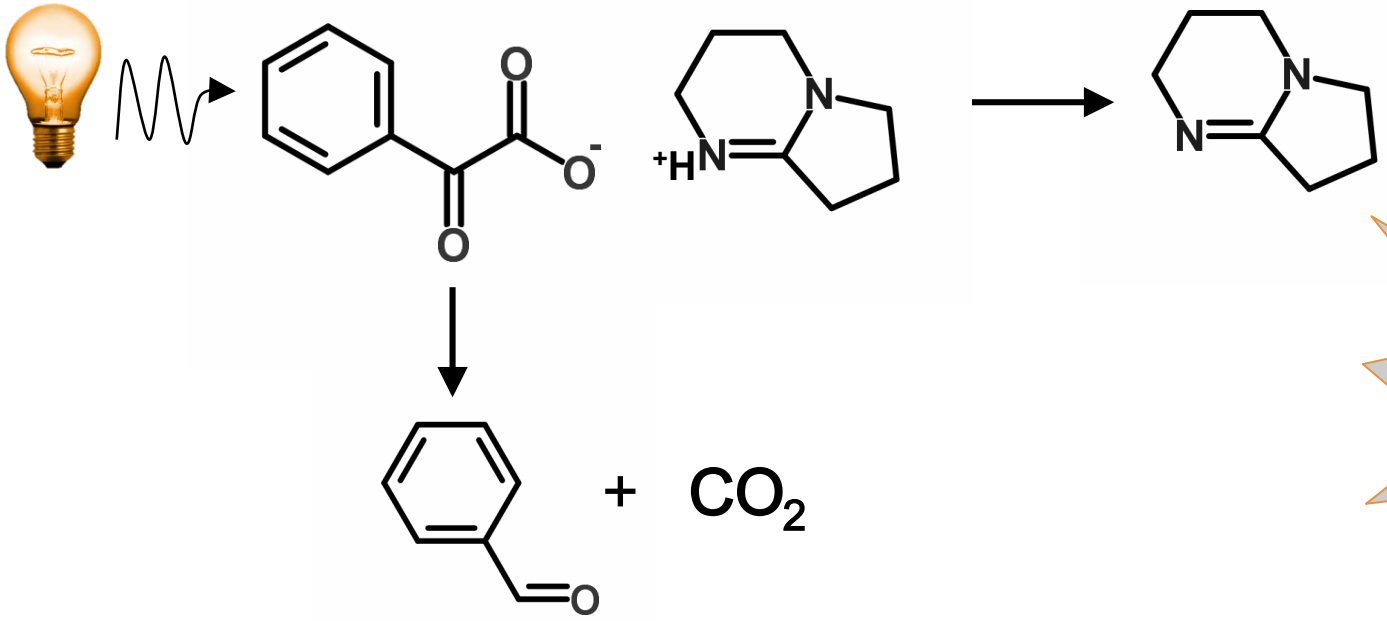
TERMINATION



Shapeways TREX

Strategy D:
Calcite

Photo Base Generator (PBG)



pH
INCREASE

Salmi et al. (2014)

Strategy D: Calcite

Hazard Endpoints	PR48 Resin	Calcite	PBG
Eye irritation	●	●	●
Skin Irritation	●	●	●
Aquatic Toxicity	●	●	●
Reproductive Toxicity	●	●	●

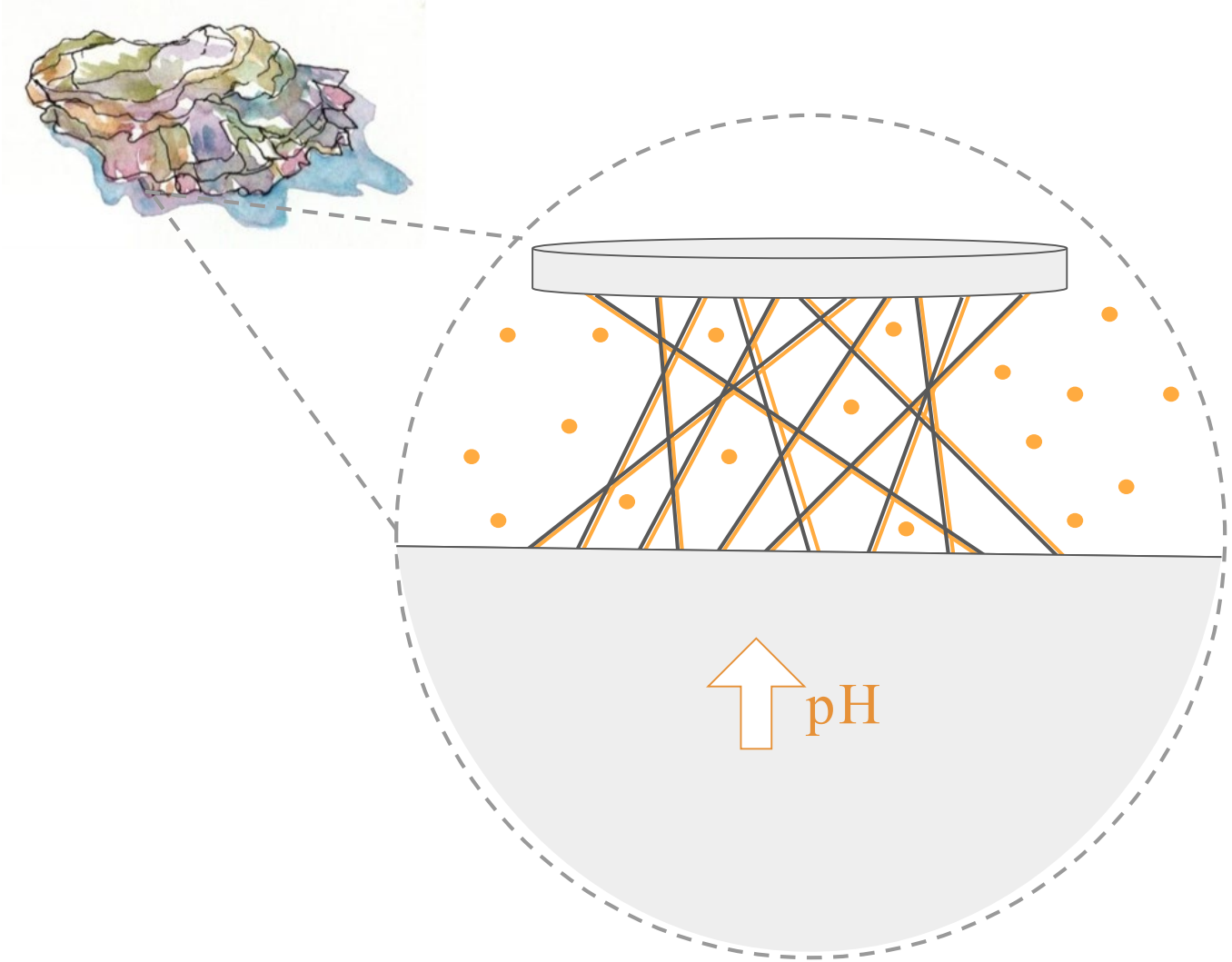
KEY: ● *Significant Data Gap* ● *Increased Hazard* ● *Decreased Hazard*

Strategy D:
Calcite

Strategy D & E:

Calcite (PBGs)

Calcium Alginate (PAGs)



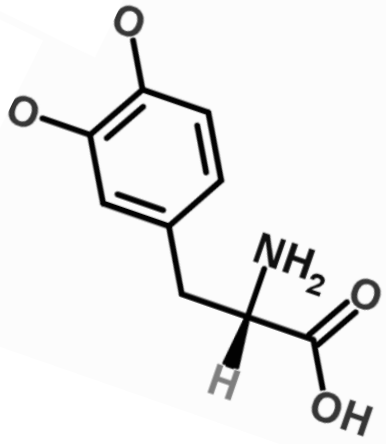
PATTERN WITH PH

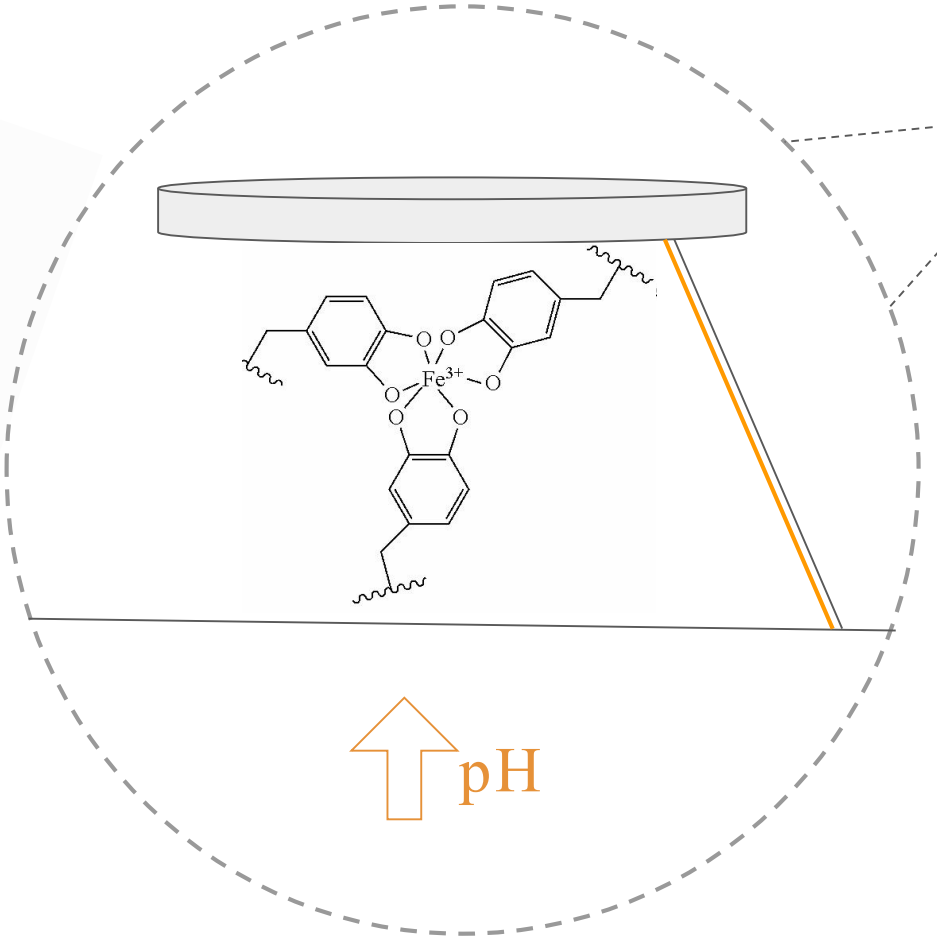
BIOLOGICAL MATERIALS

HARD & SOFT COMPOSITES


Strategy E:
Metal-Catechol Complex
BIOLOGICAL INSPIRATION
Functionally Graded Materials

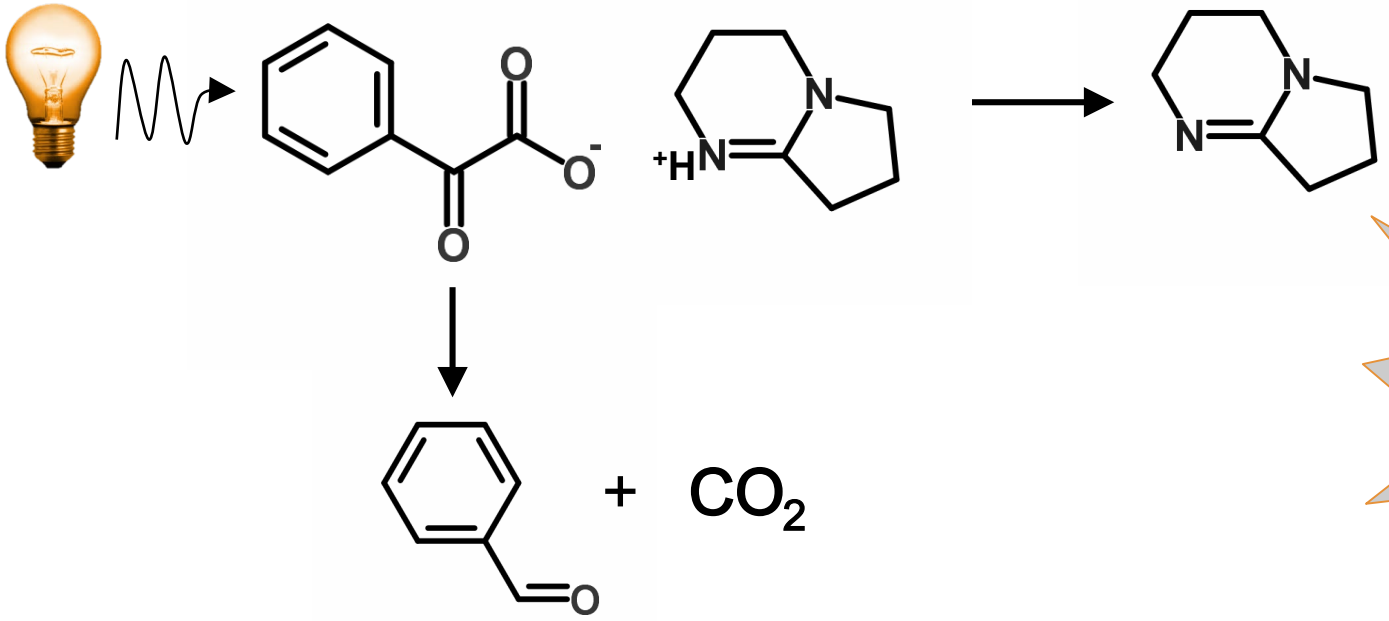
Strategy E:
Metal-Catechol Complex





Strategy E:
Metal-Catechol Complex

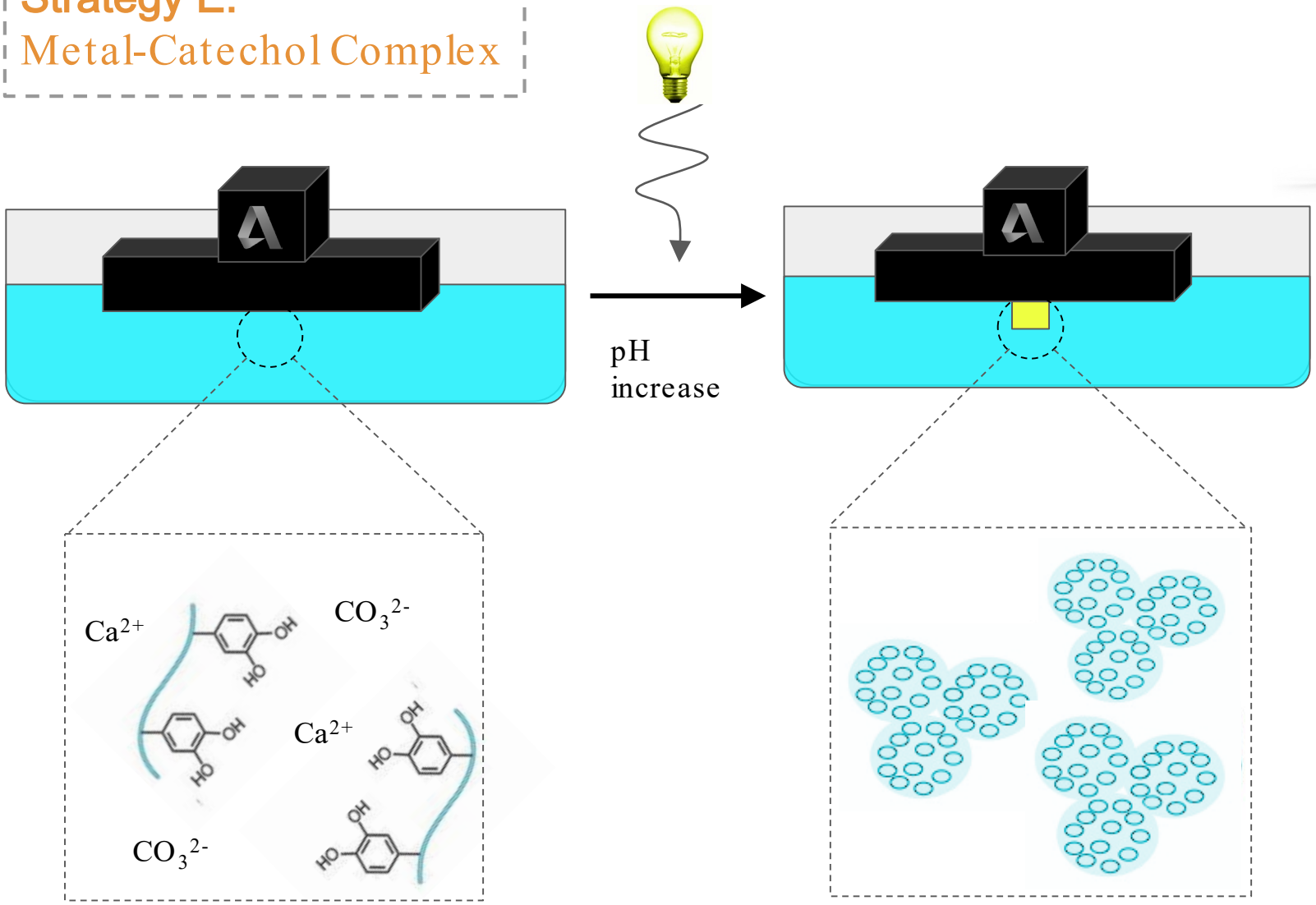
Photo Base Generator (PBG)



pH
INCREASE

Salmi et al. (2014)

Strategy E:
Metal-Catechol Complex

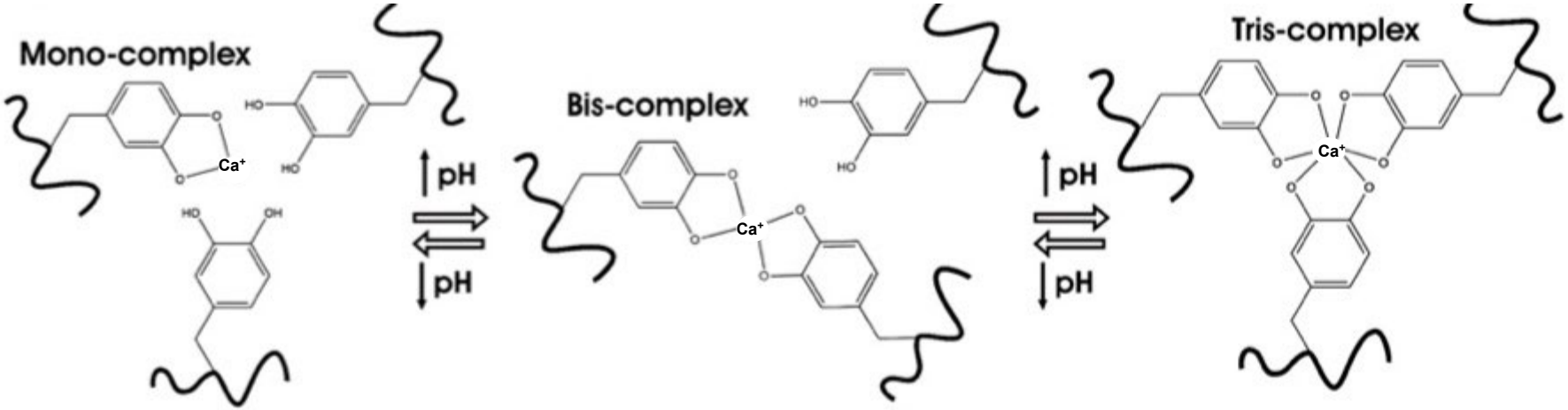


Liquid Resin

Crosslinked matrix

Stewart et al. (2004)

Strategy E:
Metal-Catechol Complex



Functionally graded materials

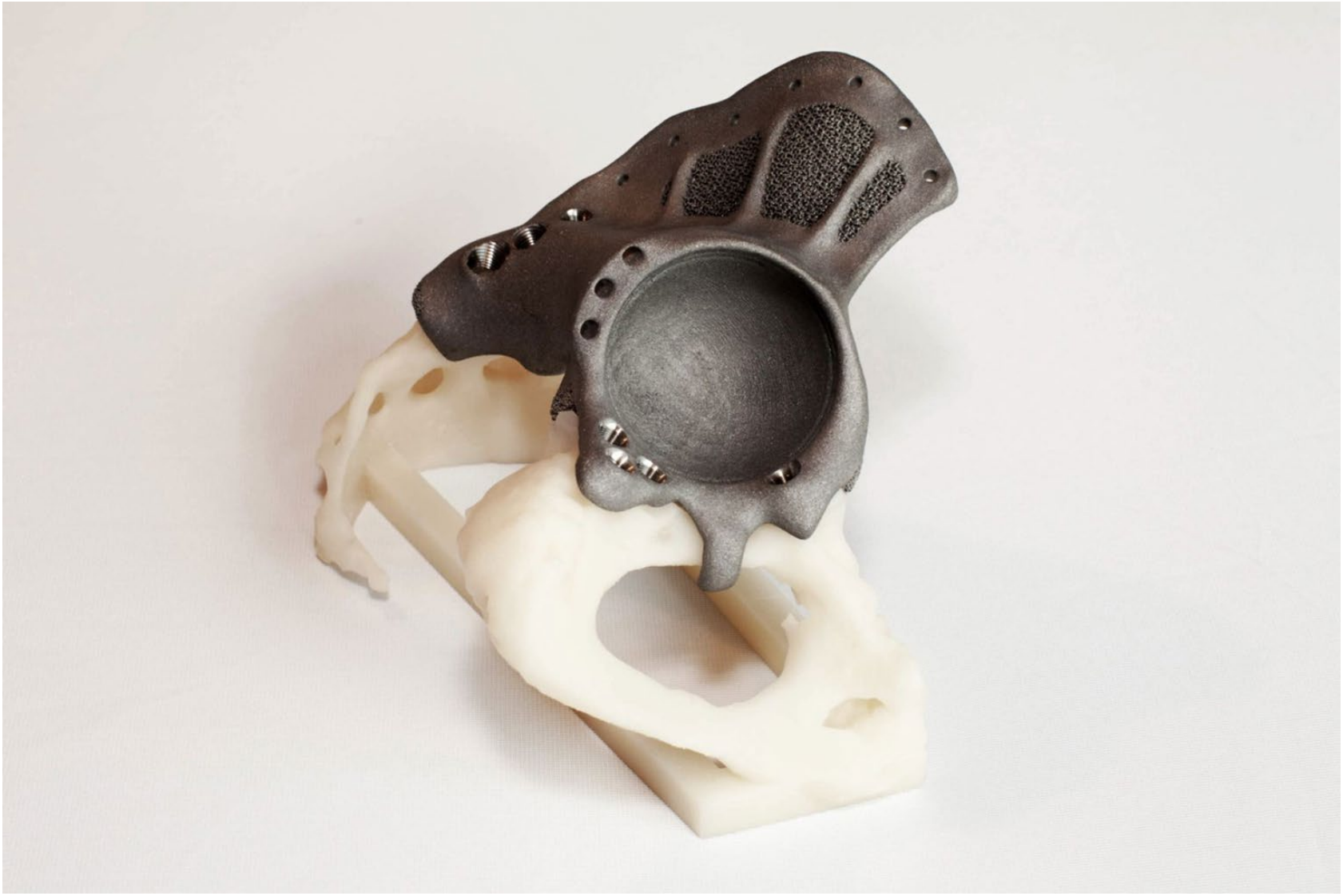
Holten-Andersen et al. (2004)

Strategy E:
Metal-Catechol Complex

Hazard Endpoints	PR48 Resin	Metal Ligand Complex	PBG
Eye Irritation	●	●	●
Skin Irritation	●	●	●
Aquatic Toxicity	●	●	●
Reproductive Toxicity	●	●	●

KEY: ● *Significant Data Gap* ● *Identified Hazard* ● *Decreased Hazard*

Strategy E:
Metal-Catechol Complex



Alternatives

I. REPLACING THE PHOTOINITIATOR

Strategy A: Curcumin & Riboflavin

II. MODIFYING ACRYLATE BASED RESINS

Strategy B: Triglycerides

Strategy C: Chitosan

III. NON-ACRYLATE RESINS via pH PHOTOINITIATION

Strategy D: Calcite

Strategy E: Metal Ligand Complexes

EVALUATION

Technical Feasibility

Hazard Potential

Use Cases

Technical Feasibility Comparison

Strategy	A: New Photo-initiators	B: Triglyceride acrylates	C: Glycol Chitosan acrylates	D: Calcite Resin	E: Metal-ligand complex
Mechanical properties	✓	?	✓	+	+
Initiation, propagation, termination	? ✓ ✓	✓ ✓ ✓	✓ ✓ ✓	? ✓ ?	✓ ✓ ?
Resolution	✓	✓	✓	✓	✓
Commercially availability	✓	✓	+	✓ –	–
Price	+	✓	–	?	?

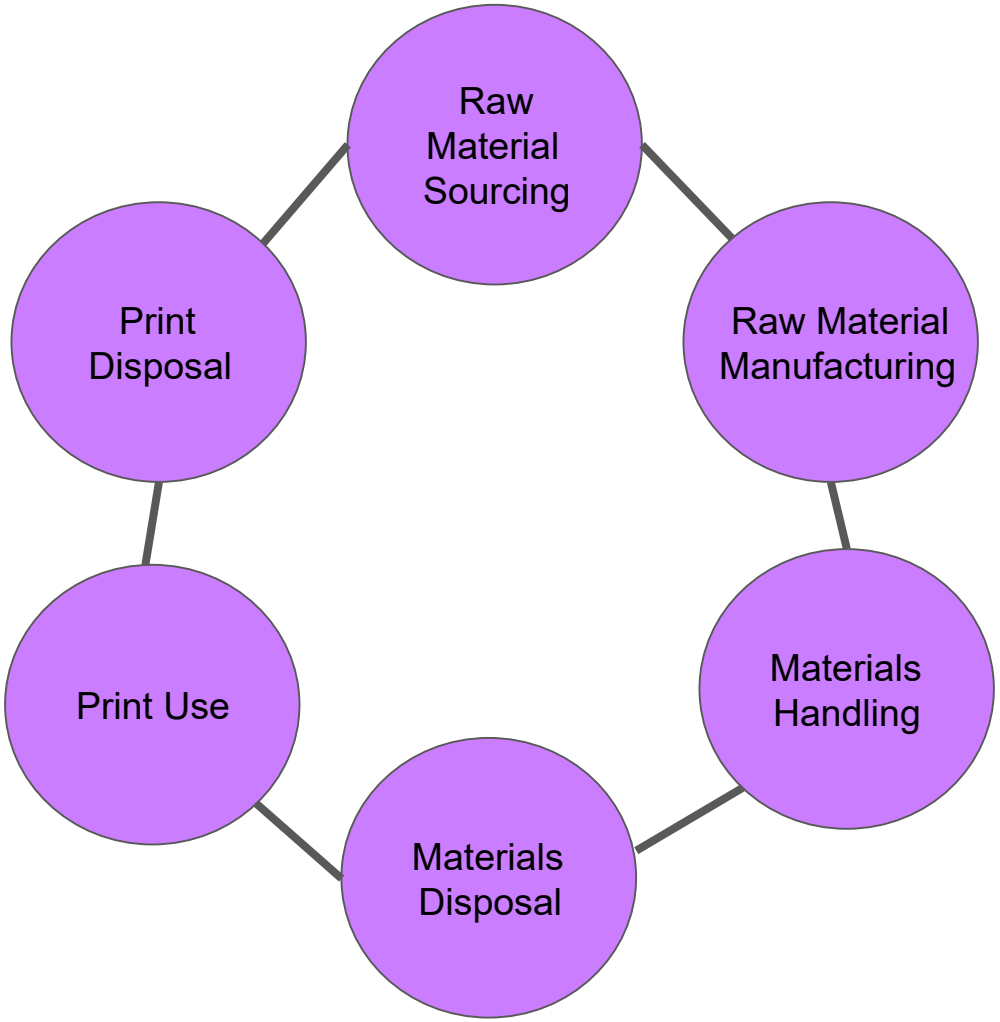
KEY: ✓ *Feasible* + *Improvement* – *Drawback* ? *Uncertain*

Material Hazard Comparison

Strategy	A: New Photo-initiators	B: Triglyceride acrylates	C: Glycol Chitosan acrylates	D: Calcite Resin	E: Metal-ligand complex
Skin sensitization	●	●	●	●	●
Eye Irritation	●	●	●	●	●
Skin Irritation	●	●	●	●	●
Aquatic Toxicity	●	●	●	●	●
Reproductive Toxicity	●	●	●	●	●

KEY: ● *Data Gaps* ● *Identified Hazard* ● *Decreased Hazard*

Future Hazard Considerations

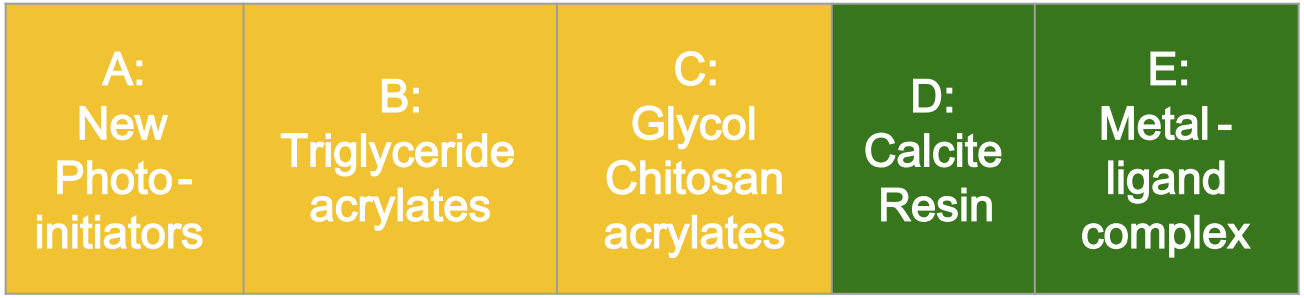


Hazard Level

Evaluation Confidence

Adapted from Justin Bours (Nov 2015)

CONCLUSIONS



Incremental → Breakthrough

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Questions?

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