UCL
Université catholique de Louvain

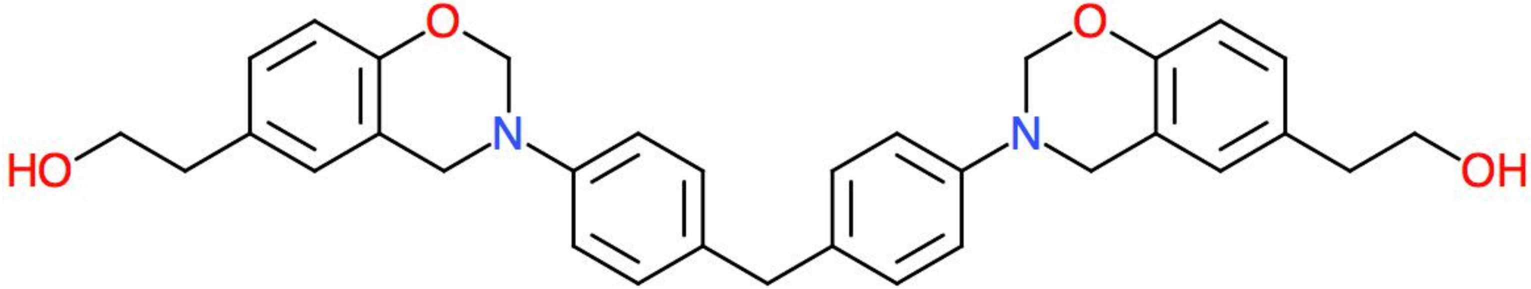
Institut de la Matière Condensée et des Nanosciences (IMCN)
Bio- and Soft MAtter (BSMA)

Using *zinc oxide* nanoparticles to improve the *thermal stability* of a new high-performance *benzoxazine* resin

J. Horion, C. van Tieghem de Ten Berghe, L. Bonnaud and C. Bailly

June 5th, 2018

ICCC 2018 - Arcachon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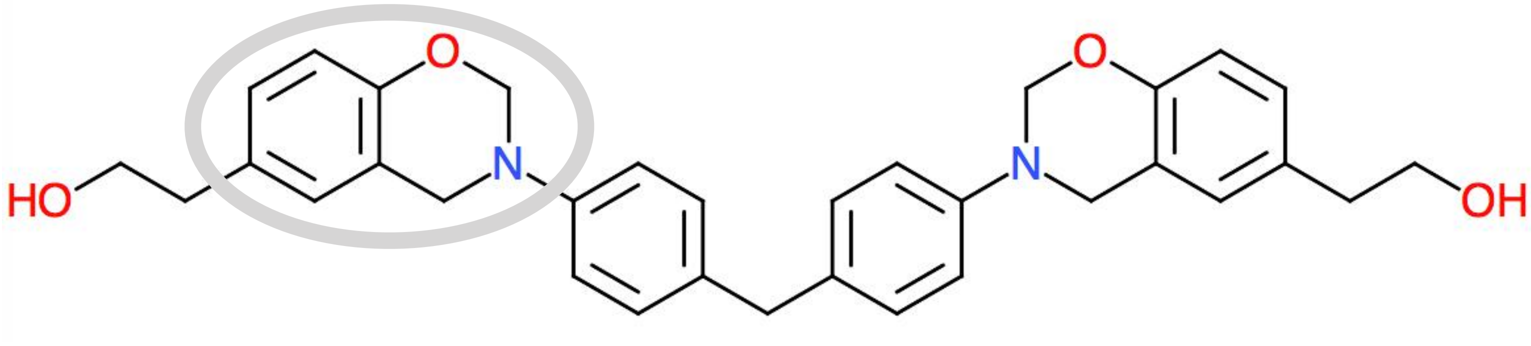

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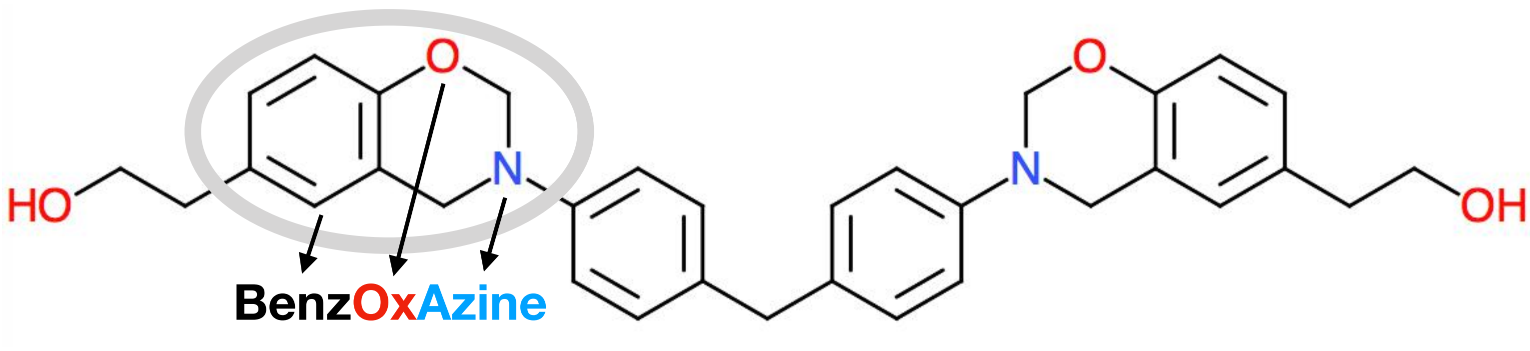
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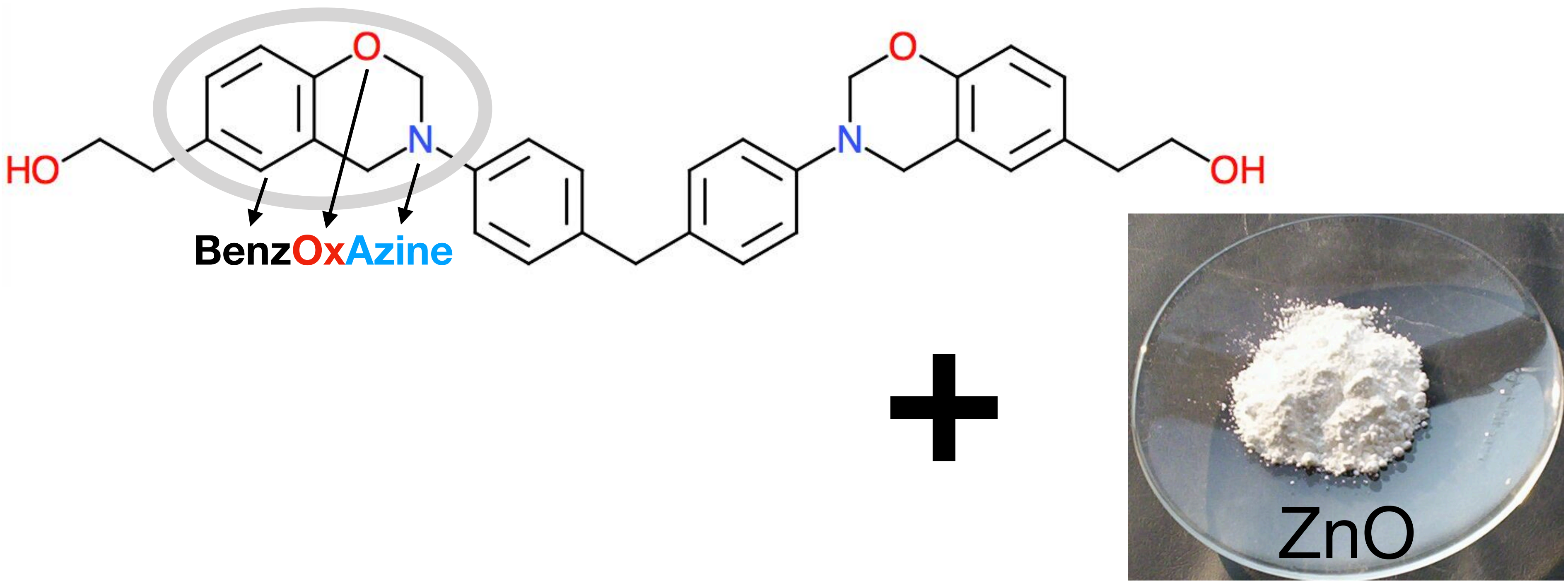
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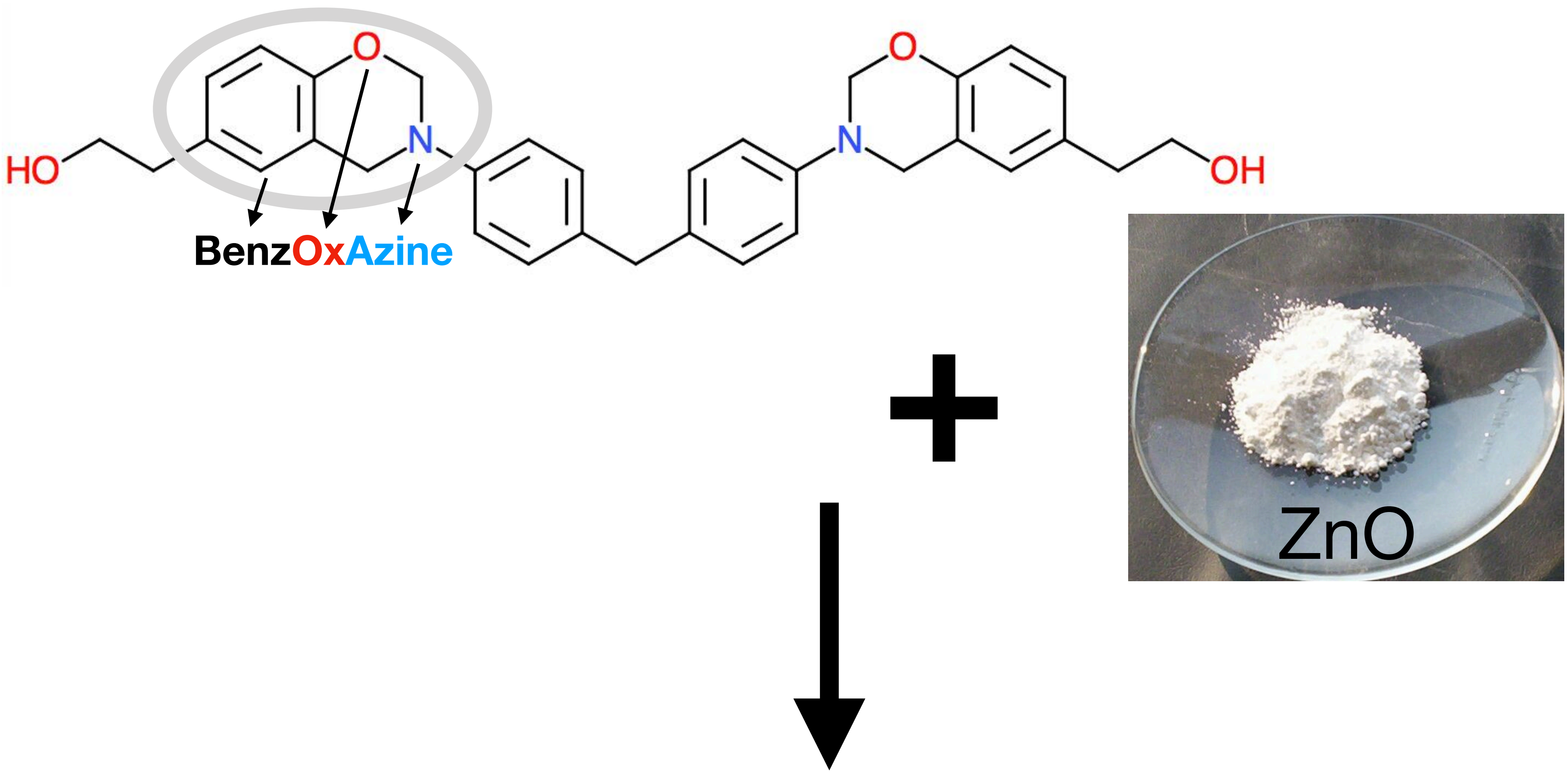
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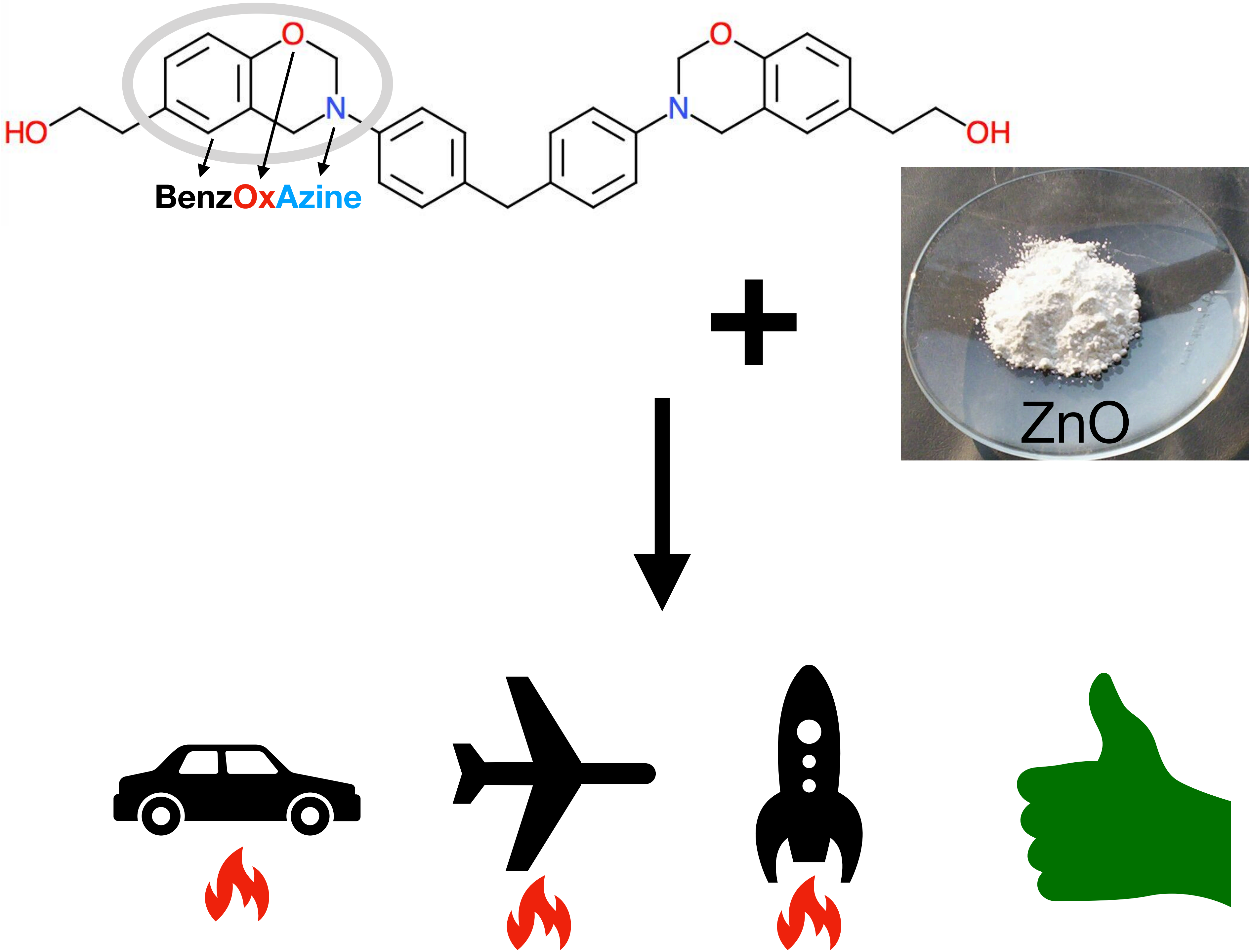

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PBZ have interesting thermo-mechanical properties

Property	Epoxy	Phenolics	Cyanate ester	PBZ
T_{cure} [°C]	25-180	150-190	180-250	160-220
T_{max} use [°C]	180	200	150-200	130-280
Cure schrinkage	$\geq$3	0.002	$\approx$3	$\approx$0
T_g [°C]	150-220	170	250-270	170-340
Tensile strength [MPa]	90-120	24-45	70-130	100-125
Tensile modulus [GPa]	3.1-3.8	3.0-5.0	3.1-3.4	3.8-4.5
Elongation [%]	3.0-4.3	0.3	2.0-4.0	2.3-2.9
T_{onset} degradation [°C]	260-340	300-360	400-420	380-400

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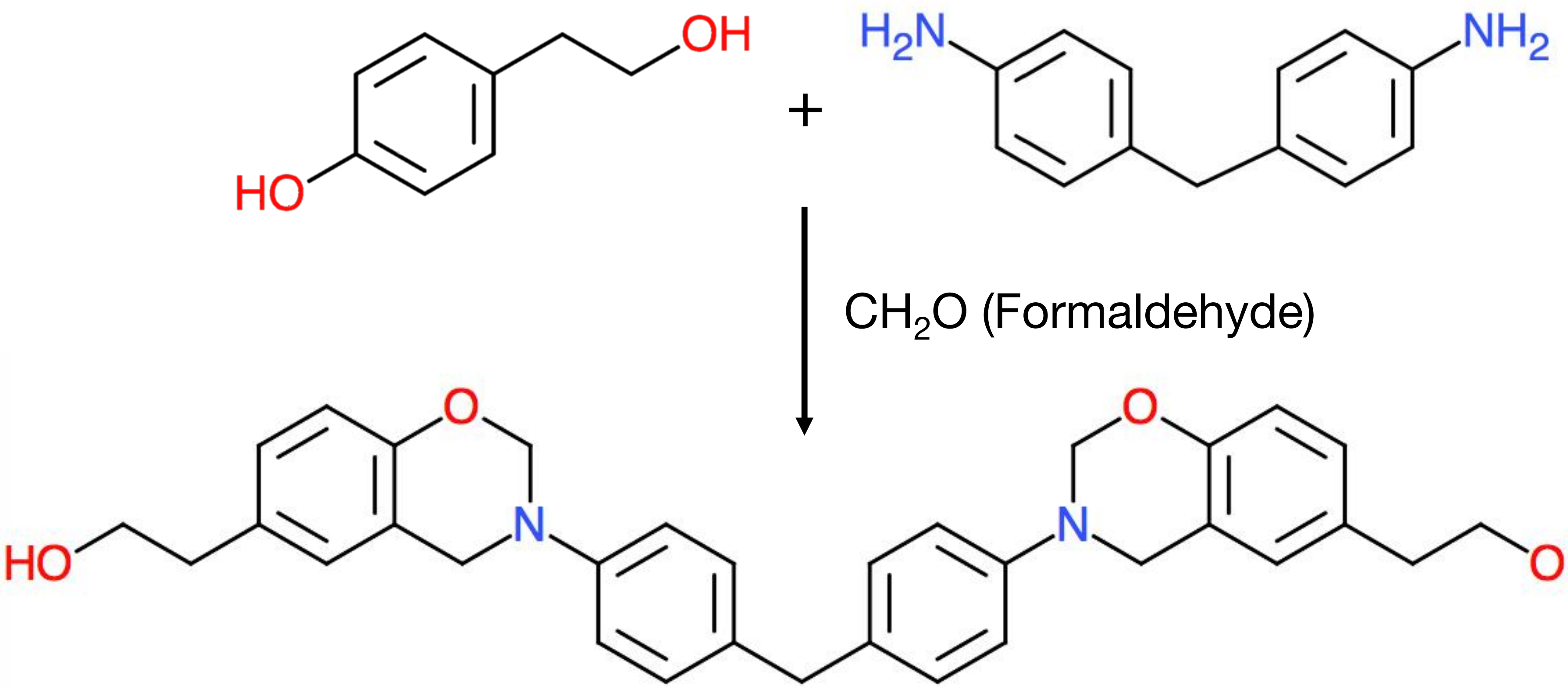
Benzoxazines are quite easy to synthesize

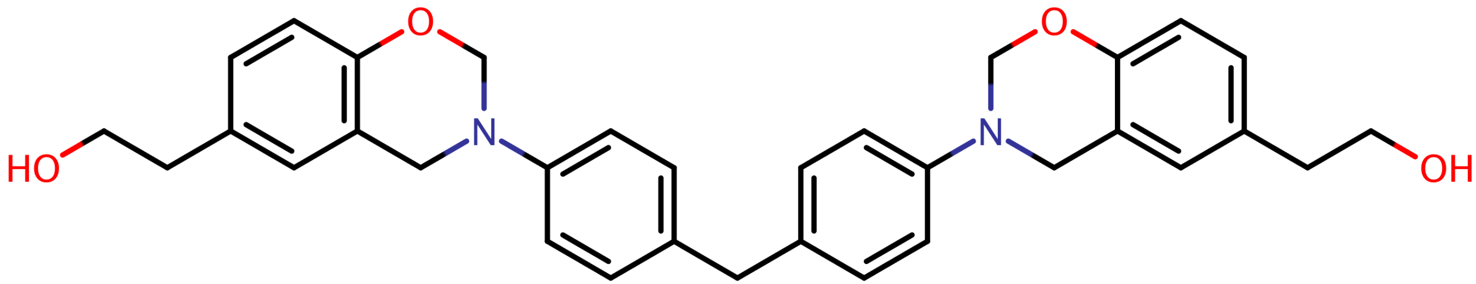
Tyrosol
4-(2-hydroxyethyl)phenol

DDM
4,4’-diaminodiphenylmethane



T-DDM benzoxazine

T-DDM is a mono-component thermoset



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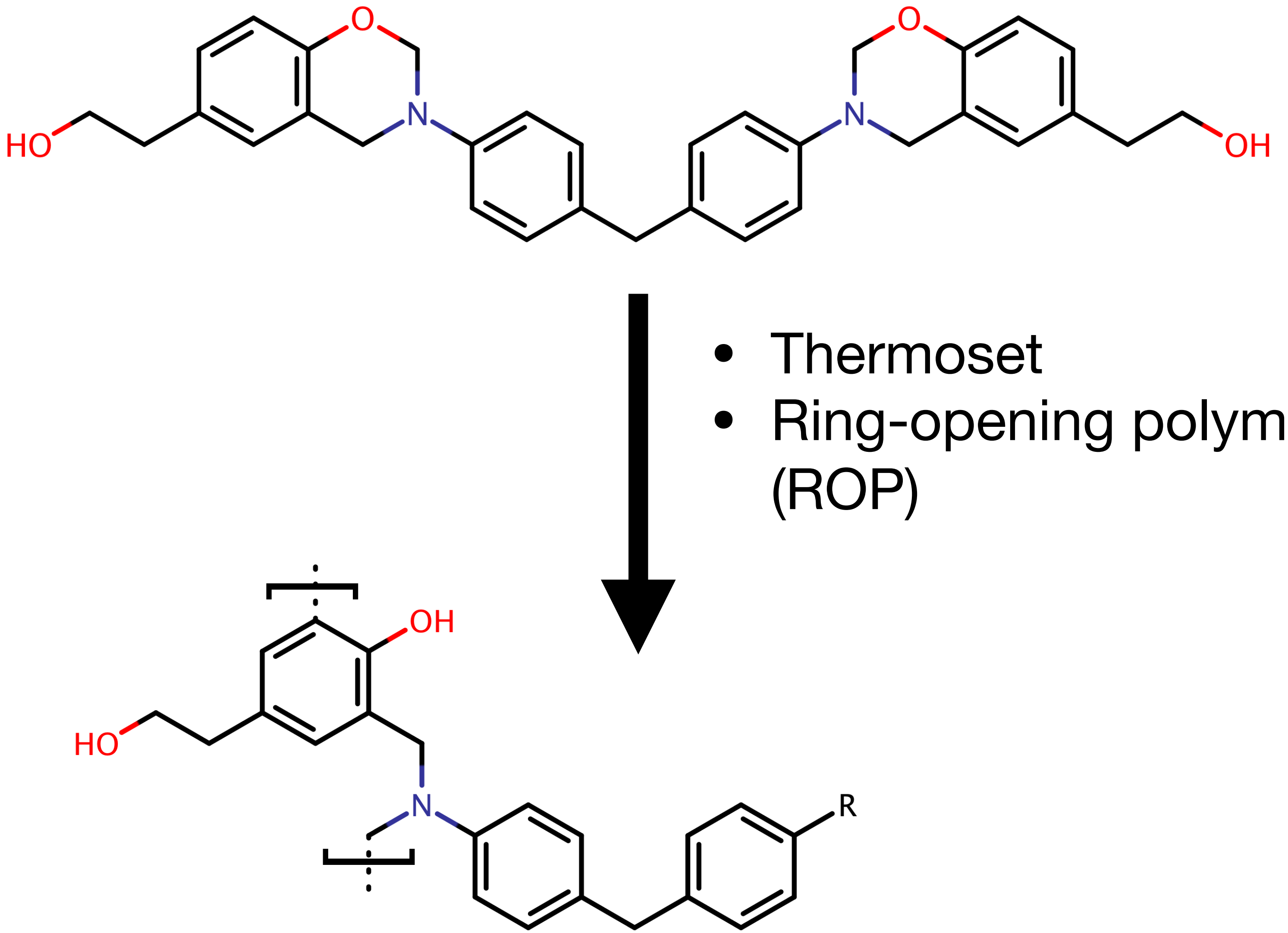

- Thermoset
- Ring-opening polymerization (ROP)

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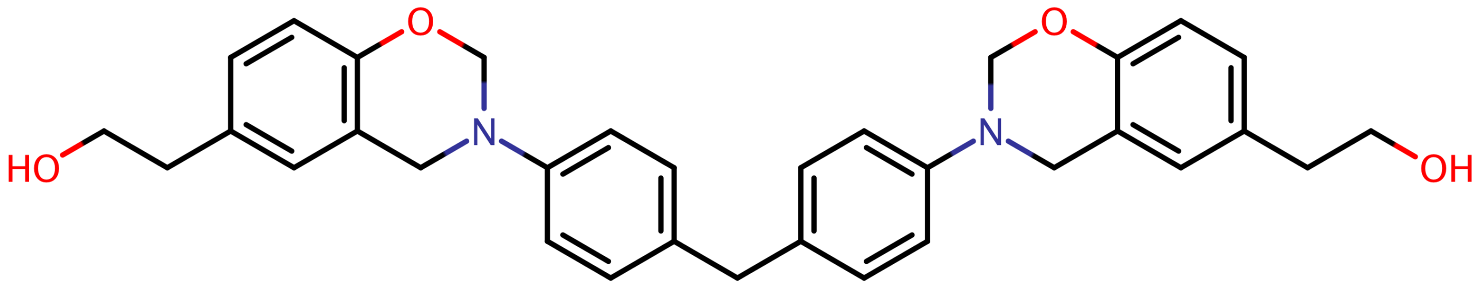
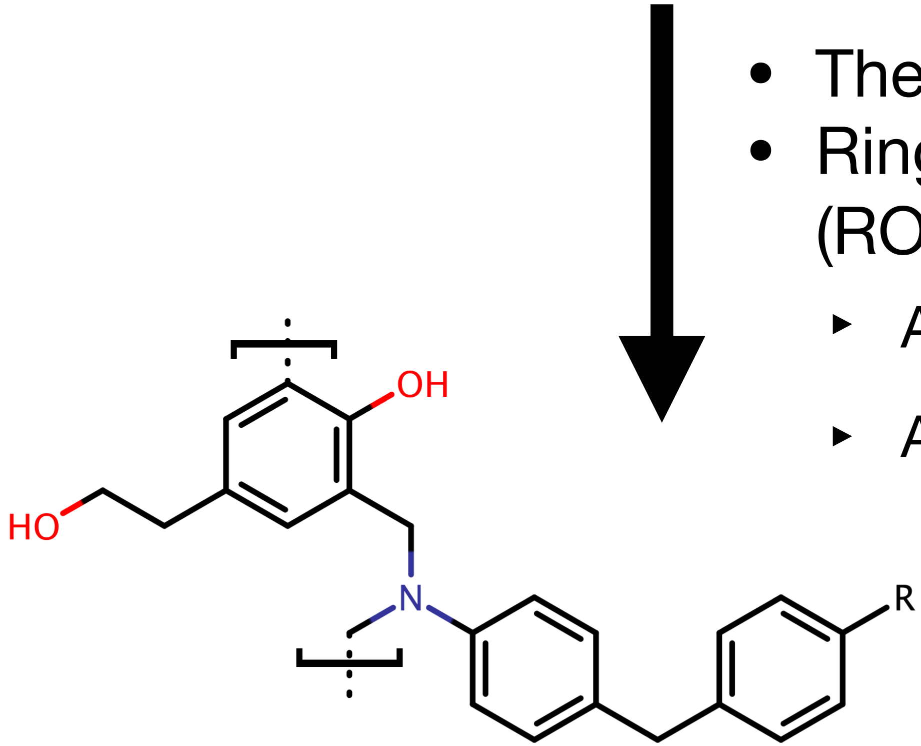




- Thermoset
- Ring-opening polymerization (ROP)
  - Activated by simple heating
  - Autocatalytic process

Activation energy ~90kJ
Order of reaction ~2.3

$$\frac{d\alpha}{dt} = k \cdot (1-\alpha)^n \cdot \alpha^m$$

Arrhenius

$$ln\left(\beta \cdot \frac{d\alpha}{dT}\right) = ln(A) - \left(\frac{E_a}{RT}\right) + n \cdot ln(1-\alpha) + m \cdot ln(\alpha)$$

- E_a in same range as peak temperature methods
- Overall order of reaction of 2.2 to 2.5

β [°C/min]	A [s^{-1}]	E_a [kJ/mol]	n	m
5	$3.99 \cdot 10^7$	90.2	1.6	0.6
10	$4.01 \cdot 10^7$	89.1	1.6	0.7
15	$4.00 \cdot 10^7$	88.0	1.7	0.8

Blend preparation is quite straightforward

1. Weighing and mixing of T-DDM and ZnO powder
2. Dissolving resin into chloroform
3. Sonication pulses (30 seconds)
4. Degassing under vacuum at 150°C in a furnace

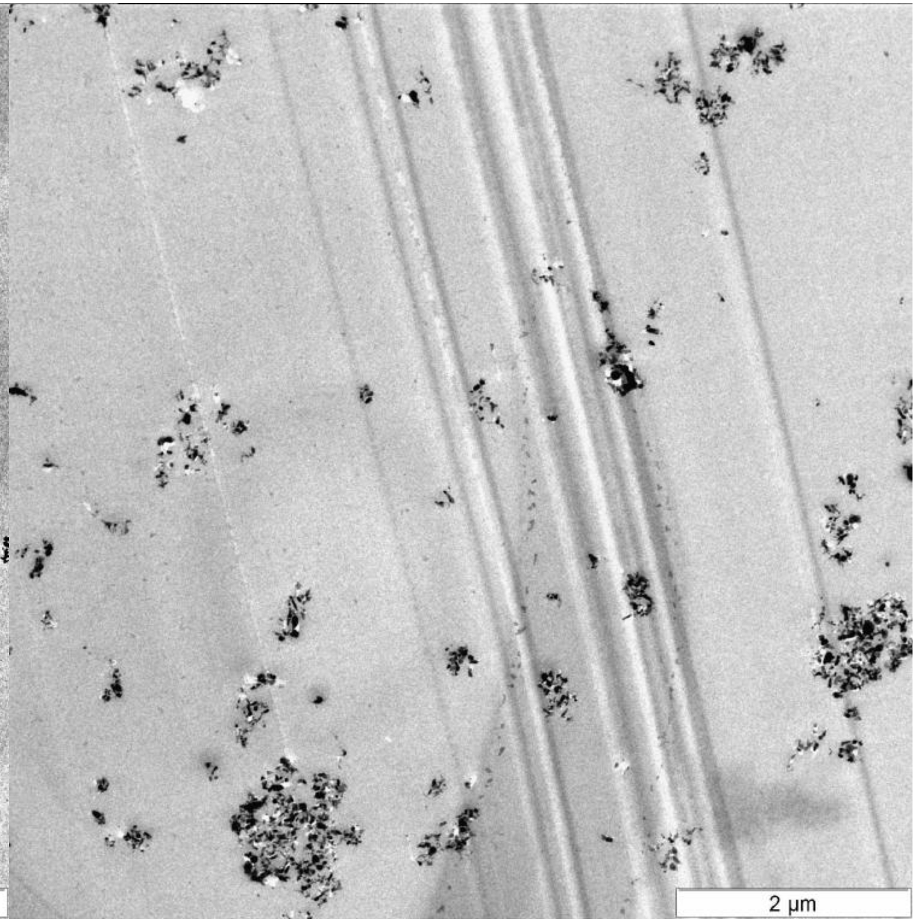
	$t_{sonication}$ [s]				
ZnO [$wt\%$]	30	90	270	360	540
0.5	X	X	X		
1.0		X			
2.5		X			
5.0	X	X	X	X	X
10.0		X			
25.0		X			
50.0		X			

Dispersions are good up to 5wt% loading

Dispersion with 90s sonication

0.5wt% ZnO

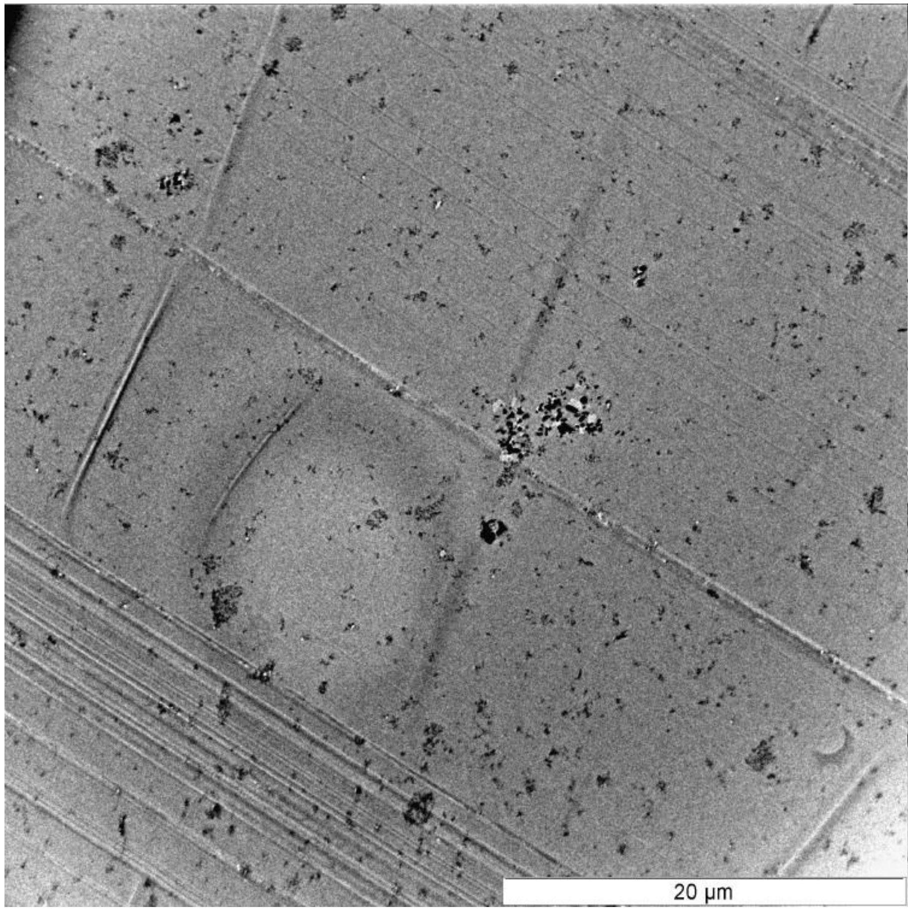
5.0wt% ZnO



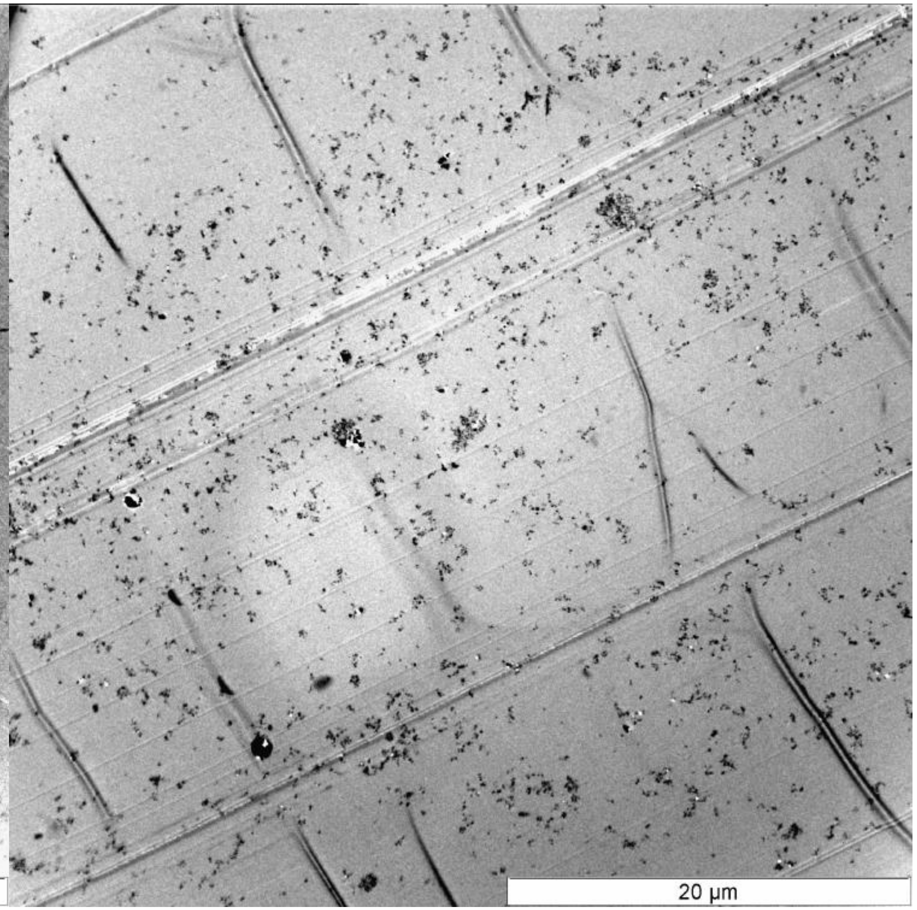
Sonication time has little influence

Dispersion at 5.0wt% ZnO

90s sonication

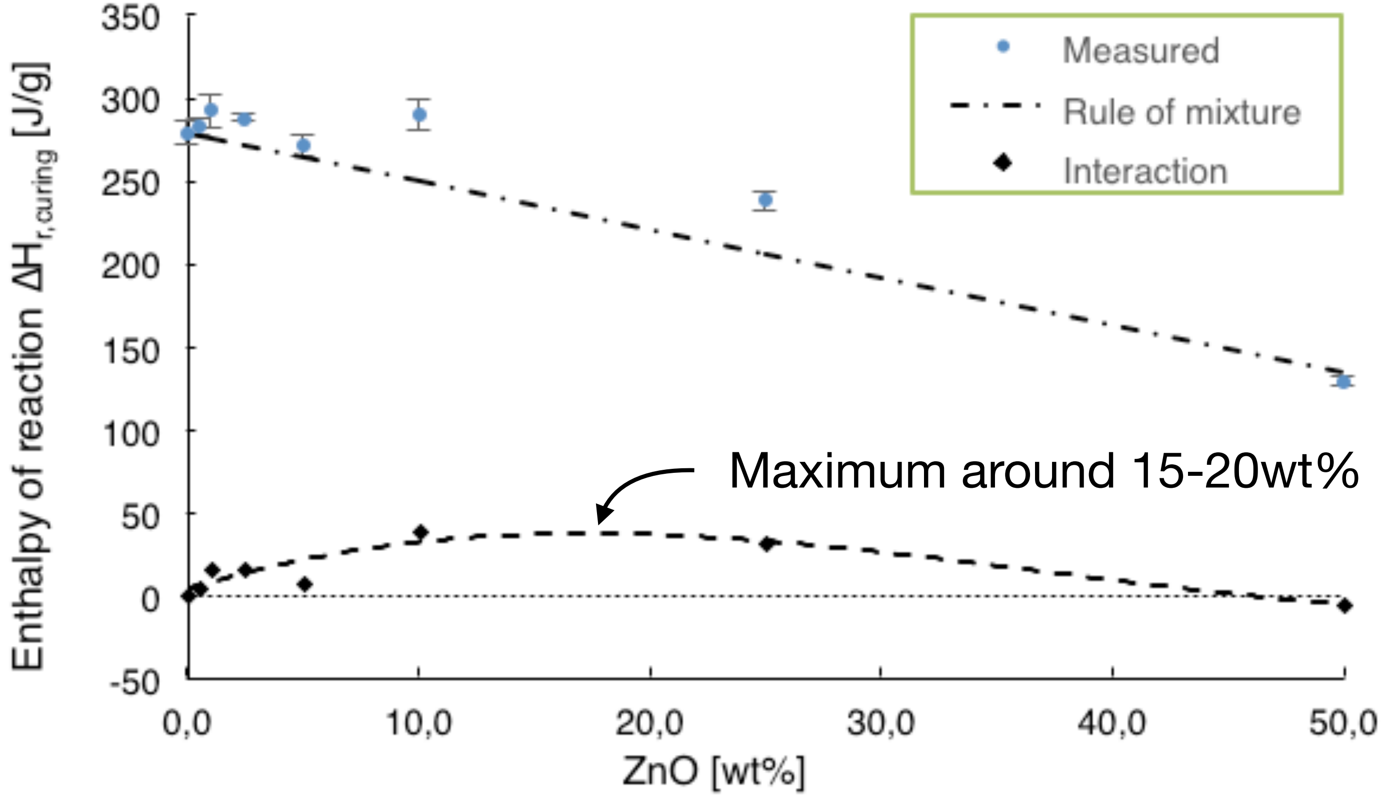


270s sonication



There is a synergic effect between ZnO and BZO

- Curing enthalpy does not follow a simple rule of mixture



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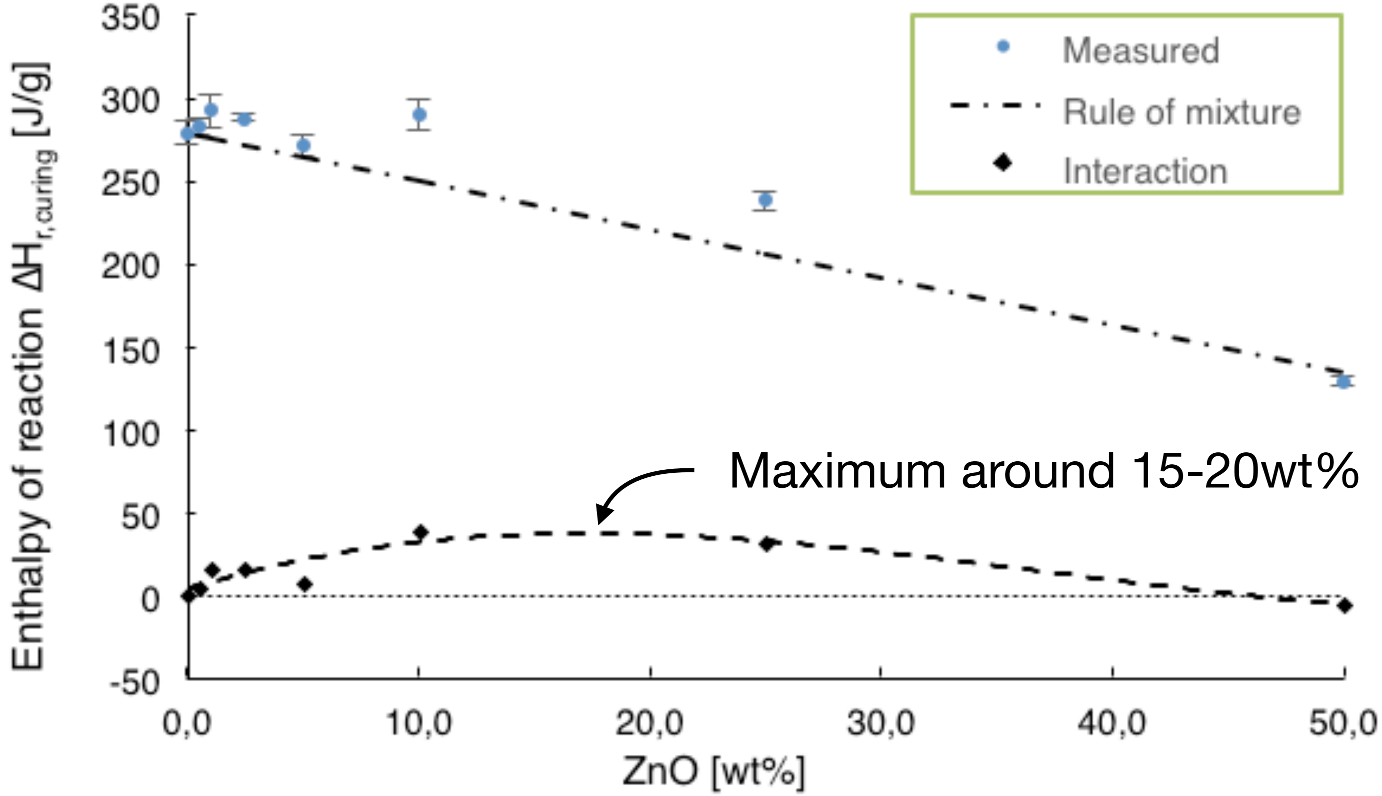
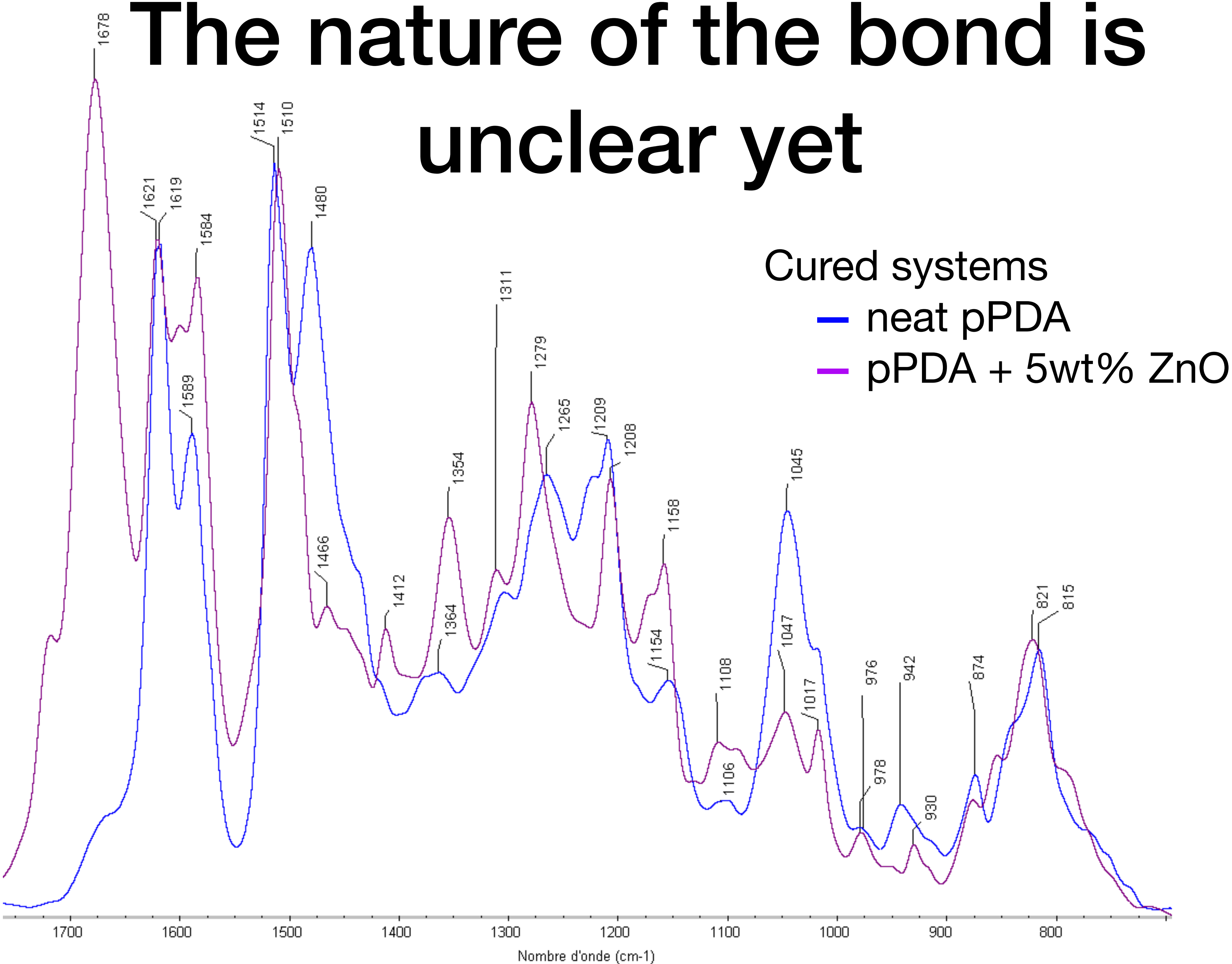


- Indicates that some chemical bonds might be formed between the resin and the nanoparticles

The nature of the bond is unclear yet



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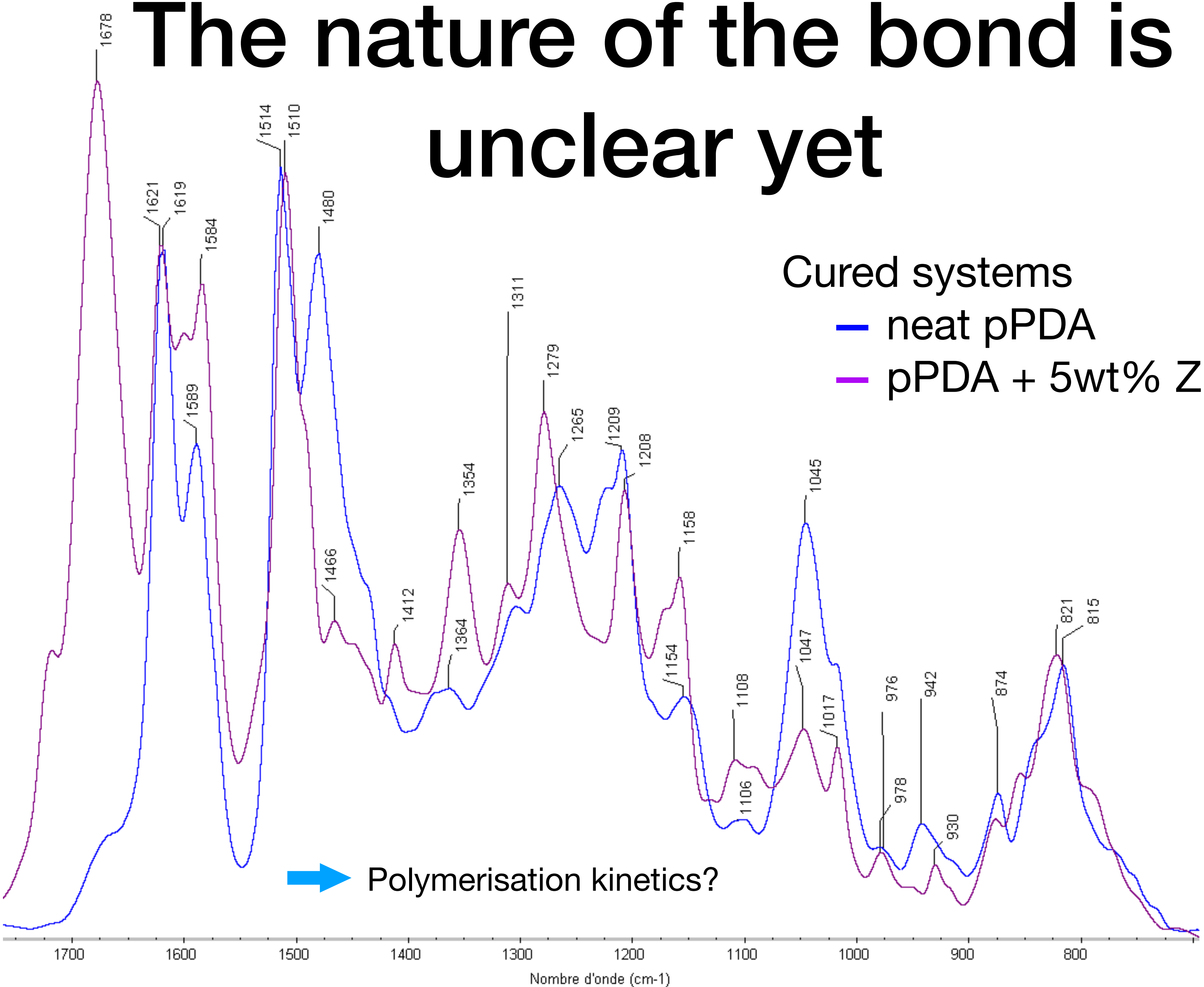
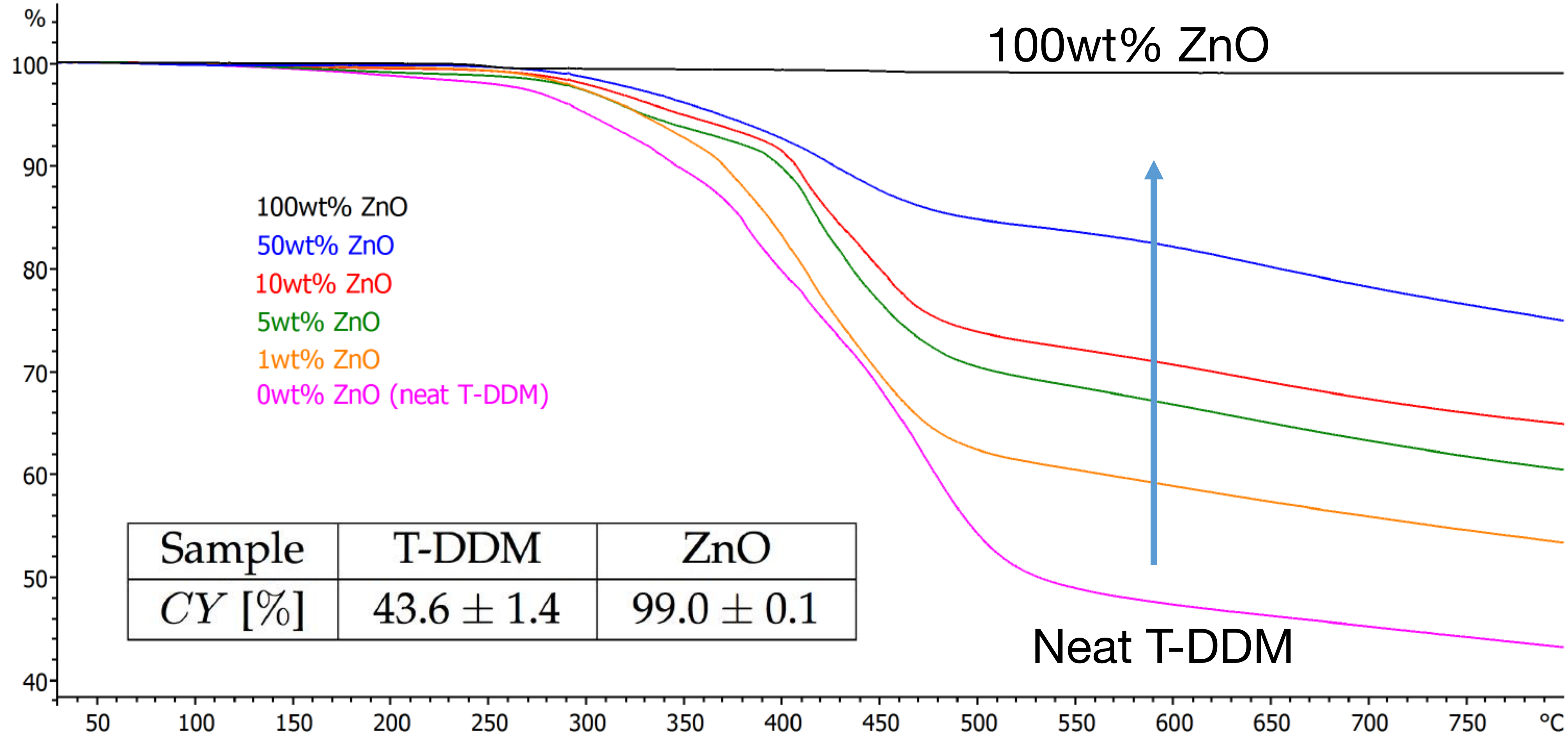


Cured systems

- neat pPDA
- pPDA + 5wt% ZnO

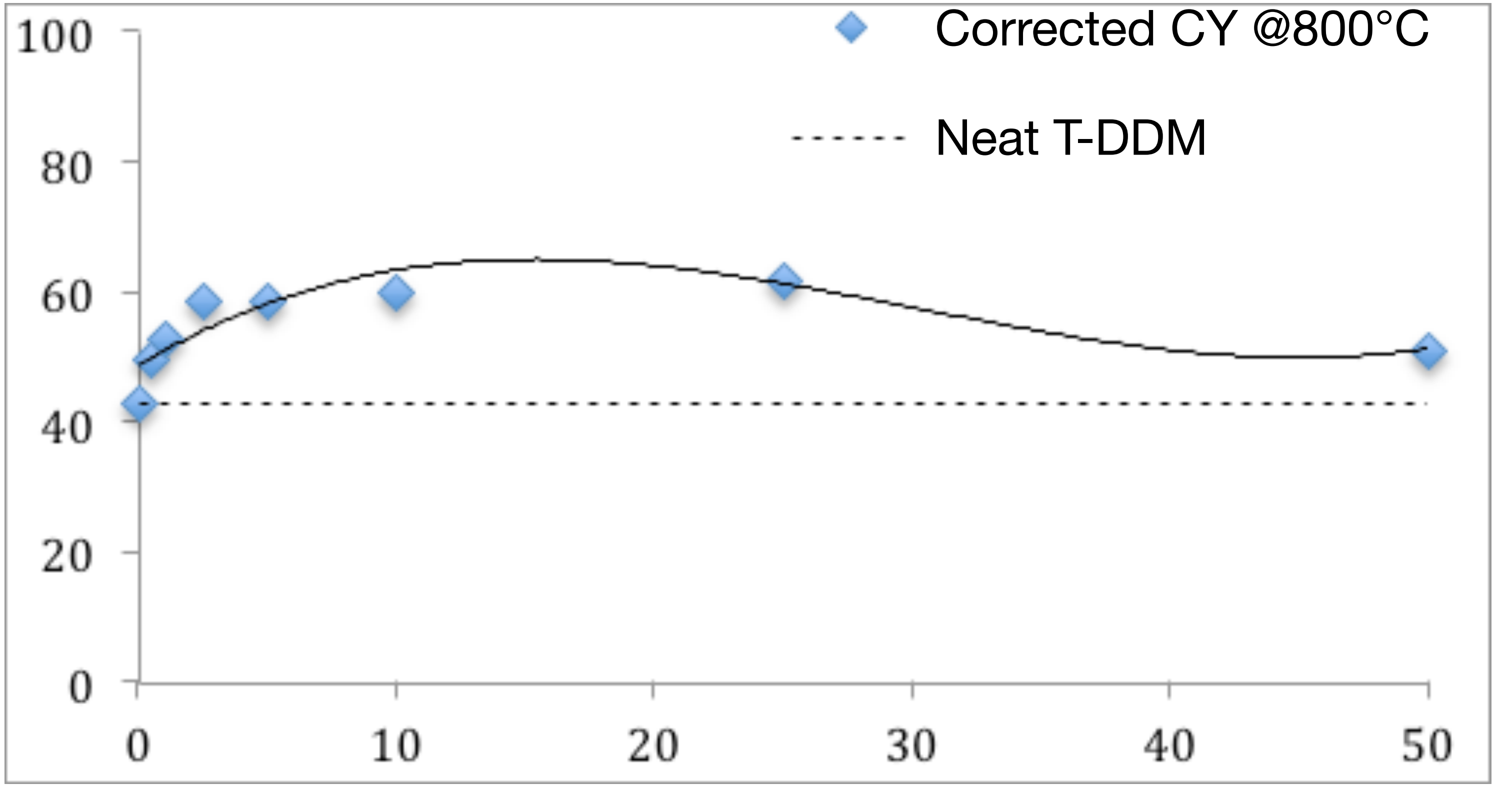
➡ Polymerisation kinetics?

The charring is greatly improved by ZnO



Sample	T-DDM	ZnO
CY [%]	43.6 ± 1.4	99.0 ± 0.1

The effect correlates with the change on kinetics



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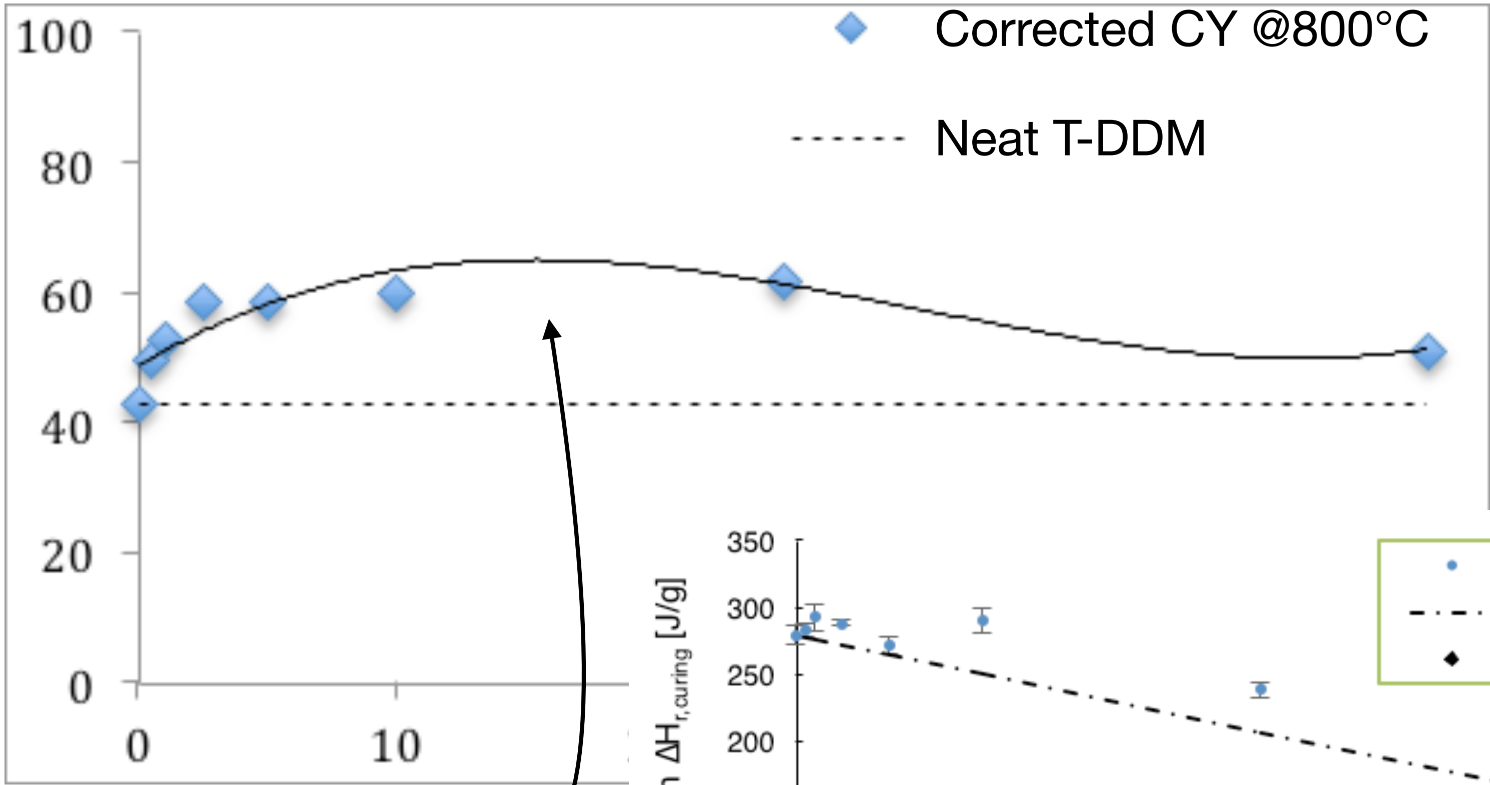
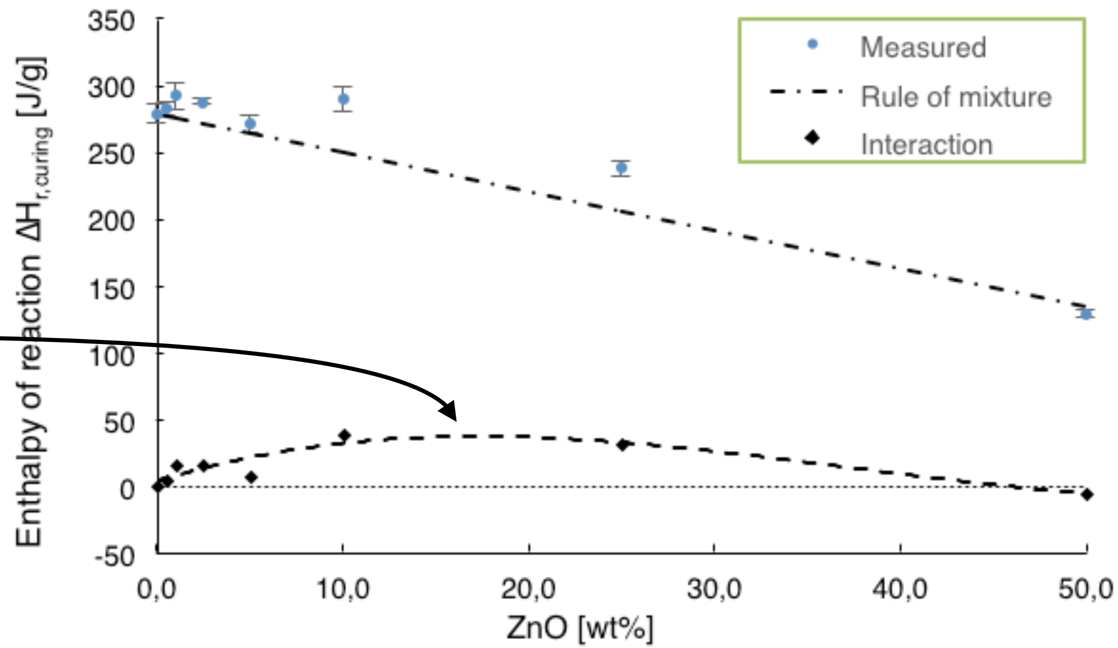
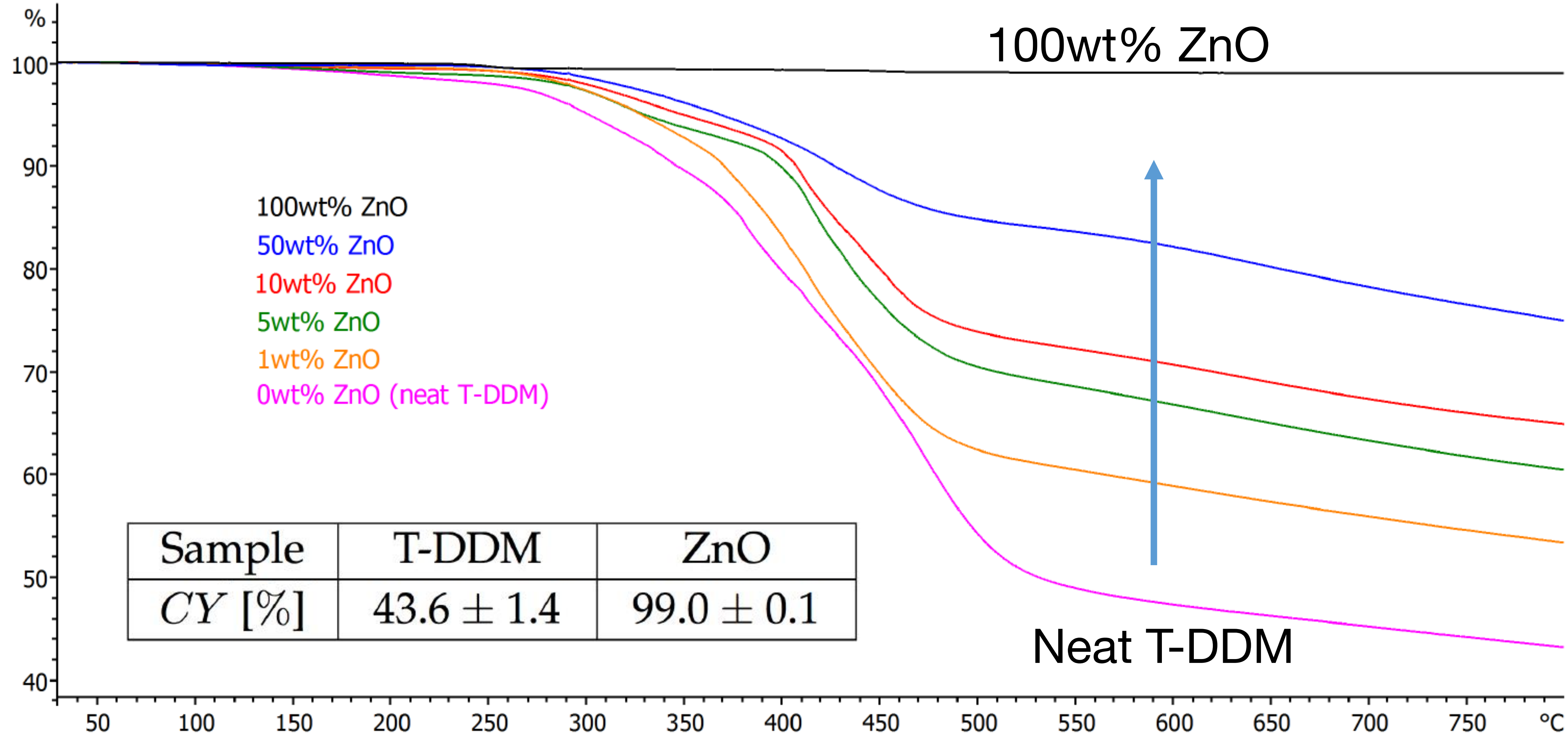


Maximum around 15-20wt%



The matrix degradation is also T°-delayed



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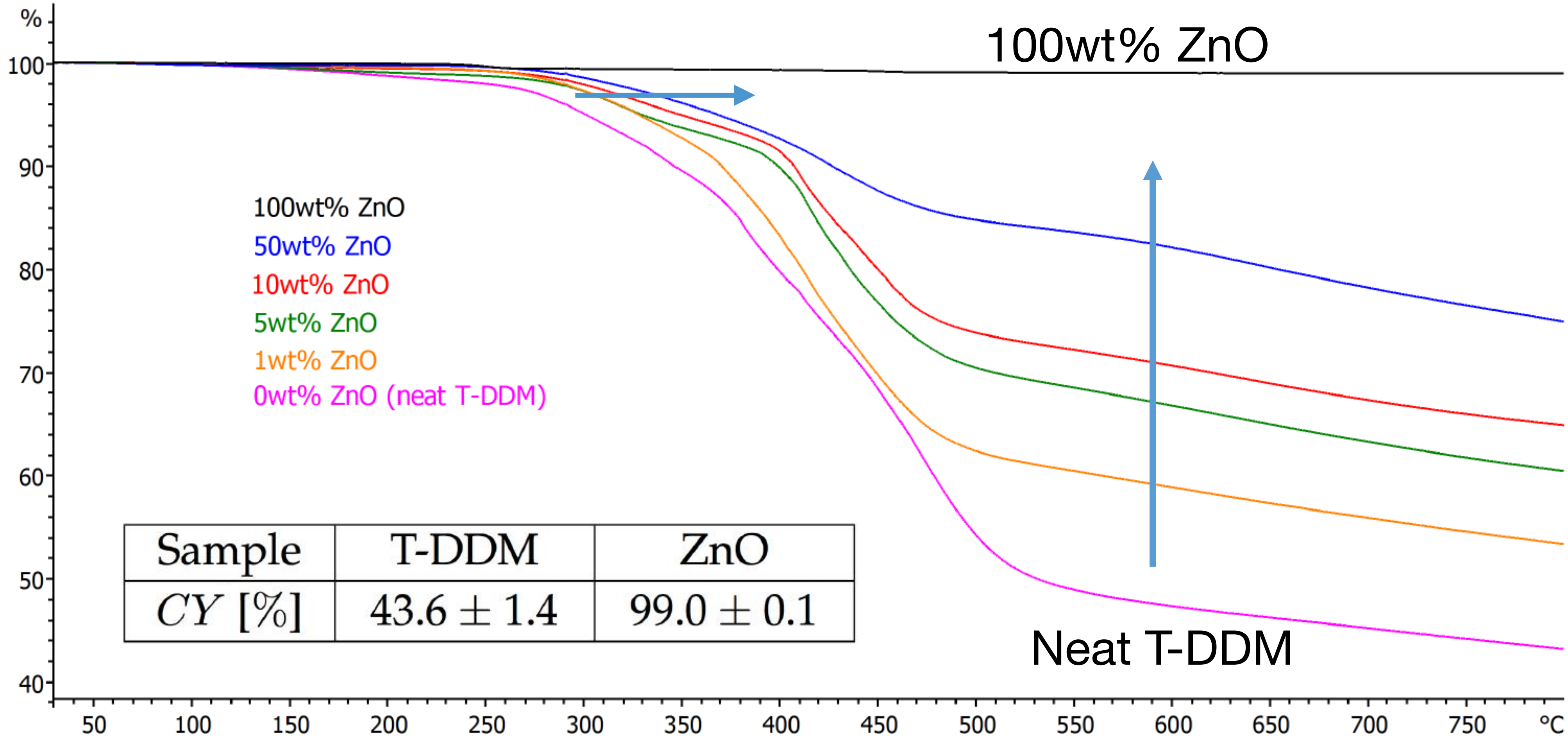

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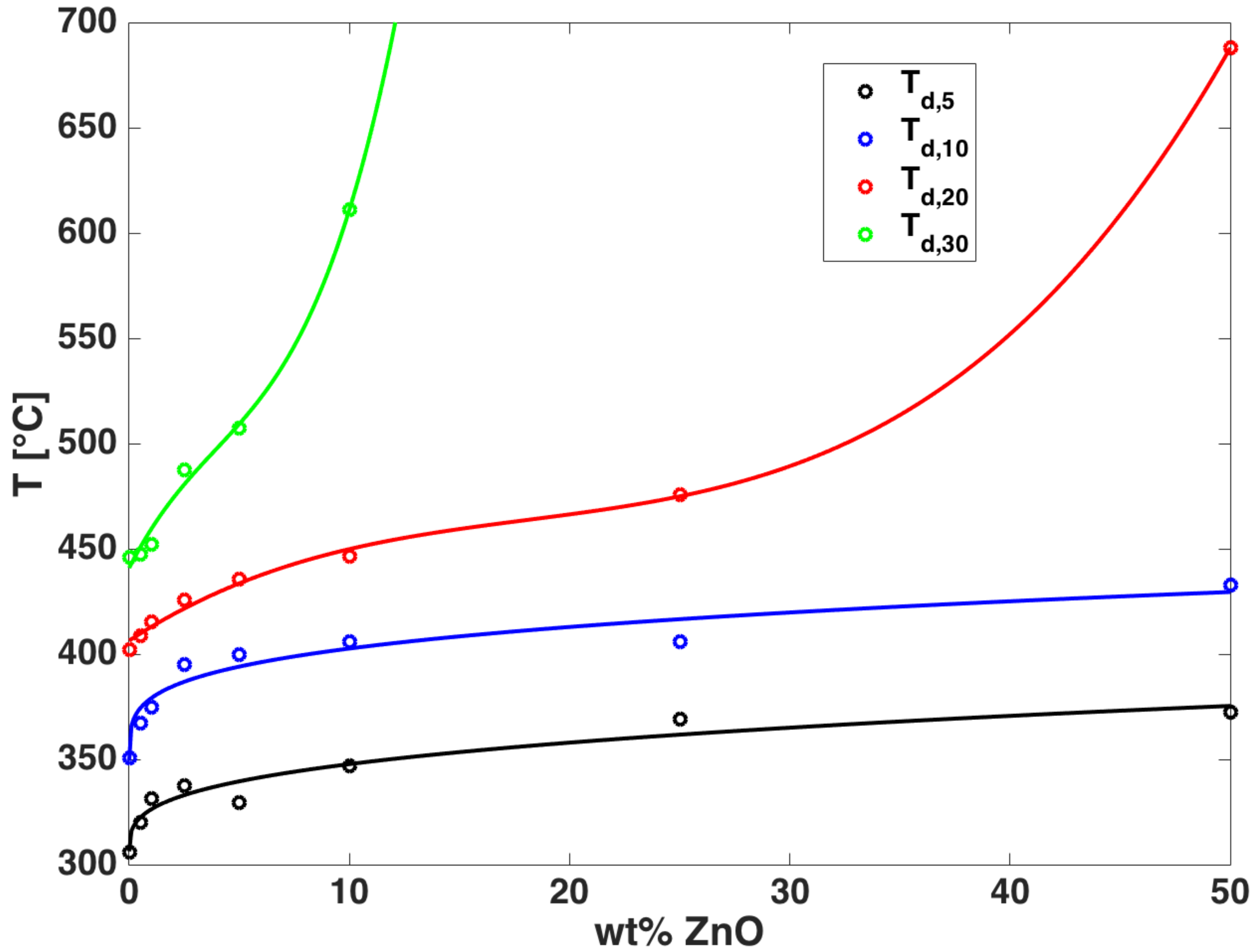

Conclusions & perspectives

Kinetics

- The activation energy for ROP of T-DDM is about 90kJ/mol
- The order of the ROP reaction is around 2.3 (between 2.2 and 2.5)

Effects of ZnO on thermal stability

- ZnO causes the formation of new chemical bonds in the system
- These bonds are likely responsible for the observed
    - charring improvement
    - fast increase of the degradation temperatures

Effect of ZnO on other benzoxazines?

Acknowledgements

- Region wallonne for financial support
- Leïla Bonnaud for providing resin and advices
- Christian Bailly for supervising this job
- Carl van Tieghem for performing most of this work

Questions?

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