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ISGS
materials through chemistry

# Flame retardant and recyclable phosphine oxide epoxy based covalent adaptable networks containing sol gel derived mixed oxides as acid catalysts


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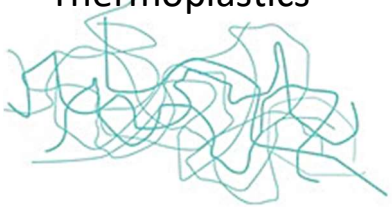
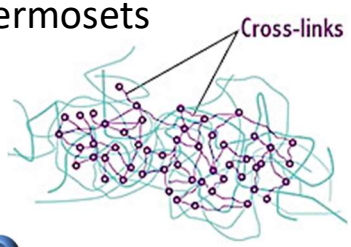
# Introduction - 1

Thermoplastics

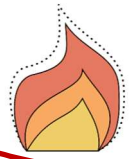


Thermosets



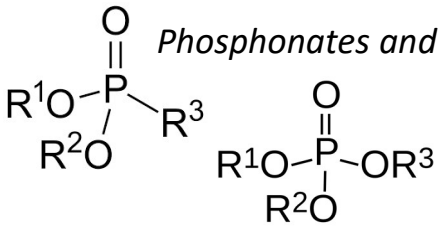

Reprocessable by associative mechanism

**VITRIMERS**

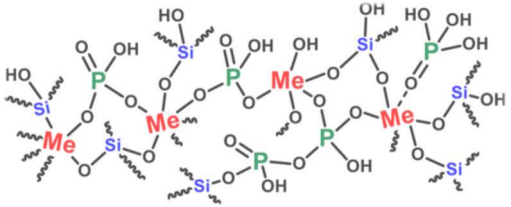


Flammability

- *Epoxies are 70% of thermosets on the market*
- *Epoxy-based vitrimers are highly desirable*



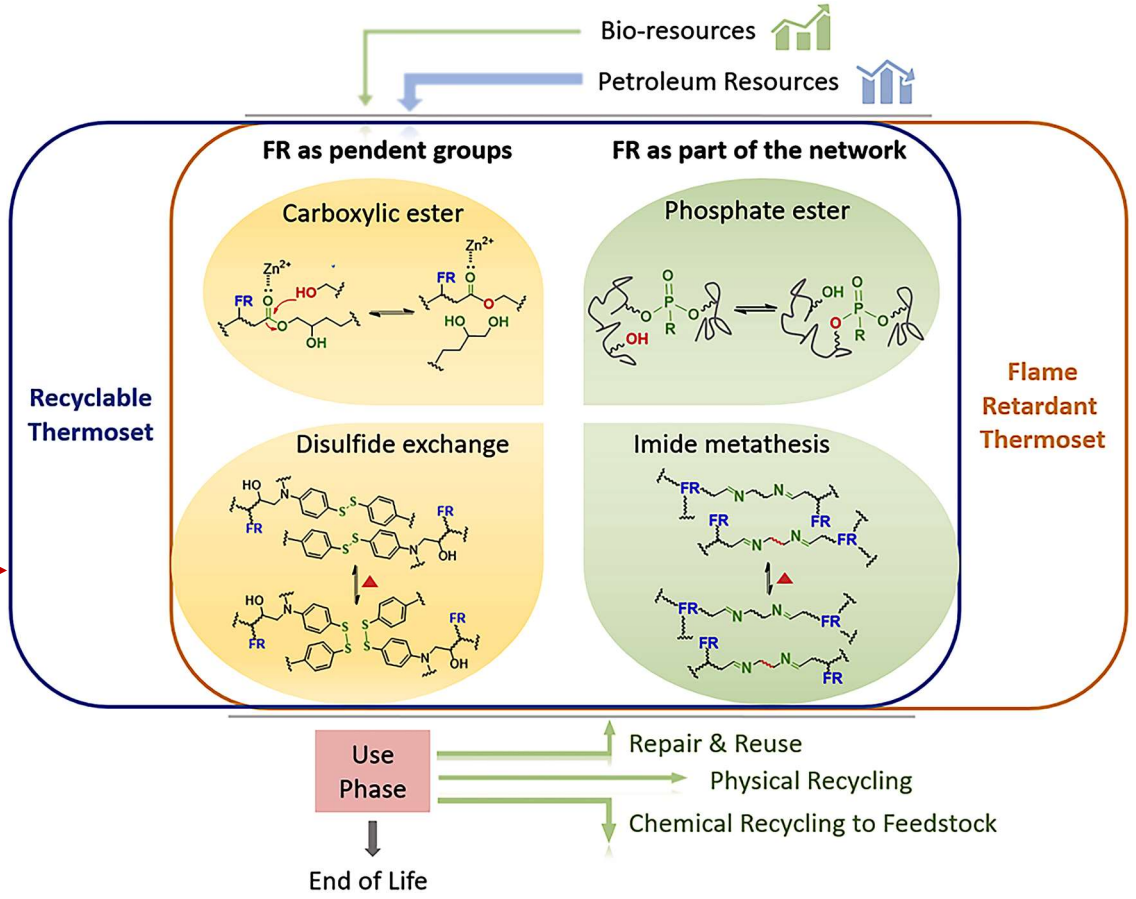
*Phosphonates and phosphine oxides*



***Via Sol-gel chemistry***

- *One-pot procedure*
- *Control*
- *High yield*
- *Low temperature*

*S.J. Demongeot et al.,* ***Polym. Chem.*** *2016, 7(27), 4486–4493*
*W.W. Klingler et al.,* ***Compos. B. Eng.*** *2023, 258, 110667*




Limits of vitrimers based on transesterification:

- Sensitive toward the hydrolysis
- High reprocessing temperatures for low activation energies/$\tau$
- Zn(II) acetate and TBD usually needed (not stable at high temperatures)
- Only one function for the catalyst, also needed at high loadings

# Synthesis of the mixed oxides - 2

*Binary and ternary oxides:*

- **$Nb_2O_5$-($P_2O_5$)-$SiO_2$ (SiNbP)**
- **$SiO_2$-$P_2O_5$ (SiP)**
- **$SiO_2$-$Nb_2O_5$ (SiNbP)**

Green sol-gel synthesis route

Metal oxide and phosphorus-based active phases finely dispersed in high-surface area porous silica matrix

Modulation of acidity (Lewis/Brønsted acid sites) and nanostructure

Catalytic activity in biomass conversion reactions (hydrolysis, dehydration, transesterification)

***Via Sol-gel chemistry***

Ammonium niobium oxalate hydrate (ANO)

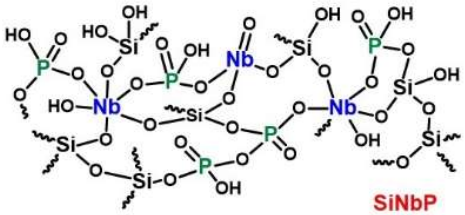
Water

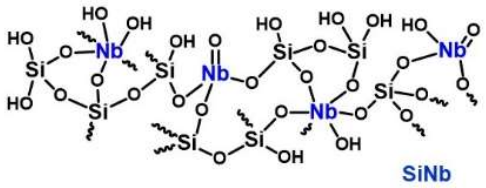
TEOS (Tetraethyl orthosilicate

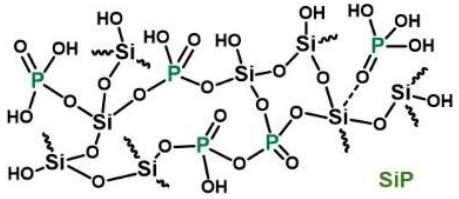
Stirring 3 days

After 1 h, $H_3PO_4$ is added and the solution is stirred at room temperature until gelation

The acidity of ANO and $H_3PO_4$ promotes TEOS hydrolysis without the need for additional acid catalysts



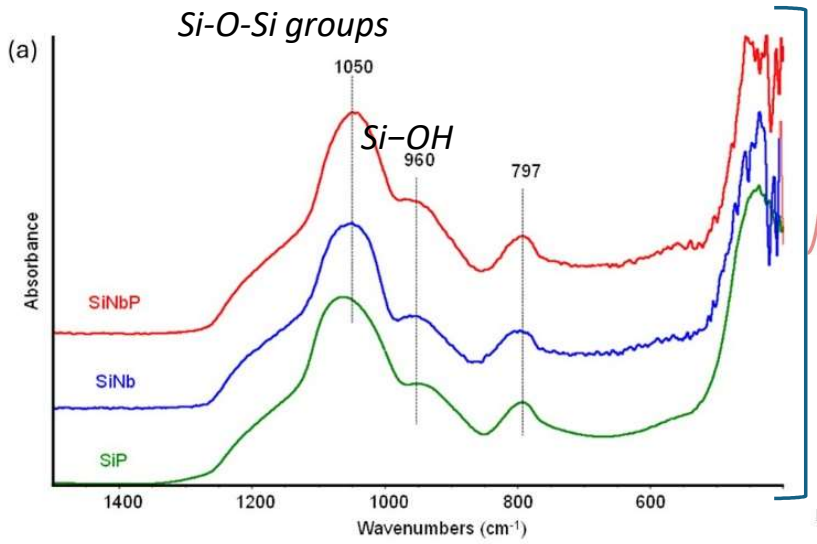



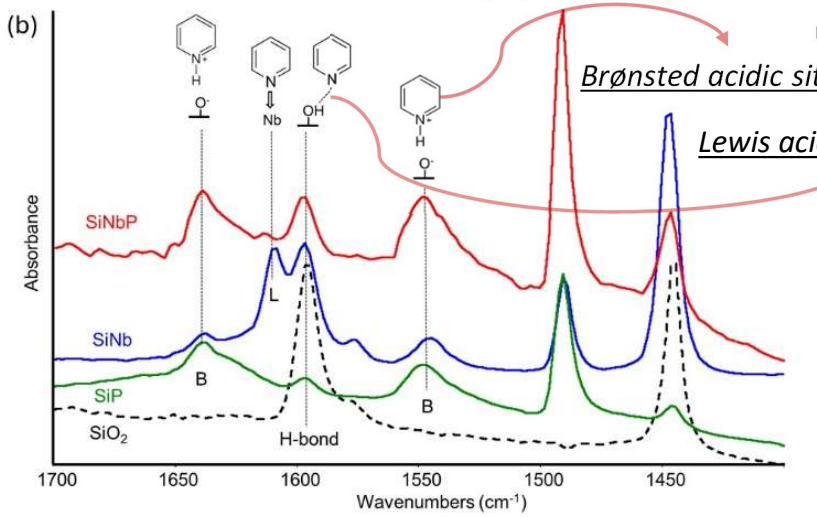




**Amorphous structures (XRD)**

*Clear homogeneous gels are obtained (3 days)*
*The gels are kept aging at room temperature (2 days)*
*Dried in air at 110 °C to white bulk xerogels*
*Ball milling and calcined in air at 500 °C for 1 h at the heating rate of 10 °C $min^{-1}$*

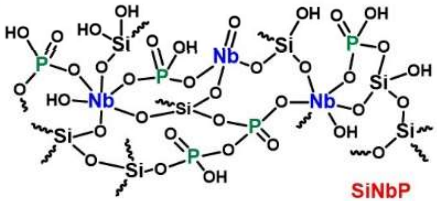
# Structural and acid properties of the mixed oxides - 2

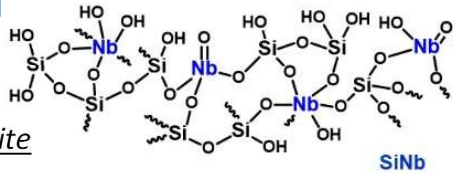


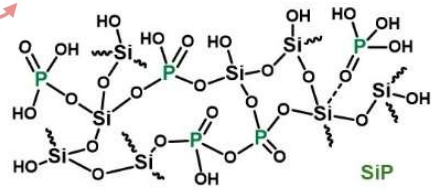




*Absence of organic compounds after calcination (500 °C)*

(c)



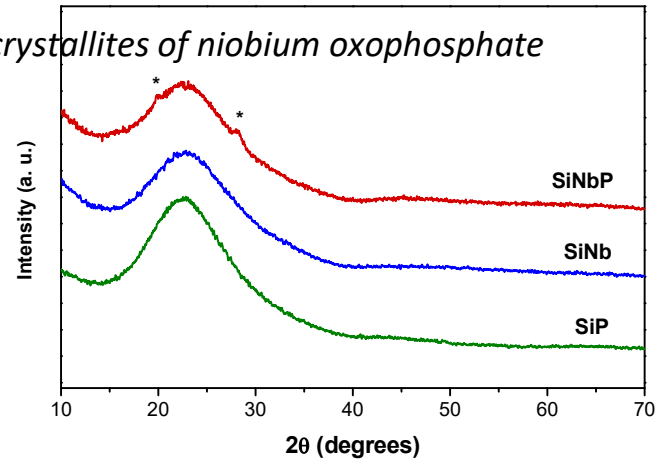




*Silicon oxide network in which Nb and P units are dispersed*

*A. Aronne et al., **J. Sol-Gel Sci. Technol.** 2007, 43(2), 193–204*

*crystallites of niobium oxophosphate*




Amorphous structure: absence of segregated $Nb_2O_5$ or $P_2O_5$ crystalline phases

$NbOPO_4$ is a well-known acidic solid characterized by a strong intrinsic Lewis/Brønsted acidity and a good thermal stability

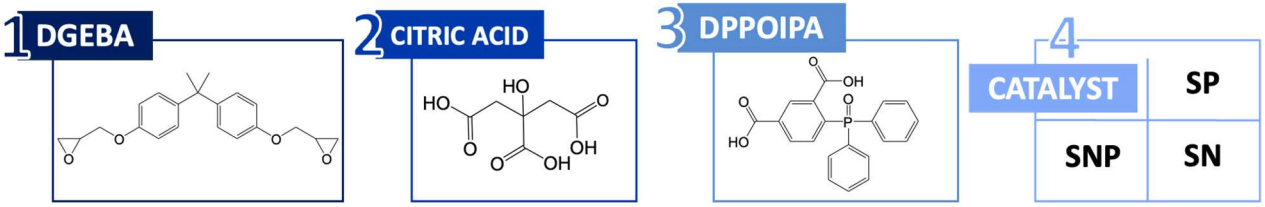
SiNbP: manly Brønsted acidity and weak Lewis acidity

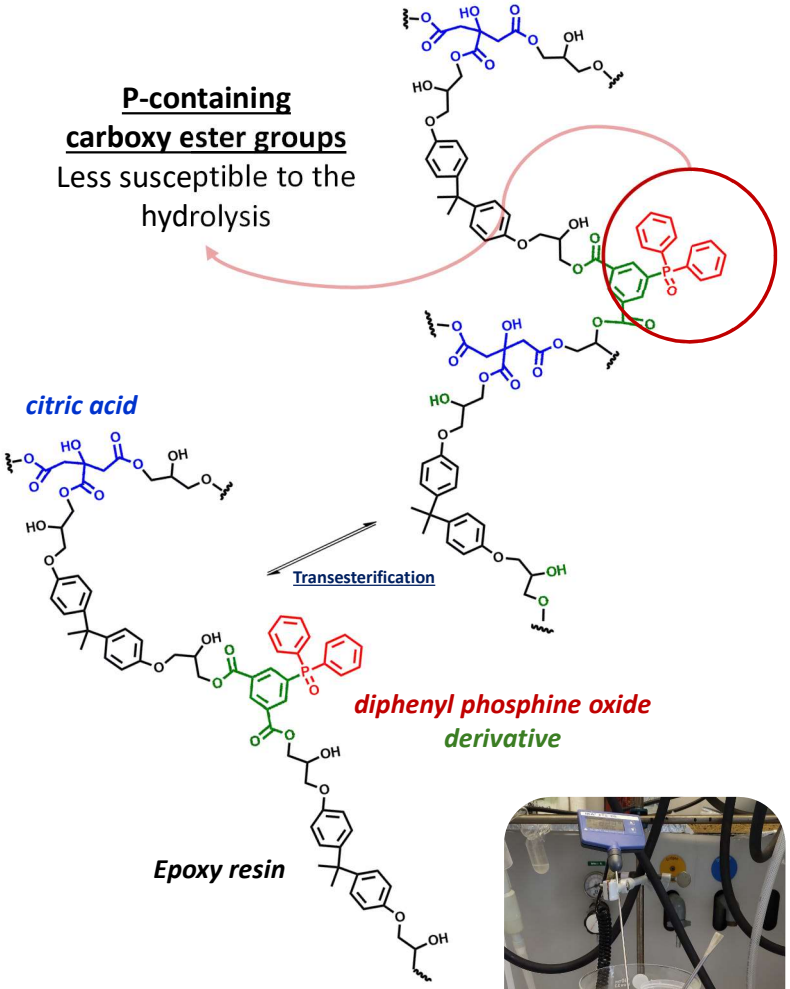
SiNb: Brønsted and medium strength Lewis acidic sites

SiP: Brønsted acidity and weakly acidic silanol groups

# Preparation of inherently recyclable and flame retardant epoxy-based vitrimers - 2

| Sample | DGEBA (mol) | CA/DGEBA (mol/mol) | DPPOIPA/ DGEBA (mol/mol) | Catalyst (10 wt.% of precured resin) | Final P content (wt.%) |
|---|---|---|---|---|---|
| EV | 1 | 0.67 | - | - | - |
| EV-SN | 1 | 0.67 | - | SiNb | - |
| EV-SP | 1 | 0.67 | - | SiP | - |
| EV-SNP | 1 | 0.67 | - | SiNbP | - |
| EVP | 1 | 0.40 | 0.40 | - | 2.0 |
| EVP-SN | 1 | 0.40 | 0.40 | SiNb | 1.8 |
| EVP-SP | 1 | 0.40 | 0.40 | SiP | 2.2 |
| EVP-SNP | 1 | 0.40 | 0.40 | SiNbP | 2.4 |






Mixing at **60°C**

***Curing*** **140°C 2h; 160°C 2h**

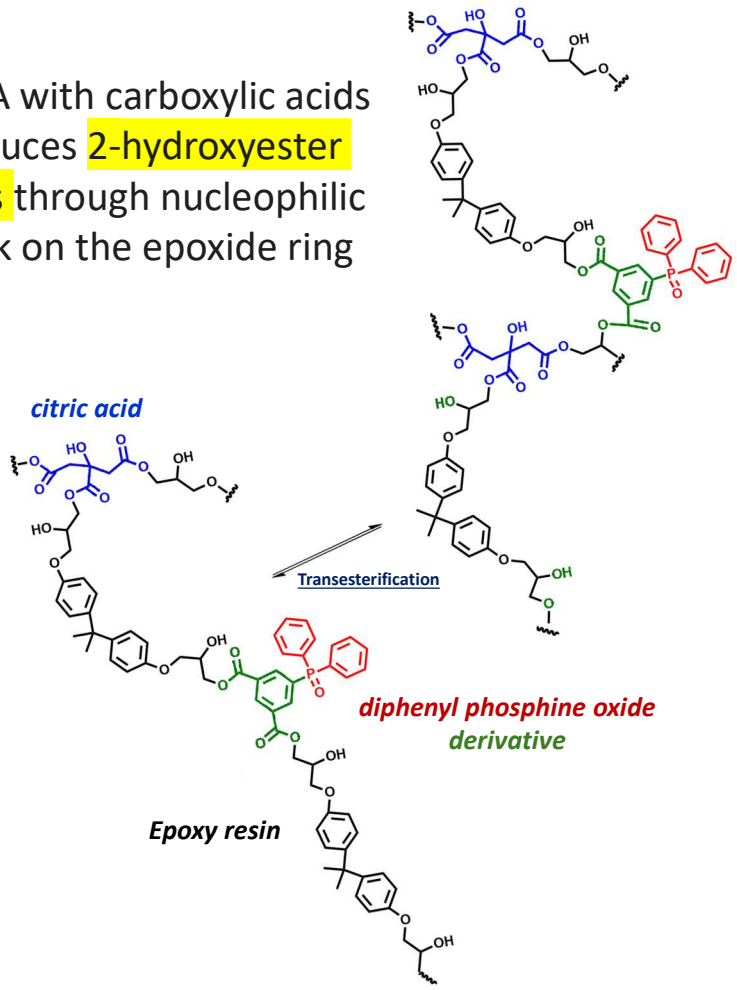
The nominal P content: 2.0 wt.%
DGEBA:CA:DPPOIPA = 1.0:0.4:0.4 (molar)
DGEBA:CA = 1:0.67 (molar)


*D. Montarnal et al.,* ***Science*** *2011, 334, 965*

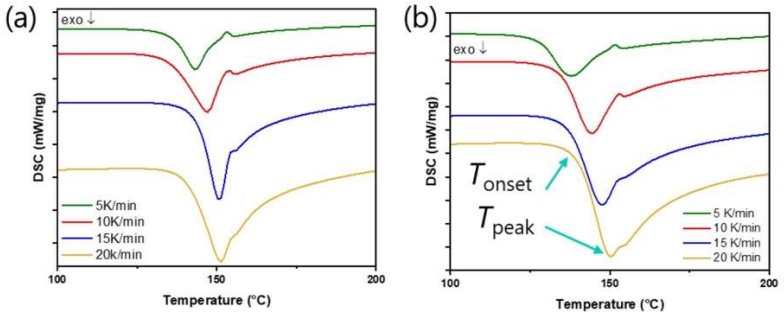
*V. Palumbo et al.,* ***Sustain. Mater. Technol.*** *2025, 45, e01477*

# Formation of the dynamic crosslinked network - 2

DGEBA with carboxylic acids produces 2-hydroxyester chains through nucleophilic attack on the epoxide ring




EV EVP




*Exothermic peak of crosslinking reactions shifts to higher temperatures and grows in magnitude as the heating rate increases*

*Model-free kinetic method: the reaction rate at constant conversion degree is simply a function of the temperature*

Mixing at **60°C**

***Curing*** **140°C 2h; 160°C 2h**

Better chemical affinity of DPPOIPA than CA

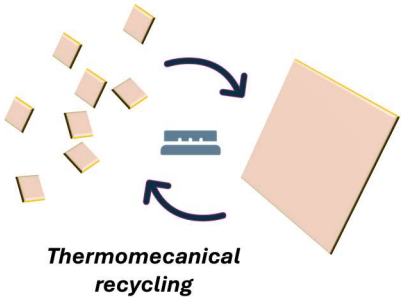
The incorporation of DPPOIPA causes a significant drop (27%) in the $E_a$ value with respect to EV reference sample

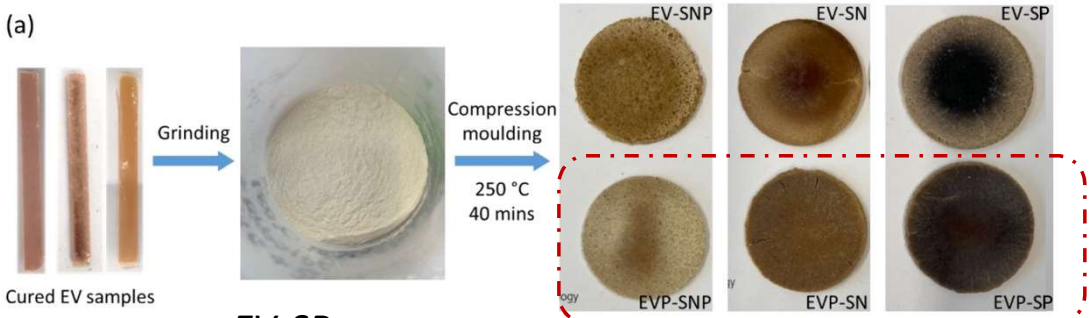
Mixed oxides appear effective in catalysing the esterification reactions, affording lower $E_a$ (up to 36%) than the one of EVP

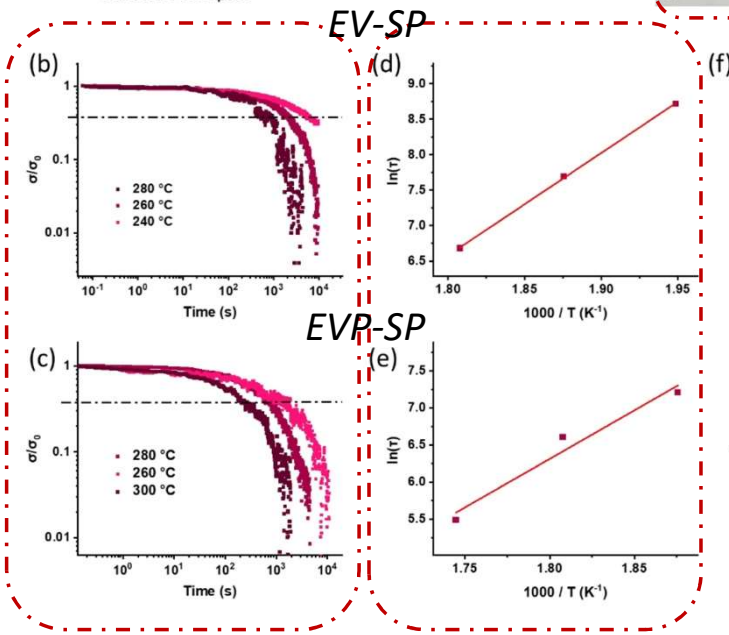
| Sample | $E_a$ (kJ mol$^{-1}$) |
|---|---|
| EV | 212 |
| EVP | 156 |
| EVP-SN | 131 |
| EVP-SP | 141 |
| EVP-SNP | 100 |

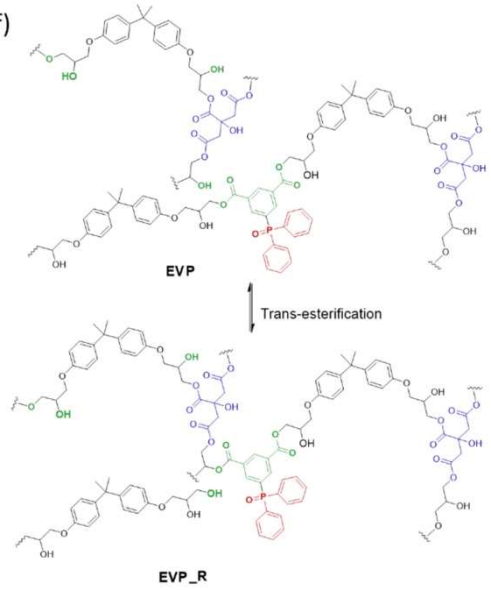
# Reprocessability of the epoxy-based vitrimers - 3

The various samples have been thermomechanically reprocessed at **250 °C for maximal**
The pressure sequence was the same for each sample, going through the following steps:
0.5 tons, 4 tons, 10 tons, and 25 tons




The better reprocessability of EVP set demonstrates that the presence of the DPPOIPA units in the network positively affects its topological rearrangement by dynamic bond exchanges

Stress relaxation follows a stretched exponential model in a range of relaxation times, especially for EV-SP and EVP-SP

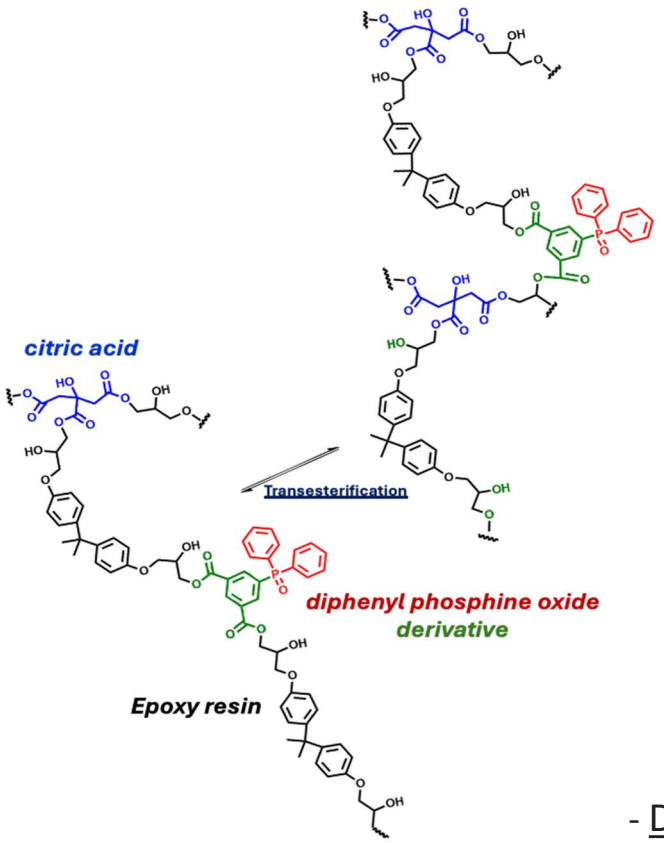
*EV-SP ($E_a$ = 120.0 kJ/mol) / (240–280 °C)*
*EVP-SP ($E_a$ = 108.7 kJ/mol) / (260–300 °C)*

$E_a$ is slightly higher compared to the values usually observed for $Zn(OAc)_2$ or $Sn(Oct)_2$



*D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, **Science** 2011, 334, 965*

# Thermal analysis of the epoxy-based vitrimers - 3




| Sample | Tg (°C) |
|---|---|
| EV | 126 |
| EV-SN | 120 |
| EV-SP | 128 |
| EV-SNP | 131 |

**DPPOIPA** →

| Sample | Tg (°C) (original) | Tg (°C) (recycled) |
|---|---|---|
| EVP | 120 | - |
| EVP-SN | 120 | 123 |
| EVP-SP | 122 | 124 |
| EVP-SNP | 99 | 101 |

*DPPOIPA introduces bulky phenyl pendant groups into the polymer chains and cause a slight plasticizing effect*

Phenyl rings of DPPOIPA negatively interfere by steric hindrance and with the establishment of hydrogen bond interactions

| Sample | Original | | Recycled | |
|---|---|---|---|---|
| | $T_{5\%}$ (°C) | Residue (wt.%) 800 °C | $T_{5\%}$ (°C) | Residue (wt.%) 800 °C |
| EV | 251 | 12 | - | - |
| EVP | 337 | 12 | - | - |
| EVP-SN | 315 | 25 | 340 | 26 |
| EVP-SP | 318 | 24 | 322 | 30 |
| EVP-SNP | 284 | 23 | 306 | 27 |

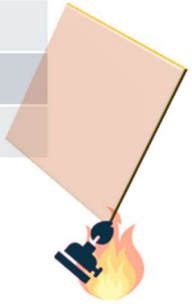
- DPPOIPA causes an increase in $T_{5\%}$
- All mixed oxides lead to an increase in residue, even higher in presence of DPPOIPA

*Condensed phase action exerted by the phosphorus-containing moieties in synergy with the mixed oxides*

# Flammability of the epoxy-based vitrimers - 3

EV-SP exhibited no dripping phenomena, probably due to the acidic characteristics of SiP, which are also beneficial for reprocessing features

| Sample | UL 94/dripping |
|---|---|
| EV | NC/YES |
| EVP | V-0/NO |
| EV-SN | NC/YES |
| EVP-SN | V-0/NO |
| EV-SP | NC/NO |
| EVP-SP | V-0/NO |
| EV-SNP | NC/YES |
| EVP-SNP | V-0/NO |



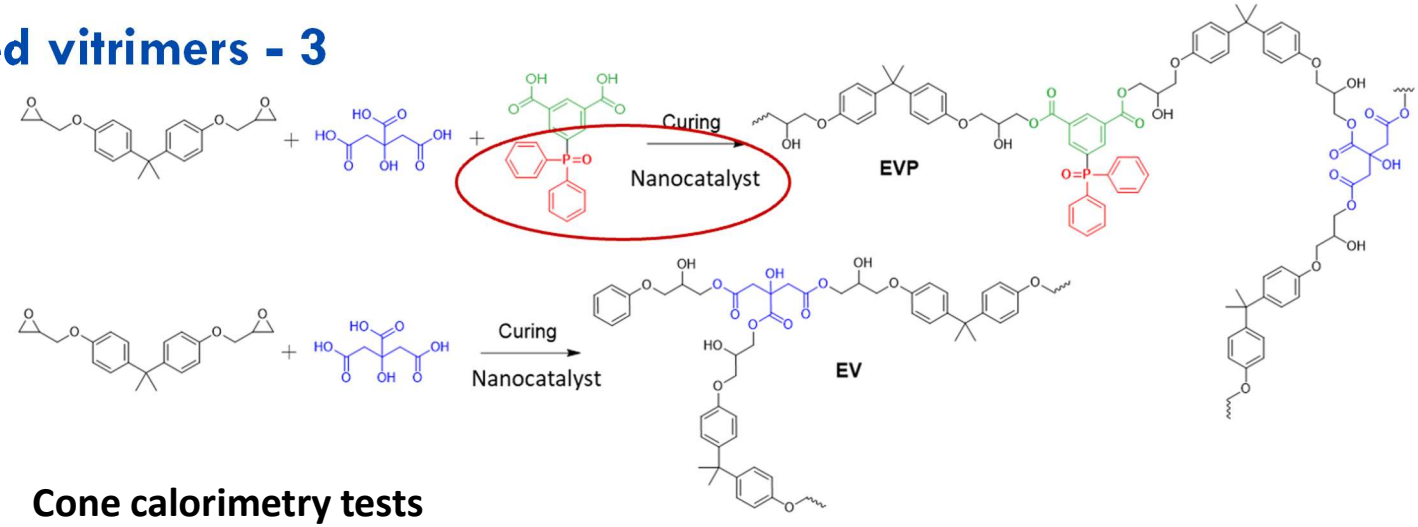
**EV-SNP**

**EVP-SNP**

Huge formation of char during the tests → acid catalysts dehydrate the polymer matrix
White smoke releasing during the tests → phosphine oxide units exert an inhibition effect

EVP with all the silica-based solid acids: no-dripping V-0 class

# Fire behaviour of the epoxy-based vitrimers - 3




The acidic characteristics of the catalysts Promote the charring of the polymer matrix, leading to the production of more carbonaceous material

The addition of SiNbP into EVP Decrease of the pHRR and THR by around 36% and 24%, respectively, together with an increase of the residue up to 5.1%

**PCFC**

| Sample | THR (kJ/g) | pHRR (W/g) | Residue (wt.%) |
|---|---|---|---|
| EV | 26 ± 0.7 | 293 ± 47 | 1.1 ± 0.1 |
| EVP | 25 ± 0.7 | 376 ± 24 | 1.4 ± 0.3 |
| EV-SN | 21 ± 0.3 | 298 ± 2 | 1.9 ± 0.1 |
| EVP-SN | 18 ± 0.1 | 291 ± 7 | 3.7 ± 0.1 |
| EV-SP | 20 ± 0.8 | 302 ± 15 | 2.0 ± 0.2 |
| EVP-SP | 18 ± 0.1 | 303 ± 3 | 3.6 ± 0.1 |
| EV-SNP | 25 ± 4 | 247 ± 3 | 1.4 ± 0.6 |
| EVP-SNP | 19 ± 0.3 | 243 ± 22 | 5.1 ± 0.5 |

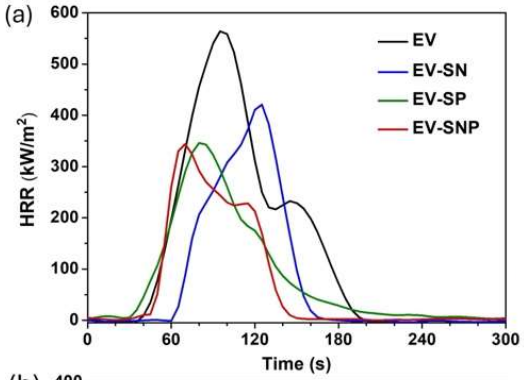
**Cone calorimetry tests**

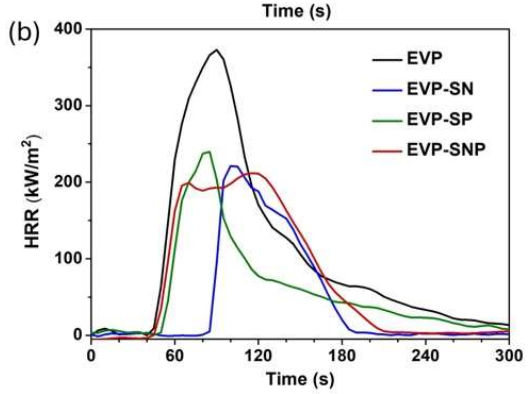
| Sample | TTI (s) | $CO/CO_2$ (-) | TSR ($m^2/m^2$) |
|---|---|---|---|
| EV | 31 ± 4 | 0.05 | 1755 ± 9 |
| EVP | 36 ± 1 | 0.14 | 2357 ± 41 |
| EV-SN | 75 ± 20 | 0.10 | 828 ± 17 |
| EVP-SN | 95 ± 12 | 0.33 | 993 ± 29 |
| EV-SP | 41 ± 9 | 0.08 | 927 ± 46 |
| EVP-SP | 54 ± 3 | 0.22 | 877 ± 16 |
| EV-SNP | 52 ± 4 | 0.08 | 777 ± 45 |
| EVP-SNP | 53 ± 1 | 0.37 | 1306 ± 19 |

Mixed oxides in EV and EVP cause a notable decrease in the total smoke release (up to 62%)

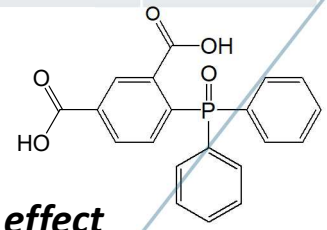
The presence of DPPOIPA leads to a remarkable increase (~70%) in the time to ignition and $CO/CO_2$ ratio

# Flame retardant mechanisms - 3

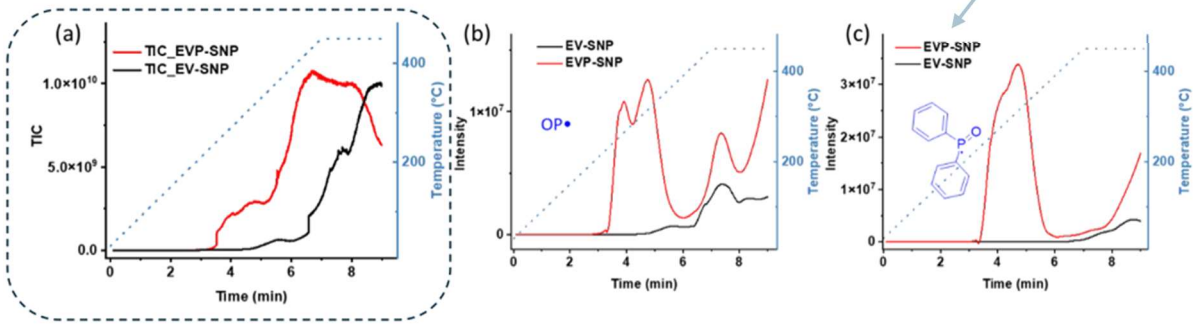


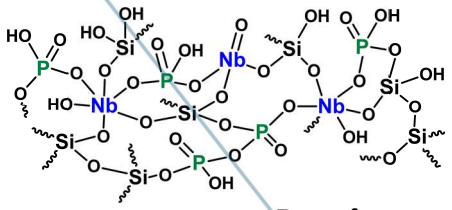

| Sample | THR (MJ/m²) | pHRR (kW/m²) |
|---|---|---|
| EV | 40 ± 1 | 573 ± 5 |
| EVP | 36 ± 2 | 390 ± 73 |
| EV-SN | 23 ± 2 | 440 ± 2 |
| EVP-SN | 14 ± 1 | 216 ± 7 |
| EV-SP | 27 ± 2 | 369 ± 34 |
| EVP-SP | 20 ± 3 | 261 ± 8 |
| EV-SNP | 20 ± 3 | 355 ± 3 |
| EVP-SNP | 25 ± 2 | 214 ± 22 |



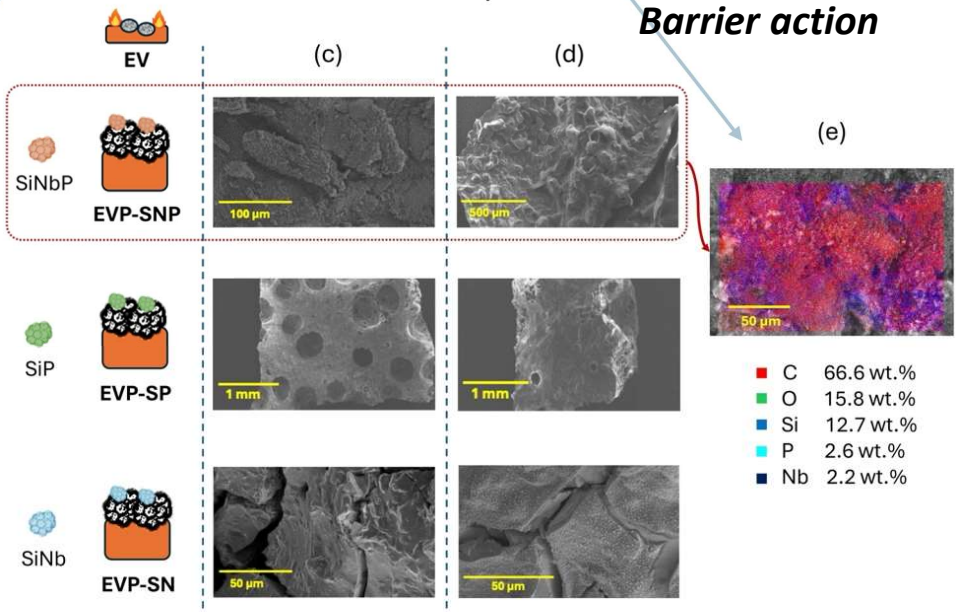

***Inhibition effect***




The incorporation of SiNbP into the P-modified epoxy system allows a significant reduction of the peak of heat release rate (~63%) and of the total heat release (~38%)

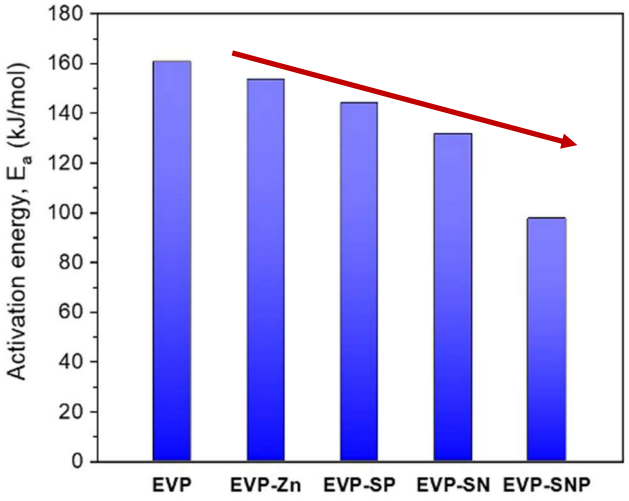


***Barrier action***



## Performance comparison between epoxy-based vitrimers obtained by using Zn(II) acetate or mixed oxides catalysts

| Sample | $E_a$ (kJ mol$^{-1}$) | Original | | Recycled | |
|---|---|---|---|---|---|
| | | $T_{5\%}$ (°C) | Tg (°C) | $T_{5\%}$ (°C) | Tg (°C) |
| EVP | 156 | 337 | 120 | - | - |
| EVP-Zn | 154 | 230 | 123 | 270 | 82 |
| EVP-SN | 131 | 315 | 120 | 340 | 123 |
| EVP-SP | 141 | 318 | 122 | 322 | 124 |
| EVP-SNP | 100 | 284 | 99 | 306 | 101 |




Esterification: crosslinking

| | Thermal stability | Tg | | Thermal stability | Tg |
|---|---|---|---|---|---|
| • SiNbP<br>• SiP<br>• SiNbP | High | Unvaried | *Thermomecanical recycling* | High | Unvaried |
| **Zn(II) acetate** | Low | Unvaried | | Low | Low |

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Catalytic effect of mixed oxides in phosphine oxide epoxy-based covalent adaptable networks: Recyclability, fire protection, and smoke suppression☆

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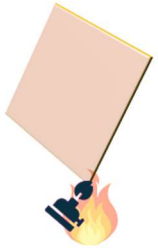
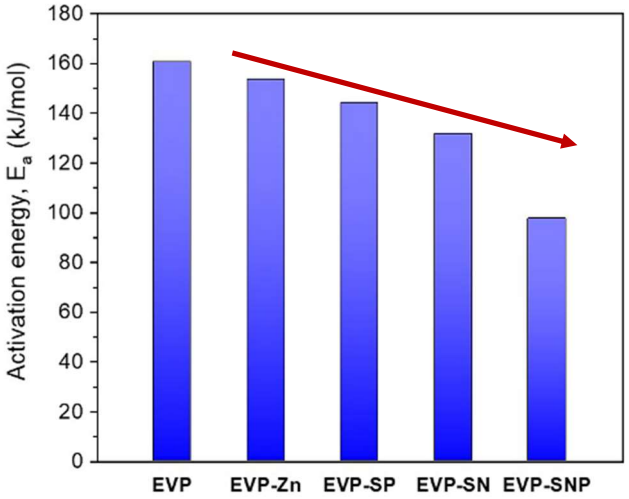
| Sample | UL 94/drip | TTI (s) | pHRR (kW/m²) | TSR (m²/m²) | CO/CO₂ (-) |
|---|---|---|---|---|---|
| EVP | V-0/NO | 36 ± 1 | 390 ± 73 | 2357 ± 41 | 0.14 |
| EVP-Zn | V-1/NO | 30 ± 12 | 320 ± 21 | 1523 ± 162 | 0.22 |
| EVP-SN | V-0/NO | 95 ± 12 | 216 ± 7 | 993 ± 29 | 0.33 |
| EVP-SP | V-0/NO | 54 ± 3 | 261 ± 8 | 877 ± 16 | 0.22 |
| EVP-SNP | V-0/NO | 53 ± 1 | 214 ± 22 | 1306 ± 19 | 0.37 |



***+ 1 master thesis in sol-gel & flame retardancy***




Esterification: crosslinking

| | Thermal stability | Tg | | Thermal stability | Tg |
|---|---|---|---|---|---|
| • **SiNbP**<br>• **SiP**<br>• **SiNbP** | High | Unvaried | ***Thermomecanical recycling*** | High | Unvaried |
| **Zn(II) acetate** | Low | Unvaried | | Low | Low |

# Conclusions - 4

Polyester vitrimers are formed by crosslinking epoxy resin with citric acid and diphenyl phosphine oxide derivative (DPPOIPA) and using sol-gel derived solid acid catalysts (SiP, SiNb, SiNbP)

The chemistry of these vitrimers allows for their reprocessing by associative mechanism of transesterification linkages. Reprocessed samples show unvaried $T_g$ compared to the original materials, and especially SiP oxide causes a reduction of curing activation energy and promotes thermomechanical recycling

This behaviour is ascribed to the significant surface acidity, mainly provided by Brønsted acid sites, driving the heat-triggered network rearrangement in vitrimers

All the DPPOIPA-containing vitrimers with acid solids are self-extinguishing, with no dripping V-0 rating in the UL 94 vertical burning test, despite the low P content (~2 wt.%)

The incorporation of SiNbP into the P-modified epoxy system allows a significant reduction of the peak of heat release rate (~63%) and of the total heat release (~38%)

For all the formulations containing an acid catalyst and DPPOIPA, the effect in the condensed phase takes place in synergy with an inhibition effect exerted by phosphorus radicals in the gas phase

Notwithstanding the gas phase action exerted by DPPOIPA, all the mixed oxides notably dwindle the TSR (up to 62%) and SEA (up to 71%) parameters during the CC tests

## Future outlooks

*Self-extinguishing flame retardant recyclable thermosets with very low smoke emissions*
*Proper tuning of the surface functionalities of such catalysts may improve fire resistance and sustainable features of final products*

# X Italian Sol-Gel Workshop

***Many thanks for your kind attention***

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