Physical aging and its effect on mechanical properties of toughened PLA films

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INTRODUCTION

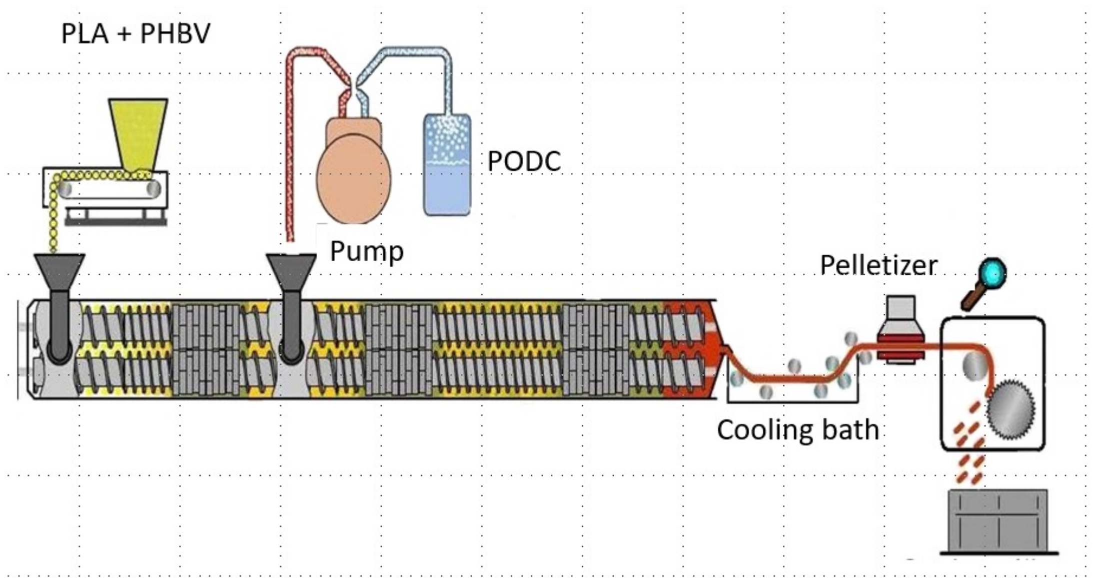
Polylactide (PLA) is one of the most promising biobased and biodegradable polymer to replace traditional petroleum thermoplastic in the packaging or textile sectors [1]. PLA features **advantages** like ease of processing, transparency, heat-sealing capacity and satisfying rigidity at room temperature. However, PLA being glassy at room temperature ($T_g \approx$ 60 °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 ± 1 % L-lactide and 11 ± 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 °C (PLA 4060D) and 80 °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 °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 mL.min-1) in 40 µL standard Aluminum pans (Mettler Toledo).

2. Tensile test

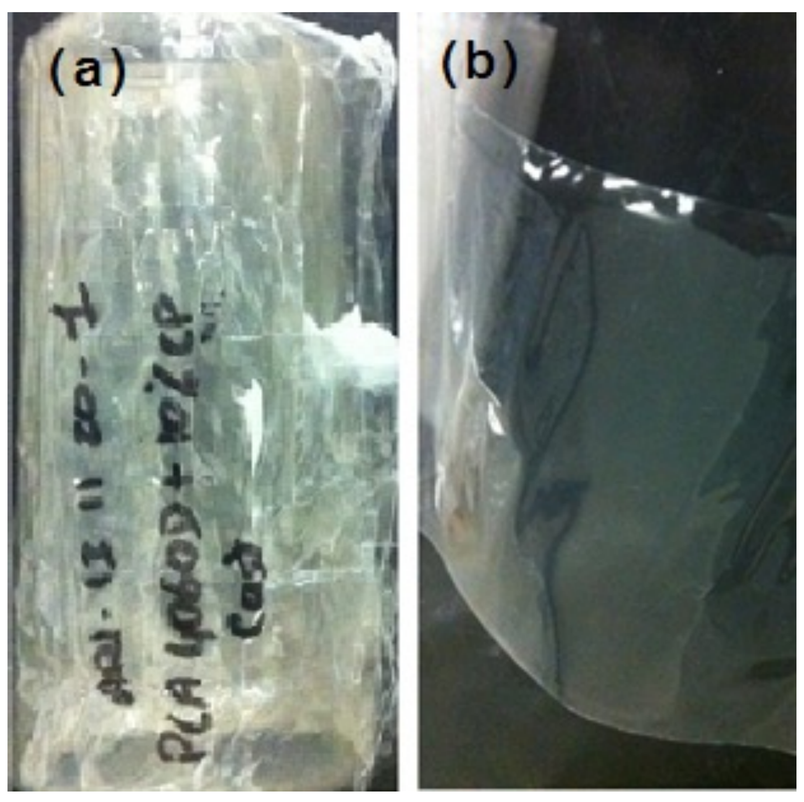
- Tensile properties investigated at 23 °C, a relative humidity (RH) 50 ± 10 % and at a cross-head speed of 5 $mm.min^{-1}$, using an universal tensile machine (Instron model 4301)

3. Physical aging

- A first physical aging carried out directly in the DSC under nitrogen (50 $mL.min^{-1}$) at a fixed distance from T_g: $T_{aging} = T_g$ – 15 °C for each formulation. The resulting aging temperatures are thus T_{aging} = 40 ± 2 °C for the PLA and PLA/PHBV samples and T_{aging} = 32 ± 2 °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 $T_{aging} = T_g$ – 15 °C under reduced pressure (0.1 bar) in order to minimize thermo-oxydation phenomena.

RESULTS

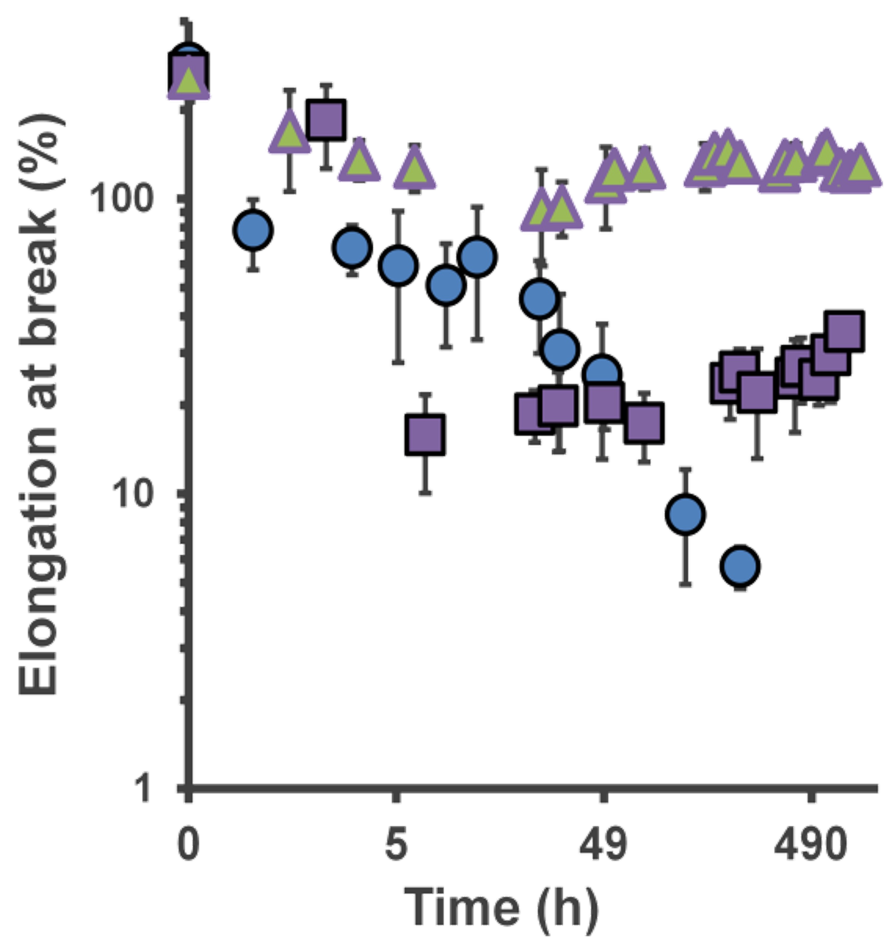
Thermal and mechanical properties of PLA/PHBV/PODC blends



Cast extruded films
(a) [PLA + 10 wt% PODC] and
(b) [90 wt% (PLA + 10 wt% PODC) + 10 wt% PHBV]
stored at 40°C during one month

	Storage	Glass transition temperature: Tg (°C)	Mechanical properties: Elongation at break (%)	Mechanical properties: Yield Stress (MPa)
PLA 4060D	1 week at 23°C	57.7 ± 0.1	6 ± 1	56 ± 3
	6 months at 40°C	56.0 ± 0.3	5 ± 2	64 ± 5
PLA 4060D + *CDHP*	1 week at 23°C	43.1 ± 0.6	135 ± 25	29 ± 2
	6 months at 40°C	48.6 ± 0.3	90 ± 25	35 ± 3
PLA 4060D + *CDHP* + *PHBV*	1 week at 23°C	44.1 ± 0.2	105 ± 15	31 ± 2
	6 months at 40°C	48.0 ± 0.3	85 ± 15	33 ± 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 Tg 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