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Alès

BIOCOMPOSITES IGNIFUGÉS POUR LA FABRICATION ADDITIVE

Valentin CARRETIER¹

Supervisors :

José-Marie Lopez-Cuesta¹

Monica Francesca Pucci²

Arnaud Regazzi²

Jean-Christophe Quantin¹

Clément Lacoste¹

¹ Polymers Composites and Hybrids (PCH), IMT Mines Ales, Ales, France

² LMGC, IMT Mines Ales, Montpellier University, CNRS, Ales, France

CONTENTS

1. **BIOBASED POLYMER MATRIX FOR 3D-PRINTING [CASE OF PLA]**
2. **BIOBASED FLAME RETARDANTS [CASE OF LIGNIN]**
3. **DESIGN OF NEW BIOCOMPOSITES FOR THE 3D-PRINTING**
4. **PROMISING RESULTS**
5. **CONCLUSION**



BIOBASED POLYMER MATRIX FOR 3D-PRINTING [CASE OF PLA]



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Biobased polymer matrix for 3D-printing

► Case of Polylactide (PLA) : A promising biobased polymer

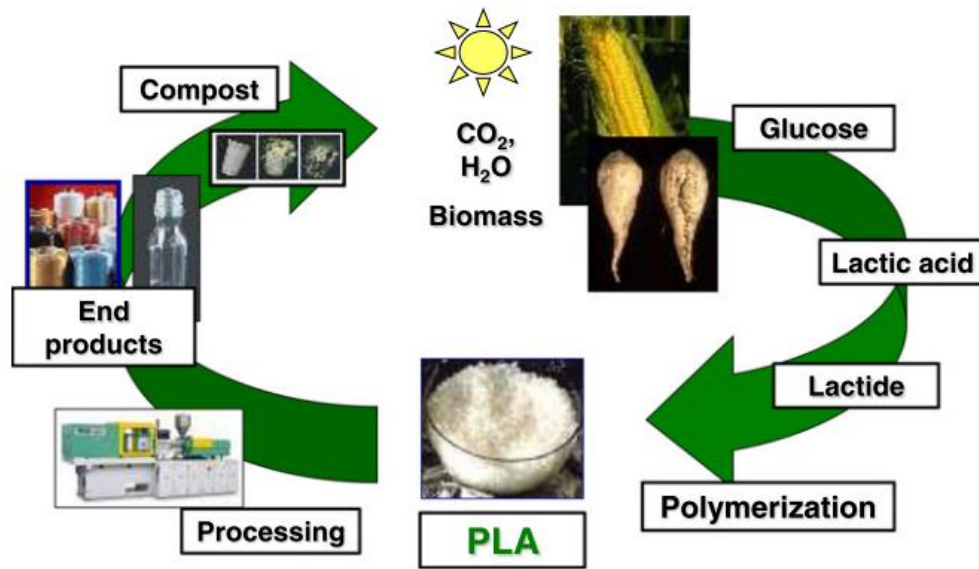


Fig. 1 : Poly(lactide acid) life cycle [1]

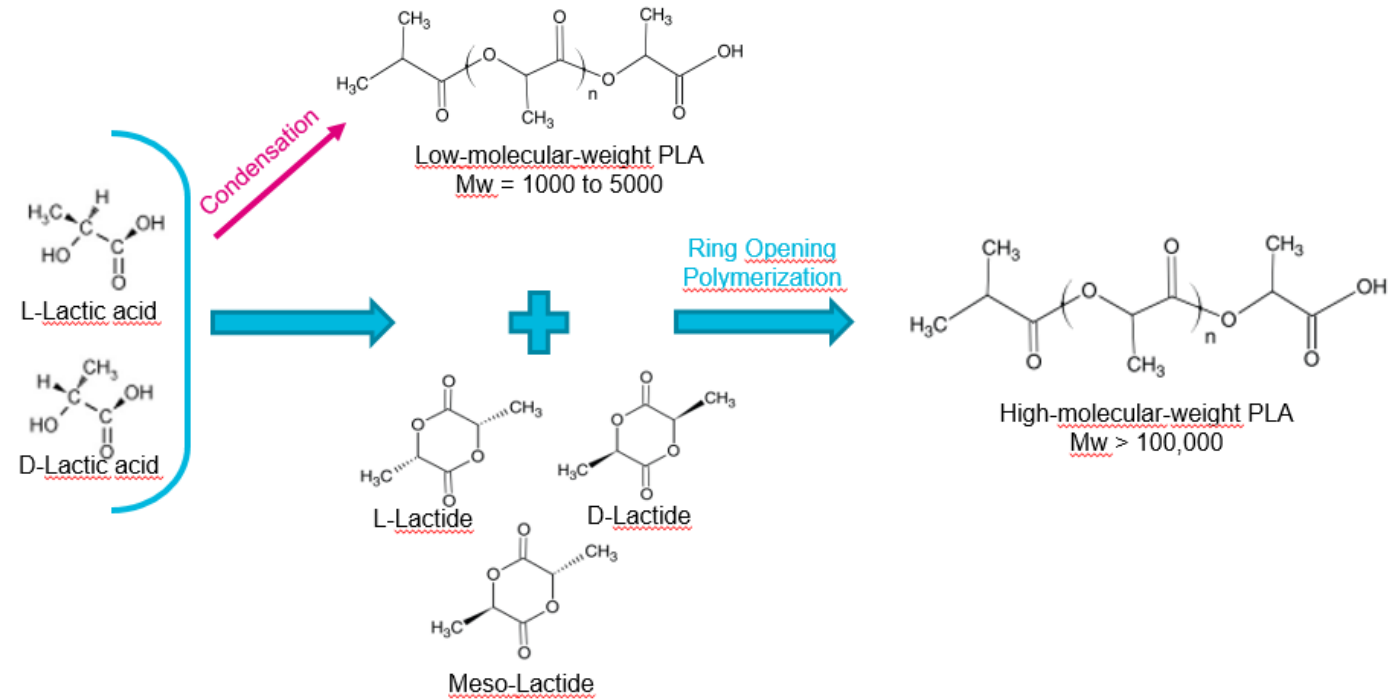


Fig. 2 : Simplified process to obtain PLA (adapted from [1])

From Biomass (biobased): Corn, sugar-beet
Biocompatible, nontoxic
Compostable, Recyclable

Global production of biopolymers in 2018/2019 :
37 Mt (270,000 t for PLA) [2]

Biobased polymer matrix for 3D-printing

- ▶ Case of Polylactide (PLA) : General properties and the use in 3D printing

General properties [3]

Density : 1.25 g/cm³
Surface Energy : 40 mJ/m²

Mechanical properties

Breaking stress: 50-60 MPa
Yield stress: 60-70 MPa
Elongation at break: 5-10 %
Elastic Modulus: 3200-3800 MPa

Thermal properties

Glass transition temperature: 50-60°C
Melt temperature: 160-200°C
Temperature On-set : 300°C

Use of PLA in 3D-printing

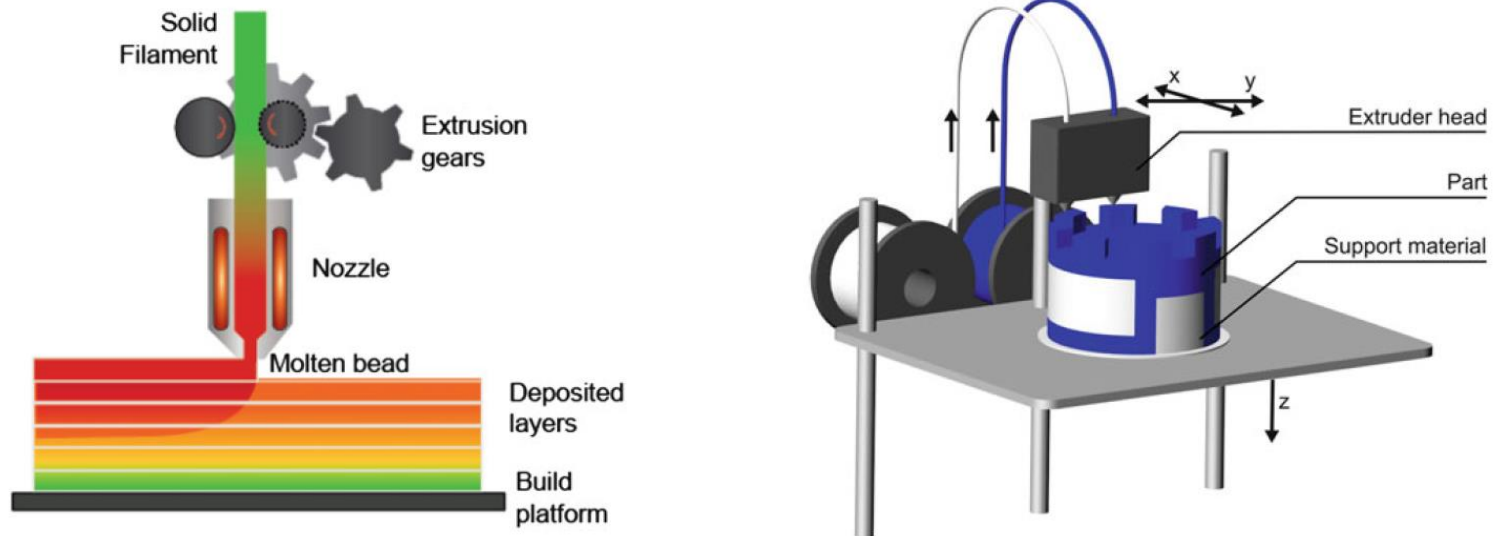


Fig. 3 : Fused Deposit Manufacturing (FDM) process [4]

Why PLA in additive manufacturing ?

- Bio-based
- Low melting temperature (nozzle temperature (190-220°C))
- Low volatile emissions
- Used for medical and bio-medical printing

BIOBASED FLAME RETARDANTS [CASE OF LIGNIN]



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Biobased flame retardants

► Case of Lignin (LG) : From paper industry to polymer industry

Biobased aromatic polymer

By-product of paper industry

Major components of trees and plants

Worldwide annual production 50 millions of tonnes / year [5]

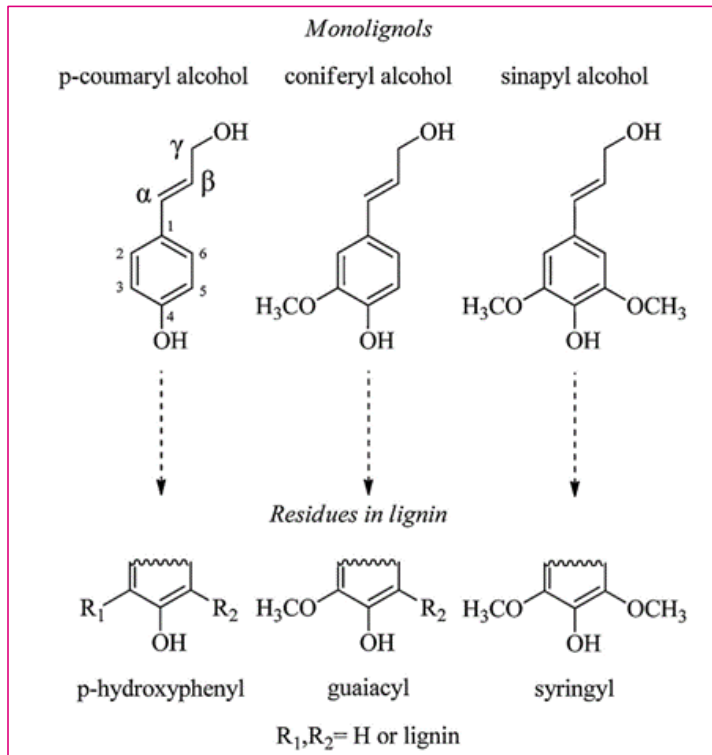


Fig. 4 : Principals lignin precursors (monolignols) and their structures in lignin macro-molecule [6]

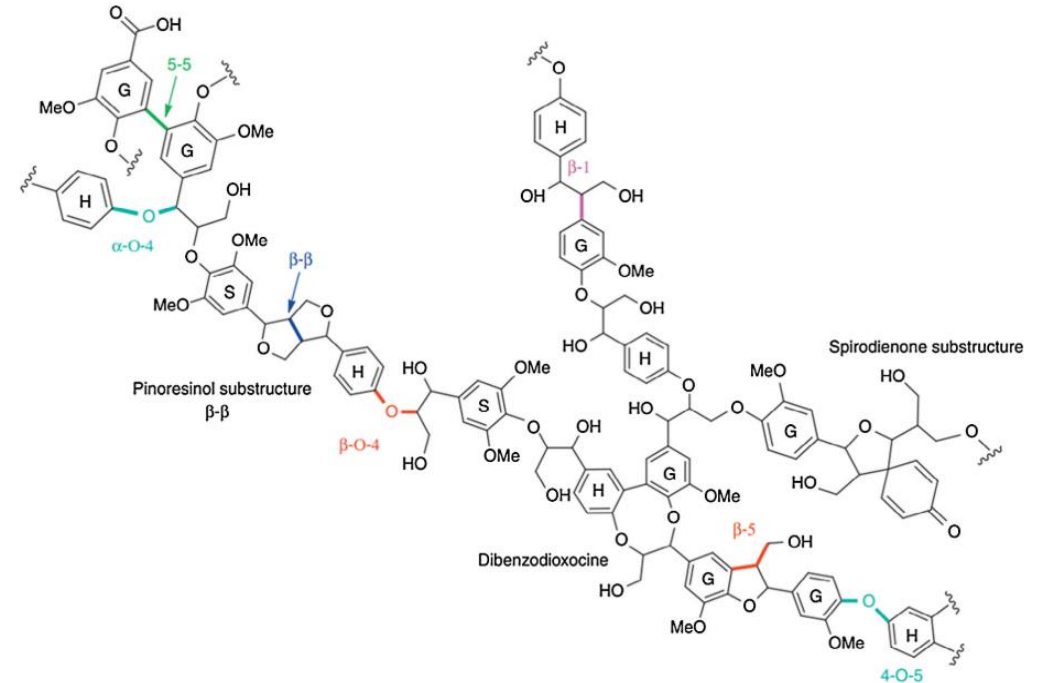


Fig. 5 : Exemple of lignin molecule [7]

For different extraction processes and different tree species [8]

- Different **molecular weight**
- Different aliphatic hydroxide, phenolic, carboxilate and sulfonate groups **concentration**
- Different solubility, reactivity

Biobased flame retardants

► Case of Lignin (LG) : General properties and applications

Few interesting properties in polymer blends :

- UV-Blocker
- **Charring agent**
- Mechanical reinforcement

Many lignin chemical modification possibilities

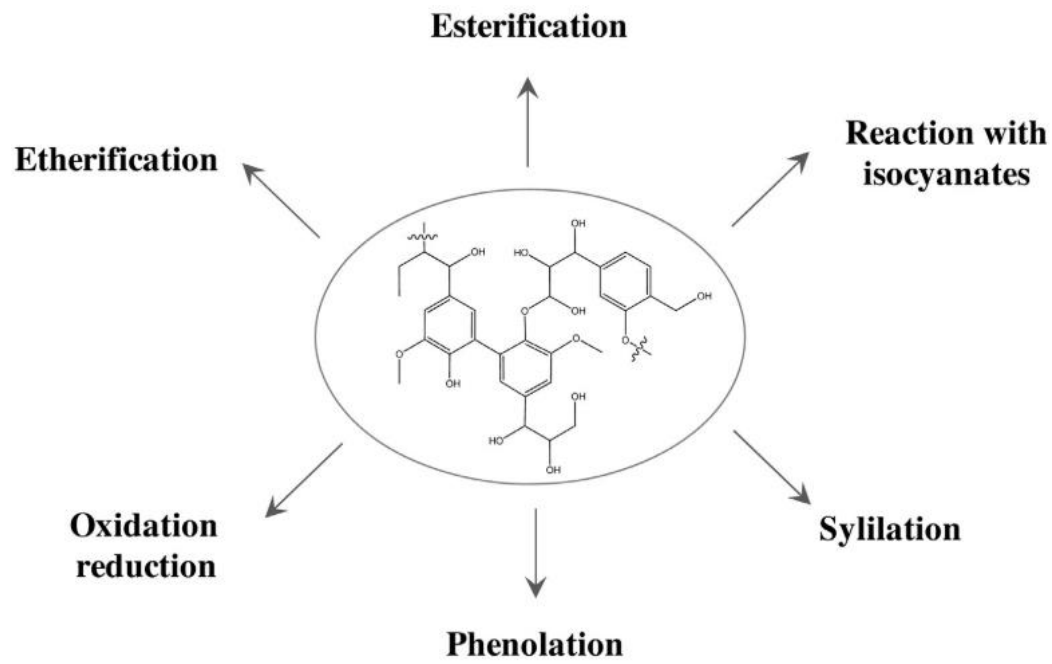


Fig. 6 : Chemical fonctionnalization of lignin hydroxyl groups [6]

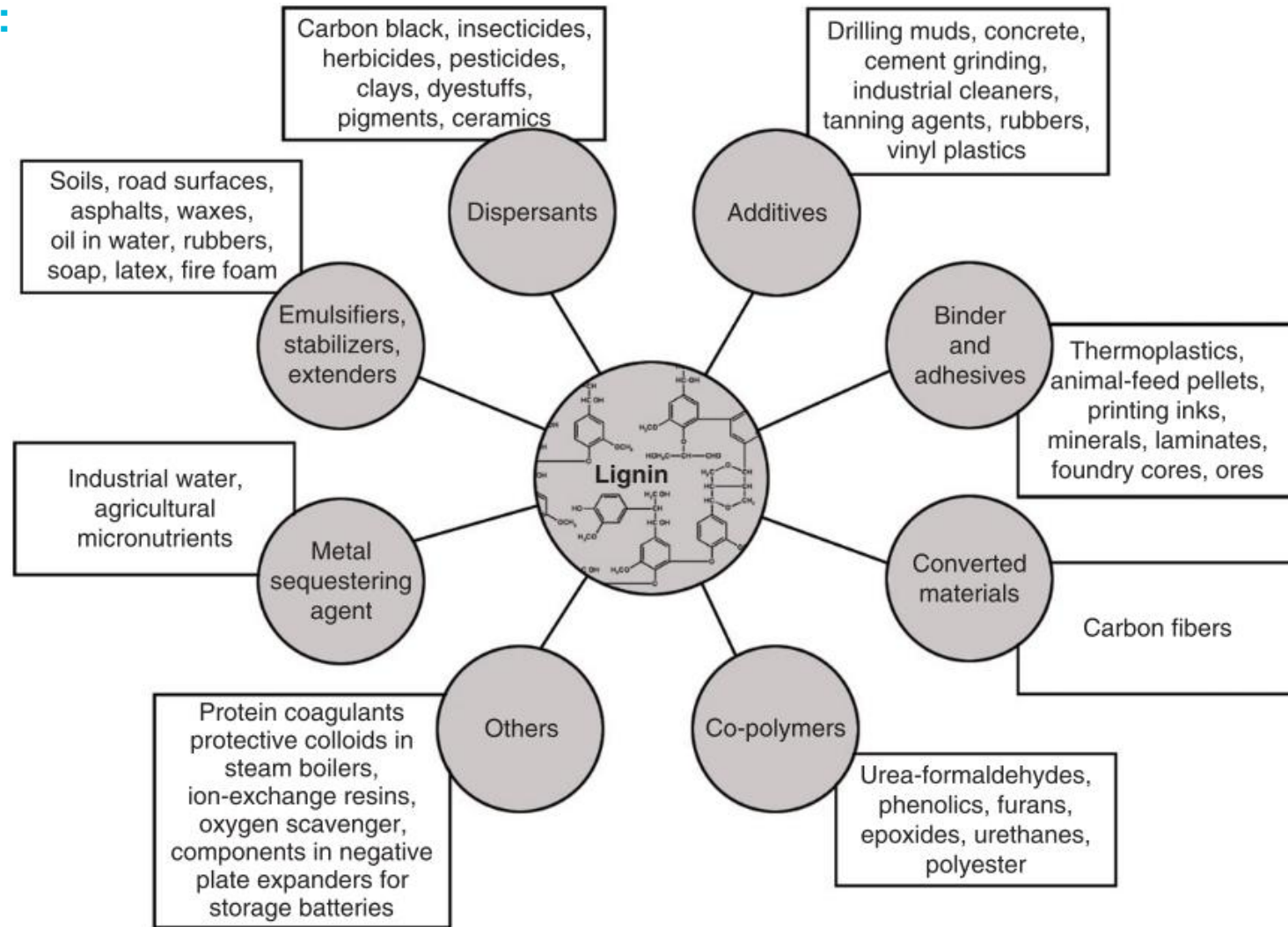


Fig. 7 : Various lignin application [9]

DESIGN OF NEW BIOCOMPOSITES FOR THE 3D-PRINTING



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- ▶ Selection of materials

Objectives :

- Improve flame retardant properties
- Use major **biobased materials**

Materials :

- **PLA** Ingeo 3251D (NatureWorks, Injection Grade)
- **APP** : Ammonium Polyphosphate (Clariant, AP423)
- **LG** : Kraft Lignin (TCI)

Biocomposites

Polymer
matrix

Intumescent Fire
retardant system

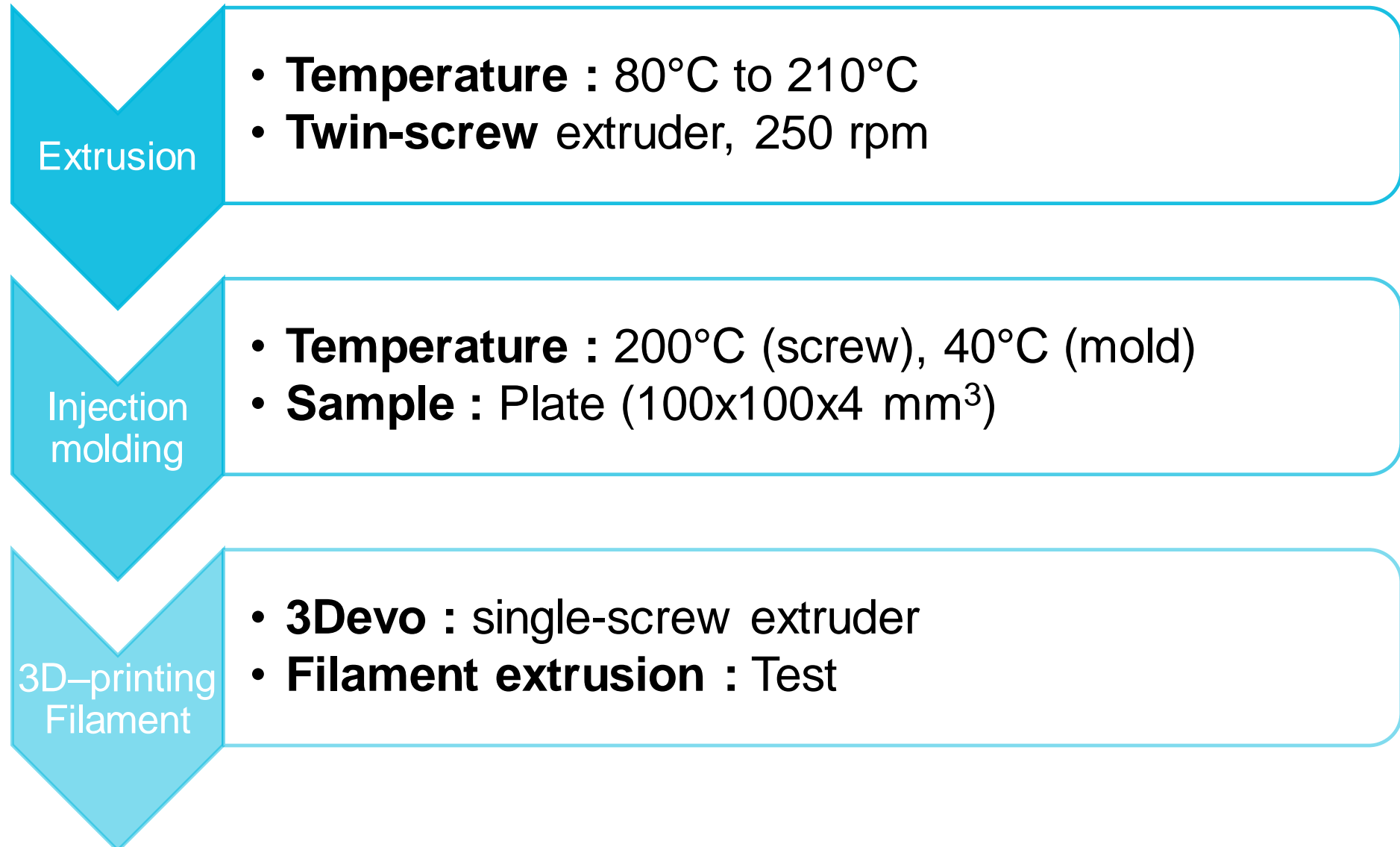
PLA

APP

Lignin

Design of new biocomposites for the 3D-printing

► Processes



► Fire behavior Characterization

Thermogravimetric analysis

- Atmosphere : N_2
- Temperature range : 30 to 900 °C
- Temperature variation : +10°C/min

Properties :

- Mass loss in relation with temperature
- Residue mass
- Temperature On-set

Cone calorimeter test

- Position : Horizontal
- Irradiance : 50 kW/m²
- Distance between sample and cone : 25 mm

Properties :

- Time To Ignition (TTI)
- Peak of Heat Release Rate (pHRR)
- Total Heat Release (THR)

PROMISING RESULTS



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Promising results

- ▶ The use of well-know flame-retardant

Polymer : PLA

Flame-retardant : APP

PLA 0 : Neat PLA

PLA 1 : PLA/APP (80w%/20w%)

TGA	T _{ON-SET} (°C)	T Max (°C)
APP	344	363
PLA 0	338	367
PLA 1	326	355

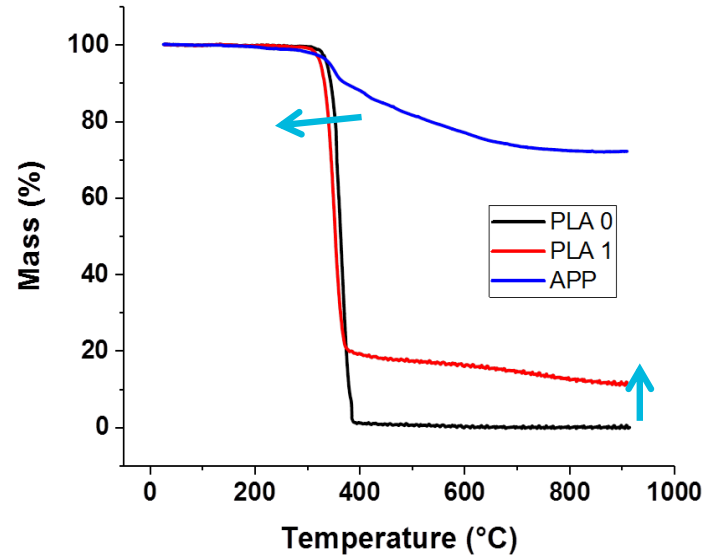


Fig. 8 : TGA results for PLA0 and PLA1

TGA :

- T_{on-set} shift due to APP degradation
- Residue for PLA1

Cone calorimetry	TTi (s)	pHRR (kW/m ²)	THR (MJ/m ²)
PLA0	33	516	108
PLA1	49	87	

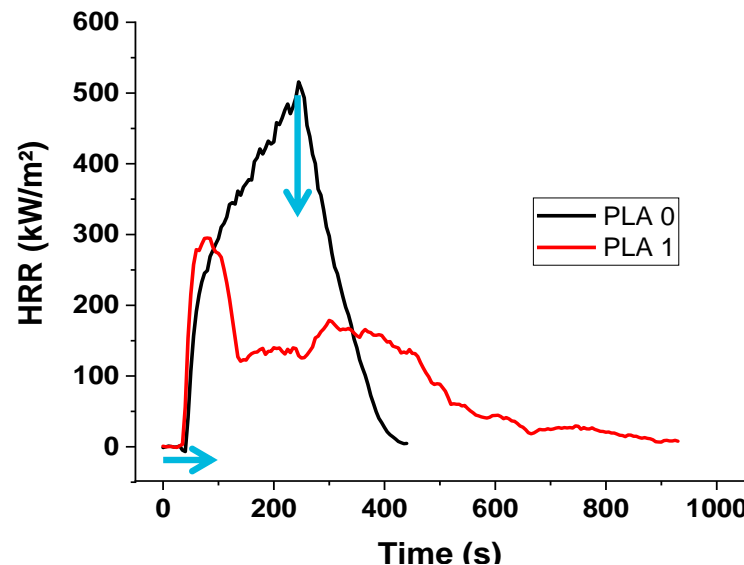


Fig. 9 : Cone calorimetry results for PLA0 and PLA1

Cone calorimetry test :

- Ignition delayed
- pHRR well decreased
- Better THR

Promising results

- ▶ The use of an intumescent fire-retardant system (IFRS)

Polymer : PLA

Flame-retardant : APP + Lignin

PLA 0 : Neat PLA

PLA 1 : PLA/APP (80w%/20w%)

PLA 5 : PLA/APP/LG (80w%/17w%/3w%)

PLA 6 : PLA/APP/LG (80w%/15w%/5w%)

PLA 7 : PLA/APP/LG (80w%/12w%/8w%)

	T _{ON-SET} (°C)	T Max (°C)
PLA0	338	367
PLA1	326	355
PLA5	326	355
PLA6	319	351
PLA7	319	351

TGA:

- T_{on-set} shift due to APP
- **Non significant** impact of lignin on residue mass

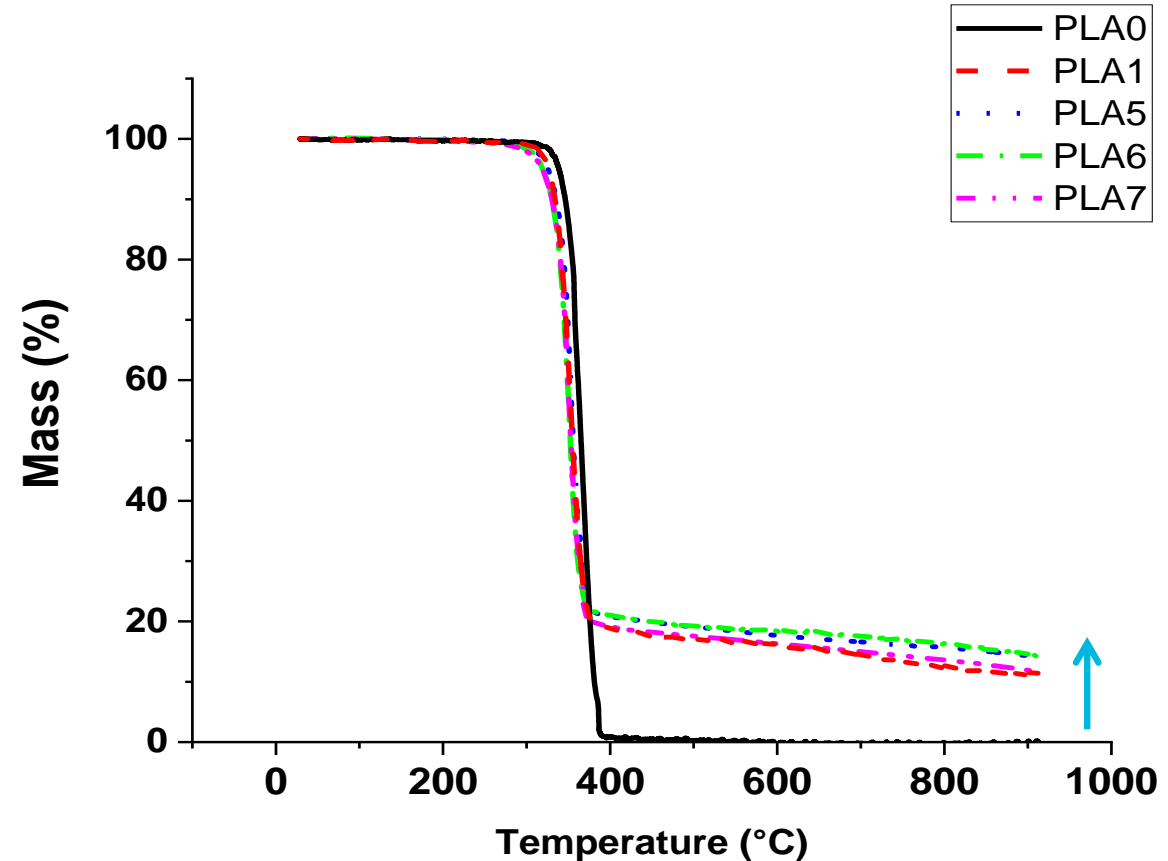


Fig. 10 : TGA results for PLA0/1/5/6/7

Promising results

► The use of an intumescent fire-retardant system (IFRS)

Polymer : PLA

Flame-retardant : APP + Lignin

PLA 0 : Neat PLA

PLA 1 : PLA/APP (80w%/20w%)

PLA 5 : PLA/APP/LG (80w%/17w%/3w%)

PLA 6 : PLA/APP/LG (80w%/15w%/5w%)

PLA 7 : PLA/APP/LG (80w%/12w%/8w%)

	TTi (s)	pHRR (kW/m ²)	THR (MJ/m ²)
PLA0	33	516	108
PLA1	49	295	87
PLA5	29	180	56
PLA6	26	229	62
PLA7	23	312	82

Cone calorimetry :

- Ignition **delayed** (earlier)
- pHRR well **reduced**
- Ratio **optimum** for APP/lignin (17/3)

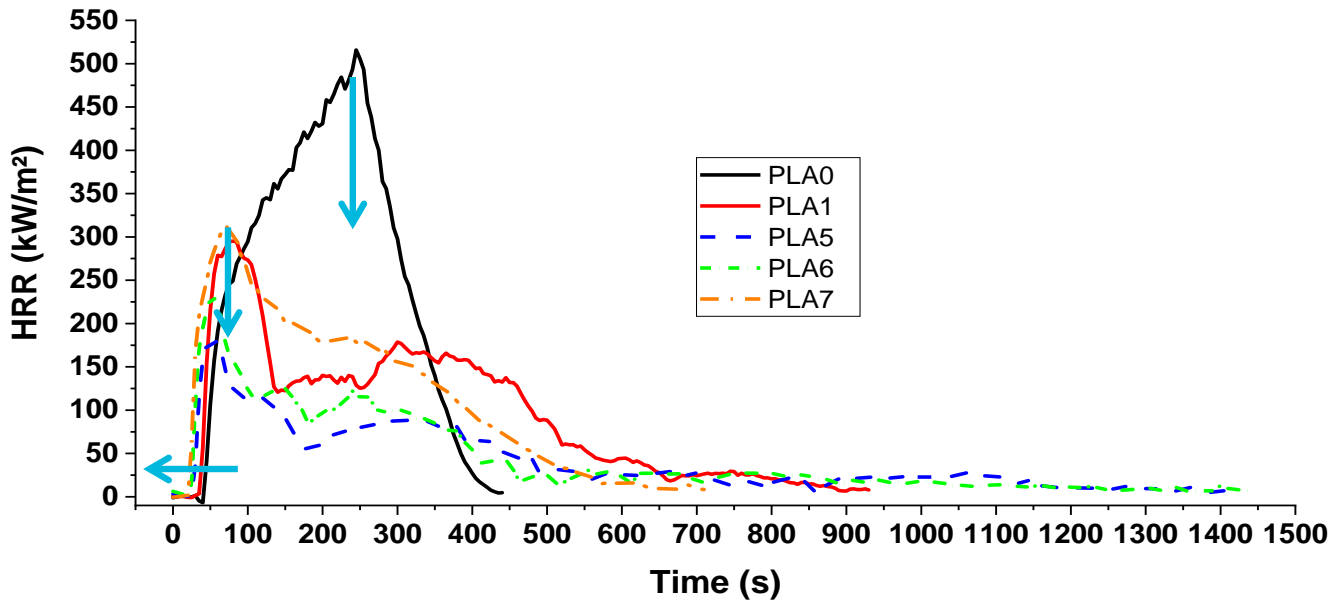


Fig. 11 : Cone calorimetry results for PLA0/1/5/6/7



Fig. 12 : Cone calorimetry residue (PLA1 and PLA5)

CONCLUSION



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PLA

- **Biobased, Biocompatible**, compostable
- Properties in adequation with **additive manufacturing**

Lignin

- **Biobased** biopolymer, paper industry by-product
- **Chemical modification** possibilities, large scale of used

What's next ?

- Lignin chemical modification to enhance fire properties
- Have a better understand of the effect of the lignin inside the polymer matrix
- Test new formulations
- Compared the effect of the 3D-printing with injection molding on the mechanical and fire properties

Process

- **Long processes** for 3D-printing composites obtention

Results

- APP + lignin = Flame-retardant Intumescent system
- **Best APP/lignin ratio: PLA5**
- **pHRR decreased by 3**

3D-printing test

- Filament preparation **possible** for PLA5 and PLA6
- Other compounds formalution are under tests

THANK YOU FOR YOUR ATTENTION

Financial Supporting :



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1 Polymers Composites and Hybrids (PCH), IMT Mines Ales, Ales, France
2 LMGCC, IMT Mines Ales, Montpellier University, CNRS, Ales, France