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Bioproducts of oil industry as toughening agents of Polylactide

Alexandre Ruellan^{1,2}, Audrey Gratia⁵, Alain Guinault³, Guillaume Chollet⁴, Cyrille Sollogoub³, Sandra Domenek², Violette Ducruet¹

1. INRA, UMR1145 Ingénierie Procédés Aliments, F91300, Massy France
2. AgroParisTech, UMR1145 Ingénierie Procédés Aliments, F91300, Massy France
3. Laboratoire PIMM, Arts et Métiers Paris Tech, 21 rue Pinel, F-75013 Paris, France
4. ITERG, 11 rue Monge, Parc Industriel Bersol 2, F-33600 Pessac, France
5. LNE, Laboratoire National de métrologie et d'Essais, Chemistry and Physical Chemistry of Materials Division. F-78197 Trappes Cedex, France

Introduction

Polylactide (PLA) which is already available in large commercial quantities shows a good potential as biobased and biodegradable polymer in several sectors. Nevertheless its low ductility narrows its usage potential needed to manufacture efficient thermoplastic films for food packaging. External plasticization is the main solution employed trying to enhance the elongation at break of PLA (1) Impact modifiers can be an alternative in order to reduce the brittleness while preserving the PLA stiffness and thermal characteristics (2). However both approaches using mainly oil-based additives reduce the biobased carbon content of the formulated material. Consequently, developing a biobased and biodegradable additive suitable for food contact material, with a low cost and a stable sourcing, could constitute a very attractive product for the industrial development of PLA food packaging. The refinery process of vegetable oil produces natural by-products with an important diversity of relevant organic molecules in particular deodorization condensate. Our study was to assess this by-product as biobased additive to improve the toughening of PLA while keeping the food safety and maintaining the biodegradability of the PLA packaging.

Materials and Methods

Amorphous PLA 4060D and semi crystalline PLA 4042D were purchased from NatureWorks. Oil deodorization condensates (ODC) were supplied by ITERG (Bordeaux, France). Melt-blending of PLA and PalmODC was done by twin-screw extrusion up to a maximum inclusion quantity of 8 wt%. Sample films were obtained by single screw cast extrusion. (Thermo Haake Ptw), Blown film of formulated PLA 4060D was done with a 30 mm diameter Mapre single-screw extruder, along the extrusion flow mounted with a film blowing machine (Dr. Collin). A blowing ratio of about 2.5 was applied and the rolls speed was adjusted to get a final film thickness of about 25 μm . Tensile properties were investigated at 23 °C, at relative humidity (RH) varying between 40 % and 60 % and at a cross-head speed of 5 $\text{mm}\cdot\text{min}^{-1}$, using an universal tensile machine (Instron model 4301). Food safety assessment of the formulated PLA was carried out according to EU Regulation 10/2011. The biodegradation of the film samples was done according to the EN 14855 standard. Microcrystalline cellulose (44 % carbon content), was used as reference material. Biodegradation was carried out at 58 °C.

Results and Discussion

The main components of Palm Oil Deodorization Condensate (PODC) are free fatty acids which reach an average amount of 95.4 %. Among these free fatty acid part, the percentage of palmitic acid and oleic acid are 49.8 % and 35 % respectively in PODC.

Table 1 shows that the addition of 8% PODC whatever the grade of PLA decreases the Tg but only by 10°C-14°C while increasing the elongation at break up to 135%. Similar trends were obtained with Rapeseed ODC, sunflower ODC and olive ODC although palm oil gave the best results. PLA can't be blown without the help of technologic additives mainly oil-based. Our results show that PODC allows the blowing of PLA 4060D while keeping it totally biobased. These two significant results could be accounted to the physical state of the fatty acids into the PLA matrix

Unsaturated fatty acid present in PODC such as linoleic acid and oleic acid are liquid at room temperature and could be solved in the amorphous part of PLA. In opposite saturated fatty acid as palmitic acid are

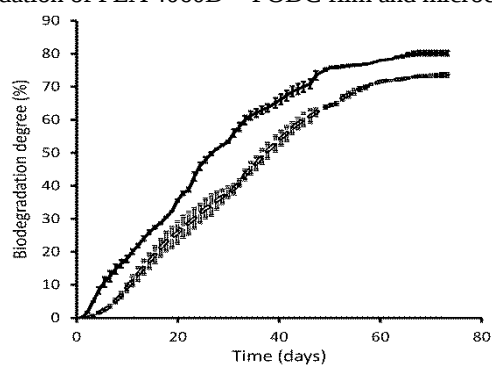
crystallized and stays at solid state in the matrix. These two behavior leads to an increase of ϵ and allows the blowing of PLA.

Table 1: Degree of crystallinity(χ_c), glass transition (T_g) and elongation at break (%) of neat PLA 4060D and PLA 4042D and formulated with PODC (8%) according to two processes.

Sample	Process	χ_c (%)	T_g ($^{\circ}\text{C}$)	Elongation at break %
PLA 4060D	Cast extrusion	-	57.7 \pm 0.1	6 \pm 1
PLA 4060D +PODC	Cast extrusion	-	43.1 \pm 0.6	135 \pm 25
PLA 4060D+PODC	Blown extrusion	-	44 \pm 0.4	100 \pm 15
PLA 4042D sheet	Cast extrusion then quenching	< 2	56.9 \pm 0.3	6 \pm 1
PLA 4042D + PODC sheet	Cast extrusion then quenching	20 \pm 2	46.1 \pm 0.4	125 \pm 45

The biodegradability rate of PLA4060D with PODC was compared to microcrystalline sample (Figure 1). It appears that the PLA sample formulated with PODC was slightly biodegraded faster and reaches the same level as the microcrystalline sample for the same duration.

Figure 1 Biodegradation of PLA 4060D + PODC film and microcrystalline cellulose



(—) cellulose reference (---) PLA 4060D + PODC cast extruded film

The overall migrations were tested at 5 $^{\circ}\text{C}$ and 40 $^{\circ}\text{C}$ by immersion of the sample in food simulants (vegetable oil, acetic acid 3% (v/v) and ethanol 50% (v/v)) defined in the EU Regulation on Food Contact Material. PLA 4060D + PODC complied with the EU regulation at 5 $^{\circ}\text{C}$ whatever the simulant and with vegetable oil at 40 $^{\circ}\text{C}$.

Conclusions

Vegetable oil deodorization condensates were used to enhance the elongation at break of polylactide (PLA) film up to 130 % while maintaining its stiffness and ecological advantages. Due to its processing aid abilities, the extrusion temperatures were significantly lowered allowing performing blown film extrusion as well as the cast one. Films specifications including biodegradability and overall migration in food simulants were assessed, defining the product about prospective applications as food packaging in particular for fatty foods and dairy products. These results allowed taking out a patent (3)

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