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## INTRODUCTION

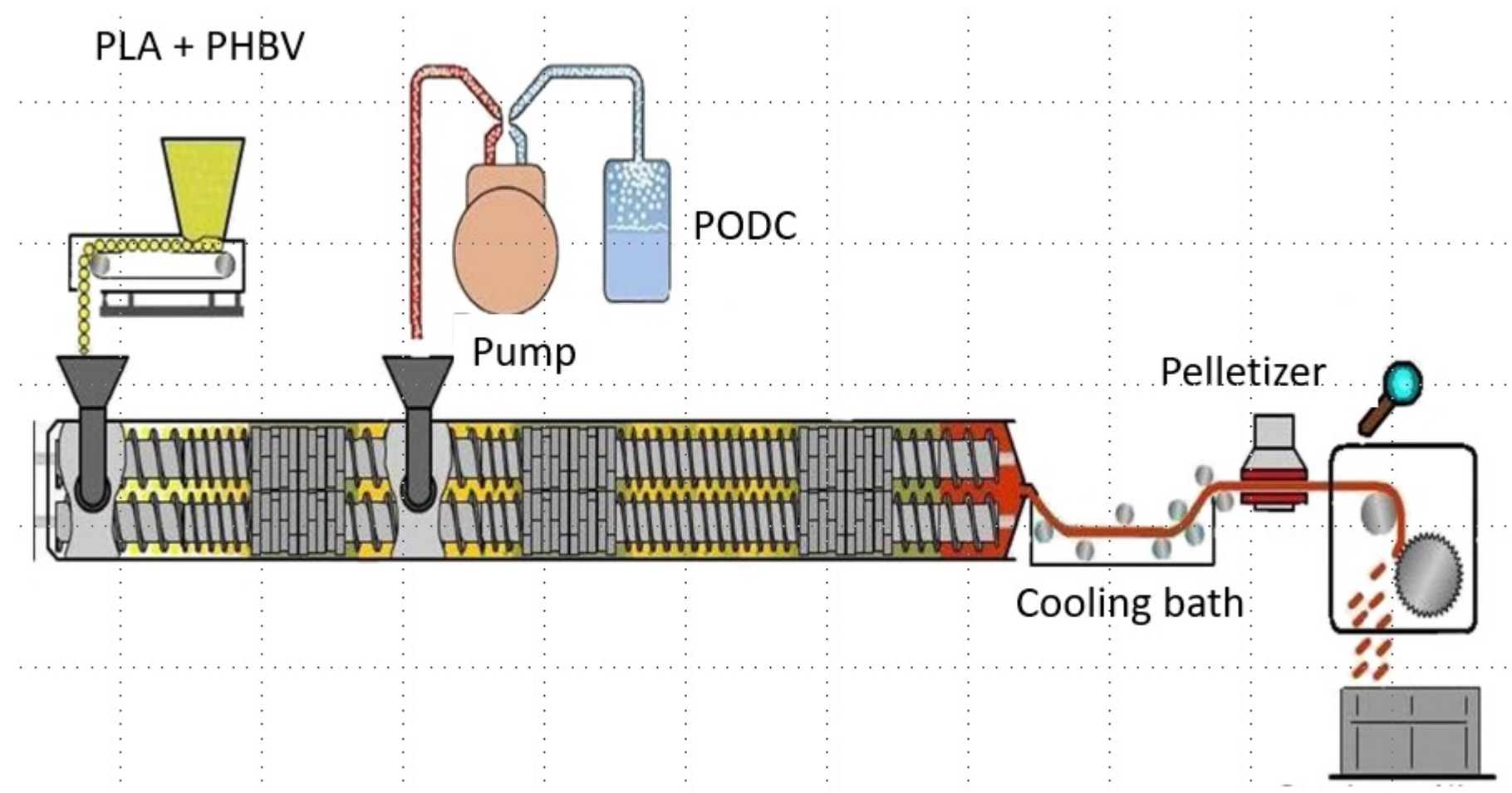
Poly(lactide) (PLA) is one of the most promising biobased and biodegradable polymer to replace traditional petroleum thermoplastic in the packaging or textile sectors [1]. PLA features **advantages** like ease of processing, transparency, heat-sealing capacity and satisfying rigidity at room temperature. However, PLA being glassy at room temperature ( $T_g \approx 60^\circ\text{C}$ ) behaves **brittle** and **possesses low heat deflection stability** after passing its glass transition [2]. In the aim **to increase the ductility and heat stability** beyond glass transition of PLA, **plasticizer and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) have been added**. Ruellan et al. [3] showed that vegetable oil deodorization condensates, being by-products of the vegetable oil industry, are highly efficient in increasing PLA ductility, although merely soluble in the polymer matrix [4]. Therefore, the effect of blending PLA with PHBV and a novel biobased and biodegradable toughening agent, palm oil deodorization condensate (PODC), on its thermal and mechanical properties has been studied. Furthermore, the **influence on polylactide physical aging of PODC and PHBV** through thermal and mechanical characterization has been investigated.

## MATERIALS

- **PLA (4060D)**: containing  $89 \pm 1\%$  L-lactide and  $11 \pm 1\%$  D-lactide units, from NatureWorks (U.S.A.)
- **PHBV (PHI 002)**: containing 97 % hydroxybutyrate and 3 % hydroxyvalerate units, from Natureplast (France)
- **Palm oil deodorization condensate (PODC)**: supplied by ITERG (Bordeaux, France).

## PREPARATION OF THE BLENDS

- **Drying** at  $60^\circ\text{C}$  (PLA 4060D) and  $80^\circ\text{C}$  (PHI 002) for 24 hours under dried air using a Motan 100 L
- **Melt blending** of PLA 4060D with PODC with or without PHI 002 was performed using a corotating twin screw extruder (Dr. Collin) with a screw diameter of 35 mm and a length to diameter ratio (L:D) 56:1.
- **Liquid addition of PODC** was done using a Robatech PuMelt D280 pump heated at  $70^\circ\text{C}$ .



[90 wt% (PLA 4060D + 10 wt% PODC) + 10 wt% PHI 002] blend was carried out in one single step

## CHARACTERIZATION

### 1. DSC

- DSC analyses performed using a Mettler Toledo DSC1 STARe System under nitrogen atmosphere ( $50\text{ mL}\cdot\text{min}^{-1}$ ) in  $40\ \mu\text{L}$  standard Aluminum pans (Mettler Toledo).

### 2. Tensile test

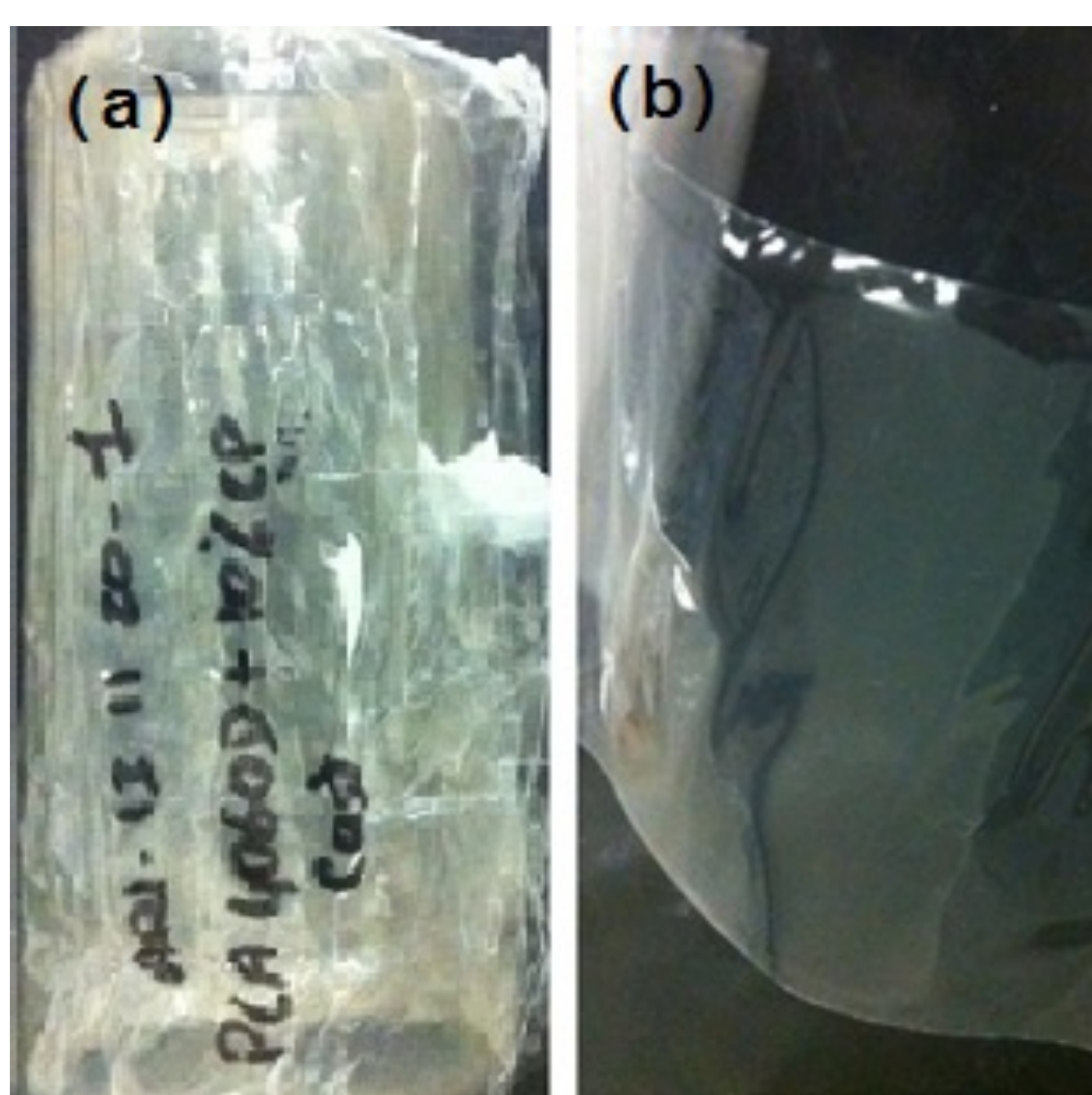
- Tensile properties investigated at  $23^\circ\text{C}$ , a relative humidity (RH)  $50 \pm 10\%$  and at a cross-head speed of  $5\text{ mm}\cdot\text{min}^{-1}$ , using an universal tensile machine (Instron model 4301)

### 3. Physical aging

- A first physical aging carried out directly in the DSC under nitrogen ( $50\text{ mL}\cdot\text{min}^{-1}$ ) at a fixed distance from  $T_g$ :  $T_{\text{aging}} = T_g - 15^\circ\text{C}$  for each formulation. The resulting aging temperatures are thus  $T_{\text{aging}} = 40 \pm 2^\circ\text{C}$  for the PLA and PLA/PHBV samples and  $T_{\text{aging}} = 32 \pm 2^\circ\text{C}$  for the PLA/PODC and PLA/PODC/PHBV samples. For this study, physical aging times varied from 0 to 100 h.
- To enable accelerated physical aging, the extruded films were stored in an oven (FisherBrand TLK 72B) at  $T_{\text{aging}} = T_g - 15^\circ\text{C}$  under reduced pressure (0.1 bar) in order to minimize thermo-oxidation phenomena.

## RESULTS

### Thermal and mechanical properties of PLA/PHBV/PODC blends

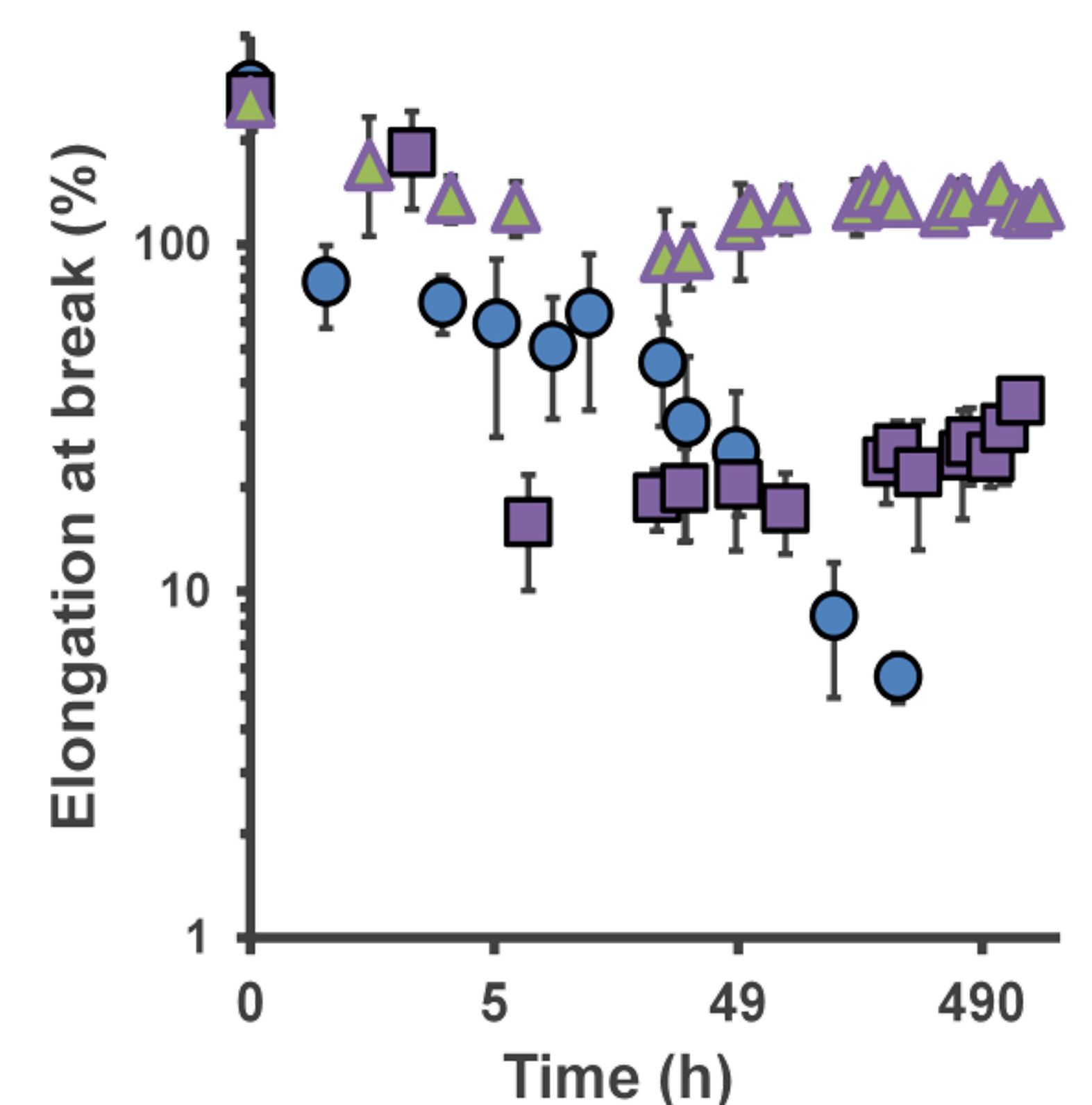


Cast extruded films

(a) [PLA + 10 wt% PODC] and  
(b) [90 wt% (PLA + 10 wt% PODC) + 10 wt% PHBV]  
stored at  $40^\circ\text{C}$  during one month

	Storage	Glass transition temperature	Mechanical properties	
		$T_g$ ( $^\circ\text{C}$ )	Elongation at break (%)	Yield Stress (MPa)
PLA 4060D	1 week at $23^\circ\text{C}$	$57.7 \pm 0.1$	$6 \pm 1$	$56 \pm 3$
	6 months at $40^\circ\text{C}$	$56.0 \pm 0.3$	$5 \pm 2$	$64 \pm 5$
PLA 4060D + CDHP	1 week at $23^\circ\text{C}$	$43.1 \pm 0.6$	$135 \pm 25$	$29 \pm 2$
	6 months at $40^\circ\text{C}$	$48.6 \pm 0.3$	$90 \pm 25$	$35 \pm 3$
PLA 4060D + CDHP + PHBV	1 week at $23^\circ\text{C}$	$44.1 \pm 0.2$	$105 \pm 15$	$31 \pm 2$
	6 months at $40^\circ\text{C}$	$48.0 \pm 0.3$	$85 \pm 15$	$33 \pm 3$

### Effect of aging time on elongation at break



(○) PLA ; (□) PLA/PHBV ; (Δ) PLA/PODC/PHBV

## CONCLUSIONS

- Physical aging plays an important role in determining the long terms performance of polymers, especially PLA, whose  $T_g$  is close to ambient temperature.
- Considering long term performances, PLA/PHBV/PODC blends are the most promising materials for the toughening of PLA. Indeed, for these blends significant improvement in the strain at break was observed, along with a limited depression of the Young modulus and the stress at yield in comparison to neat PLA, as well as an improved thermal stability.

[1] R. Auras, B. Harte, S. Selke, *Macromol. Bioscience*, **4**(9), 835-864, 2004

[2] S. Domenek, C. Courgneau, V. Ducruet, in *Biopolymers: Biomedical and Environmental Applications*, S. Kalia and L. Avérous, Editors, John Wiley & Sons., 183-223, 2011

[3] A. Ruellan, A. Guinault, C. Sollogoub, V. Ducruet, S. Domenek, *J. Appl. Polym. Sci.*, **32**(48), 2015

[4] A. Ruellan, V. Ducruet, A. Gratia, L. Saelices Jimenez, A. Guinault, C. Sollogoub, G. Chollet, S. Domenek, *Polym. Int.*, **65** (6), 683-690, 2016