Use of Agricultural and Forestry Products in Thermosetting Polymers

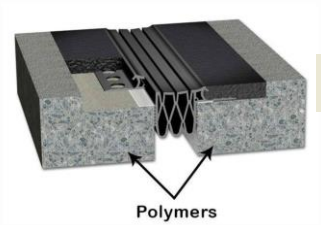
Dean C. Webster
Coatings and Polymeric Materials
North Dakota State University
Fargo, North Dakota, USA

U.S. DEPARTMENT OF ENERGY
arpa·e
CHANGING WHAT'S POSSIBLE

Carbon Negative Building Materials Workshop
March 23 and 25, 2021

Polymers and Resins in Building Construction

Structural Foams, Composite Wood Prods.



Polymer Concrete

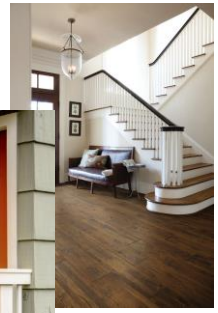
Pipes, tubing, plumbing ware

Synthetic Marble

Adhesives and Sealants

Paints and Coatings

Fire Retardant



Bio-based Material Initiatives

CSMS
CENTER FOR
SUSTAINABLE MATERIALS SCIENCE

Center for Bioplastics and Biocomposites

Team of 15 Researchers
- Chemistry
- Polymers
- Engineering

NSF Industry-University Cooperative Research Center (IUCRC)
~30 Member companies
Four Universities:

NDSU NORTH DAKOTA STATE UNIVERSITY

ND EPSCoR
Established Program to Stimulate Competitive Research

IOWA STATE UNIVERSITY

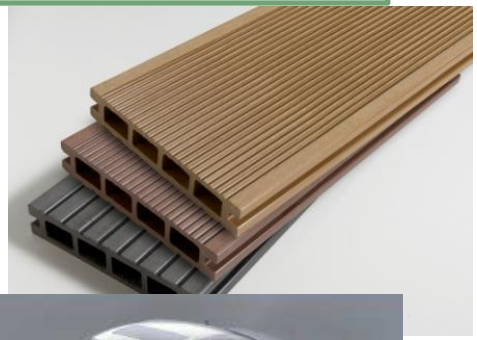
WASHINGTON STATE UNIVERSITY

1785
The University of Georgia

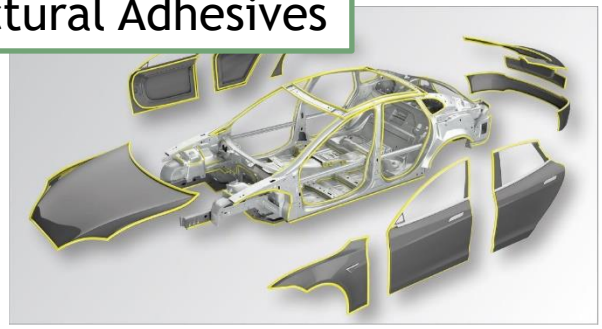
Thermoset Polymer Applications

Industrial and OEM Coatings

Composites and Foams

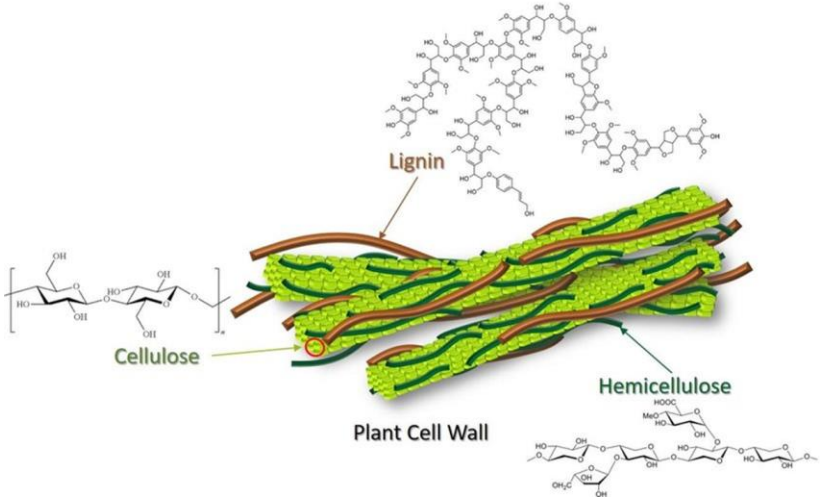


Structural Adhesives



Agricultural Sources of Chemicals

Drying Oils
Semi-Drying Oils
Glycerol
Fatty Acids



Cellulose
Hemi-cellulose
Starch
Lignin
Rosin
Tall Oil FA
Terpenes

Topics

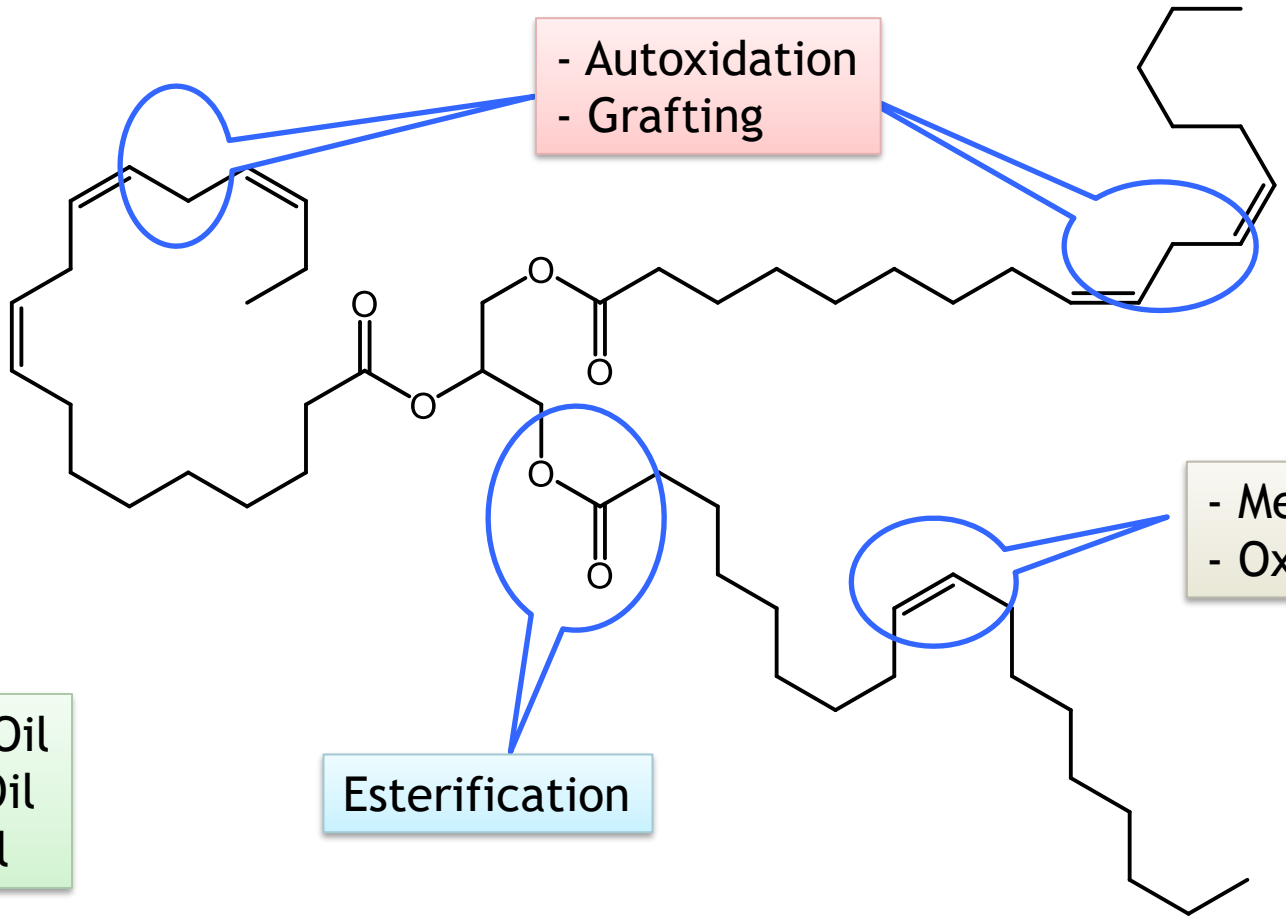
Soybean Oil-Based
High Functionality Resins
for Thermosets

Monomers from Biomass

Non-isocyanate
Polyurethanes

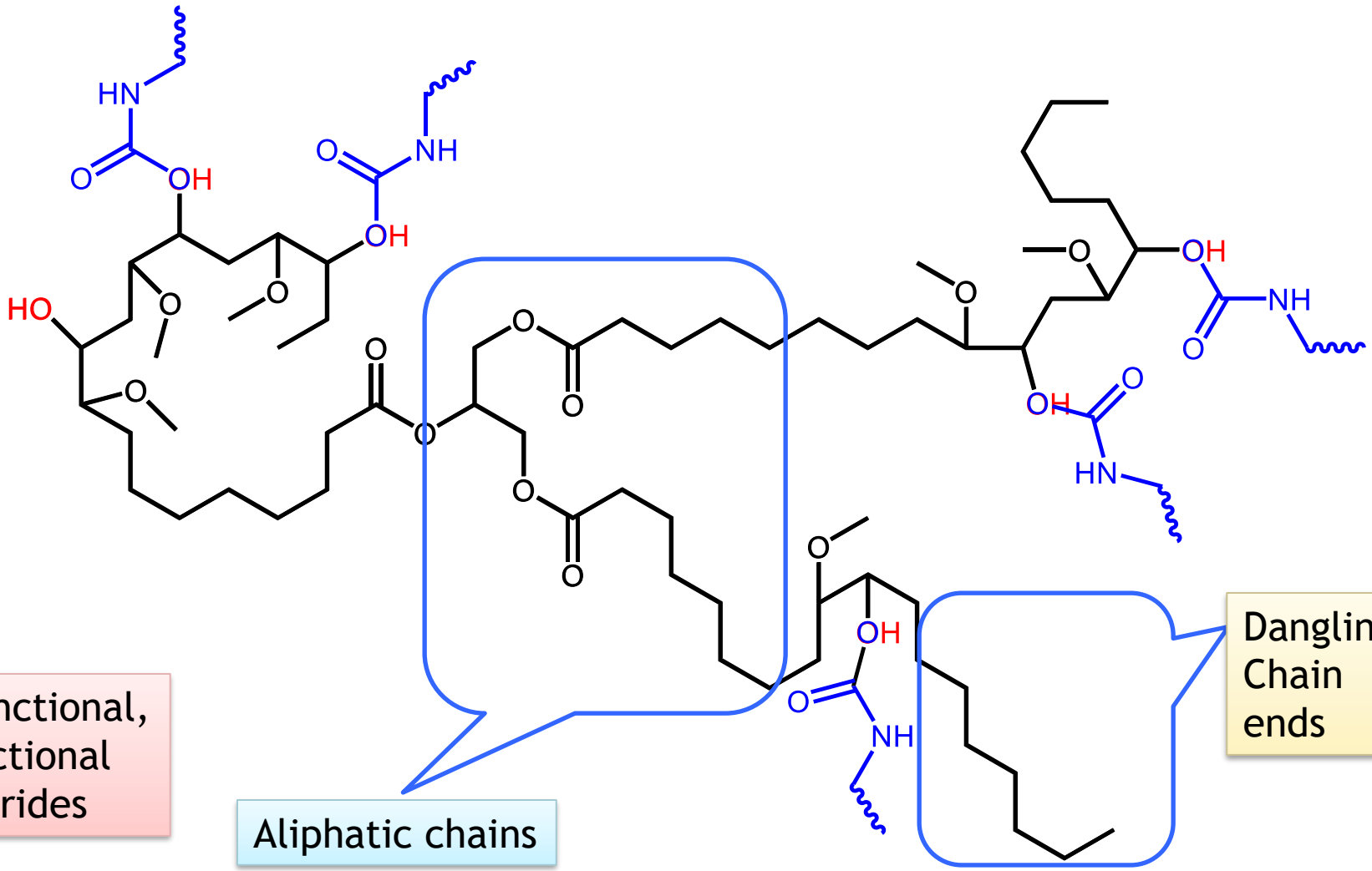
Fast Curing Resins for
Rigid Foams

Seed/Vegetable Oils



Soybean Oil
Linseed Oil
Castor Oil

Polyol in Polyurethane



Monofunctional, Nonfunctional Triglycerides

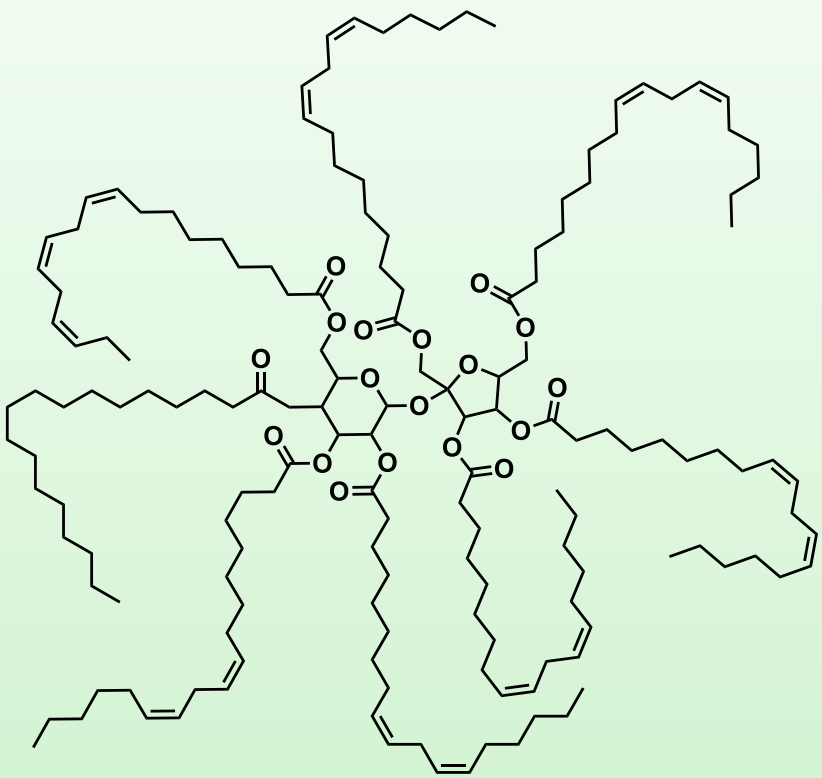
Aliphatic chains

Dangling Chain ends

Question?

Is it possible to make a high strength thermoset from a vegetable oil?

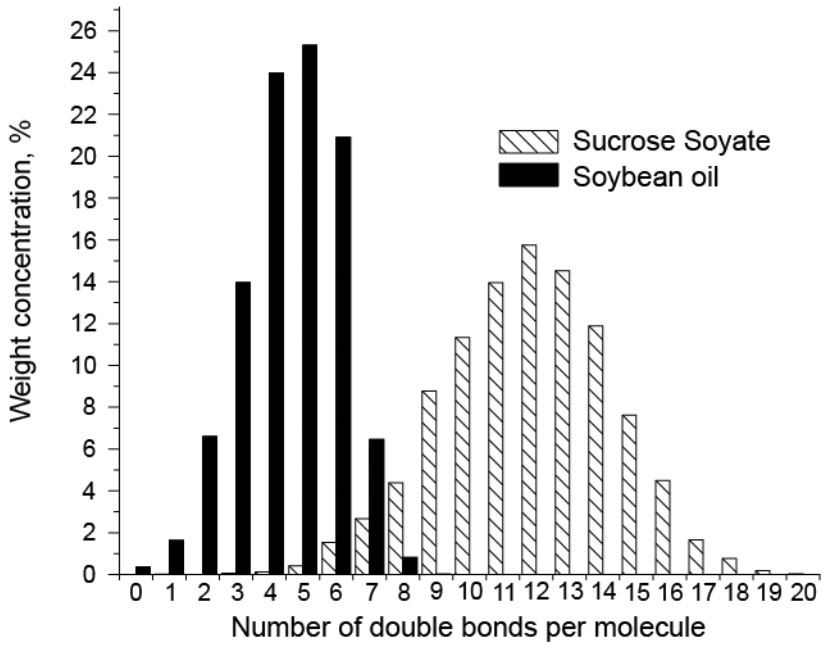
Sucrose Ester Resins of Vegetable Oil FAs



- Synthesized from sucrose and methyl esters of FAs
- Known in the 1960s
- Procter & Gamble Chemicals: "SEFOSE"
- Low Viscosity at 100% Solids
- Useful as an "alkyd resin"
  - 2009 U.S. Presidential Green Chemistry Award to P&G and CCP

Sucrose Ester	Viscosity (mPa·s)
Sucrose linseedate	236
Sucrose safflowerate	393
Sucrose soyate	425
Sucrose soyate B6	890

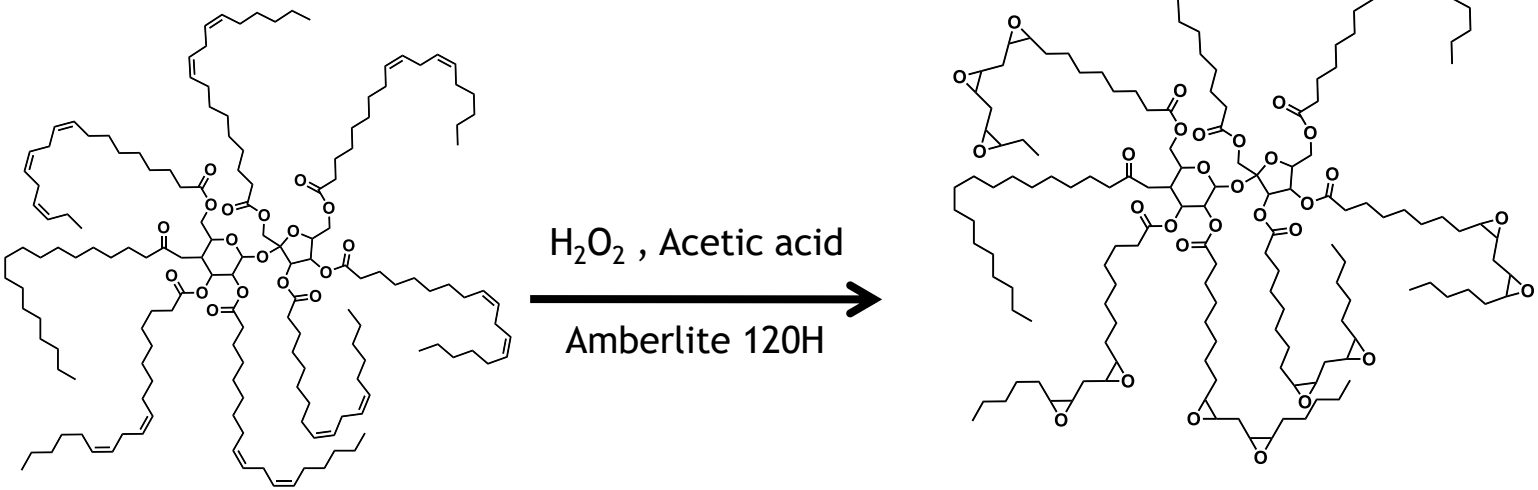
Triglyceride vs. Sucrose Ester



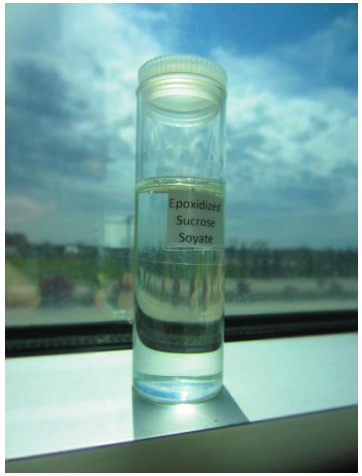
- Sucrose Ester
  - Higher average functionality
  - Broad distribution of functionality
  - No non-functional molecules
  - Minimum functionality ~4-5

Epoxidation of Sucrose Esters

- Prilezhaev reaction
- Near 100% conversion of double bonds to epoxies
  - No side reactions observed

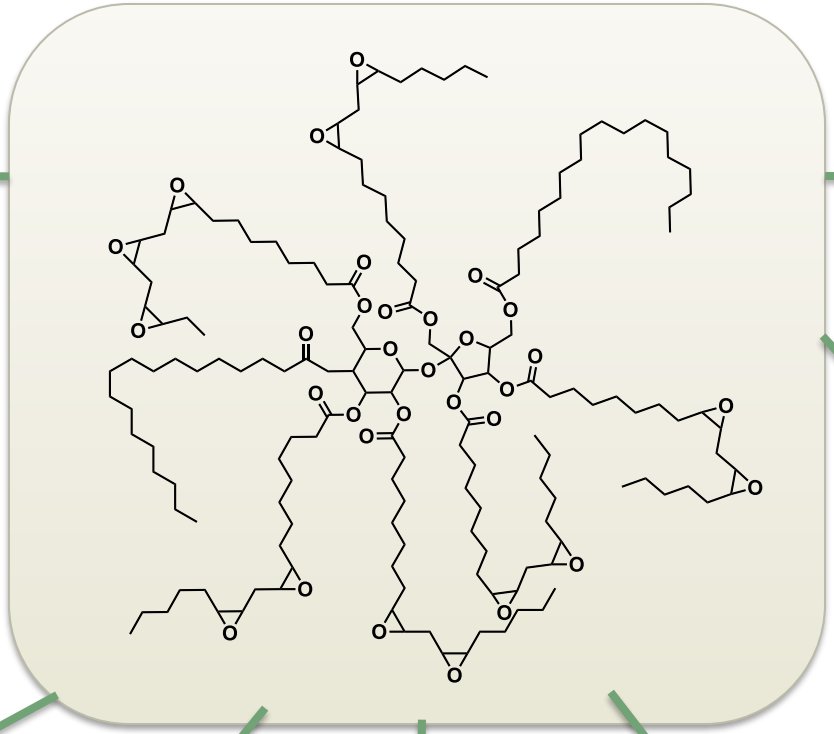


Epoxy	The average degree of sucrose substitution	Average molecular weight, MW (g/mol)	Epoxide equivalent weight, EEW (g/eq.)	Epoxide functionality per molecule	Viscosity (mPa-s)	Density (g/cm^3)
ESL	7.7	2,700	183	15.0	8000	1.05
ESSF	7.7	2,645	230	11.6	5000	1.04
ESS	7.7	2,628	248	10.6	2200	1.02
ESSB6	6	2,048	256	8.0	5500	1.03
ESO (Control)	3	993	231	4.3	420	0.99



Pan, Sengupta, Webster, *Green Chemistry*, 13, 965-975 (2011).

ESE Resins: A Platform Technology



Polyols

Crosslinking

Carbonate

Thermal Crosslinking - Blocked Acids

Water-assisted acid crosslinking

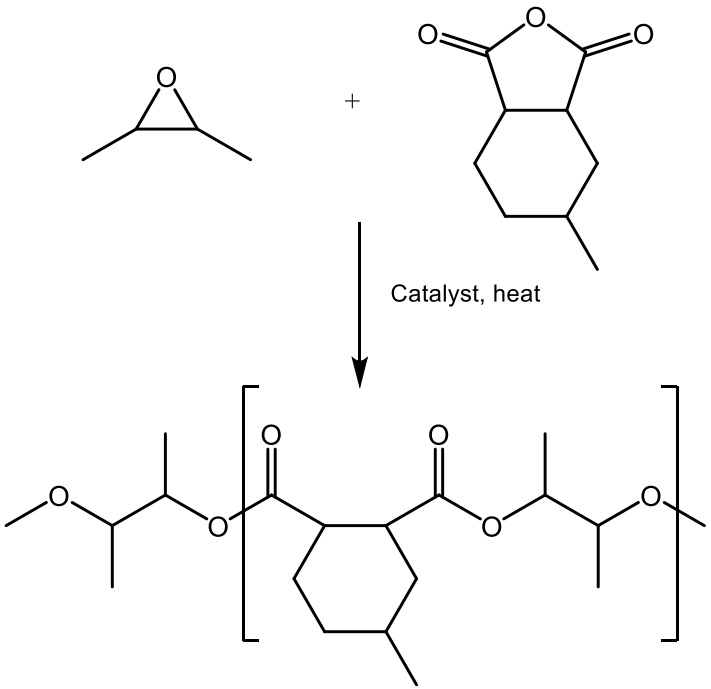
Thermal Crosslinking - Anhydrides

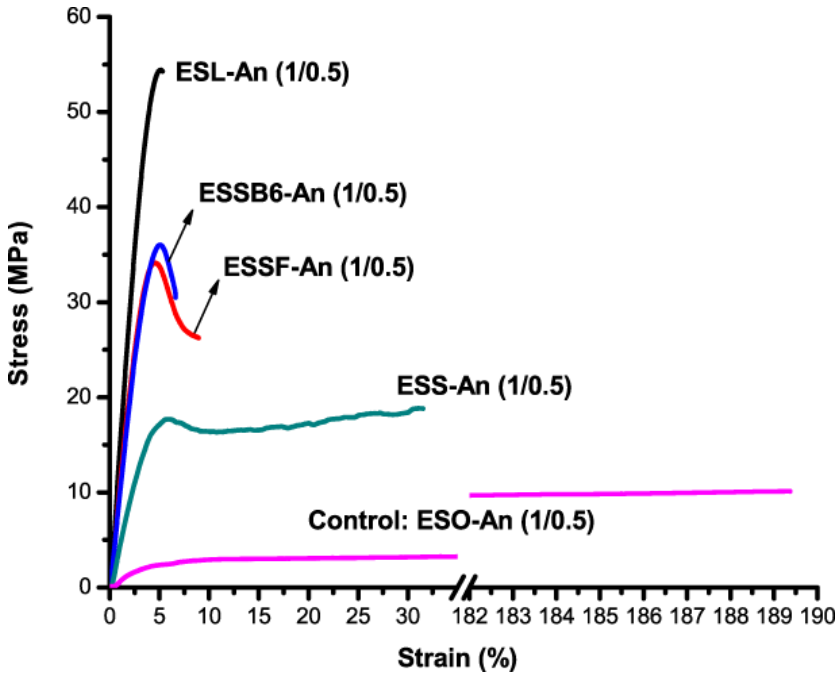
Photo-polymerization

(Meth)acrylates

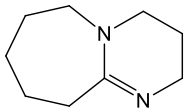
Thermal Crosslinking

Anhydride Curing





Initial studies:
Curing: 80°C, 12 Hrs
Catalyst: DBU



Remarkable tensile properties for a seed oil based system

Pan, Sengupta, Webster, *Biomacromolecules*, 2011, 12, 2416-2428.

Composites with Natural Fibers

Bio-based resin gives equivalent or better performance than petrochemical resin

Reinforcement: Loose flax fibers

	Untreated Fiber			NaOH Treated Fiber	
Category	Araldite	ESS F1	ESS F2	Araldite	ESS F2
Tens. Str. MPa	158.09 ± 21.69	154.16 ± 6.77	152.58 ± 15.99	NA	178.31 ± 38.93
Flex. Str. MPa	195.65 ± 24.64	252.42 ± 24.20	340.30 ± 28.17	242.00 ± 22.5	259.45 ± 12.36
Sht. Beam Str. MPa	12.65 ± 1.56	22.32 ± 3.16	25.63 ± 2.46	23.32 ± 0.25	25.35 ± 1.76

Data courtesy of C. Taylor, T. Krosbakken, Chad Ulven, NDSU Mechanical Engineering

ESS in Wood Composites

ESS shows promise as a resin system for wood composites

Lap shear using yellow birch

Cure Temperature [°C]	100% MDI Cure Time* 20 m (MPa)	100% MDI Cure Time* 40m (MPa)	75% MDI 25% ESS Cure Time 20 m (MPa)	75% MDI 25% ESS Cure Time 40m (MPa)	50% MDI 50% ESS Cure Time 20 m (MPa)	50% MDI 50% ESS Cure Time 40m (MPa)	25% MDI 75% ESS Cure Time 20 m (MPa)	25% MDI 75% ESS Cure Time 40m (MPa)	74% ESS 24%MHHPA 2%DBU Cure Time 60 m (MPa)
150	2.75	3.65	3.48	3.53	2.45	2.30	1.84	1.47	4.2
165	3.20	3.18	2.54	3.45	2.70	2.60	1.48	1.65	4.1

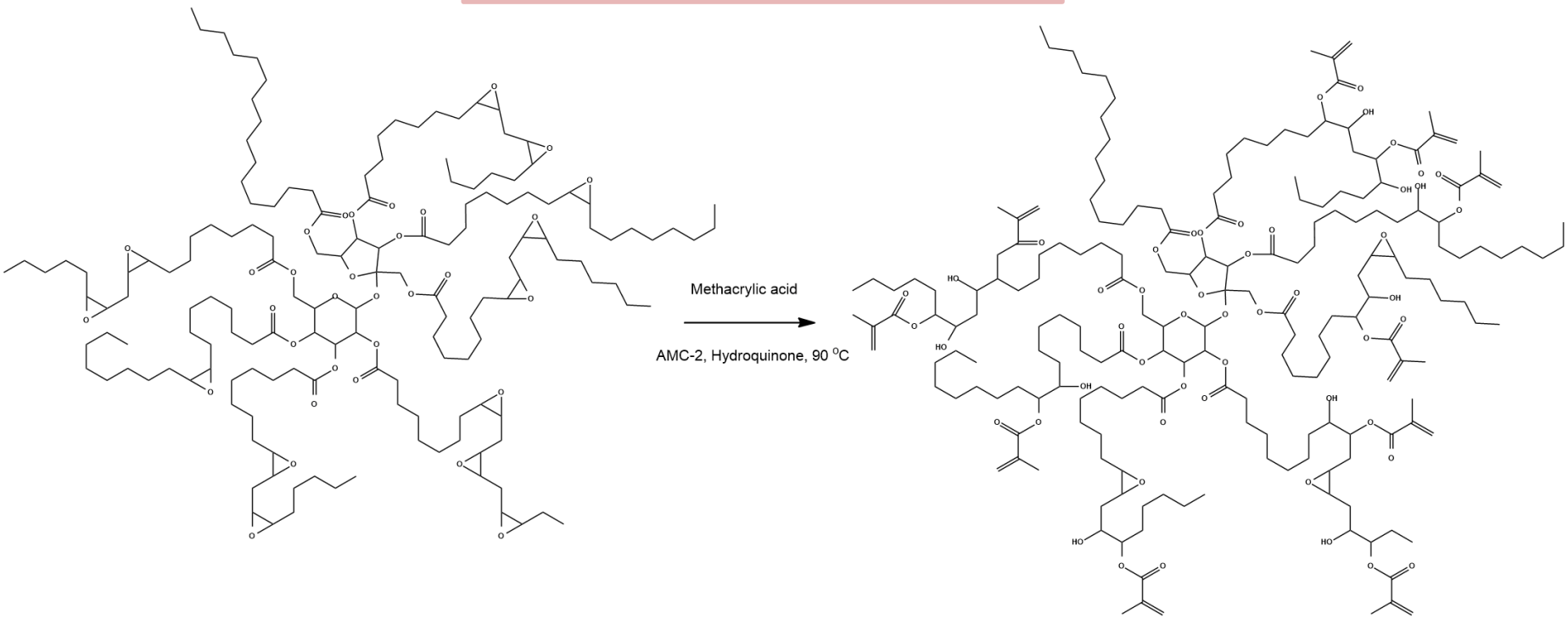
Composites with soy and wheat straw

Formulation	Modulus [MPa]	Internal Bond [kPa]	Screw Withdrawal [N]	Surface Hardness [N]
Soy-ESSANH	BC - 364.5 +/- 177.7	CD - 9.3 +/- 3.2	C - 182.1 +/- 40.4	C - 1863.2 +/- 559.8
Soy-ESSMDI	AB - 699.4 +/- 378.4	CD - 45.6 +/- 31.3	B - 408.5 +/- 72.5	BC - 2446.4 +/- 468.0
Soy-MDI	A - 788 +/- 387.2	C - 49.9 +/- 17.7	B - 445.6 +/- 90.0	A - 3878.8 +/- 416.7
Wheat- ESSANH	C - 76.8 +/- 38.9	D - 3.3 +/- 0.4	D - 39.2 +/- 6.2	D - 878.6 +/- 257.0
Wheat-ESSMDI	A - 754.5 +/- 156.2	A - 186.8 +/- 60.5	A - 578.8 +/- 105.4	A - 3247.4 +/- 519.6
Wheat-MDI	AB - 681.2 +/- 223.4	B - 133.2 +/- 50.6	A - 648.6 +/- 148.8	B - 2518.2 +/- 266.4

Sitz, et al., *Ind. Crops Products*, 2017, 107, 400-408

Methacrylated ESS for Composites

A bio-based "Vinyl ester" resin

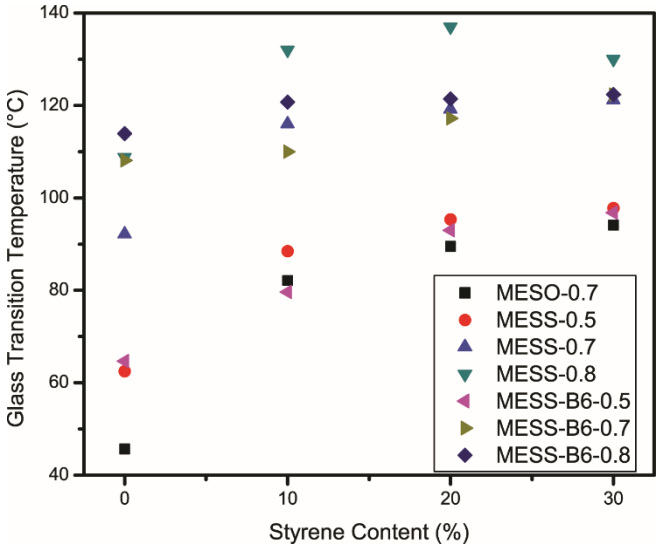


Cure Catalysts: Luperox P, Luperox 10M75
Cure Schedule:
150 °C for 1 hour, 175 °C for 1 hour, and 200 °C for five hours

Yan, Webster, Green Materials, 2014, 2, 132-143

Thermoset Properties

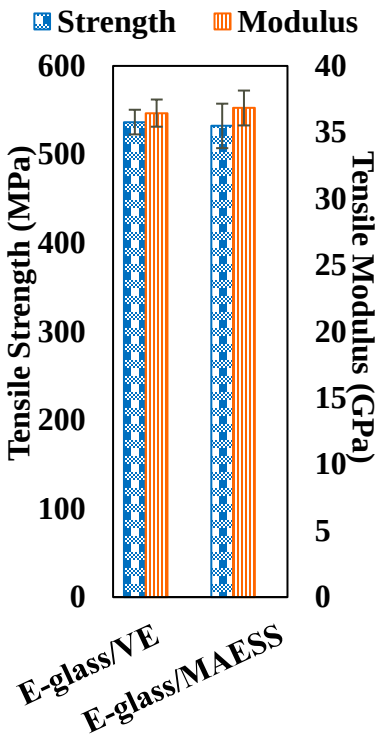
Formulation		Biobased content (%)	T_g (°C)	v_e (10^{-3} mol/mm^3)	$T_{5\%}$ (°C)	Gel content (%)
Resin	% Styrene					
MESO	0	79.7	46	3.11	295	97.2
MESO	10	69.5	82	2.18	309	95.8
MESO	20	59.9	90	2.00	299	97.1
MESO	30	50.9	94	1.13	297	94.5
MESS-0.5	0	85.1	63	4.30	305	97.8
MESS-0.5	10	74.3	89	3.06	294	98.2
MESS-0.5	20	64.2	95	2.56	302	96.1
MESS-0.5	30	54.6	98	1.87	302	98.5
MESS-0.7	0	80.4	92	4.46	306	97.5
MESS-0.7	10	70.0	116	6.87	302	97.8
MESS-0.7	20	60.3	119	4.16	297	97.2
MESS-0.7	30	51.2	121	2.91	285	95.9
MESS-0.8	0	78.5	109	5.17	300	96.8
MESS-0.8	10	68.4	132	7.42	304	97.9
MESS-0.8	20	58.8	137	5.57	307	96.4
MESS-0.8	30	49.9	130	4.81	308	96.0

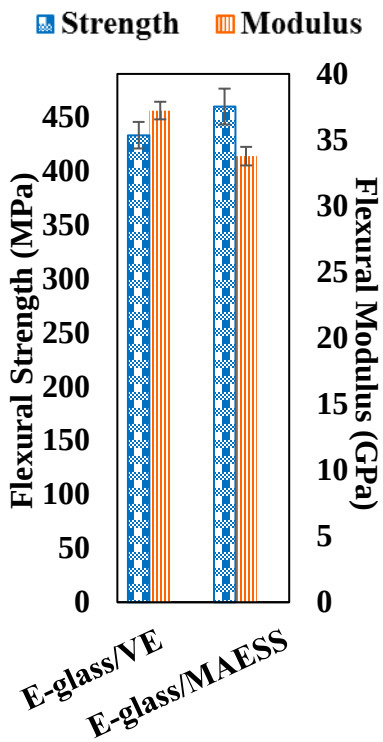


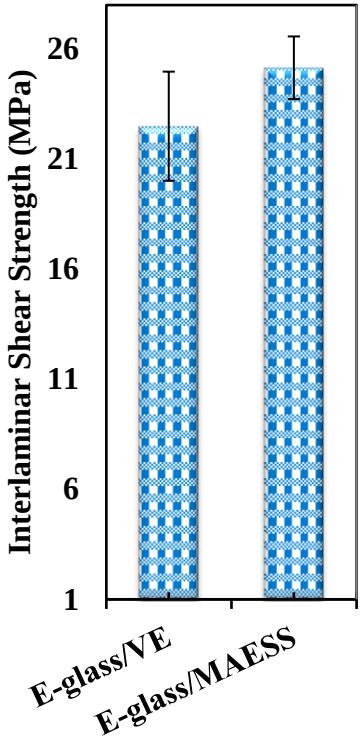
Excellent Performance Properties for a Bio-based Thermoset
Very High Glass Transition temperature, modulus
Low styrene content

Glass Fiber Composites

MESS Resin System Comparable or Better Than Vinyl Ester (VE)



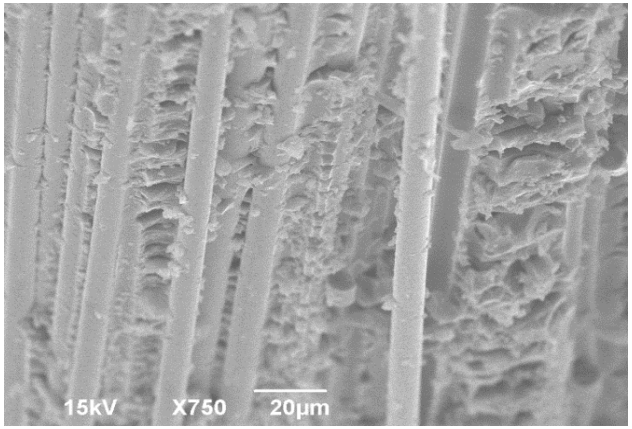


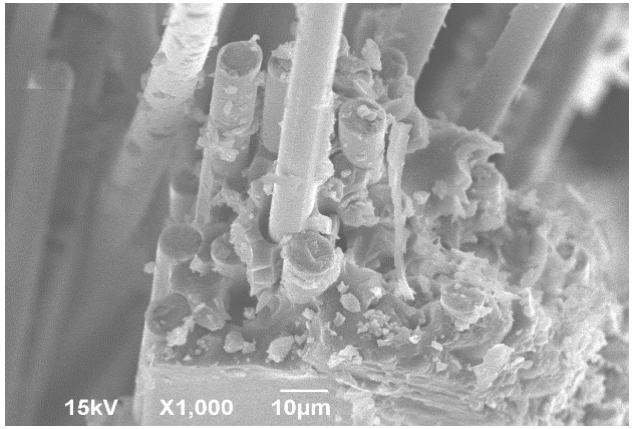


Data from: Nassibeh Hosseini, Chad Ulven, NDSU Mechanical Engineering

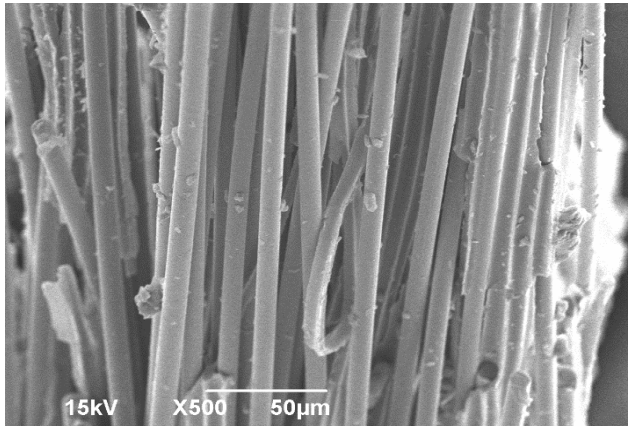
Fiber-Resin Adhesion

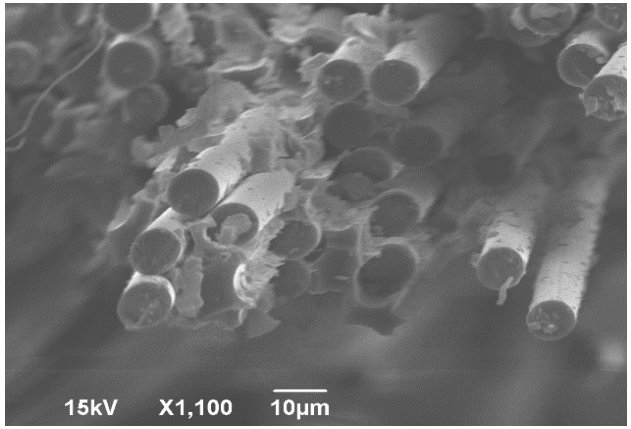
E-glass with MAESS





E-glass with Vinyl Ester Resin

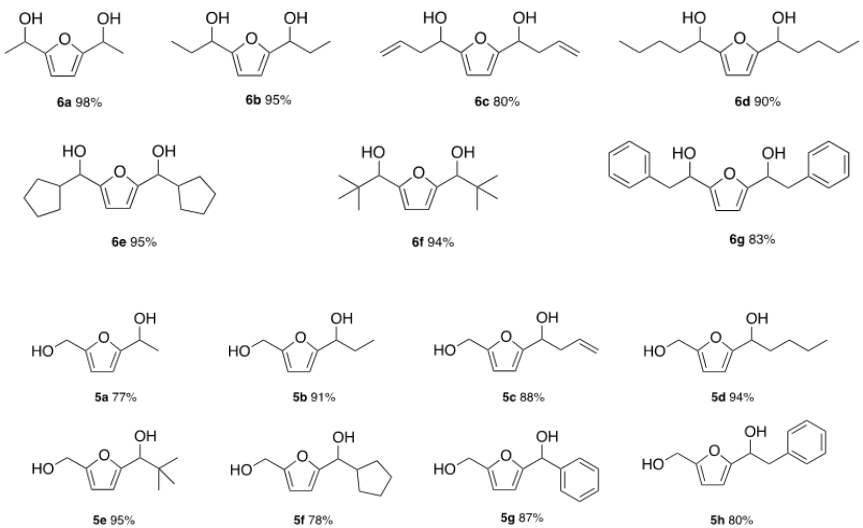




Interfacial adhesion appears to be better when using MAESS resin system

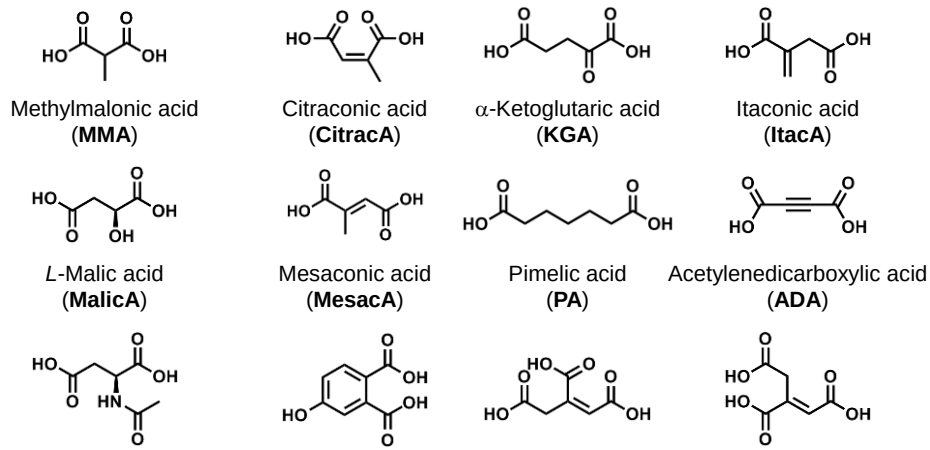
Monomers from Biomass

Many opportunities for polymer building blocks and curing agents



- Bisphenol-A replacements
- Epoxy resins
- Polyesters, polycarbonates

ACS Sustainable Chem. Eng., 2020, 8, 18824-18829



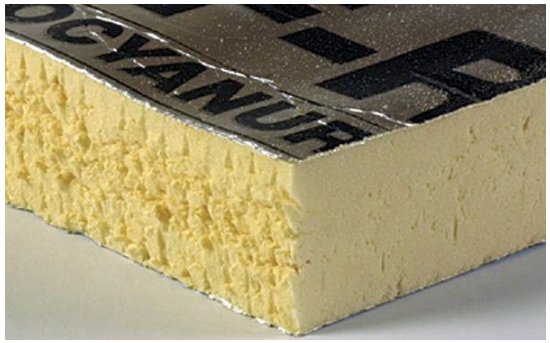
- Epoxy curing agents
- Polyesters

ACS Sustainable Chem. Eng., 2020, 8, 5750-5762
J. Polym. Sci., 2021, online

zymergen

Polyurethanes

Important family of high-performance polymers

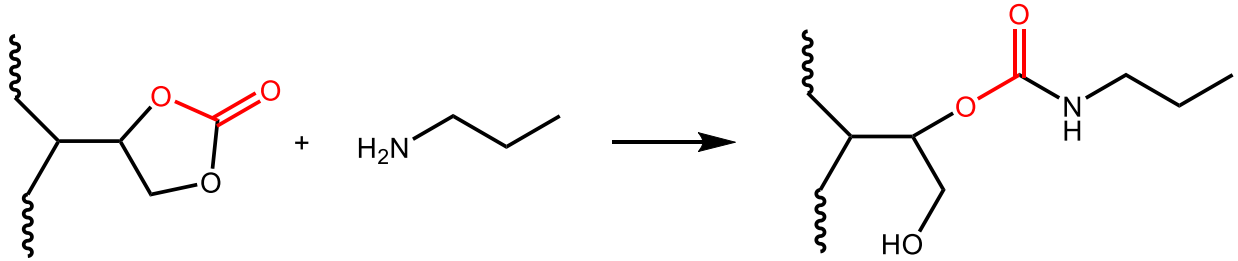


Polyurethanes are made using isocyanates
Health concerns over exposure

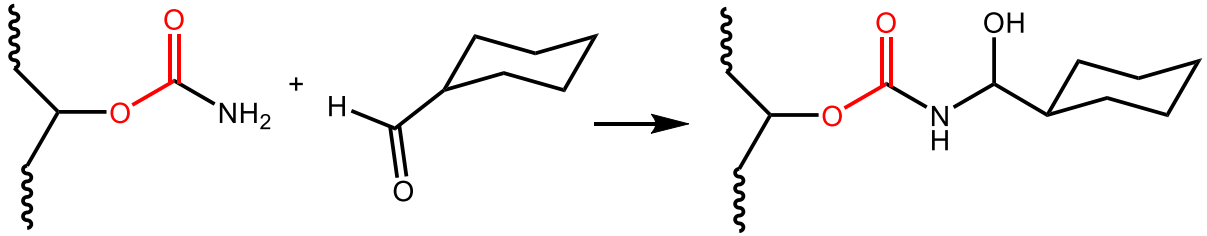
Non-Isocyanate Polyurethanes

Objective: Make polyurethanes without isocyanates

Cyclic carbonate + Amine



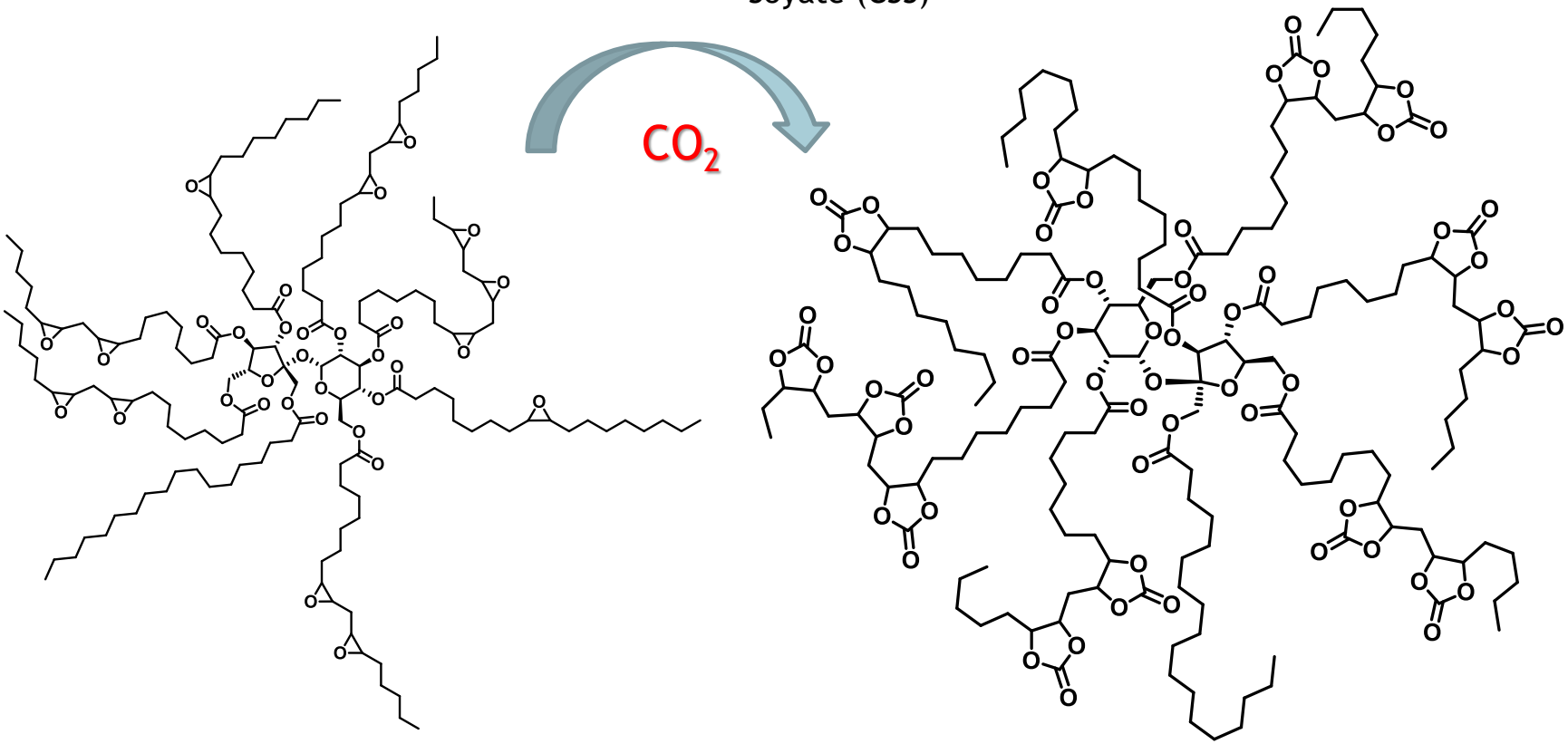
Carbamate + Aldehyde



Carbonated Sucrose Soyate

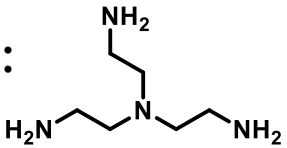
Epoxidized Sucrose Soyate (ESS)

Carbonated Sucrose Soyate (CSS)

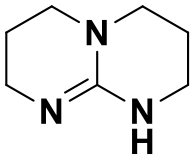


J. Coat. Technol. Res. 2019, 16: 41-57

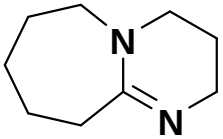
NIPU Coatings Properties

Curing agent: 

Tris(2-aminoethyl)amine (TAEA)

Catalysts: 

Triazabicyclodecane (TBD)

or 

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)

+ LiOTf

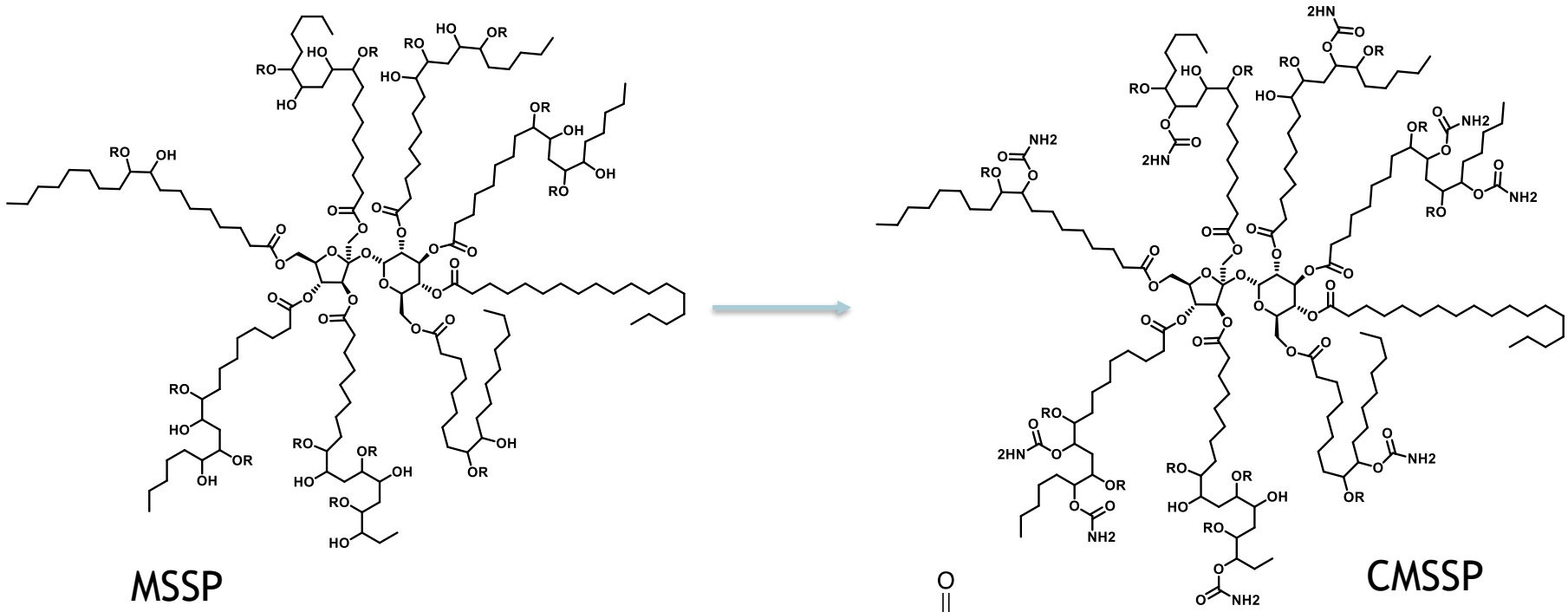
Entry	Resin	1% catalyst	Solvents (1:3)	Thickness (μm)	MEK DRs	König (sec)	Pencil Hardness
1	CSBO	TBD	EEP:toluene	44.2	122	18	HB
2	CSS			45.5	>400	37	H
3	CSBO	DBU		47.2	109	16	HB
4	CSS			34.2	>400	38	H
5	CSBO	TBD	EEP:BA (*n*-butyl acetate)	56.1	129	23	H
6	CSS			46.2	139	42	HB
7	CSBO	DBU		53.9	73	21	H
8	CSS			42.2	211	39	H
9	CSBO	TBD	EEP:PM (2-methoxy-1-propanol)	41.1	135	24	F
10	CSS			41.9	391	46	H
11	CSBO	DBU		38.1	130	25	HB
12	CSS			41.1	>400	47	H
13	CSBO	TBD	EEP:TBOH (*t*-butanol)	50.5	115	21	H
14	CSS			41.7	340	43	F
15	CSBO	DBU		36.6	98	18	H
16	CSS			46.4	>400	61	F

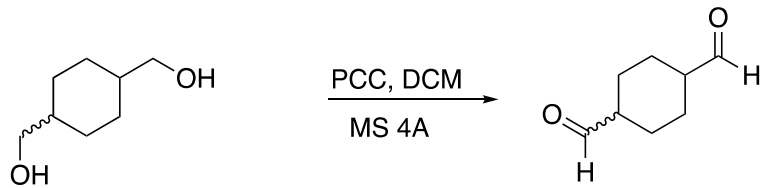
Cure conditions: 80°C, 45 minutes, Reverse impact: 172 in•lbs, X-hatch adhesion: 5B

J. Coat. Technol. Res. 2019, 16: 41-57

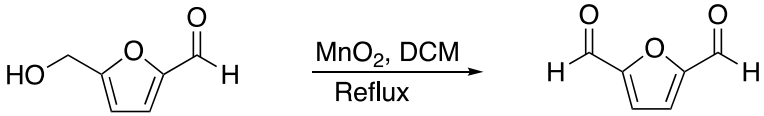
Bio-based Carbamate-Aldehyde System

Highly functional bio-based carbamate resin + Bio-based Aldehydes





CHDA



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ACS Sustainable Chem. Eng., 7, 19621-19630 (2019)

Coatings Properties

Formulation	Curing Conditions	Thickness (μm)	Konig Hardness (s)	Pencil	Cross-hatch	Rev. Impact (in-lbs)	MEK DRs	Tack Free (min)	Gel Content (%)
DFF-CMSSP	Ambient (1 week/3 months)	37.3 ± 3	122/127	HB/F	0B/0B	<3.92	116/225	8	91.4
	120 °C	27.9 ± 3	135	H	0B	<3.92	>400	N/A	96.6
CHDA-CMSSP	Ambient (1 week/3 months)	32.3 ± 2	70/143	2B/HB	0B/4B	<3.92	44/200	7	67.5
	120 °C	35.1 ± 2	101	2B	0B	<3.92	196	N/A	75.0

Substrate: Aluminum

Substrate: iron phosphate treated steel:

Formulation	Crosshatch Adhesion	Impact Resistance (For/Rev, in-lbs)
DFF-CMSSP	4B	78.4/<3.92
CHDA-CMSSP	5B	86.2/11.8

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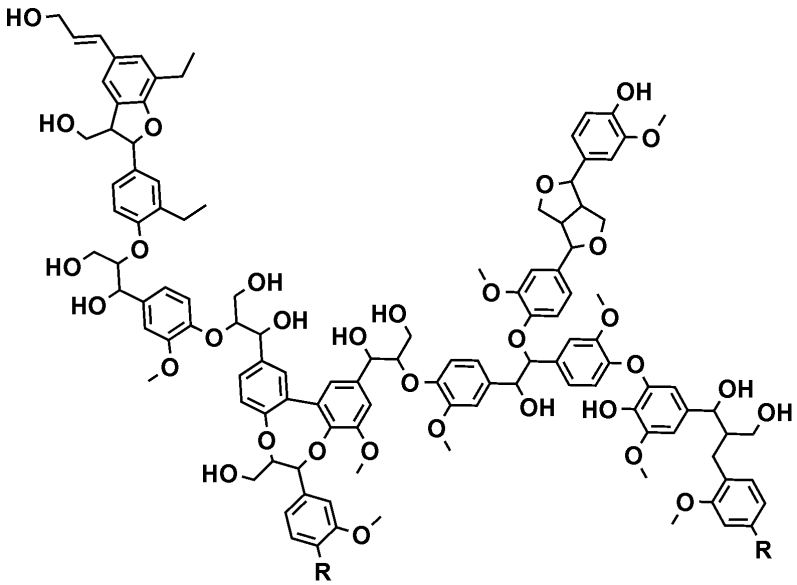
Lignin

Lignin is the second most abundant biopolymer on earth
High aromatic content; by-product of paper pulping, other processes

"You can make anything from lignin, except money"

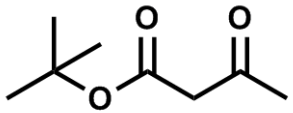


- Most abundant aromatic biopolymer
- Mostly used as fuel
- Difficult to extract useful chemicals
- High numbers of hydroxyl groups

Solvent-Free Functionalization of Lignin

Kraft Lignin

Diluent



Functionalizing reagent

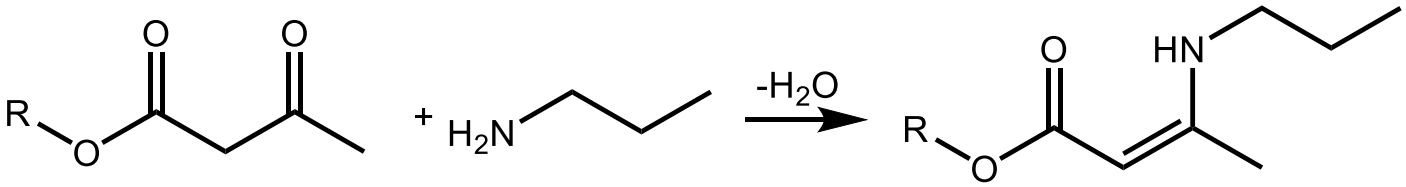
Ethylene glycol
1,3-Propane diol
1,4-Butane diol
Glycerol

Functionalized Lignin/Diluent

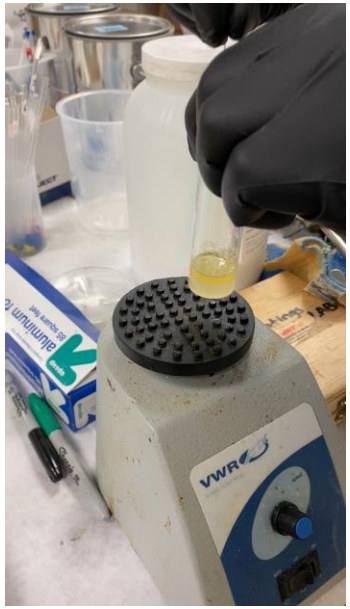
- Acetoacetylated Kraft Lignin
- Low viscosity resin
- Crosslinking:
  - Melamine Formaldehyde
  - Amine
  - Michael Addition
- Extendable to other functional groups

U. S. Pat. No. 10,851,244
Other Patents Pending

Non-isocyanate Foams

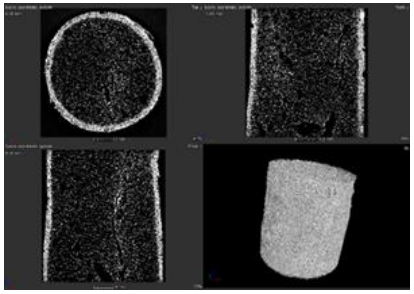


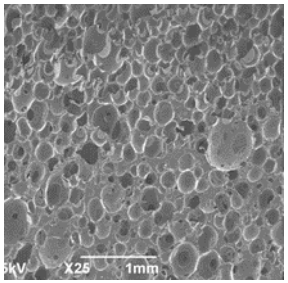
- Reaction with amines occurs at room temperature
- Highly exothermic
- Can be used to volatilize low boiling solvent
- Can also use a polysilane foaming agent → H_2



Lignin-based rigid foams:
Density (g/cm^3): 0.10 – 0.25
Comp. Str. (kPa): 900 - 6800
Glass transition temp (°C): 60 - 97

Comparative PU Foams:
Density (g/cm3): 0.08 – 0.19
Comp. Str. (kPa): 760-2550





Summary

- Abundant opportunities to use bio-based materials in building products
- Direct incorporation of CO_2 into polymers
- Use underutilized agricultural/forestry resources
- Biobased materials to replace other materials

Bio-based composite roofing tile
Dr. Chad Ulven, NDSU

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Postdocs
Jingbo Wu
Ivan Hevus

Staff
Olena Shafranska

Former Students
AliReza Rahimi
Samantha Silbert
Eric Krall
Arvin Yu
Adlina Paramarta
T.J. Nelson
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Songqi Ma
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