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

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ABSTRACT

In this study, biodegradable and compostable compositions, derived from totally natural feedstock/raw materials, namely polylactide (PLA), potato thermoplastic starch (TPS) and plant glycerin have been made by melt extrusion with epoxydized soybean oil (ESO) as reactive modifier in order to improve PLAs ductility and reduce the products cost without compromising biodegradation. The obtained PLA/mTPS (0,5ESO) [75/25] and PLA/mTPS (2ESO) [75/25] compositions provides satisfactory mechanical properties comparable to native PLA. Addition of 25% TPS and 0,5-2% ESO to PLA, improved impact strength from 13,70 kJ/m^2 to 16,69 kJ/m^2 compared to neat PLA and increase elongation at break from 2,6% to 8,8%. The addition of ESO into PLA/TPS composition enhanced water resistance and improved impact strength to over 16 kJ/m2 for PLA/TPS(2%ESO)[75/25]composition. The thermal, rheological and morphology of fractured surface were also studied. Finally, biodegradability and compostability of prepared samples was specified by stimulated composting process (according to PN-EN 14806:2010 standard). Possibility of replacing up to 25% of PLA by TPS and ESO, allows to reduces the costs of the product as well as maintain quite similar properties and ability to composting relative to native PLA.

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

1. Introduction

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

Currently, the most common biodegradable polymers are polylactide (PLA), poly(hydroxybutyrate) (PHB), poly(glycolic acid) (PGA) and natural-based polymers like starch and cellulose (Kale et al., 2007; Mohanty et al., 2000; Shen et al., 2009). Each of these polymers has many different advantages and disadvantages. One of the ways of extracting the positive features of these materials is their mutual blending. The benefit of this approach is the possibility of using already known manufacturing methods and conventional machinery. PLA or PHB are very universal but also expensive polymers, therefore their modification via blending with a naturally occurring polymers may cause reduction of material costs, without compromising biodegradation (Martin and Avérous, 2001; Parulekar and Mohanty, 2007; Zhang and Sun, 2004). On the other hand, in most cases biopolymer pairs are thermodynamically immiscible - this prevents to mix them at the molecular level (Teixeira et al., 2012; Wang et al., 2008). In order to enhance the interfacial adhesion and improve compatibility between the polymers matrix a number of different agents, may be added. There are many reports which indicates that an incorporation of enhancing additives, such as: acrylic acid (AA) (Wu, 2005), maleic anhydrite (MA) (Clasen et al., 2015; Huneault and Li, 2007; Leadprathom et al., 2010; Zhang and Sun, 2004), methylene-diphenyldiisocyanate (MDI) (Carmona et al., 2015; Wang et al., 2001), fillers, e.g. montmorillonite (MMT) (Guarás et al., 2016; Jalalvandi et al., 2015), or phenyl diisocyanate (PDI) (Karagoz and Ozkoc, 2013), might contributed to a significant improvement of miscibility biodegradable blends. Consequently, the production of bio-blends containing solely of fully natural raw materials is a challenging.

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

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

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

2. Materials and methods

2.1. Materials

Each formulation was prepared with the use of biodegradable and compostable materials made from renewable resource of plant origin. Native potato starch was purchased from ZetPezet, Poland (humidity max. 16%, pH= 5.5-7.5). PLA (7032D, MFR = 7g/10min at 210ºC, 2.16kg, density 1.25g/cm^3, humidity 3%) was supplied by NatureWorks LLC (USA), as a transparent injection grade. Plant pharmaceutical grade glycerin (TechlandLab, Poland, density$_{20ºC}$ 1.26 g/cm^3, purity 99.5%), was used as a starch plasticizer. Epoxidized soybean oil (ESO) (Brenntag, Germany) with oxirane oxygen about 6-10 gO_2/100g and iodine number approximately 3 gI_2/100g, served as a starch reactive modifier.

2.2. Preparation and modification of TPS

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

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

2.3. PLA/TPS compositions fabrication

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

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

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

2.4. Melt Flow Rate (MFR)

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

2.5. Mechanical characterization

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

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

Hardness was measured by using Shore method according to PN-EN ISO 868:2004. Obtained data were presented with Shore D degree (°Sh D). For each PLA/TPS blend 10 samples were examined and the results were averaged.

2.6. Morphology characterization

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

2.7. Thermal properties

The thermal properties of prepared blends were characterized by differential scanning calorimetry (DSC) on a TA Instrument (model Q100). Firstly, the samples were conditioned at 30 ºC for 2 min. Then, measurements were carried out from -50 to 190 ºC, at a heating rate of 10 ºC/min, under a nitrogen atmosphere.

2.8. Water resistance

Water resistance was studied as follows; Samples of PLA/TPS blends of 20x10x4 mm were dried in a laboratory oven at 60 ºC until constant weight was achieved (m_0). Samples cooled down to the room temperature. Immediately afterwards, specimens were immersed in the containers filled with 25 ml of tap water. The incubation process was carried out for 1 month and the control time points were after 1h, 8h, 24h, 48h, respectively. Water resistance was calculated according to the formula 1 and formula 2. Formula 1 express the swelling ratio (i_{tx}) of the samples, which was determined by the mass of adsorbed solvent (m_1) in storage period (t_x). Formula 2 is associated with the samples mass loss *(ml%)* after each time point, where samples were removed out of container, dried to the constant mass and weighted *(m_z)*.

$$i_{t_x} = \frac{(m_1 - m_0) * 100}{m_o} \qquad (1)$$

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

2.9. Stimulated composting

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

3. Results and discussion

3.1. Melt Flow Rate (MFR)

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

Therefore, the resulting PLA/TPS compositions exhibit also improved degree of flow in comparison to the pure PLA, remaining at a level of 6g/10min (Figure 3). In PLA/TPS compositions containing of 12% TPS, different presence of ESO does not significantly affect the MFR value. Increasing the content of TPS up to 25%, the similar trend in MFR is observed like for TPS modified by ESO (mTPS Figure 2). For 1 % of ESO concentration in PLA/TPS with 25% of TPS, MFR values reached the highest point (7.39 g/10min). Further increasing the content of the ESO up to 2% results in a reduction of the melt flow rate (5.26 g/10min). Our findings correlate with Yu-Qiong Xu (Yu-Qiong Xu, 2009) studies. They noted that increasing addition of ESO in the PLA is characterized by a sinusoidal change in value of MFR. In our case, addition of ESO caused plasticization effect by increasing of MFR value. The lack of a catalyst could have contributed to the absence of the branching and cross-linking effect in compositions. However, it should be noted that this effect is not noticeable for the composition containing 12.5% TPS, because of too small ESO content relative to PLA.

3.2. *Mechanical characterization*

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

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

Another parameter that describes the functional properties of polymers is impact strength. A slight improvement in impact strength was achieved by blending of unmodified TPS with PLA. It was believed that addition of a ductile and flexible material such as TPS resulted in reduction of brittleness of the PLA. From Table 3 it could be seen the impact-energy absorption of the PLA/TPS blends raising with increasing of ESO content. For the samples with 25% of TPS the highest impact strength value has reached PLA/TPS composition with 2% of ESO (16.96 kJ/m^2). It can be assumed that the PLA/mTPS(2ESO)[75/25] sample show the highest adhesion between PLA and TPS. In turn, for the samples with 25% of TPS and 0.5% or 1% of ESO, the impact strength is unnoticeable (13.92 kJ/m2 and 14.03 kJ/m2, respectively) and probably it is due to too small amount of ESO. Therefore, it should be attributed a significant effect of the addition of ESO to the blends toughness, but only if the ESO content is at least 2%. The impact strength value of all obtained compound does not falls below 10 kJ/m^2, which allows for a statement that as a result of preparing PLA/TPS/ESO blends do not reduce impact strength, compared to pure PLA.

Table 3 summarized the mechanical properties of pure PLA and obtained blends. In terms of mechanical properties our results are passable enough but cannot be strictly comparable to the results found by other researches. Yu-Qiong Xu et al. (Yu-Qiong Xu, 2009) and Vijayarajan et al. (Vijayarajan et al., 2014) added much larger amounts of epoxidized soybean oil to PLA matrix (in the range of 3 up to 20 wt% of ESO). This has led to great improvement of impact strength (up to 47 J/m) and ductility (Vijayarajan et al., 2014) as well as positively influenced on melt strength and rheological properties of PLA (Yu-Qiong Xu, 2009). On the other hand, research on the impact of ESO on the mechanical properties of TPS were led by Belhassen et al. (Belhassen et al., 2014). They proved occurrence of the condensation reaction between the oxirane rings of ESO and the TPS hydroxyl groups. This resulted in enhancement in Young's modulus and tensile strength of TPS/ESO samples, but also caused rigidification effect (lower elongation at break).

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

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^2	ºSh 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

3.3. *Morphology characterization*

The morphology of PLA/TPS[75/25] blends with a various ESO content was examined by SEM and shown in Figure 5. As the content of the ESO increases, the surface morphology changes. For the unmodified sample (PLA/TPS[75/25]), the morphology is highly inhomogeneous. There are numerous gaps between the TPS and the PLA matrix. Moreover, discontinuities in the structure are visible. TPS occurs in the form of granules (particle size ranges from 0.5 to 2 µm) and tubes (particle length ranges from 3 to 20 µm), suggesting poor dispersion and miscibility of TPS in the PLA matrix due to a large difference in polarity between TPS and PLA polymers. Similar morphology was observed in Ferri et al. study (Ferri et al., 2016). The addition of ESO improved compatibility between TPS and PLA molecules. The addition of only 0.5% ESO (Figure. 5b) resulted in disappearance of the tubes particles and reduction in the number and size of TPS granules. Increasing the ESO content to 2% caused enhancement of interfacial bonding between TPS and TPS phases. Significantly decreased number of black particles were observed, representing TPS granules “ripped out’’ from PLA matrix. The structure of PLA/mTPS (2ESO) [75/25] is more homogeneous. The TPS granules appear to be strongly embedded in the PLA matrix (Figure. 5d). Hence, the assumption that the addition of ESO improves the miscibility and interphase adhesion of TPS to PLA molecules. Similar effect of ESO presence in PLA/TPS composition was observed by Xiong et al. (Xiong et al., 2013).

3.4. *Thermal properties*

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

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

Composition	T_g [°C]	T_{cc} [°C]	ΔH_{cc} [J/g]	Main T_m [°C]	ΔH_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

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

3.5. Water resistance

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

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

3.6. *Stimulated composting*

According to ASTM D5338-98, 2003 (ASTM D5338-98, 2003) standard, composting is a controlled process of biological degradation with the use of microorganisms under strictly controlled conditions. A biodegradable material is converted to CO2, water, inorganic compounds and biomass. The microorganisms in the process of polymer degradation release enzymes which cause a chain scission of the polymer into monomers (Lau et al., 2009). To confirm the suitability of the obtained innovative materials for use in the short-life application packaging industry as an alternative for commonly used petroleum-based polymers, compostable tests was commissioned. The composting processes is illustrated in Figure 9. The data from testing by COBRO lab clearly confirm that the materials decomposed completely. During 57 days of incubation, all samples were disintegrated to dimension smaller than 2mm in diameter. According to PN-EN 14806:2010 standard, all were completely degraded in the composting conditions.

4. Conclusions

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

References

Akrami, M., Ghasemi, I., Azizi, H., Karrabi, M., Seyedabadi, M., 2016. A new approach in compatibilization of the poly(lactic acid)/thermoplastic starch (PLA/TPS) blends. Carbohydr. Polym. 144, 254–262. https://doi.org/10.1016/j.carbpol.2016.02.035

Ali, F., Chang, Y.-W., Kang, S.C., Yoon, J.Y., 2009. Thermal, mechanical and rheological properties of poly (lactic acid)/epoxidized soybean oil blends. Polym. Bull. 62, 91–98. https://doi.org/10.1007/s00289-008-1012-9

ASTM D5338-98, 2003. Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions.

Auras, R., Harte, B., Selke, S., 2004. An overview of polylactides as packaging materials. Macromol. Biosci. 4, 835–864. https://doi.org/10.1002/mabi.200400043

Ayana, B., Suin, S., Khatua, B.B., 2014. Highly exfoliated eco-friendly thermoplastic starch (TPS)/poly (lactic acid)(PLA)/clay nanocomposites using unmodified nanoclay. Carbohydr. Polym. 110, 430–439. https://doi.org/10.1016/j.carbpol.2014.04.024

Belhassen, R., Vilaseca, F., Mutjé, P., Boufi, S., 2014. Thermoplasticized starch modified by reactive blending with epoxidized soybean oil. Ind. Crops Prod. 53, 261–267. https://doi.org/10.1016/j.indcrop.2013.12.039

Carmona, V.B., Corrêa, A.C., Marconcini, J.M., Mattoso, L.H.C., 2015. Properties of a Biodegradable Ternary Blend of Thermoplastic Starch (TPS), Poly(ε-Caprolactone) (PCL) and Poly(Lactic Acid) (PLA). J. Polym. Environ. 23, 83–89. https://doi.org/10.1007/s10924-014-0666-7

Cartier, L., Okihara, T., Ikada, Y., Tsuji, H., Puiggali, J., Lotz, B., 2000. Epitaxial crystallization and crystalline polymorphism of polylactides. Polymer (Guildf). 41, 8909–8919. https://doi.org/10.1016/0032-3861(94)90933-4

Clasen, S.H., Müller, C.M.O., Pires, A.T.N., 2015. Maleic Anhydride as a Compatibilizer and Plasticizer in TPS/PLA Blends. J. Braz. Chem. Soc. https://doi.org/10.5935/0103-5053.20150126

Ferri, J.M., Garcia-Garcia, D., Sánchez-Nacher, L., Fenollar, O., Balart, R., 2016. The effect of maleinized linseed oil (MLO) on mechanical performance of poly(lactic acid)-thermoplastic starch (PLA-TPS) blends. Carbohydr. Polym. 147, 60–68. https://doi.org/10.1016/j.carbpol.2016.03.082

Gregory, M.R., 2009. Environmental implications of plastic debris in marine settings--entanglement, ingestion, smothering, hangers-on, hitch-hiking and alien invasions. Philos. Trans. R. Soc. Lond. B. Biol. Sci. 364, 2013–2025. https://doi.org/10.1098/rstb.2008.0265

Guarás, M.P., Alvarez, V.A., Ludueña, L.N., 2016. Biodegradable nanocomposites based on starch/polycaprolactone/compatibilizer ternary blends reinforced with natural and organo-modified montmorillonite. J. Appl. Polym. Sci. 133. https://doi.org/10.1002/app.44163

Huneault, M.A., Li, H., 2007. Morphology and properties of compatibilized polylactide/thermoplastic starch blends. Polymer (Guildf). 48, 270–280. https://doi.org/10.1016/j.polymer.2006.11.023

Imre, B., Pukánszky, B., 2013. Compatibilization in bio-based and biodegradable polymer blends. Eur. Polym. J. 49, 1215–1233. https://doi.org/10.1016/j.eurpolymj.2013.01.019

Jalalvandi, E., Majid, R., Ghanbari, T., Ilbeygi, H., 2015. Effects of montmorillonite (MMT) on morphological, tensile, physical barrier properties and biodegradability of polylactic acid/starch/MMT nanocomposites. J. Thermoplast. Compos. Mater. 28, 496–509. https://doi.org/10.1177/0892705713486129

Janik, H., Sienkiewicz, M., Wawrowska, M., Wiecierzycka, K., Przybytek, A., 2017. Degradation of modified TPS in natuaral and industrial compost, in: Mukbaniani, O., Abadie, M., Tatrishvili, T. (Eds.), Chemical Engineering of Polymers. Production of Functional and Flexible Materials. Apple Academic Press, CRC Press, pp. 397–406.

Kale, G., Kijchavengkul, T., Auras, R., Rubino, M., Selke, S.E., Singh, S.P., 2007. Compostability of bioplastic packaging materials: An overview. Macromol. Biosci. 7, 255–277. https://doi.org/10.1002/mabi.200600168

Karagoz, S., Ozkoc, G., 2013. Effects of a diisocyanate compatibilizer on the properties of citric acid modified thermoplastic starch/poly(lactic acid) blends. Polym. Eng. Sci. 53, n/a-n/a. https://doi.org/10.1002/pen.23478

Kaseem, M., Hamad, K., Deri, F., 2012. Thermoplastic starch blends: A review of recent works. Polym. Sci. Ser. A 54, 165–176. https://doi.org/10.1134/S0965545X1202006X

Khan, B., Bilal Khan Niazi, M., Samin, G., Jahan, Z., 2016. Thermoplastic Starch: A Possible Biodegradable Food Packaging Material-A Review. J. Food Process Eng. 0. https://doi.org/10.1111/jfpe.12447

Khoo, R., Chow, W., 2015. Mechanical and thermal properties of poly(lactic acid)/sugarcane bagasse fiber green composites. J. Thermoplast. Compos. Mater. https://doi.org/10.1177/0892705715616857

Lau, A.K., Cheuk, W.W., Lo, K.V., 2009. Degradation of greenhouse twines derived from natural fibers and biodegradable polymer during composting, Journal of Environmental Management. https://doi.org/10.1016/j.jenvman.2008.03.001

Leadprathom, J., Suttiruengwong, S., Threepopnatkul, P., Seadan, M., 2010. Compatibilized Polylactic Acid/Thermoplastic Starch by Reactive Blend. J. Met. Mater. Miner. 20, 87–90.

Lim, L.-T., Auras, R., Rubino, M., 2008. Processing technologies for poly(lactic acid). Prog. Polym. Sci. 33, 820–852. https://doi.org/10.1016/j.progpolymsci.2008.05.004

Luckachan, G.E., Pillai, C.K.S., 2011. Biodegradable Polymers- A Review on Recent Trends and

Emerging Perspectives. J. Polym. Environ. 19, 637–676. https://doi.org/10.1007/s10924-011-0317-1

Madhavan Nampoothiri, K., Nair, N.R., John, R.P., 2010. An overview of the recent developments in polylactide (PLA) research. Bioresour. Technol. 101, 8493–8501. https://doi.org/10.1016/j.biortech.2010.05.092

Martin, O., Ârous, L.A., 2001. Poly(lactic acid): plasticization and properties of biodegradable multiphase systems. Polymer (Guildf). 42, 6209–6219.

Martin, O., Avérous, L., 2001. Poly(lactic acid): plasticization and properties of biodegradable multiphase systems. Polymer (Guildf). 42, 6209–6219. https://doi.org/10.1016/S0032-3861(01)00086-6

Mohanty, A.K., Misra, M., Hinrichsen, G., 2000. Biofibres, biodegradable polymers and biocomposites: An overview. Macromol. Mater. Eng. 276–277, 1–24. https://doi.org/10.1002/(SICI)1439-2054(20000301)276:1<1::AID-MAME1>3.0.CO;2-W

Müller, C.M.O., Pires, A.T.N., Yamashita, F., 2012. Characterization of thermoplastic starch/poly(lactic acid) blends obtained by extrusion and thermopressing. J. Braz. Chem. Soc. 23, 426–434. https://doi.org/10.1590/S0103-50532012000300008

Nafchi, A.M., Moradpour, M., Saeidi, M., Alias, A.K., 2013. Thermoplastic starches: Properties, challenges, and prospects. Starch/Staerke 65, 61–72. https://doi.org/10.1002/star.201200201

Parulekar, Y., Mohanty, A.K., 2007. Extruded Biodegradable Cast Films from Polyhydroxyalkanoate and Thermoplastic Starch Blends: Fabrication and Characterization. Macromol. Mater. Eng. 292, 1218–1228. https://doi.org/10.1002/mame.200700125

PlasticsEurope, 2016. Plastics – the Facts 2016. An analysis of European plastics production, demand and waste data.

Shen, L., Haufe, J., Patel, M.K., 2009. Product overview and market projection of emerging bio-based plastics.

Siracusa, V., Rocculi, P., Romani, S., Rosa, M.D., 2008. Biodegradable polymers for food packaging: a review. Trends Food Sci. Technol. 19, 634–643. https://doi.org/10.1016/j.tifs.2008.07.003

Tábi, T., Sajó, I.E., Szabó, F., Luyt, A.S., Kovács, J.G., 2010. Crystalline structure of annealed polylactic acid and its relation to processing. Express Polym. Lett. 4, 659–668. https://doi.org/10.3144/expresspolymlett.2010.80

Teixeira, E. de M., Curvelo, A.A.S., Corrêa, A.C., Marconcini, J.M., Glenn, G.M., Mattoso, L.H.C., 2012. Properties of thermoplastic starch from cassava bagasse and cassava starch and their blends with poly (lactic acid). Ind. Crops Prod. 37, 61–68. https://doi.org/10.1016/j.indcrop.2011.11.036

Vijayarajan, S., Selke, S.E.M., Matuana, L.M., 2014. Continuous Blending Approach in the Manufacture of Epoxidized Soybean-Plasticized Poly(lactic acid) Sheets and Films. Macromol. Mater. Eng. 299, 622–630. https://doi.org/10.1002/mame.201300226

Wang, H., Sun, X., Seib, P., 2001. Strengthening blends of poly(lactic acid) and starch with methylenediphenyl diisocyanate. J. Appl. Polym. Sci. 82, 1761–1767. https://doi.org/10.1002/app.2018

Wang, N., Yu, J., Chang, P.R., Ma, X., 2008. Influence of formamide and water on the properties of thermoplastic starch/poly(lactic acid) blends. Carbohydr. Polym. 71, 109–118. https://doi.org/10.1016/j.carbpol.2007.05.025

Wootthikanokkhan, J., Kasemwananimit, P., Sombatsompop, N., Kositchaiyong, A., Isarankura na Ayutthaya, S., Kaabbuathong, N., 2012. Preparation of modified starch-grafted poly(lactic acid) and a study on compatibilizing efficacy of the copolymers in poly(lactic acid)/thermoplastic starch blends. J. Appl. Polym. Sci. 126, E389–E396. https://doi.org/10.1002/app.36896

Wu, C.-S., 2005. Improving Polylactide/Starch Biocomposites by Grafting Polylactide with Acrylic Acid - Characterization and Biodegradability Assessment. Macromol. Biosci. 5, 352–361. https://doi.org/10.1002/mabi.200400159

Xing, C., Matuana, L.M., 2016. Epoxidized soybean oil-plasticized poly(lactic acid) films performance as impacted by storage. J. Appl. Polym. Sci. 133, 1–8. https://doi.org/10.1002/app.43201

Xiong, Z., Yang, Y., Feng, J., Zhang, X., Zhang, C., Tang, Z., Zhu, J., 2013. Preparation and characterization of poly(lactic acid)/starch composites toughened with epoxidized soybean oil. Carbohydr. Polym. 92, 810–816. https://doi.org/10.1016/j.carbpol.2012.09.007

Yang, Y., Tang, Z., Xiong, Z., Zhu, J., 2015. Preparation and characterization of thermoplastic starches and their blends with poly(lactic acid). Int. J. Biol. Macromol. 77, 273–279. https://doi.org/10.1016/j.ijbiomac.2015.03.053

Yu-Qiong Xu, J.-P.Q., 2009. Mechanical and Rheological Properties of Epoxidized Soybean Oil Plasticized Poly(lactic acid). J. Appl. Polym. Sci. 112, 3185–3191. https://doi.org/10.1002/app

Zhang, J.-F., Sun, X., 2004. Mechanical Properties of Poly(lactic acid)/Starch Composites Compatibilized by Maleic Anhydride. Biomacromolecules 5, 1446–1451. https://doi.org/10.1021/bm0400022

Zhang, Y., Rempel, C., Liu, Q., 2014. Thermoplastic Starch Processing and Characteristics—A

Review. Crit. Rev. Food Sci. Nutr. 54, 1353–1370. https://doi.org/10.1080/10408398.2011.636156

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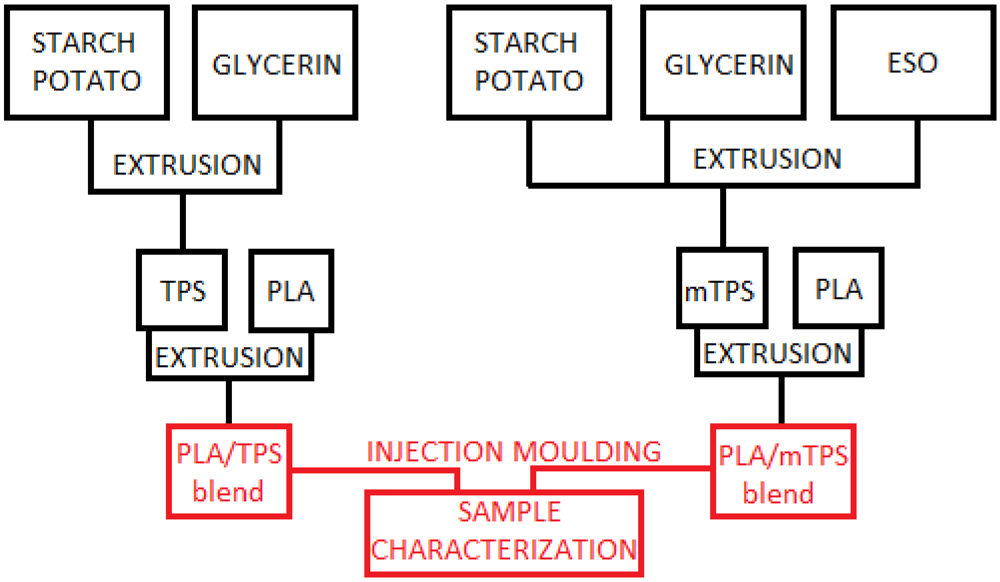
Fig 1.



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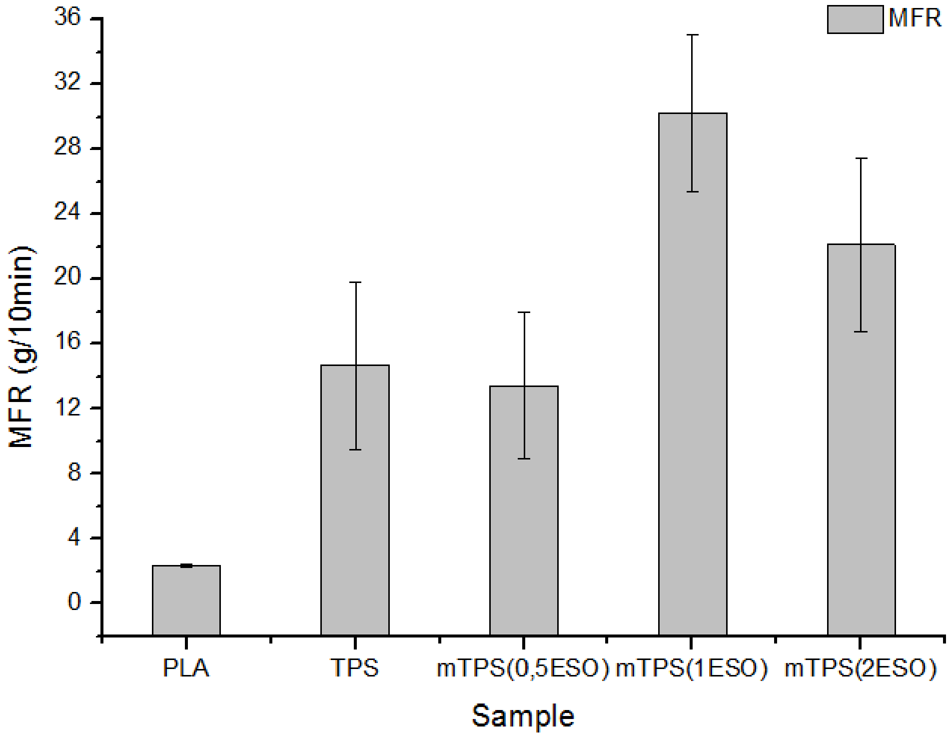

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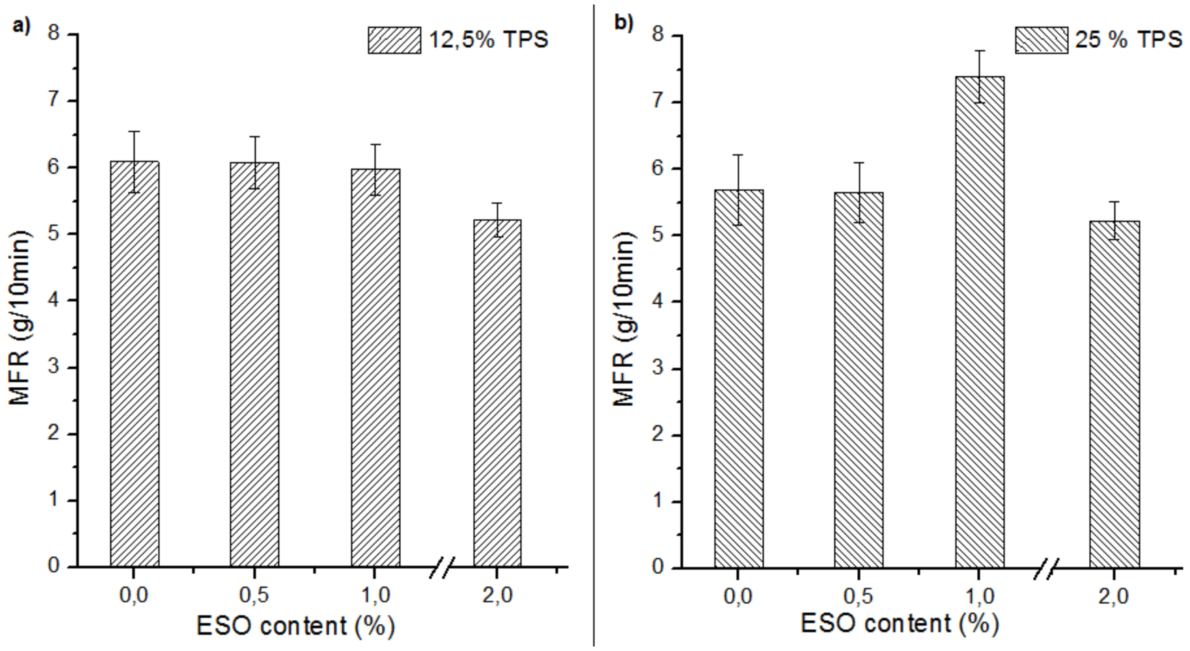
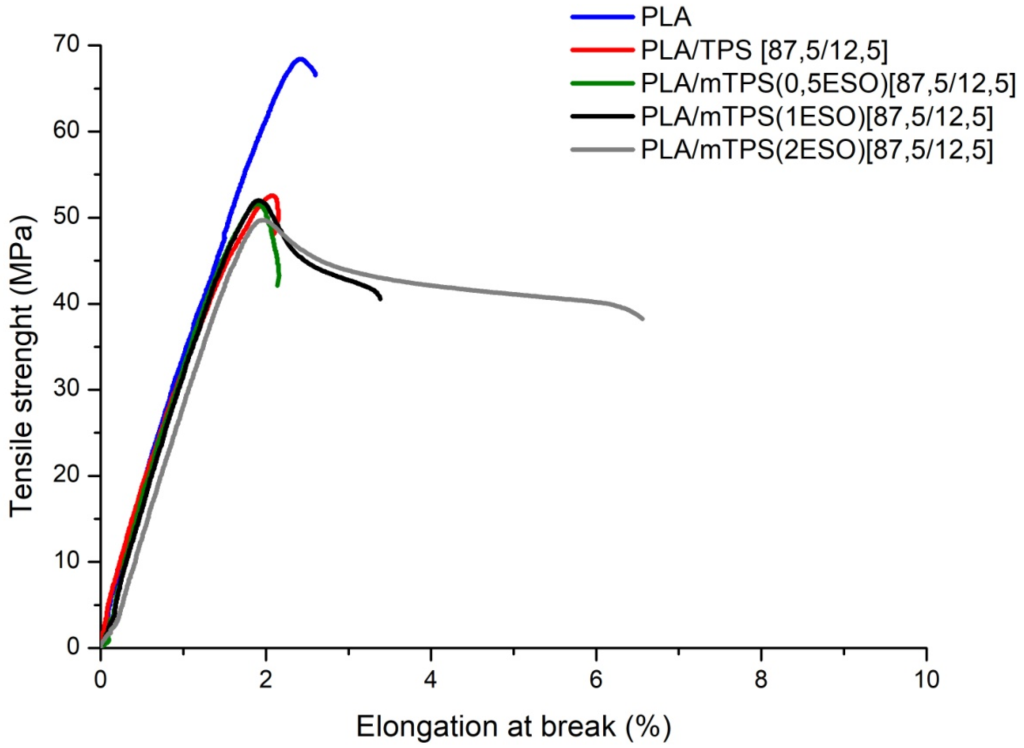


Fig. 4a



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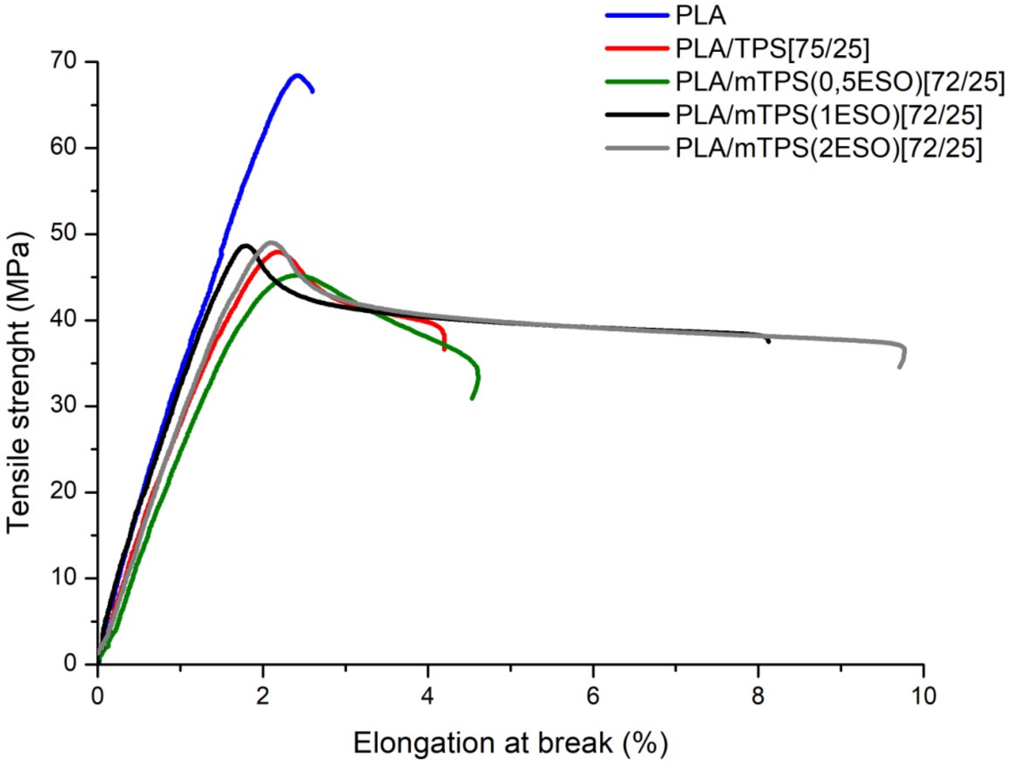
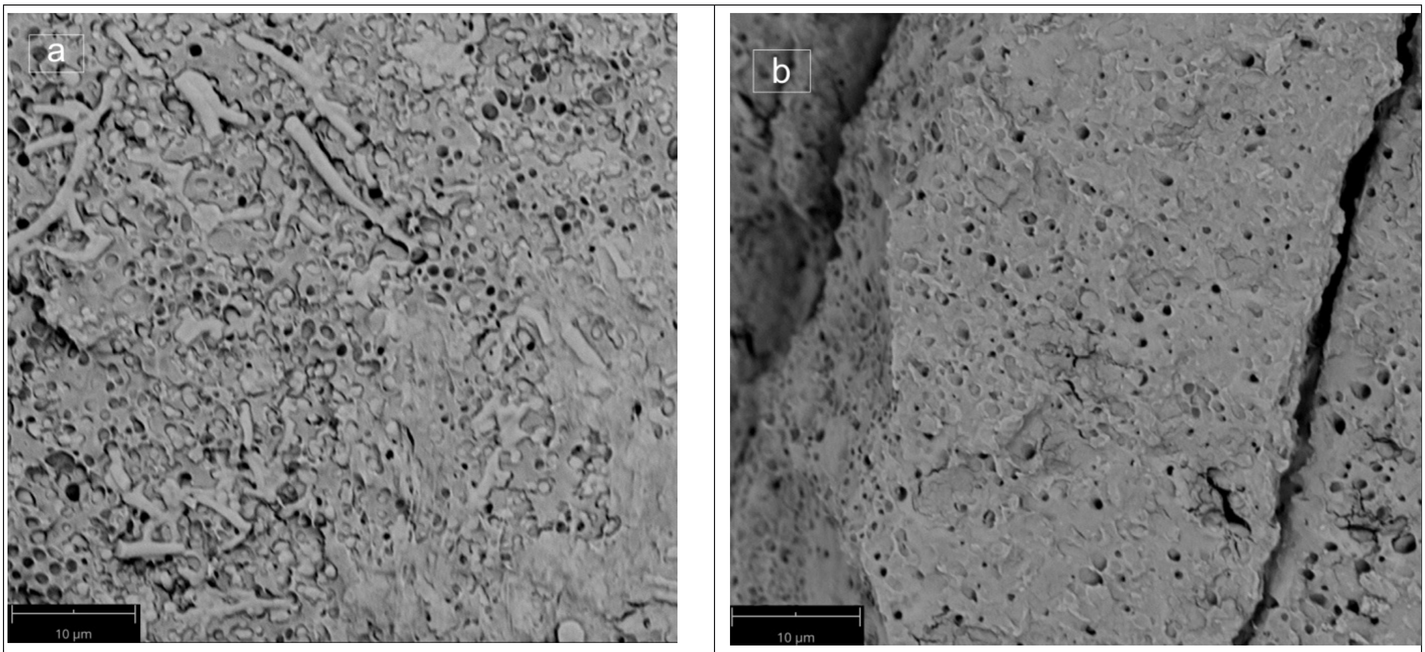

PLA
PLA/TPS[75/25]
PLA/mTPS(0,5ESO)[72/25]
PLA/mTPS(1ESO)[72/25]
PLA/mTPS(2ESO)[72/25]
Tensile strenght (MPa)
0
10
20
30
40
50
60
70
Elongation at break (%)
0
2
4
6
8
10

Fig 5


a
10 µm
b
10 µm

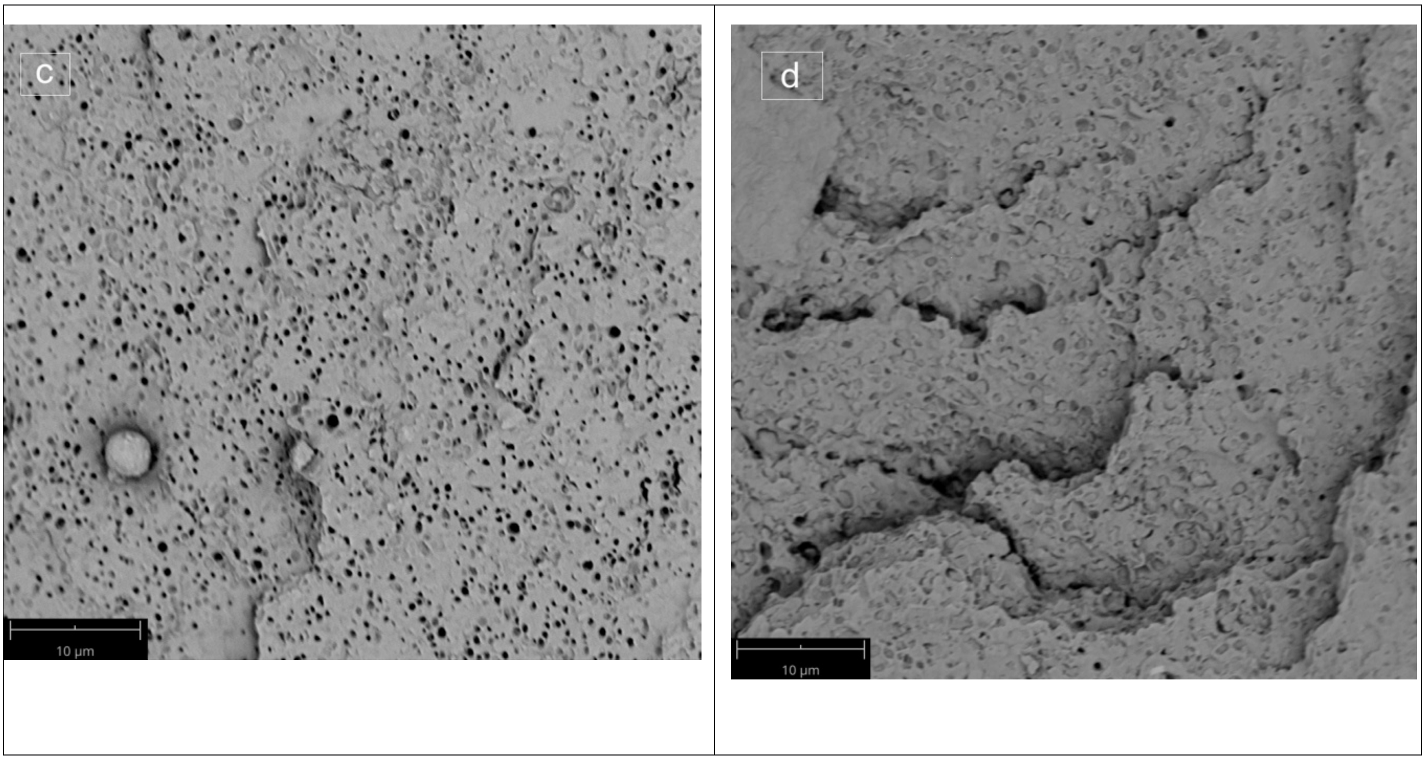

c
10 µm
d
10 µm

Fig 6a

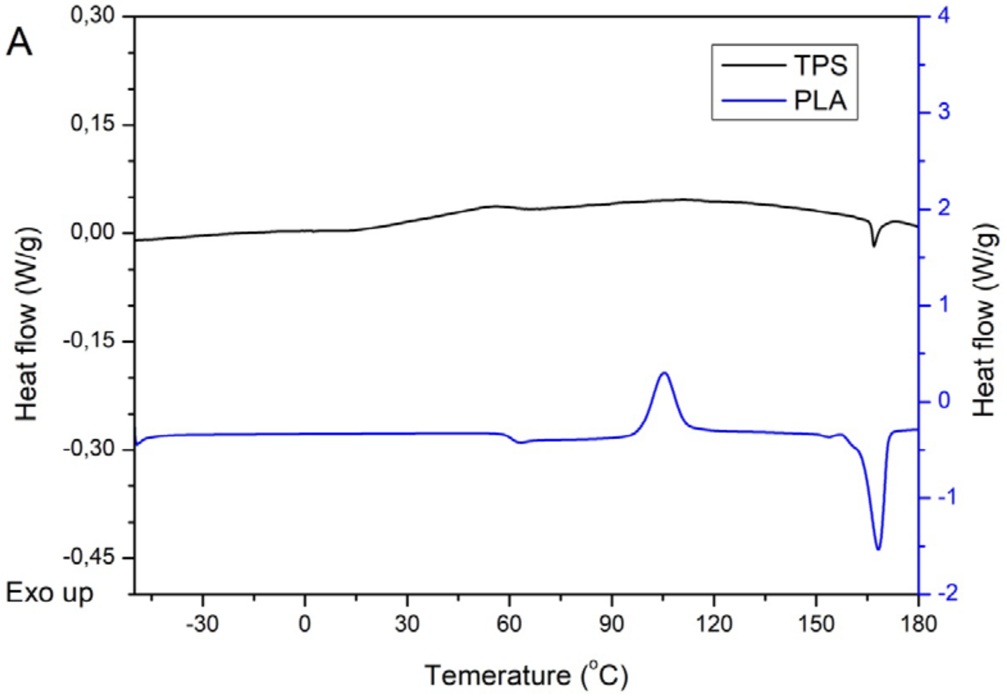
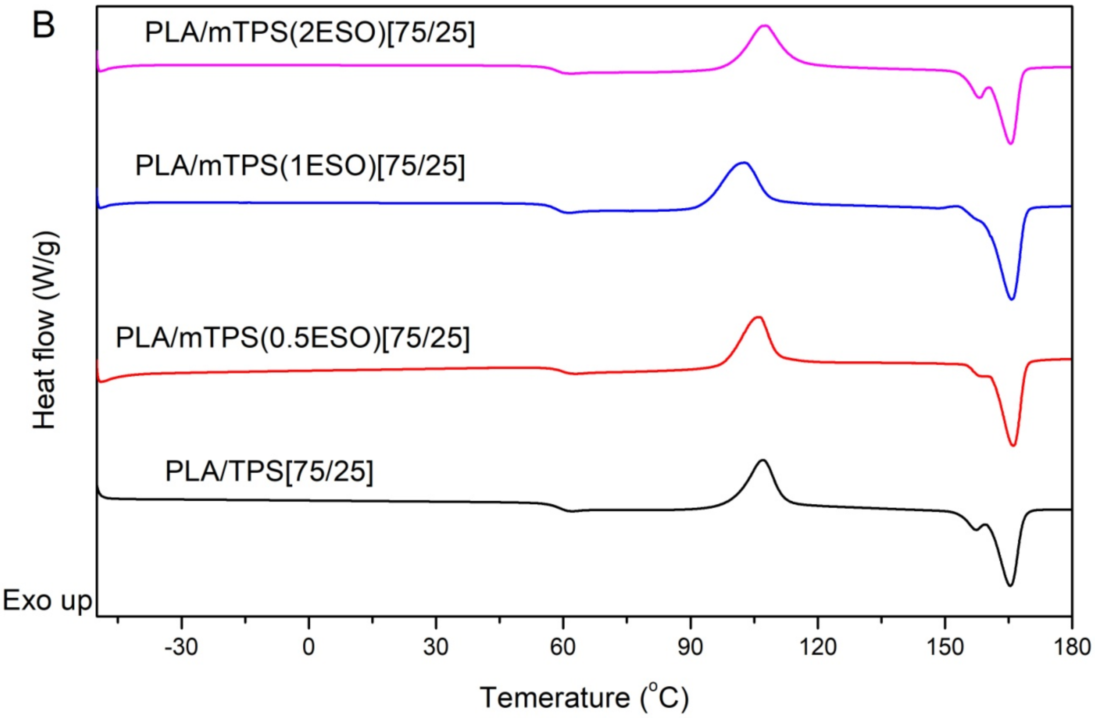

A
TPS
PLA
0,30
0,15
0,00
-0,15
-0,30
-0,45
Exo up
Heat flow (W/g)
4
3
2
1
0
-1
-2
Heat flow (W/g)
-30
0
30
60
90
120
150
180
Temerature (°C)

Fig 6b.



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553 Fig 6c.

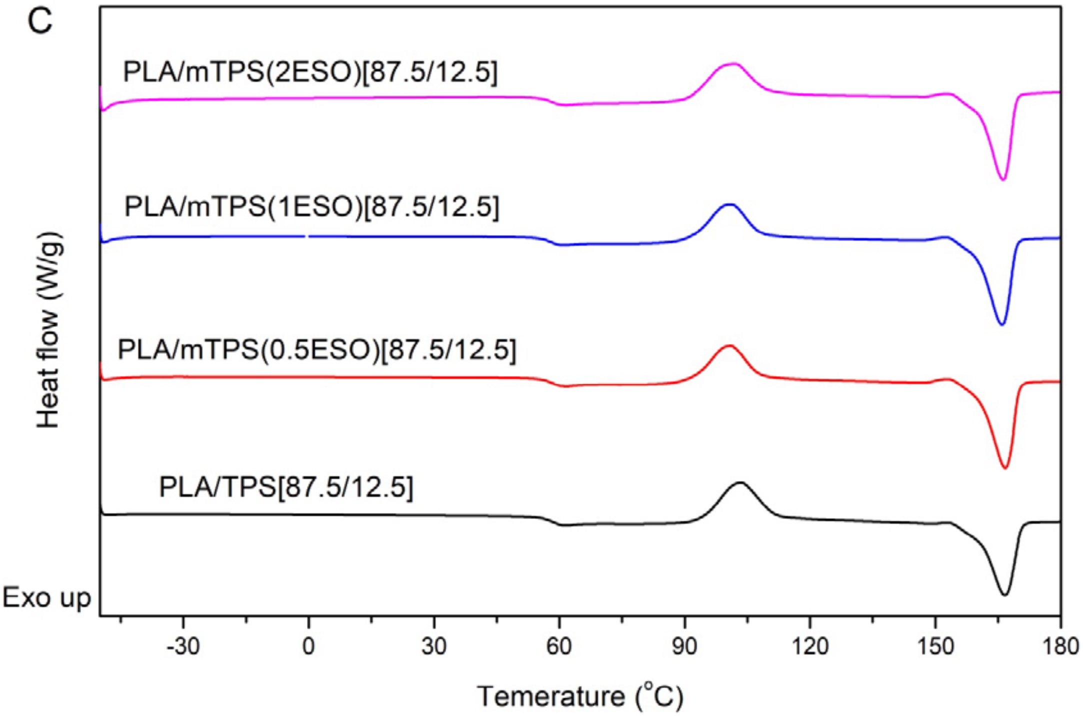

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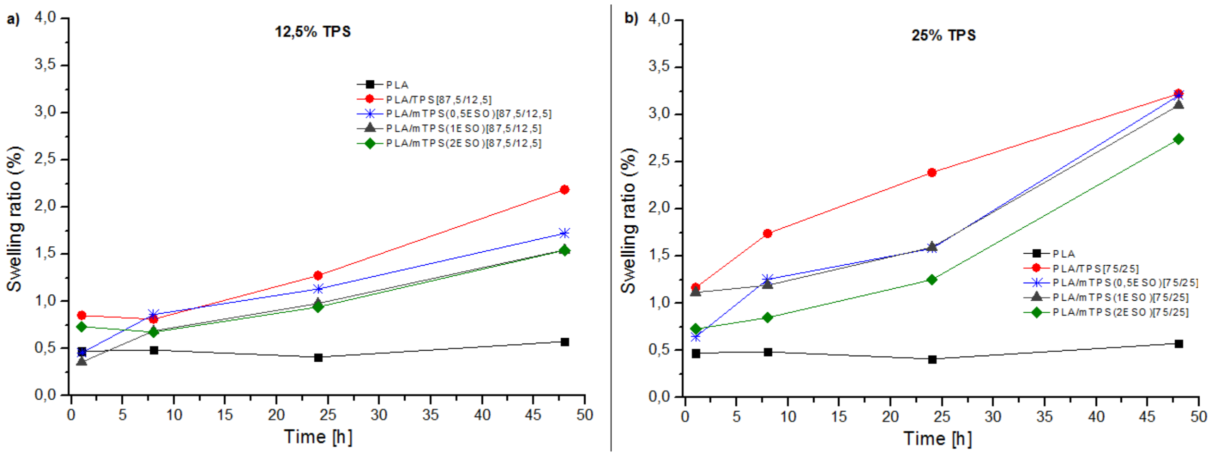
Fig 7.



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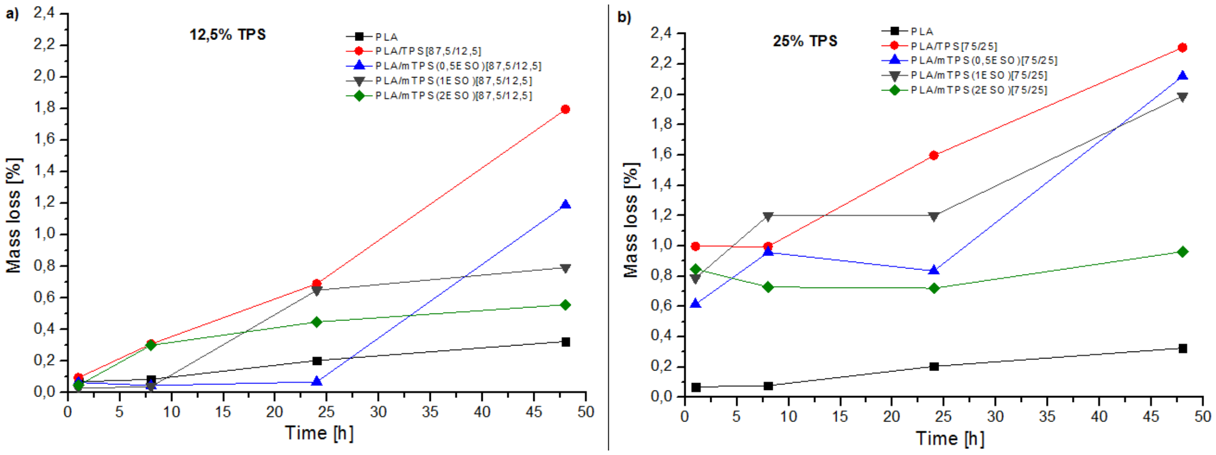
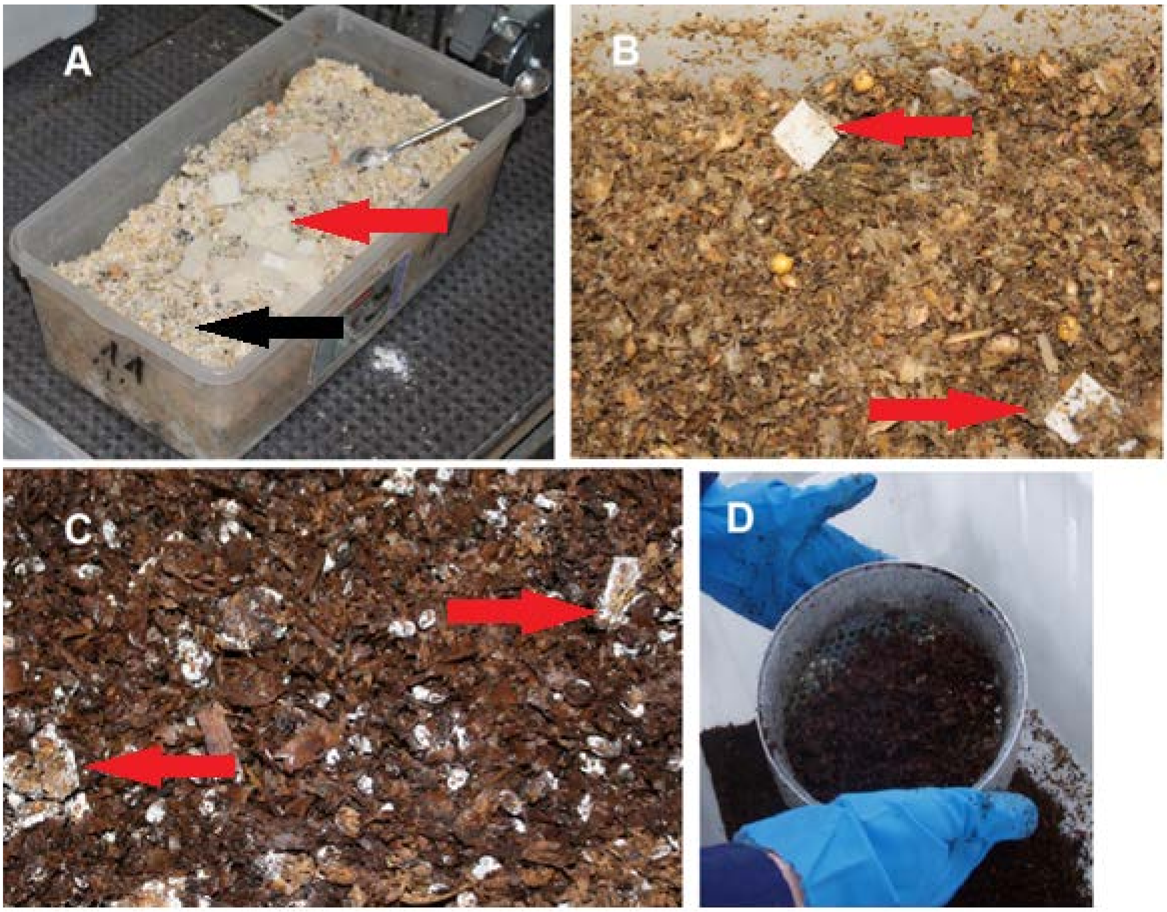


Fig 9.


A
B
C
D