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THE FOLLOWING ARTICLE:**

Volpe, V., De Feo, G., De Marco, I., Pantani, R.
"USE OF SUNFLOWER SEED FRIED OIL AS AN ECOFRIENDLY PLASTICIZER FOR STARCH AND APPLICATION OF
THIS THERMOPLASTIC STARCH AS A FILLER FOR PLA"
Industrial Crops and Products
Volume 122, 15 October 2018, Pages 545-552
DOI: 10.1016/j.indcrop.2018.06.014

WHICH HAS BEEN PUBLISHED IN FINAL FORM AT
<https://www.sciencedirect.com/science/article/abs/pii/S0926669018305156>

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1 **Use of sunflower seed fried oil as an ecofriendly plasticizer for starch and**
2 **application of this thermoplastic starch as a filler for PLA**

3 V. Volpe*, G. De Feo, I. De Marco, R. Pantani

4 *Department of Industrial Engineering, University of Salerno*

5 *Via Giovanni Paolo II, 132, 84084 Fisciano (SA), Italy*

6
7 *Corresponding author: Department of Industrial Engineering, University of Salerno, Via Giovanni Paolo II, 132, 84084
8 Fisciano (SA), Italy. Email address: vavolpe@unisa.it (V. Volpe)

9
10 **Abstract**

11 The high cost of the Poly(lactic) Acid when compared to its durable competitors is a significant drawback
12 that inhibits its diffusion for many industrial applications. A common solution is the compounding with
13 other polymers that preserve biodegradability, and thermoplastic starch (TPS) is a conventional choice. The
14 innovation proposed in this work is to replace into the starch plasticization process part of the glycerol with
15 a sunflower seed oil resulting from the frying process in a fast food. The so plasticized TPS was compared to
16 the TPS plasticized with only glycerol and then mixed to the PLA. The replacement of a certain percentage
17 of glycerol with fried edible sunflower oil as plasticizer for starch results in an improvement in material
18 properties of the TPS and does not change the properties of the PLA/TPS blends. Plasticization of starch
19 with fried oil has been proven to be the most environmentally sound solution also from a Life Cycle
20 Assessment.

21
22 **Keywords:** Poly(lactic) acid, thermoplastic starch, sustainability

24 **1. Introduction**

25 Biodegradable polymers are currently used as an alternative to durable polymers in many applications for
26 large consumption goods. The most widespread biodegradable polymer is poly(lactic) acid, PLA (De Santis
27 et al., 2017; Garlotta, 2001; Husarova et al., 2014; Lim et al., 2008; Sanyang and Sapuan, 2015; Volpe and
28 Pantani, 2015). However, although presenting the successful property of being biodegradable, it presents
29 also the significant drawback of being relatively expensive when compared to its durable competitors (i.e.
30 polyolefins). One of the methods currently adopted by industries in order to mitigate the cost of the raw
31 material is to use a significant fraction of additives (De Santis and Pantani, 2015; Mohanty et al., 2000b; Yu
32 et al., 2006). In this case, a slight decrease in the properties of the part is generally considered an
33 acceptable side effect for the sake of having a cheaper product. Obviously, the property of being
34 biodegradable should not be harmed, and thus the filler should be biodegradable itself (Gorrasi and
35 Pantani, 2018).

36 Several natural additives have been proposed as possible fillers for PLA. For instance, polymer-
37 lignocellulose composites have been explored in recent times (Lee et al., 2008; Mohanty et al., 2000a).
38 Lignocellulose, in fact, is an inexpensive filler that increases material toughness and improve the thermal
39 stability by reducing tool wear (Way et al., 2012). However, the highly hydrophilic nature of the fibers often
40 needs compatibilisation to improve the polymer-fiber interface (Murariu and Dubois, 2016). Other natural
41 additives have been experimented in these years. Manshor et al. in 2014 presented a novel idea of utilizing
42 durian skin waste as reinforcing fiber for PLA. They found that 30 wt% PLA can be replaced by durian skin
43 fibers without altering the impact strength, flexural modulus and thermal properties of the material with
44 respect to the unreinforced PLA (Manshor et al., 2014). In 2017 Kocaman suggested surface-modified
45 grinded coconut waste (CW) particles as bio-fillers to prepare polymeric composite materials with
46 enhanced properties (Kocaman et al., 2017).

47 One of the most common biodegradable additives of the PLA is the Thermoplastic Starch (TPS), a
48 renewable and biodegradable material very interesting because of its worldwide availability and its low
49 cost (Tester and Karkalas, 2001). Different kinds of starches (wheat, corn, sorghum, yucca, potato, etc.) are

50 conventionally used to produce industrial TPSs. The poor processability because of higher melting point
51 compared to its decomposition temperature is the most important limiting factor for starch, which imposes
52 the use of plasticizers (glycerol, sorbitol, maltose, glucose, water, urea, citric acid etc.) (Ma et al., 2006;
53 Mahieu et al., 2015; Poutanen and Forssell, 1996; Shi et al., 2007; Tang et al., 2008; Teixeira et al., 2007).
54 Plasticizers reduce the tension of deformation, hardness, density, viscosity and electrostatic charge of a
55 polymer, while increasing the polymer chain flexibility, resistance to fracture and dielectric constant
56 (Rosen, 1993). Glycerol and sorbitol are the most widely used polyol plasticizers for starch-based films due
57 to the close similarity between their chemical structures and the structure of starch polymer (Mali et al.,
58 2005). Müller et al. (Muller et al., 2016) have recently studied component interactions, structure and
59 properties of blends prepared from poly(lactic) acid and thermoplastic starch plasticized with glycerol at
60 two different weight percentages. They found that blending of the two components results in
61 heterogeneous, two phase structures at all compositions. For this reason, they concluded that useful
62 materials can be produced from PLA and TPS only with the development of an appropriate coupling
63 strategy. Akrai et al. in 2016 (Akrami et al., 2016) synthesized a new compatibilizer based on maleic
64 anhydride grafted poly-ethylene glycol grafted starch to improve the compatibility of the PLA/TPS blends.
65 They demonstrated that compatibilizer enhanced interfacial adhesion without to influence the
66 biodegradability behavior. In the same year Ferri et al. (Ferri et al., 2016) proposed a plasticization strategy
67 that involves the addition to glycerol of an environmentally friendly plasticizer derived from vegetable oils,
68 maleinized linseed oil (MLO), obtaining a remarkable compatibilizing effect. The possibility of adopting as a
69 plasticizer a mixture of glycerol and sorbitol with different percentages of sunflower seed oil was also
70 recently explored (Vieira et al., 2011). It was shown that the presence of the oil not only increases the
71 barrier properties to water vapor, but also enhances the mechanical properties of the starch films.
72 Obviously, the use of a substance which is potentially useful for human nutrition can cause ethical
73 problems. For this reason, in this work we decided to study the possibility of adopting fried sunflower seed
74 oil as a plasticizer. In particular, this oil is the waste of the frying process of a fast food. The use of this oil
75 can present the twofold advantage of reducing the cost of the plasticizer and reuse a waste product. Blends

76 of PLA and TPS plasticized with glycerol and fried sunflower seed oil were examined by rheological, thermal
77 and mechanical characterization. Furthermore, Life Cycle Assessment (LCA) study was carried out in order
78 to compare the environmental impacts related to the different plasticized starches' productions.

79

80

81 **2. Materials and methods**

82 A corn starch powder C* Gel 03401, supplied by Cargill, containing 75% amylose and 25% amylopectin was
83 plasticized with glycerol and edible sunflower seed oil, both raw and fried in a fast food. This latter was
84 filtered before any further use. The analysis on oils were carried out according to the procedures described
85 by Memoli et al. (Memoli et al., 2017). Table 1 shows features and composition of the two oils.

86

87 **Table 1**

88 Features and composition of the raw and fried oil.

	Raw oil	Fried oil
Peroxides [meq O₂/kg]	9.45	11.59
Acidity [g oleic acid/100 g oil]	0.14	0.59
Palmitic Acid [%]	6.56	7.93
Palmiticoleic Acid [%]	0.13	0.13
Stearic Acid [%]	3.27	4.73
Oleic Acid [%]	25.34	31.6
Linoleic Acid [%]	63.12	56.39

89

90 As expected, peroxides increase as a consequence of frying. Furthermore, the percentages of shorter fatty
91 acids increase.

92 A Poly(lactic) Acid (PLA), Ingeo™ Biopolymer 4043D, supplied by NatureWorks LLC (Minnetonka, MN, USA)
93 was adopted for producing blends with the previously tested thermoplastic starch. The adopted PLA has a
94 density of 1.24 g/cm³ and weight average molecular weight of 10⁵ g/mol.

95

96 *2.1 Micro compounder*

97 The plasticization of the corn starch powder with glycerol and edible sunflower seed oil was carried out by
98 a micro compounder with conical twin-screws Thermo Scientific Haake MiniLab II (Victoria, Australia), at a
99 temperature of 110 °C, a screw rotation of 100 rpm and a cycle time of 5 min. Table 2 shows the weight
100 percentage of starch, glycerol and edible sunflower seed oil, both raw (R) and fried (F), contained in the
101 produced blends, which are referred to considering oil/glycerol ratio (namely TPS 0.2 R stands for blend
102 containing an Oil/Glycerol ratio equal to 0.2, obtained by using Raw sunflower seed oil).

103 Larger oil/glycerol ratios with respect to 10/15, keeping the amount of starch close to 70%, could not be
104 adopted due to solubility problems: overcoming this ratio led to difficulties in obtaining a homogenous TPS
105 blend. This ratio can be thus considered as a limit for this kind of blends. Before mixing, the pellets of PLA
106 and the corn starch powder were dried for 24 h under vacuum at a temperature of 45°C. The extruded
107 materials were then kept dry under vacuum conditions.

108

109 **Table 2**

110 TPS blends.

Blend	Oil/Glycerol ratio [-]	Starch [%]	Glycerol [%]	Raw sunflower oil [%]	Fried sunflower oil [%]
TPS	0	70	30	-	-
TPS 0.2 R	0.2	70	25	5	-
TPS 0.2 F	0.2	70	25	-	5
TPS 0.5 R	0.5	70	20	10	-
TPS 0.5 F	0.5	70	20	-	10
TPS 0.7 R	0.7	75	15	10	-
TPS 0.7 F	0.7	75	15	-	10

111

112 TPS obtained as described above was then mixed to PLA by means of the same equipment, always keeping
113 the percentage of PLA at 70% in weight. In this case, temperature was set at 170 °C while the screw
114 rotation and the cycle time have not changed. Results obtained from PLA/TPS blends were compared with
115 the behaviour of the neat PLA .

116

117 *2.2 Compression molding*

118 Amorphous films of thermoplastic starch (TPS) with an average thickness of 200 µm were obtained by
119 compression molding using a Carver hydraulic press. In particular, the pellets and the extruded materials
120 were preheated in the mold at 85 °C for 10 min and, then, under a pressure of 3500 bar for an holding time
121 of 10 min.

122 PLA/TPS films were also produced by Carver hydraulic press at 170 °C with a preheating of 5 min and
123 compression at 3500 bar for 10 min. Before any test, the films were dried for 12 h under vacuum at 45°C.

124

125 *2.3 Thermogravimetric analysis (TGA)*

126 In order to analyze the behavior at high temperatures of the TPS and of the PLA/TPS blends, a
127 thermogravimetric analysis (TGA) by means of a Pyris Diamond TG/DTA from PerkinElmer (USA) was
128 performed. Each sample was kept in inert atmosphere by a continuous nitrogen flow at 25°C for 5 minutes
129 and then heated at the rate of 5 °C min⁻¹ from 25 °C to 600 °C.

130

131 *2.4 Mechanical Analysis*

132 All films produced by compression molding were subjected to mechanical analysis in tension. In particular,
133 rectangular TPS films having a geometry of 10 mm x 5 mm x 200 µm were subjected to uniaxial tensile
134 elongation by a PerkinElmer DMA 8000, with a maximum load equal to 2 N and a load rate of 0.1 N/min.

135 The PLA/TPS blends were instead subjected to tensile tests by a dynamometer INSTRON 4301 equipped
136 with a load cell of 100 N. The clamps distance was equal to 10 mm and the crosshead speed was set at 5
137 mm/min. The difference in the used techniques is due to the high brittleness of TPS film, which did not
138 allow a reliable analysis by the dynamometer.

139

140 *2.5 Rheological tests*

141 A rheological characterization of the PLA/TPS blends was carried out by a Haake Mars II (Thermo scientific)
142 rotational rheometer in an oscillatory dynamic mode with parallel plates configuration under a nitrogen
143 atmosphere. The experiments were performed at 160 °C and 180 °C. Master curves of each PLA/TPS blend
144 were then built at 160°C.

145

146 *2.6 Gel Permeation Chromatography (GPC)*

147 The measurements of molecular weight distribution were carried out by a Waters Breeze 2 HPLC system on
148 neat PLA (both in form of pellet and extruded) and on the blends PLA/TPS 0.5 R and PLA/TPS 0.5 F. The
149 samples were dissolved in tetrahydrofuran (THF) at 58 °C and then the solution was filtered by means of a
150 Chromafil PTFE 0.45 mm filter.

151

152 *2.7 Differential scanning calorimetry (DSC)*

153 PLA/TPS blends were subjected to differential scanning calorimetry (DSC) by means of a differential
154 scanning calorimeter DSC 822TM from Mettler Toledo Inc. The samples were heated from 25 to 200 °C at 5
155 °C/min, kept at 200 °C for 5 min to erase the previous thermal history and subsequently cooled to 25 °C at 5
156 °C/min. The same protocol was then repeated a second time. In order to assess the effect of the TPS on the
157 crystallization kinetics of the PLA, the samples were also subjected to the following heat protocol:

- 158 • from 25 °C to 170 °C at 10 °C/min;
- 159 • at 170 °C for 5 min;
- 160 • from 170 °C to 110 °C to 10 °C/min;
- 161 • at 110 °C for 3 h.

162

163 *2.8 Life Cycle Assessment (LCA)*

164 The Life Cycle Assessment (LCA) methodology is one of the most used tools for the evaluation of
165 environmental performance of product, processes and services. LCA allows comparing different systems
166 considering the consumption of resources as well as the emission of pollutants that may occur during their
167 life cycle, which may include extraction of raw materials, production and processing of materials,
168 packaging, transport, phase of use and, finally, end of life. LCA methodology consists of four steps: (1) goal
169 and scope definition, (2) inventory analysis, (3) impact assessment and (4) improvement assessment.

170 The goal of this LCA study is to analyze and compare the environmental impacts related to the different
171 plasticized starches' productions. The chosen functional unit is 10 grams of plasticized starch.

172 Data were analyzed using SimaPro 8.0.5 software, whereas the Ecoinvent 3.1 database and primary data
173 were used for the life cycle inventory, according to the reference standard for LCA (i.e., ISO 14040-14044).

174 The environmental impacts were evaluated with the ReCiPe 2008 H. This method combines a midpoint
175 level approach (problem-oriented) with an endpoint approach (damage-oriented). Eighteen impact
176 categories are considered at the midpoint level: climate change (CC), ozone depletion (OD), terrestrial
177 acidification (TA), freshwater eutrophication (FE), marine eutrophication (ME), human toxicity (HT),

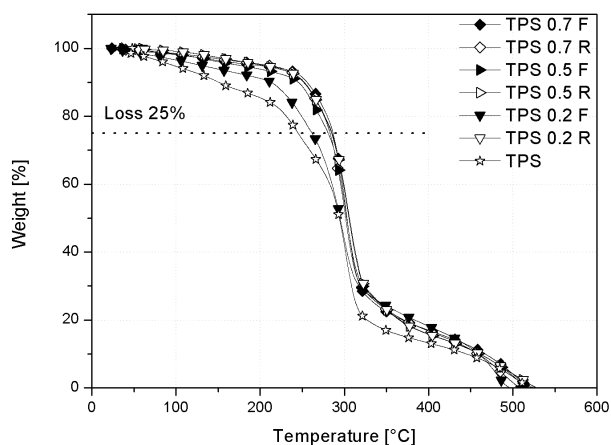
178 photochemical oxidant formation (POF), particulate matter formation (PMF), terrestrial ecotoxicity (TET),
179 freshwater ecotoxicity (FET), marine ecotoxicity (MET), ionising radiation (IR), agricultural land occupation
180 (ALO), urban land occupation (ULO), natural land transformation (NLT), water depletion (WD), metal
181 depletion (MD) and fossil depletion (FD).such as ozone depletion, agricultural land occupation, fresh water
182 depletion, fossil fuel depletion, etc. The hierarchist perspective (H) is based on the most common policy
183 principles concerning the time frame and other issues. At the endpoint level, most of these midpoint
184 impact categories have to be further converted and aggregated into the following three endpoint
185 categories: damage to human health (HH), damage to ecosystem (E) and damage to resources (R)
186 (Goedkoop et al., 2009).

187

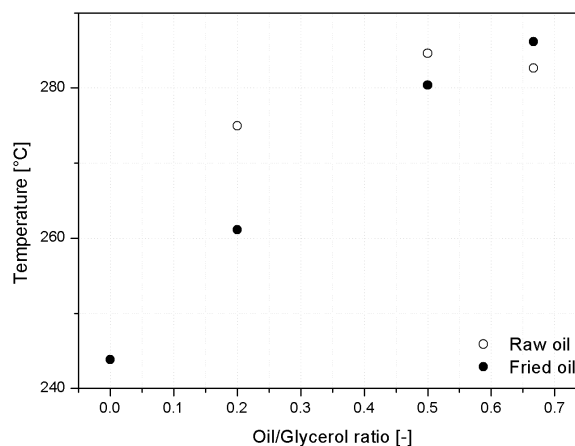
188 **3. Results and discussion**

189 *3.1 Thermoplastic starch*

190 The corn starch powder is commonly plasticized by small hydrophilic molecules, such as amino acids,
191 glycolic or polyols. Among these, the most commonly used is glycerol, substance rather expensive because
192 of the laborious production process. As mentioned above, the innovation proposed in this work is to
193 replace into the starch plasticization process part of the glycerol with a fried oil as result of a fast food, in
194 order to reduce the costs due to glycerol and simultaneously reuse a waste product. In particular, different
195 percentages of glycerol were replaced by raw and fried oil, in order to compare their plasticizing
196 capabilities. The properties of the so plasticized TPS were compared with those of the TPS plasticized only
197 with glycerol. The TPS produced by micro compounder were subjected to thermogravimetric analysis, in
198 order to evaluate the behavior of the TPSs at high temperatures. Figure 1 shows the weight reduction on
199 increasing temperature for all TPS blends (Fig. 1a), and the temperature corresponding to a weight loss of
200 25% (Fig. 1b) of the TPS blends with raw and fried oil at all the oil/glycerol ratios.



(a)



(b)

201

202

203 **Fig. 1.** TGA of the starch/glycerol/sunflower oil blends (a); temperature corresponding to a weight loss of 25% of the
 204 TPS blends with raw and fried oil at all the oil/glycerol ratios (b).

205

206 The TGA analysis showed main stages of thermal degradation. The first stage, observed between 50 and
 207 250°C, can be attributed to the elimination of water, glycerol and other low molecular weight compounds.

208 The second stage of thermal degradation, at ~320 °C, represents the degradation of TPS components
 209 amylose and amylopectin. The third stage corresponds to oil decomposition (Lendvai et al., 2017;

210 Schlemmer et al., 2010). From Fig. 1b it is possible to observe that the temperature corresponding to a
 211 weight loss equal to 25% increases with the oil/glycerol ratio. TPS with raw oil and TPS with fried oil show

212 the same behavior during heating. From thermogravimetric analysis, it is possible to conclude that the
 213 starch plasticized with oil has a better stability at high temperatures compared to the starch plasticized only

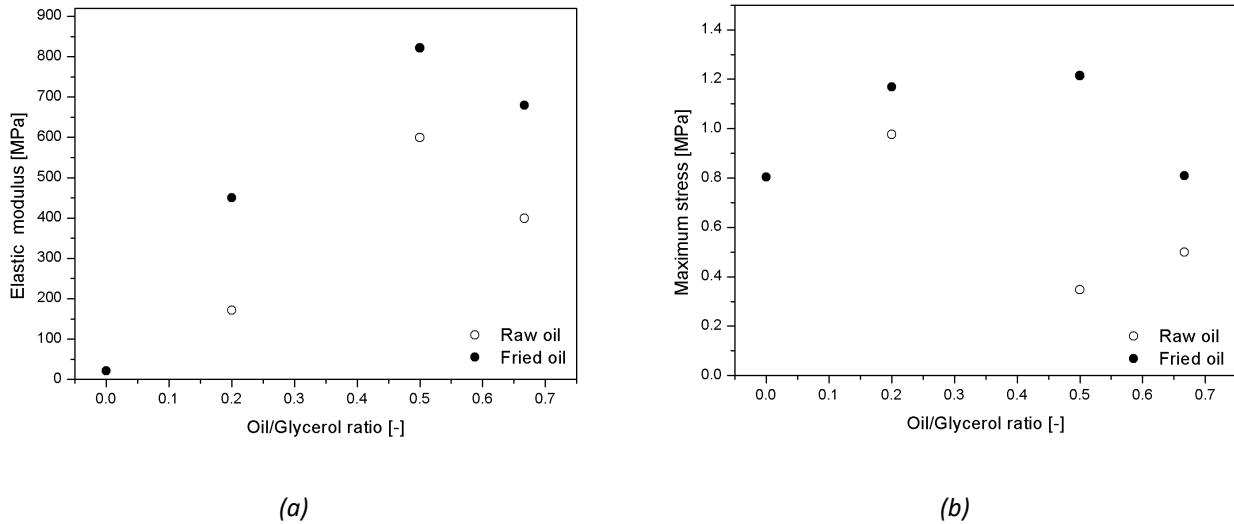
214 with glycerol. This thermal stability is strictly dependent on the chemical structures of vegetable oils, and in
 215 particular to the content of unsaturated fatty acid (Schlemmer et al., 2010).

216 200 µm thick films were subjected to uniaxial tensile elongation, from which elastic modulus and maximum
 217 stress were evaluated. TPS with only glycerol presents a lower modulus than those with oil. The elastic

218 modulus increases with the oil/glycerol ratio until a maximum value, corresponding to oil/glycerol ratio
 219 equal to 0.5 (Fig. 2a). The maximum stress presents a similar trend (Fig. 2b). It is also important to note that

220 TPS with fried oil present a larger modulus and a larger maximum stress with respect to TPS with raw oil.

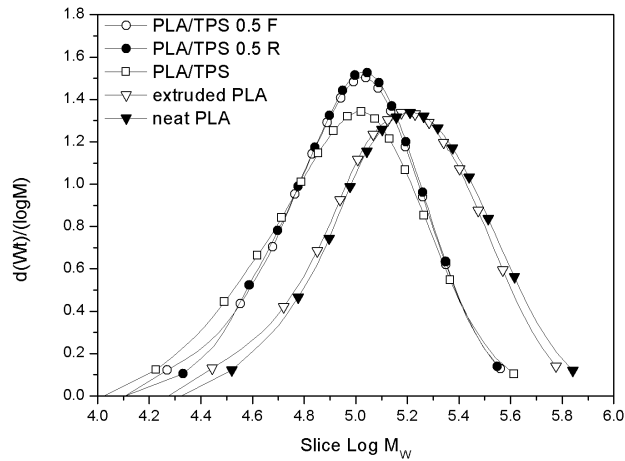
221 It can therefore be concluded that the replacement of a percentage of glycerol with edible sunflower seed
222 oil, especially fried, as a plasticizing for the starch results in an improvement in thermal stability and
223 mechanical properties of TPS.



224
225 (a) (b)
226 **Fig. 2.** Elastic modulus (a) and maximum stress (b) of the TPS blends with raw and fried oil at all the oil/glycerol ratios.
227
228

229 3.2 PLA/TPS

230 All PLA/TPS blends were analyzed by gel permeation chromatography (GPC) in order to evaluate the
231 molecular weight distribution of the different blends. Fig. 3 shows the curves obtained from the GPC
232 analysis. By comparing the data of the extruded PLA with the data of the different PLA/TPS blends, in which
233 the PLA has been subjected to the same extrusion process, it is possible to note a shift of the latter towards
234 lower molecular weight, symptom of a slight degradation of PLA due to the blending with TPS.
235 Furthermore, it is important to note that the PLA/TPS plasticized with raw and fried oil have a slightly
236 narrower distribution compared to the PLA/TPS blend with only glycerol, as it is possible to appreciate also
237 from the polydispersity index. A possible explanation may be related to the presence of peroxides in the oil,
238 that stabilize the PLA by deactivating the catalyst residues (Maharana et al., 2009). This means that the
239 presence of oil to replace glycerol preserves the PLA, which therefore undergoes less degradation as result
240 of the blending with TPS. Moreover, no significant difference can be observed between the blend with raw
241 oil and that with fried oil.



242

243 **Fig. 3.** GPC of neat PLA, extruded PLA and PLA/TPS blends with raw and fried oil/glycerol ratio 0.5.

244

245 **Table 3**

246 Average molecular weights and polydispersity index of neat PLA, extruded PLA and PLA/TPS blends with raw and fried
247 oil/glycerol ratio 0.5.

Sample	M_n [Da]	M_w [Da]	PDI [-]
<i>Neat PLA</i>	73659	115427	1.57
<i>Extruded PLA</i>	66231	104850	1.58
<i>PLA/TPS</i>	40043	65478	1.64
<i>PLA/TPS 0.5 R</i>	45761	66655	1.46
<i>PLA/TPS 0.5 F</i>	43719	66037	1.51

248

249 The differential Scanning Calorimetry (DSC) analysis made on each blend allowed to evaluate their melting
250 temperature and glass transition temperature (Table 4). For both the characteristic temperatures, the
251 PLA/TPS blends are positioned below the value of the neat PLA. Minor differences between the
252 formulations with glycerol alone, with raw oil and with fried oil can be observed.

253 The effect of adding TPS to the PLA on the crystallization kinetics can be appreciated from the thermograms
254 in Fig. 4, obtained during isotherm at 110°C. It is clear that the curves of extruded PLA and PLA/TPS
255 (plasticized only with glycerol) have a very similar pattern. Blends with oil (PLA/TPS 0.5 F and PLA/TPS 0.5
256 R), instead, show a peak at longer times. Therefore, the addition of oil (both raw and fried) seems to slower

257 the crystallization kinetics of the material. This effect is not surprising: it is quite well known that
258 plasticization may have opposite effects on the crystallization behavior. This happens because a plasticizer
259 can act in reducing both the glass transition temperature and the equilibrium melting temperature
260 (Saeidlou et al., 2012). If the glass transition temperature depression is larger than the decrease in
261 equilibrium melting temperature, an increase of crystallization rate is normally found. If the opposite takes
262 place, a decrease in crystallization rate is measured. This is the condition of our blends, as also reported in
263 Table 4. The result reported in Fig. 4 suggests that sunflower oil acts differently from glycerol as a
264 plasticizer, as it was expected being completely different from a chemical point of view, but no differences
265 are found between raw and fried oil.

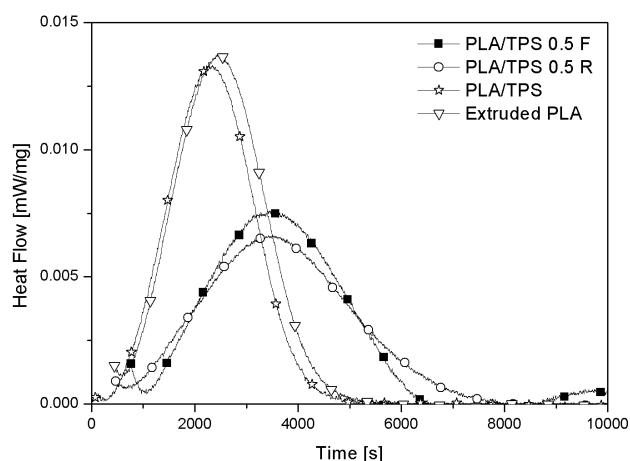
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267 **Table 4**

268 Melting temperature and glass transition temperature of the PLA/TPS blends with raw and fried oil at all the
269 oil/glycerol ratios.

	Melting temperature [°C]	Glass transition temperature [°C]
<i>Neat/Extruded PLA</i>	150.2	60.3
<i>PLA/TPS</i>	145.8	57.3
<i>PLA/TPS 0.2 R</i>	145.2	56.2
<i>PLA/TPS 0.2 F</i>	146.3	57.3
<i>PLA/TPS 0.5 R</i>	145.2	56.6
<i>PLA/TPS 0.5 F</i>	145.8	55.9
<i>PLA/TPS 0.7 R</i>	147.5	55.8
<i>PLA/TPS 0.7 F</i>	146.0	56.0

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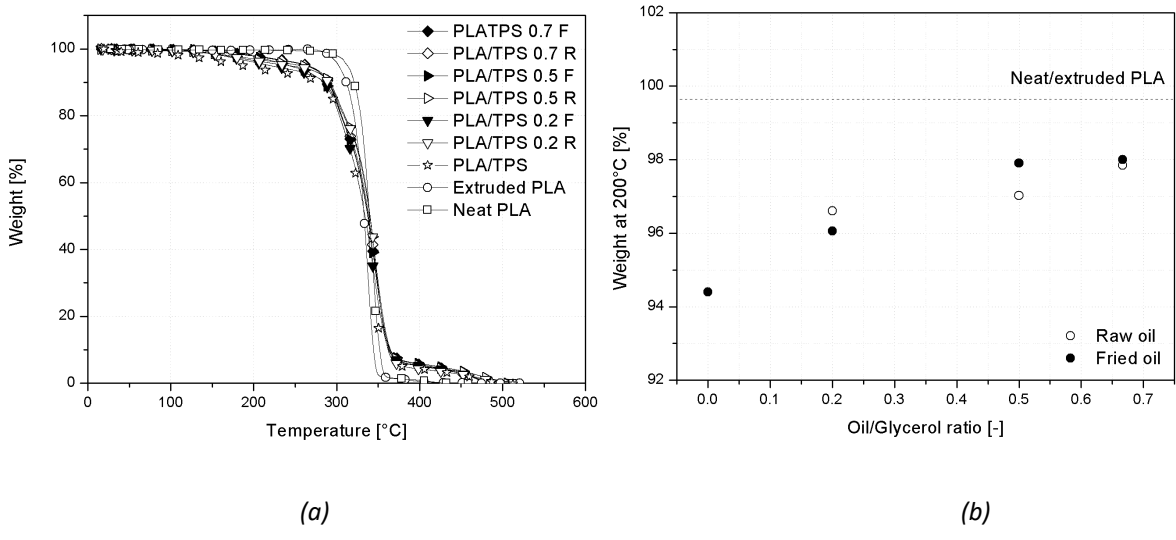


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272 **Fig. 4. DSC experimental curves during isotherm at 110°C corresponding to neat PLA, extruded PLA and PLA/TPS**
 273 **blends with raw and fried oil/glycerol ratio 0.5 (b).**

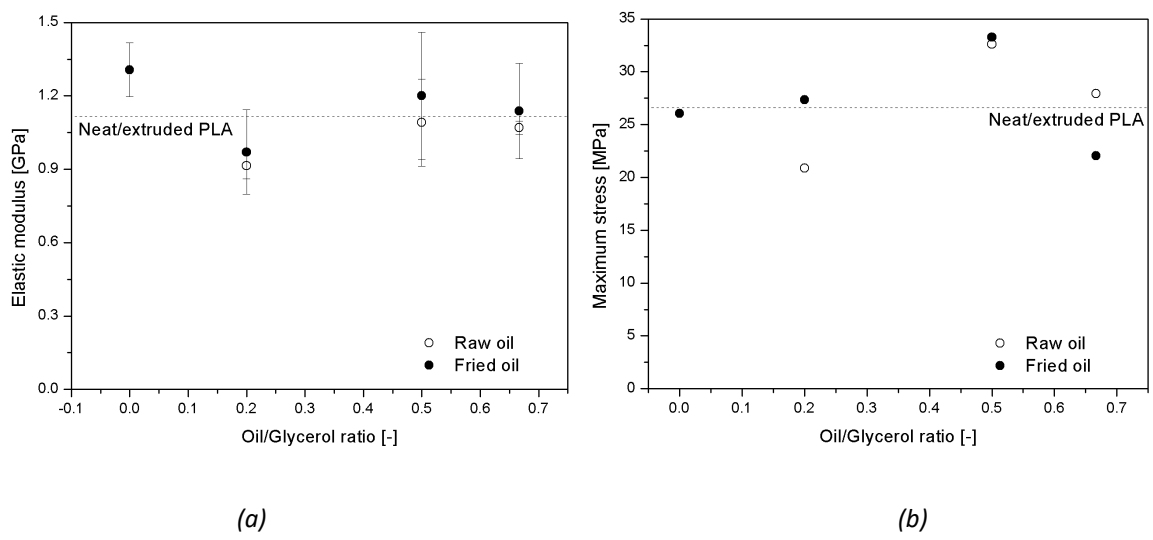
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275 Also in this case, as for TPS, the blends were subjected to thermogravimetric analysis in order to evaluate
 276 their behavior at high temperatures. Curves in Fig. 5a show that the degradation of all the PLA/TPS blends
 277 starts at lower temperatures and ends at higher temperatures with respect to the neat and extruded PLA.
 278 Furthermore, it is possible to observe that at 200 °C, a commonly adopted processing temperature for PLA,
 279 the weight loss percentage decreases on increasing oil/glycerol ratio (Fig. 5b). In conclusion, a positive
 280 effect of oil on overall thermal stability of PLA/TPS blends is found, with an improved resistance to thermal
 281 degradation temperature as the oil/glycerol ratio increases.



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Fig. 5. TGA of the PLA/TPS blends (a); weight percentage at 200°C of the PLA/TPS blends with raw and fried oil at all the oil/glycerol ratios (b).

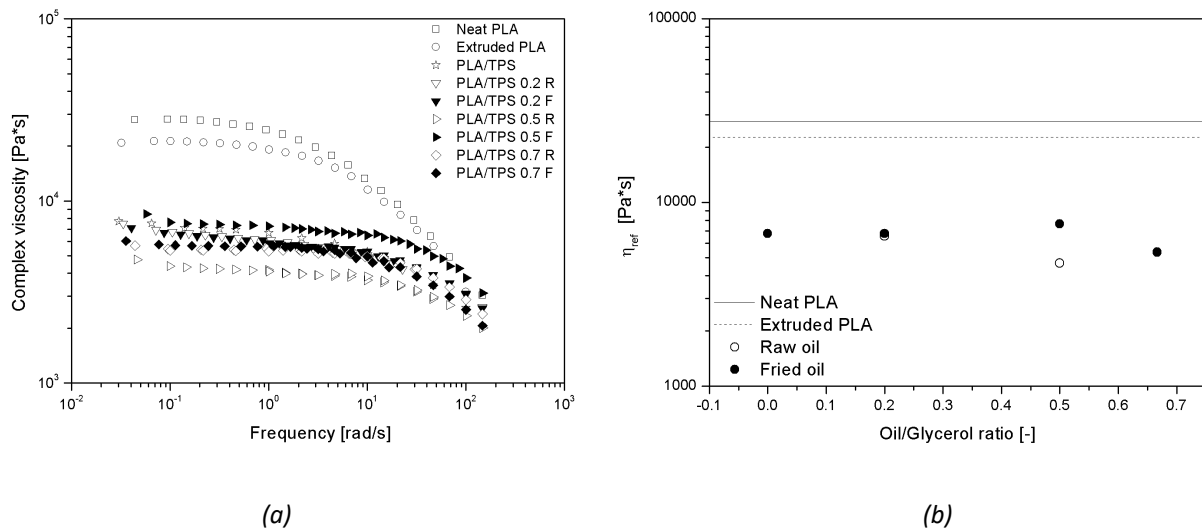


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Fig. 6. Elastic modulus (a) and maximum stress (b) of the PLA/TPS blends with raw and fried oil at all the oil/glycerol ratios.

The mechanical properties of the PLA/TPS blends were assessed by tensile tests. In Fig. 6 it is also possible to observe the elastic modulus (Fig. 6a) and the maximum stress of the blends (Fig. 6b) with raw and fried oil at all the oil/glycerol ratios. For all the PLA/TPS blends, values of both parameters were comparable and in some cases higher than the values obtained for neat and extruded PLA. In particular, the PLA/TPS blend with oil/glycerol ratio of 0.5 presents the largest value of maximum stress.

297 In Fig. 7a the master curves at 160°C of the dependence of viscosity upon frequency is reported for all the
 298 materials. The rheological analysis showed that the addition of thermoplastic starch to the PLA results in a
 299 reduction in viscosity. This is known from the literature to be due to the plasticizer adopted for the starch:
 300 indeed, for blends of PLA with starch plasticized with different percentages of glycerol, it is reported
 301 (Jacquel et al., 2008) that the reduction of viscosity is larger for larger percentages of glycerol. In our
 302 blends, the viscosity reduction results to be similar on replacing the glycerol with oil. This suggests that
 303 sunflower oil is an effective replacement of glycerol from the rheological point of view.



304
 305 (a) (b)
 306 **Fig. 7.** Complex viscosity vs shear rate (mastercurve at 160°C) (a) and Newtonian viscosity at 160°C (b) of the PLA/TPS
 307 blends with raw and fried oil at all the oil/glycerol ratios.

309 **Table 5**

310 Cross Model parameters.

	η_{ref} [Pa s]	λ_{ref} [s]	n
<i>Neat PLA</i>	29000	0.145	0.31
<i>Extruded PLA</i>	21873	0.087	0.18
<i>PLA/TPS</i>	7342	0.026	0.36
<i>PLA/TPS 0.2 R</i>	6623	0.013	0.45
<i>PLA/TPS 0.2 F</i>	6373	0.011	0.35

<i>PLA/TPS 0.5 R</i>	4255	0.008	0.25
<i>PLA/TPS 0.5 F</i>	7267	0.009	0.16
<i>PLA/TPS 0.7 R</i>	5413	0.009	0.14
<i>PLA/TPS 0.7 F</i>	5711	0.013	0.15

311

312 The data shown in Fig. 7a were fitted by a Cross model (Eq. 1):

313

$$314 \quad \eta = \frac{\eta_{ref}}{1+(\lambda_{ref}\omega)^{1-n}} \quad (1)$$

315

316 where η_{ref} is the Newtonian viscosity, λ_{ref} is a characteristic relaxation time (namely the reciprocal of the
317 shear rate at which the viscosity starts to decrease from the Newtonian plateau), and n is the flow index.

318 Table 5 shows the parameters of the Cross equation obtained by fitting the rheological data showed in Fig.

319 7a. As also shown in Fig. 7b, the Newtonian viscosity of the blends with oil is comparable to that of the
320 blend obtained only with glycerol. Furthermore, the replacement of certain percentages of glycerol with oil,

321 both raw and fried, results in a wider Newtonian plateau, as testified by the decrease of λ_{ref} . A decrease in
322 relaxation time can be ascribed to the presence of low molecular weight molecules which act as lubricants.

323 From this point of view, on the basis of the results reported in Fig. 7, it can be concluded that from a
324 rheological point of view, the partial replacement of glycerol with fried oil results in a more effective
325 lubrication, and no significant differences can be found between raw and fried oil.

326

327

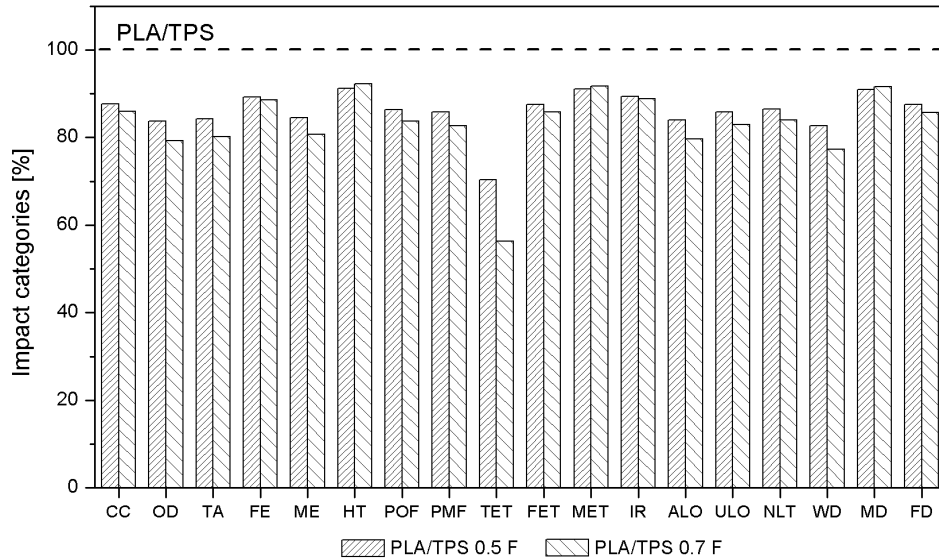
328 3.3 Life cycle assessment (LCA)

329 The LCA analysis was performed comparing the impacts obtained for three different plasticized starches:

- 330 • PLA/TPS: starch (70 %) +glycerol (30 %);
- 331 • PLA/TPS 0.5 F: starch (70 %) + glycerol (20 %) + fried oil (10 %);

332 • PLA/TPS 0.7 F: starch (75 %) + glycerol (15 %) + fried oil (10 %).

333 The results at the midpoint level are reported in Fig. 8 (the numerical values were added in the
334 supplementary data).



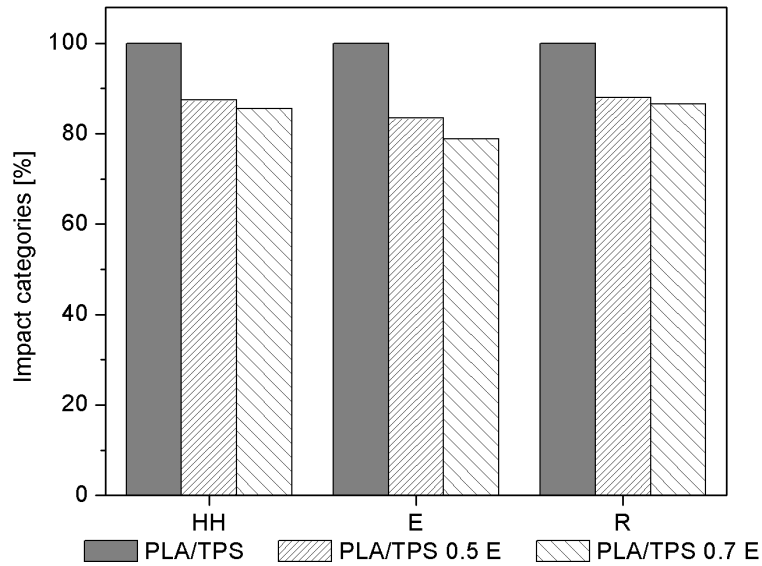
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336 **Fig. 8.** Comparison of the impacts, evaluated with the method ReCiPe 2008 H, at the midpoint level of the different
337 plasticized starches per FU. The PLA/TPS blend is set to 100% in all the impact categories under analysis.

338

339 From Fig. 8 it is possible to observe that the substitution of part of the glycerol with fried oil generates a
340 reduction of the impacts in terms of all the categories under analysis. Indeed, the solution PLA/TPS is
341 always the most impactful one. Comparing the two solutions that use fried oil, we can note that the
342 solution with fried oil/glycerol ratio equal to 0.5 is preferable in terms of human toxicity, marine ecotoxicity
343 and metal depletion, whereas, on the other 15 categories, the solution with fried oil/glycerol ratio equal to
344 0.7 generates lower impacts.

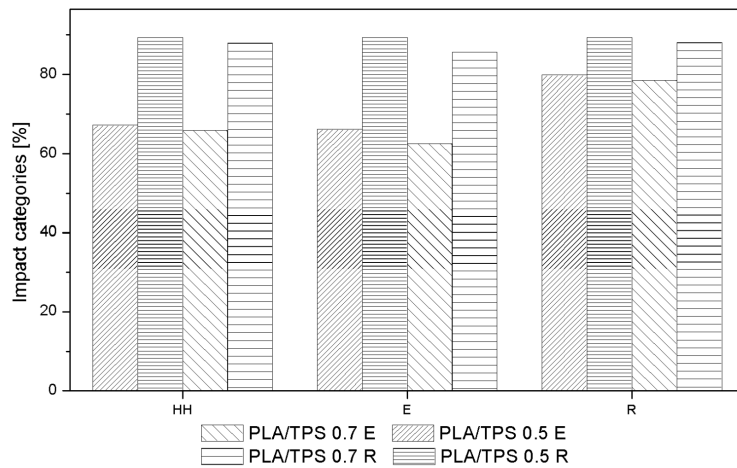
345 Therefore, the three solutions were compared at normalized endpoint level, as reported in Fig. 9.



346
 347 **Fig. 9.** Comparison of the impacts at the endpoint level of the different plasticized starches per FU.

348 From Fig. 9, it is clear that the most environmentally sound solution is the third one (higher fried
 349 oil/glycerol ratio) on the three damage categories.

350 In order to understand which would be the impacts related to the usage of a vegetable raw sunflower oil,
 351 the solutions were analyzed substituting the fried sunflower oil with a raw sunflower oil. The results are
 352 reported in Fig. 10.



353
 354 **Fig. 10.** Comparison of the impacts at endpoint level of the different plasticized starches obtained using fried and raw
 355 oil per FU.

356 It is evident that the use of raw oil is not recommended not only from an ethical point of view, but also
 357 from the environmental one.

358 4. Conclusions

359 In this work, different percentages of glycerol were substituted by raw and fried sunflower seed oil into the
360 starch plasticization process. The material thus compounded was thermally and mechanically
361 characterized. The results showed that the replacement of a percentage of glycerol with edible sunflower
362 seed oil, especially if fried, as a plasticizer for the starch results in an improvement in thermal stability and
363 mechanical properties of the material. The elastic modulus and the maximum stress increases with the
364 oil/glycerol ratio until a maximum value corresponding to an oil/glycerol ratio equal to 0.5.

365 In the second part of the work, the previously tested thermoplastic starches were adopted for producing
366 blends with a Poly(lactic) Acid. The different characterizations have led to the following results:

- 367 • the molecular weight of the PLA/TPS blends undergoes a slight decrease with respect to the neat
368 PLA extruded through the same process, symptom of a slight degradation of the material. However,
369 the presence of oil to replace glycerol preserves the PLA, which therefore undergoes less
370 degradation as result of the blending with TPS;
- 371 • the presence of thermoplastic starch results in a slight decrease in molecular weight of the PLA.
372 Furthermore, the PLA/TPS plasticized with raw and fried oil have a slightly narrower molecular
373 weight distribution compared to the PLA/TPS blend with only glycerol, indicative of a lower
374 degradation;
- 375 • at 200 °C, process temperature commonly adopted for PLA, the weight loss percentage of the
376 PLA/TPS blends decreases with increasing oil/glycerol ratio;
- 377 • the mechanical properties of the PLA/TPS blends were comparable and in some cases better than
378 the properties of neat and extruded PLA;
- 379 • the addition of thermoplastic starch to the PLA results in a reduction in viscosity. Furthermore,
380 from a rheological point of view, the partial replacement of glycerol with fried oil results in a more
381 effective lubrication, and no significant differences can be found between raw and fried oil.

382 Life Cycle Assessment study assesses that the plasticization of corn starch with fried edible sunflower seed
383 oil is the most environmentally sound solution, while the use of raw oil is not recommended not only from
384 an ethical point of view, but also from the environmental one.

385

386 **5. Acknowledgments**

387 The authors wish to thanks "AcciPizza" in Giffoni V. P. (SA) for providing raw and fried oil, the group led by
388 prof. M. Di Matteo at UNISA for the characterization of the oils, the group led by prof. G. Gorrasi for the
389 help in characterizing the mechanical properties of the films.

390

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