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POLYMERS AND COMPOSITES FROM PLANT OIL-BASED RESIN

Alejandrina Campanella

Dixie Chemical
The Element of Open Innovation

3rd International Conference and Exhibition on Materials Science & Engineering
October 06-08, 2014 San Antonio, USA

OUTLINE

- Market Drivers

- Bio-Polymers from Plant Oils
  - Plant oil overview
  - Bio-resins:
    - Monomers: MAESO, MAELO
    - Diluents: styrene, MFA, …
  - Bio-Thermoset Polymer

- Bio-Composites Applications
  - BMC
  - VARTM

- Summary

DIXIE CHEMICAL

Dixie Chemical is a global supplier of specialty chemicals in four key market segments:

- **Thermoset Materials**
- Alkaline Paper Sizing
- Fuel and Lube Additives
- Life Sciences

BIO-COMPOSITES MARKET DRIVERS

- Reduce dependence on petroleum based products
- Increase the use of renewable resources
- Reduce emissions and impacts on the environment and health
- Improve working conditions and worker safety
- Sustainable materials with comparable properties
- Ability to differentiate from competitive offerings (Bio-based)
- Open new markets throughout the supply chain
- Rural community stability and development (USDA BioPreferred)
- Improve product life cycle footprint

BIO-COMPOSITES MARKET DRIVERS

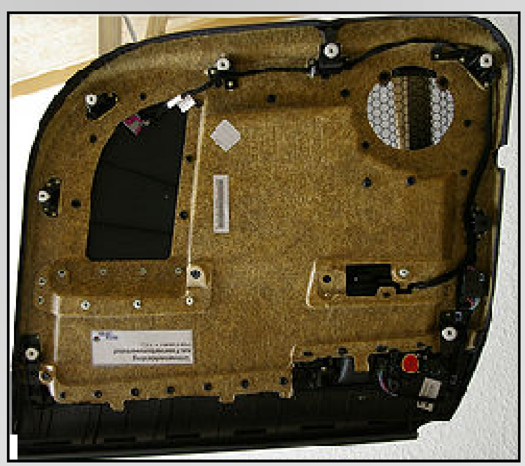
- Expand options for end of life recycle/re-use
- Help customers adapt to Local, Regional and Federal regulation
- Increasing consumer interest in sustainable products
- Produce a sustainable product that is certified and/or labeled by:

BIO-POLYMERS FROM PLANT OILS

Dixie Chemical

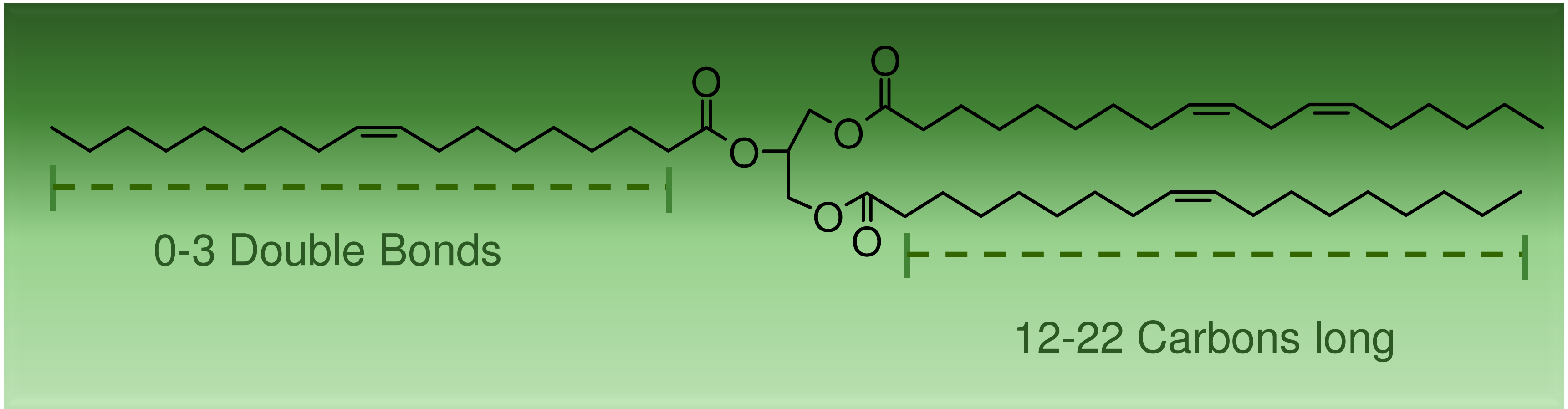
The Element of Open Innovation

BIO-BASED COMPOSITE MATERIALS

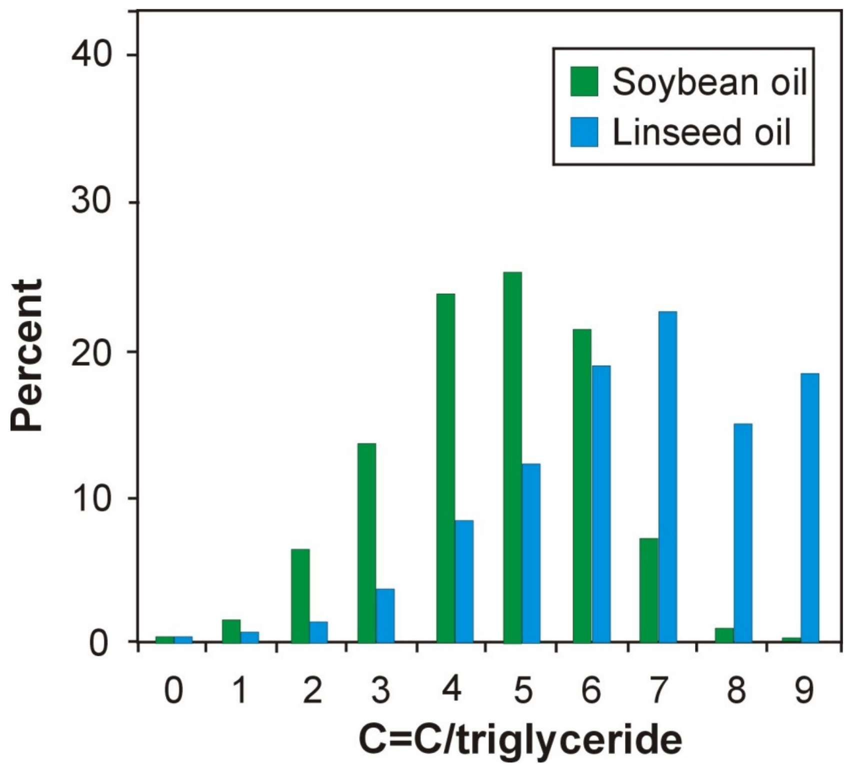


PLANT OIL OVERVIEW

Soybean, Corn, Sunflower, Linseed…



FATTY ACID DISTRIBUTION



# Carbons	# Double bonds	Soybean oil % Comp.	Linseed oil % Comp.
14	0	0.1	0.0
14	1	0.0	0.0
16	0	11.0	5.5
16	1	0.1	0.0
18	0	4.0	3.5
18	1	23.4	19.1
18	2	53.2	15.3
18	3	7.8	56.6
20	0	0.3	0.0
20	1	0.0	0.0
22	0	0.1	0.0
22	1	0.0	0.0

Soybean oil

4.6 double bonds per triglyceride

Linseed oil

6.6 double bonds per triglyceride

BIO-RESINS DEFINITION

MAESO/MAELO + Reactive Diluent

Reactive Diluent: styrene, MFA, vinyl toluene and others

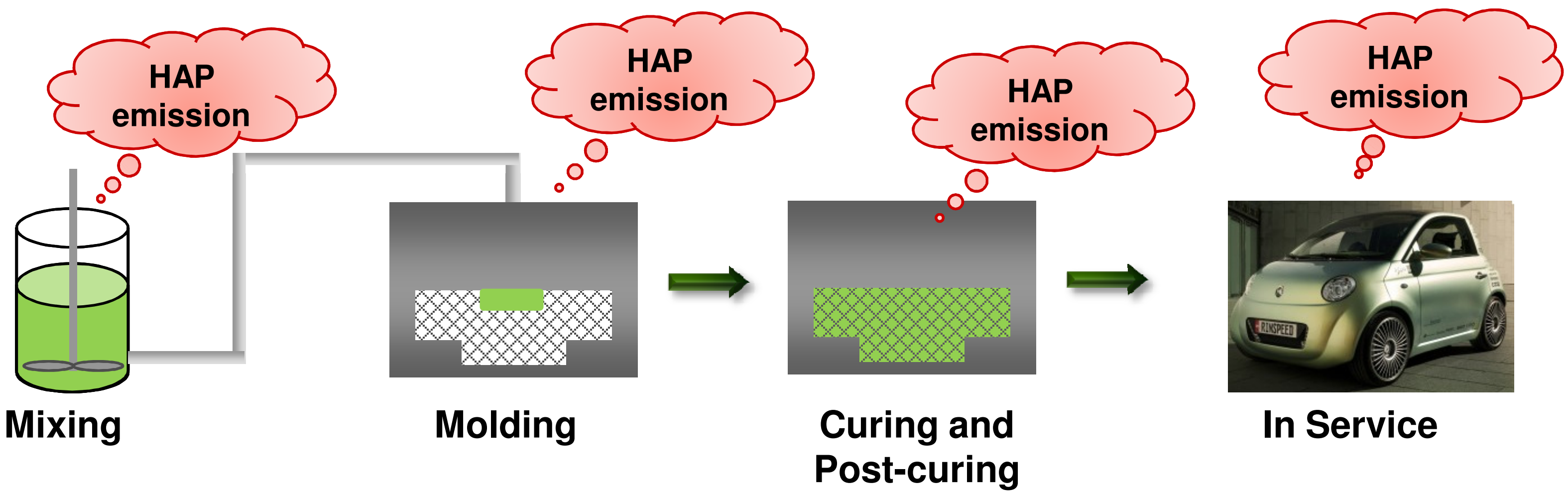
BIO-THERMOSETTING POLYMER

Resin	MAESO	MAELO	Iso-UPR	Ortho-UPR
T_g (^oC)	108	120	110	120
Flexural strength (MPa)	77.1	95.6	80.0	130.0
Flexural modulus (GPa)	2.7	2.8	3.5	3.6
Tensile strength (MPa)	39.7	58	55	75
Tensile modulus (GPa)	2.2	2.8	3.5	3.4

MAESO: Maleinated acrylated epoxidized soybean oil
MAELO: Maleinated acrylated epoxidized linseed oil
UPR: Unsaturated polyester resin

VOC/HAP EMISSIONS

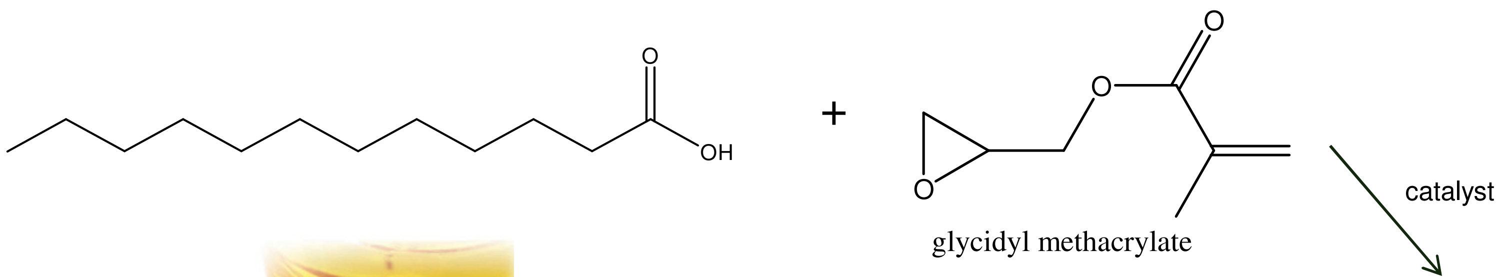
Liquid resins used in molding large scale composites are a significant source of Hazardous Air Pollutants.



Composites industry consumes 9% of the styrene, but accounts for 79% of styrene emissions.

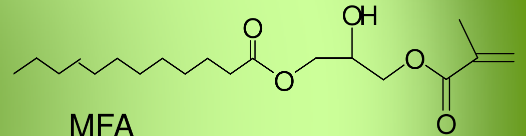
Lacovara, 1999

METHACRYLATED FATTY ACID



La Scala et al., Polymer, 2005

BIO-THERMOSETTING POLYMER

+ 

MFA
(Styrene Offset)

+ Initiator

Heat

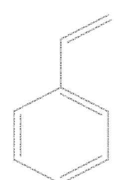
Use fatty acid monomers to reduce styrene content.

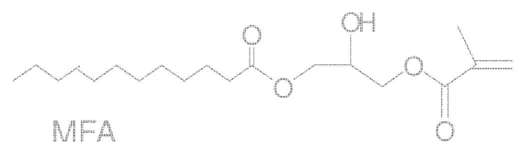
- Non-volatile
- Maintain low viscosity
- Increase bio-based content

Bio-Based Thermoset Polymer

MAESO WITH STYRENE/MFA

Resin	1	2	3
Styrene (wt%)	33	20	13
MFA (wt%)	0	13	20
T_g (°C)	108	85	69
E'(MPa)	1889	1385	911
Crosslink density (mol/m³)	3848	2165	1253
M_c (g/mol)	285	500	877
BBC	57	65	69

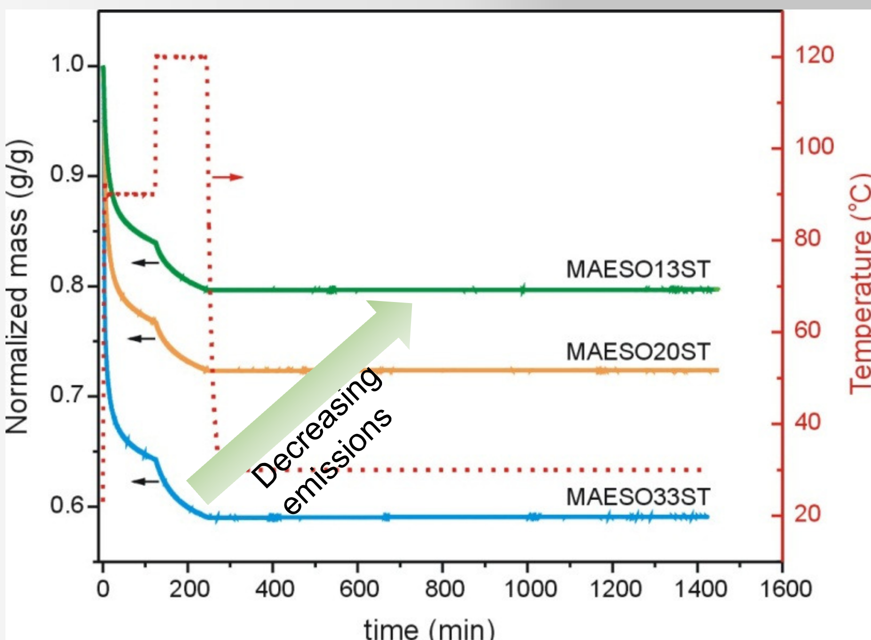




BBC = bio-based content

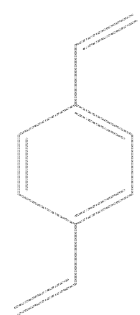
STYRENE EMISSION STUDY

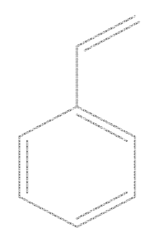
Mass Loss: Reactive diluents

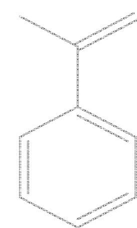


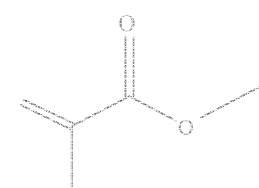
MAESO WITH DIFFERENT DILUENTS

Resin	DB	S	VT	MMA
Diluent (wt%)	33	33	33	33
T_g (°C)	122	108	109	67
E'(MPa)	2120	1889	1838	1690
Crosslink density (mol/m³)	4620	3848	3207	2575
M_c (g/mol)	127	285	342	427









S: styrene
DB: divinyl benzene
VT: vinyl toluene
MMA: methyl methacrylate

BIO-COMPOSITES APPLICATIONS

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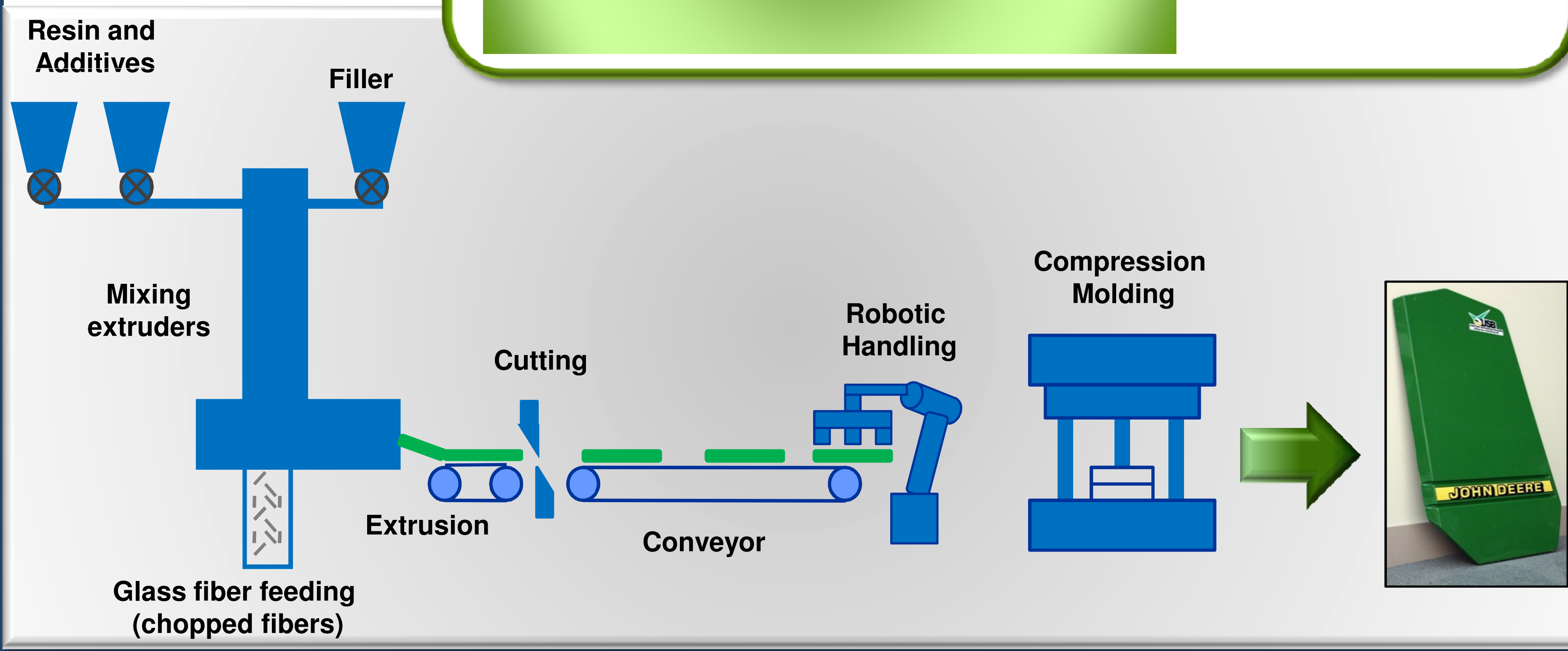
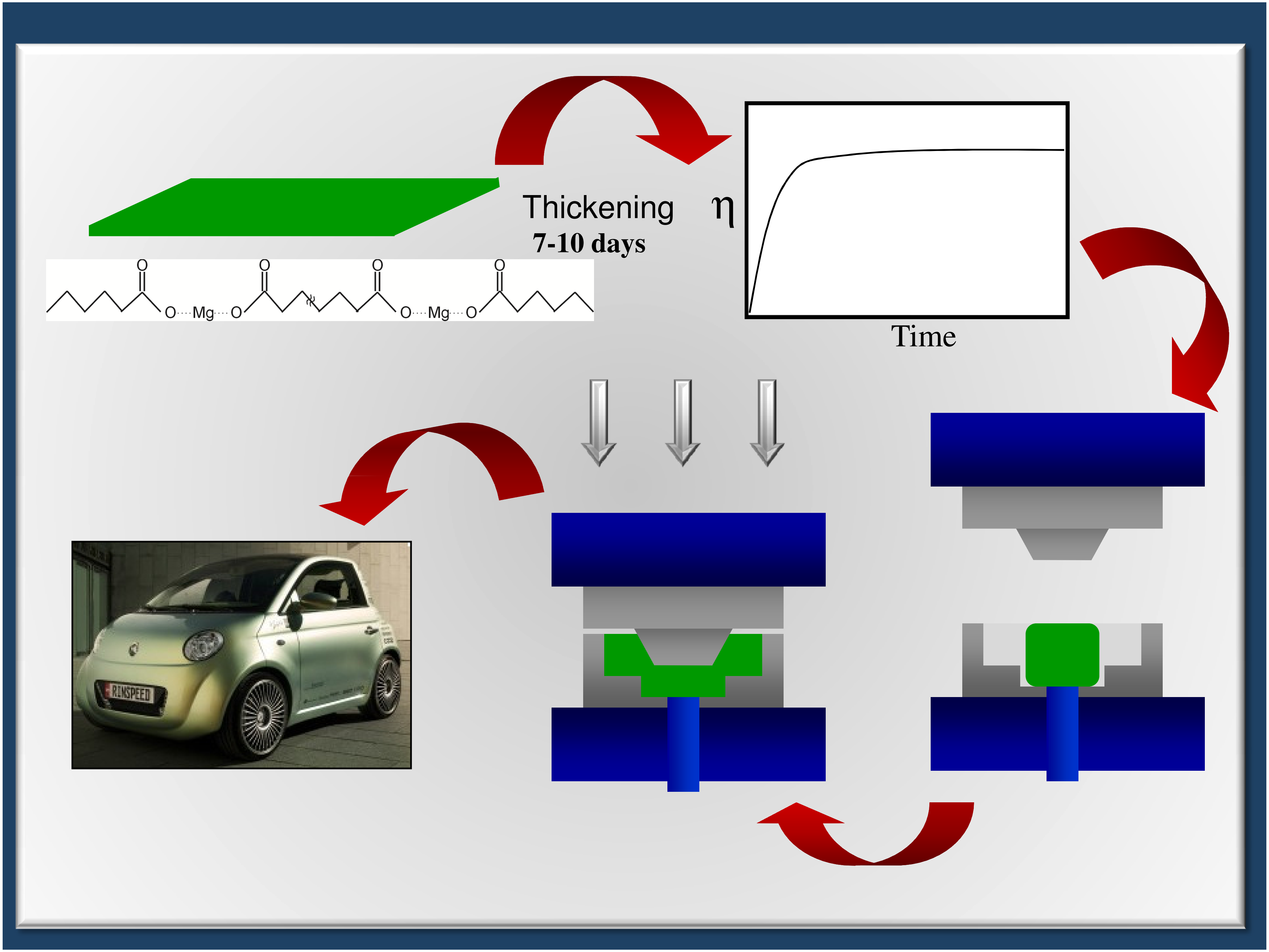
SMC – BMC APPLICATIONS

+ Filler + MgO

+ Fibers + Initiator




Thickening
7-10 days
η
Time
RINSPEED

BMC MANUFACTURING

Dixie Chemical PREMIX

Resin & Initiator

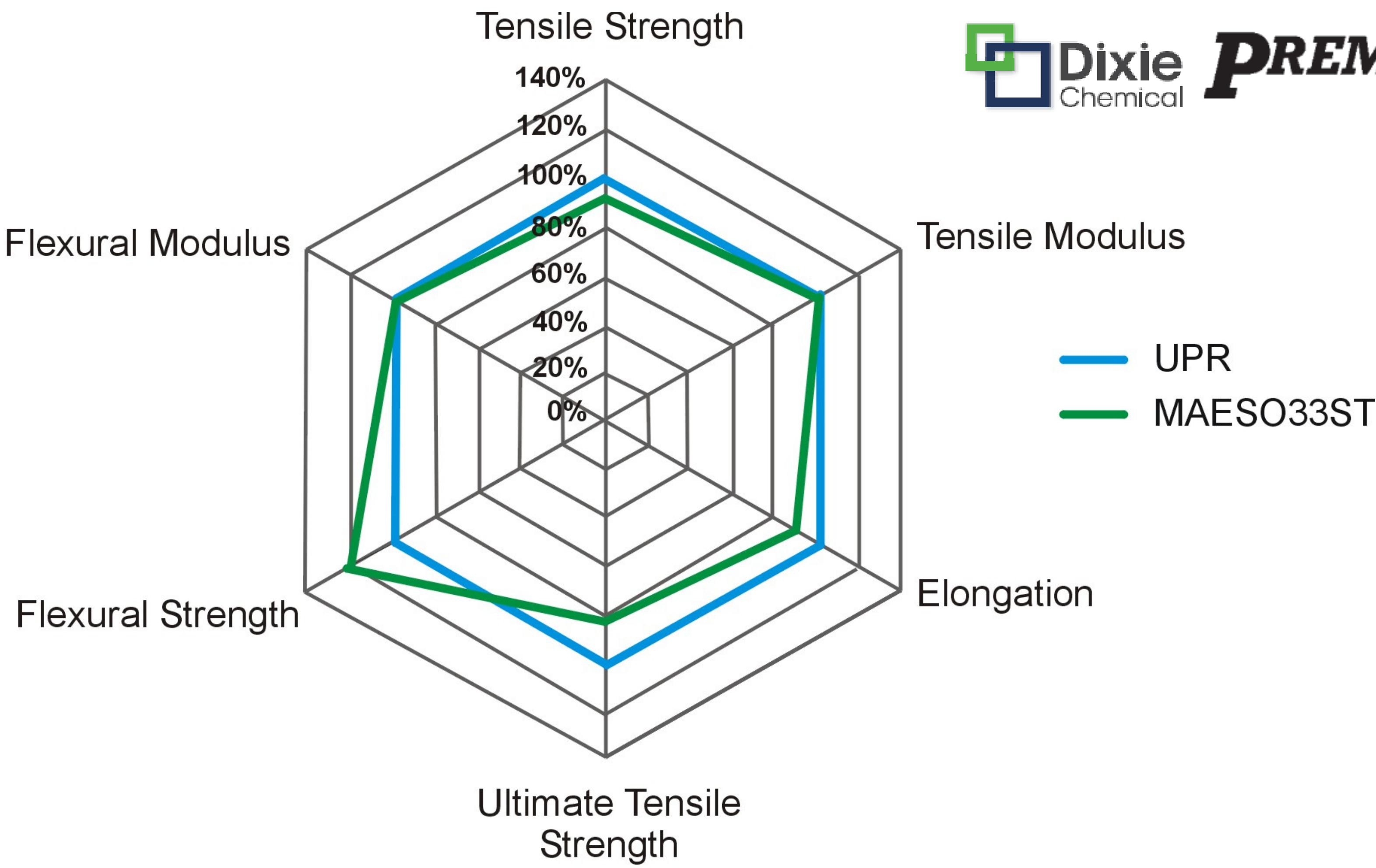
Filler added

Mixed

Fiber glass added

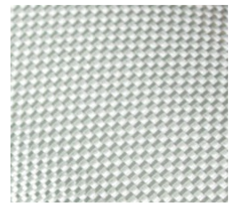
Mixed

BMC PROPERTIES



VARTM/RTM APPLICATIONS

+

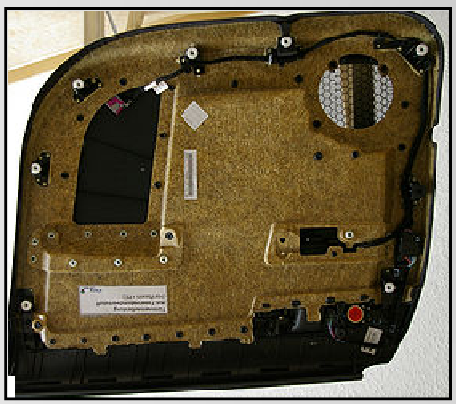


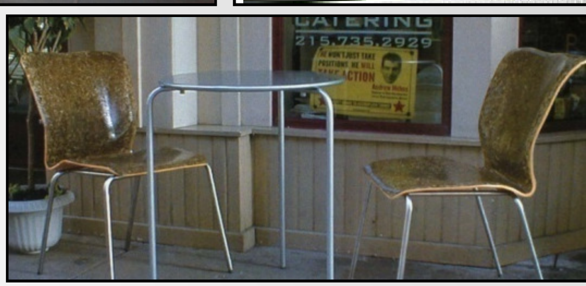
Synthetic Fiber

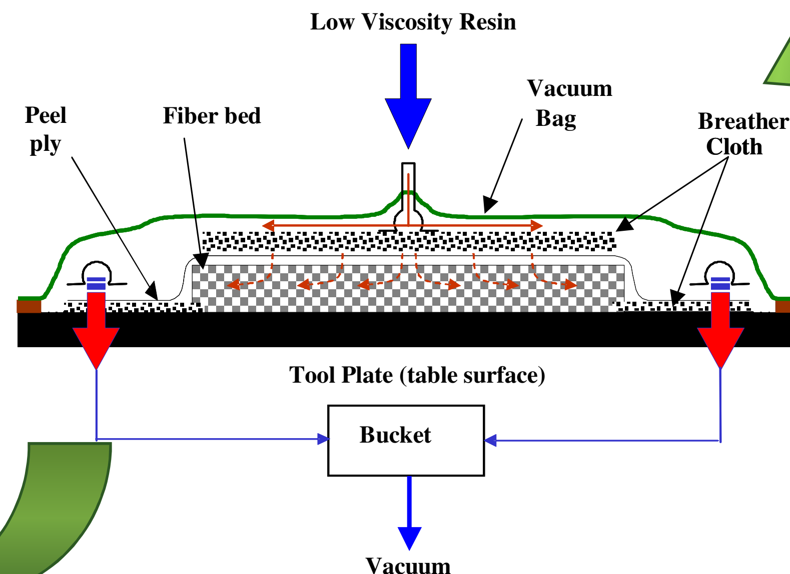
and/or

Natural Fiber

+ Initiator







VARTM

Composite made from Bio-Resin and Fiberglass

Resin	MAESO	MAESO
Glass Fiber	-	44 vol%
T_g (°C)	96	120
E' (MPa)	1310	20578
Flexural strength (MPa)	61.8	304.1
Flexural modulus (GPa)	1.6	21.1
Tensile strength (MPa)	39.7	291.8
Tensile modulus (GPa)	2.2	11.4
BBC	57	57

MAESO = MAESO33ST

Dixie Chemical

CREY BIORESINS, INC.

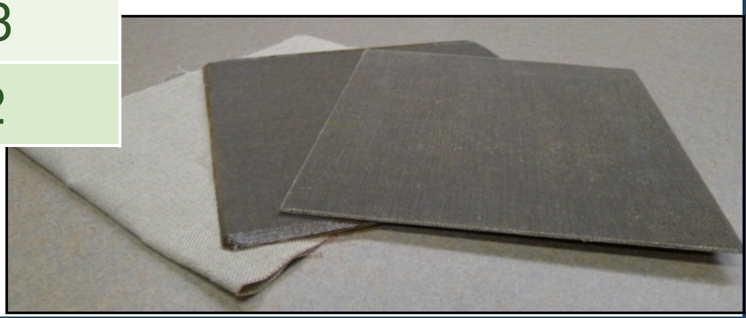
VARTM

Composite made of Bio-Resin and Flax Fiber

Dixie Chemical

CREY BIORESINS, INC.

Resin	MAESO	MAESO
Glass Fiber	-	44 vol%
T_g (°C)	96	100
E' (MPa)	1310	4373
Flexural strength (MPa)	61.8	78.9
Flexural modulus (GPa)	1.6	3.9
Tensile strength (MPa)	39.7	81.9
Tensile modulus (GPa)	2.2	3.3
BBC	57	72



MAESO = MAESO33ST

SUMMARY

- Functionalized plant oils can be used with or in place of petroleum based resins.
- Selection of oils (such as soybean or linseed oil) and reactive diluent (such as styrene, MFA and others) can be used to customize the physical and mechanical properties.
- Methacrylated fatty acids (MFA) can be used to increase the bio-based content, and reduce styrene emissions and related health and environmental risk.
- Bio-resins from MAESO/MAELO are suitable for BMC and VARTM.
- Bio-composites can be produced with good mechanical properties and high bio-content.

ACKNOWLEDGEMENT

- Dr. G. Macdonell, M. Gromacki, Dr. C. Shen, A. Grous (Dixie Chemical)
- Prof. R. Wool (University of Delaware, Center of Composite Materials and Crey Bioresins)
- Dr. M. Zhang (Crey Bioresins)
- Mrs. P. Watts. (Premix)
- Dr. J. La Scala (ARL)
- Prof. G. Palmese (Drexel University)

THANK YOU!!!!!

QUESTIONS?

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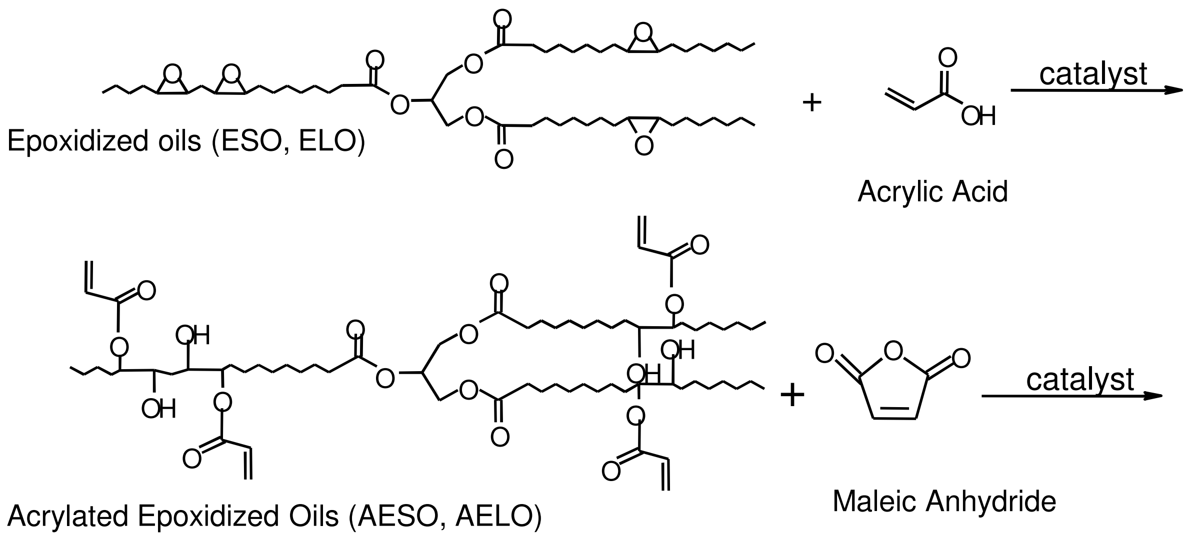
The Element of Open Innovation

MALEINATED ACRYLATED EPOXIDIZED OILS



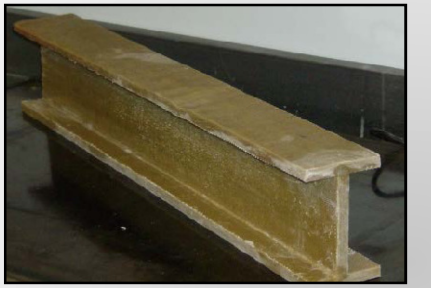
Maleinated Acrylated Epoxidized Oils (MAESO, MAELO)

Wool and Sun, Bio Based Polymers and Composites, 2005

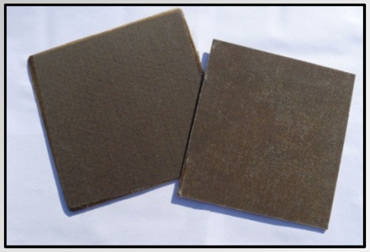
BIO-THERMOSETTING POLYMER

+ Initiator

Heat

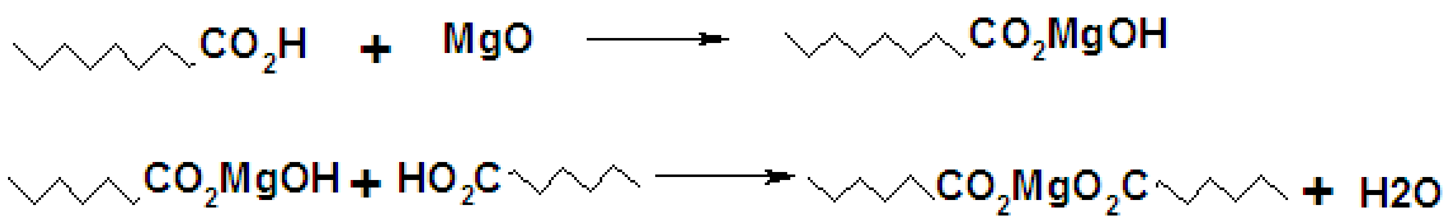


Bio-Based Thermoset Polymer

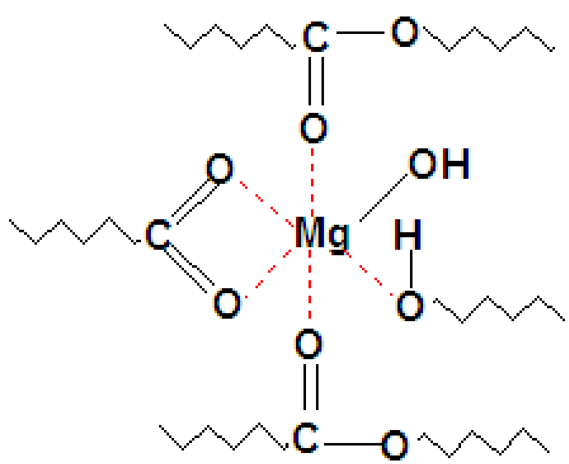


THICKENING FOR SMC BIO-RESINS

The first-stage reaction

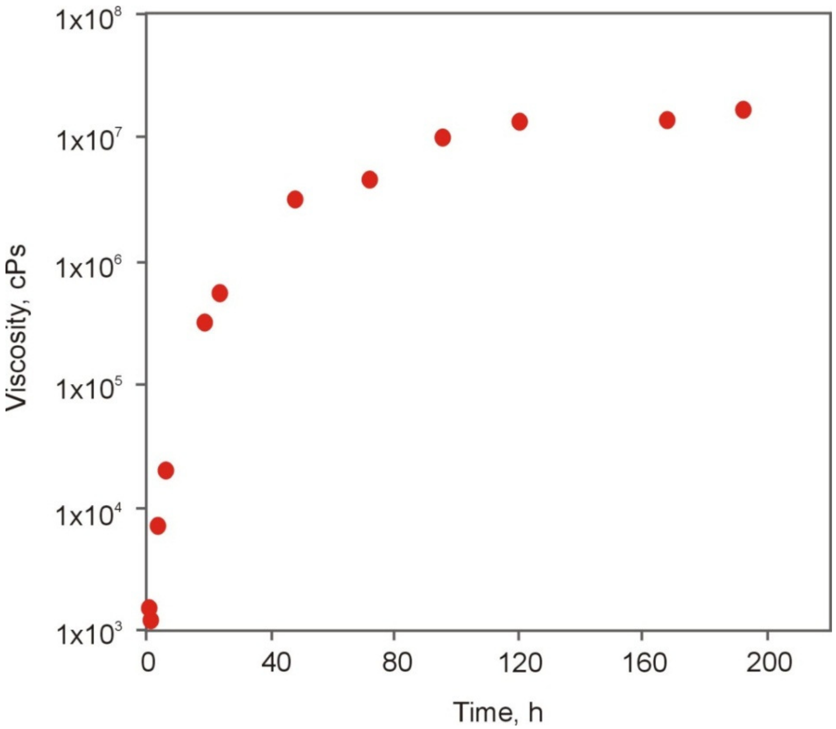


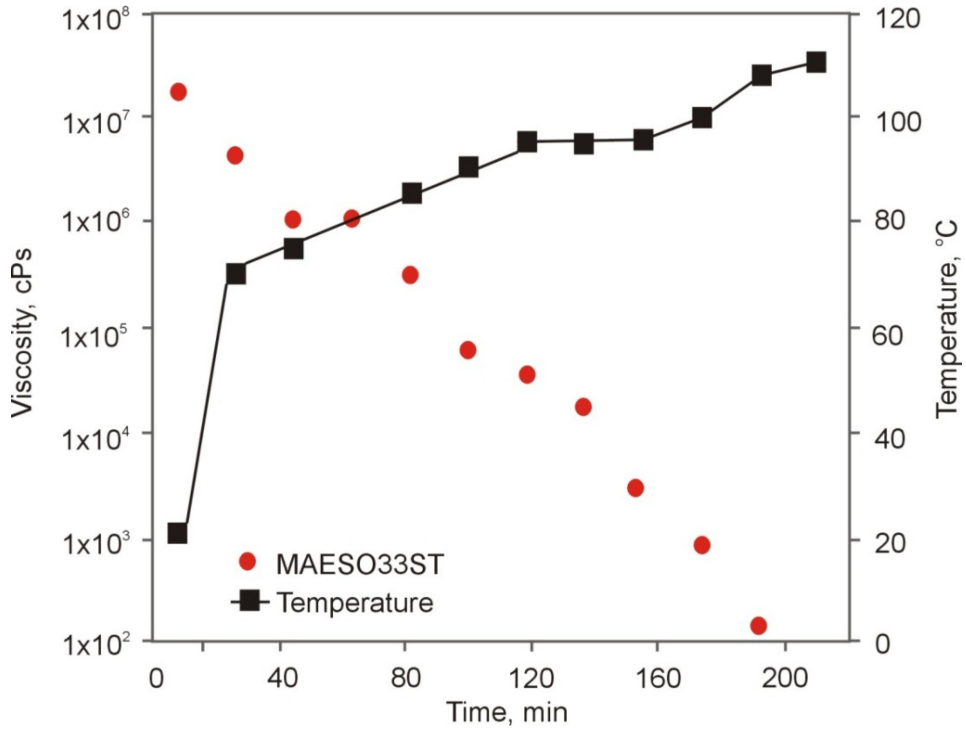
The second-stage reaction



Lu, PhD thesis, University of Delaware, 2005

THICKENING BEHAVIOR

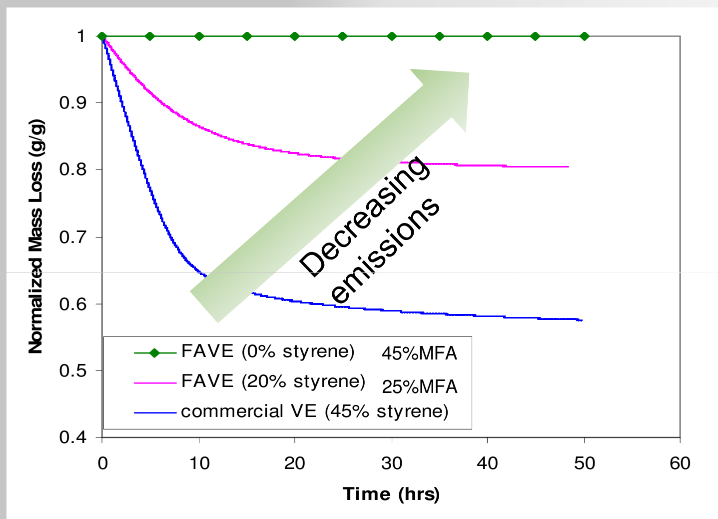


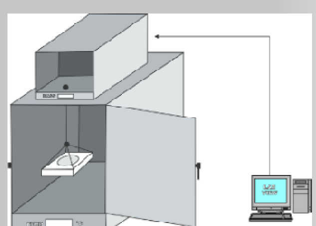


Lu, PhD thesis, University of Delaware, 2005

STYRENE EMISSION STUDY

Mass Loss: Resins

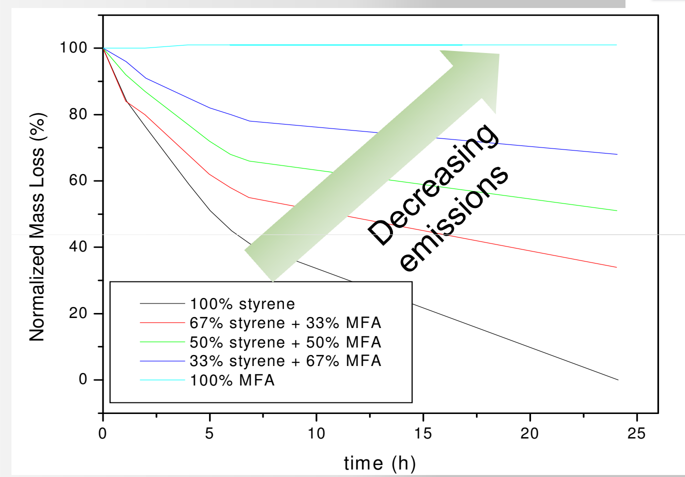




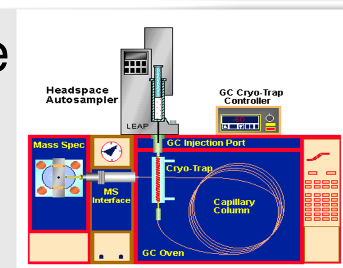
Low HAP resin systems reduce emissions by 40-80%[1]

[1] La Scala *et al.*, Clean Techn Environ Policy, 2009

Mass Loss: Reactive diluents



Head Space CGMS



BIO-BASED CONTENT

$$\text{Bio-Based Content} = \frac{\text{Amount of bio-based carbon}}{\text{Amount of bio-based carbon + Amount of petroleum based carbon}} \times 100$$

http://www.biopreferred.gov

BIO-BASED CONTENT

- MAESO33ST (MAESO with 33 wt% styrene) **57% BBC**
- MAESO20ST (MAESO with 20 wt% styrene and 13 wt% MFA) **65% BBC**
- MAESO13ST (MAESO with13 wt% styrene and 20 wt% MFA) **69% BBC**
- MAESO33MFA (MAESO 33 wt% MFA) **77% BBC**

MAESO is compatible with VE and UPR resins

- Resin made of MAESO (32.5%) and VE/UPR (32.5%) with 33wt% styrene **28% BBC**
- Resin made of MAESO (32.5%) and VE/UPR (32.5%) with 33wt% MFA **48% BBC**

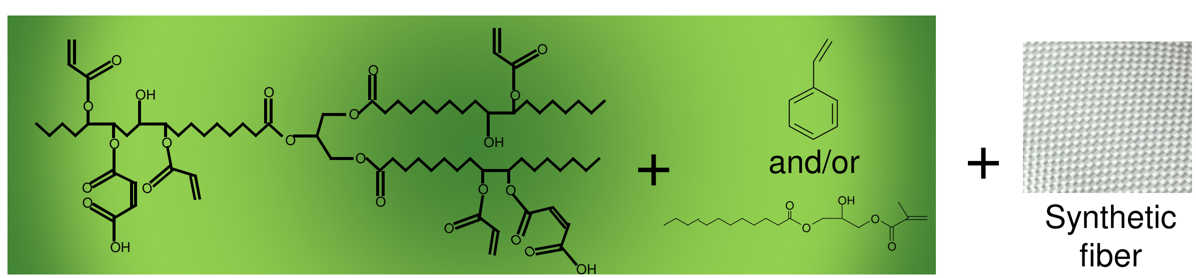
BIO-BASED CONTENT

Composites prepared with bio-resin and fiber glass

Bio-resin			BBC		
Monomer	**Styrene (wt%)**	**MFA (wt%)**	**Neat polymer**	**Composite Example 1 [a]**	**Composite Example 2 [b]**
MAESO	33	0	57%	57%	57%
MAESO	20	13	65%	65%	65%
MAESO	13	20	69%	69%	69%
MAESO	0	33	77%	77%	77%

[a] 50 wt% fiber glass

[b] 70 wt% fiber glass

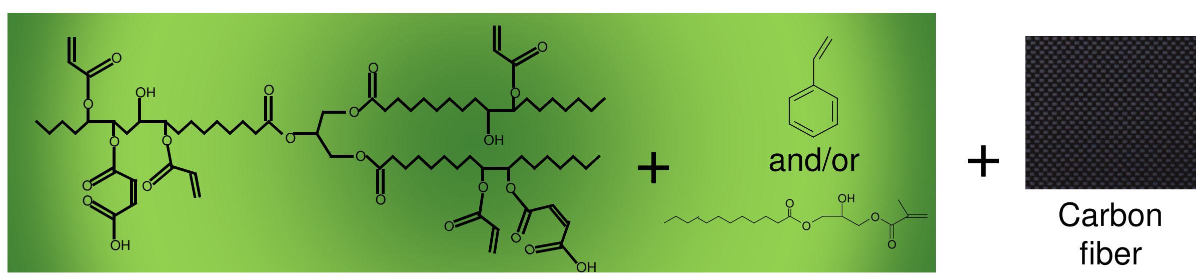


BIO-BASED CONTENT

Composites prepared with bio-resin and of carbon fiber

Bio-resin			BBC		
Monomer	Styrene (wt%)	MFA (wt%)	Neat polymer	Composite Example 1 [a]	Composite Example 2 [b]
MAESO	33	0	57%	27%	17%
MAESO	20	13	65%	30%	19%
MAESO	13	20	69%	32%	20%
MAESO	0	33	77%	36%	23%

[a] 50 wt% carbon fiber
[b] 70 wt% carbon fiber

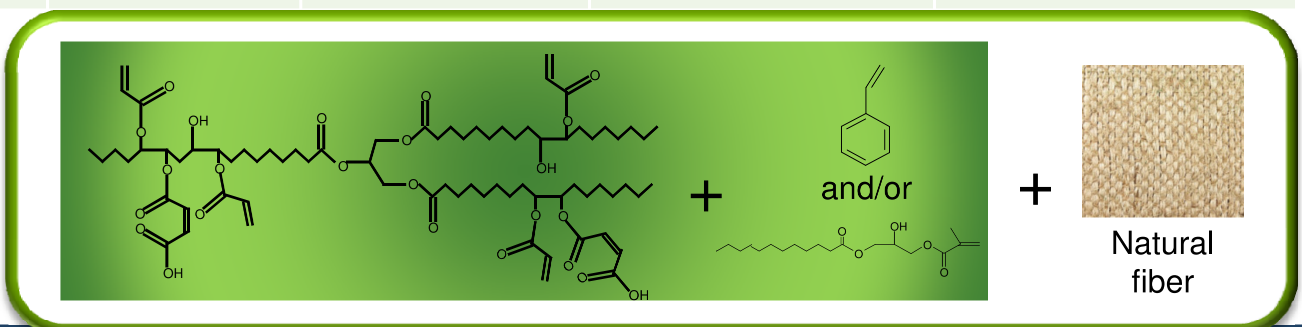


BIO-BASED CONTENT

Composites prepared with bio-resin and of natural fibers

Bio-resin			BBC		
Monomer	**Styrene (wt%)**	**MFA (wt%)**	**Neat polymer**	**Composite Example 1 [a]**	**Composite Example 2 [b]**
MAESO	33	0	57%	78%	87%
MAESO	20	13	65%	82%	89%
MAESO	13	20	69%	84%	90%
MAESO	0	33	77%	87%	93%

[a] 50 wt% natural fiber
[b] 70 wt% natural fiber



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