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Industrial vegetable oil by-products increase the ductility of polylactide

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Abstract. The use of industrial by-products of the vegetable oil industry as ductility increasing additives of polylactide (PLA) was investigated. Vegetable oil deodorization condensates were melt-blended by twin-screw extrusion up to a maximum inclusion quantity of 20 wt% without preliminary purification. Sample films were obtained by single screw cast extrusion. Compounded PLA films featured largely improved ductility in tensile testing with an elongation at break up to 180%. The glass transition temperature remained higher than room temperature. The native mixture of molecules, which composed the deodorization condensates, had superior performance compared to a synthetic mixture of main compounds. The investigation of the correlation between composition of the additives and the ductility of the PLA blends by Principal Component Analysis showed synergy in property improvement between fatty acids having a melting point below and beyond the room temperature. Furthermore, a compatibilizing effect of molecules present in the native mixture was evidenced. Oil deodorization condensates, which are a price competitive by-product of the vegetable oil industry, are therefore a very promising biobased and biodegradable additive for improving the ductility of PLA.

Keywords: biodegradable polymers, poly(lactic acid), ductility, vegetable oil by-products, crazing

1. Introduction

Biodegradable and/or biobased polymers are widely studied to replace petroleum-based materials with the aim of contributing to higher sustainability of plastics. However, in many cases these new products still do not meet economical or functional requirements to be competitive in commodity applications. Polylactide (PLA) is one of the polymers which can potentially enter high volume markets, mostly in the food packaging [1–3] or textile [4] sector. Polylactide is a biobased and compostable polymer [5–7] issued from polymerization of lactic acid produced by fermentation of starch, potatoes or beets [7, 8]. Although it has been known before [9], production cost reduction in the 1990s and 2000s thanks to breakthroughs in the polymerization technology [10, 11], made it economically competitive with petroleum-based materials. PLA offers many interests such as a glass transition higher than room temperature, ease of processing, high transparency, printability, glossy aspect [1, 12, 13]. However, its mechanical properties still remain an obstacle for many applications. In fact, PLA features high tensile strength and modulus but also high brittleness [14]. In order to enhance the PLA ductility, melt-blending with rubbery materials as poly(ether)urethane [15,

16], polyamide elastomer [17], acrylonitrile-butadiene-styrene copolymer, or various impact modifiers [18–26] is effective. Furthermore, plasticizers such as citrate esters [27–37], polyethylene glycols [27, 33, 38–44] or manifold other molecules [29, 43, 45–48] can be used. Unfortunately, impact modifiers are often not biodegradable nor biobased and plasticizers are generally derived from fossil resources, degrading one important environmental advantage of employing PLA. Therefore biobased and biodegradable additives have been and are investigated for toughening PLA. Chemically modified vegetable oils have received important research interest, because ester or epoxy groups can be degraded by microorganisms [49], maintaining the biodegradability of blends with PLA. Polymerized soybean oil derivatives prepared by crosslinking double bonds of alkyl chains afforded ductility increase after melt-blending with PLA and using a compatibilizer [50]. Improvements were also obtained with conjugated soybean oil which was reactively compatibilized with PLA by unsaturated triglycerides [51]. Epoxidized soybean oil [52–55] and epoxidized palm oil [56–58] also showed some positive effects on PLA toughness. Another approach consists in using rigid particles, which usually increased stiffness but is ineffective, or even detrimental for the ductility. Nonetheless, NatureWorks [59] reported the use of EMforce®, a mineral additive, able to change the polymer failure mode from brittle to ductile. In fact, the efficient crack initiation in glassy PLA, which was provided by the well-dispersed additive with good interfacial adhesion to the matrix, enhanced the PLA elongation at break.

Expertise from plasticizing polyvinylchloride teaches that mixtures of different plasticizers are efficient for increasing toughness, because they make use of different mechanisms available for ductility improvement [49]. For example, a mixture of tributyl citrate (TBC) and a block copolymer PLA-g-polyethyleneglycol yielded a material with high elongation at break and satisfying stress at yield [30]. Al-Mulla *et al*. [55] successfully used modified nanoclays in combination with epoxidized soybean oil to increase stiffness and ductility. The combination of PLA with rubber and compatibilizers has also been investigated by several authors, showing important gains in ductility, with an elongation at break of up to 160% for high rubber concentrations [60] or bicontinous phases [61], and up to 200% when using

compatibilizers [62, 63]. However, these solutions often require the inclusion of several additives, chemically modified and costly components that increase the price of the final formulation, which is inappropriate for a large volume production. Finding a low cost biobased and biodegradable toughening agent would therefore help PLA to conquer new markets.

Vegetable oils contain a number of potentially interesting molecules for PLA toughening and the refinery of vegetable oils gives rise to several by-products. Among those, oil deodorization condensates represent a high-volume by-product, which is chemically close to the vegetable oil. They are obtained by distillation in the aim of purifying the raw oil from odorous compounds, which are negative for the sensorial properties of vegetable oils. Deodorization condensates contain free fatty acids, glycerides and unsaponifiable molecules. The objective of this study was to use vegetable oils and the by-product deodorization condensate as produced for toughening PLA. The individual molecules which make up oils and deodorization condensates were tested on the mechanical properties and several vegetable oils were screened.

2. Experimental
2.1. Materials
PLA 4060D was supplied by NatureWorks (U.S.A.) and consists of 89±1% L-lactic acid and 11±1% D-lactic acid units, making it unable to crystallize under common conditions [1, 64]. The glass transition temperature (T_g) obtained from differential scanning calorimetry (DSC) measurements was 56°C. Average molecular weights obtained from size exclusion chromatography (SEC) measurements were M_w = 236 800 g·mol^{-1}, M_n = 103 700 g·mol^{-1} and dispersity M_w/M_n = 2,28.

Hydrogenated palm oil (HPO), Hydrogenated Copra Oil (HCO), Rapeseed Oil Deodorization Condensate (RODC), Soybean Oil Deodorization Condensate (SODC), Olive Oil Deodorization Condensate (OODC) and Palm Oil Deodorization Condensate (PODC) were supplied by ITERG (Bordeaux, France).

Palmitic acid (purity >98%) *i.e.* hexadecanoic acid (C16:0), oleic acid (purity >96%) *i.e.* 9-octadecenoic acid (C18:1), squalene (purity >98%) *i.e.* (6E,10E,14E,18E)-2,6,10,15,19,23-hexamethyltetracosa-2,6,10,14,18,22-hexaene, and alpha-toco-

pherol (purity >96%) *i.e.* (2R)-2,5,7,8-tetramethyl-2-[(4R,8R)-(4,8,12-trimethyltridecyl)]-6-chromanol, were supplied by Sigma-Aldrich (France).

2.2. Film fabrication

Prior to melt-blending, PLA pellets were dried at 60°C for 24 h under dried air using a SOMOS 60L. Relative humidity of dried pellets was controlled to be lower than 350 ppm using an Aboni FMX Hydrotracer (France). Melt-mixing of PLA with or without additives was carried out using a twin screw extruder (Thermo Haake Ptw 16-40D, France), having a screw diameter of 16 mm and a length to diameter ratio (*L/D*) 40:1. A temperature of 180°C was used to process by twin-screw extrusion the PLA pellets as reference material, while the temperature profile of the 7 heating zones decreased from 180 to about 150/130°C along the extrusion flow, depending on the nature and the amount of additive. Screw

speed was 300 rpm. The exact temperature profile for each formulation is given in Table 1. To properly control the feed rate of additives, which are solid at room temperature, a home-made apparatus consisting in a heated syringe was used. Obtained pellets were stored into hermetic sealed metalized bags to avoid PLA rehydration.

Films of about 0.8 mm thickness containing palmitic acid, oleic acid, hydrogenated palm oil, hydrogenated copra oil, squalene, α-tocopherol and some combinations of these products were obtained using a single screw extruder (Scamex Rheoscam, France), mounted with a screw of 20 mm diameter and a length to diameter ratio (*L/D*) 12:1 and a flat die of 40 mm width and 1 mm thickness. Films were stretched and cooled with chill rolls. Due to the short length of the screw, an increasing temperature profile from 180 to 195°C over the 3 heating zones was used for PLA, while it was decreasing from 180

Table 1. Processing conditions of melt-mixing twin screw extrusion

Formulation		Temperature profile [°C]
Neat PLA		175/180/190/190/190/190/180
PLA + 10 wt% C16:0		175/180/180/170/170/170/170
PLA + 10 wt% C18:1		175/180/180/170/170/170/170
PLA + 10 wt% [50 wt% C16:0 + 50 wt% C18:1]		175/180/180/170/170/170/170
PLA + 10 wt% [95 wt% (50 wt% C16:0 + 50 wt% C18:1) + 5 wt% HPO]		175/180/180/170/170/170/170
PLA +	5 wt% HCO	175/180/180/180/180/170/170
	10 wt% HCO	175/180/180/180/180/170/170
	15 wt% HCO	175/180/180/180/170/170/160
PLA +	5 wt% HPO	175/180/180/180/180/170/170
	10 wt% HCO	175/180/180/180/180/170/170
	15 wt% HCO	175/180/180/180/180/170/170
PLA +	5 wt% α-tocopherol	175/180/180/180/180/180/180
	10 wt% α-tocopherol	175/180/180/180/180/180/170
	15 wt% α-tocopherol	175/180/180/180/180/170/170
PLA +	5 wt% squalene	175/180/180/180/180/180/180
	10 wt% squalene	175/180/180/180/180/170/170
	15 wt% squalene	175/180/180/180/180/170/170
PLA +	5 wt% RODC	175/180/180/180/180/175/170
	10 wt% RODC	175/180/180/180/180/170/160
	15 wt% RODC	175/180/180/180/180/170/160
	20 wt% RODC	175/180/180/180/170/160/150
PLA +	5 wt% SODC	175/180/180/180/180/175/170
	10 wt% SODC	175/180/180/180/180/170/160
	15 wt% SODC	175/180/180/180/180/170/160
	20 wt% SODC	175/180/180/180/170/160/150
PLA +	5 wt% OODC	175/180/180/170/170/170/170
	10 wt% OODC	175/180/180/170/170/170/170
	15 wt% OODC	175/180/180/170/170/160/160
	20 wt% OODC	175/180/180/170/160/150/150
PLA +	5 wt% PODC	175/180/180/180/180/175/170
	10 wt% PODC	175/180/180/180/170/160/155
	15 wt% PODC	175/180/180/180/170/160/150
	20 wt% PODC	175/180/180/170/160/150/135

Table 2. Processing conditions of cast films extrusion

Formulation		Temperature profile [°C]	Die temperature [°C]
Neat PLA		180/190/195	185
PLA + 10 wt% C16:0		180/180/175	170
PLA + 10 wt% C18:1		180/180/175	170
PLA + 10 wt% [50 wt% C16:0 + 50 wt% C18:1]		180/180/175	170
PLA + 10 wt% [95 wt% (50 wt% C16:0 + 50 wt% C18:1) + 5 wt% HPO]		180/180/175	170
PLA +	5 wt% HCO	180/180/180	180
	10 wt% HCO	180/170/170	170
	15 wt% HCO	180/170/170	170
PLA +	5 wt% HPO	180/180/180	170
	10 wt% HPO	180/170/170	170
	15 wt% HPO	180/170/170	170
PLA +	5 wt% α-tocopherol	180/180/180	180
	10 wt% α-tocopherol	180/180/180	180
	15 wt% α-tocopherol	180/175/170	170
PLA +	5 wt% squalene	180/180/180	180
	10 wt% squalene	180/180/175	170
	15 wt% squalene	180/180/170	170

to about 170°C for blends. The specific temperatures depending on the nature and the amount of additive are given in Table 2.

In the case of the deodorization condensates of the vegetable oils (RODC, SODC, OODC, PODC), the available quantity was insufficient for carrying out a single screw extrusion in the aim to obtain films. In that case PLA sheets of 1 mm thickness were thermo-moulded by compression at 220 bar (Laboratory Press Gibitre Instruments 20 tons, Italy). For this, pellets were pre-melted at 180°C without pressure during 180 seconds then heating plates were closed with progressive increase in pressure during 120 seconds to eliminate air bubbles.

2.3. Chemical and physical chemical characterization of vegetable oils and deodorization condensates

Glyceride composition of fats was determined according to the IUPAC 6.002 and EN 14105 standards using a Shimadzu GC-2010 Plus gas chromatograph (France) equipped with a Zebron ZB 5 HT Inferno (15 m, 0.25 mm, 0.1 μm) column and a flame ionization detector set at 380°C. The vector gas was H_2 at a flow rate of 1.17 mL·min^{-1}. Both the injector and the oven temperature were set at 60°C for 3 min, then raised to 370°C at 10°C·min^{-1} and held at 370°C for 12 min. Direct on-column injection was performed.

Fatty acid composition was determined according to the ISO 12966-2 standard using a Shimadzu GC-2010 Plus gas chromatograph (France) equipped with a BPX70 (50 m, 0.22 mm, 0.25 μm) column, and a flame ionization detector set at 250°C. The vector gas was H_2 at a flow rate of 0.32 mL·min^{-1}. The oven temperature was set at 60 C for 2 min, raised to 170°C at 20°C·min^{-1}, held at 170°C for 25 min, raised to 230°C at 4°C·min^{-1} and held at 230°C for 10 min. The injector temperature was set at 250°C and a split ratio of 200 was used.

Acid value was determined according to the ISO 660 standard using a mixture of ethanol 95% and diethylic ether as solvent, potassium hydroxide 0.5 mol·L^{-1} in ethanol 95% as titrant and alkali blue 6B as indicator.

Saponification value was determined according to the ISO 3657 standard. Samples were saponified with potassium hydroxide 0.5 mol·L^{-1} in ethanol 95% boiled under reflux during 2 h. Hydrochloric acid 0.5 mol·L^{-1} was used as titrant and alkali blue 6B as indicator.

Water content was measured using a Mettler Toledo HB43 S Halogen Moisture Analyzer set (France) at 103°C.

Melting point of free fatty acids was determined from literature [65]. Estimation of mono, di- and triglycerides average chemical structure of oil deodorization condensates was based on the averages unsaturation number and the alkyl chains length of the corresponding free fatty acids composition profile (Table 3). Average glycerides melting point was estimated calculating a weighted average of the

Table 3. Composition of hydrogenated vegetable oils and vegetable oil deodorization condensates

Type		HPO	HCO	RODC	SODC	OODC	PODC
Glyceride composition [%]	Free fatty acids	0.0	0.0	39.0	43.1	39.2	95.4
	Monoglycerides	0.2	0.0	11.2	2.9	2.0	1.7
	Diglycerides	10.6	0.0	2.7	9.0	8.4	2.2
	Triglycerides	88.9	100	12.2	16.8	33.5	0.7
	Sterols (α-tocopherol)	0.0	0.0	25.7	9.8	1.6	0.0
	Hydrocarbons (Squalene)	0.0	0.0	0.0	13.8	13.0	0.0
	Unidentified	0.3	0.0	9.2	4.6	2.3	0.0
Acid value [mg KOH·g^{-1}]		0.1	0.1	65.3	68.4	47.7	201.0
Saponification value [mg KOH·g^{-1}]		198.6	255.2	125.1	157.9	162.2	205.7
Water content [%]		0.11	0.10	0.55	0.34	0.37	0.16
Fatty acid composition [%]	Caproic acid C6:0	0.0	0.5	0.0	0.0	0.0	0.0
	Caprylic acid C8:0	0.0	6.8	0.0	0.0	0.0	0.0
	Capric acid C10:0	0.0	5.7	0.0	0.0	0.1	0.0
	Lauric acid C12:0	0.5	47.5	0.0	0.8	0.0	0.4
	Myristic acid C14:0	1.2	18.1	0.0	0.4	0.0	1.3
	Palmitic acid C16:0	43.6	9.4	7.4	12.3	11.3	49.8
	Palmitoleic acid C16:1	0.0	0.0	0.0	0.0	0.0	0.2
	Stearic acid C18:0	53.8	10.8	3.4	4.1	2.5	4.1
	Oleic acid C18:1	0.0	1.0	27.3	21.7	69.5	35.2
	Linoleic acid C18:2	0.0	0.0	42.4	49.7	10.9	7.8
	Linolenic acid C18:3	0.0	0.0	1.5	6.4	0.6	0.3
	Arachidic acid C20:0	0.5	0.1	0.5	0.3	0.4	0.3
	Eicosenoic acid C20:1	0.0	0.0	0.3	0.2	0.4	0.1
	Behenic acid C22:0	0.1	0.0	1.0	0.5	0.0	0.0
	Lignoceric acid C24:0	0.1	0.0	0.5	0.2	0.1	0.0
	Unidentified	0.5	0.1	0.2	15.7	13.4	4.2
Average alkyl chain carbon quantity		17.1	13.0	17.9	17.7	17.8	16.9
Average alkyl chain unsaturation quantity		0.0	0.0	1.4	1.5	1.0	0.5

specific melting points of the contained molecules taken from references [65–67]. Physical properties of molecules are given in Table 4.

2.4. Calculation of solubility parameters

Molar volumes and molar attraction constants of polylactide and additives were determined according to the van Krevelen and Hoftyzer atomic group contribution method [68]. Average molar volumes and average molar attraction constants of mono, di and triglycerides of oil deodorization condensates were estimated based on average chemical structures previously determined.

Hansen Solubility parameters were calculated using Equations (1), (2) and (3) [69, 70]. Used molar constant values [68] are presented in Table 5:

$$\delta_d = \frac{\sum F_{dt}}{\sum V_i} \tag{1}$$

$$\delta_p = \frac{\sqrt{\sum F_{Pi}^2}}{\sum V_i} \tag{2}$$

$$\delta_h = \frac{\sqrt{\sum E_{hi}}}{\sum V_i} \tag{3}$$

where δ_d is the dispersion component of the solubility parameter in J$^{1/2}$·cm$^{-3/2}$, δ_p the polar component of the solubility parameter in J$^{1/2}$·cm$^{-3/2}$, δ_h the hydrogen bonding component of the solubility parameter in J$^{1/2}$·cm$^{-3/2}$, F_d the dispersion contribution of the molar attraction constant in (J$^{1/2}$·cm$^{-3/2}$)·mol^{-1}, F_p the polar contribution of the molar attraction constant in (J$^{1/2}$·cm$^{-3/2}$)·mol^{-1}, E_h the hydrogen bonding energy contribution of the molar attraction constant in J·mol^{-1} and V the molar volume contribution of the chemical group involved in cm^3·mol^{-1}.

The solubility of the molecules in PLA (Table 4) was assessed using the HSP Relative Energy Difference (RED) from Equations (4) and (5):

$$Distance = \sqrt{4(\delta_{d_{molec}} - \delta_{d_{PLA}})^2 + (\delta_{P_{molec}} - \delta_{P_{PLA}})^2 + (\delta_{h_{molec}} - \delta_{h_{PLA}})^2} \tag{4}$$

$$RED = \frac{Distance}{Radius} \tag{5}$$

Table 4. Physical properties and solubility parameters of fatty acids, mono-, di-, and triglycerides contained in the hydrogenated vegetable oils and oil deodorization condensates

			Molar weight [g·mol⁻¹]	Molar volume [cm³·mol⁻¹]	Melting point [°C]	Hansen Solubility Parameters (HSP)			Distance with PLA	RED with PLA
						δ_d [J$^{1/2}$·cm$^{-3/2}$]	δ_p [J$^{1/2}$·cm$^{-3/2}$]	δ_h [J$^{1/2}$·cm$^{-3/2}$]		
PLA 4060D			242800	–	–	18.6	9.9	6.0	(radius: 10.7)	–
Free fatty acids	Caproic acid	C6:0	116	126	–3[a]	16.06	3.32	8.89	8.80	0.82
	Caprylic acid	C8:0	144	159	16[a]	16.20	2.65	7.94	8.91	0.83
	Capric acid	C10:0	172	191	31[a]	16.30	2.20	7.24	9.05	0.85
	Lauric acid	C12:0	200	223	44[a]	16.37	1.88	6.70	9.20	0.86
	Myristic acid	C14:0	228	255	55[a]	16.42	1.65	6.26	9.34	0.87
	Palmitic acid	C16:0	256	287	63[a]	16.46	1.46	5.90	9.46	0.88
	Palmitoleic acid	C16:1	254	282	1[a]	16.27	1.49	5.95	9.62	0.90
	Stearic acid	C18:0	285	320	70[a]	16.49	1.31	5.59	9.58	0.89
	Oleic acid	C18:1	283	314	13[a]	16.32	1.34	5.64	9.71	0.91
	Linoleic acid	C18:2	280	309	–9[a]	16.14	1.36	5.69	9.86	0.92
	Linolenic acid	C18:3	278	304	–14[a]	15.95	1.38	5.74	10.03	0.94
	Arachidic acid	C20:0	313	352	75[a]	16.52	1.19	5.33	9.68	0.90
	Eicosenoic acid	C20:1	311	347	23[a]	16.36	1.21	5.37	9.80	0.92
	Behenic acid	C22:0	341	384	80[a]	16.54	1.09	5.10	9.77	0.91
	Lignoceric acid	C24:0	369	416	84[a]	16.55	1.01	4.90	9.85	0.92
Monoglycerides	HPO	(HO)$_2$–Gly–(C17.1:0)	346	346	68–76[b]	17.14	2.49	11.66	9.77	0.91
	RODC	(HO)$_2$–Gly–(C17.9:1.4)	354	351	10–22[b]	16.92	2.45	11.56	9.89	0.92
	SODC	(HO)$_2$–Gly–(C17.5:1.5)	351	348	8–18[b]	16.56	2.47	11.63	10.17	0.95
	OODC	(HO)$_2$–Gly–(C17.8:1.0)	354	352	25–32[b]	16.98	2.44	11.56	9.84	0.92
	PODC	(HO)$_2$–Gly–(C16.9:0.5)	342	340	45–55[a, c]	17.07	2.53	10.00	8.93	0.83
Diglycerides	HPO	HO–Gly–(C17.1:0)$_2$	600	630	65–72[b]	16.82	1.36	7.34	9.35	0.87
	RODC	(HO)–Gly–(C17.9:1.4)$_2$	617	642	2–12[b]	16.59	1.33	6.49	9.48	0.89
	SODC	(HO)–Gly–(C17.7:1.5)$_2$	611	634	–4–8[b]	16.57	1.35	7.32	9.56	0.89
	OODC	(HO)–Gly–(C17.8:1.0)$_2$	615	643	10–20[b]	16.66	1.33	7.27	9.50	0.89
	PODC	(HO)–Gly–(C16.9:0.5)$_2$	592	619	42–48[b]	16.74	1.38	7.41	9.41	0.88
Triglycerides	HCO	Gly–(C13:0)$_3$	681	717	8–42	16.68	1.18	5.41	9.54	0.89
	HPO	Gly–(C17.1:0)$_3$	854	915	62–66[c]	16.70	0.93	4.79	9.82	0.92
	RODC	Gly–(C17.9:1.4)$_3$	879	932	–30––26[c]	16.46	0.91	4.75	10.03	0.94
	SODC	Gly–(C17.7:1.5)$_3$	870	921	–32––28[c]	16.44	0.92	4.78	10.04	0.94
	OODC	Gly–(C17.8:1.0)$_3$	877	933	–14––10[c]	16.53	0.91	4.74	9.98	0.93
	PODC	Gly–(C16.9:0.5)$_3$	842	898	15–25[c]	16.61	0.95	4.84	9.87	0.92
Others	α-tocopherol	–	431	436	2[a]	17.63	1.47	7.27	8.74	0.82
	Squalene	–	411	477	–7[a]	16.10	0.00	0.00	12.61	1.18

[a]from [65], [b]from [66], [c]from [67]

Table 5. Used group contribution molar constants

Group	F_d $[(J^{1/2} \cdot cm^{-3/2}) \cdot mol^{-1}]$	F_p^2 $[(J \cdot cm^{-3}) \cdot mol^{-1}]$	E_h $[J \cdot mol^{-1}]$	Molar volume $[cm^3 \cdot mol^{-1}]$
–CH₃	420	0	0	33.5
–CH₂–	270	0	0	16.1
=CH–	200	0	0	13.5
>CH–	80	0	0	−1.0
>C<	−70	0	0	−1
=C<	70	0	0	−5.5
–COO–	390	240 100	7 000	18
–COOH	530	176 400	10 000	28.5
–OH	210	250 000	20 000	10
Ring	190	0	0	16

where δ_d, δ_p, and δ_h are the components of the solubility parameter of the molecules and the PLA obtained from Equations (1), (2) and (3), where the radius value is the maximal distance obtained from [71] beyond which the molecules are not miscible anymore with the polymer. Therefore, the closer the RED value to zero, the better the compatibility. A RED value higher than 1 means a theoretical non-miscibility of the additive with PLA.

2.5. Physical-chemical characterization PLA blends

Differential Scanning Calorimetry (DSC) analyses were performed using a Mettler Toledo (France) DSC1 STARe System under nitrogen atmosphere (50 mL·min⁻¹) in 40 µL standard Aluminum pans (Mettler). Calibration of the device was done using Indium and Zinc standards. Calorimetric scans of additives were performed from –80 to 220°C at a heating rate of 2°C·min⁻¹. Experiments were carried out in duplicate. Calorimetric scans of blended PLA samples were done at a heating/cooling rate of 10°C·min⁻¹. The first heating scan for sample rejuvenation was performed from 25 to 75°C with an isotherm at 75°C during 2 min. Then, the cooling scan was from 75 to –20°C and the second heating scan from –20 to 100°C. The glass transition temperature (T_g) was taken at the midpoint of the second heating scan. Experiments were done in triplicate.

Tensile properties were investigated at 23°C, relative humidity (RH) 50±10 % and cross-head speed of 25 mm·min⁻¹, using an universal tensile machine (Instron model 4301, France) equipped with a load cell 1000±1 N and without extensiometer. The dog bone shaped samples (ISO 527-2, type 5A) were directly cut from the materials. Prior to tensile testing, samples were conditioned at 23°C and 50±10% RH for at least 72 h. Each mechanical characteristic value is an average of 8 measurements.

Uniaxial deformation under an optical microscope was done in cutting rectangular samples of 20 mm length, 4 mm width, and 0.8 mm thickness from blank PLA, PLA + 10 wt% C16:0, PLA + 10 wt% C18:1 and PLA + 10 wt% PODC films. They were stretched at 5 mm·min⁻¹ using a homemade tensile machine placed under an Olympus Japan optical microscope mounted with WHK 10×/20 L ocular lens and MD Plan 10 0.25 objective lens. Observations were performed in optical transmission light mode using a Sony CCD-IRIS Model DXC-107P camera (France).

The morphology of the dispersed phase of PLA + 10 wt% C16:0, PLA + 10 wt% C18:1 and PLA + 10 wt% PODC materials before and after being stretched was observed with Scanning Electron Microscopy (SEM) (Hitachi 4800 II, France). Observations were directly conducted on the longitudinal surface of the dog bone shaped samples without any previous preparation.

2.6. Principal component analysis (PCA)

PCA was carried out considering the contents of each free fatty acid, mono, di and triglyceride types, hydrocarbons, sterols and water, the acid and saponification values and the measured elongation at break [%], Young modulus and T_g values of the PLA formulations tested. PCA was done with XLstat software.

3. Results and discussion

3.1. Effects of free fatty acids, glycerides, α-tocopherol and squalene on PLA ductility

Individual components present in vegetable oils, which could feature toughening ability for PLA, as free fatty acids, glycerides, and the unsaponifiable

components as α-tocopherol and squalene were tested. In order to achieve the most efficient formulation, the solubility of a molecule in the polymer matrix is one determinant for its plasticizing power [37]. Therefore the Hansen Solubility Parameters (HSP) of each compound was calculated. HSP (Table 4) shows low solubility of the different compounds in the PLA matrix. All the obtained values are close to one, which marks the solubility limit. The highest solubility (although still modest) was displayed by small fatty acids and α-tocopherol. The mechanical and thermal properties of the corresponding compounds are given in Table 6. The raw data of typical stress/strain curves of blends are presented in Figure 1. The DSC thermograms of neat additives in Figure 2 and of blends in Figure 3 for further information.

Literature studies on the use of vegetable oil as toughening agent of PLA showed that generally chemical modification is required to obtain positive effects [50, 52–54, 56–58, 72]. Not surprisingly due to their low solubility in PLA, the impact of the tested fatty acids (C16:0, C18:1), vegetable oils (HPO and HCO) and unsaponifiable compounds on T_g was negligible. However, despite the low solubility of the compounds, PLA ductility was increased in some cases. In particular, HCO, which contains mainly triglycerides, but with short chain length, improved the PLA ductility and lowered the apparent Young modulus, stress and elongation at yield. HPO, which mostly contains triglycerides and some diglycerides with higher chain length did not bring significant ductility enhancement nor T_g decrease. HSP of di- and triglycerides from HPO and triglycerides from HCO

Table 6. Mechanical and thermal properties of formulations

Formulation		Elongation at break [%]	app. Young modulus[a] [MPa]	Elongation at yield [%]	Stress at yield [MPa]	T_g [°C]
PLA (twin screw pellets)		6±1	1760±90	4.2±0.4	64±5	56.3±0.2
PLA + 10 wt% C16:0		4±1	1720±60	3.2±0.1	50±3	49.3±0.1
PLA + 10 wt% C18:1		16±5	1440±50	2.2±0.1	28±2	45.2±0.2
PLA + 10 wt% [50 wt% C16:0 + 50 wt% C18:1]		45±12	1590±80	2.2±0.1	31±2	40.7±0.3
PLA + 10 wt% [95 wt% (50 wt% C16:0 + 50 wt% C18:1) + 5 wt% HPO]		74±15	1550±120	2.2±0.2	25±4	39.8±0.4
PLA +	5 wt% HCO	9±3	1680±70	3.6±0.2	51±1	54.1±0.2
	10 wt% HCO	9±6	1540±80	3.6±0.2	42±2	54.1±0.1
	15 wt% HCO	11±5	1460±70	3.8±0.2	38±2	54.8±0.3
PLA +	5 wt% HPO	55±20	1610±50	2.7±0.1	38±1	52.6±0.2
	10 wt% HPO	85±15	1420±70	2.6±0.2	26±2	54.4±0.4
	15 wt% HPO	91±14	1300±80	2.4±0.1	26±1	53.9±0.3
PLA +	5 wt% α-tocopherol	6±2	1150±90	3.8±0.2	41±4	51.3±0.2
	10 wt% α-tocopherol	5±2	1070±60	4.0±0.4	31±3	49.8±0.2
	15 wt% α-tocopherol	8±3	990±70	3.9±0.3	29±4	47.1±0.2
PLA +	5 wt% squalene	38±7	1180±90	3.3±0.4	36±7	51.4±0.2
	10 wt% squalene	51±9	990±60	3.1±0.9	28±3	49.5±0.2
	15 wt% squalene	29±7	890±80	2.9±0.7	19±2	49.4±0.1
PLA +	5 wt% RODC	22±3	1530±80	3.2±0.2	40±3	52.6±0.2
	10 wt% RODC	55±7	1490±140	2.4±0.2	28±4	49.1±0.1
	15 wt% RODC	65±15	1380±155	2.3±0.3	23±4	48.8±0.1
	20 wt% RODC	73±20	1270±150	2.2±0.3	20±4	48.5±0.3
PLA +	5 wt% SODC	29±8	1550±110	3.3±0.3	41±7	50.6±0.1
	10 wt% SODC	73±18	1510±90	2.3±0.2	25±5	49.4±0.3
	15 wt% SODC	80±13	1340±80	2.2±0.3	23±3	48.7±0.1
	20 wt% SODC	52±15	1220±100	2.1±0.4	16±4	47.5±0.1
PLA +	5 wt% OODC	49±6	1430±90	3.1±0.3	34±4	49.5±0.2
	10 wt% OODC	85±17	1490±90	2.6±0.2	31±2	49.0±0.1
	15 wt% OODC	88±16	1360±70	2.1±0.2	20±3	48.5±0.1
	20 wt% OODC	67±16	1370±110	2.2±0.2	21±3	48.7±0.1
PLA +	5 wt% PODC	51±17	1680±110	2.5±0.2	36±2	45.3±0.1
	10 wt% PODC	132±18	1460±40	2.1±0.2	24±1	39.2±0.2
	15 wt% PODC	179±15	1180±130	2.3±0.3	18±2	35.1±0.2
	20 wt% PODC	84±31	1130±60	2.0±0.4	14±3	33.8±0.2

[a]apparent Young modulus for comparison reasons obtained without extensiometer
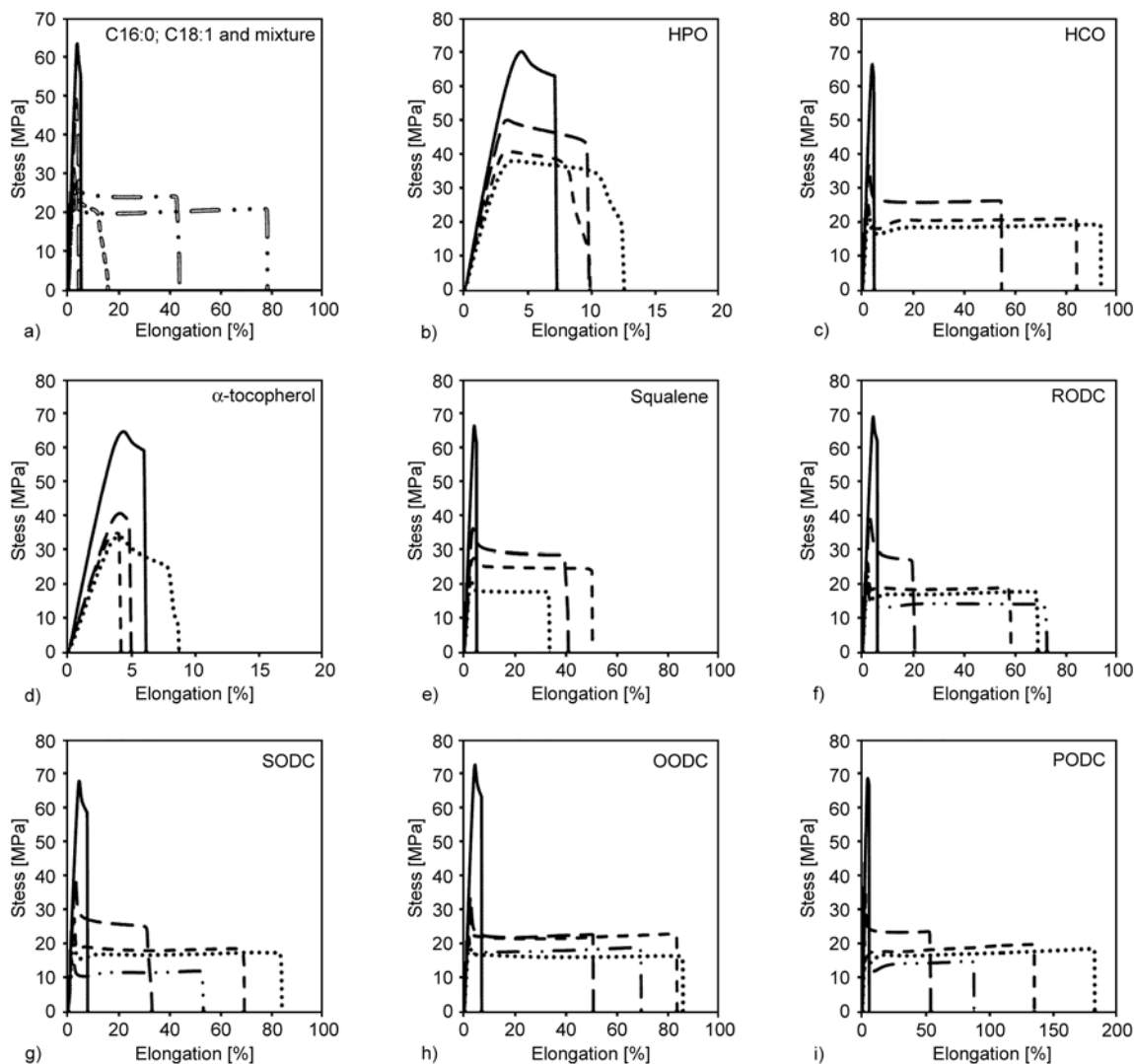
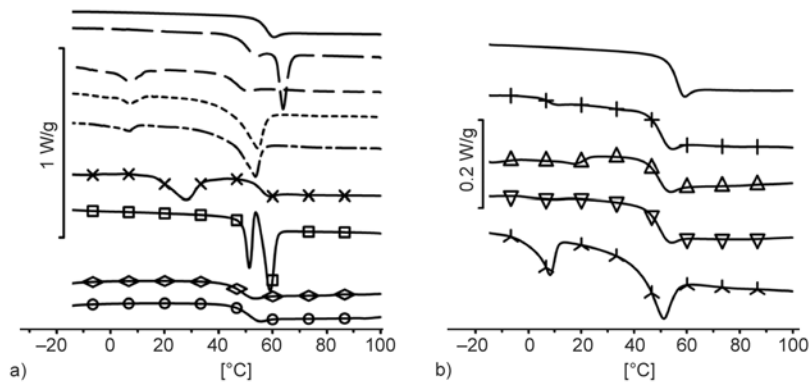**Figure 1.** Stress/strain curves of PLA blends with free fatty acids, hydrogenated vegetable oils (HPO and HCO), unsaponifiable compounds (squalene, α-tocopherol), and vegetable oil deodorization condensates (palm oil PODC, olive oil OODC, soybean oil SODC and rapeseed oil RODC); (——) neat PLA; (== ==) PLA + 10 wt% C16:0; (= =) PLA + 10 wt% C18:1; (== •) PLA+ 10 wt% [50 wt% C16:0 + 50 wt% C18:1]; (== • •) PLA + 10 wt% [95 wt% (50 wt% C16:0 + 50 wt% C18:1) + 5 wt% HPO]; (— —) PLA + 5 wt% additive; (- - -) PLA + 10 wt% additive; (• •) PLA + 15 wt% additive; (— • •) PLA + 20 wt% additive
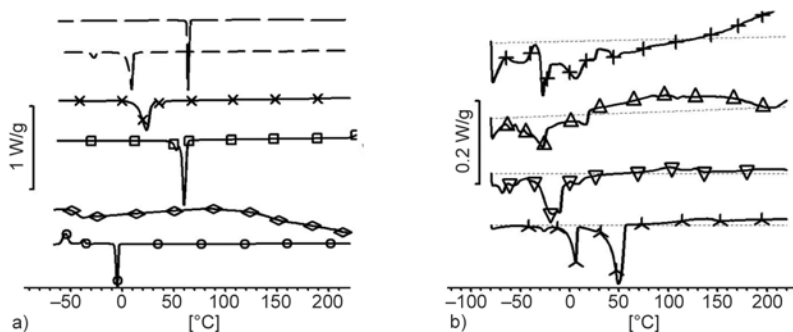
Figure 2. Thermograms (first heating scan) of free fatty acids, hydrogenated vegetable oils (HPO and HCO), unsaponifiable compounds (squalene, α-tocopherol), and vegetable oil deodorization condensates (palm oil PODC, olive oil OODC, soybean oil SODC and rapeseed oil RODC); (— —) C16:0; (– –) C18:1; (×) HCO; (□) HPO; (◊) α-tocopherol; (○) squalene; (+) RODC; (Δ) SODC; (▽) OODC; (⤴) PODC

Figure 3. Thermograms (second heating scan) of PLA blends with free fatty acids, hydrogenated vegetable oils (HPO and HCO), unsaponifiable compounds (squalene, α-tocopherol), and vegetable oil deodorization condensates (palm oil PODC, olive oil OODC, soybean oil SODC and rapeseed oil RODC); (—) neat PLA; (— —) PLA + 10 wt% C16:0; (– –) PLA + 10 wt% C18:1; (- - -) PLA + 10 wt% [50 wt% C16:0 + 50 wt% C18:1]; (— -) PLA + 10 wt% [95 wt% (50 wt% C16:0 + 50 wt% C18:1) + 5 wt% HPO]; (×) PLA + 10 wt% HCO; (□) PLA + 10 wt% HPO; (◊) PLA + 10 wt% α-tocopherol; (○) PLA + 10 wt% squalene; (+) PLA + 10 wt% RODC; (Δ) PLA + 10 wt% SODC; (▽) PLA + 10 wt% OODC; (⅄) PLA + 10 wt% PODC

were close, while the average molar volume and molecular weight of triglycerides from HCO are smaller than the ones from HPO (Table 2). Testing of single fatty acids with longer chain length (C16:0, C18:1) showed that they were not able to increase PLA ductility. This is coherent with existing literature. For example, Jacobsen and Fritz [73] studied PLA blends with fatty acid esters. No significant ductility improvement was observed. The blending with the unsaponifiable compound α-tocopherol showed small gains in elongation at break, which extends already existing knowledge. It was already shown that the use of α-tocopherol as a natural antioxidant in PLA at small quantities (<4 wt%) induced a slightly T_g decrease [74] but no increase in elongation at break [75]. Here, no elongation at break improvement upon was found using greater α-tocopherol amounts, despite solubility was assessed to be higher than other molecules (such as HPO and HCO, Table 4) and a T_g decrease was observed (Table 3). Squalene, which is a natural tri-terpene found in vegetable oils, showed some toughening abilities (Table 6) despite its low solubility in PLA (Table 4). In fact, the creation of a dispersed phase promoting crazing was most probably responsible for this effect [37].

The most interesting result was obtained upon mixing different compounds. A mix of C18:1 and C16:0 fatty acids increased the PLA ductility much more than using them separately. The Young modulus and the T_g remained higher than using only C18:1 likely because of its lower content involved, while the stress and elongation at yield were lessened as much as adding only C18:1. Mixture made of [95 wt% (50 wt% C16:0 + 50 wt% C18:1) + 5 wt% HPO] at a total content of 10 wt% in PLA, further enhanced the ductility. There was apparently a synergistic effect between compounds, which can be possibly exploited.

3.2. Properties of PLA blends with vegetable oil deodorization condensates

Deodorization oil condensates are mixtures of different molecules contained in vegetable oils, the composition of which depends on the botanic source and oil refinery process. Four kinds of oil deodorization condensates (RODC, SODC, OODC and PODC) were blended with PLA, each at four concentrations (5, 10, 15 and 20 wt%). As shown in Table 3, content in free fatty acids, mono di or triglycerides, sterols (mainly alpha-tocopherol) and hydrocarbons (mainly squalene) was highly variable, as well as unsaturation degree of fatty acids. From the composition, an average HSP was calculated and is given in Table 4. As observed in Table 4, the longer and/or more unsaturated the alkyl chain is, the lower the solubility in PLA. However, except for very short fats alkyl chains and organic compounds as α-tocopherol or squalene, HSP of involved molecules appear to be rather similar. Mechanical and thermal properties of PLA/oil deodorization condensates blends are given in Table 6 and typical curves of raw data are shown in the Figure 1. Significant increases in elongation at break were obtained, especially with the PODC. Addition of too much additive, *i.e.* about 20 wt%, induced a stagnation or decrease in the elongation at break. All the deodorization condensates led to a

lowering in the stress and elongation at yield. Interestingly, the apparent Young modulus of materials remained high. The stress/strain curves (Figure 1) showed that the yielding peak shrunk and flattened with the increase in additive content, as if the yield critical stress would tend to meet the plateau value where the stress remains constant with the strain. There is thus an important gain of using native mixtures of fatty acids present in deodorisation condensates for PLA ductility increase.

3.3. Study of the deformation mechanisms involved in PLA/oil deodorization condensates blends

In all samples the T_g remained higher than the measurement temperature, the main deformation mechanism was thus crazing of the glassy polymer [37]. The yield process in glassy amorphous polymers can be described as a stress induced glass-transition. In fact, because PLA Poisson's ratio is less than 0.5 ($v_{PLA} = 0.36$) [76], the volume of PLA increases when subjected to tensile stress. Correspondingly, samples experienced important stress whitening, which appeared simultaneously with yielding. Stress whitening is caused by the formation of sizeable microvoids in the polymer matrix due to cavitation and crazes [77]. Crazes can also be initiated inside non-miscible inclusions in the polymer matrix or on the interface between inclusion and polymer in the case of low compatibility. The addition of oil deodorization condensates initiated crazes at stress levels substantially below those of the brittle failure of neat PLA, which propagated perpendicularly to the stretching direction. Morphological analysis of the form and size of inclusions of PODC, C16:0 and C18:1 was done to help interpretation. Figure 4 shows SEM micrographs of [PLA/C16:0], [PLA/C18:1] and [PLA/PODC] 90 wt%/ 10 wt% blends. [PLA/C16:0] blends exhibit rods of about 5 to 10 µm length and 1 to 2 µm width, corresponding to fatty acid crystals. [PLA/C18:1] showed small spher-

ical domains of fatty acids of about 0.5 µm diameters and some aggregates of about 3 to 5 µm diameters. The [PLA/PODC] blend micrograph showed both rods and aggregates of droplets, where the droplets appear to be distributed all around the crystals.

Figure 5 shows optical micrographs in transmission mode of stretched samples under the microscope taken at different percentages of elongation. Many small cracks started appear in neat PLA when approaching the yield peak, which is common for glassy amorphous polymers. Addition of C16:0, *i.e.* rod like crystals, increased both the occurrence and the length of cracks. Cracks quantity upon stretching caused the material to become opaque.

Failure of the blend revealed PLA fibrils. C18:1, *i.e.* small spherical liquid domains, induced fewer but much larger cracks as if their extensibility was eased. PODC, *i.e.* mostly a combination of C16:0 and C18:1 and some minor constituents, showed a high number of cracks but with smaller width as if using only C18:1. The mixture of palmitic acid crystals and liquid inclusions of oleic acid had thus a synergistic effect allowing for efficient craze initiation by the crystals and by cavitation inside the liquid inclusions. The superior performance of the PODC blends seems thus to be linked to the chemical composition in fatty acids and the presence of the minor constituents.

3.4. Role of the chemical composition of deodorization condensates in PLA ductility improvement

A Principal Components Analysis (PCA) was carried out including composition data and physico-chemical characteristics of the deodorization condensates and of the PLA samples. Figure 6 shows the principal components projection plot of F1 and F2 of the data set. Only 50% of the total variance in these PLA samples is extracted according to F1 and F2 axes. In fact, scores of formulations containing
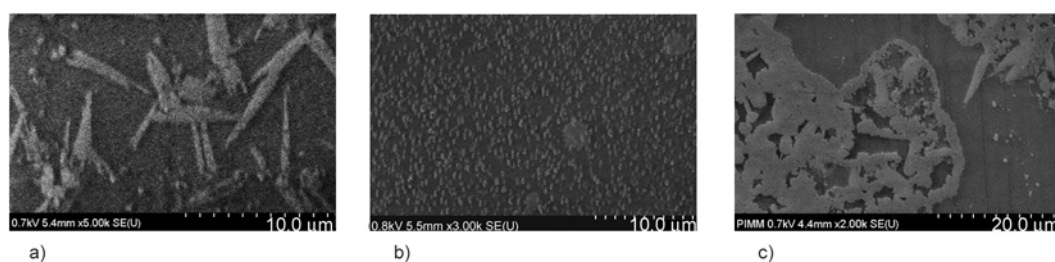

Figure 4. SEM micrographs of (a) C16:0, (b) C18:1 and (c) PODC blends with PLA at 10 wt%
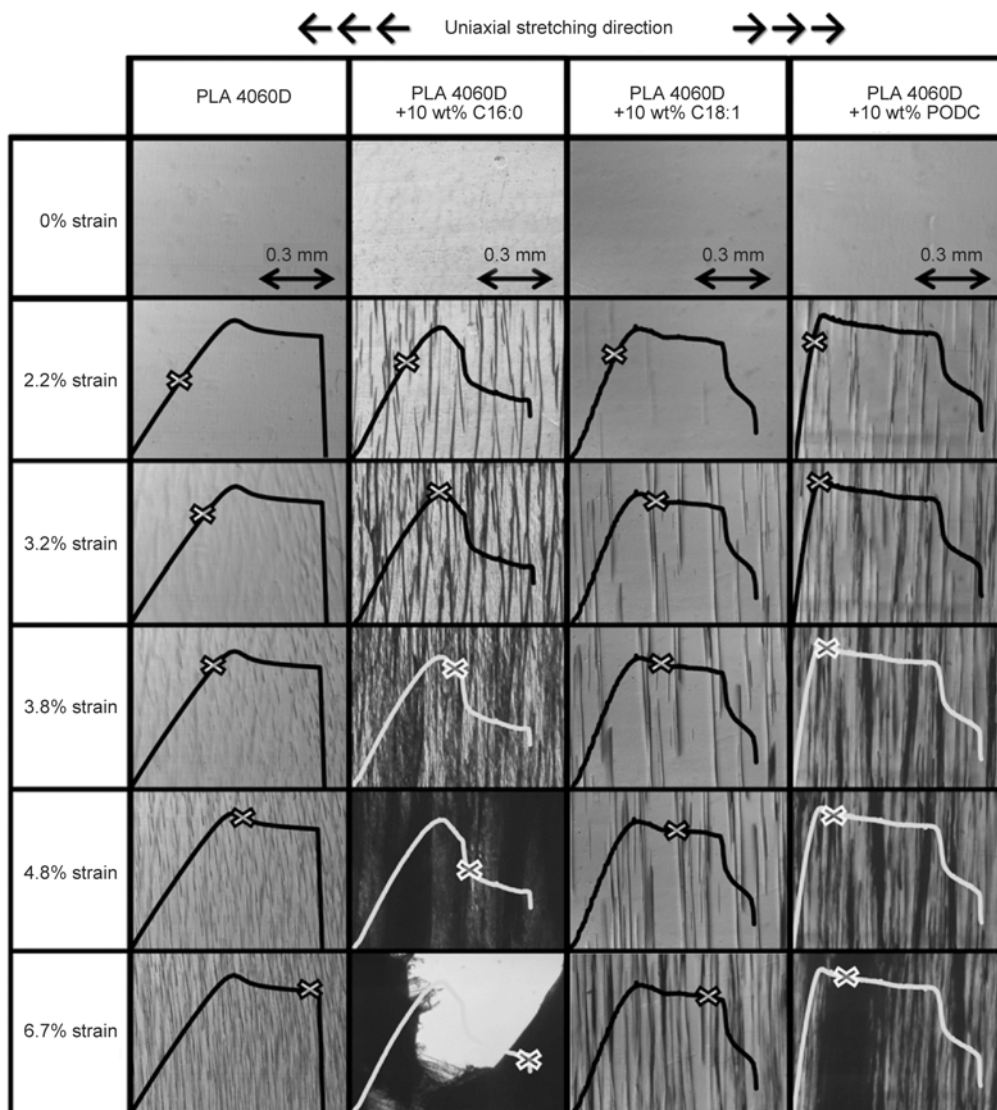
Figure 5. Optical micrographs of uniaxially stretched PLA and PLA blends with free fatty acids (C16:0, C18:1) and palm oil deodorization condensate (PODC) at different strain

squalene, α-tocopherol, HPO, HCO and mixtures of C16:0, C18:1 and HPO are not discriminated. However discrimination of PLA samples containing deodorization condensates of each kind of vegetable oils and according to their respective amount is obtained. Corresponding loadings are plotted in Figure 7. The positive part of F1 axis appears to be mainly governed by the elongation at break and as opposed to its negative part with the T_g. The F2 axis mostly separates fats as a function of the unsaturation and length of their alkyl chains. Looking at the elongation at break improvement, unsaturation of alkyl chains appears to be required, but the lower the ratio, the larger the enhancement was. Medium alkyl chain length, *i.e.* from lauric (C12) to stearic (C18) acid, also tends to be preferable than the long
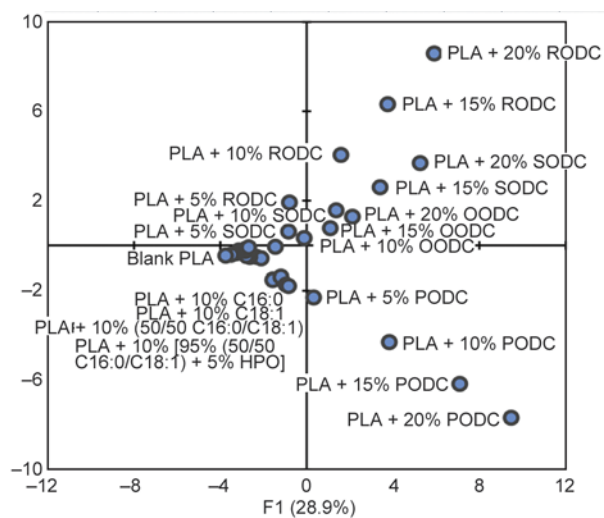
Figure 6. Principal components projection plot of F1 and F2 of the data set
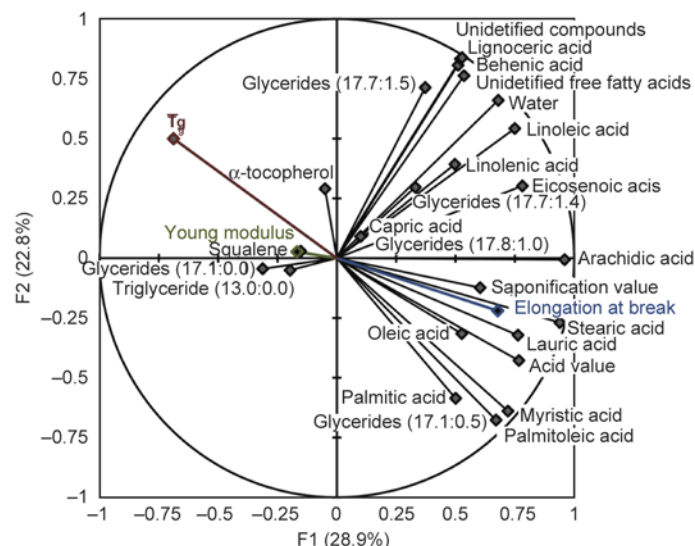
Figure 7. Loadings plot of the Principal Components Analysis of the dataset

ones as behenic (C22) or lignoceric (C24) acids. Both the unsaturation and the length of alkyl chains are main physical factors governing the melting point of fats. One common point is that unsaturation decreases melting points while length increases it. Therefore, efficiency of fats in toughening PLA appeared to be linked to medium melting point properties. A mixture of crystalline and liquid fatty acids at room temperature seemed favorable. This could explain the ability of HCO triglycerides to increase the PLA ductility while HPO did not, although their HSP were similar, as their ability to depress the T_g of PLA. In fact, due to short alkyl chains, HCO triglycerides are waxy at room temperature. The DSC thermogram (Figure 2) shows a broad melting peak going from 8 to 42°C of HCO while it is beyond 55°C for HPO. Literature shows that combining liquid and solid additives can sometimes be effective for PLA [78]. Acid and saponification values are related to the elongation at break improvement (Figure 7). Therefore, the higher the esterified fats and/or the free fatty acid contents, the better the efficiency of the additive. In opposite, unidentified compounds, *i.e.* mostly unsaponifiable compounds, are not favorable to the ductility increase. Therefore, the superiority in toughening abilities of the PODC compared to the alike mixture made of [95 wt% (50 wt% C16:0 + 50 wt% C18:1) + 5 wt% HPO] can be attributed to the complex and favorable mixture of fatty acids having different chain length.

4. Conclusions

By-products of the vegetable oils industry, namely deodorization condensates, were investigated as biobased additives for ductility improvement of PLA. The deodorization condensates improved substantially the elongation at break of PLA up to 180%. The glass transition was merely decreased which brought ductility to the still glassy polymer. The deformation mechanism was efficient craze initiation delaying failure. Most importantly, it was shown that the industrial by-product of the palm oil refinery had superior properties compared to mixtures of fatty acids and vegetable oils because it contained a mixture of fatty acids with melting points below and beyond room temperature. This makes deodorization condensates efficient and low price additives for PLA able to be used in commodity applications such as food packaging.

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