In-service materials performance

AB2021 6th International Conference on Adhesive Bonding 2021

Effect of the addition of lignin on thermal and bonding properties of an epoxy adhesive

J. Abenojar, S. López de Armentia, M. A. Martínez, J.C del Real

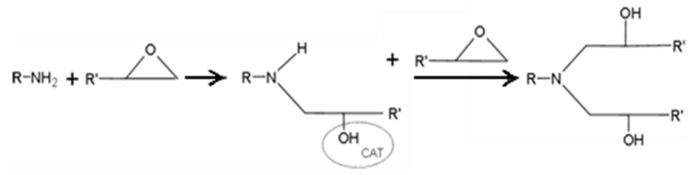
Materials Science and Eng. Dept. Universidad Carlos III de Madrid, Spain
Mechanical Eng. Dept. Universidad Pontificia Comillas, Madrid, Spain

Epoxy resins have many oxirane groups per molecule which opening begins the polymerizing reaction. However, the cured resin may not contain these oxirane groups. Most epoxy resins are derivates from the reaction between A-bisphenol and epichlorohydrin. The addition of these two products creates linear chains with hydroxyl groups and epoxy groups which allow a further crosslinking through amines compost. Lignin has already been used as a filler in epoxy resins in order to reduce the amount of bisphenol A. Lignin can substitute the epoxy resin or the curing agent (hardener).

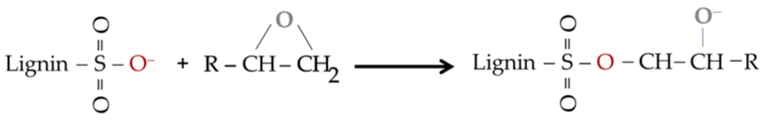
In this study, the effect of the addition of ligno-sulfonic acid in a commercial epoxy resin, reducing the amount of both resin and hardener, has been studied from a thermal and adhesive properties point of view. Therefore, the aim of this study is to obtain an epoxy resin adhesive with less resin and hardener.

Catalytic process produced by OH

The OH groups generated in the polymerization reaction increases the initial reaction rate.

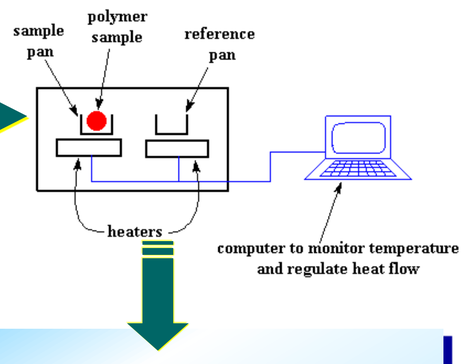


But a similar effect can be produced for lignin-sulfonic groups, opening the oxirane rings



EXPERIMENTAL PROCEDURE

Araldite 1564 + Aradur 3405 (100:36 and 100:20) + **Lignin (10, 25 and 50 wt.%)** → Sonication processes → **8 - 8.5 mg mix**

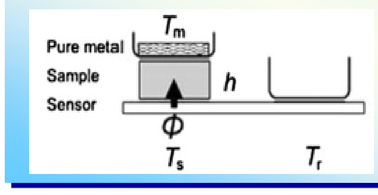


Cured for 8 h at 80 ºC

Thermogravimetric Analyse

- Non-Isothermal method (20 ºC/min) from 25 to 600 ºC
- 30-32 mg

Thermal Conductivity
From 28 to 38 ºC at 0,5ºC/min



$$\lambda = \frac{\phi}{\Delta T}\frac{h}{A}$$

$$\lambda = \frac{1}{\left(\frac{1}{S_G} - \frac{1}{S_S}\right)}\frac{h}{A}$$

Adhesion Test

- Pull off

Substrate: Cork

- Non-Isothermal method (5, 10, 15 and 20 ºC/min) from -20 to 250 ºC

MFK model

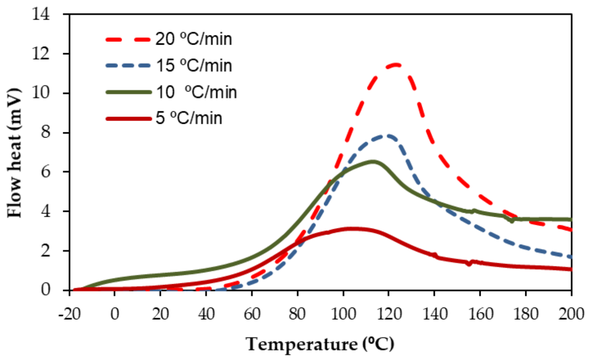
- Non-Isothermal method (20 ºC/min)

T_g

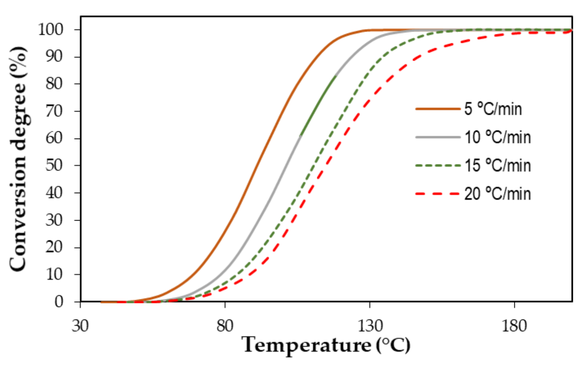
RESULTS

Kinetics - MFK

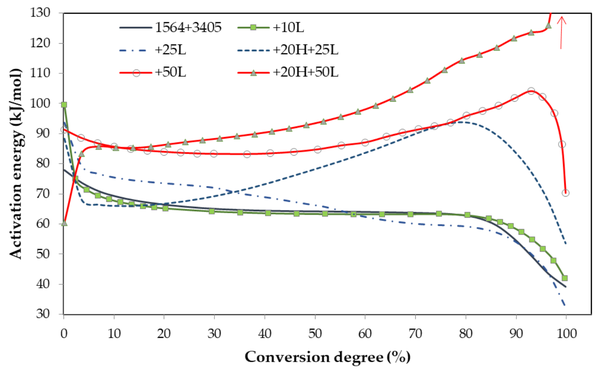
Thermograms at different rates



Conversion degree curves

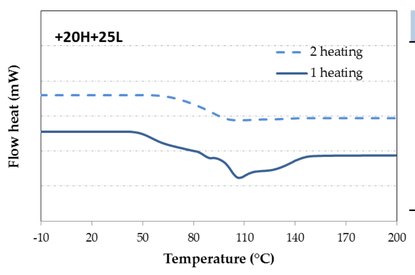


Activation energy



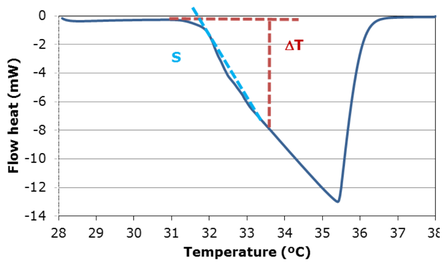
	Activation Energy (kJmol^{-1})		
	Initial	Middle	Final
1564+3405	74	64	39
+10L	99	63	42
+25L	94	66	32
20H+25L	88	79	54
+50L	91	85	70
20H+50L	60	94	172

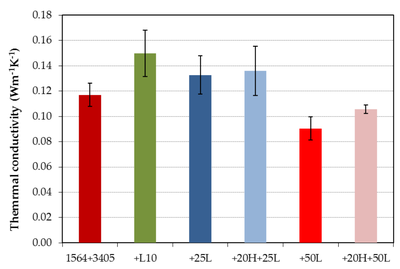
T_g



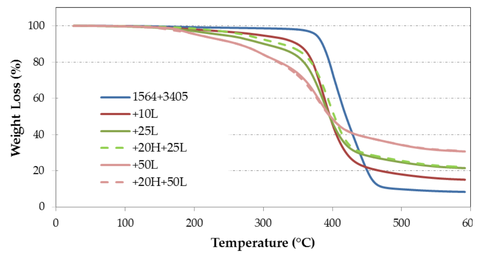
	T_g	
1564+3405	89	±1
+10L	89	±1
+25L	89	±1
+20H+25L	89	±1
+50L	86	±1
+20H+50L	81	±1

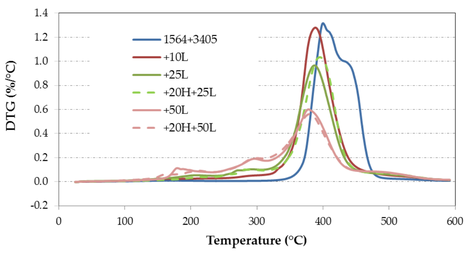
Thermal conductivity





TGA - DTG





Residue is greater as the percentage of lignin increases.

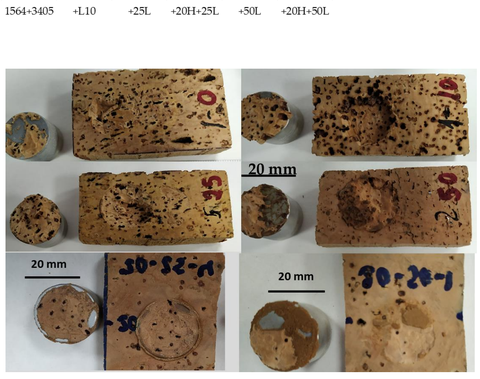
Lignin decomposition

- 190 ºC - softening and melting of the lignin.
- 280 ºC - cleavage of C-H groups between aromatic rings and aliphatic chains.
- 380 ºC - thermal decomposition of aromatic rings.
- 460 ºC - carbon gratification.

Adhesion tests

	Strength (MPa)	Strain (%)
1564+3405	1.06 ± 0.03	78.00 ± 1
+10L	1.34 ± 0.14	79.00 ± 1
+25L	1.46 ± 0.17	78.00 ± 2
+20H+25L	1.28 ± 0.03	76.00 ± 1
+50L	1.24 ± 0.22	107.00 ± 1
20H+50L	0.82 ± 0.05	77.00 ± 2

Substrate failure



CONCLUSIONS

- The addition of lignin to the epoxy resin used in this study does not significantly change the curing kinetics. However, the beginning and the end require higher activation energy for curing. When less hardener and 50 wt.% Lignin is added (+20H+50L), the curing reaction needs higher activation energy to finish curing.
- T_g also decreases for +50L and +20H+50L, but remains the same as neat epoxy resin for the rest of adhesives with lignin.
- Thermal conductivity increases for adhesives + 10L, + 25L and + 20H + 25L, but decreases for those containing 50%. This may be due to less crosslinking as the T_g decreases.
- The decomposition of lignin begins earlier than neat epoxy resin. By increasing the amount of lignin, the processes that take place are better appreciated. Also the carbon residue increases with the amount of lignin. The amount of hardener has not influence on decomposition.
- Adhesion tests show that all lignin adhesives have good strength to cork, even higher than the epoxy resin itself. The only exception is for the adhesive +20H+50L, but still the strength is good. Substrate failures are observed in all cases.