



IMT Mines Alès  
École Mines-Télécom



La Région  
Occitanie  
Pyrénées - Méditerranée

Journées scientifiques et techniques – Fabrication Additive  
des Composites – 14-15 Octobre 2020



École Doctorale  
Sciences Chimiques Balard

# FUSED FILAMENT FABRICATION OF NEW FIRE-RETARDED BIOCOMPOSITES

Valentin CARRETIER<sup>1</sup>

Supervisors:

José-Marie Lopez-Cuesta<sup>1</sup>

Monica Francesca Pucci<sup>2</sup>

Arnaud Regazzi<sup>2</sup>

Jean-Christophe Quantin<sup>2</sup>

Clément Lacoste<sup>1</sup>

<sup>1</sup> Polymers Composites and Hybrids (PCH), IMT Mines Ales, Ales, France  
<sup>2</sup> LMGC, IMT Mines Ales, Montpellier University, CNRS, Ales, France

# CONTENTS

1. CONTEXT
2. PLA AND FIRE RETARDANCY
3. METHODS
4. RESULTS AND DISCUSSION
5. CONCLUSION



**IMT Mines Alès**  
École Mines-Télécom

# CONTEXT



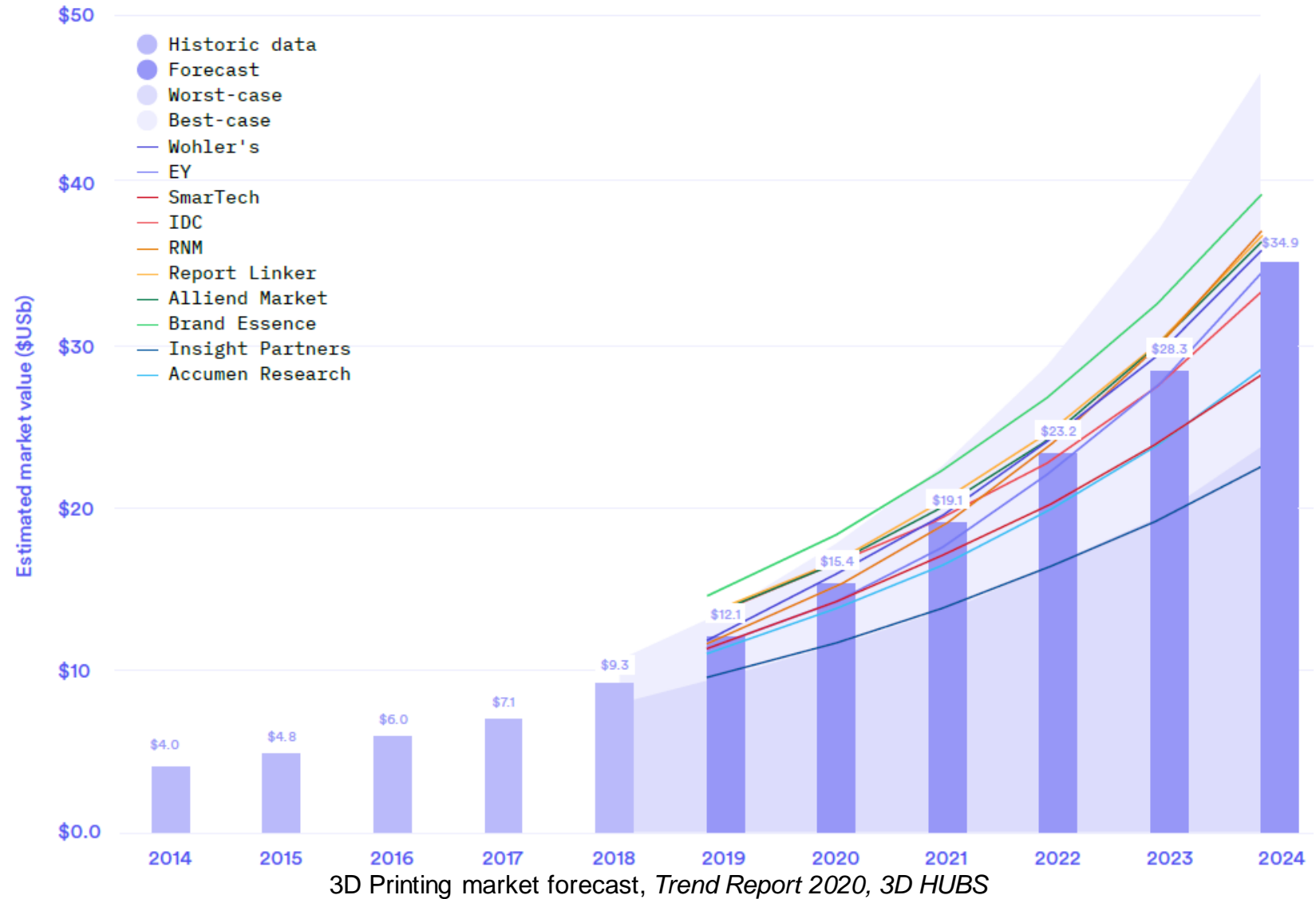
**IMT Mines Alès**  
École Mines-Télécom

# CONTEXT

## ► 3D-Printing Markets

France: **Ranked #4** for the investment, adoption, awareness by the Ultimaker 3D Printing Sentiment Index (Ultimaker, 2019)

The world market will grow strongly in the coming years.



- ▶ 3D-Printing markets

## Plastic and polymers are widely used in additive manufacturing

### 3 sources of pollution and security problems:

- Printing wastes
- Volatiles emission
- Better fire security



### Needs:

- Biobased materials
- Low volatiles emission
- Flame retarded materials



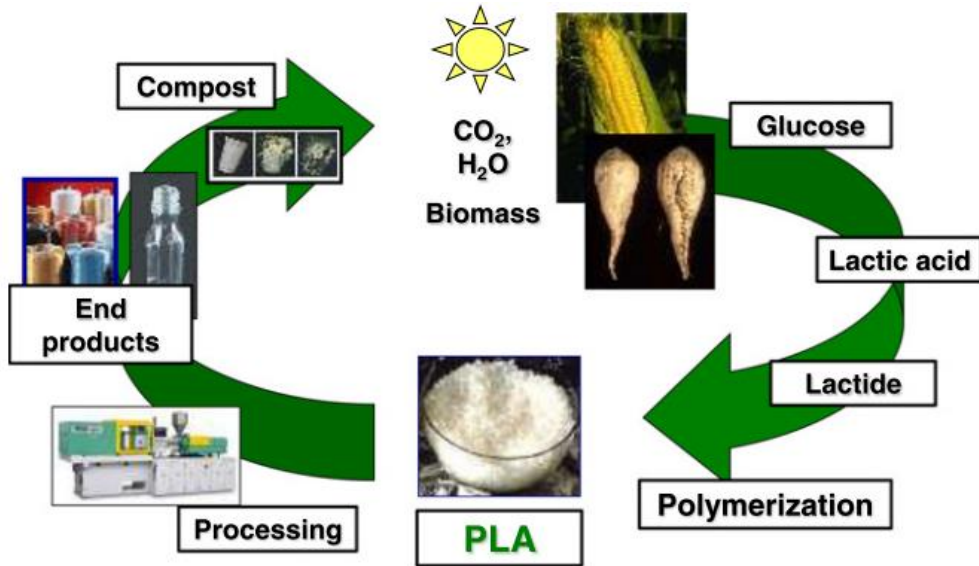
# PLA AND FIRE RETARDANCY



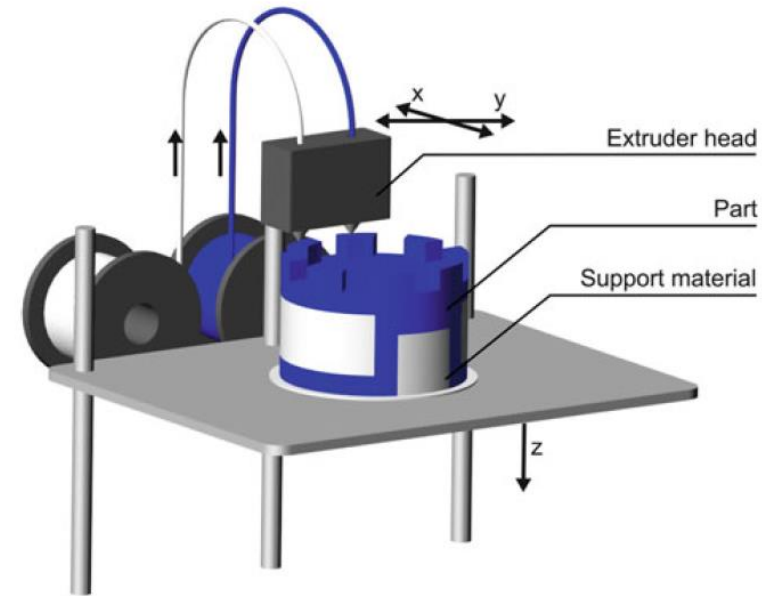
**IMT Mines Alès**  
École Mines-Télécom

# PLA AND FIRE RETARDANCY

► Polylactide (PLA): A promising biobased polymer



Poly(lactic acid) life cycle [1]



Fused Filament Fabrication (FFF) process [2]

**From Biomass (biobased):** Corn, sugar beet

**Biocompatible**, non-toxic

**Compostable**, Recyclable

**Global production of biopolymers in 2018/2019:**

**37 Mt (270,000 t for PLA) [2]**

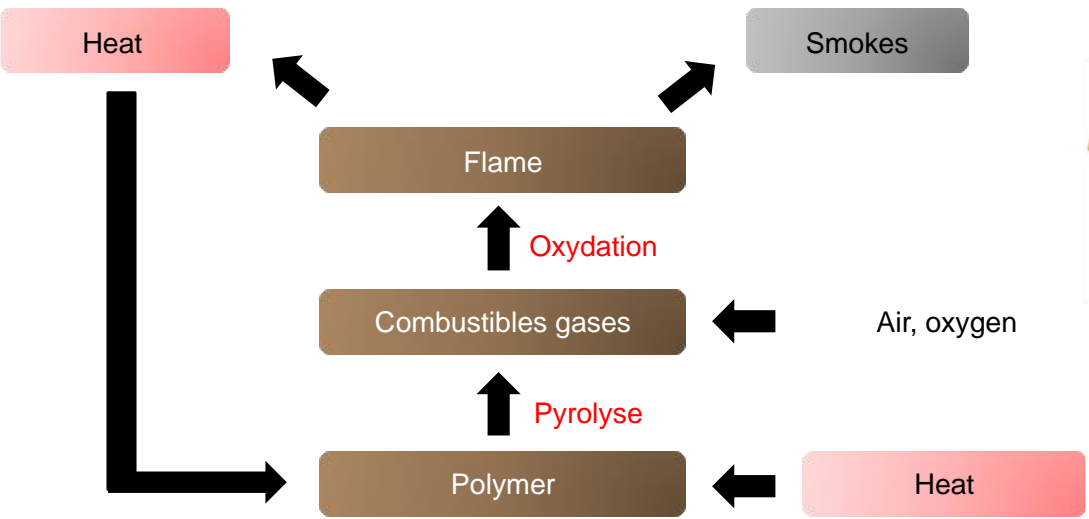
## Why PLA in additive manufacturing?

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

# PLA AND FIRE RETARDANCY

- ▶ 4 ways for flame retardancy

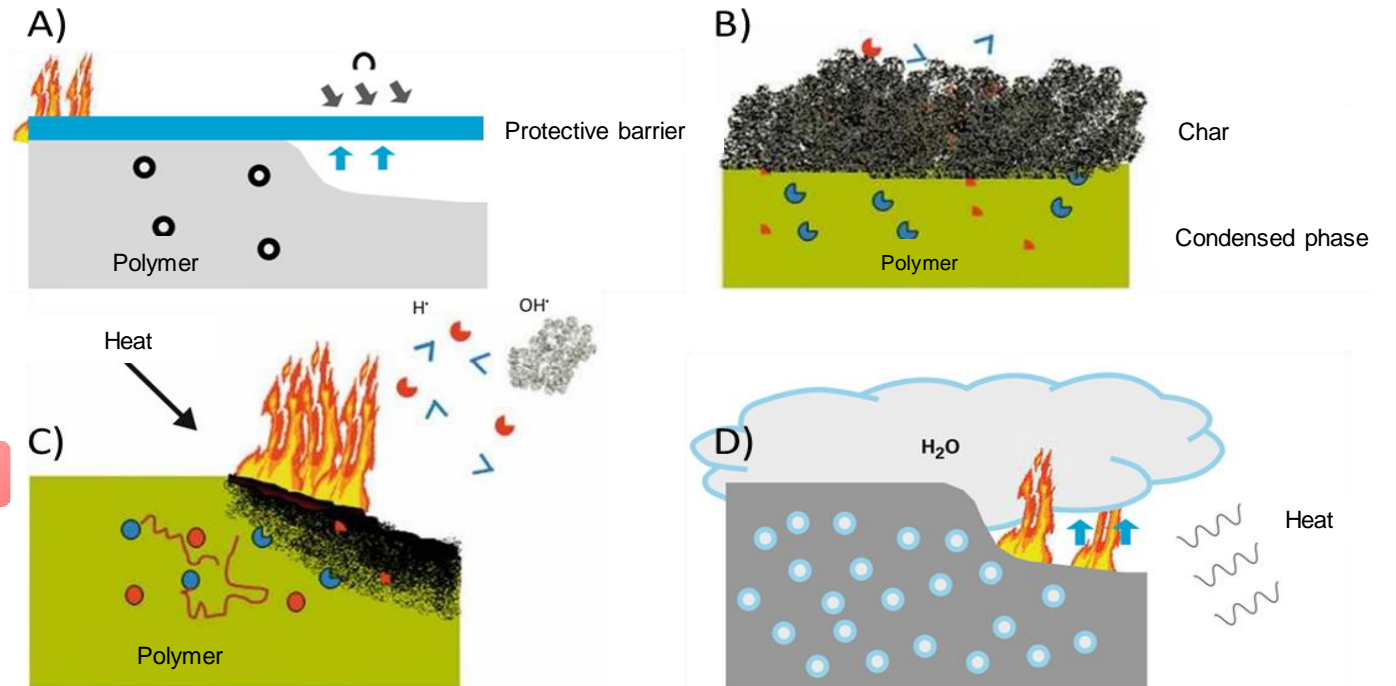
**Polymers are good combustible!**



Polymer Combustion representation, adapted from [3]

There are 4 ways to fireproof a polymer [4]:

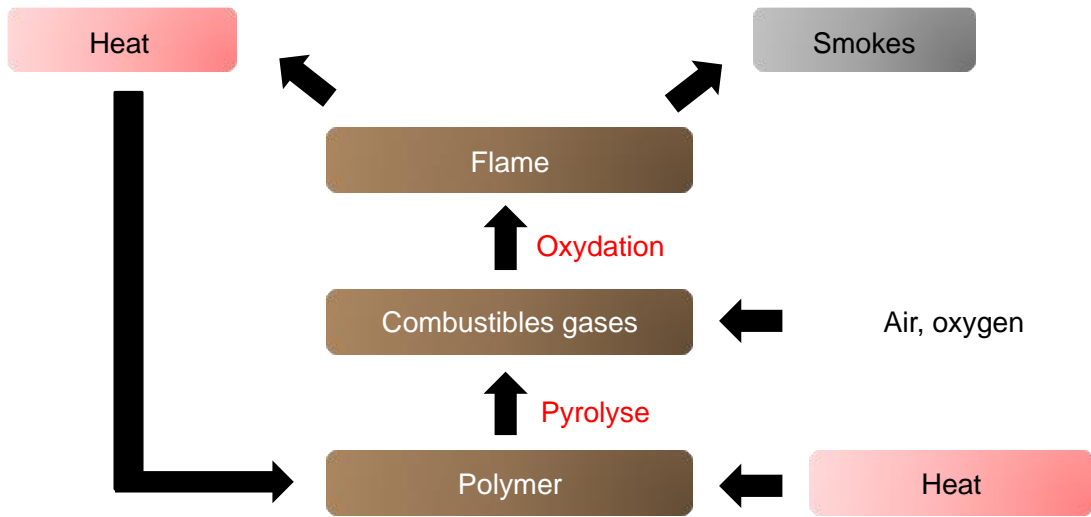
- A) Protective barrier
- B) Intumescent system
- C) Gases chemical modification
- D) Water release





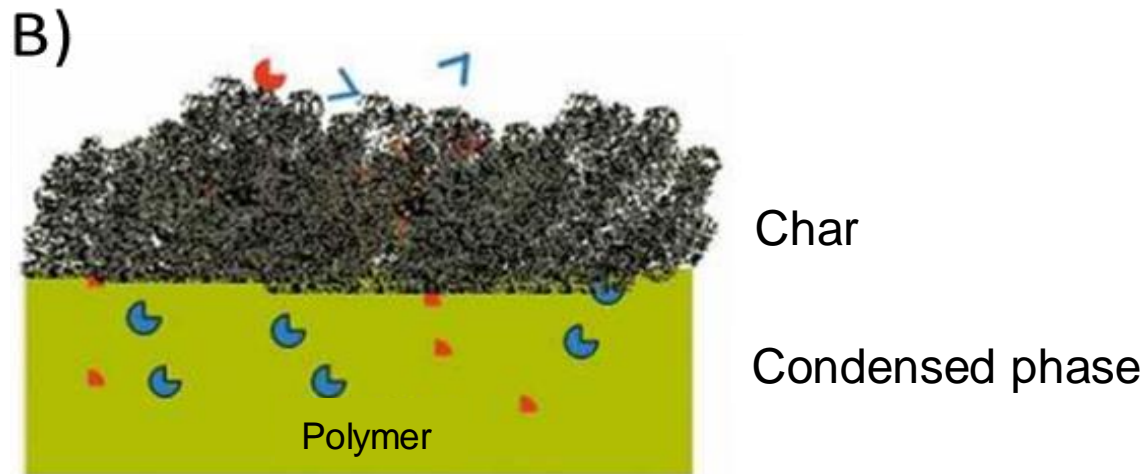
# PLA AND FIRE RETARDANCY

## ▶ Intumescent Fire Retardant System (IFRS)



## Composition of IFRS

1. Charring agent (Source of carbon)
2. Acid source
3. Blowing agent



# PLA AND FIRE RETARDANCY

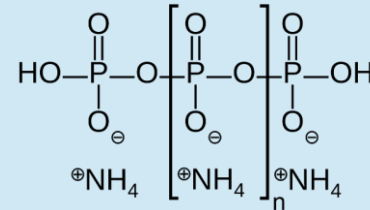
## ► Fire retardancy: Intumescent Fire Retardant System (IFRS)

### Lignin

- Biobased aromatic polymer
- By-product of paper industry
- Major components of trees and plants
- Worldwide annual production 50 millions of tons / year [6]
- **Charring Agent**

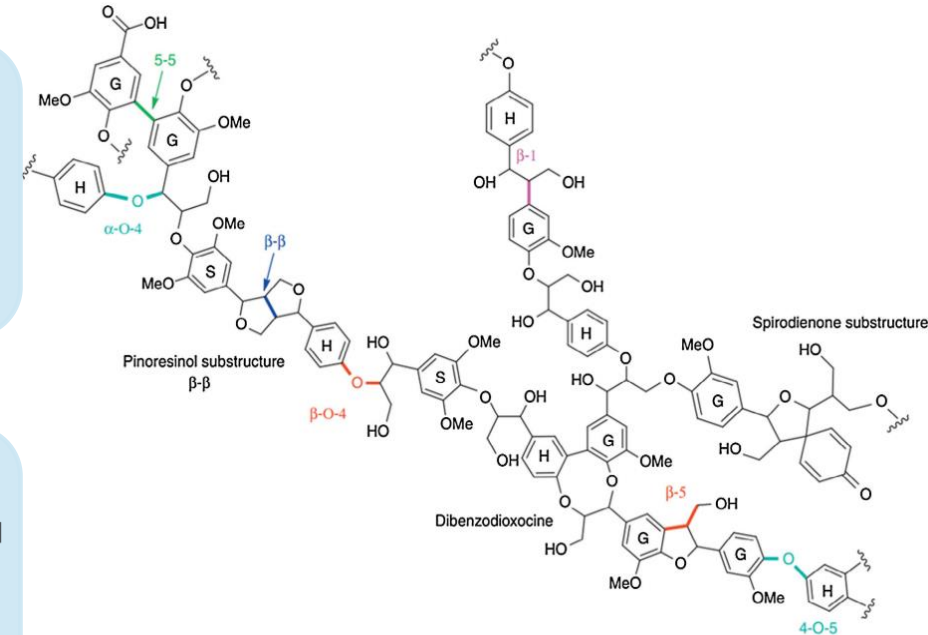
### Ammonium Polyphosphate (APP)

- Fire-retardant widely used
- **Blowing agent** with the release of NH<sub>3</sub>
- Phosphoric acid source



- **Halloysite (HNT)**
  - Phyllosilicate, Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>
- **Layered Double Hydroxide (LDH)**
  - Containing phosphorus

Enhancement of the formed char



Example of lignin molecule [7]

- ▶ Designed biocomposites

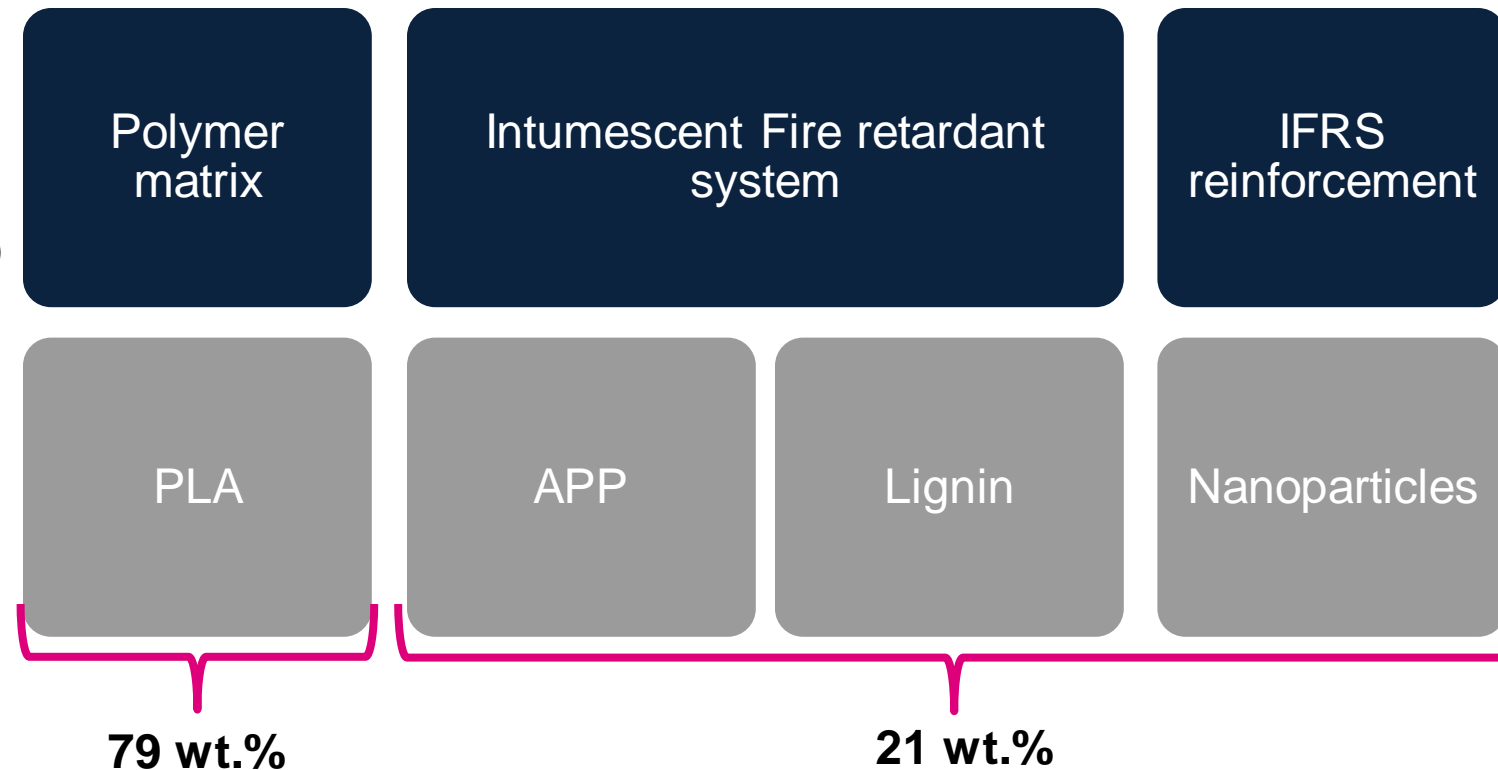
## Objectives:

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

## Materials:

- **PLA** Ingeo 2003D (NatureWorks, Extrusion Grade)
- **APP**: Ammonium Polyphosphate (Clariant, AP423)
- **LG**: Alkaline Lignin (TCI)
- **Nanoparticles**: LDH (Prolabim and Tefarm) and Halloysite (Applied Minerals)

# Biocomposites



# METHODS



**IMT Mines Alès**  
École Mines-Télécom

## Compounding:

- Temperature: 80 °C to 210 °C
- Twin-screw extruder, 250 rpm

## Injection-molding (IM): Sample preparation

- Temperature: 200 °C (melt), 40 °C (mold)
- Samples: Plate (100x100x4 mm<sup>3</sup>) and dog-bone

## Extrusion: Filament preparation

- Temperature: 180 °C to 195 °C
- Single screw extruder, 5 rpm
- Diameter : 2.85 mm

## 3D-Printing (3DP): Sample preparation

- Nozzle diameter: 0.8 mm
- Nozzle temperature: 200 °C
- Layer thickness: 0.2 mm
- Infill: ± 45°
- Nominal speed: 60 mm/s

## Cone calorimeter test

- ISO 5660-1:2015
- Position: Horizontal
- Irradiance: 50 kW/m<sup>2</sup>
- Distance between sample and cone: 25 mm
- Duration: Until flame out

### Properties:

- Time To Ignition (TTI)
- Peak of Heat Release Rate (pHRR)
- Total Heat Release (THR)
- Maximal Average Rate of Heat Emission (MARHE)

## Tensile test

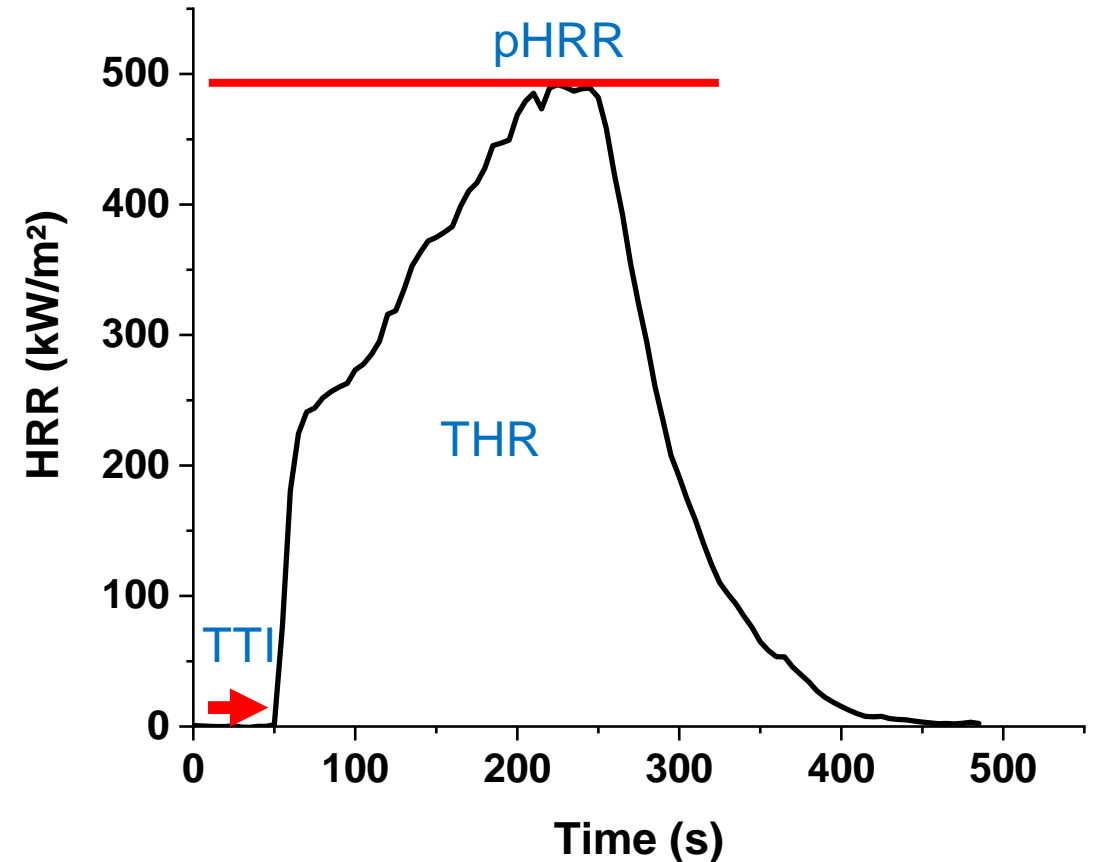
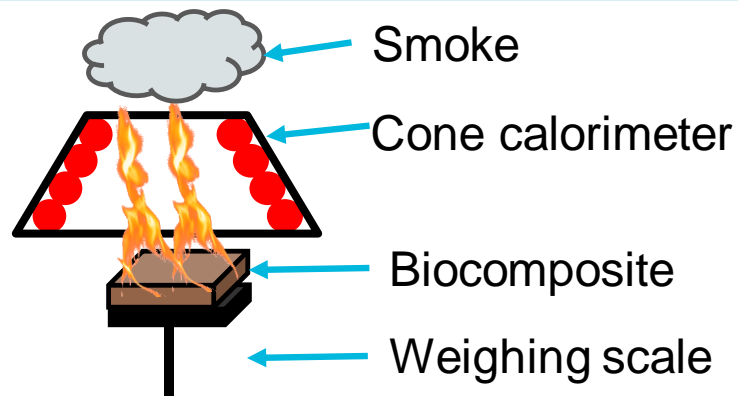
- ISO 527-1:2019
- Load cell: 2500 N
- Speed:
  - 1 mm/min for Young Modulus
  - 10 mm/min for break

### Properties:

- Young's modulus
- Elongation at break
- Tensile strength

## Cone calorimeter test

- ISO 5660-1:2015
- Position: Horizontal
- Irradiance: 50 kW/m<sup>2</sup>
- Distance between sample and cone: 25 mm
- Duration: Until flame out



# RESULTS AND DISCUSSION



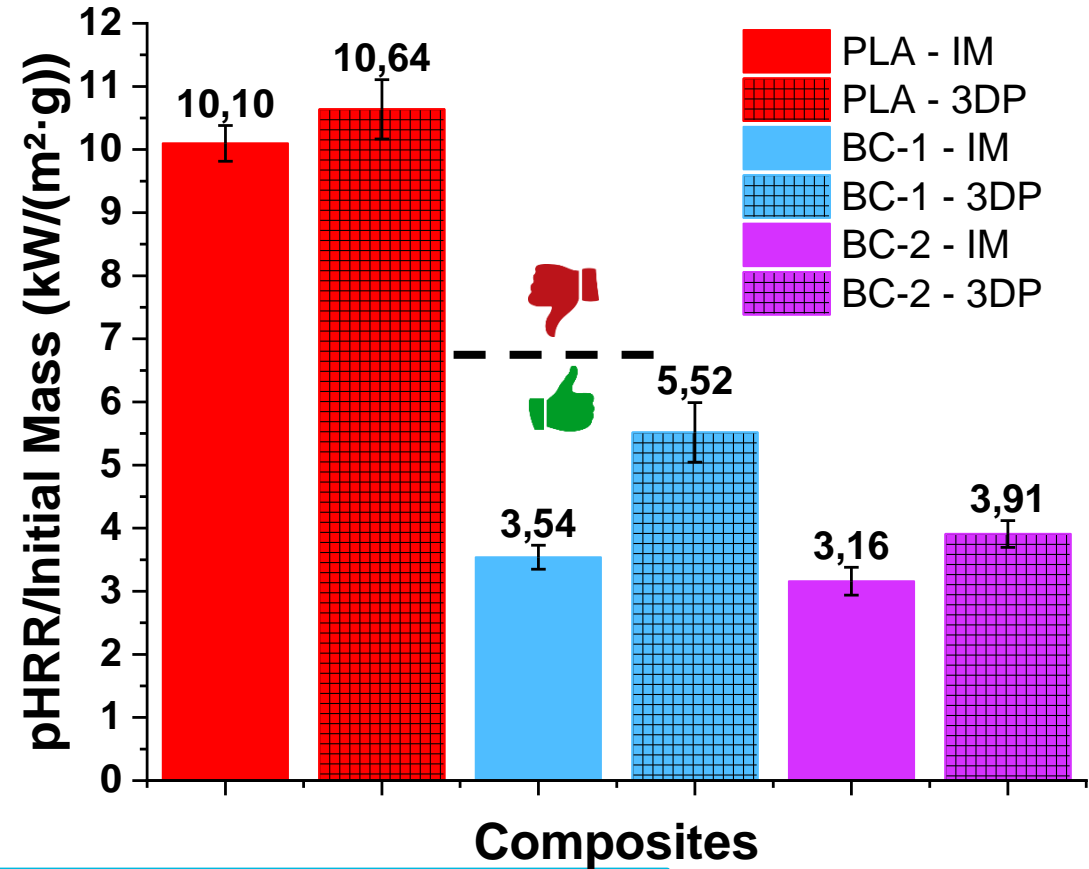
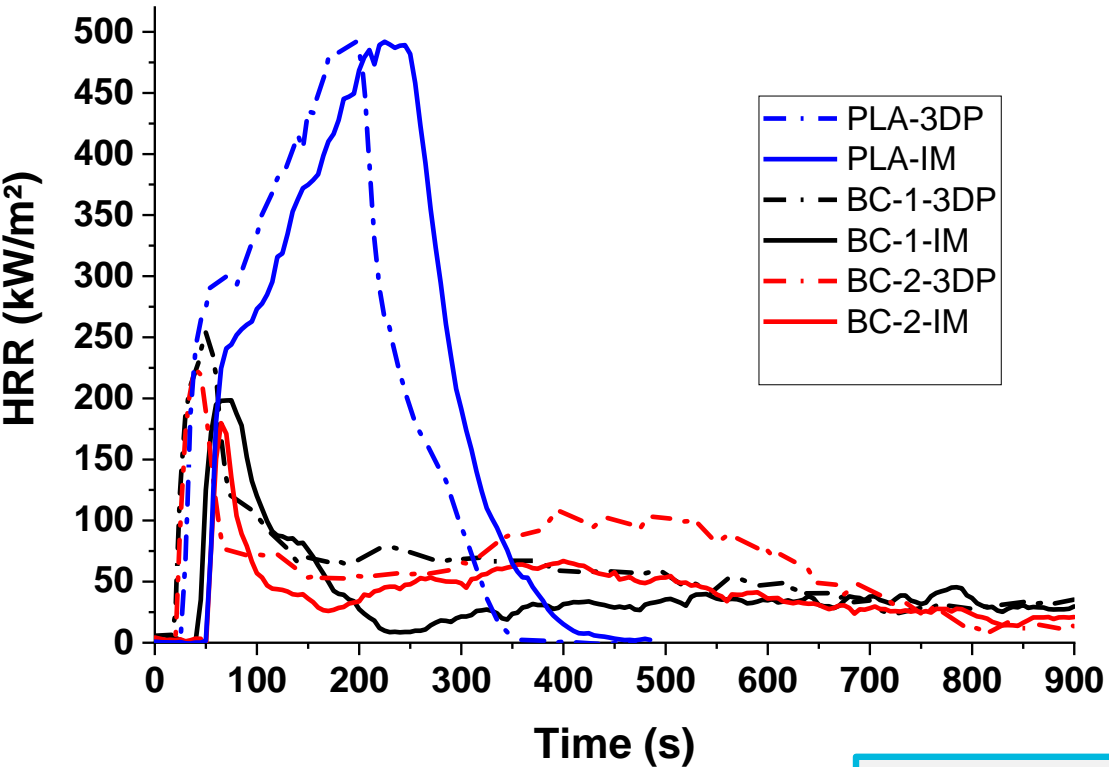
**IMT Mines Alès**  
École Mines-Télécom



# Results and discussion

## ► Fire behavior

Polymer: PLA  
 Flame-retardant: APP + Lignin + nanoparticles  
 BC-1: PLA/APP/LG/LDH  
 BC-2: PLA/APP/LG/HNT

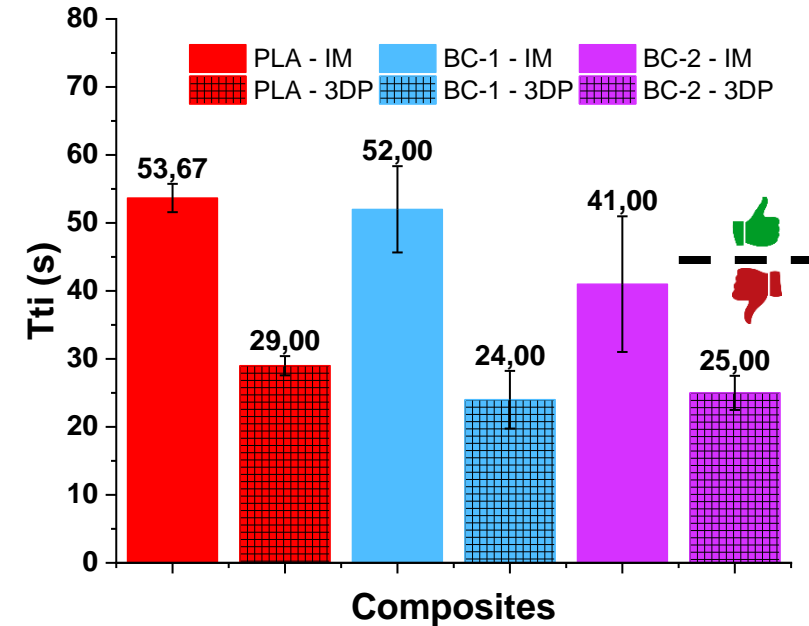
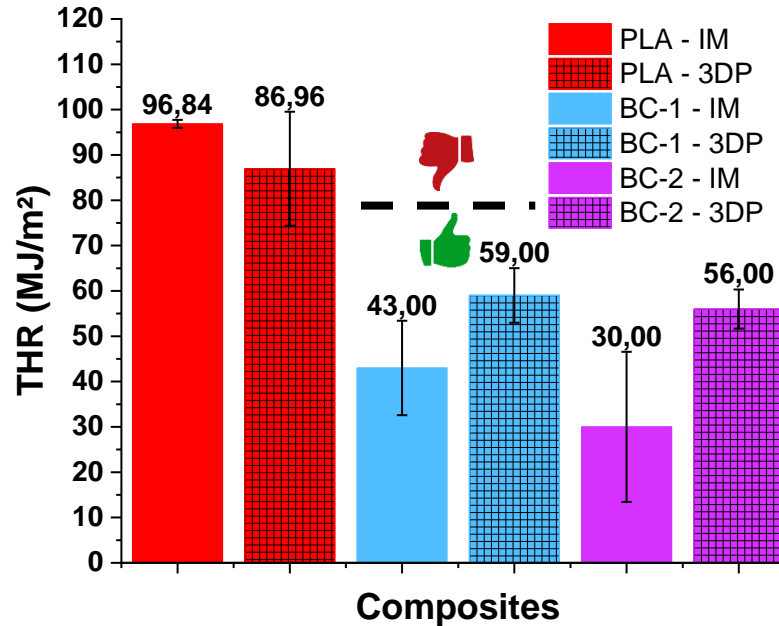
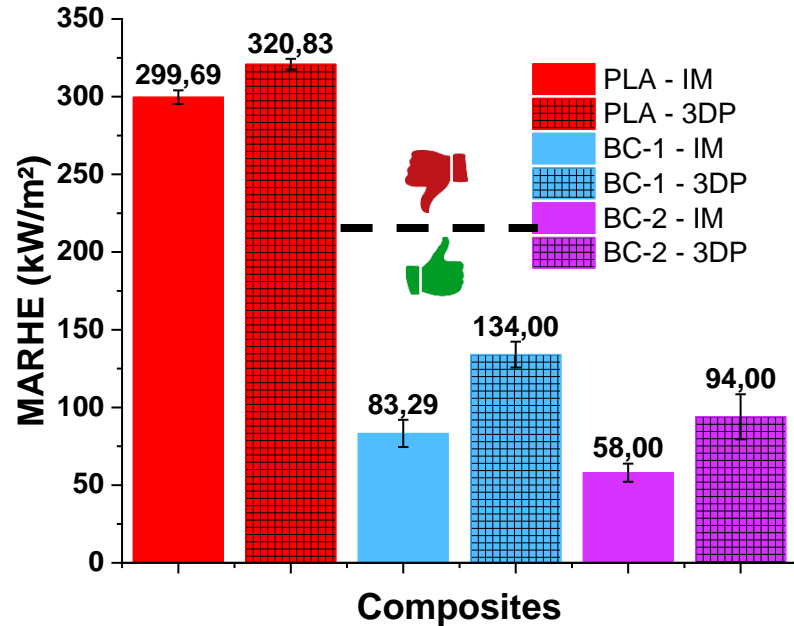


**Cone calorimetry:**  
 Ignition time delayed for 3DP  
 Higher pHRR for 3D-printing Biocomposites  
 This not seems to be due to the density of the sample

# Results and discussion

## ► Fire behavior

BC-1: PLA/APP/LG/LDH  
 BC-2: PLA/APP/LG/HNT



### Cone calorimetry:

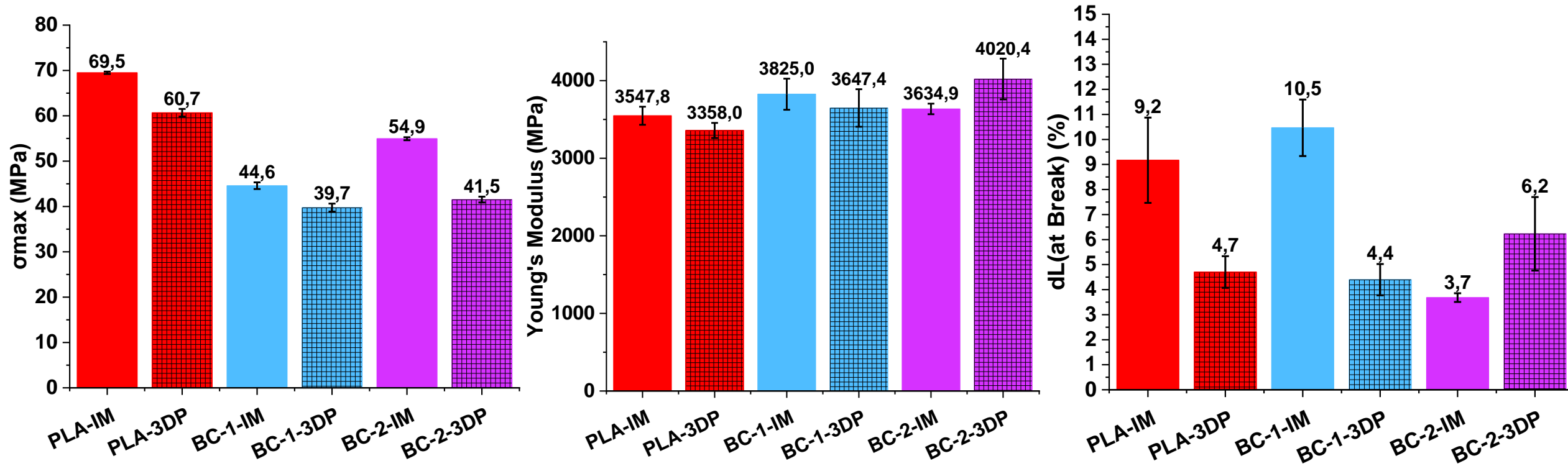
BC-2 have a lower MAHRE, THR  
 BC-1 have the higher ignition time (TTI)

The difference between IM and 3DP, **2 hypotheses** :

- Entrapped air inside porosity can help to have good flaming condition.
- Biocomposite degradation during 3DP process steps

# Results and discussion

## ► Mechanical properties



**Mechanical properties:**  
The 3DP samples seems to conserve the same properties  
The 3DP samples have a higher elongation at break than the IM samples  
The biocomposites are more rigid but more brittle  
BC-2 have the best mechanical properties for the biocomposites samples

# CONCLUSION



**IMT Mines Alès**  
École Mines-Télécom

## Fire behavior

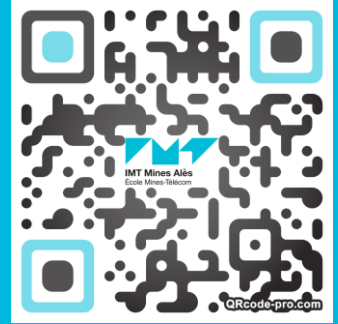
- Biocomposite have a better fire behavior
- Effect of the process on the properties
- HNT seems to be better than LDH
- LDH have the highest TTI

## Mechanical test

- Biocomposite are more rigid but more brittle
- The process has not an important impact on the properties

## What's next ?

- Understand the difference between IM/3DP fire properties
- Characterize the char formed by XRD
- Optimization of the 3DP process



# THANK YOU FOR YOUR ATTENTION

## Financial Supporting :



École Doctorale  
Sciences Chimiques Balard



IMT Mines Alès  
École Mines-Télécom



La Région  
**Occitanie**  
Pyrénées - Méditerranée

## Supervisors :

José-Marie Lopez-Cuesta<sup>1</sup>  
Monica Francesca Pucci<sup>2</sup>  
Arnaud Regazzi<sup>2</sup>  
Jean-Christophe Quantin<sup>2</sup>  
Clément Lacoste<sup>1</sup>

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