

# Gas-esterification of cellulose particles for the production of PHBV based biocomposites

Grégoire David<sup>1</sup>, Nathalie Gontard<sup>1</sup>, Laurent Heux<sup>2</sup>, Hélène Angellier-Coussy<sup>1</sup>

<sup>1</sup>UMR-IATE (CIRAD, INRA, Montpellier SupAgro, Université de Montpellier), Place Viala, 34060 Montpellier Cedex 01, France

<sup>2</sup>CERMAV-CNRS, Grenoble, 38000, France

Corresponding author. Tel: (+33) 499612200; E-mail: gregoire.david@umontpellier.fr



## Background and objectives

### NoAW project

NoAW (No Agricultural Waste) is an European-Chinese project.

**Objective:** Be closer to a zero-waste society, elaborating a circular economy approach for agro-wastes on a territorial and seasonal basis.

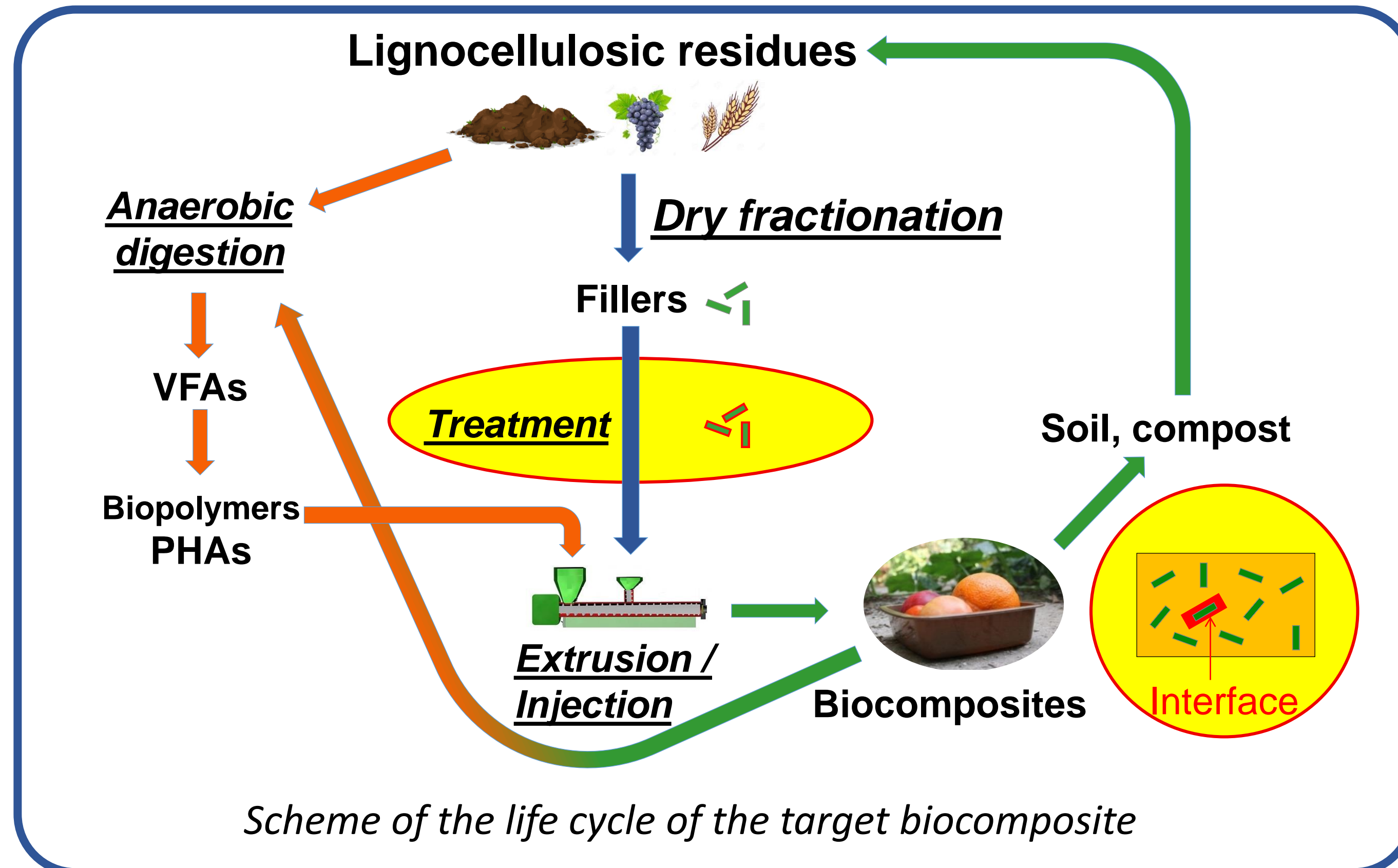
- Bio-refinery concept
- Early eco-design method
- Eco-efficient products: bioenergy, biomolecules, biofertilizers and biocomposites

A part is devoted to new biocomposite materials from solely agro-wastes :

- PHBV, poly(hydroxy-butyrate-co-valerate), a bacterial polyester as matrix
- Lignocellulosic fillers produced from vine shoots

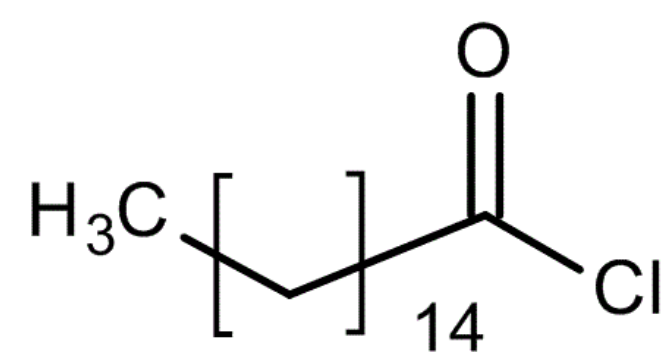
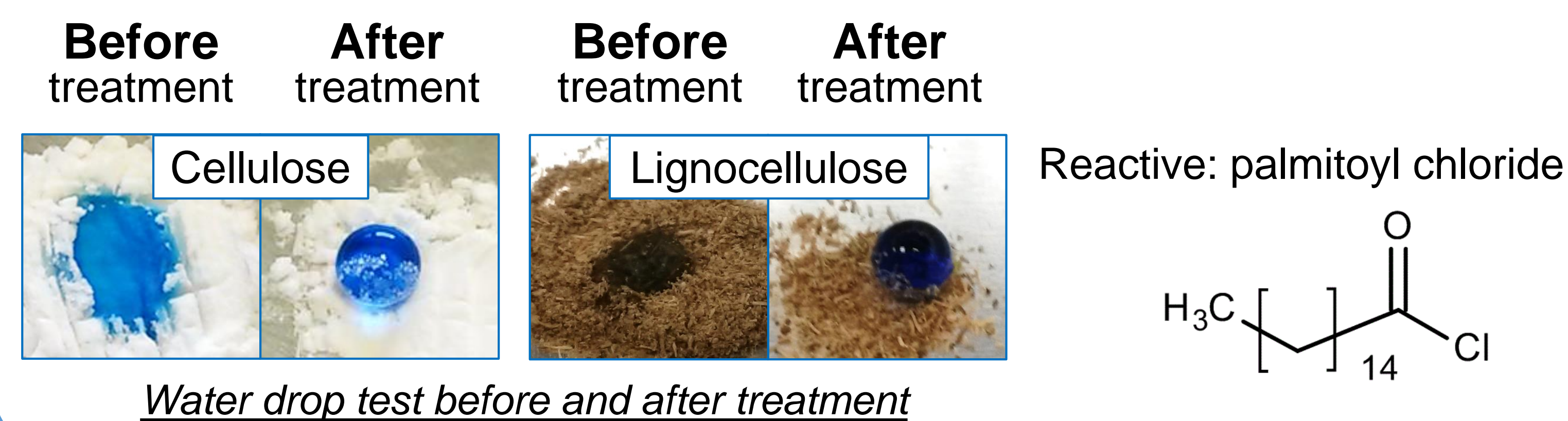
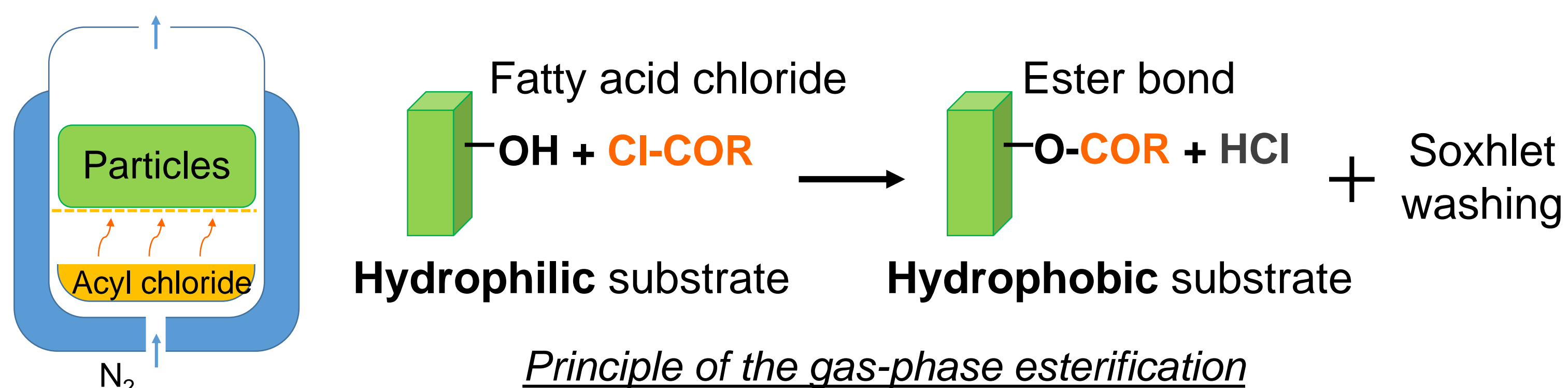
**Scientific problem:** Poor adhesion at the interface filler/matrix.

**Explored solution:** Gas phase esterification as pre-treatment to reduce hydrophilic character of lignocellulose particles.



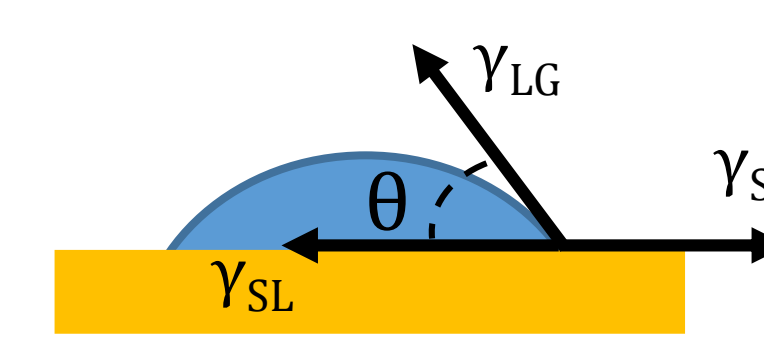
## Progress and main results

### Pre-treatment: Gas-phase esterification



### Surface energy

$$\gamma = \gamma^D + \gamma^P$$



Owens-Wendt model:

$$\frac{(1 + \cos(\theta)) \gamma_L}{2 \sqrt{\gamma_L^D}} = \sqrt{\gamma_S^P} \sqrt{\frac{\gamma_L^P}{\gamma_L^D}} + \sqrt{\gamma_S^D}$$

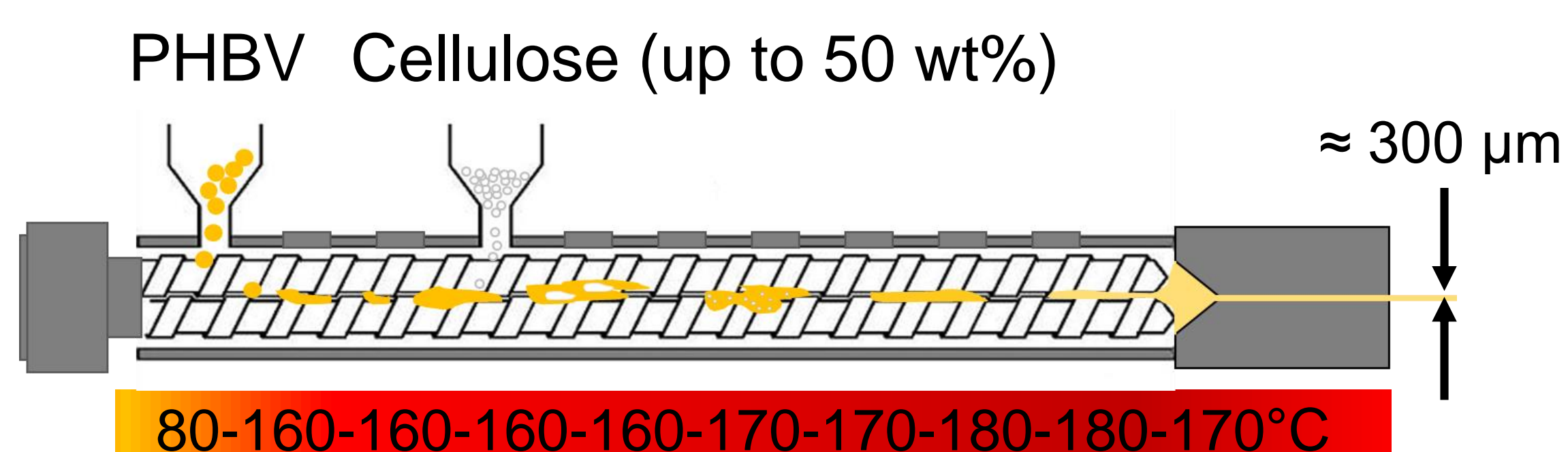
Esterification of cellulose			Contact angle with water (°)	Polar component $\gamma^P$ (mN/m)	Dispersive component $\gamma^D$ (mN/m)	Surface energy $\gamma$ (mN/m)
Time (h)	T (°C)	DS* by FT-IR				
3	100	$8.7 \cdot 10^{-3}$ **	$105 \pm 2$	0.2	22.2	22.4
7	120	$1.4 \cdot 10^{-1}$	$105 \pm 2$	0.1	21.5	21.6
15	100	$5.9 \cdot 10^{-2}$	$109 \pm 2$	0.2	23.5	23.7
15	120	$2.3 \cdot 10^{-1}$	$103 \pm 3$	0.1	20.1	20.2
Pure cellulose			$44 \pm 2$	17.7	32.1	49.8

\*DS: Degree of Substitution (number of acid chlorides grafted per anhydroglucose unit)  
\*\*Confirmed by <sup>13</sup>C NMR

DS and contact angles with water confirm that the grafting of long aliphatic chains on the cellulose surface brings hydrophobicity. DS does not need to be high to have effects. The surface energy of grafted cellulose is reduced, particularly the polar component has collapsed to nearly zero.

### Melt extrusion of composites

- Lab-scale twin-screw extruder: Eurolab D: 16 mm – L/D: 40 from ThermoFisher Scientific
- PHBV pellets and cellulosic particles (d50 = 20 μm) were dried in an oven at 60 °C at least 24 h.



Grafted and non-grafted cellulosic particle contents in the biocomposite were formulated from 5% to 50% by weight.

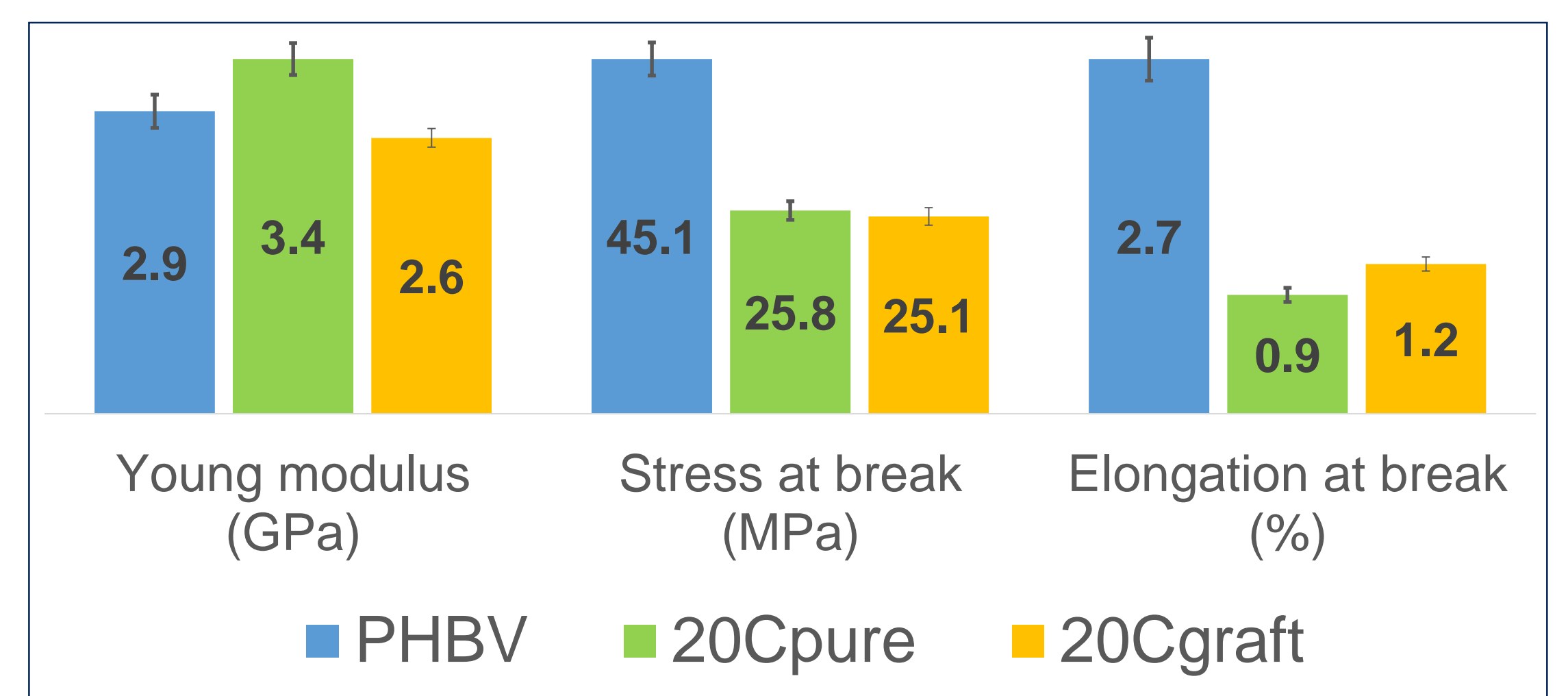
### Mechanical tests

- Initial grip distance: 45mm
- Cross-head speed: 1mm.min<sup>-1</sup>

Test specimen from film are stored in an oven at 20 °C and 50%RH.



Results of the tensile test carried on pure PHBV (PHBV), 20% cellulose composite (20Cpure) and 20% grafted cellulose (20Cgraft)



In both cases, adding particles weakens the biopolymers. Grafting of cellulosic particles makes the composite slightly more ductile than the classic one, so more processable. The stress at break is not improved as expected.



## Conclusion and perspectives

- A gas-phase esterification of lignocellulosic particles was applied to improve interfacial adhesion with the matrix for biocomposite application.
- Hydrophobic character is provided to cellulose: high contact angle with water and collapse of the polar component of surface energy.
- Mechanical properties of final composites still need to be improved.
- Mass transfer properties of final composites are under study.
- A life cycle assessment of this treatment is on progress.
- Composites with lignocellulosic fillers, grafted or not, will be extruded.