



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



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ABSTRACT

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

1. Introduction

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

Several natural additives have been proposed as possible fillers for PLA. For instance, polymer-lignocellulose composites have been explored in recent times (Lee et al., 2008; Mohanty et al., 2000a). Lignocellulose, in fact, is an inexpensive filler that increases material toughness and improve the thermal stability by reducing tool wear (Way et al., 2012). However, the highly hydrophilic nature of the fibers often needs compatibilisation to improve the polymer-fiber interface (Murariu and Dubois, 2016). Other natural additives have been

experimented in these years. Manshor et al. in 2014 presented a novel idea of utilizing durian skin waste as reinforcing fiber for PLA. They found that 30 wt% PLA can be replaced by durian skin fibers without altering the impact strength, flexural modulus and thermal properties of the material with respect to the unreinforced PLA (Manshor et al., 2014). In 2017 Kocaman suggested surface-modified grinded coconut waste (CW) particles as bio-fillers to prepare polymeric composite materials with enhanced properties (Kocaman et al., 2017).

One of the most common biodegradable additives of the PLA is the Thermoplastic Starch (TPS), a renewable and biodegradable material very interesting because of its worldwide availability and its low cost (Tester and Karkalas, 2001). Different kinds of starches (wheat, corn, sorghum, yucca, potato, etc.) are conventionally used to produce industrial TPSs. The poor processability because of higher melting point compared to its decomposition temperature is the most important limiting factor for starch, which imposes the use of plasticizers (glycerol, sorbitol, maltose, glucose, water, urea, citric acid etc.) (Ma et al., 2006; Mahieu et al., 2015; Poutanen and Forsell, 1996; Shi et al., 2007; Tang et al., 2008; Teixeira et al., 2007). Plasticizers reduce the tension of deformation, hardness, density, viscosity and electrostatic charge of a polymer, while increasing the polymer chain flexibility, resistance to fracture and dielectric constant (Rosen, 1993). Glycerol and sorbitol are the most widely used polyol plasticizers for starch-based films due to the close similarity between their chemical structures and the structure of starch polymer (Mali et al., 2005). Müller et al. (Müller et al., 2016) have recently studied component interactions, structure and properties

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of blends prepared from poly(lactic) acid and thermoplastic starch plasticized with glycerol at two different weight percentages. They found that blending of the two components results in heterogeneous, two phase structures at all compositions. For this reason, they concluded that useful materials can be produced from PLA and TPS only with the development of an appropriate coupling strategy. Akrami et al. (2016) synthesized a new compatibilizer based on maleic anhydride grafted poly-ethylene glycol grafted starch to improve the compatibility of the PLA/TPS blends. They demonstrated that compatibilizer enhanced interfacial adhesion without to influence the biodegradability behavior. In the same year Ferri et al. (2016) proposed a plasticization strategy that involves the addition to glycerol of an environmentally friendly plasticizer derived from vegetable oils, maleinized linseed oil (MLO), obtaining a remarkable compatibilizing effect. The possibility of adopting as a plasticizer a mixture of glycerol and sorbitol with different percentages of sunflower seed oil was also recently explored (Vieira et al., 2011). It was shown that the presence of the oil not only increases the barrier properties to water vapor, but also enhances the mechanical properties of the starch films. Obviously, the use of a substance which is potentially useful for human nutrition can cause ethical problems. For this reason, in this work we decided to study the possibility of adopting fried sunflower seed oil as a plasticizer. In particular, this oil is the waste of the frying process of a fast food. The use of this oil can present the twofold advantage of reducing the cost of the plasticizer and reuse a waste product. Blends of PLA and TPS plasticized with glycerol and fried sunflower seed oil were examined by rheological, thermal and mechanical characterization. Furthermore, Life Cycle Assessment (LCA) study was carried out in order to compare the environmental impacts related to the different plasticized starches' productions.

2. Materials and methods

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

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

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

2.1. Micro compounder

The plasticization of the corn starch powder with glycerol and edible sunflower seed oil was carried out by a micro compounder with conical twin-screws Thermo Scientific Haake MiniLab II (Victoria, Australia), at a temperature of 110 °C, a screw rotation of 100 rpm and a cycle time of 5 min. Table 2 shows the weight percentage of starch,

Table 1
Features and composition of the raw and fried oil.

	Raw oil	Fried oil
Peroxides [meq O ₂ /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

Table 2
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 0.5F	0.5	70	20	–	10
TPS 0.7 R	0.7	75	15	10	–
TPS 0.7 F	0.7	75	15	–	10

glycerol and edible sunflower seed oil, both raw (R) and fried (F), contained in the produced blends, which are referred to considering oil/glycerol ratio (namely TPS 0.2 R stands for blend containing an Oil/Glycerol ratio equal to 0.2, obtained by using Raw sunflower seed oil).

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

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

2.2. Compression molding

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

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

2.3. Thermogravimetric analysis (TGA)

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

2.4. Mechanical analysis

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

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

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