ESCD CONGRESS 2022

JUNE 8-10, 2022 - AMSTERDAM - THE NETHERLANDS

Nature-Inspired Epoxy Resins: PinoDGE

I HILL W. T

Dr. Niamh O'Boyle Trinity College Dublin, Ireland nioboyle@tcd.ie

ESCD Congress 2022 Thursday 9th June Session: Acrylates and resins

INTRODUCTION | EPOXY RESINS

Epoxy chemicals are implicated in both occupational and non-occupational contact allergy.

11.7 – 12.5%



A, et al. Contact Dermatitis (2010) 62: 55 N et al. Contact Dermatitis (2012) 67: 73

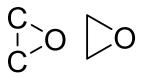
0.9 - 2.3%

OCCUPATIONAL CONTACT ALLERGY | EPOXY RESINS

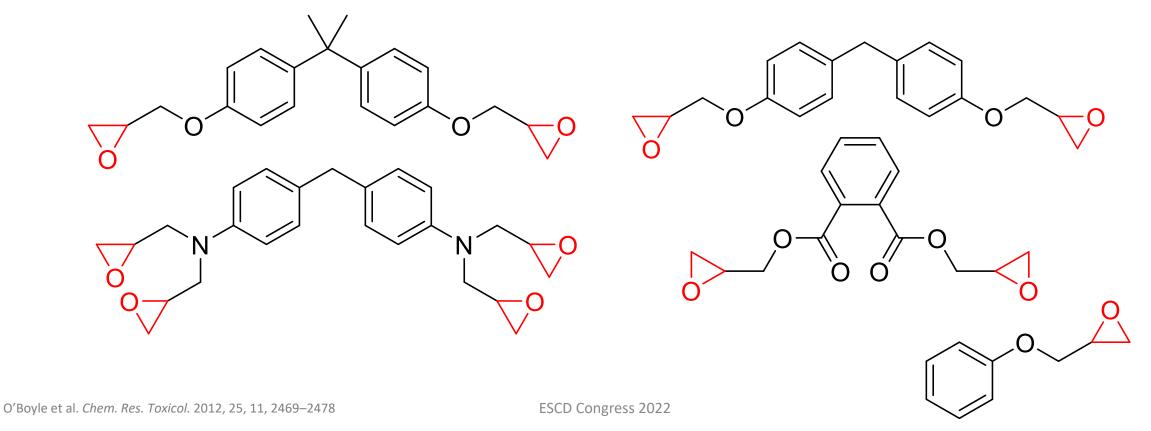


Higgins, C, Cahill, J, Jolanki, R, et al. (2018) Epoxy Resins. In Kanerva's Occupational Dermatology (3rd edit)

INTRODUCTION | EPOXY RESINS



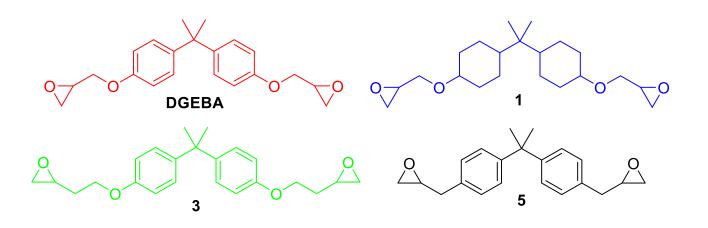
- Global market volume: 3.0 million tonnes per annum
- Allergenicity depends on the terminal epoxide group

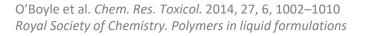


AIM

Our aim is to develop epoxy resins that:

- 1. Have less skin sensitizing properties
- 2. Have excellent technical properties
- 3. Are derived from sustainable sources





ESCD Congress 2022





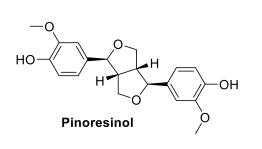
Polymers in liquid formulations

Opportunities for a sustainable future

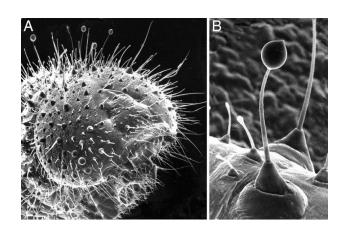
PINORESINOL

- A lignan found in many plant species, including *Forsythia*
- Also found in the secretions of a caterpillar, *Pieris rapae*

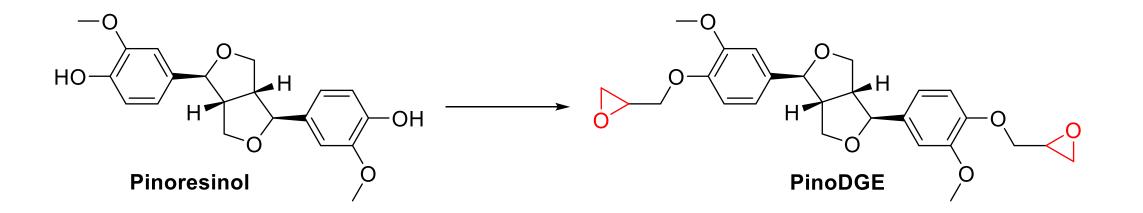








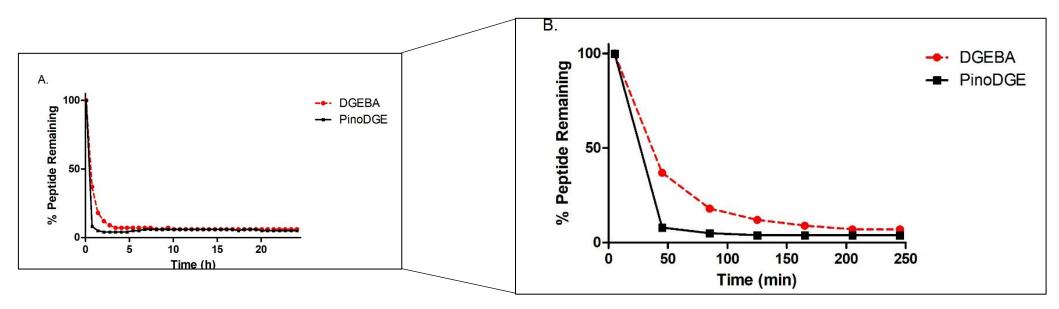
PinoDGE | SYNTHESIS FROM PINORESINOL



Reagents and conditions: (±)-Epichlorohydrin (22 eq.), NaOH (4 eq.), EtOH, 80 °C, microwave irradiation, 40 min, **88 %**

PinoDGE | PEPTIDE REACTIVITY

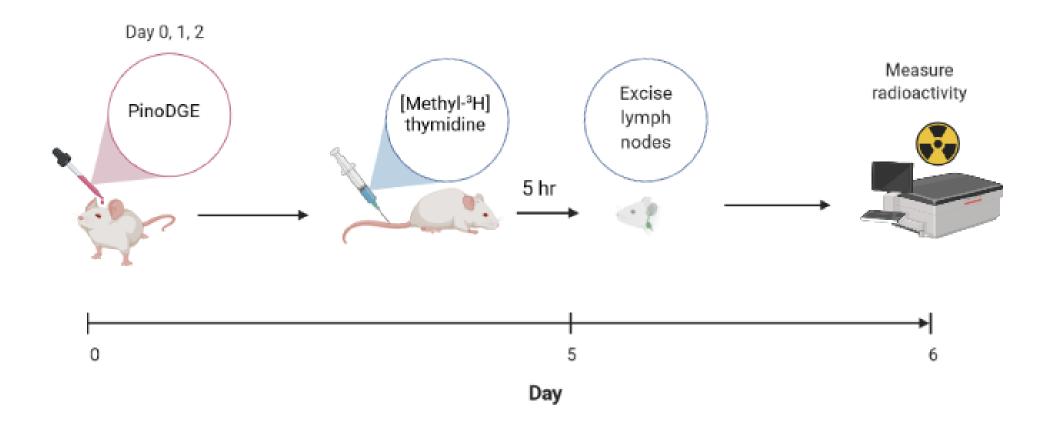
- Model peptide AcPHCKRM
 - Contains cysteine and histidine amino acids
- React with DGEBA or PinoDGE for 24 hours
- Measure reactivity by LC/MS



PinoDGE | KeratinoSens ASSAY

| Compound | ا _{max} (fold induction) ^ه | Classification ^b | EC _{κs} 1.5 (μM) ^c | EC _{κs} 4.5 (μM) ^c | Cytotoxicity IC ₅₀ (μM) ^d |
|----------|---|------------------------------------|--|--|--|
| DGEBA | 13 | Sensitizer | 5.2 | 10 | 22 |
| PinoDGE | 246 | Sensitizer | 2.5 | 7.4 | 24 |

PinoDGE | LLNA ASSAY



PinoDGE | LLNA ASSAY

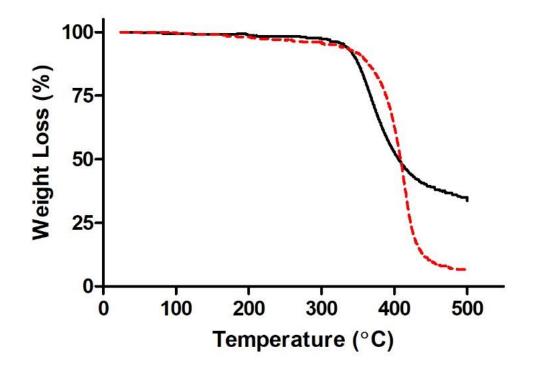
- PinoDGE was not classified as a skin sensitizer in the LLNA at concentrations up to 0.17 M
 - DGEBA EC3 = 0.036 M

| Solvent | Test concentration | Test concentration | (³ H)thymidine incorporation | SI | EC3 | |
|----------|--------------------|--------------------|--|------|-------------------|-------------------|
| | (% w/v) | (M) | (dpm/lymph node) | | (% w/v) | (M) |
| AOO 4:1 | Control | | 298 | | n. a ^b | n. a ^t |
| | 0.10 | 0.0021 | 280 | 0.94 | | |
| | 1.0 | 0.021 | 368 | 1.23 | | |
| | 2.5 | 0.053 | 166 | 0.56 | | |
| | 3.0 | 0.064 | 325 | 1.09 | | |
| | 5.0 | 0.11 | 327 | 1.10 | | |
| AOO 16:1 | Control | _ | 248 | _ | n. a ^b | n. a ^t |
| | 2.0 | 0.043 | 130 | 0.52 | | |
| | 4.0 | 0.085 | 180 | 0.73 | | |
| | 6.0 | 0.13 | 195 | 0.79 | | |
| | 8.0 | 0.17 | 480 | 1.94 | | |
| | 10 ^c | 0.21 ^c | 180 | 0.73 | | |

Table 2. Detailed results from the LLNA of pinoresinol diglycidylether (PinoDGE)^a in AOO 4:1 and in AOO 16:1.

PinoDGE | TECHNICAL PROPERTIES

- Thermogravimetric analysis
- Initial decomposition temperature
 - PinoDGE: 338 °C
 - DGEBA: 358 °C



Thermogravimetric thermograms showing % weight loss at increasing temperatures of epoxy resins based on different ERMs in N2. DGEBA and PinoDGE. N=3.

SUMMARY | FUTURE WORK

Epoxy resins that:

- ✓ Have less skin sensitizing properties
- Have excellent technical properties*
- ✓Are derived from sustainable sources
 - Investigate a wider range of plantderived material



THANK YOU FOR LISTENING

ACKNOWLEDGEMENTS

University of Gothenburg Dr. Ida B. Niklasson Dr. David J Ponting Dr. Miguel A Ortega Dr. Tina Seifert Prof. Kristina Luthman Prof. Ann-Therese Karlberg

Givaudan Schweiz AG Dr. Andreas Natsch