EPOXY RESINS

From today’s challenges to safe & sustainable alternatives

SPECIFIC POLYMERS

1 INTRODUCTION

2 STAKES & STRATEGY

3 BIOBASED & BPA FREE RESINS

1

INTRODUCTION

INTRODUCTION

Epoxides : history and properties

Discovery

Early 1890s

Nikolai Prilezhaev

First patent

1934

Paul Schlack

Simultaneous discovery

1940

Dr. Pierre CASTAN

Ciba SA

BASF Performance products

First industrial application

1946

Dr. Sylvan GREENLEE

Devoe & Reynolds

Schlack, P. & Germany, B.-T. United States Patent Office Manufacture of Amines of High Molecular Weight, Wich Are Rich on Nitrogen. (1938)

INTRODUCTION

Epoxides : history and properties

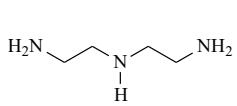
*« Is commonly called epoxy a compound that contains one or several **oxirane moieties**»*

Ring strain
114 kJ/mol3
High reactivity

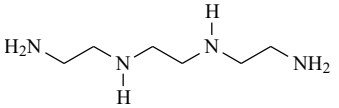
Various hardeners
- **Amines**
- Anhydrides
- Thiols
- Phenols

AMINES

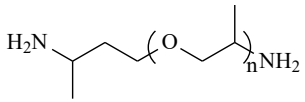
Aliphatic



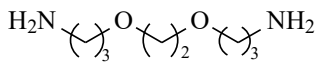
Diethylenetriamine (DETA)



Triethylenetetramine (TETA)

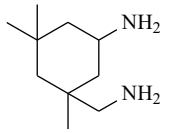


Poly(oxypropylene diamine)

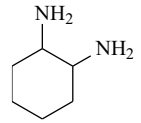


Poly(glycol amine)

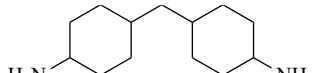
Cycloaliphatic



Isophorone diamine IPDA

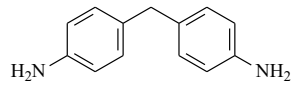


1,2- Diaminocyclohexane (DACH)

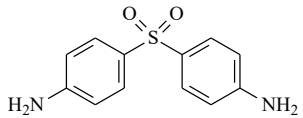


Bis(4-aminocyclohexyl) methane (PACM)

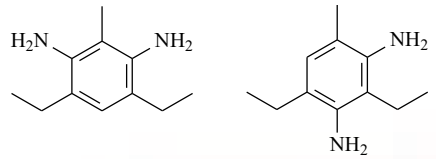
Aromatic



4,4'-Diamino- diphenylmethane (DDM)



4,4-Diaminodiphenyl sulfone (DDS)



Diethyltoluenediamine (DETDA)

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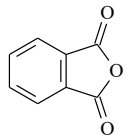
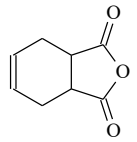
- **Anhydrides**
- Thiols
- Phenols

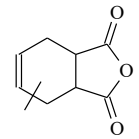
ANHYDRIDES



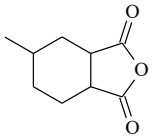
Phthalic anhydride (PA)



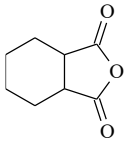
Tetrahydrophthalic anhydride (THPA)



Methyltetrahydrophthalic anhydride (MTHPA)



Methyl hexahydrophthalic anhydride (MHHPA)



Hexahydrophthalic anhydride (HHPA)

INTRODUCTION

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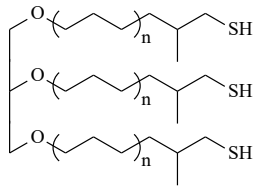
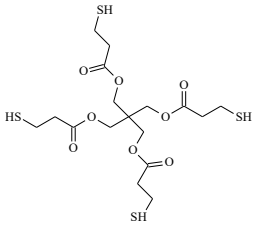
- Phenols

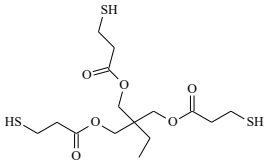
POLYTHIOLS



Polymercaptans



Pentaerythritol
tetrakis(3-mercaptopropionate)



Trimethylolpropane
tris(3-mercaptopropionate)

INTRODUCTION

Epoxides : history and properties

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Ring strain
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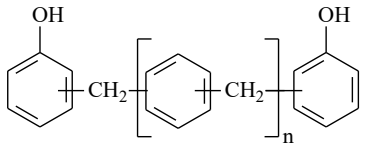
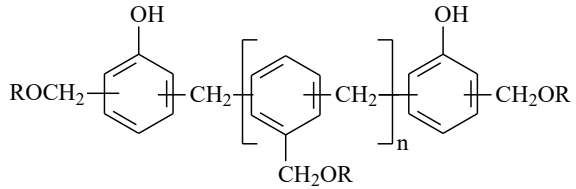
Various hardeners

- Amines
- Anhydrides
- Thiols
- **Phenols**

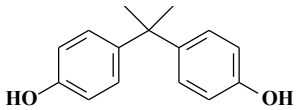
PHENOLIC COMPOUNDS



Phenol Novolac resin



Phenol-formaldehyde resin



Bisphenol A

INTRODUCTION

Epoxides : history and properties

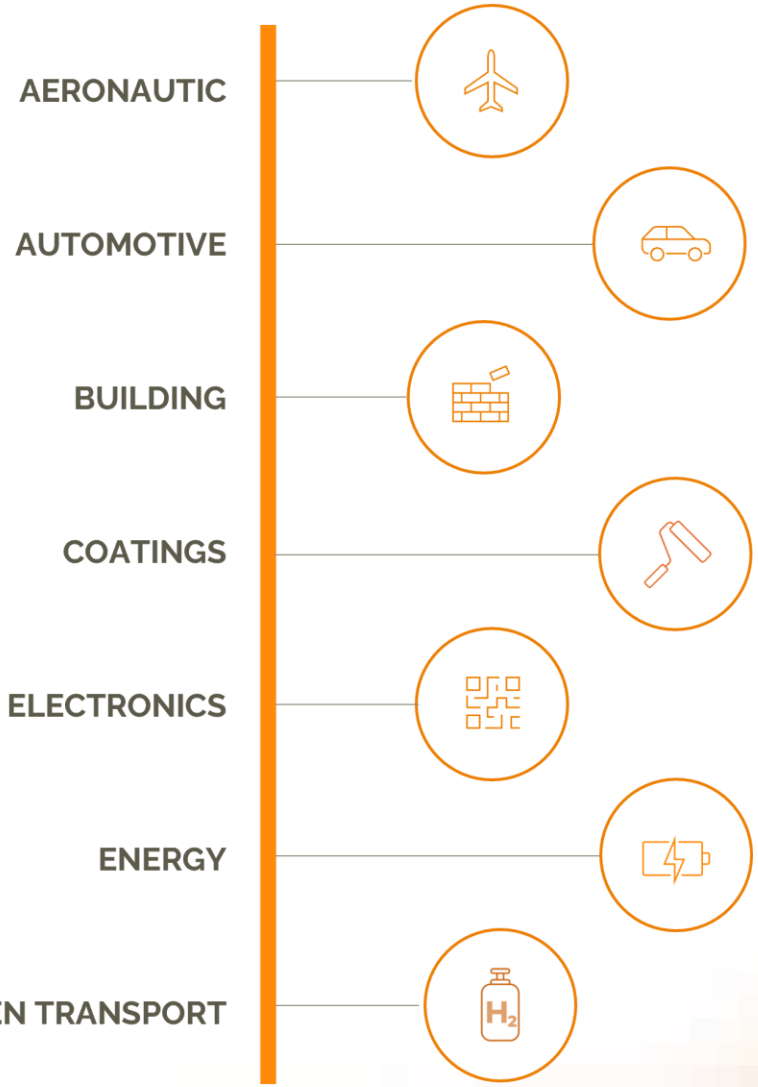
*« Is commonly called epoxy a compound that contains one or several **oxirane moieties**»*

Ring strain
114 kJ/mol3
High reactivity

Wide range of properties
- Thermomechanical performances
- Chemical resistance
- Electrical insulating properties

Various hardeners
- Amines
- Anhydrides
- Thiols
- Phenols

APPLICATIVE FIELDS

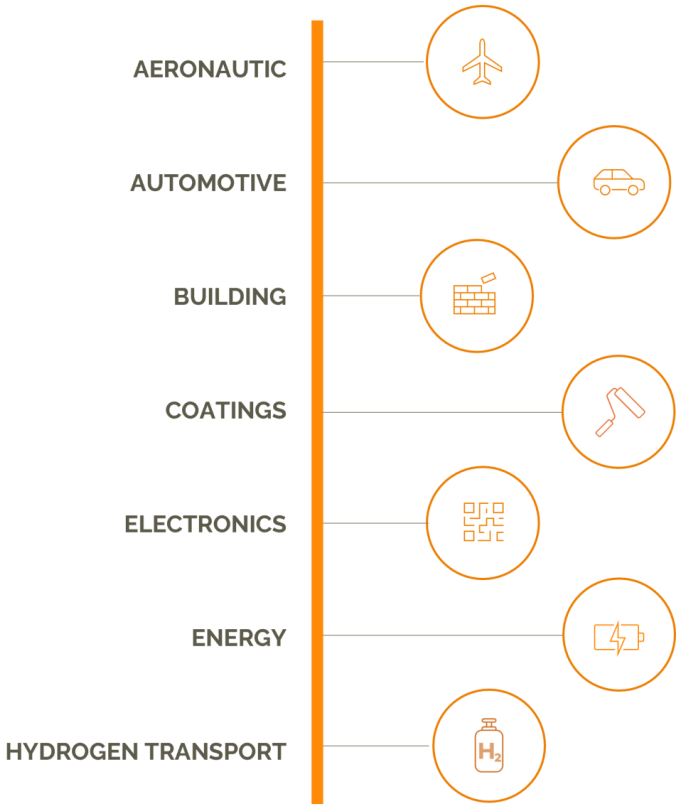


Jin, F. L., Li, X. & Park, S. J. Synthesis and application of epoxy resins: A review. J. Ind. Eng. Chem. 29, 1–11 (2015).

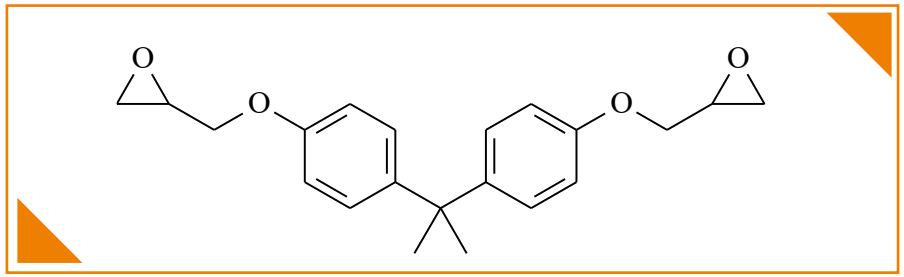
INTRODUCTION

Today's challenges

APPLICATIVE FIELDS



Most used epoxy compound



Diglycidylether of bisphenol A (**DGEBA**)

Olin EPOXY

Sicomin Epoxy Systems

HUNTSMAN

SPECIFIC POLYMERS

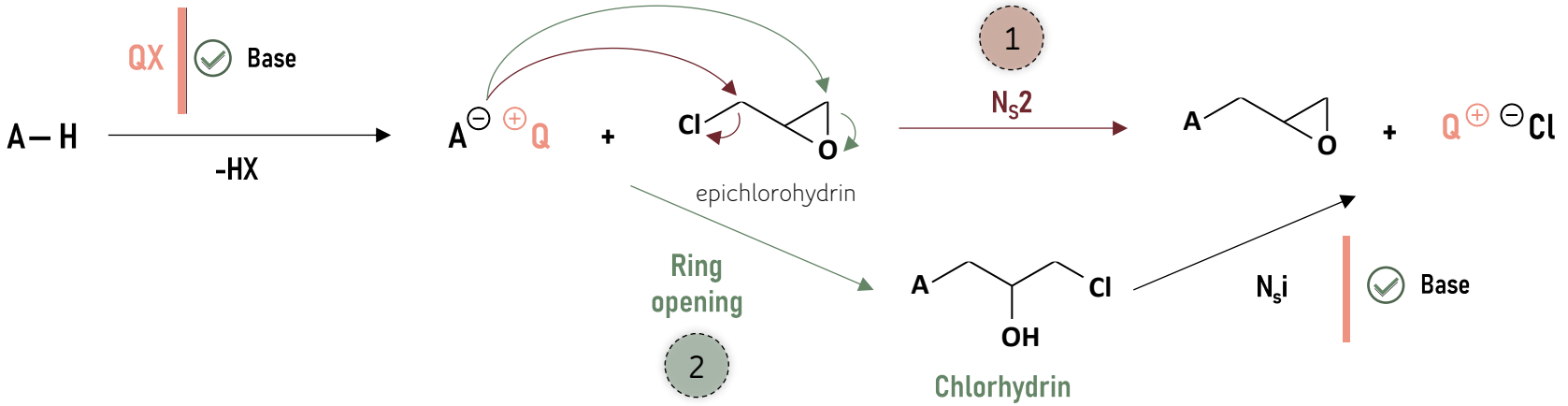
HORIZON 2020

Circular Bio-based Europe Joint Undertaking

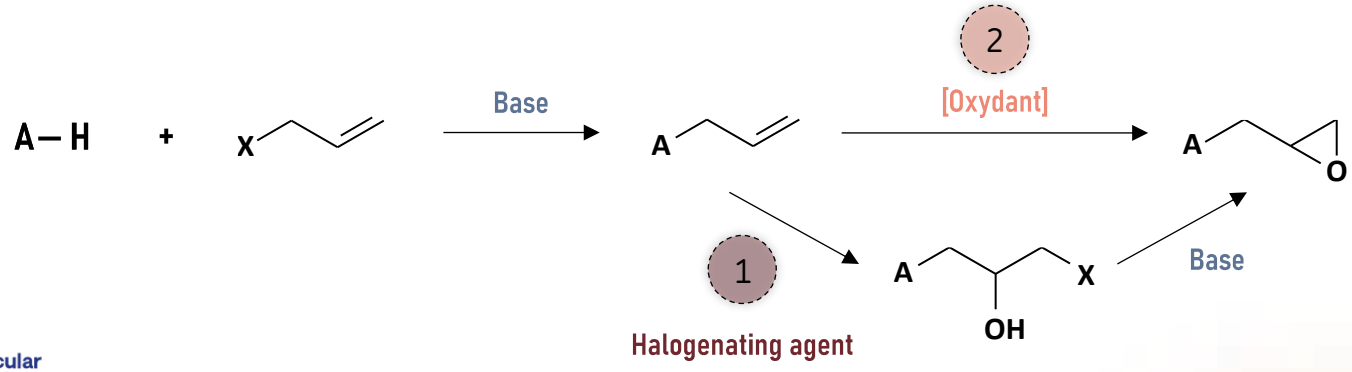
INTRODUCTION

Epoxy synthesis

1. Direct pathway using epichlorohydrin



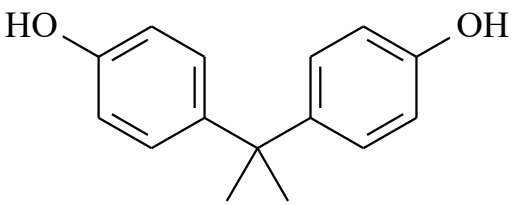
2. Indirect pathway - allylation / epoxydation



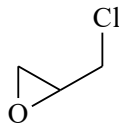
INTRODUCTION

Today's challenges

DGEBA precursor

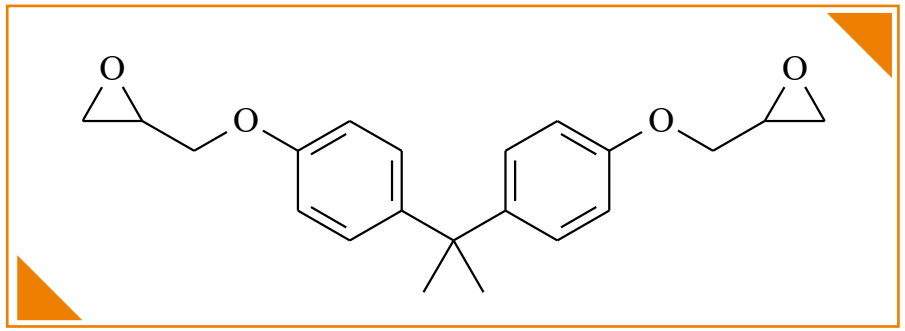


Bisphenol A



Epichlorohydrin

Most used epoxy compound



Diglycidylether of bisphenol A (**DGEBA**)

Precursor in **85 %** of the world production of **epoxy resins**[1]
Adverse effects on human health and environment (activation of estrogen receptor)
Highly regulated on food contact material and **banned in nurse bottles** since 2011

Harmful + Petro-based compounds

[1]Baroncini, E. A., Kumar Yadav, S., Palmese, G. R. & Stanzione, J. F. Recent advances in bio-based epoxy resins and bio-based epoxy curing agents. J. Appl. Polym. Sci. 133, 1-19 (2016).

2

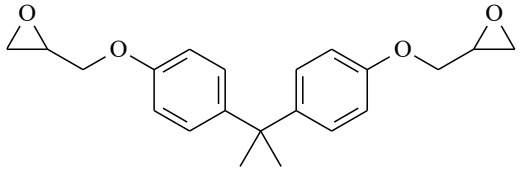
STAKES & STRATEGY

STAKES & STRATEGY

Overview

Epoxy material

1



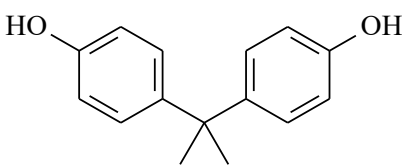
DGEBA

2

HARDENER

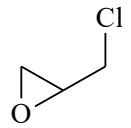
Finding safe & sustainable epoxy materials alternatives means ...

1.1



Bisphenol A

1.2



Epichlorohydrin

STAKES & STRATEGY

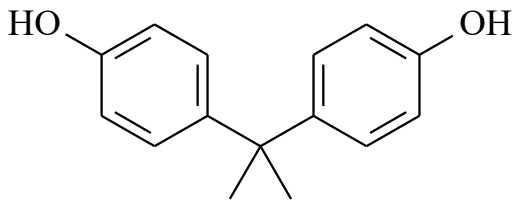
Alternatives in biobased epoxy resins

- Researches in finding safe & biobased alternatives to BPA
- Researches in finding biobased alternatives to epichlorohydrin
- Researches in finding biobased hardeners

INTRODUCTION

Today's challenges

DGEBA precursor



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→ Finding relevant alternatives to BPA means…

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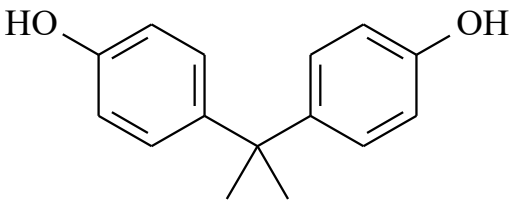

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1. Design a structure which not able to activate estrogen receptor

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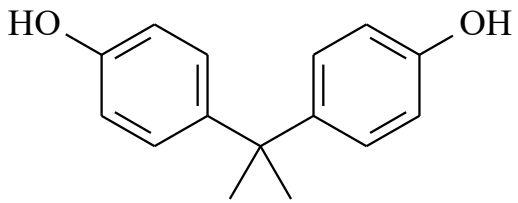

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2. Use sustainable resources

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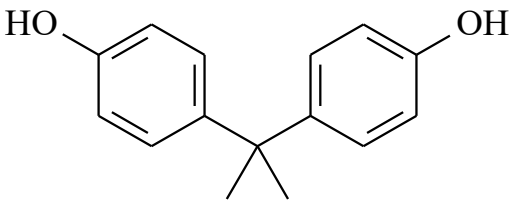

Bisphenol A

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2. Use sustainable resources

3. Target similar performances

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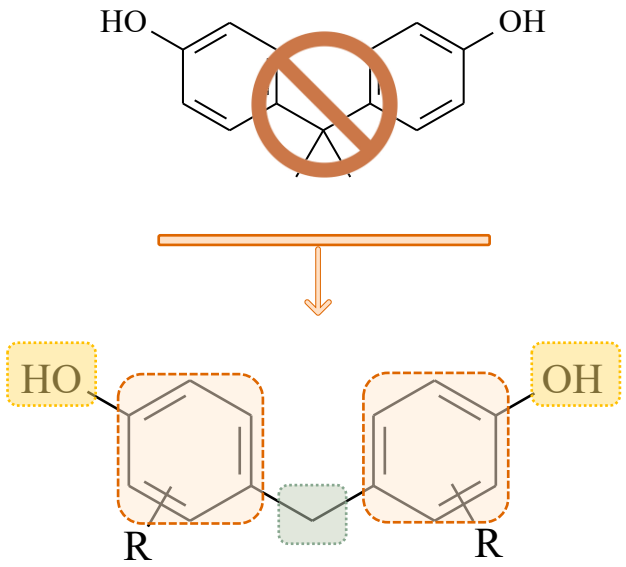
STAKES & STRATEGY

By-passing bisphenol-A : toward safer epoxy resins



- 2 phenols moieties
- 2 aryl groups
- 1 carbon spacer

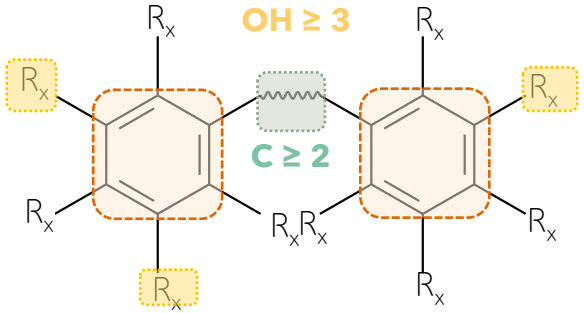
Structural part

Target DGEBA main performances

Involve **mono-aryl phenols**

Rx : OH, or H or another functional group

Involve **polyphenols**

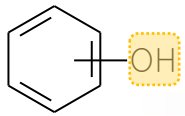


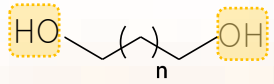
R_x : H, OH or another functional group (methoxy, aldehyde..)

Epoxy reactive diluents

Fine tuning of properties

Involve **monophenol, aliphatic diols**





STAKES & STRATEGY

Alternatives in biobased epoxy resins

Researches in finding biobased alternatives to BPA

- Plant oil
- Sugar derivatives
- Natural phenols & polyphenols
- Natural resins
- Lignin & derivatives

STAKES & STRATEGY

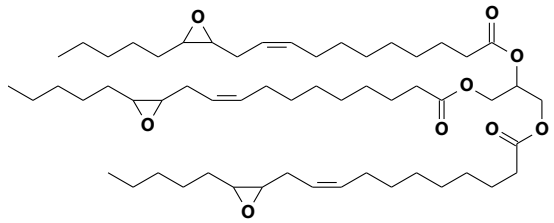
Alternatives in biobased epoxy resins

Researches in finding biobased alternatives to BPA

From → Plant oil
- Sugar derivatives
- Natural phenols & polyphenols
- Natural resins
- Lignin & derivatives

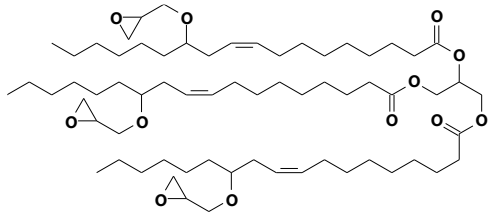
\+

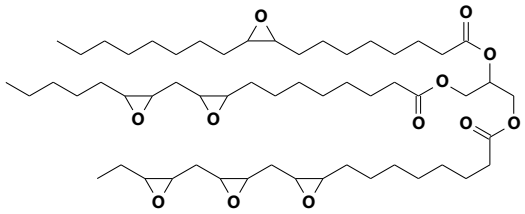
- Nontoxic
- Low cost
- Widely available



Vernonia oil

Castor oil





Soybean oil

- Long aliphatic chain
  → ≈ low performances
- Material T_g ∝ epoxy index

[1]Baroncini, E. A., Kumar Yadav, S., Palmese, G. R. & Stanzione, J. F. Recent advances in bio-based epoxy resins and bio-based epoxy curing agents. J. Appl. Polym. Sci. 133, 1-19 (2016).

STAKES & STRATEGY

Alternatives in biobased epoxy resins

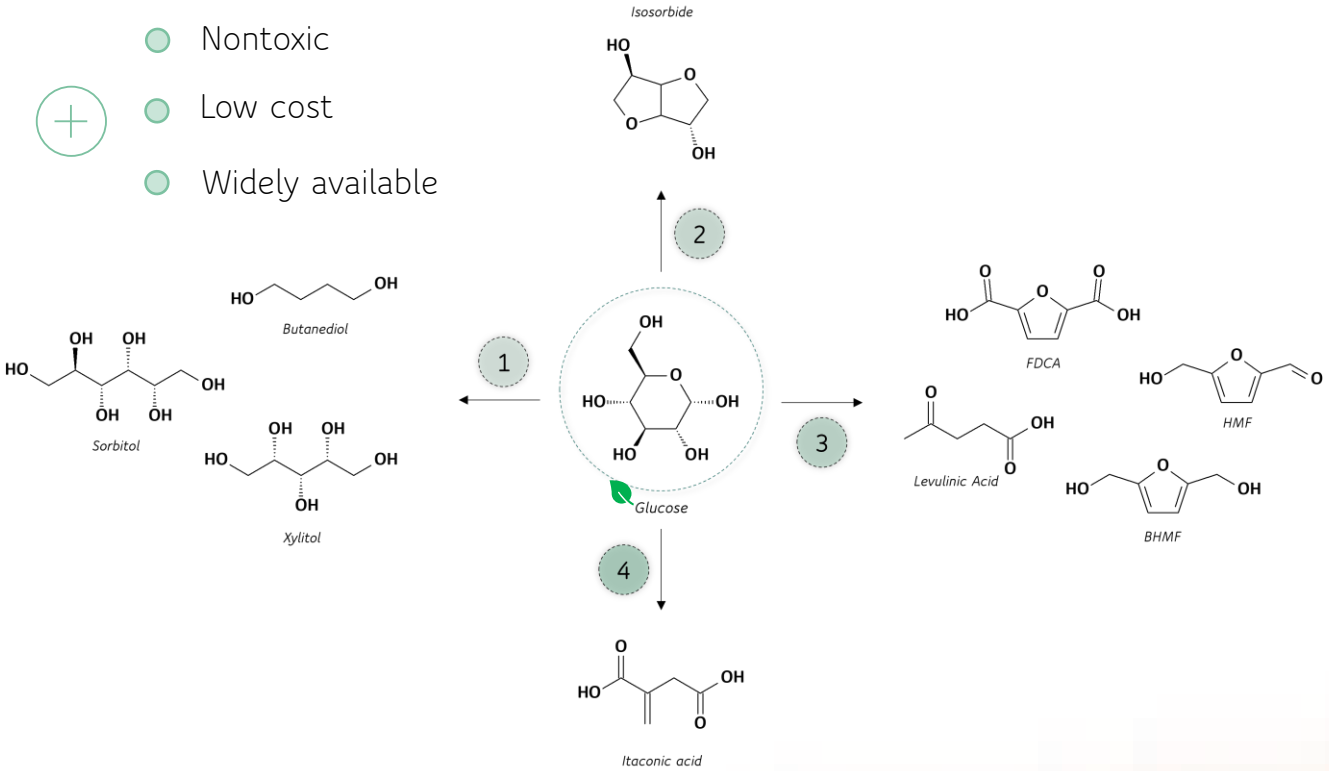
Researches in finding biobased alternatives to BPA

From

- Plant oil
- Sugar derivatives
- Natural phenols & polyphenols
- Natural resins
- Lignin & derivatives

Precursors platform from Glucose

- Nontoxic
- Low cost
- Widely available



[1]Baroncini, E. A., Kumar Yadav, S., Palmese, G. R. & Stanzione, J. F. Recent advances in bio-based epoxy resins and bio-based epoxy curing agents. J. Appl. Polym. Sci. 133, 1-19 (2016).

STAKES & STRATEGY

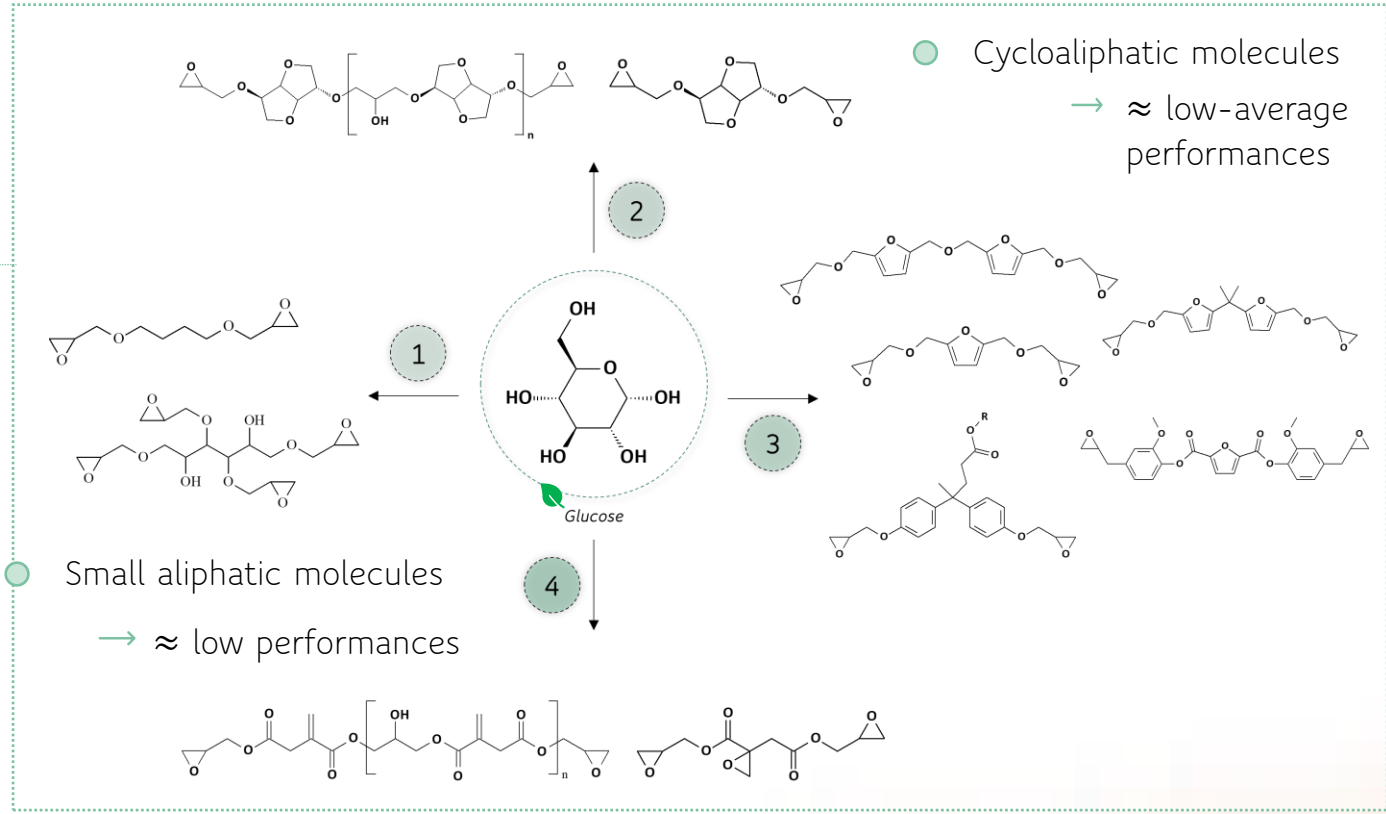
Alternatives in biobased epoxy resins

Researches in finding biobased alternatives to BPA

From →

- Plant oil
- Sugar derivatives
- Natural phenols & polyphenols
- Natural resins
- Lignin & derivatives

Epoxy platform from Glucose



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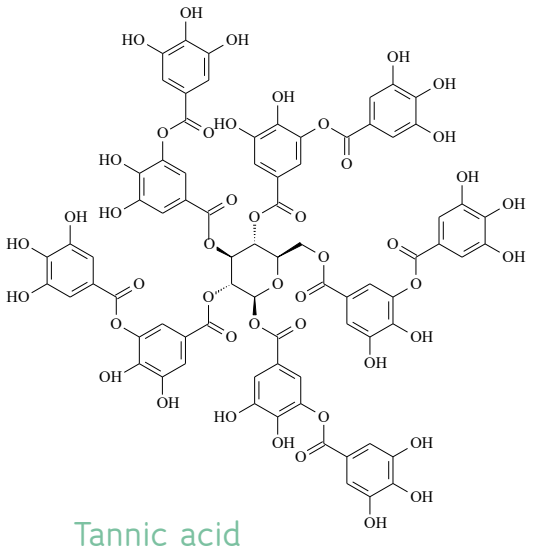
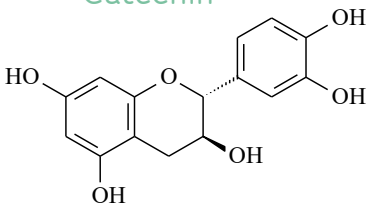
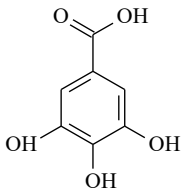


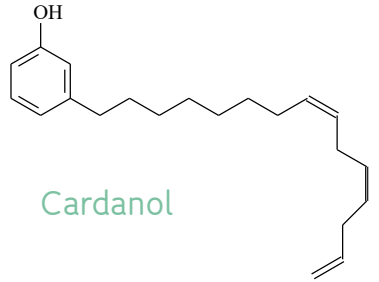
Tannic acid

Catechin





Gallic acid



Cardanol

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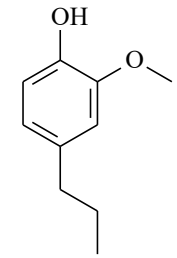
STAKES & STRATEGY

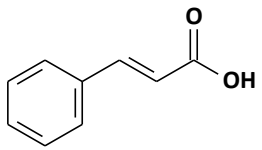
Alternatives in biobased epoxy resins

Researches in finding biobased alternatives to BPA

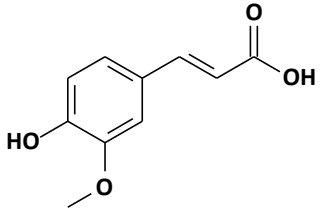
- Plant oil
- Sugar derivatives
- Natural phenols & polyphenols
- Natural resins
- From ⟹ Lignin & derivatives



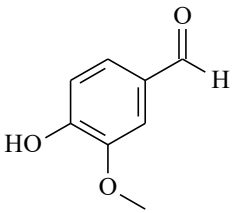
Dihydroxy eugenol



Cinnamic acid



Ferulic acid



Vanillin

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STAKES & STRATEGY

Alternatives in biobased epoxy resins

- Researches in finding biobased alternatives to BPA
- Research in finding biobased alternatives to epichlorohydrin
- Research in finding biobased hardeners

STAKES & STRATEGY

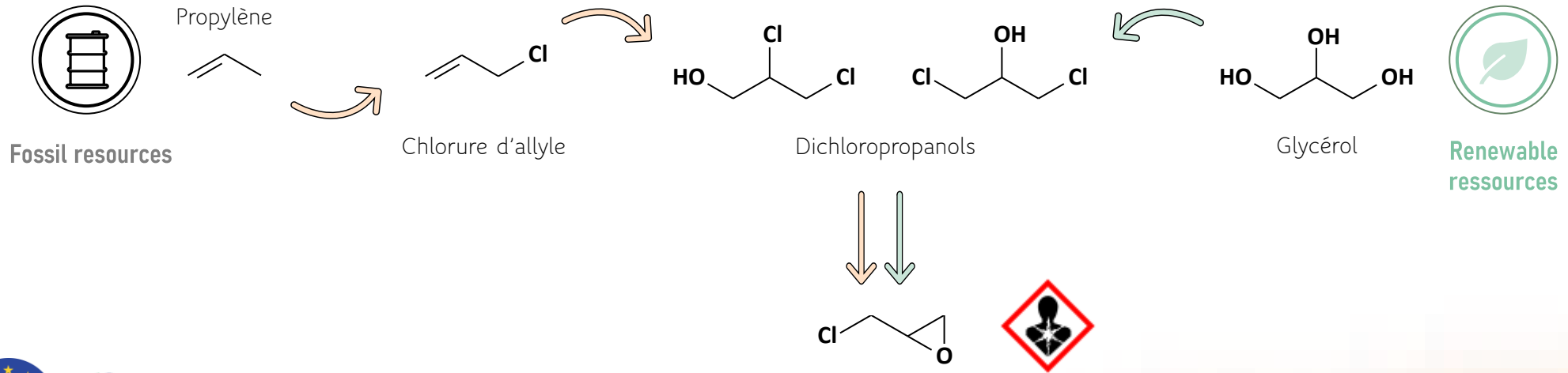
Alternatives in biobased epoxy resins

Researches in finding biobased alternatives to Epichlorohydrin (ECH)

Possible synthesis from **Glycerol** (GTE process)

Commercial solution : **Epicerol®** Technology

Cost very close to petrobased ECH : 2$/kg



STAKES & STRATEGY

Alternatives in biobased epoxy resins

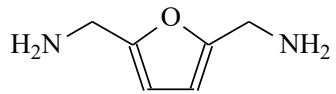
- Researches in finding biobased alternatives to BPA
- Researches in finding biobased alternatives to epichlorohydrin
- Researches in finding biobased hardeners

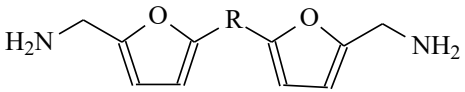
STAKES & STRATEGY

Alternatives in biobased epoxy resins

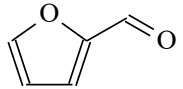
Researches in finding biobased hardeners

- Amines
- Amino acids
- Acids
- Anhydrides
- Phenols

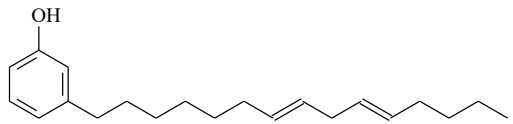




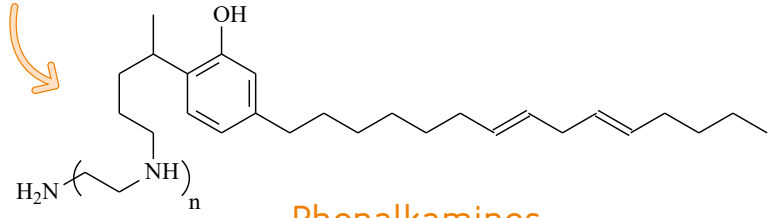
HMF



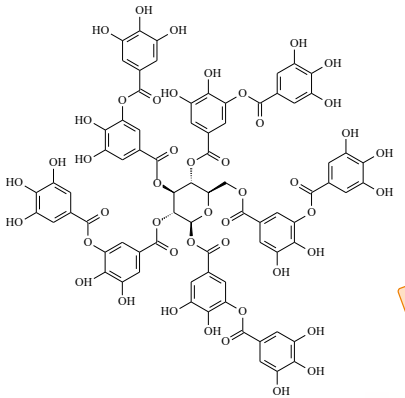
Furfural



Cardanol



Phenalkamines



Tannic acid

3

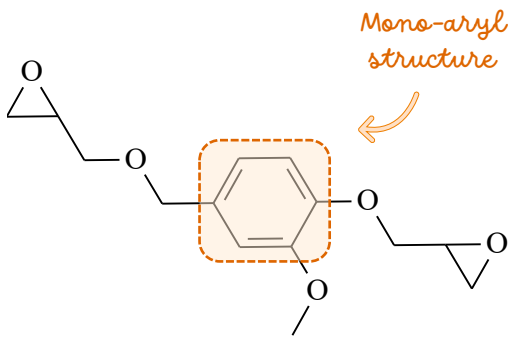
BIOBASED
&
BPA-FREE RESINS

BIOBASED & BPA FREE RESINS

Epoxy building-blocks : SP's strategy

kgs

DGEVA SP-9S-5-005



Diglycidylether of vanillyl alcohol

- Crystalline white solid
- Structural epoxy resin
- Low viscosity – 25 °C 500 mPa.s | 50 °C 70 mPa.s
- Available in 3 BBCs 0 % | 40 % | 100 %
- Low performances

Thermal cure

Cycloaliphatic amine hardener. $T_g \approx 95$ °C

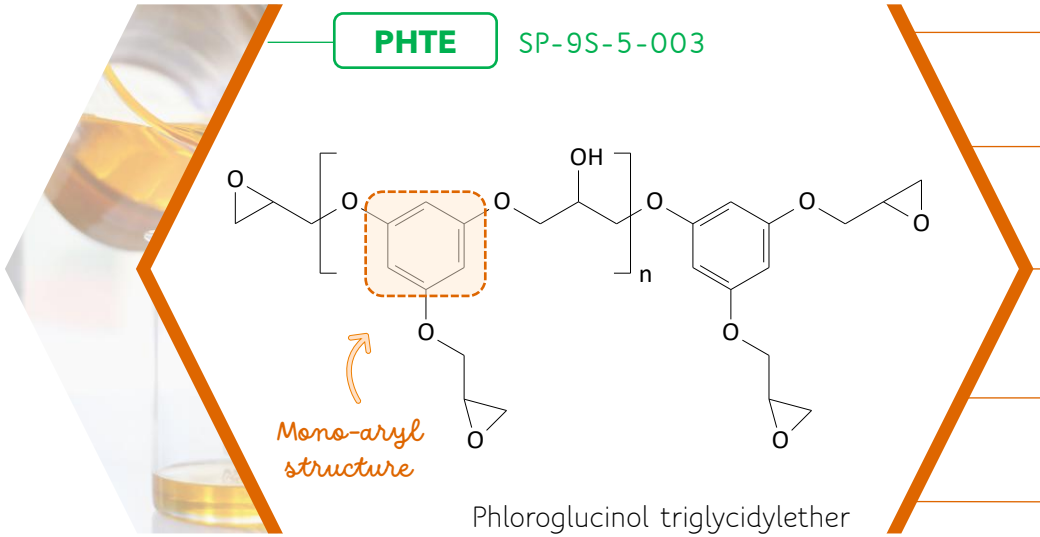
Aromatic amine hardener. $T_g \approx 110$ °C

SPECIFIC POLYMERS

BIOBASED & BPA FREE RESINS

Epoxy building-blocks : SP's strategy

kgs



PHTE SP-9S-5-003

Phloroglucinol triglycidylether

- Orange viscous liquid
- Structural epoxy resin
- High viscosity – 30 °C 7000 - 9000 mPa.s | 50 °C 600 – 700 mPa.s
- Available in 2 BBCs 0 % | 60 %
- High performances

Thermal cure

Cycloaliphatic amine hardener. $T_g \approx 250$ °C (DMA)
Aromatic amine hardener. $T_g \approx 225$ °C (DMA)

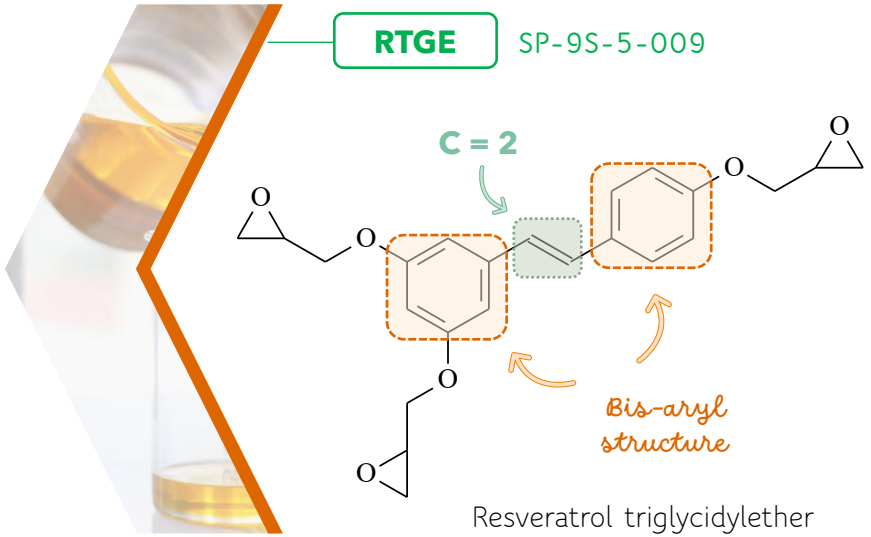
BIOBASED & BPA FREE RESINS

Epoxy building-blocks : SP's strategy

COMING SOON

kgs

g to 1 kg



RTGE SP-9S-5-009

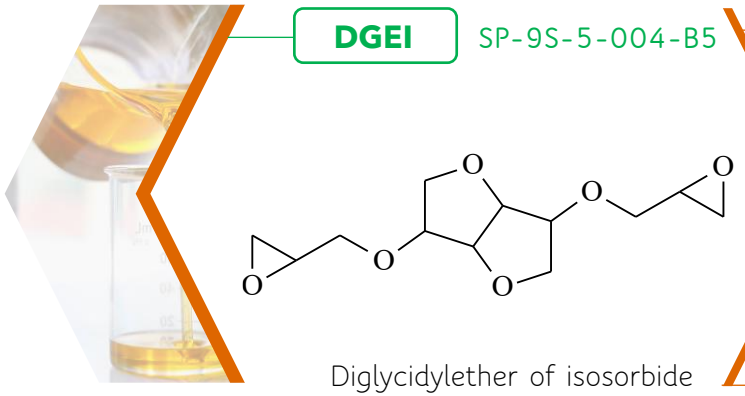
Resveratrol triglycidylether

- Brown viscous liquid
- Structural epoxy resin
- Very high viscosity – 30 °C 200 k – 450 k mPa.s | 80 °C 500 – 700 mPa.s
- High performances
- Available in 2 BBCs: 0 % | 60 % | COMING SOON 100 %

Approximating PHTE ⇦

BIOBASED & BPA FREE RESINS

Epoxy building-blocks : SP's strategy

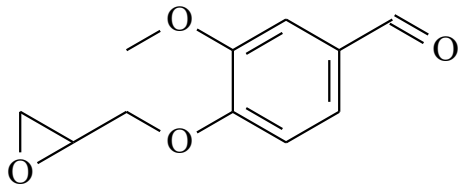


DGEI SP-9S-5-004-B5

Diglycidylether of isosorbide

- Liquid
- Powder
- Epoxy reactive diluent
- Very low viscosity
- Very low performances

SP-9S-5-008 **MGEV**



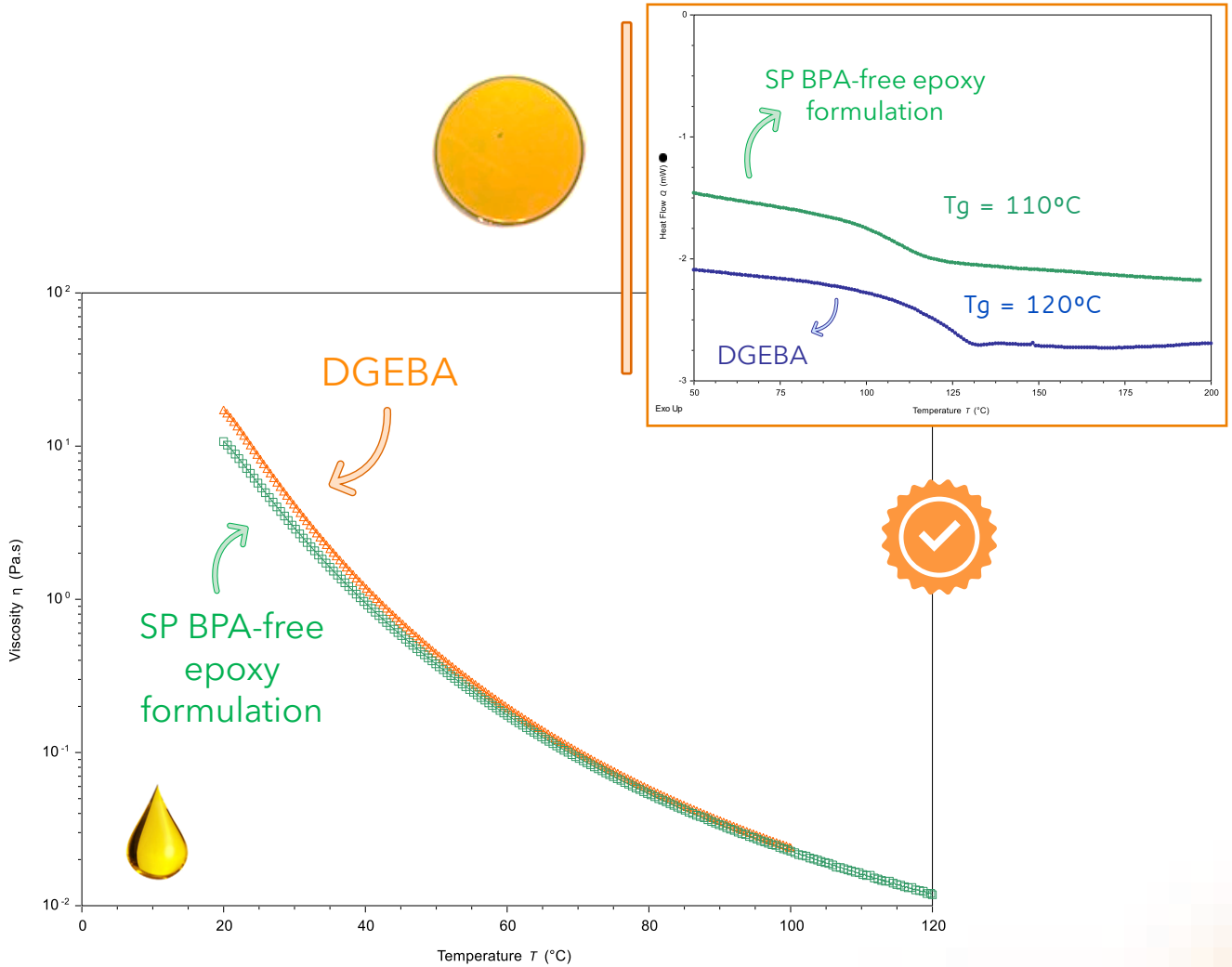
Vanillin monoglycidylether

- Bifunctional bicyclic epoxy
- Low molecular weight
- Viscosity at 25 °C = 250 mPa.s

- Monofunctional aryl epoxy
- Low molecular weight
- Powder at 25 °C,

BIOBASED & BPA FREE RESINS

Epoxy formulations : SP achievement



THANK YOU FOR YOUR ATTENTION

Fiona Magliozzi
fiona.magliozzi@specificpolymers.fr

SPECIFIC POLYMERS

CUBIC

HORIZON 2020

Circular Bio-based Europe Joint Undertaking