

# Preparation and characterization of biodegradable and compostable PLA/TPS/ESO compositions

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1 ABSTRACT

2 In this study, biodegradable and compostable compositions, derived from totally natural  
3 feedstock/raw materials, namely polylactide (PLA), potato thermoplastic starch (TPS) and  
4 plant glycerin have been made by melt extrusion with epoxydized soybean oil (ESO) as  
5 reactive modifier in order to improve PLAs ductility and reduce the products cost without  
6 compromising biodegradation. The obtained PLA/mTPS (0,5ESO) [75/25] and PLA/mTPS  
7 (2ESO) [75/25] compositions provides satisfactory mechanical properties comparable to  
8 native PLA. Addition of 25% TPS and 0,5-2% ESO to PLA, improved impact strength from  
9 13,70 kJ/m<sup>2</sup> to 16,69 kJ/m<sup>2</sup> compared to neat PLA and increase elongation at break from  
10 2,6% to 8,8%. The addition of ESO into PLA/TPS composition enhanced water resistance  
11 and improved impact strength to over 16 kJ/m<sup>2</sup> for PLA/TPS(2%ESO)[75/25]composition.  
12 The thermal, rheological and morphology of fractured surface were also studied. Finally,  
13 biodegradability and compostability of prepared samples was specified by stimulated  
14 composting process (according to PN-EN 14806:2010 standard). Possibility of replacing up  
15 to 25% of PLA by TPS and ESO, allows to reduces the costs of the product as well as  
16 maintain quite similar properties and ability to composting relative to native PLA.

17 **KEYWORDS:** potato thermoplastic starch, biodegradable/composting polymers, polylactide,  
18 epoxydized soybean oil, renewable raw resources

19

## 20 1. Introduction

21 In Europe, packaging applications are the largest application sector for the plastics industry  
22 and represent 39,6% of the total plastics demand (PlasticsEurope, 2016). Conventional  
23 plastic packages are post-consumer wastes which are difficult for disposal and constitute a  
24 burden to the environment, due to their large volume and inability to biodegrade or to  
25 compost (Gregory, 2009; Imre and Pukánszky, 2013; Kale et al., 2007; Siracusa et al.,  
26 2008). Mainly, municipal solid wastes (MSW) consist of a containers and packaging wastes  
27 (Kale et al., 2007). The continuous increase in the amount of packaging wastes contributed  
28 to significant growing interest in raw materials derived from renewable sources. The current  
29 environmental protection requirements necessitate withdrawal commonly used petroleum  
30 based polymers. This has led to an enormous development of innovative bio-polymers and  
31 biotechnologies (Luckachan and Pillai, 2011).

32 Currently, the most common biodegradable polymers are polylactide (PLA),  
33 poly(hydroxybutyrate) (PHB), poly(glycolic acid) (PGA) and natural-based polymers like  
34 starch and cellulose (Kale et al., 2007; Mohanty et al., 2000; Shen et al., 2009). Each of  
35 these polymers has many different advantages and disadvantages. One of the ways of  
36 extracting the positive features of these materials is their mutual blending. The benefit of this  
37 approach is the possibility of using already known manufacturing methods and conventional  
38 machinery. PLA or PHB are very universal but also expensive polymers, therefore their  
39 modification via blending with a naturally occurring polymers may cause reduction of material  
40 costs, without compromising biodegradation (Martin and Avérous, 2001; Parulekar and  
41 Mohanty, 2007; Zhang and Sun, 2004). On the other hand, in most cases biopolymer pairs  
42 are thermodynamically immiscible - this prevents to mix them at the molecular level (Teixeira  
43 et al., 2012; Wang et al., 2008). In order to enhance the interfacial adhesion and improve  
44 compatibility between the polymers matrix a number of different agents, may be added.  
45 There are many reports which indicates that an incorporation of enhancing additives, such

46 as: acrylic acid (AA) (Wu, 2005), maleic anhydrite (MA) (Clasen et al., 2015; Huneault and Li,  
47 2007; Leadprathom et al., 2010; Zhang and Sun, 2004), methylene-diphenyldiisocyanate  
48 (MDI) (Carmona et al., 2015; Wang et al., 2001), fillers, e.g. montmorillonite (MMT) (Guarás  
49 et al., 2016; Jalalvandi et al., 2015), or phenyl diisocyanate (PDI) (Karagoz and Ozkoc,  
50 2013), might contributed to a significant improvement of miscibility biodegradable blends.  
51 Consequently, the production of bio-blends containing solely of fully natural raw materials is  
52 a challenging.

53 Polylactide (PLA) is obtained by the condensation of lactic acid or ring opening  
54 polymerization of cyclic-lactides and has one of the most advantageous properties for the  
55 fabrication of high-quality, eco-friendly packaging materials (Lim et al., 2008). PLA  
56 possesses good mechanical properties (high Young's modulus and tensile strength), high  
57 degree of transparency and is easily processable same as conventional petro-based plastics  
58 (Auras et al., 2004). Unfortunately due to the high price and some drawbacks (brittleness,  
59 low flexibility), PLA still cannot completely replace a conventional plastics from a widespread  
60 use. One of a simple solution to reduce the costs of PLA, seems to be blending with  
61 thermoplastic starch (TPS) - a polymer obtained by mechanical and thermal processing of  
62 native starch with a plasticizer (Zhang et al., 2014). TPS is a highly biodegradable,  
63 inexpensive and abundantly available biopolymer, capable of serve as a PLA filler. The main  
64 function of a plasticizer is to decrease the melting point of native starch, thereby allowing use  
65 of traditional plastic processing techniques, such as extrusion and injection molding.  
66 Furthermore, the plasticizer lowers the glass transition temperature ( $T_g$ ) and increases  
67 flexibility. In turn, the major drawbacks of starch are: unsatisfactory mechanical properties,  
68 migration of plasticizers from the matrix – retrogradation and hydrophilic character (Kaseem  
69 et al., 2012; Khan et al., 2016; Nafchi et al., 2013). However, the literature shows that in the  
70 most cases PLA/TPS blends exhibited very poor interfacial adhesion (Ayana et al., 2014;  
71 Müller et al., 2012; Wootthikanokkhan et al., 2012; Yang et al., 2015). On the other hand

72 improving properties of PLA/TPS blends could be achieved by incorporation of reactive  
73 modifier.

74 Epoxidized soybean oil (ESO) belongs to a wide group of vegetable oils (Khoo and Chow,  
75 2015), natural resources-based substance, commonly used as a polymer plasticizer  
76 (Vijayarajan et al., 2014; Xiong et al., 2013). There are some data on the addition of  
77 epoxidized vegetable oils as a plasticizer and modifiers to improve the brittleness and low  
78 flexibility of PLA (Ali et al., 2009; Xing and Matuana, 2016; Yu-Qiong Xu, 2009), what is  
79 mainly manifested by an increase in elongation at break with the simultaneous reduction in  
80 tensile strength properties. There are another paper in which the addition ESO to TPS  
81 presents different trend. Belhassen et al. (Belhassen et al., 2014), modified in situ  
82 thermoplastic starch (pre-plasticized with glycerol) with epoxidized soybean oil (ESO) using  
83 reactive blending. It was found the condensation reaction between the oxirane rings of ESO  
84 and the hydroxyl groups (starch and glycerol) by FTIR spectra. It led to an increase in tensile  
85 strength, modulus of elasticity and hydrophobicity of the resulting materials. The enormous  
86 potential of ESO is likely due to the molecule construction, i.e. high molecular weight,  
87 occurrence of reactive oxirane rings and long carbon chains. Moreover, biodegradability and  
88 non-toxicity encourages further research on this unconventional polymers modifier.

89 The aim of our research is to prepare fully biodegradable polymer compositions using  
90 materials originating solely from renewable resources. For this purpose, polylactide (PLA)  
91 was blended with modified by epoxidized soybean oil (ESO) thermoplastic starch (TPS)  
92 using melt extruding. The present study also aimed to receive the less expensive  
93 biodegradable blends for the use in packaging industry, that will have similar properties to  
94 PLA. The mechanical, thermal and rheological properties of the obtained materials were  
95 characterized by the static tensile test, impact strength, hardness, the melt flow rate (MFR)  
96 and DSC analysis. Morphology of fractured surface and resistant to water were also studied.  
97 Finally, biodegradability and compostability of prepared samples were specified by



98 stimulated composting process.

## 99 2. Materials and methods

### 100 2.1. Materials

101 Each formulation was prepared with the use of biodegradable and compostable materials  
102 made from renewable resource of plant origin. Native potato starch was purchased from  
103 ZetPezet, Poland (humidity max. 16%, pH= 5.5-7.5). PLA (7032D, MFR = 7g/10min at  
104 210°C, 2.16kg, density 1.25g/cm<sup>3</sup>, humidity 3%) was supplied by NatureWorks LLC (USA),  
105 as a transparent injection grade. Plant pharmaceutical grade glycerin (TechlandLab, Poland,  
106 density<sub>20°C</sub> 1.26 g/cm<sup>3</sup>, purity 99.5%), was used as a starch plasticizer. Epoxidized soybean  
107 oil (ESO) (Brenntag, Germany) with oxirane oxygen about 6-10 gO<sub>2</sub>/100g and iodine number  
108 approximately 3 gl<sub>2</sub>/100g, served as a starch reactive modifier.

### 109 2.2. Preparation and modification of TPS

110 At preliminary stage, native potato starch and glycerol (contents 25 wt%), were manually  
111 mixed and stored at ambient conditions for 24h. The resulting blends were placed into co-  
112 rotating twin-screw extruder (Laboratory extruder IQLINE EHP 2x20 IQ, ZAMAK, Poland).  
113 The temperature was in the range of 120-170 °C in nine heating zones. The screw speed  
114 was between 60 and 80 rpm. The extruded material was granulated after air-cooling.  
115 Modified thermoplastic starch (mTPS) was obtained by adding ESO (0.5, 1 or 2 wt%) and the  
116 same processing as previously described. The final composition of prepared compound was  
117 shown in Table 1.

118 Table 1 Composition of TPS mixtures used in the study.

Formulation	Starch (%)	Glycerol (%)	ESO (%)
TPS	75	25	-
mTPS(0,5ESO)	74,5	25	0,5
mTPS(1ESO)	74	25	1
mTPS(2ESO)	73	25	2

119

### 120 2.3. PLA/TPS compositions fabrication

121 The PLA/TPS blends were prepared by using twin-screw extrusion process. PLA was mixed  
122 with a varying amounts of unmodified or modified thermoplastic starch (12.5 or 25 wt% TPS)  
123 granulates. Then, prepared PLA/TPS blends were extruded. The processing conditions were  
124 similar to those described previously, i.e. 130-180 °C and 40-60 rpm (Figure 1). PLA/TPS  
125 blends, in form of strands, were cooled in air, granulated and stored in sealed aluminum tins  
126 at room temperature.

127 Obtained PLA/TPS blends were injection molded (hydraulic injection molding machine HM  
128 45/130, BATTENFELD, Poland), into normalized molds. Prepared PLA/TPS blends were  
129 used for further static tensile test study. All samples were pre-conditioned at room  
130 temperature for at least 48h prior to testing. Symbols of the prepared PLA/TPS blends, with  
131 their brief explanation, were given in Table 2.

132 Table 2 Composition and description of obtained PLA/TPS samples.

Formulation	PLA (%)	Starch (%)	Glycerol (%)	ESO (%)
PLA/TPS [87.5/12.5]	87.5	9.375	3.125	-
PLA/TPS [75/25]	75	18.75	6.25	-
PLA/mTPS(0.5ESO) [87.5/12.5]	87.5	8.875	3.125	0.5
PLA/mTPS(1ESO) [87.5/12.5]	87.5	8.375	3.125	1
PLA/mTPS(2ESO) [87.5/12.5]	87.5	7.375	3.125	2
PLA/mTPS(0.5ESO) [75/25]	75	18.25	6.25	0.5
PLA/mTPS(1ESO) [75/25]	75	17.75	6.25	1
PLA/mTPS(2 ESO) [75/25]	75	16.75	6.25	2

### 133 2.4. Melt Flow Rate (MFR)

134 MFR was performed by using plastometer (M-Flow BFN-001, ZWICK, Poland), according to  
135 the PN-EN ISO 1133:2005 standard (180°C, load of 2.16 kg). The value of MFR is expressed  
136 as a X g of material extruded through the standard capillary placed in a heating nozzle during  
137 10 min [g/10min].

### 138 2.5. Mechanical characterization

139 The static tensile test was performed on Zwick/Roell Z020 testing machine according to the  
140 PN-EN ISO 527:2004 standard (dumb-bell-shaped test specimen, type A). The crosshead  
141 speed was of 5 mm/min and the initial force was equal to 2N. For each PLA/TPS blend 5  
142 samples were examined and the results were averaged.

143 The impact strength test was performed on Zwick/Roell HIT5.5P according to the PN-EN ISO  
144 180:2004 standard. A 5.5J pendulum was used and U-shaped hammer was taken. Bar-  
145 shaped specimens (10x80x4mm) without notch were tested. For each PLA/TPS blend 5  
146 samples were examined and the results were averaged.

147 Hardness was measured by using Shore method according to PN-EN ISO 868:2004.  
148 Obtained data were presented with Shore D degree ( $^{\circ}\text{Sh D}$ ). For each PLA/TPS blend 10  
149 samples were examined and the results were averaged.

#### 150 *2.6. Morphology characterization*

151 The morphology of obtained blends was investigated using scanning electron microscope  
152 Phenom TM with a magnification range: 80 – 100.000  $\times$ , digital zoom: 12  $\times$  (ProX/Pro), at  
153 5kV voltage. The samples were prepared from cryogenically fractured surface of injection  
154 molded parts under liquid nitrogen. The surface was sputter coated with gold prior to  
155 observation.

#### 156 *2.7. Thermal properties*

157 The thermal properties of prepared blends were characterized by differential scanning  
158 calorimetry (DSC) on a TA Instrument (model Q100). Firstly, the samples were conditioned  
159 at 30  $^{\circ}\text{C}$  for 2 min. Then, measurements were carried out from -50 to 190  $^{\circ}\text{C}$ , at a heating  
160 rate of 10  $^{\circ}\text{C}/\text{min}$ , under a nitrogen atmosphere.

#### 161 *2.8. Water resistance*

162 Water resistance was studied as follows; Samples of PLA/TPS blends of 20x10x4 mm were  
163 dried in a laboratory oven at 60 °C until constant weight was achieved ( $m_0$ ). Samples cooled  
164 down to the room temperature. Immediately afterwards, specimens were immersed in the  
165 containers filled with 25 ml of tap water. The incubation process was carried out for 1 month  
166 and the control time points were after 1h, 8h, 24h, 48h, respectively. Water resistance was  
167 calculated according to the formula 1 and formula 2. Formula 1 express the swelling ratio ( $i_{t_x}$ )  
168 of the samples, which was determined by the mass of adsorbed solvent ( $m_t$ ) in storage  
169 period ( $t_x$ ). Formula 2 is associated with the samples mass loss ( $ml\%$ ) after each time point,  
170 where samples were removed out of container, dried to the constant mass and weighted  
171 ( $m_z$ ).

$$172 \quad i_{t_x} = \frac{(m_t - m_0) * 100}{m_0} \quad (1)$$

$$173 \quad ml = \frac{(m_0 - m_z) * 100}{m_0} \quad (2)$$

#### 174 2.9. Stimulated composting

175 Preliminary evaluation of the disintegration of packaging materials under simulated  
176 composting conditions in a laboratory scale test was commissioned to carry by COBRO -  
177 Polish Packaging Research Institute, according to PN-EN 14806:2010 standard. As a  
178 compost was used organic fertilizer obtained by the biodegradability of the mixture consisting  
179 essentially of plant residues. The initial pH of compost was equal to 5.95. Material for the  
180 study was provided in the form of sheets with dimensions of 25 x 25 x 2 mm. Three samples  
181 were made for each prepared material. Prior to study, samples were dried in a laboratory  
182 dryer (60°C, 24h) and weighted. The samples were then put into polypropylene (PP) reactors  
183 and placed in a bioreactor. The incubation process was carried out for 64 days maintaining  
184 constant temperature of 58 °C. The degree of degradation was determined after composting  
185 cycle (64 days) by sieving through a sieve of 2 mm. The material that passed through the

186 sieve is treated as totally biodegradable.

### 187 **3. Results and discussion**

#### 188 *3.1. Melt Flow Rate (MFR)*

189 MFR as an important parameter of the plastics processing was investigated. It facilitates the  
190 selection of the factors of the technological process which shortens the time and reduces the  
191 cost of production preparation. To be able to determine the influence of ESO to MFR of  
192 different compositions, starting materials (PLA, TPS, mTPS) and finished blends (PLA/TPS,  
193 PLA/mTPS) were examined. It was observed that in all cases the values of MFR were higher  
194 than those of pure PLA (2.34 g/10min). The results in Figure 2 show influence of  
195 incorporation ESO to TPS. For the content of 0.5% ESO in TPS, no significant change in  
196 MFR value was noted. Increasing the ESO content to 1% caused a rapid increase in the  
197 MFR value to 30,23 g/10min. This indicates the plasticizing effect of ESO added to TPS. In  
198 this study cross-linking effect was not observed, differently to (Belhassen et al., 2014) study,  
199 that observed a decrease of MFR and proved the act of epoxy groups on cross-linking  
200 process of TPS. In our work, a catalyst was not used so the cross-linking effect was not  
201 observed. Probably, ESO molecules have diffused between TPS chains, acting as a  
202 plasticizer and destroyed the occurring hydrogen bonds, what leads to decrease of MFR.

203 Therefore, the resulting PLA/TPS compositions exhibit also improved degree of flow in  
204 comparison to the pure PLA, remaining at a level of 6g/10min (Figure 3). In PLA/TPS  
205 compositions containing of 12% TPS, different presence of ESO does not significantly affect  
206 the MFR value. Increasing the content of TPS up to 25%, the similar trend in MFR is  
207 observed like for TPS modified by ESO (mTPS Figure 2). For 1 % of ESO concentration in  
208 PLA/TPS with 25% of TPS, MFR values reached the highest point (7.39 g/10min). Further  
209 increasing the content of the ESO up to 2% results in a reduction of the melt flow rate (5.26  
210 g/10min). Our findings correlate with Yu-Qiong Xu (Yu-Qiong Xu, 2009) studies. They noted

211 that increasing addition of ESO in the PLA is characterized by a sinusoidal change in value  
212 of MFR. In our case, addition of ESO caused plasticization effect by increasing of MFR  
213 value. The lack of a catalyst could have contributed to the absence of the branching and  
214 cross-linking effect in compositions. However, it should be noted that this effect is not  
215 noticeable for the composition containing 12.5% TPS, because of too small ESO content  
216 relative to PLA.

### 217 3.2. Mechanical characterization

218 Stress – strain curves of pure PLA and PLA/TPS blends are shown in Figure 4 (a,b). It can  
219 be seen that addition of unmodified (TPS) and modified (mTPS) starch into PLA significantly  
220 changed the course of the stress-strain curve. PLA/TPS blends exhibit evident yield point.  
221 According to literature reports (Akrami et al., 2016; Ayana et al., 2014; Ferri et al., 2016;  
222 Huneault and Li, 2007) the incorporation of thermoplastic starch (TPS) to PLA matrix leads to  
223 the increase of flexibility and reduce of tensile strength. In our study, presence of epoxycized  
224 soybean oil intensified these effect. The elongation at break increases progressively with the  
225 addition of the ESO, reaching up to 5.52% (in samples with 12.5 wt % of TPS and 2% ESO,  
226 Figure 4a) and 8,80% (in samples containing 25 wt % of TPS and 2% ESO, Figure 4b),  
227 respectively. Compared to the pure PLA (2.67%), it is over three-fold increase in the value of  
228 elongation at break (Table 3). The tensile strength decrease up to value approximately 50  
229 MPa in PLA/TPS blends generally, relative to the pure PLA (68.14 MPa). It was noticed that,  
230 increasing the content of TPS modified by ESO in PLA blends, does not reduce significantly  
231 the tensile strength, what is a proof of elastomeric and toughening effect of ESO. Similar  
232 observations were reported by Xiong et al. (Xiong et al., 2013). In their study, with the  
233 increase of ESO content in PLA and starch matrixes, tensile strength decreased and  
234 elongation and break increased. They observed that ESO acted as a plasticizer and also as  
235 a compatibilizer which improved interfacial bonding between PLA and starch.



236 With regard to the hardness, we recorded slightly decreasing tendency with increasing of  
237 TPS content (Table 3). The Shore D hardness of pure PLA is 83.53° and it is decreasing up  
238 to 82.81° for the PLA/TPS[87.5/12.5] sample. In turn, addition to the PLA/TPS compositions  
239 ESO leads to further softening of the material. The evidence is the noticeable decrease in  
240 hardness to the value of 77.70° (sample containing 2% ESO, 25%TPS), while hardness of  
241 unmodified PLA/TPS with 25% of TPS is equal to 81.55°. This is another confirmation of  
242 plasticizing effect of ESO added into PLA/TPS compositions.

243 Another parameter that describes the functional properties of polymers is impact strength. A  
244 slight improvement in impact strength was achieved by blending of unmodified TPS with  
245 PLA. It was believed that addition of a ductile and flexible material such as TPS resulted in  
246 reduction of brittleness of the PLA. From Table 3 it could be seen the impact-energy  
247 absorption of the PLA/TPS blends raising with increasing of ESO content. For the samples  
248 with 25% of TPS the highest impact strength value has reached PLA/TPS composition with  
249 2% of ESO (16.96 kJ/m<sup>2</sup>). It can be assumed that the PLA/mTPS(2ESO)[75/25] sample show  
250 the highest adhesion between PLA and TPS. In turn, for the samples with 25% of TPS and  
251 0.5% or 1% of ESO, the impact strength is unnoticeable (13.92 kJ/m<sup>2</sup> and 14.03 kJ/m<sup>2</sup>,  
252 respectively) and probably it is due to too small amount of ESO. Therefore, it should be  
253 attributed a significant effect of the addition of ESO to the blends toughness, but only if the  
254 ESO content is at least 2%. The impact strength value of all obtained compound does not  
255 falls below 10 kJ/m<sup>2</sup>, which allows for a statement that as a result of preparing PLA/TPS/ESO  
256 blends do not reduce impact strength, compared to pure PLA.

257 Table 3 summarized the mechanical properties of pure PLA and obtained blends. In terms of  
258 mechanical properties our results are passable enough but cannot be strictly comparable to  
259 the results found by other researches. Yu-Qiong Xu et al. (Yu-Qiong Xu, 2009) and  
260 Vijayarajan et al. (Vijayarajan et al., 2014) added much larger amounts of epoxidized  
261 soybean oil to PLA matrix (in the range of 3 up to 20 wt% of ESO). This has led to great



262 improvement of impact strength (up to 47 J/m) and ductility (Vijayarajan et al., 2014) as well  
 263 as positively influenced on melt strength and rheological properties of PLA (Yu-Qiong Xu,  
 264 2009). On the other hand, research on the impact of ESO on the mechanical properties of  
 265 TPS were led by Belhassen et al. (Belhassen et al., 2014). They proved occurrence of the  
 266 condensation reaction between the oxirane rings of ESO and the TPS hydroxyl groups. This  
 267 resulted in enhancement in Young's modulus and tensile strength of TPS/ESO samples, but  
 268 also caused rigidification effect (lower elongation at break).

269 Summarizing, the improved mechanical characteristic in a presence of ESO in the PLA/TPS  
 270 blends mainly might be associated with enhanced interfacial adhesion between PLA and  
 271 TPS. However, to confirm this thesis in a next step, morphology study was conducted.

272 Table 3 Summary of results from the mechanical tests of PLA/TPS compositions.

Composition	Tensile strength	Elongation at break	Impact strength	Hardness
	MPa	%	kJ/m <sup>2</sup>	°Sh D
PLA	68.14 ± 0.24	2.67 ± 0.07	13.71 ± 0.27	83.57 ± 1.26
PLA/TPS [87,5/12,5]	52.65 ± 0.34	2.20 ± 0.16	16.64 ± 1.91	82.81 ± 0.78
PLA/TPS [75/25]	47.87 ± 0.32	4.83 ± 0.52	14.07 ± 0.98	81.55 ± 0.57
PLA/mTPS (0,5ESO) [87,5/12,5]	51.60 ± 0.57	2.57 ± 0.66	13.56 ± 0.95	79.88 ± 1.47
PLA/mTPS (0,5ESO) [75/25]	45.82 ± 0.78	3.78 ± 0.61	13.92 ± 1.14	78.73 ± 2.03
PLA/mTPS (1ESO) [87,5/12,5]	52.00 ± 0.16	3.81 ± 1.01	11.84 ± 1.59	80.12 ± 1.87
PLA/mTPS (1ESO) [75/25]	48.76 ± 0.56	7.19 ± 0.91	14.03 ± 2.66	79.14 ± 1.74
PLA/mTPS (2ESO) [87,5/12,5]	48.26 ± 1.88	5.52 ± 1.62	10.29 ± 3.86	80.49 ± 1.25
PLA/mTPS (2ESO) [75/25]	49.04 ± 0.16	8.80 ± 1.04	16.96 ± 3.54	77.70 ± 1.89

273

### 274 3.3. Morphology characterization

275 The morphology of PLA/TPS[75/25] blends with a various ESO content was examined by  
 276 SEM and shown in Figure 5. As the content of the ESO increases, the surface morphology  
 277 changes. For the unmodified sample (PLA/TPS[75/25]), the morphology is highly  
 278 inhomogeneous. There are numerous gaps between the TPS and the PLA matrix. Moreover,  
 279 discontinuities in the structure are visible. TPS occurs in the form of granules (particle size  
 280 ranges from 0.5 to 2 μm) and tubes (particle length ranges from 3 to 20 μm), suggesting

281 poor dispersion and miscibility of TPS in the PLA matrix due to a large difference in polarity  
 282 between TPS and PLA polymers. Similar morphology was observed in Ferri et al. study (Ferri  
 283 et al., 2016). The addition of ESO improved compatibility between TPS and PLA molecules.  
 284 The addition of only 0.5% ESO (Figure. 5b) resulted in disappearance of the tubes particles  
 285 and reduction in the number and size of TPS granules. Increasing the ESO content to 2%  
 286 caused enhancement of interfacial bonding between TPS and TPS phases. Significantly  
 287 decreased number of black particles were observed, representing TPS granules “ripped out”  
 288 from PLA matrix. The structure of PLA/mTPS (2ESO) [75/25] is more homogeneous. The  
 289 TPS granules appear to be strongly embedded in the PLA matrix (Figure. 5d). Hence, the  
 290 assumption that the addition of ESO improves the miscibility and interphase adhesion of TPS  
 291 to PLA molecules. Similar effect of ESO presence in PLA/TPS composition was observed by  
 292 Xiong et al. (Xiong et al., 2013).

### 293 3.4. Thermal properties

294 Table 4 and Figure 6 (a,b,c) present the results of differential scanning calorimetry (DSC) of  
 295 PLA/TPS compositions with different content of TPS and ESO. The glass transition  
 296 temperature ( $T_g$ ), cold crystallization temperature ( $T_{cc}$ ), melting temperature ( $T_m$ ) and the  
 297 heats of melting and cold crystallization ( $\Delta H_m$ ,  $\Delta H_{cc}$ ) are given.

298 Table 4. Thermal analysis data for pure PLA and the respective compositions with different content of  
 299 TPS and ESO.

Composition	$T_g$ [°C]	$T_{cc}$ [°C]	$\Delta H_{cc}$ [J/g]	Main $T_m$ [°C]	$\Delta H_m$ [J/g]
PLA	60.6	105.6	35.6	168.1	46.3
TPS	52.6	-	-	166.1	0.6
PLA/TPS [87,5/12,5]	58.4	103.3	33.9	166.8	34.4
PLA/TPS [75/25]	58.1	106.8	27.1	165.2	29.6
PLA/mTPS (0,5ESO) [87,5/12,5]	58.2	100.5	26.2	166.8	34.5
PLA/mTPS (0,5ESO) [75/25]	59.0	106.0	24.7	166.2	28.4
PLA/mTPS (1ESO) [87,5/12,5]	57.6	100.7	29.0	165.8	33.6
PLA/mTPS (1ESO) [75/25]	55.7	102.2	30.5	165.8	34.5
PLA/mTPS (2ESO) [87,5/12,5]	57.2	101.1	30.3	166.2	33.0

PLA/mTPS (2ESO) [75/25]	57.7	107.39	23.45	165.50	27.48
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300

301 The neat PLA shows a glass transitions ( $T_g$ ) at 60.6 °C, a cold crystallization peak ( $T_{cc}$ ) at  
 302 105.6 °C and a sharp melting peak ( $T_m$ ) about 168 °C. In turn,  $T_g$  of TPS is about 52.6 °C,  $T_m$   
 303 reaches 166.1 °C and the  $T_{cc}$  does not appear (Figure 6a). In case of all prepared  
 304 compositions  $T_g$  is between  $T_g$  of pure PLA and TPS, what suggests the good miscibility  
 305 between the components. However according to the literature the immiscibility of PLA and  
 306 TPS was proved by Muller et al. (Müller et al., 2012), which is also in accordance with our  
 307 SEM results as we very clearly observe two-phase morphology for all compositions studied.  
 308 The examined compositions have small amounts of TPS and due to this some thermal  
 309 parameters for it are not traced in DSC thermograms. Moreover the thermal transitions for  
 310 TPS are very weak in comparison of PLA. Occurrence of two endothermic peaks is attributed  
 311 to the phenomenon of lamellar rearrangement and polymorphism of PLA crystalline structure  
 312 (Cartier et al., 2000; Martin and Ârous, 2001; Tábi et al., 2010). Moreover TPS is known as a  
 313 good crystallization nucleate for PLA (Madhavan Nampoothiri et al., 2010). Some slight  
 314 increase in  $T_{cc}$  of PLA in PLA/TPS/ESO composition are observed after the addition 2% of  
 315 ESO (Figure 6b), suggesting small disturbing effect in PLA crystallization (decrease in delta  
 316  $H_{cc}$ ), thus stimulating effect in partial miscibility at the phase border. This might be very  
 317 valuable information for the processing of the blends. Additionally, adding of 2% of ESO to  
 318 the composition PLA/mTPS (2ESO)[75/25] decreases  $T_g$  and  $T_m$  of blends, what confirms it  
 319 as a good plasticizer for the composition of PLA and TPS. Summarizing the data of DSC, it  
 320 should be noted that  $T_g$  of potato TPS and PLA are very close, what can complicate the  
 321 interpretation of the results of DSC and speculations on the morphology of compositions.

### 322 3.5. Water resistance

323 Water resistance of PLA/TPS blends was analyzed by the swelling ratio and mass loss  
 324 behavior during storage in water under ambient condition. The results shown in Figure 7 and



325 Figure 8 revealed that in all cases pure PLA shows minimal swelling ratio and mass loss rate  
326 with less than 0.55% and 0.35% after 48h, respectively. As was presumed, the increase of  
327 the starch content in the compound manifested by the higher values in both cases.  
328 Contemplating the effect of the ESO adjunct on the resistance to water of prepared  
329 compounds found that ESO delays the two processes. In presence of 2%ESO the swelling  
330 ratio reaches about 1.5% and 2.75% after 48h, at a content of 12.5% and 25% TPS,  
331 respectively. The mass loss test exhibit similar behavior. Unmodified PLA/TPS[87,5/12,5],  
332 PLA/TPS[75/25] showed the greatest mass loss (about 1.5% and 2.3% after 48h). While, the  
333 increase of ESO content brought the reduction in value which reflect the amount of the  
334 0.55% for PLA/TPS(2ESO)[87.5/12.5] and 0.95% for PLA/TPS(2ESO)[75/25], respectively. It  
335 is assumed that presence of plasticized starch (TPS) promoted hydrolytic degradation,  
336 thereby causing reduction of dimensional stability. However, presence of ESO resulting in  
337 improved the swelling ratio and mass loss behavior, relative to unmodified PLA/TPS  
338 compositions.

### 339 3.6. Stimulated composting

340 According to ASTM D5338-98, 2003 (ASTM D5338-98, 2003) standard, composting is a  
341 controlled process of biological degradation with the use of microorganisms under strictly  
342 controlled conditions. A biodegradable material is converted to CO<sub>2</sub>, water, inorganic  
343 compounds and biomass. The microorganisms in the process of polymer degradation  
344 release enzymes which cause a chain scission of the polymer into monomers (Lau et al.,  
345 2009). To confirm the suitability of the obtained innovative materials for use in the short-life  
346 application packaging industry as an alternative for commonly used petroleum-based  
347 polymers, compostable tests was commissioned. The composting processes is illustrated in  
348 Figure 9. The data from testing by COBRO lab clearly confirm that the materials  
349 decomposed completely. During 57 days of incubation, all samples were disintegrated to  
350 dimension smaller than 2mm in diameter. According to PN-EN 14806:2010 standard, all

351 were completely degraded in the composting conditions.

#### 352 **4. Conclusions**

353 This work is motivated by current demands of the market which seeks for less expensive  
354 alternatives for PLA. In this study, a new compositions based on PLA, modified by TPS and  
355 ESO was prepared to improve PLAs ductility and reduce the products cost without  
356 compromising biodegradation. To confirm the efficiency of drafted compositions, their  
357 rheological, mechanical and thermal properties, water resistance and ability to composting  
358 were studied. Growth in MFR value leads to an increased susceptibility to injection and blow  
359 molding processes. From the technological point of view these increases the variety of  
360 products for short life application. Further, to confirm the suitability of obtained PLA/TPS  
361 blends in various branches of the packaging industry, the mechanical properties were  
362 characterized. The addition of ESO leads to softer materials, improved impact strength (up to  
363 16,69 kJ/m<sup>2</sup>), tensile and ductile properties (elongation at break ~ 8.8%), compared to the  
364 native PLA, what has been confirmed by SEM examination of fractured surfaces. The  
365 presence of ESO in the compositions delayed the water diffusion into blends matrix. This  
366 might improve products dimensional stability, exposed to short-term water acting. The  
367 prepared thermoplastic starch (TPS) modified by epoxidized soybean oil (ESO) requires the  
368 same machines as well to the processing of pure PLA. Possibility of replacing up to 25% of  
369 PLA through modified mTPS allows to reduces the costs of the product as well as maintain  
370 quite similar properties and ability to composting relative to pure PLA. Moreover in our  
371 previous studies on TPS/ESO it is clear that ESO added to TPS speeds up composting  
372 processing time (Janik et al., 2017).

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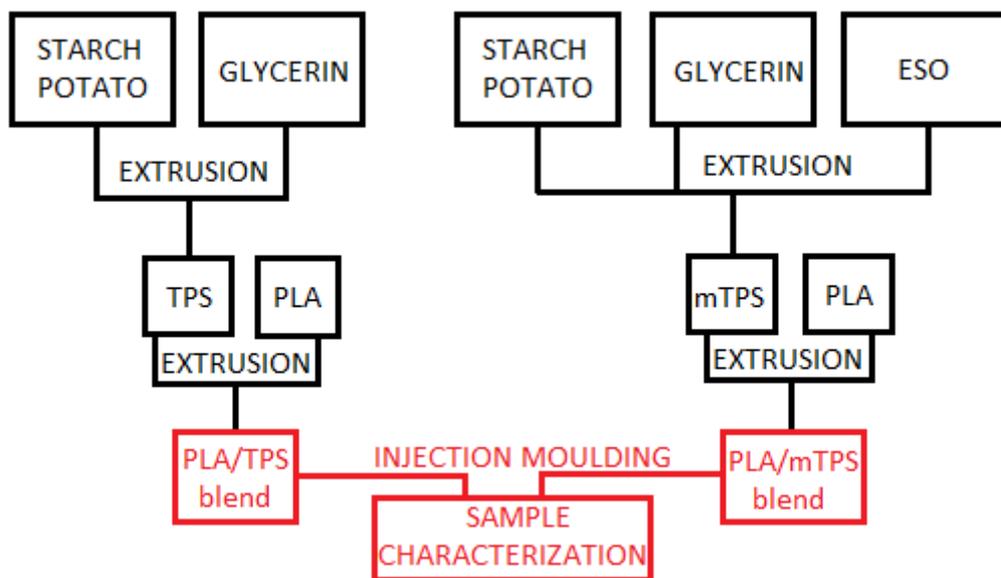
532 Table 1. Composition of TPS mixtures used in the study.

533 Table 2 Composition and description of obtained PLA/TPS samples.

534 Table 3. Summary of results from the mechanical tests of PLA/TPS compositions.

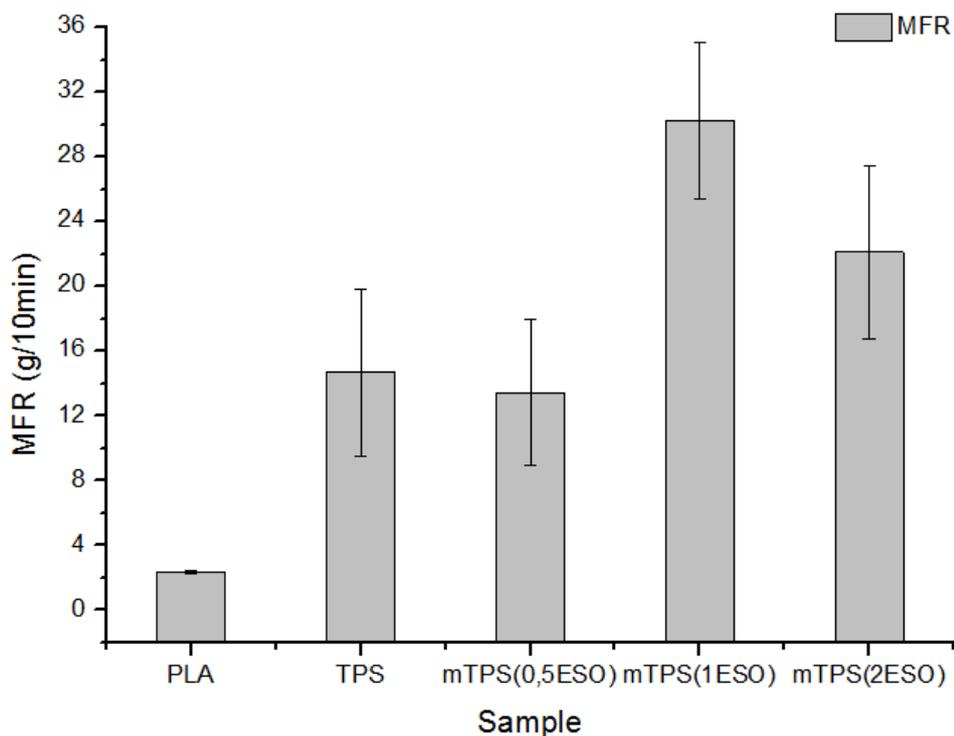
535 Table 4. Thermal analysis data for pure PLA and the respective compositions with different  
536 content of TPS and ESO.

537 Fig 1.



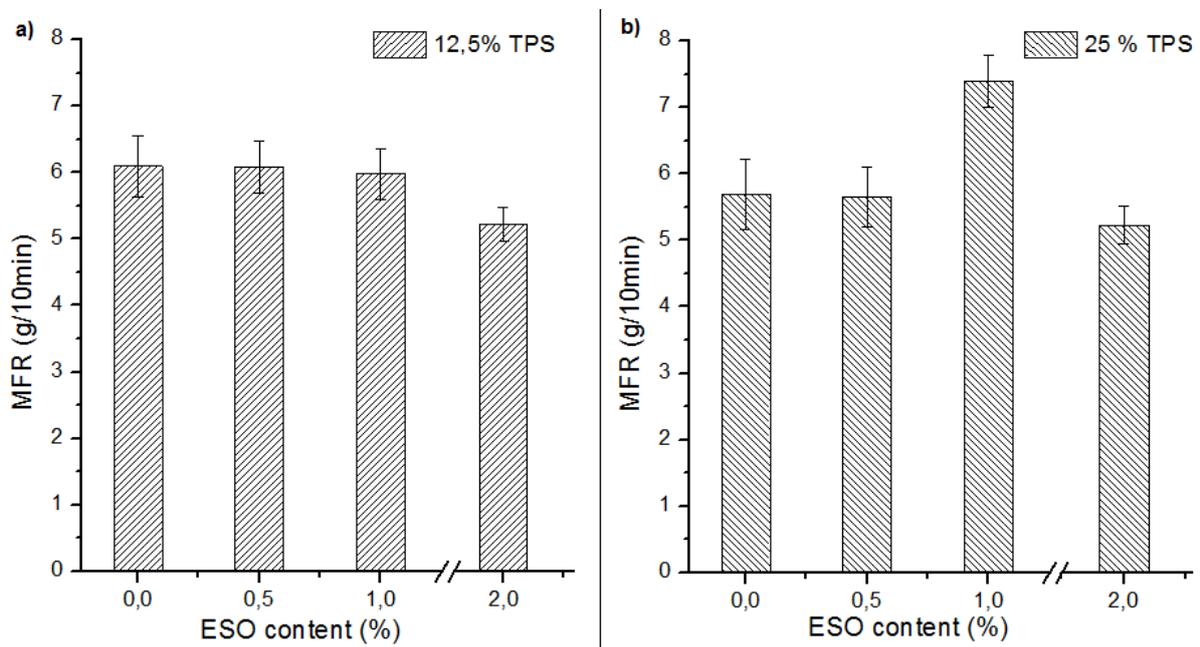
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539 Fig 2.



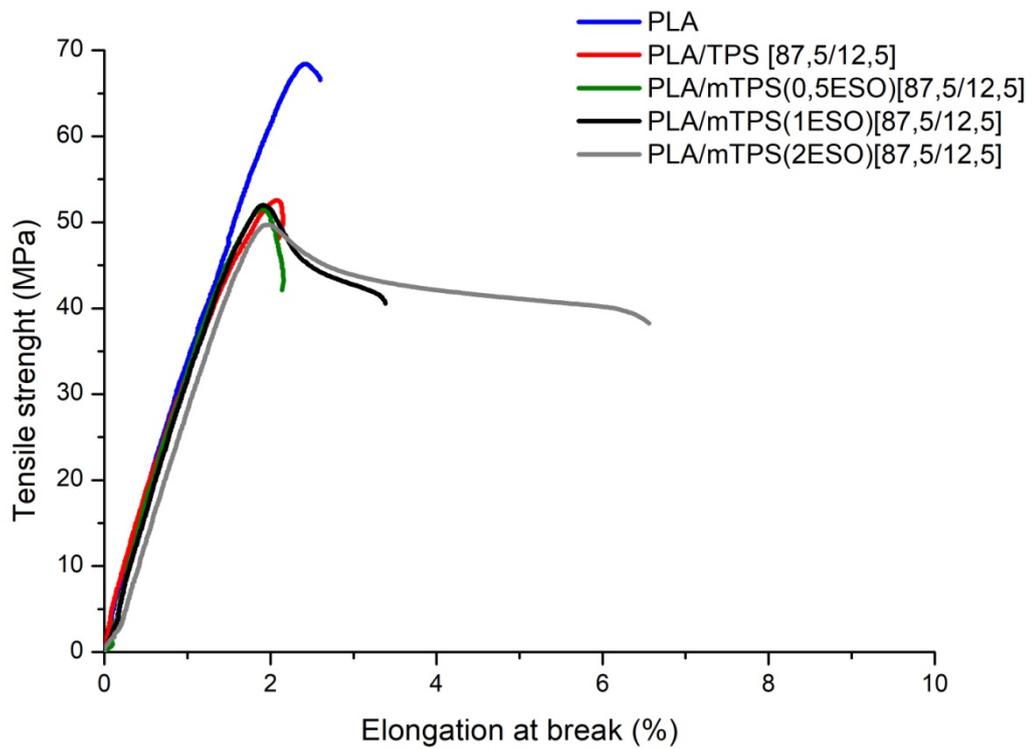
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541 Fig 3.



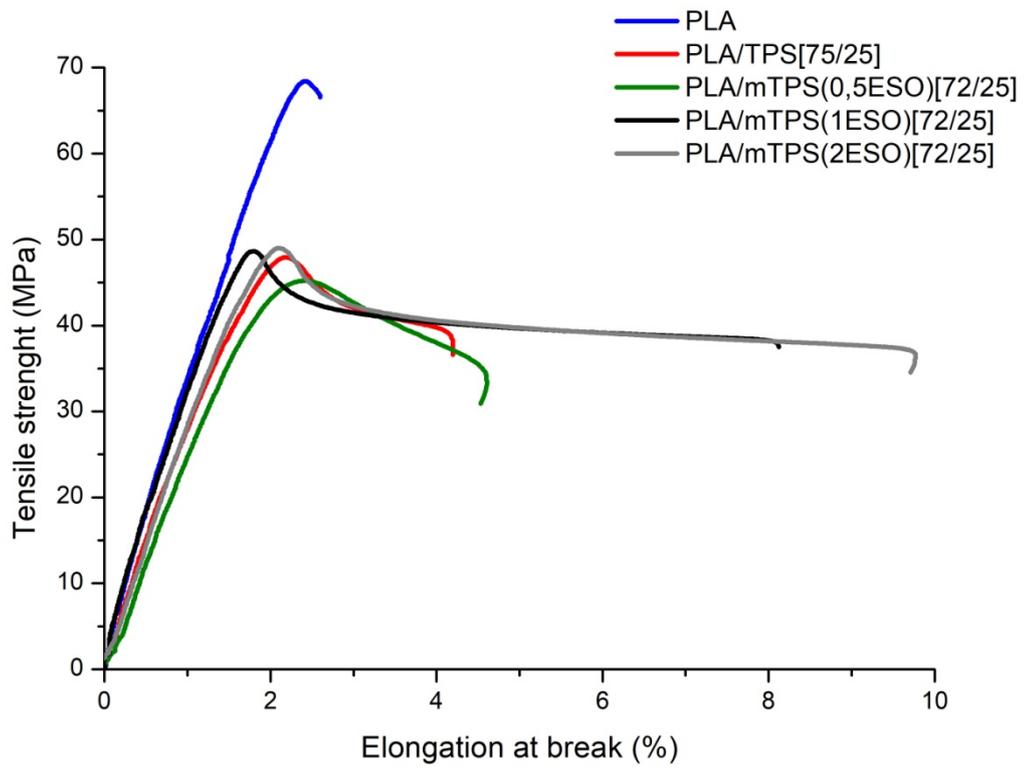
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543 Fig. 4a



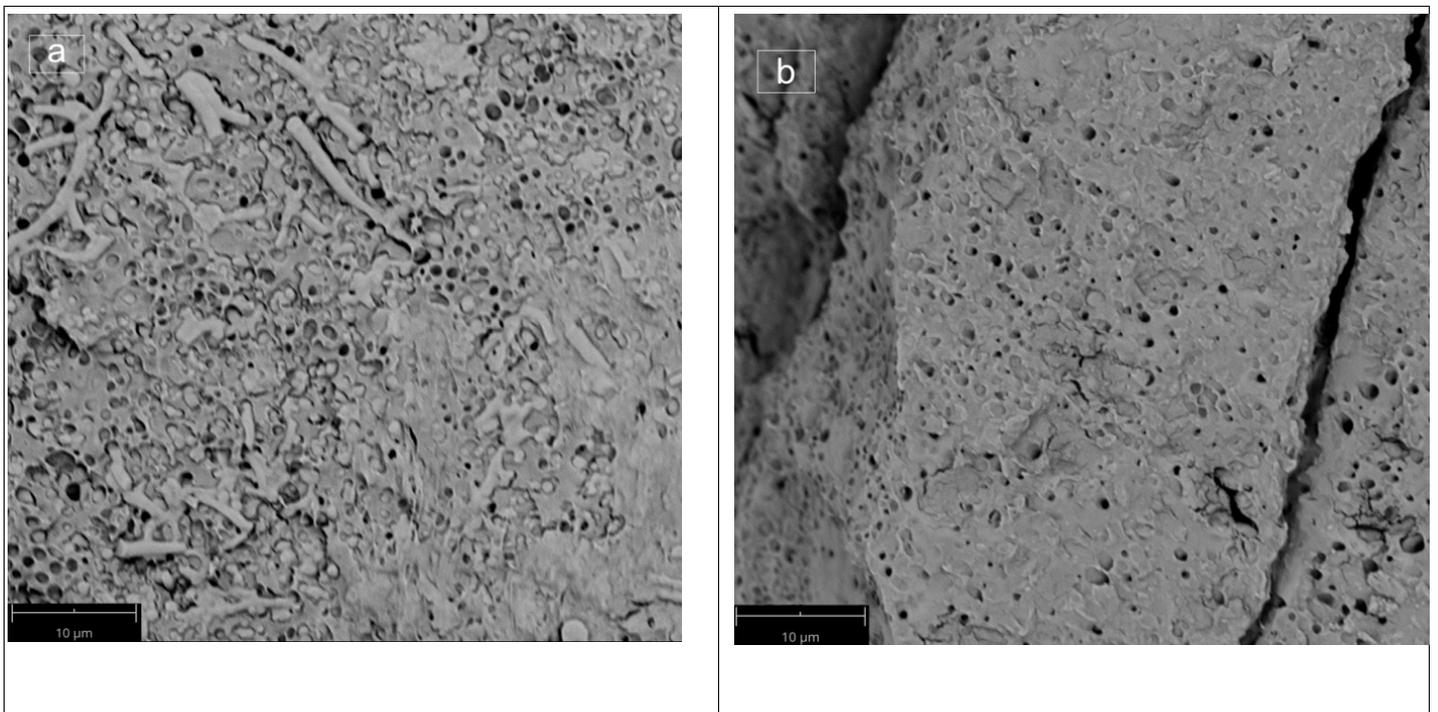
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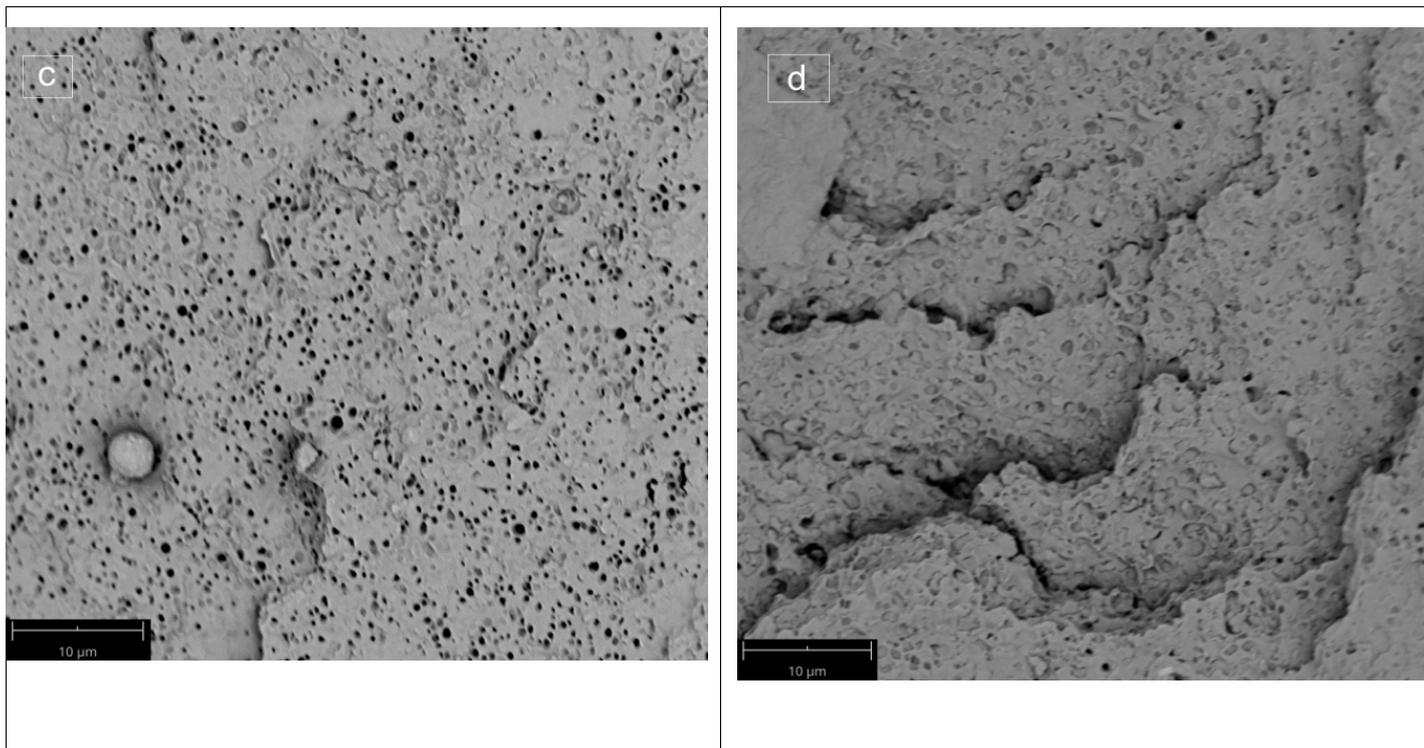
545 Fig 4b.



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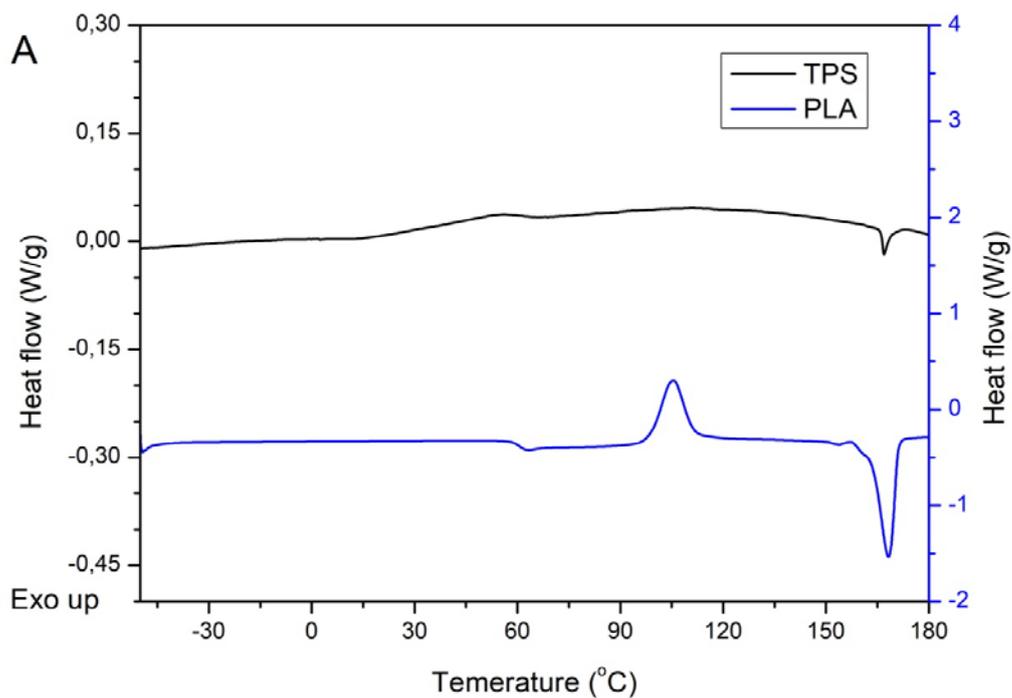
547 Fig 5





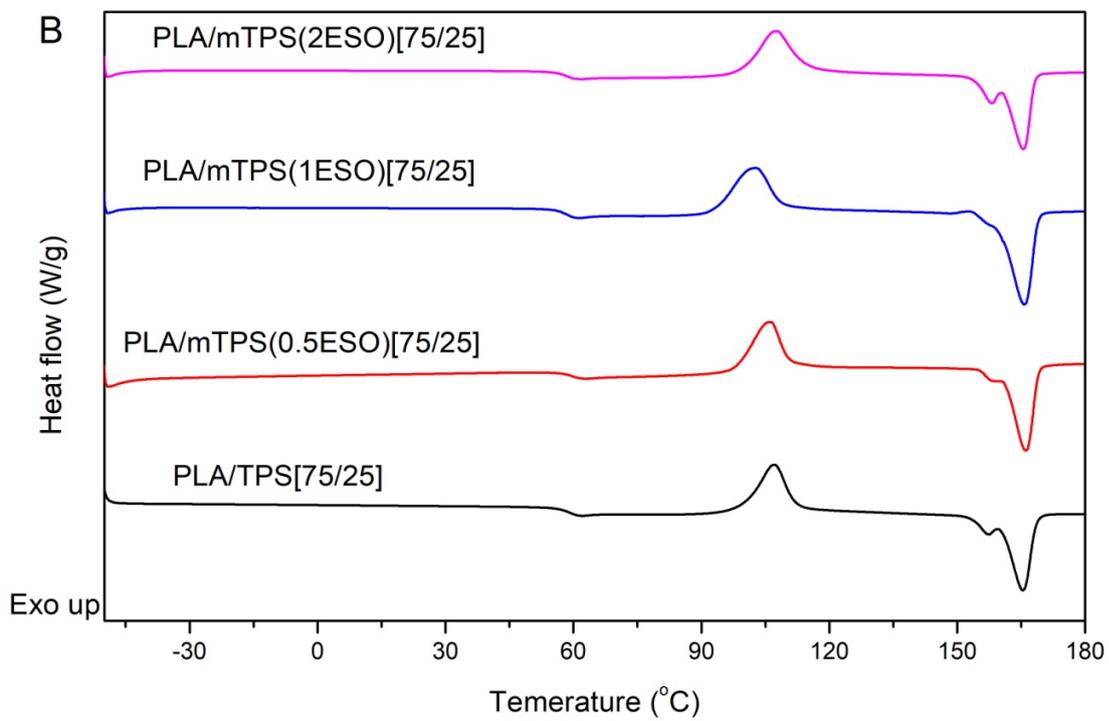
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549 Fig 6a



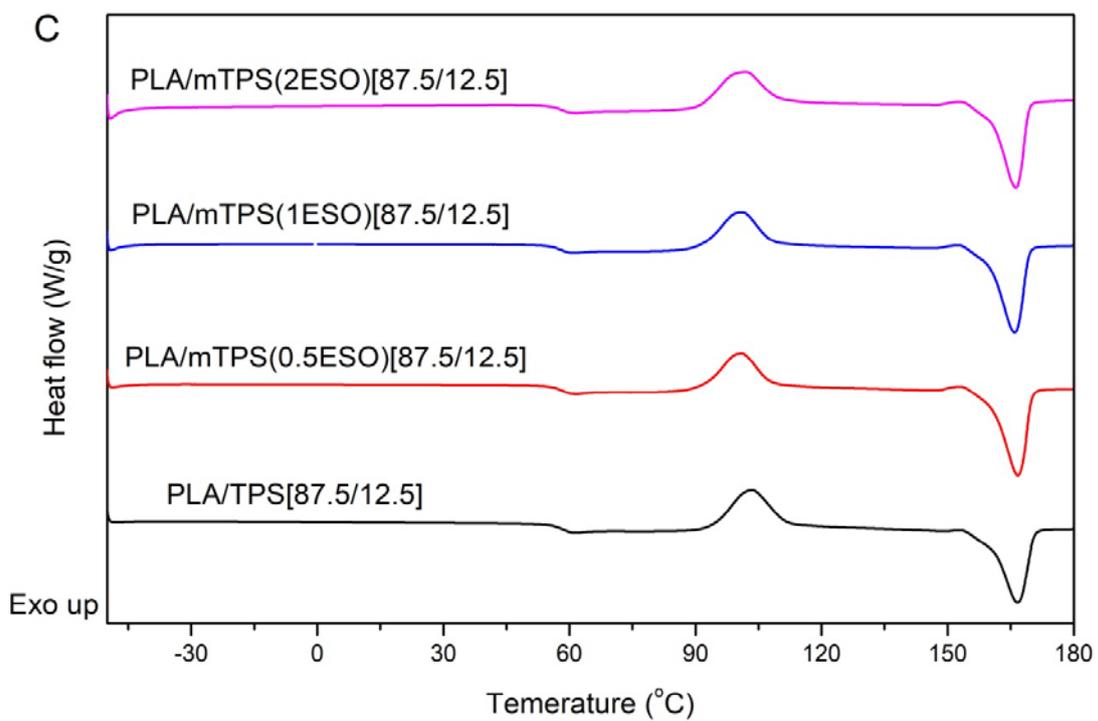
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551 Fig 6b.



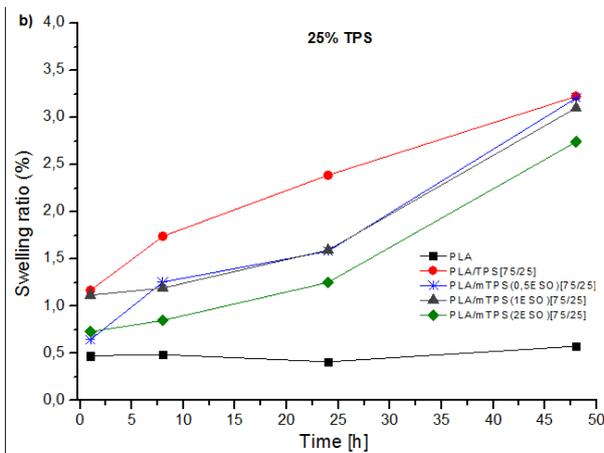
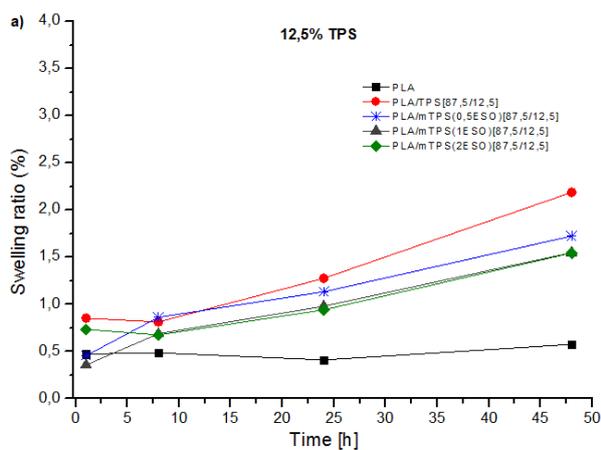
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553 Fig 6c.



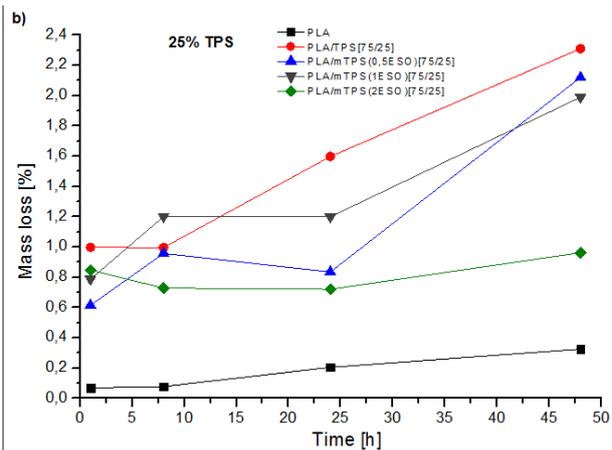
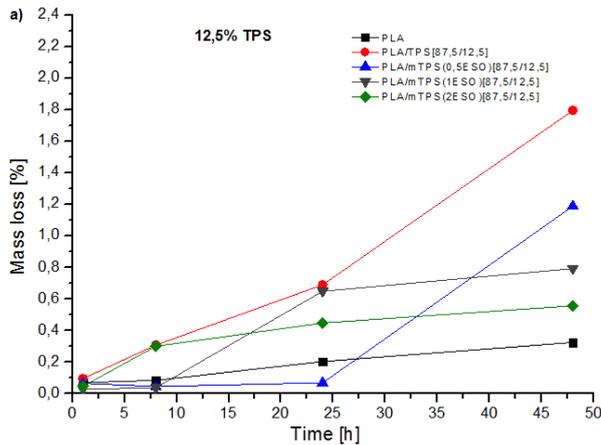
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555 Fig 7.



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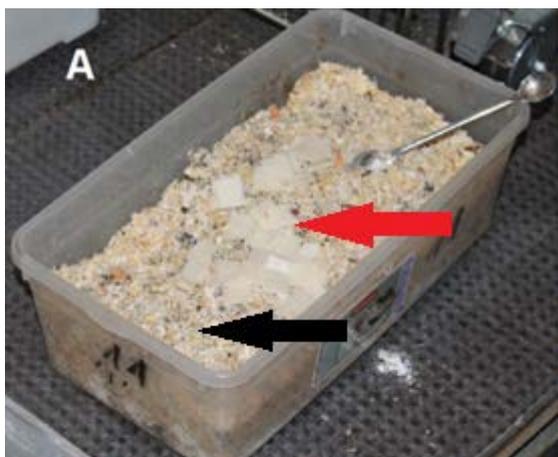
557 Fig 8.



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559

560 Fig 9.



561