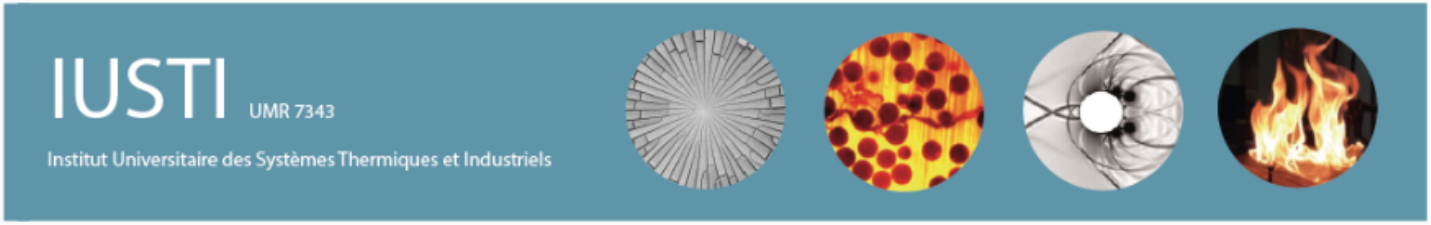


06 et 07 juin 2019, Marseille

GDR – Groupement de Recherche « Feux »

GDR CNRS n°2864

Étude du comportement au feu d'une résine polybenzoxazine – Applications aux matériaux composites

Prof. Sophie DUQUESNE, Dr. Fabienne SAMYN

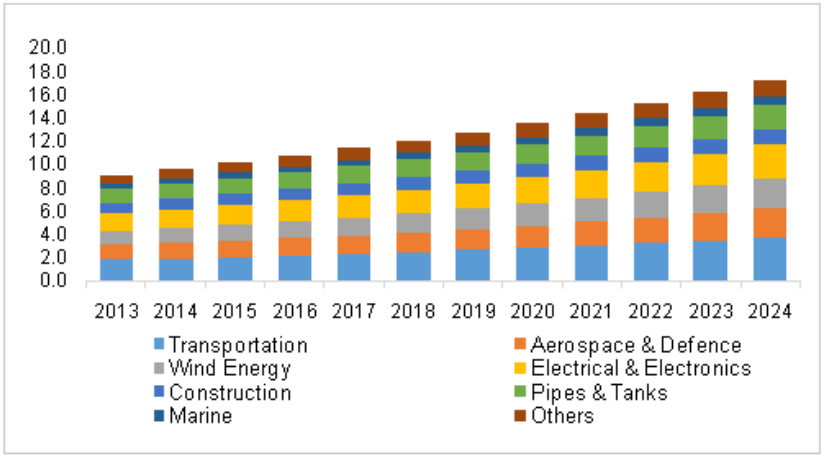
École Nationale Supérieure de Chimie de Lille
UMET - UMR-CNRS 8207
Villeneuve d'Ascq, France

Dr. Leila BONNAUD

MateriaNova,
Mons, Belgique

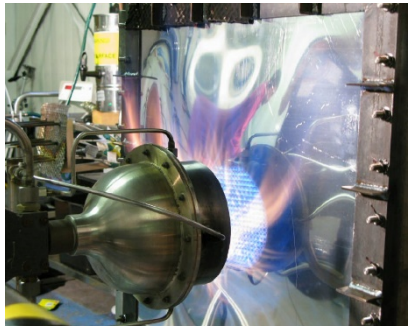
Composites and fire

U.S. composites market revenue by application, 2013 - 2024, (USD Billion)



http://www.grandviewresearch.com/industry-analysis/composites-market

Stringent fire safety regulations



Composites and fire

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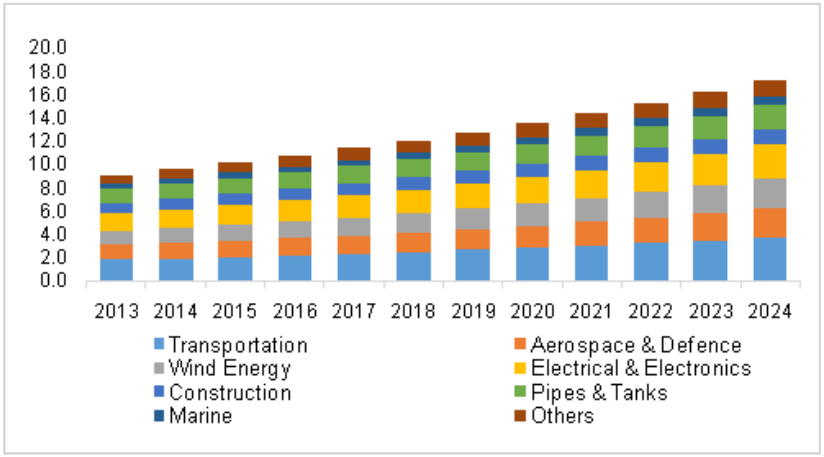

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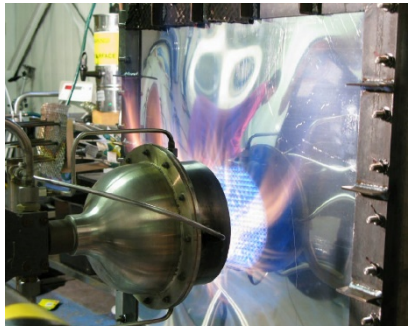
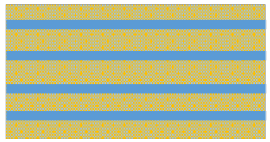


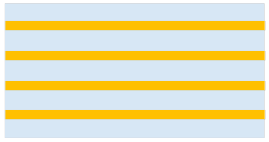
- ✓ ***High performance resin***
- ✓ ***Modification of the resin***

  Incorporation of FR additives (loading15 to 40% FR)



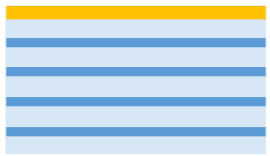
- ✓ ***Treatment on the fibres***

  *Padding of fibres with **FR solutions***



- ✓ ***Protection from the surface***

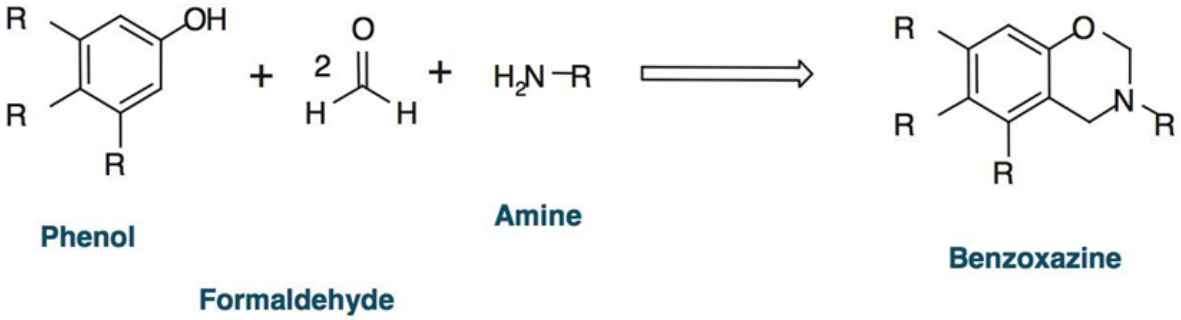
  Insulative materials like intumescent/ ceramic coatings or fabrics



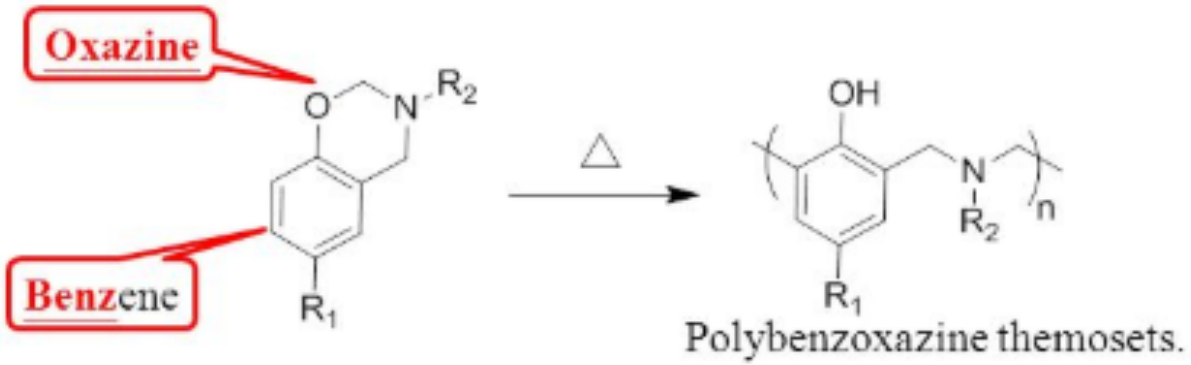
Benzoxazine resins

Chemistry discovered in the 1930's

Synthesis of benzoxazine

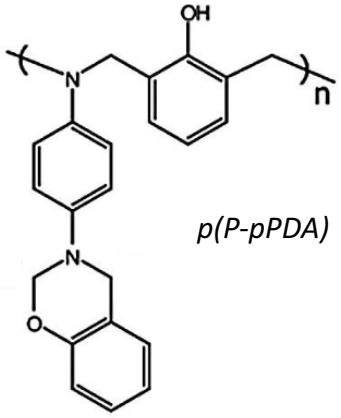


Synthesis of polybenzoxazine (PBA)

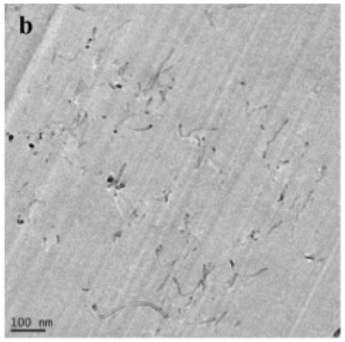


- **Low cost high performance resin**
- **High glass transition temperature**
- **Good flammability resistance**
- **No by product**
- **Low water absorption**
- **Good electrical properties**
- **Low shrinkage in curing**
- **Bio-based precursor**

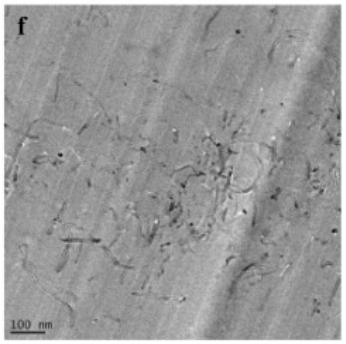
Fire retardancy of Benzoxazine resins



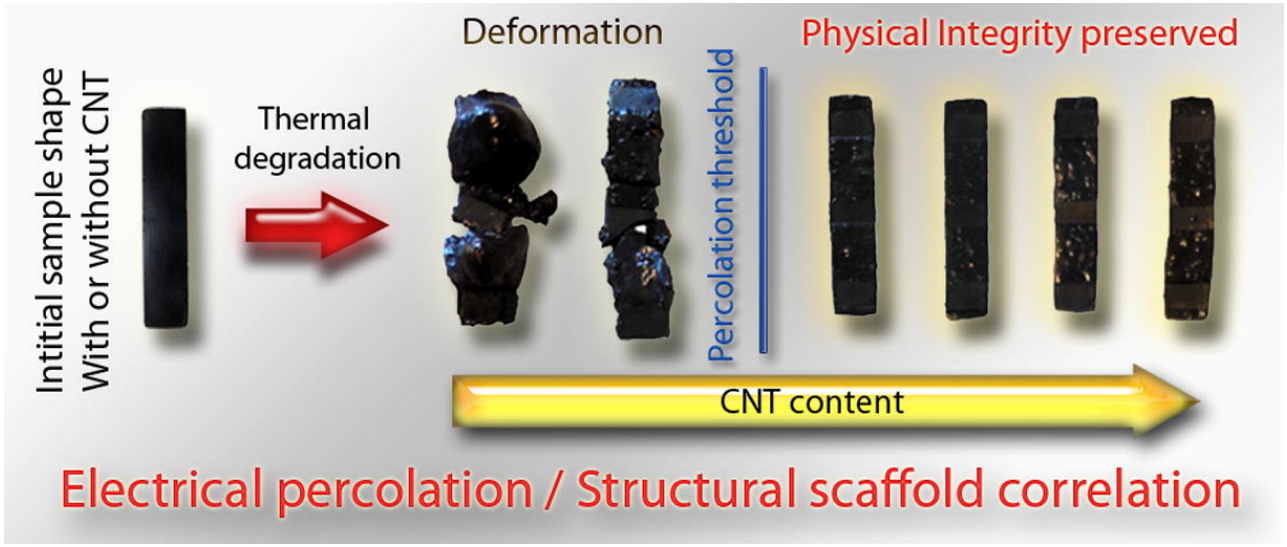
p(P-pPDA)



p(P-pPDA)+0,1% CNT



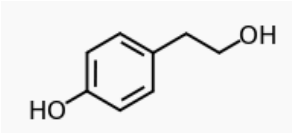
p(P-pPDA)+1% CNT



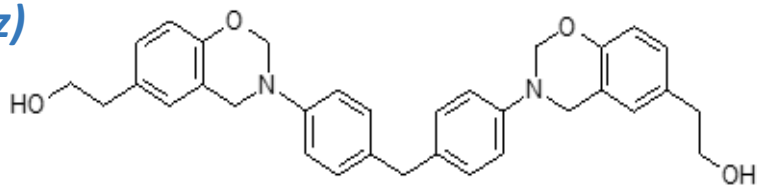
Picture of p(P-pPDA) burned in a rich oxygen atmosphere (38.5%)

European Polymer Journal, Volume 58, September 2014, Pages 218-225

Materials and methods

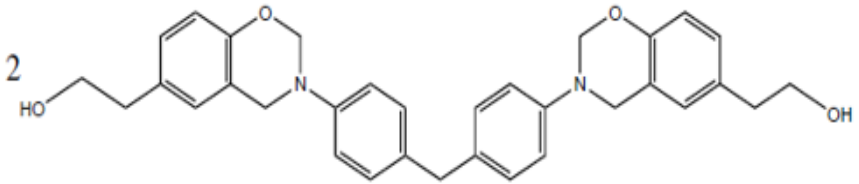


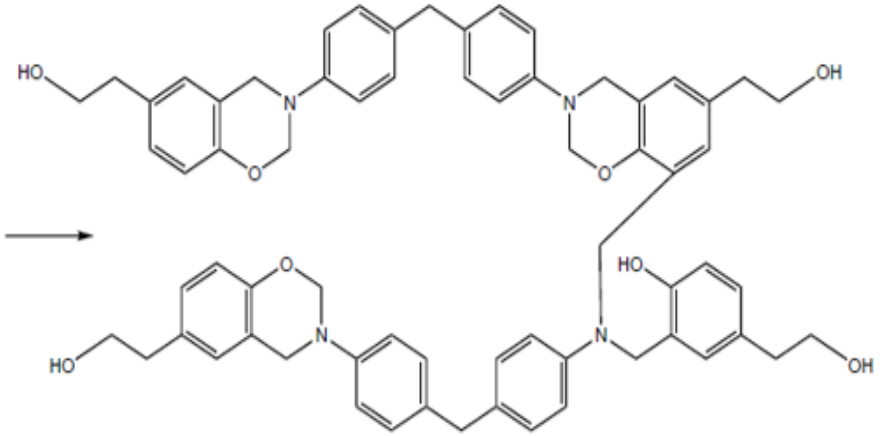
Benzoxazine (Bz)

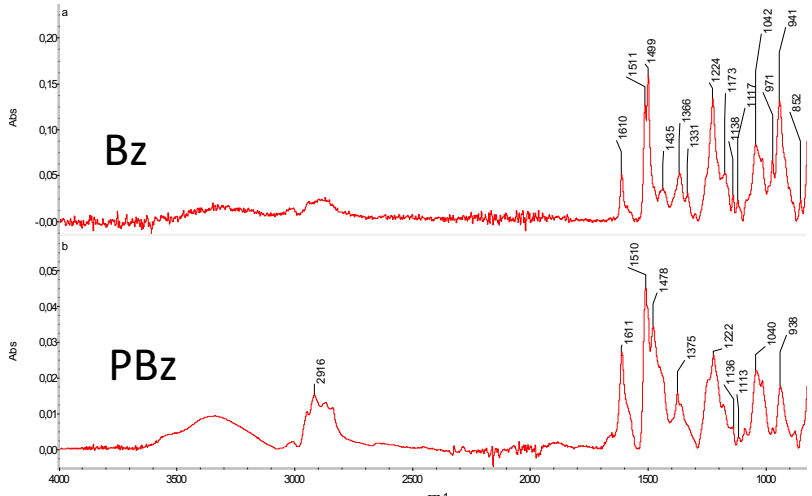


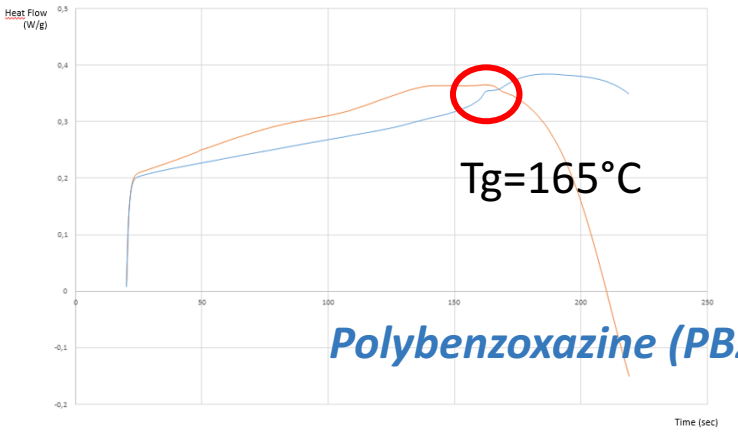
T-DDM precursors synthesized from natural phenol
Tyrosol => yellow and semi-cristalline powder (Tm=120°)

Ring opening polymerisation





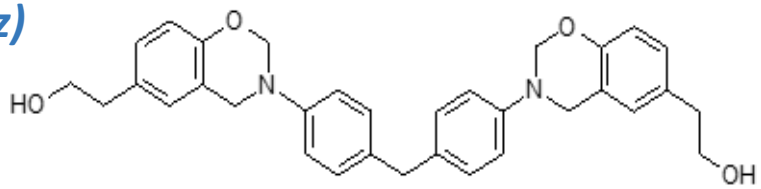




Polybenzoxazine (PBz)

Materials and methods

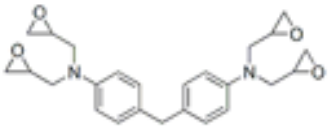
Benzoxazine (Bz)

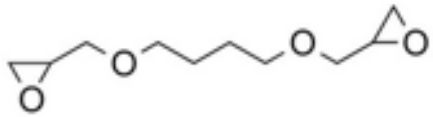


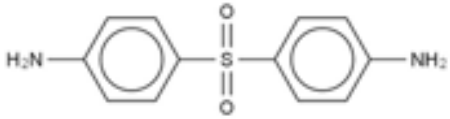
T-DDM precursors synthesized from natural phenol Tyrosol => yellow and semi-cristalline powder (Tm=120°)

Epoxy resin

1,4-Butanediol diglycidyl ether (obtained from Capot) and 4,4'-Methylenebis(N,N-diglycidylaniline) (obtained from Alfa Aesar) with 4,4'-Diaminodiphenyl sulfone (obtained from Alfa Aesar)

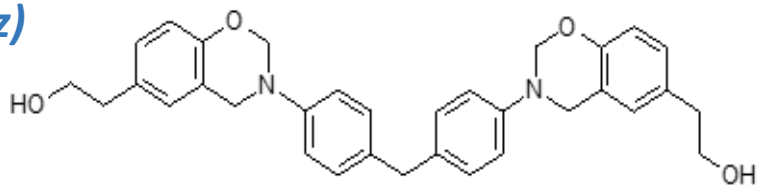






Materials and methods

Benzoxazine (Bz)



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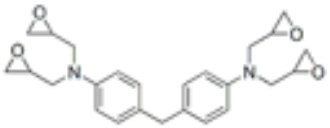

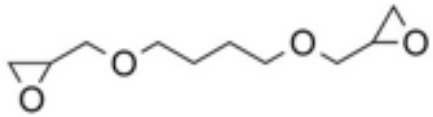

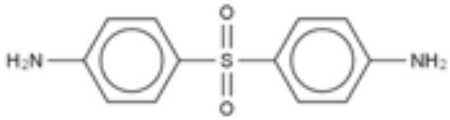

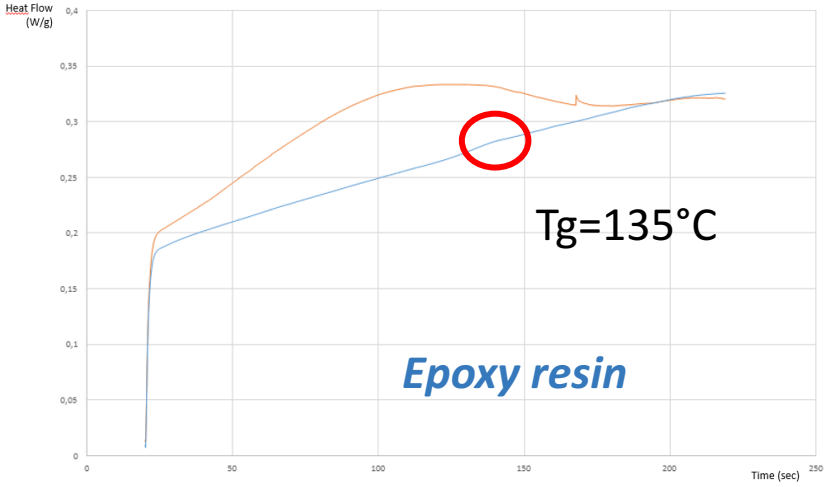

Materials and methods

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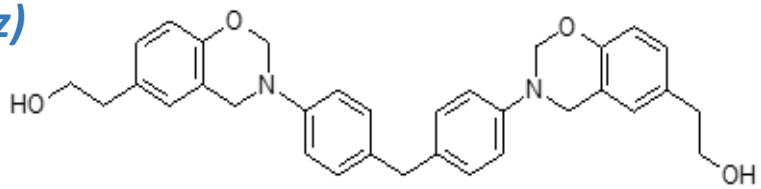

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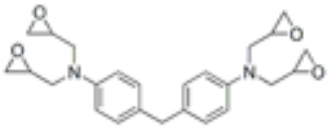
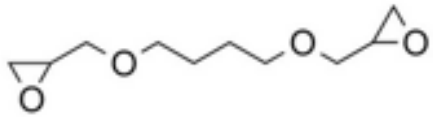
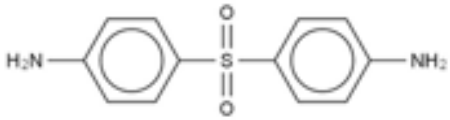
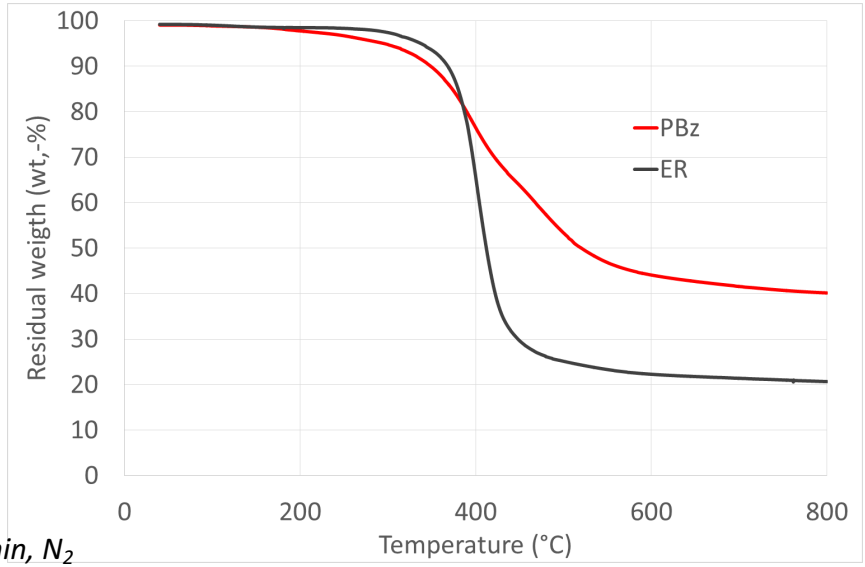
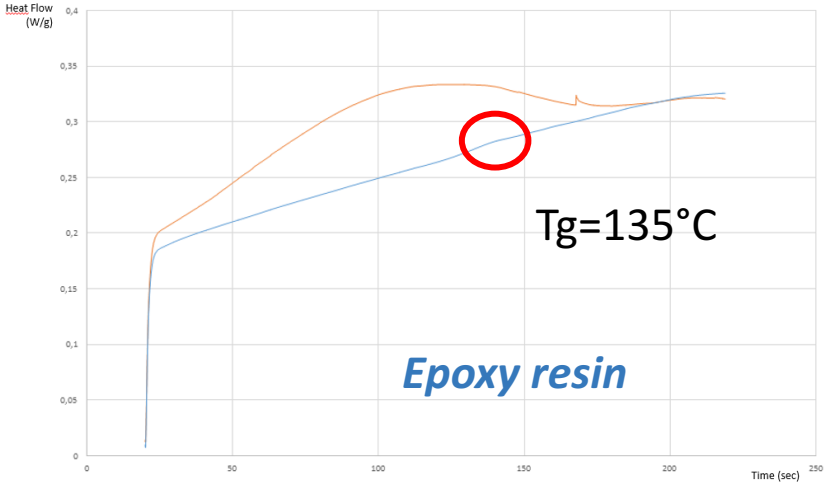




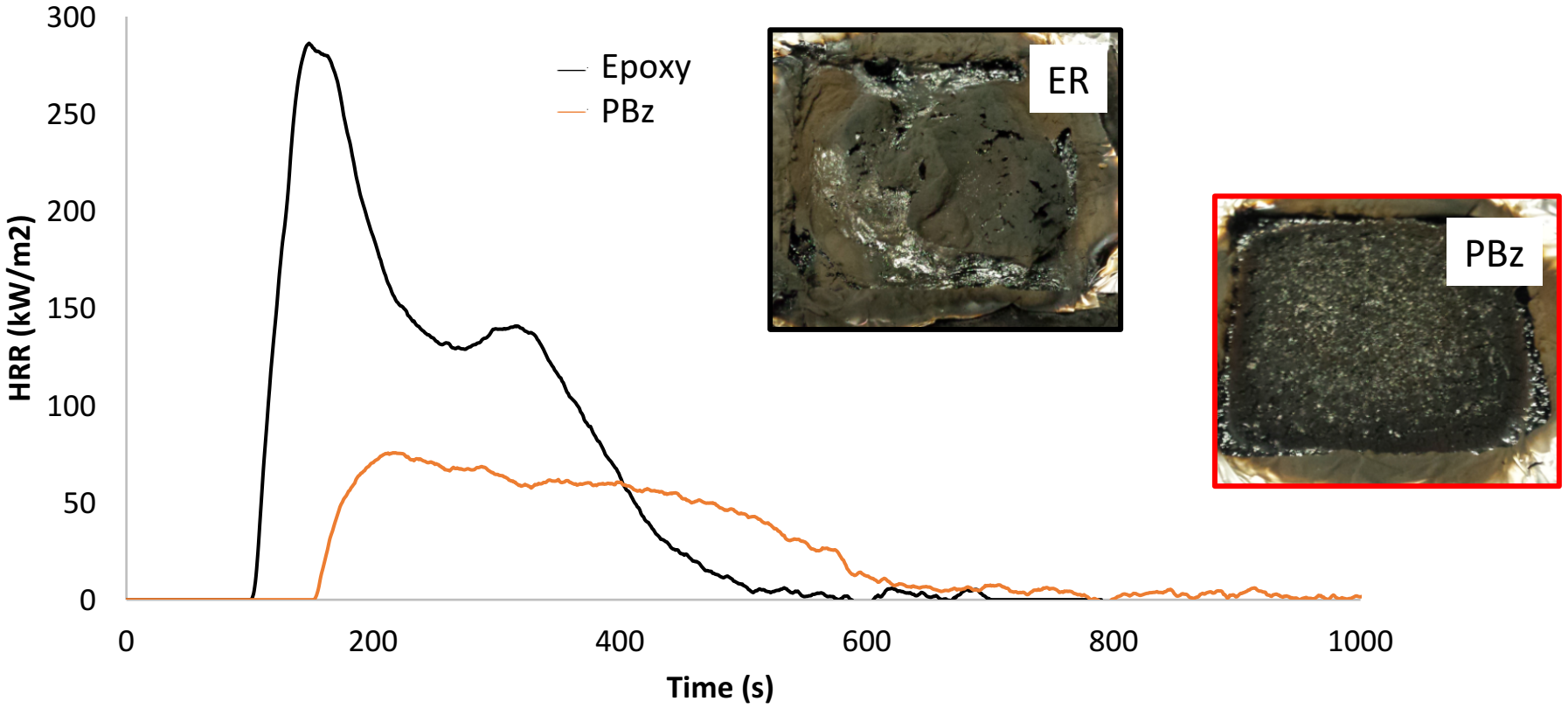




10°C/min, N_2



Fire retardant performance of pure resins

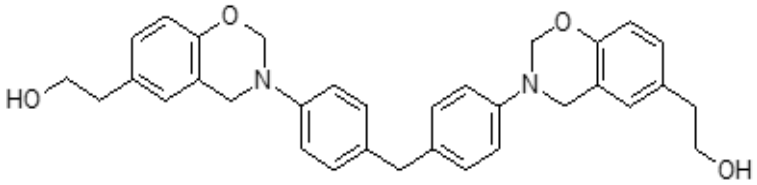


Sample		% mass after test	tign [s]	tfout [s]	t flaming [s]	pHRR [kW/m²]	% reduction pHRR	tpHRR [s]	THR [MJ/m²]	% reduction THR
Epoxy	1	27	104	469	365	286		148	49	
T-DDM	2	55	155	644	489	76	73	217	24,5	50

Better performance for polybenzoxazine

Materials and methods

Benzoxazine



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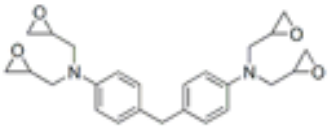
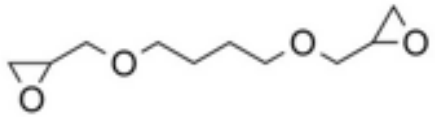
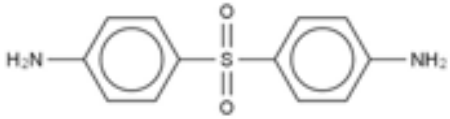
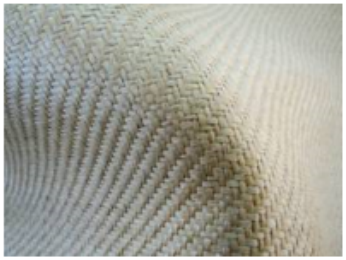
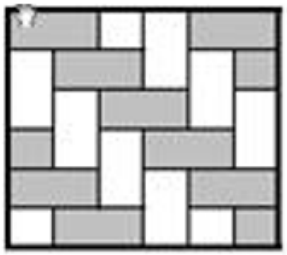




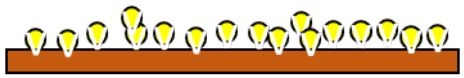


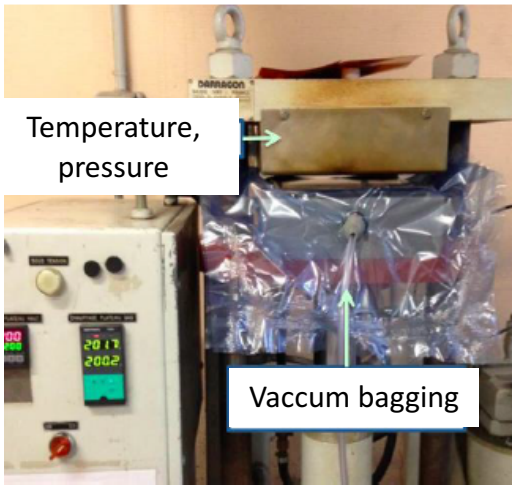
Flax fabric (twill weave, 360g/m²)



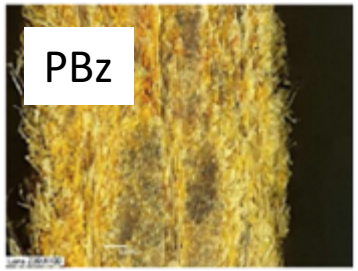


Depestele, Bourguebus, France





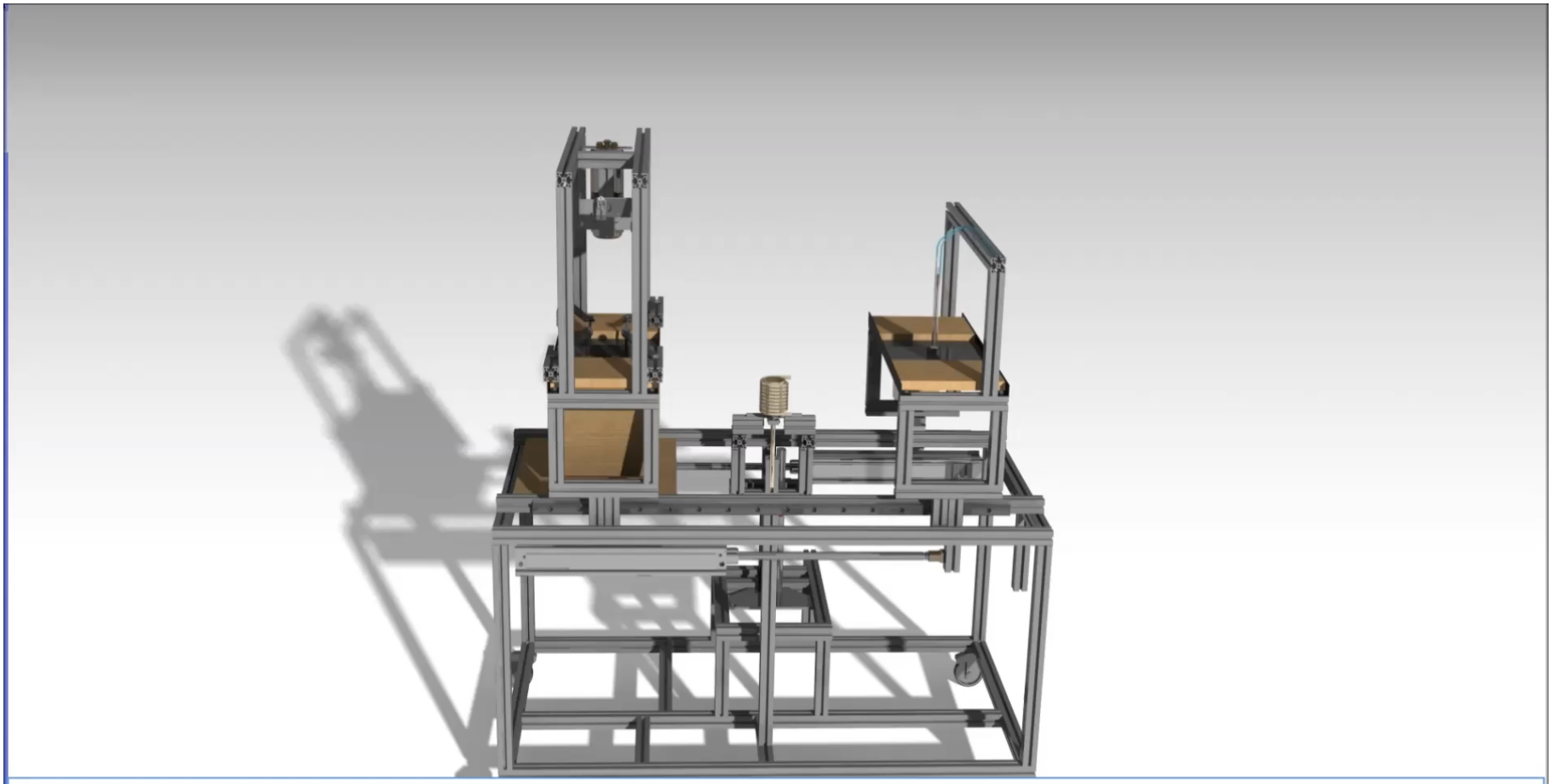
+ post-curing (180°C / 3h)



a

d

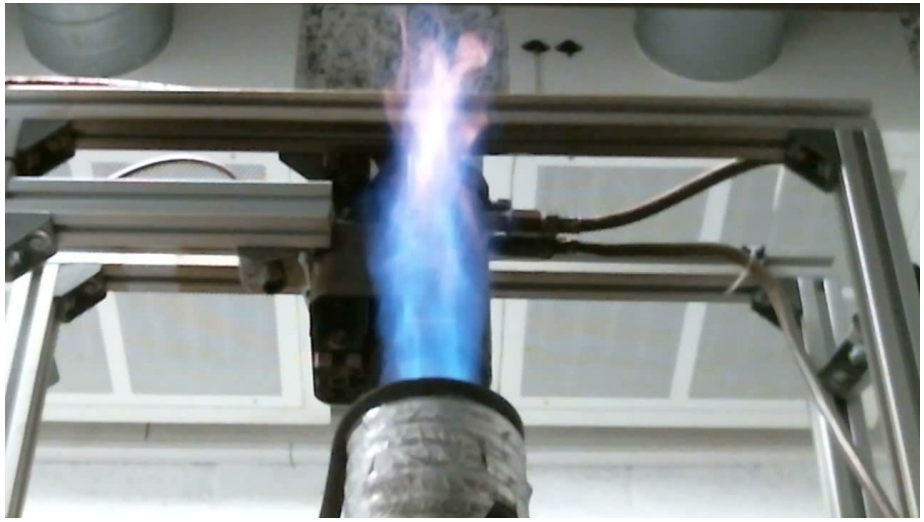
Materials and methods



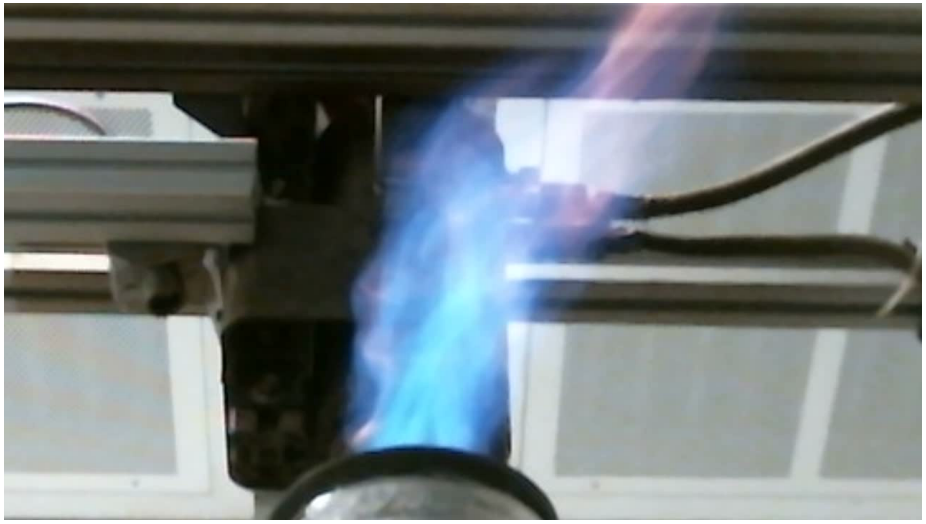
Safran Project:

Design and improvement of a test bench to fire a reduced scale

Fire performance of the composites

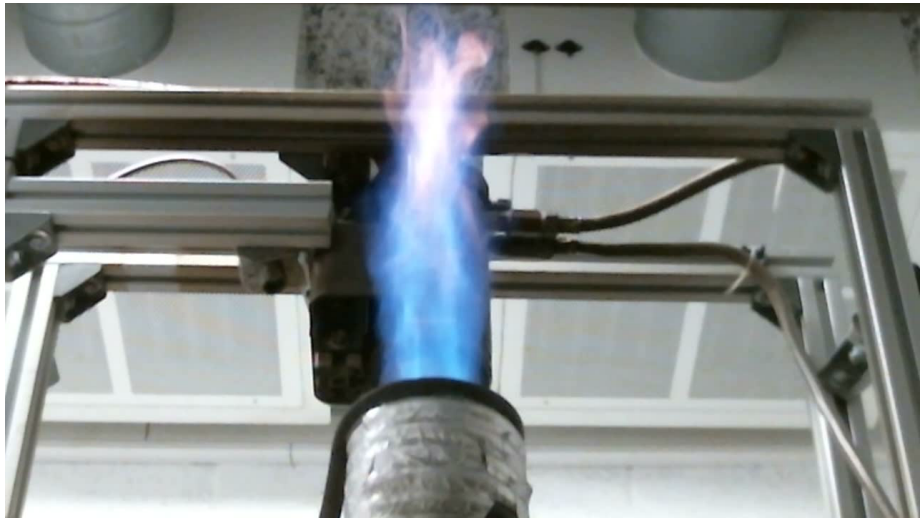


Epoxy resin



Polybenzoxazine

Fire performance of the composites



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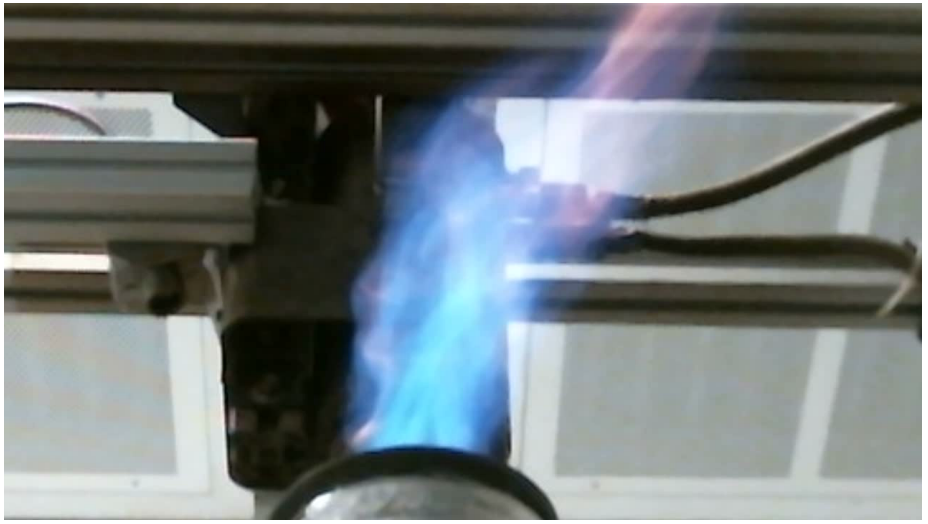


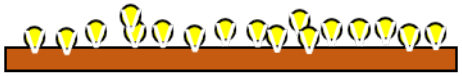
Polybenzoxazine

Material	ER-based composite	TDDM-based composite
Time of Failure	133sec	91sec

low deformability of the important char formed during PBz decomposition => cracks and failure of the test

Scheme of composite preparation

STEP 1

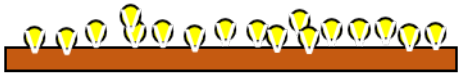


T-DDM precursor application on Carbon or Basalt fabric

- ✓ *Basalt fabric from Basaltex (Twill 2,2 – 220g/m²)*
- ✓ *Carbon fabric from Bally Ribbon Mills (plain woven fabric Twill Balanced IM7 12k)*

Scheme of composite preparation

STEP 1



T-DDM precursor application on Carbon or Basalt fabric

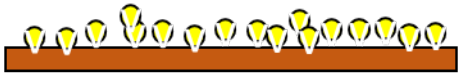
- ✓ *Basalt fabric from Basaltex (Twill 2,2 – 220g/m²)*
- ✓ *Carbon fabric from Bally Ribbon Mills (plain woven fabric Twill Balanced IM7 12k)*

STEP 2

T-DDM precursor melting (130°C), Fabric impregnation (30 min, 130°C), Thermoforming (130°C, 1 bar)

Scheme of composite preparation

STEP 1



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Stacking of composite layers

Scheme of composite preparation

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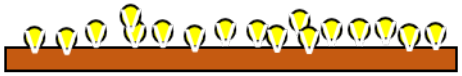

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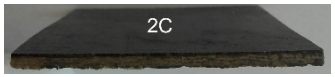
STEP 3

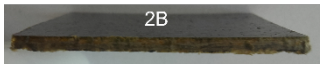
Stacking of composite layers

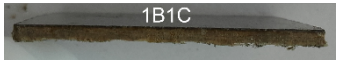
STEP 4

Thermocuring of T-DDM based pre-pregs layers (1h30 at 150°C + 20min at 180°C under 1 bar)

Fire performance of the composites

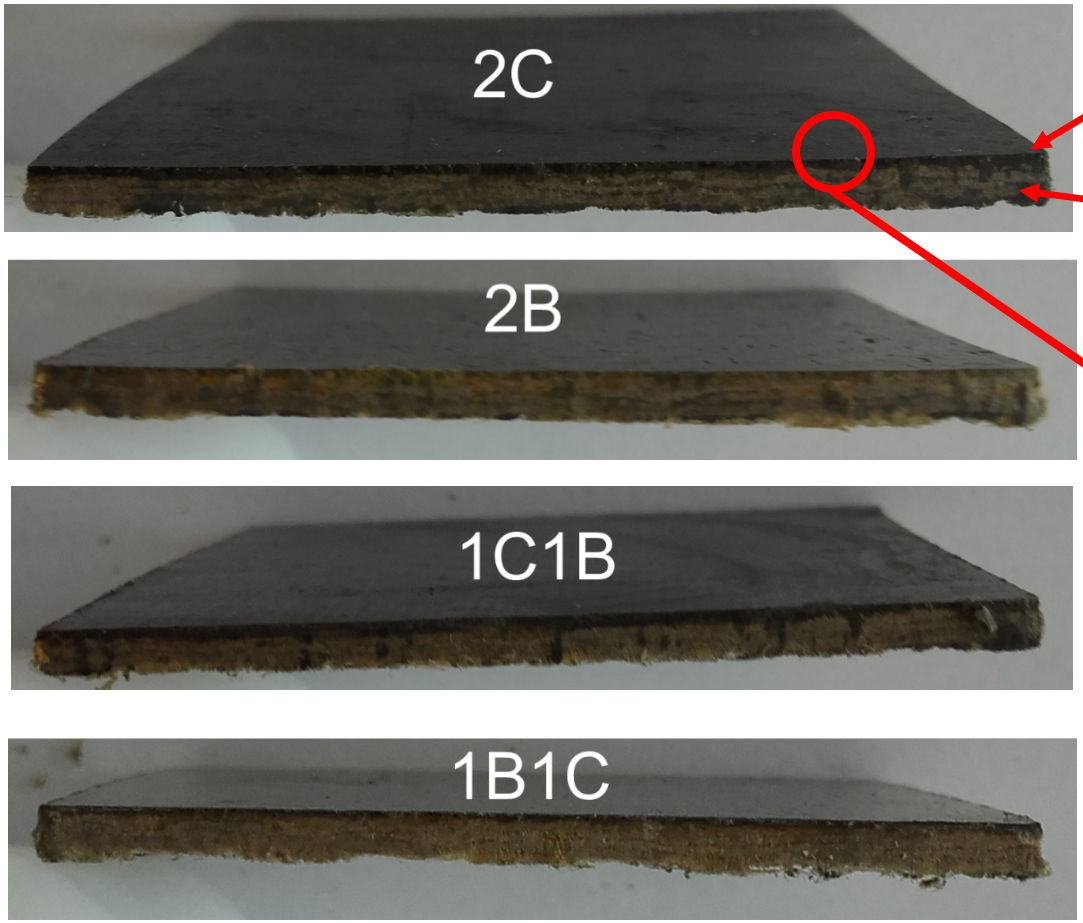






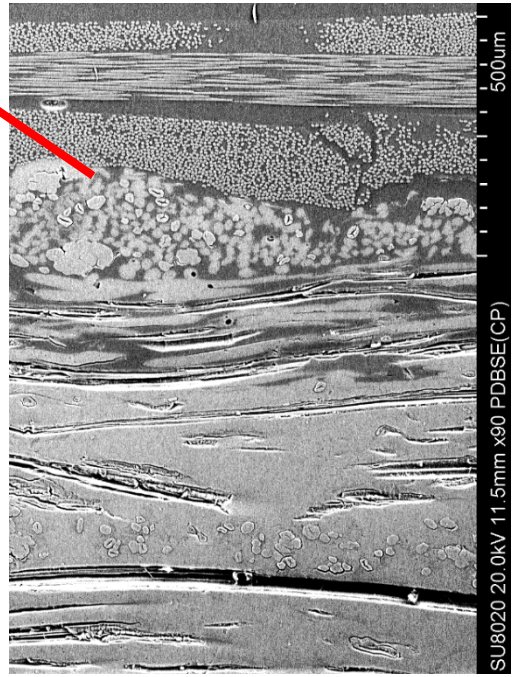
	2C	2B	1C1B	1B1C
Layer 1/ Layer 2	T-DDM+Carbon / T-DDM+Carbon	T-DDM+Basalt / T-DDM+Basalt	T-DDM+Carbon / T-DDM+Basalt	T-DDM+Basalt / T-DDM+Carbon
Thickness of the composite (mm)	2.11±0.08	2.07±0.01	2.02±0.03	2.07±0.03
Thickness of protective layers (µm)	300±71	245±49	335±21	310±57

Morphology of the composites



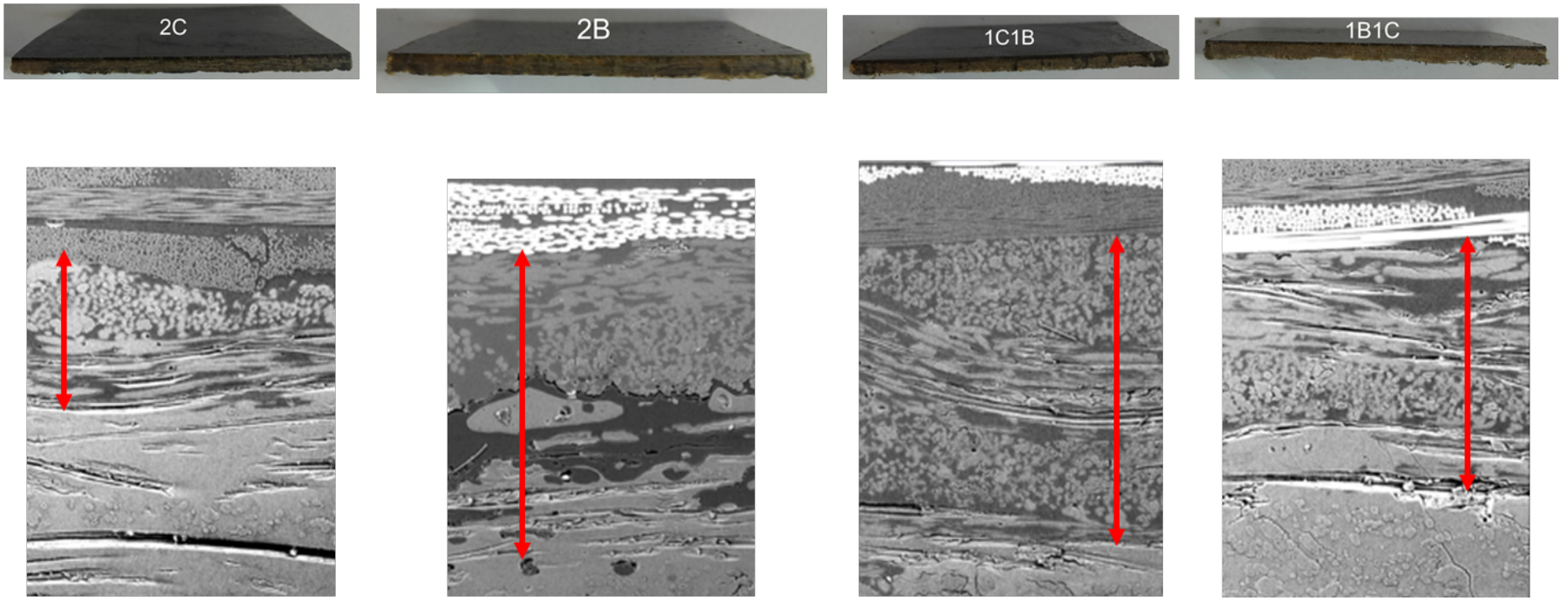
Protective structure
PBZ + Carbon

PLA / Flax composites



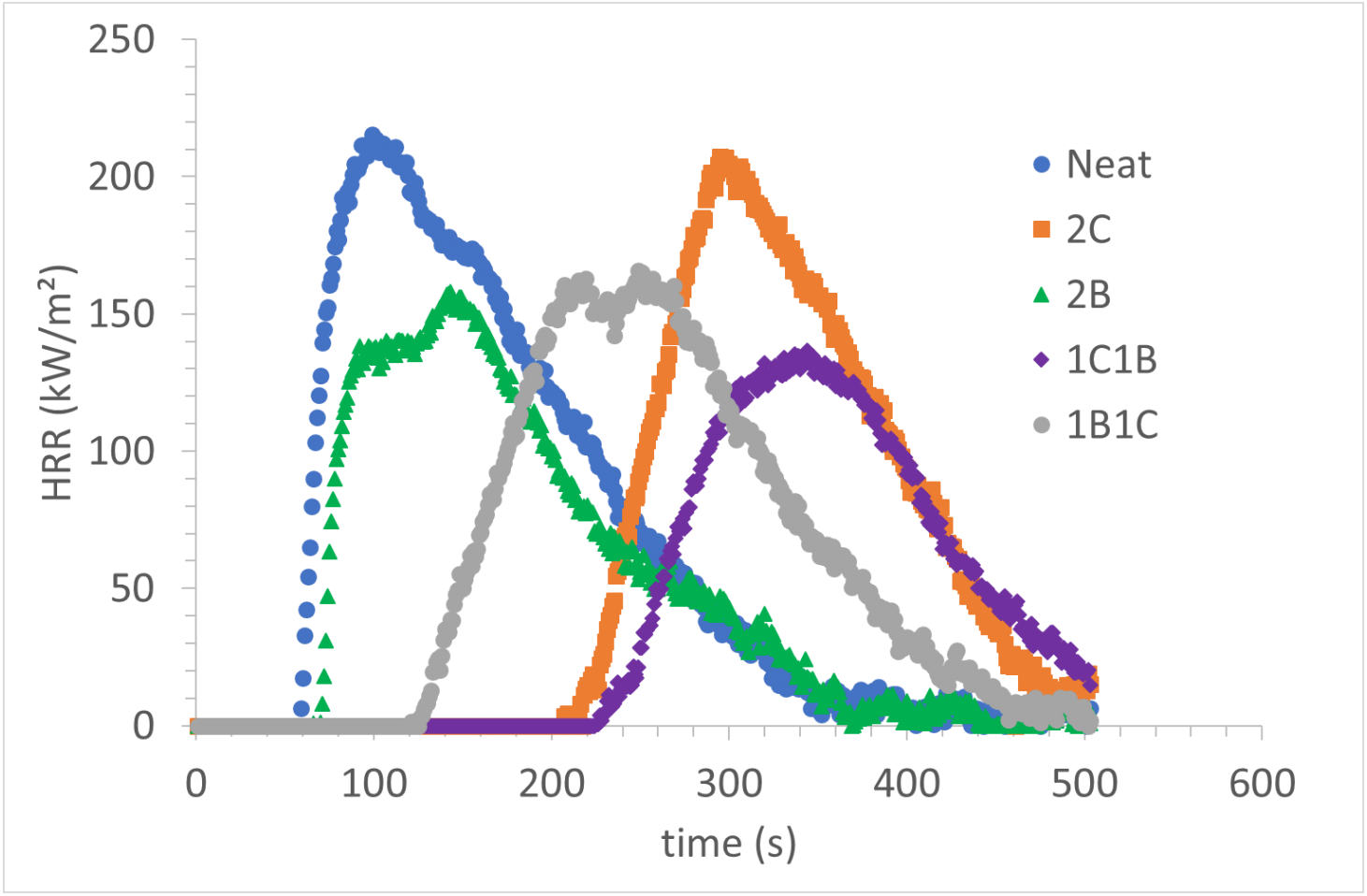
What about interface?

Morphology of the composites



Formation of a large interphase (0.5-1mm) upon curing
=> Strong adhesion of T-DDM layers to PLA/flax composite

Fire retardancy of the composites



Heat source, 35kW/m²

The performance varies depending on the composition of the protective layer

Fire retardancy of the composites

Composite	$t_{ignition}$ (s)	$t_{flame\ out}$ (s)	time of flaming (s)	pHRR (kW/m²)	time to pHRR (s)	THR (MJ/m²)	Residue after the test (%)
Neat	54±4	262±37	209±37	213±22	116±26	30±2	10±9
2C	247±43	518±55	271±39	182±27	334±35	28±2	41±9
2B	**75±6**	365±39	290±41	164±37	139±37	26±2	46±3
1C1B	201±67	420±96	218±40	180±39	280±77	23±3	48±5
1B1C	144±24	426±37	281±25	182±29	244±24	25±3	45±3

Benzoxazine based pre-pregs can improve significantly the FR properties of PLA/flax composites

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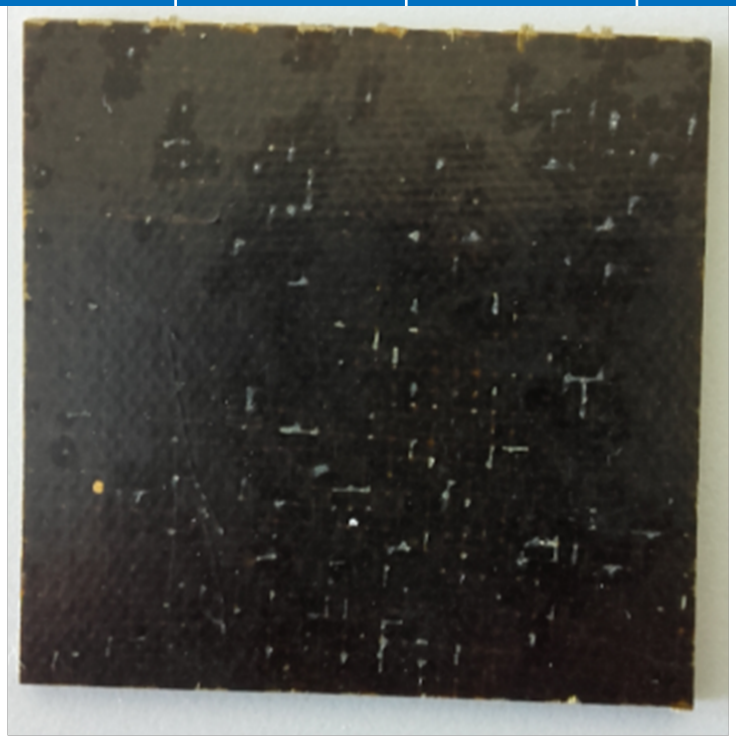
1B1C	144±24						

Benzoxazine I



Presence of PLA on the surface of the composite 2B

Fire retardancy of the composites

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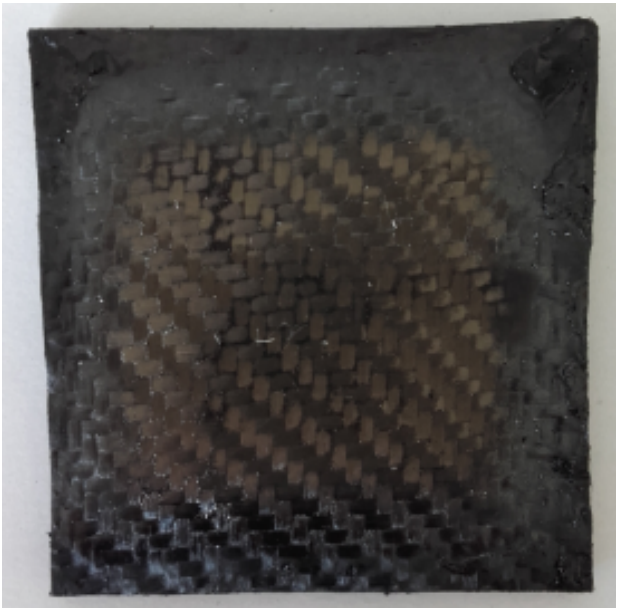
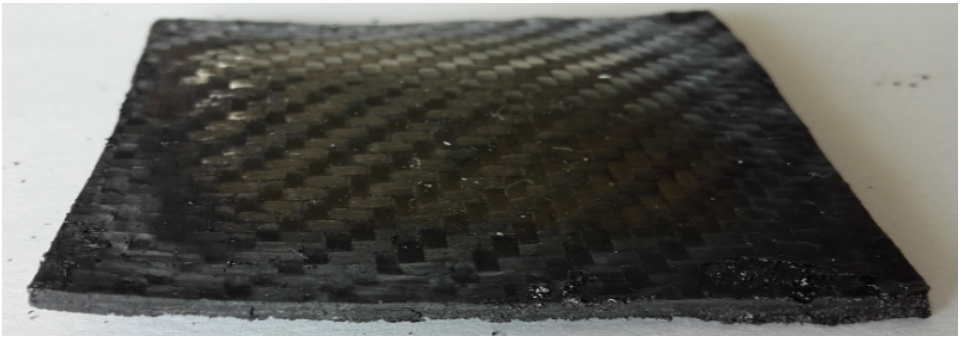
Residue of PLA/flax composite

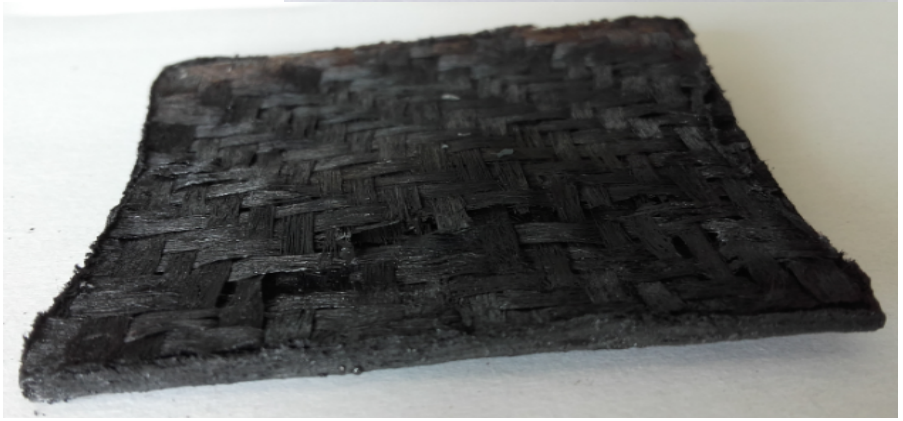
Residue composite 1C1B



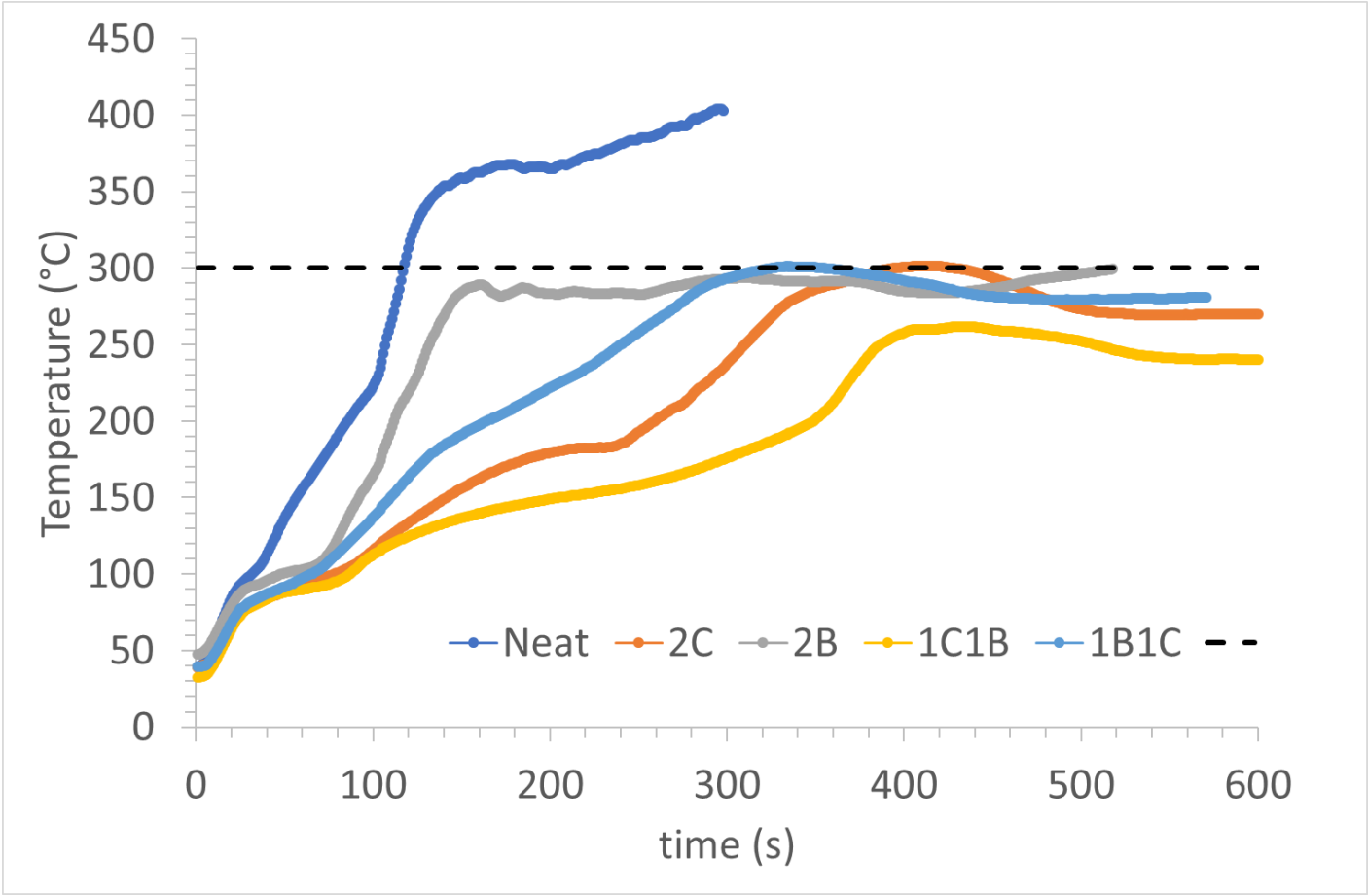
Benzo side



PLA side



Evolution of the temperature on PLA/flax side during the test



Conclusion

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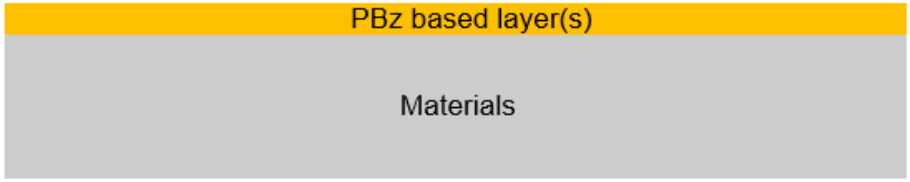
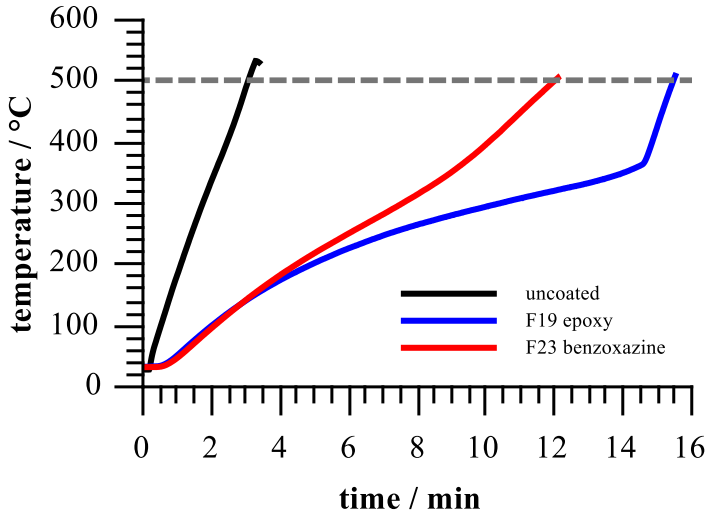
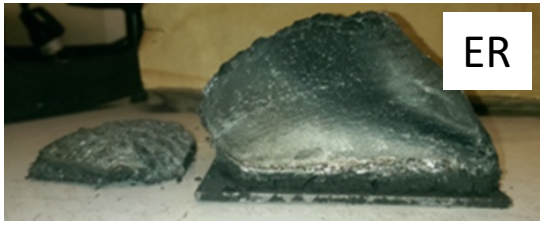


- ✓ What about intumescent and PBz?





Acknowledgments

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UNION EUROPÉENNE
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