AMADE
ANALYSIS AND ADVANCED MATERIALS FOR STRUCTURAL DESIGN

Novel vanillin-derived epoxy resin: Curing kinetics, thermal, rheological and mechanical properties

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September 5th to 6th, 2024

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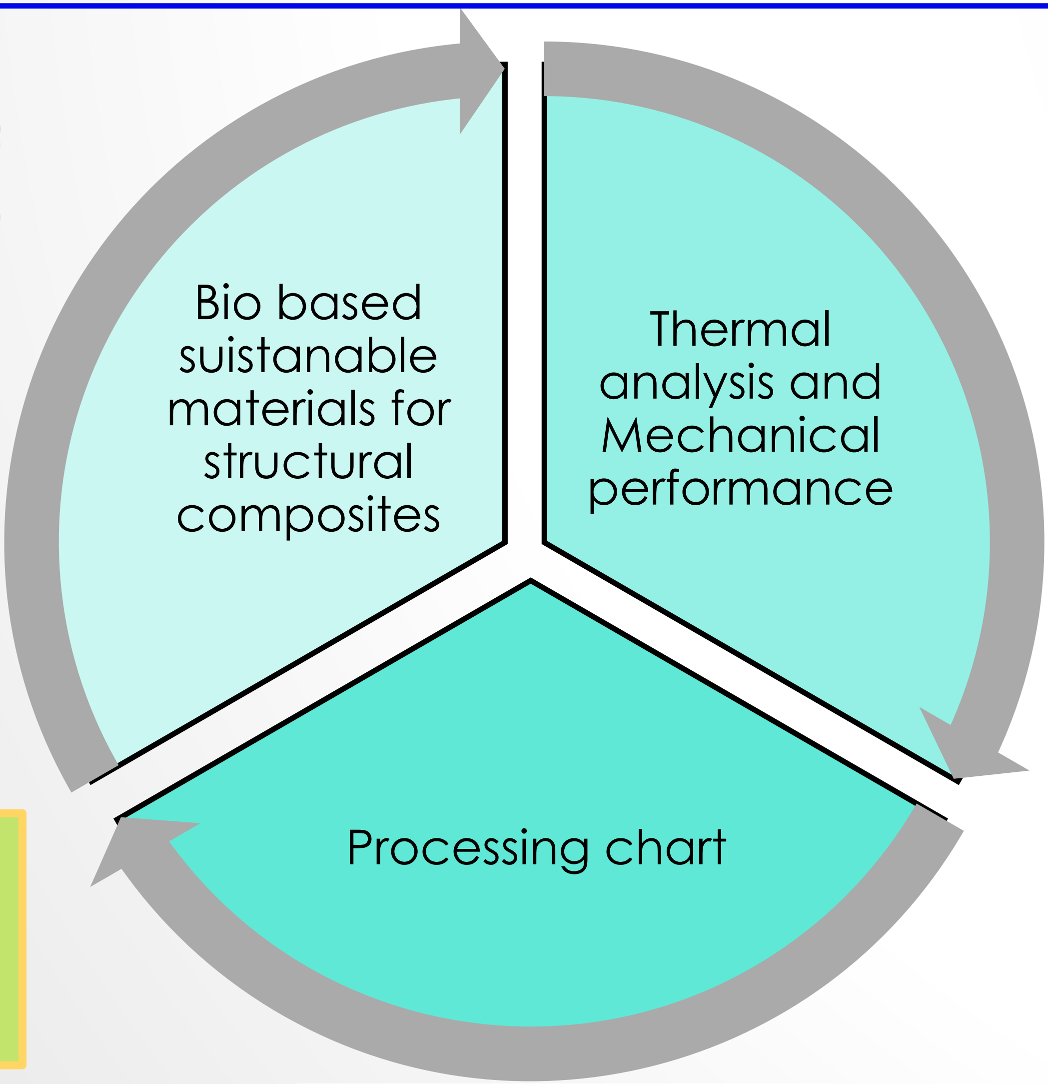
The main goals of the project

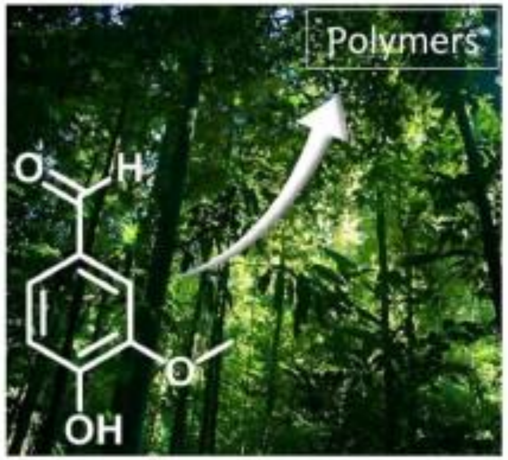
Universitat de Girona
Grup de Recerca en Materials i Termodinàmica



Bio-Based Epoxy Resins: A successful Solution
to sustainability challenges in thermostes

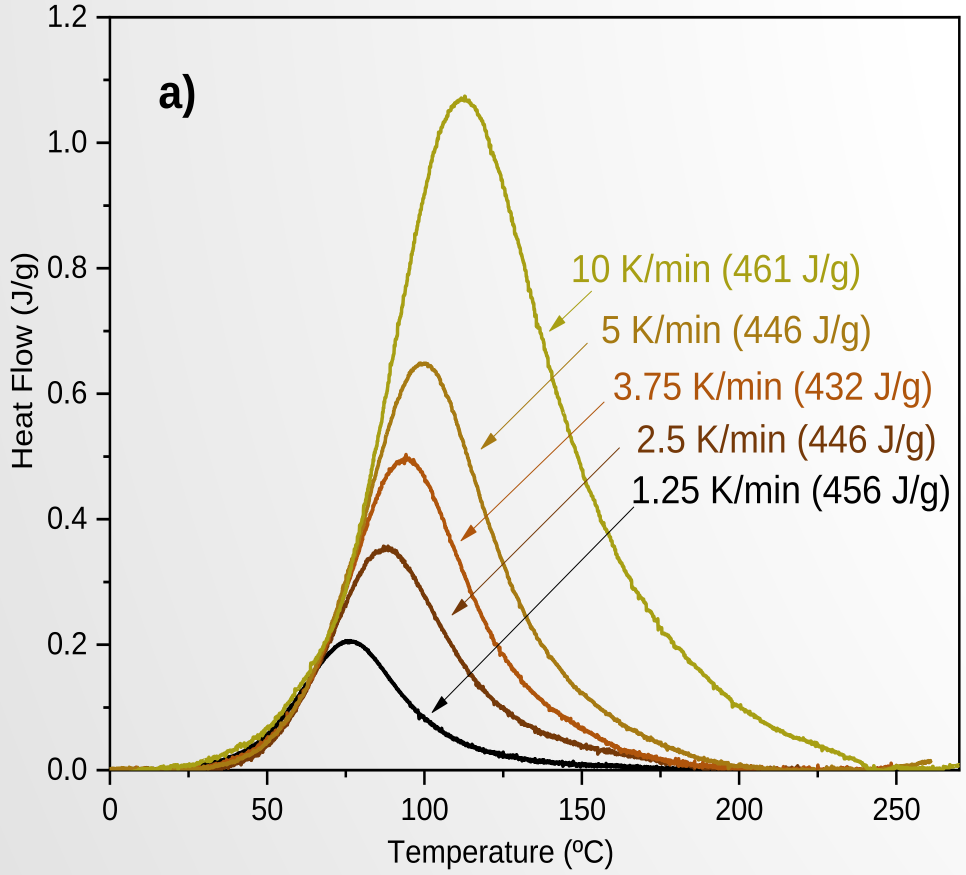
Why vanillin bio based epoxy resins?

- comparable mechanical properties to DGEBA.
- synthesized from wood on an industrial scale
- are promising substitutes to bisphenol A for designing high-performance thermosets

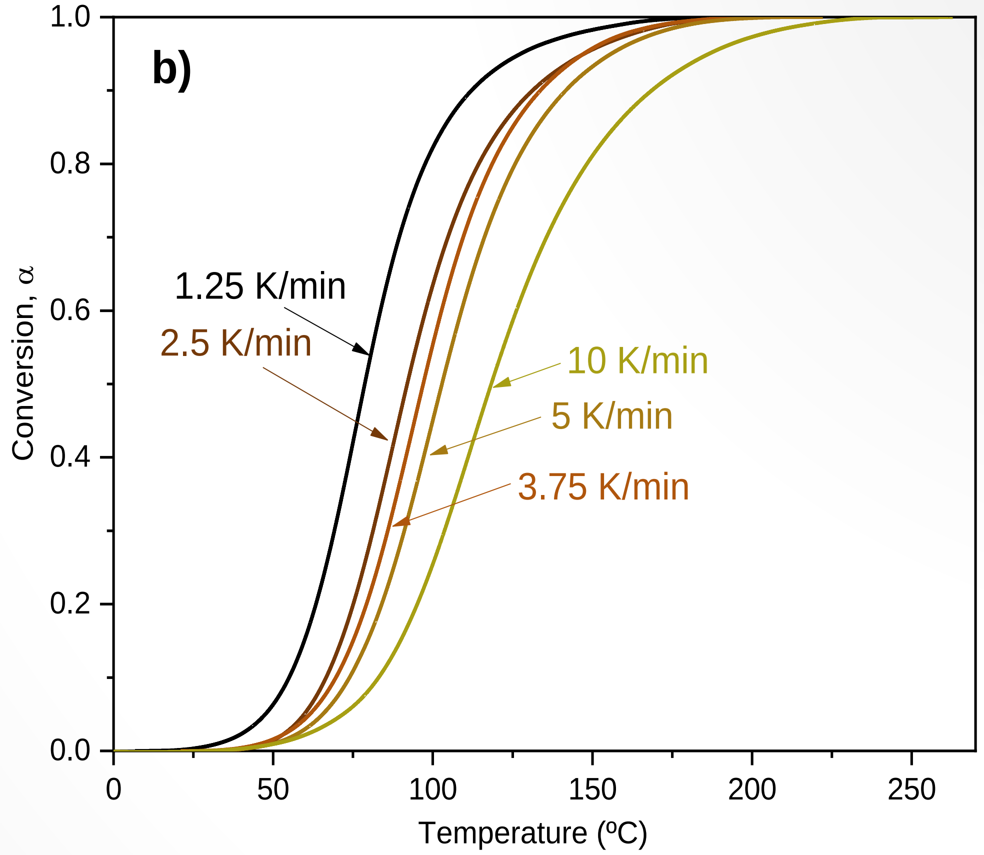


Isothermal processing chart

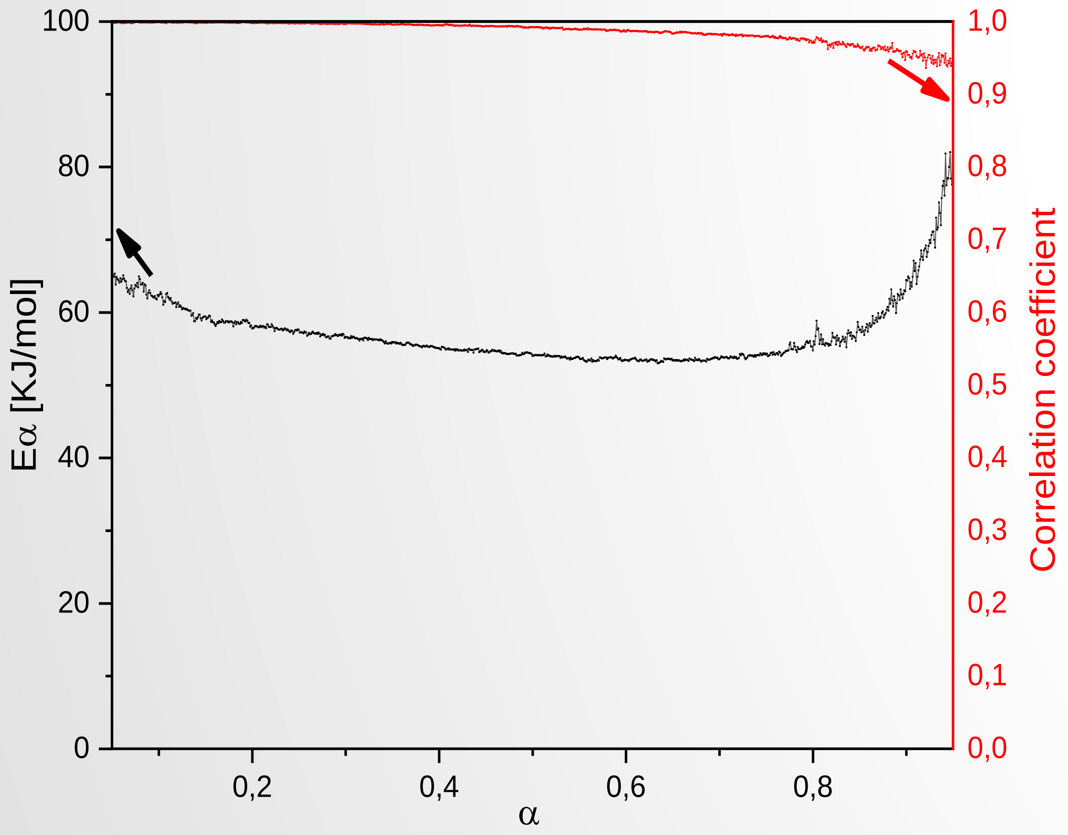
Curing kinetics



DSC thermograms of the bio-based epoxy system when curing at different heating rates



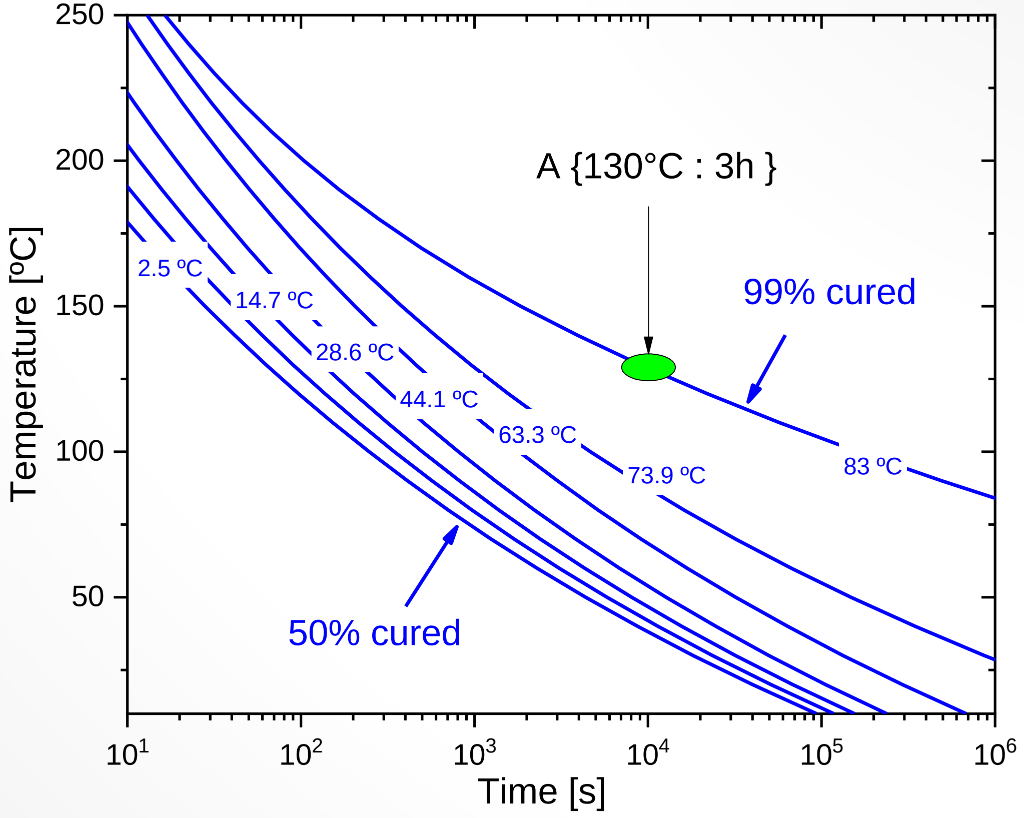
Corresponding degree of cure as a function of temperature obtained from the integration of DSC thermograms.



dependence of the apparent activation energy, Ea, on the degree of curing, a

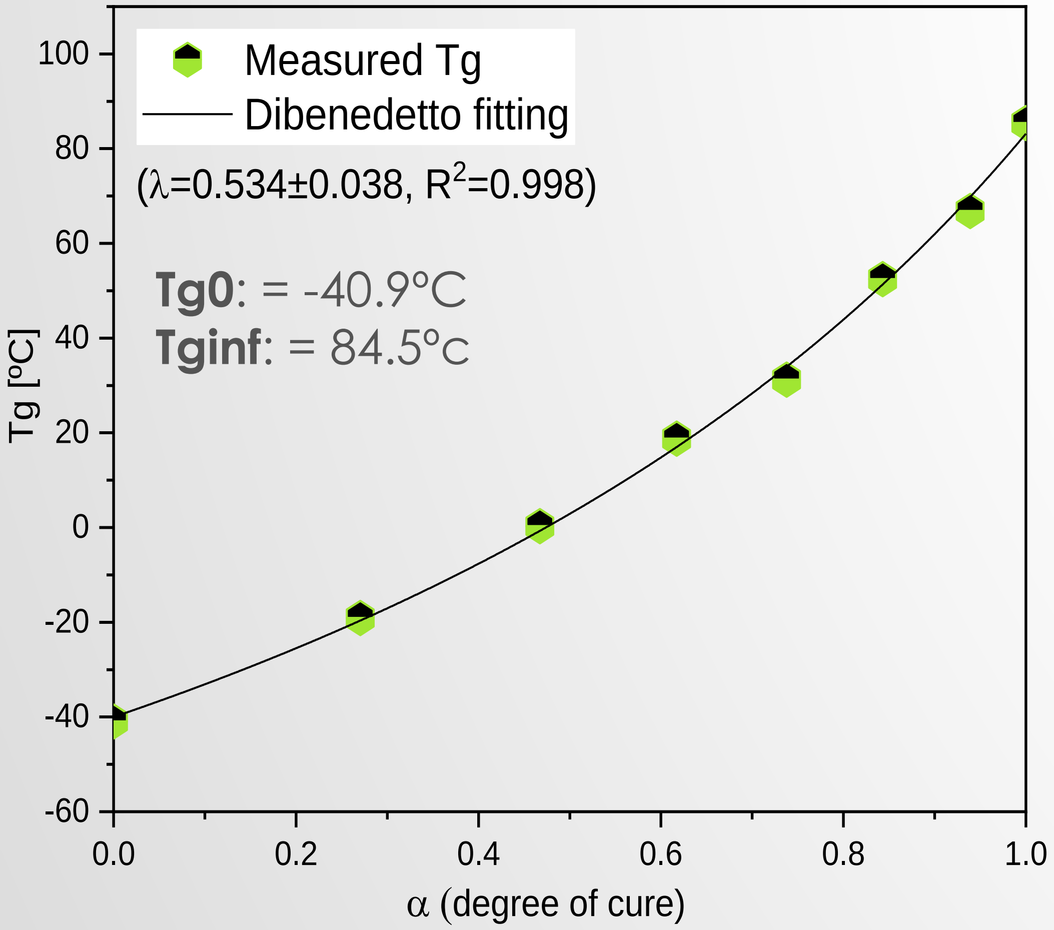
$$ln\left[\left(\frac{d\alpha}{dt}\right)_{T\alpha,i}\right] = ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{RT_{\alpha,i}}$$

E_α and A(t)are determined by Friedman's differential isoconversional method under isothermal condition



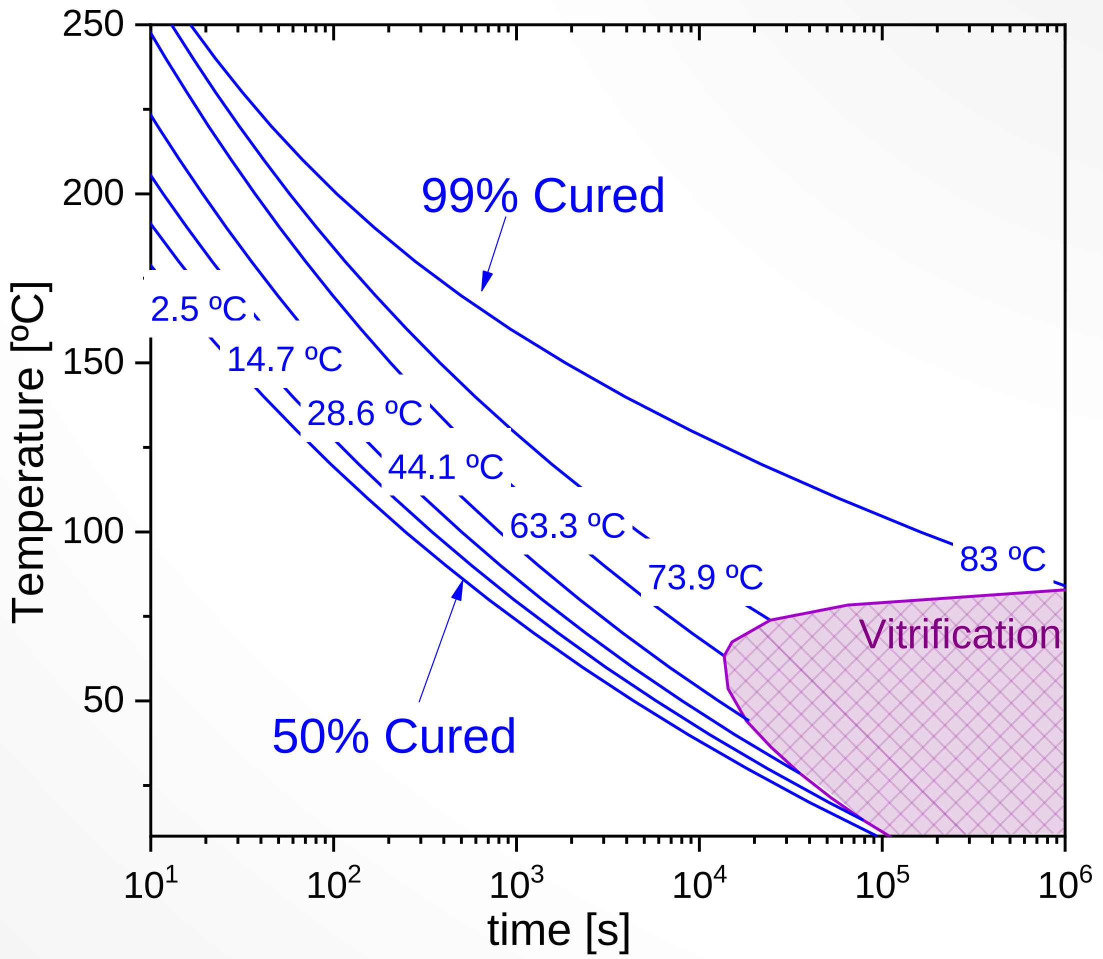
Time-temeparture-transformation chart of the curing

Vitrification: Glass transition temperature vs curing degree α



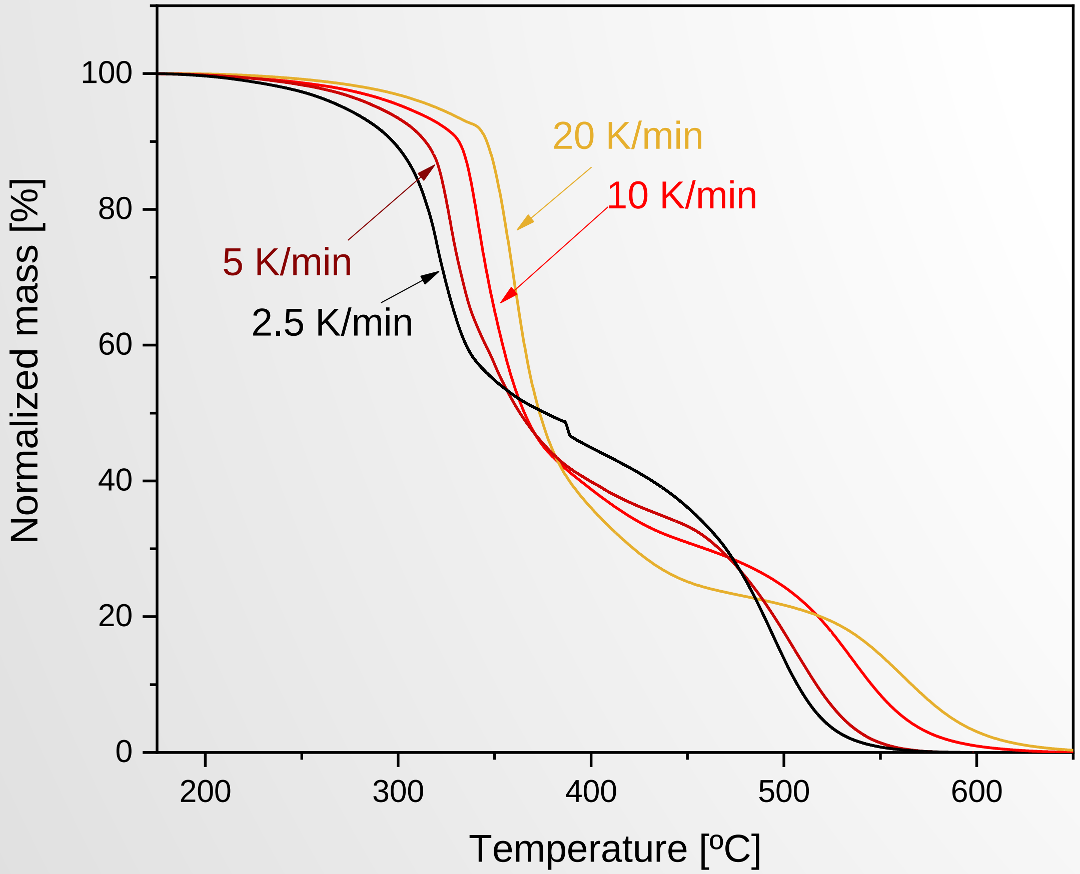
Evolution of the glass transition temperature, Tg, with the degree of cure.

Dibenedetto: $$\frac{(T_g - T_{g0})}{(T_{g\infty} - T_{g0})} = \frac{\lambda\alpha}{(1-(1-\lambda)\alpha)}$$

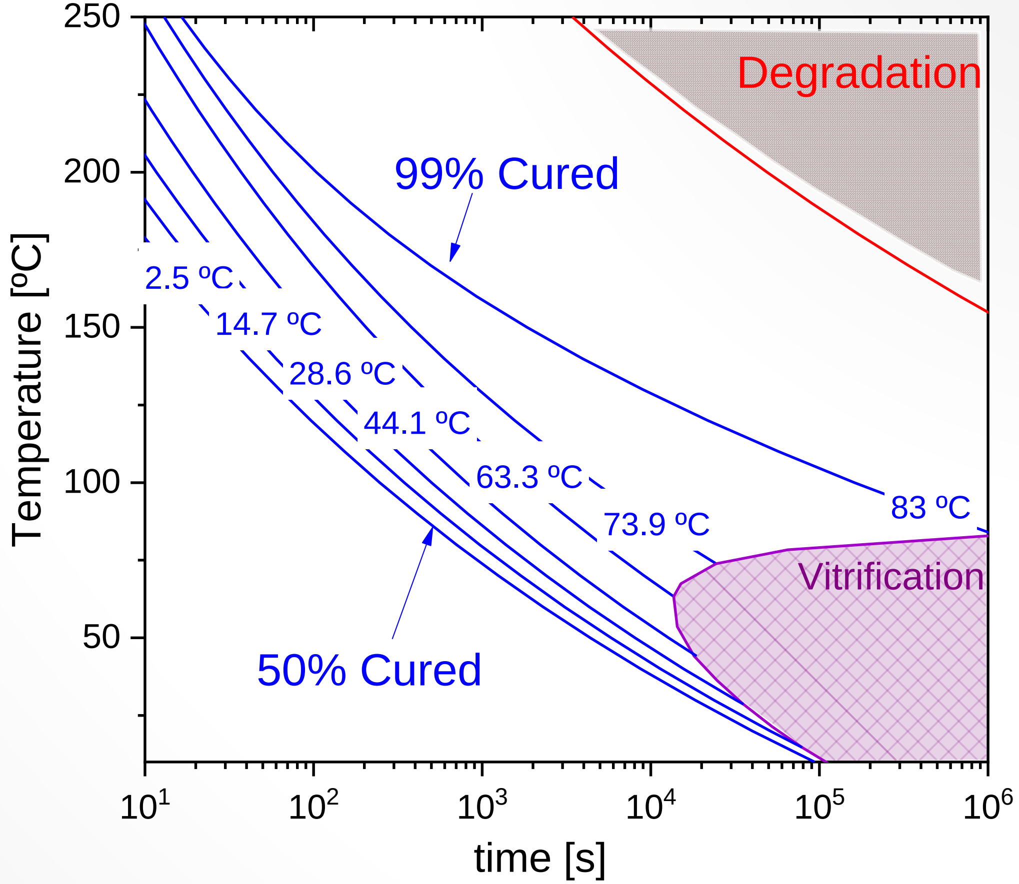


Time-temeparture-transformation chart including the curing and vitfrication

Thermal degradation process

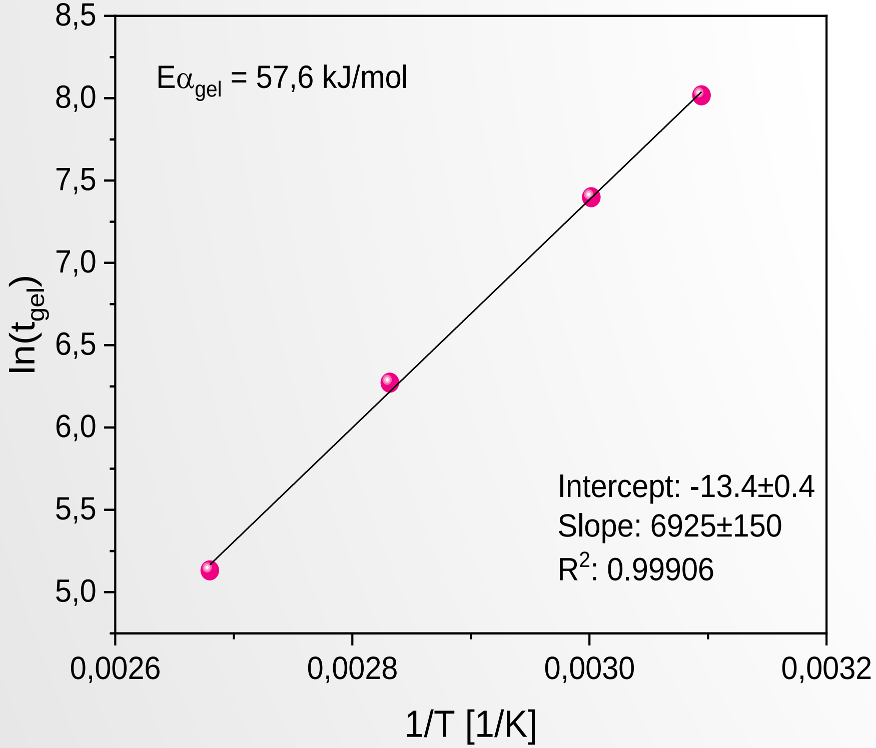


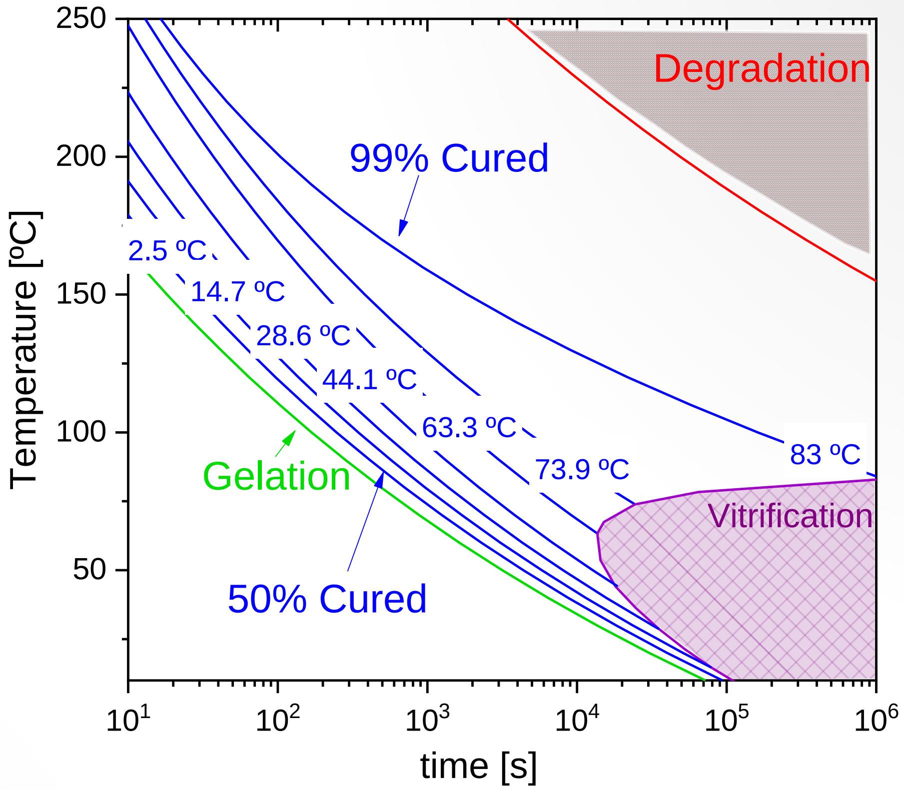
TG thermograms of the cured resin heated at different heating rates.



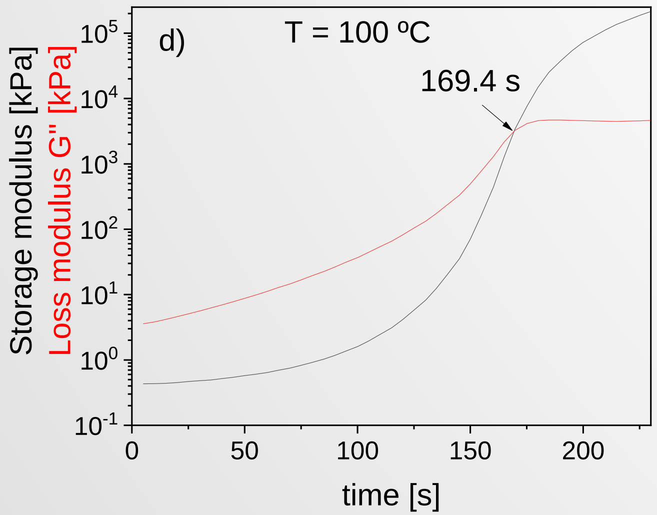
Time-temepararture-transformation chart including the curing, vitfrication and degradation

Rheological properties



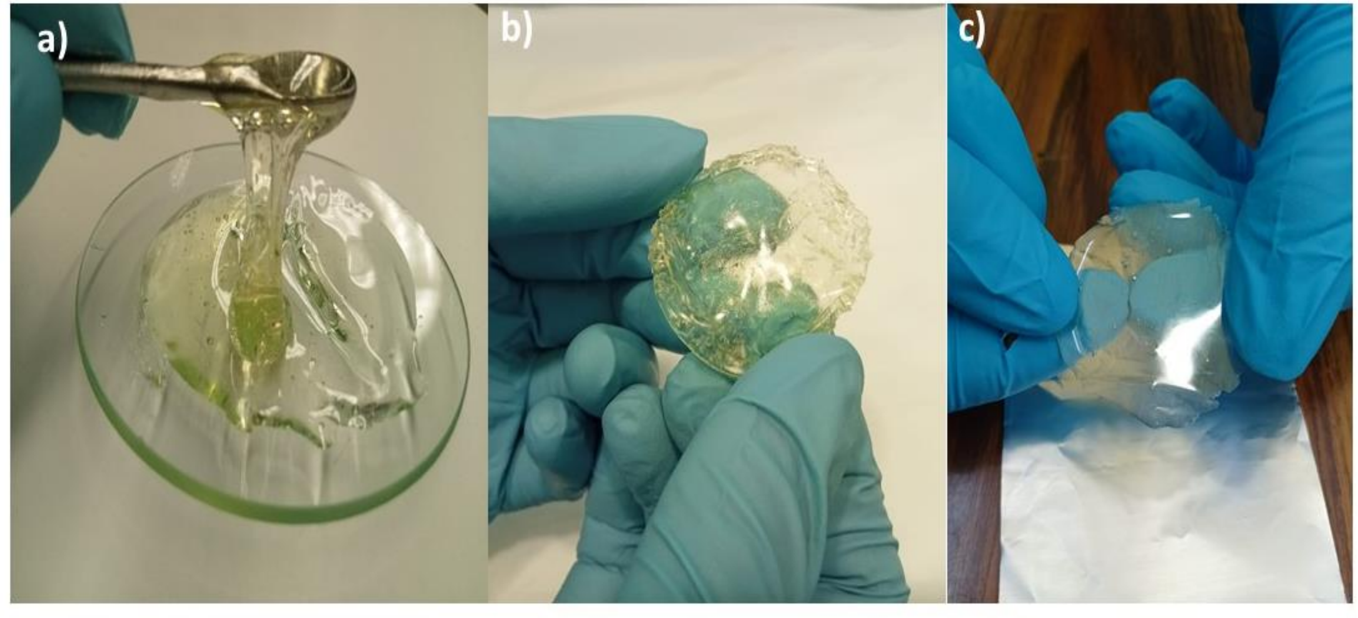


Processing map of the bio based epoxy



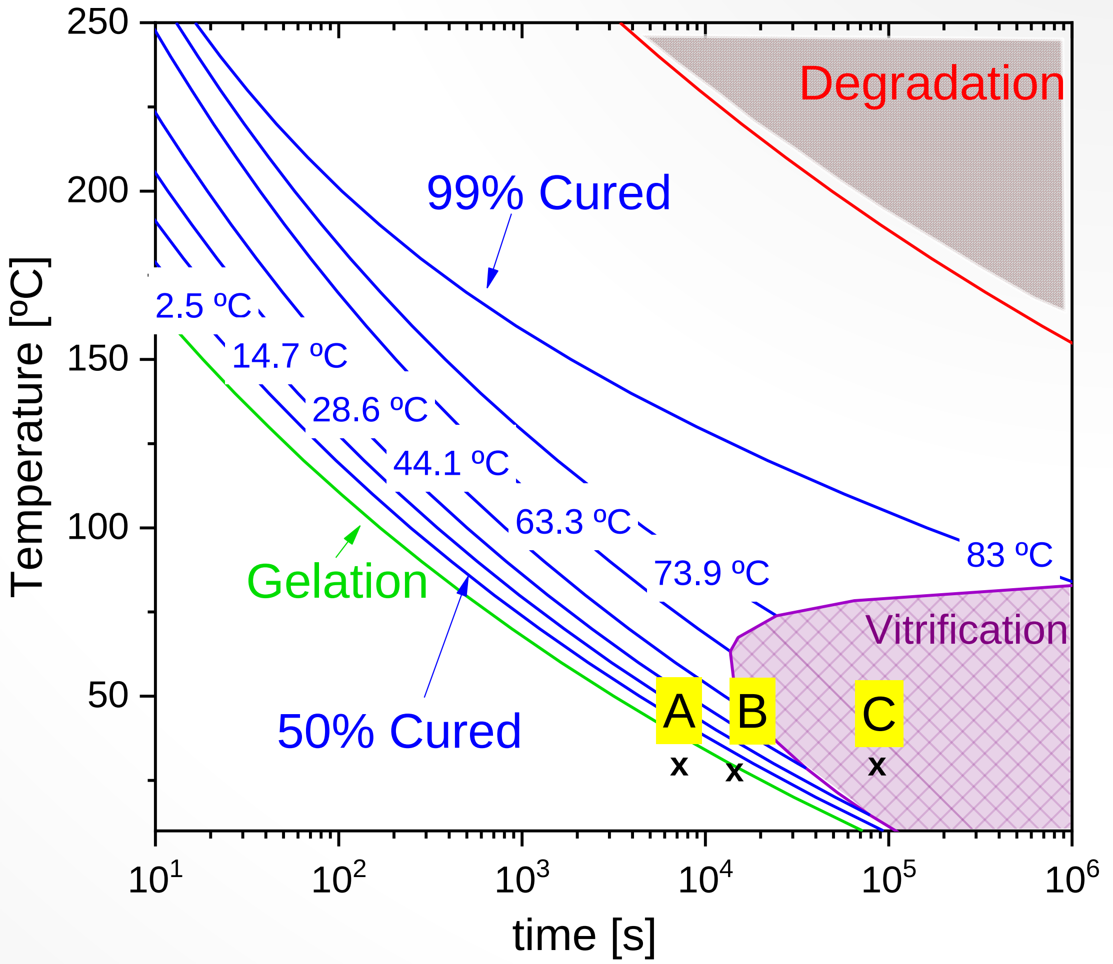
Analysis done under isothermal condition at different temperatures : 50°C, 60°C, 80°C and 100°C

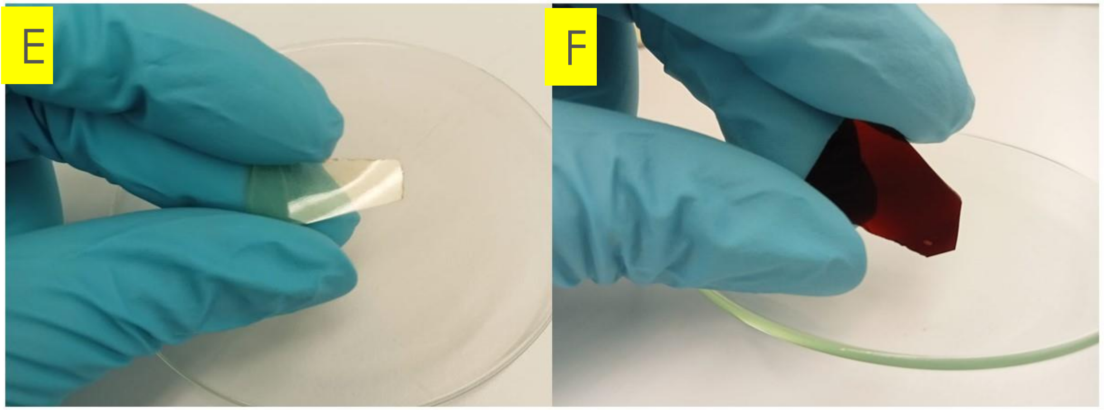
Isothermal processing chart: Experimental validation



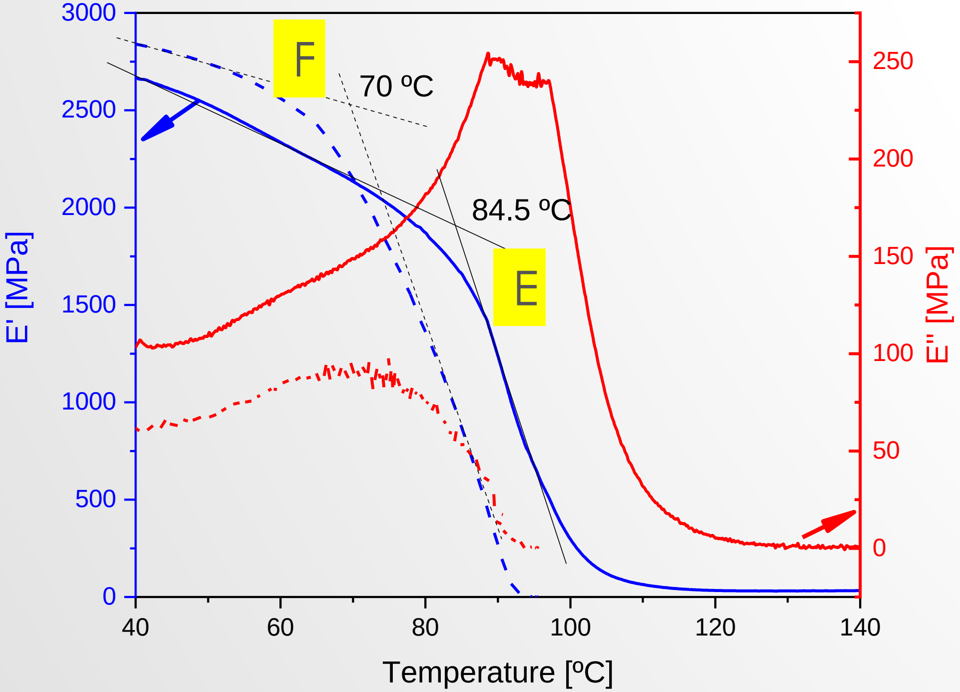
A B C

The observed progression of these rheological properties is in full agreement with our diagram. Thus validating its low temperature curing

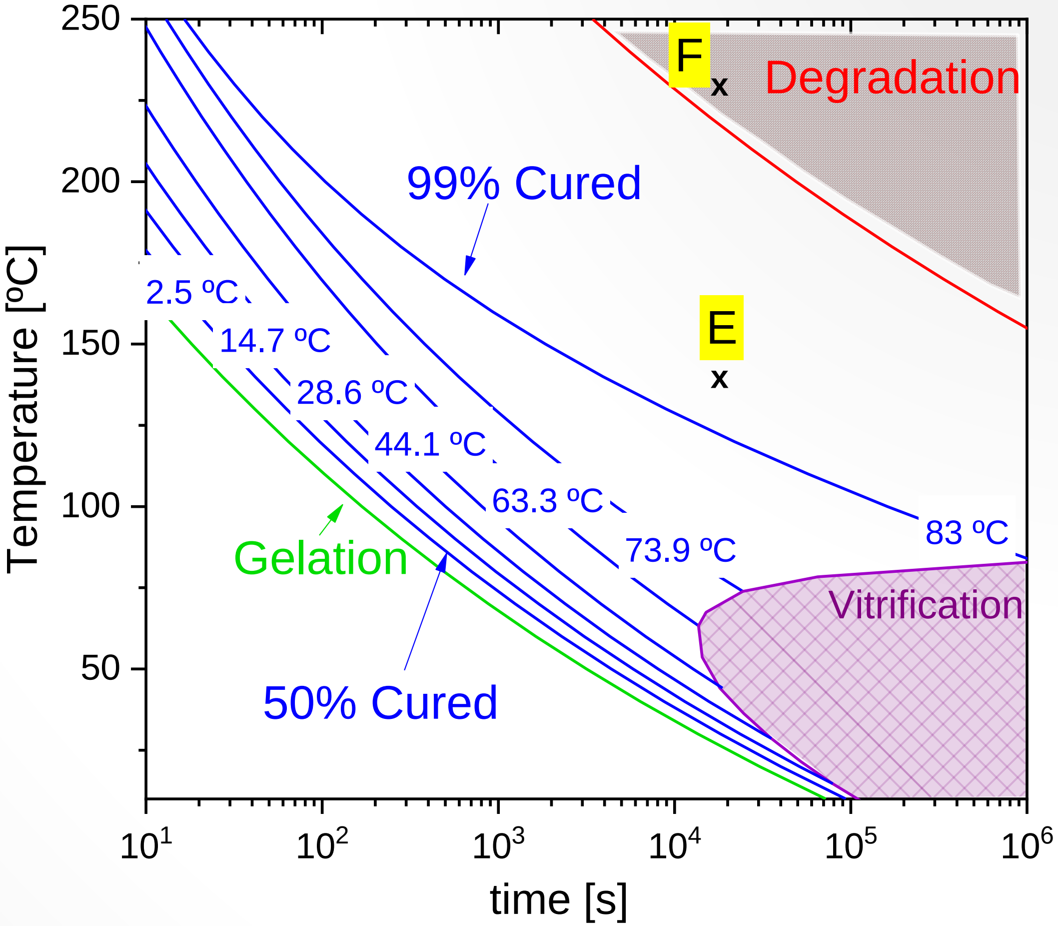




a) -Sample post-cured at 140ºC for 5h; b) sample post-cured at 230 ºC for 5h



DMA thermograms showing the evolution of the tensile storage and loss moduli as a function of temperature



Thermomechanical properties

Epoxy name	E' (storage modulus)	Tg (100% curing)
DGEBA	3.12 GPa	89 °C
Vanillin bio based epoxy	2.7 GPa	85.4 °C

The storage modulus (G'= 2.7 GPa) of this bio-based resin is comparable to that of other vanillin-based structural epoxies with thermomechanical properties on par to DGEBA(Bisphenol A diglycidyl ether)

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Conclusions

- Curing and degradation kinetics of the resin have been thoroughly characterized allowing the construction of a TTT diagram that reveals the optimal processing conditions of the sample.
- An optimal post-curing of the resin allows obtaining thermomechanical properties similar to those obtained with commercial resins based on DGEBA..
- The activation energy of the curing and degradation obtained using friedman's isoconvertional method ranges between 55 and 65 kJ/mol for a conversion of less than 80%,in line with the typical behavior observed in epoxy-amine

Polymer Degradation and Stability 223 (2024) 110743

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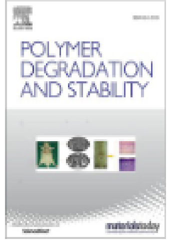

Optimal processing conditions of a bio-based epoxy synthesized from vanillyl alcohol

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ARTICLE INFO

Keywords:
Processability map
Thermoset
Bio-based
Epoxy resins
Vanillin
Thermal oxidation

ABSTRACT

This work provides a comprehensive thermomechanical and rheological characterization of a high-performance epoxy resin synthesized from a vanillin derivative, vanillyl alcohol. The study includes a complete analysis of the curing and decomposition kinetics that enabled a Time-Temperature-Transformation plot accounting for gelation, vitrification, and resin degradation to be developed. These plots allow one to determine the optimal time and temperature processing conditions that will yield the best mechanical properties. Kinetic predictions and experimental results showed that this resin can be cured at room temperature in just a few hours, forming a solid gelled glass. Enhanced mechanical properties are achieved by post-curing the resin at temperatures above $T_{g\infty}$ = 85.4 °C. With a dynamic storage modulus of 2.7 GPa, this bio-based resin proves to be a sustainable alternative to fossil-based resins whose primary source is the ever-prevalent bisphenol A diglycidyl ether. Thermal oxidation is the main cause of the mechanical deterioration at high temperatures, as revealed by FTIR spectroscopy.

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Acknowledgments

- UDG and CSIC Project
- AMADE and the GRMT project (PID2021–126989OB-I00 financed by the MCI, Spain)
- The Catalan Government for their support through 2017SGR1378.
- the Beatriu de Pinós Programme and the Ministry of Research and Universities of the Government of Catalonia (Fellowship BP00069)
- The SABIO project (PID2020–119546RJ-I00) financed by the MCIN/AEI, Spain

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