



Effect of carboxylic acids as compatibilizer agent on mechanical properties of thermoplastic starch and polypropylene blends



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ABSTRACT

In this work, polypropylene/thermoplastic starch (PP/TPS) blends were prepared as an alternative material to use in disposable packaging, reducing the negative polymeric environmental impact. Unfortunately, this material displays morphological characteristics typical of immiscible polymer blends and a compatibilizer agent is needed. Three different carboxyl acids: myristic (C14), palmitic (C16) and stearic acids (C18) were used as natural compatibilizer agent (NCA). The effects of NCA on the mechanical, physical, thermal and morphological properties of PP/TPS blends were investigated and compared against PP/TPS with and **without** PP-grafted maleic anhydride (PPgMA). When compared to PP/TPS, blends with C18, PPgMA and C14 presented an improvement of 25, 22 and 17% in tensile strength at break and of 180, 194 and 259% in elongation at break, respectively. The highest increase, 54%, in the impact strength was achieved with C14 incorporation. Improvements could be seen, through scanning electron microscopy (SEM) images, in the compatibility between the immiscible components by acids incorporation. These results showed that carboxylic acids, specifically C14, could be used as compatibilizer agent and could substitute PPgMA.

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1. Introduction

There has been an increased interest in producing environmentally friendly materials. Starch-based materials seems to be an attractive source for the development of biodegradable materials (St-Pierre, Favis, Ramsay, Ramsay, & Verhoogt, 1997). Starch is a natural carbohydrate storage material accumulated by green plants. It is an important polysaccharide composed of a linear and branched chain of glucose molecules, named as amylose and amylopectin, respectively. It is an inexpensive, renewable and naturally biodegradable polymer (Yu, Prashantha, Soulestin, Lacrampe, & Krawczak, 2013).

Native starch itself does not show thermoplastic behavior, due to its intra and inter-molecular hydrogen bonds between hydroxyl groups of starch structures, which represent their crystallinity and, consequently, damaging the mechanical properties (Lu, Xiao, & Xu, 2009). In order to improve its properties, various methods have been developed to enhance starches positive characteristics, like physical or chemical modifications methods

and the use of plasticizer such as glycerol (Carvalho, Curvelo, & Gandini, 2005; Da Róz, Zambon, Curvelo, & Carvalho, 2011; Morán, Cyras, & Vázquez, 2013). The addition of plasticizers and exposition to thermo-mechanical energy leads to disruption of the semi-crystalline structure, resulting in an amorphous material called thermoplastic starch (TPS). This characteristic allows the use of traditional processing conditions (extrusion, blow and injection molding) (Corradini, Carvalho, Curvelo, Agnelli, & Mattoso, 2007; Lin, Huff, Parsons, Iannotti, & Hsieh, 1995; Liu, Xie, Yu, Chen, & Li, 2009; Prachayawarakorn, Sangnitidej, & Boonpasith, 2010).

The available hydroxyl groups on the starch chain makes the TPS, evidently, a very hydrophilic material with limited performance. This characteristic leads to a poor processability, dimensional stability and mechanical properties for its ends products. Therefore, thermoplastic starch is not used directly and blending with a synthetic thermoplastic is still necessary (Kahar, Ismail, & Othman, 2012; Ning, Jiugao, Xiaofei, & Ying, 2007; Pedroso & Rosa, 2005; Rodriguez-Gonzalez, Ramsay, & Favis, 2003; Roy, Ramaraj, Shit, & Nayak, 2011).

However, an inconvenient issue is the incompatibility between hydrophilic TPS and hydrophobic synthetic polypropylene (PP). The resulting products of polymer/starch compound do not possess satisfying or favorable properties. The compatibility of starch filled polymer blending system has to be enhance, once it is utmost

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important to avoid loss of advance properties on materials. Compatibilizers reduce the interfacial energy and homogenizes the polar starch with synthetic polymer, improving the interfacial tensions between phases. One of the foremost approaches to improve compatibility was through maleated blending methods. The maleic anhydride (MA) is widely used to connect olefin polymers to dissimilar materials (Huneault & Li, 2012; Kaseem, Hamad, & Deri, 2012; Rahmat, Rahman, Sin, & Yussuf, 2009; Shujun, Jiugao, & Jinglin, 2005; Taguet, Huneault, & Favis, 2009).

Nevertheless, MA is expensive, difficult to manufacture and like petroleum based polymers, non biodegradable (Shujun et al., 2005). In order to find a compatibilizer agent from renewable source, the use of carboxylic acids has been a good possibility to replace synthetic agents, once they have a compatible chemical structure, high environmental availability and biodegradability (Poletto, Zattera, & Santana, 2014).

In the specific case of polypropylene (PP) and TPS blends, long hydrocarbon chain carboxylic acids has a polar end group (–COOH) that could reacts with the hydroxyl groups of starch through secondary bonds forces, as hydrogen bonding. While, its apolar fraction interacts with the PP matrix through secondary bonds forces, as Van der Waals forces. This allows the carboxylic acid to place itself at the interface and it acted as adhesion enhancer between PP/TPS during melt blending. Moreover, it has the advantage of being from renewable sources and been biodegradable. However, to our knowledge, detailed studies on the mechanical, thermal and morphological properties of using carboxylic acids on PP/TPS blends have not been reported in literature.

Myristic acid (tetradecanoic acid) is used in the food industry as a flavor ingredient. It is found distributed in fats throughout the plant and animal kingdom, including common human foodstuffs, such as nutmeg, butterfat and coconut (Burdock & Carabin, 2007). Palmitic acid (hexadecanoic acid) is widely distributed, being found in practically all vegetable oils and animal (including marine animal). Its appearance ranges from a hard, white or faintly yellow, slightly glossy crystalline solid to a white or yellow-white powder or white crystals. Stearic acid (octadecanoic acid) is one of the useful types of saturated fatty acid that comes from many animal and vegetable fats and oils. It is a white solid with a mild odor (Table 1).

The aim of this research was to explore the use of carboxylic acids as compatibilizer agents from renewable resources as an alternative to currently employed commercially. Hence, the influence of three different organic carboxylic acids as compatibilizer agent in the mechanical, thermal and morphological properties of blends of polypropylene (PP) and thermoplastic starch (TPS) were studied.

2. Materials and methods

2.1. Materials

Native regular cornstarch was purchased in local trade in the city of Porto Alegre, RS, Brazil. The plasticizer, glycerol and the natural compatibilizer agents (NCA): myristic acid (C14), palmitic acid (C16) and stearic acid (C18) were provided by Vetec Fine Chemicals. Pure polypropylene (PP), melt flow index 40 g/min (230 °C, 2.16 kg) was supplied by Braskem (Triunfo, RS, Brazil) and the commercial compatibilizer agent used was the PP grafted with maleic anhydride (PPgMA) had a concentration equal to 1% of maleic anhydride according to Polybond 3200 informations.

2.2. Blend preparation

For obtaining the thermoplastic starch (TPS), starch granules were plasticized with glycerol in a weight ratio of starch/glycerol

70/30, as shown in Fig. 1, part I. The components were mixed at room temperature for 30 min. The obtained pulp was dried in an oven at 60 °C for 48 h.

The PP/TPS (70/30) blends with and without compatibilizer agent were manufactured in the twin-screw extruder (Haake Rheomex, model PTW16/25) with screw diameter of 16 mm, L/D ratio of 25 and 120 rpm. The extrusion was conducted using a temperature profile from 160 to 180 °C (Fig. 1, part II). Table 2 shows the composition of each blend developed. The compatibilizer agents were used at constant amount of 3% w/w in all cases throughout the study. This amount was chosen according to Liu, Wang, & Sun (2003), who studied the critical interfacial concentration of a type of compatibilizer on starch blends with a polyolefin.

After mixing in the extruder, the materials were pelletized (SEIBT, model PS50) as showed in Fig. 1, part III. The obtained samples were dried in an oven for 24 h at 60 °C. Thereafter, the blends in the pellets form were molded in an injection molding machine (Thermo Scientific Haake, MiniJet II). The temperature adopted was 190 °C, with a mold temperature of 40 °C and 500 bar pressure, producing tensile and impact specimens test.

2.3. Physical tests

The density of the samples was determined by the Archimedes method based on ASTM D792-1. The liquid medium used was ethanol. The extruded and injection molded specimens were used for this test (± 1 g). Analyzes were performed in triplicate. Density of the material was determined by the following equation:

$$\rho = \frac{a}{(a + w - b)} \times 0.7859 \quad (1)$$

where ρ is the material density in g/cm^3 , a the weight of the specimen in air, b apparent mass of specimen completely immersed and of the wire partially immersed in liquid, and w apparent mass of totally immersed sinker and of partially immersed wire, 0.7859 is the density of alcohol at 23 °C.

The void content was based on ASTM D2374, the densities used were obtained experimentally. The equation for calculating the void content is (Eq. (2)):

$$V = 100 - M_d \left(\frac{r}{dr} + \frac{g}{dg} \right) \quad (2)$$

where V represents the void content (%), M_d the measured density (g/m^3), r the fraction of resin (%), g the starch fraction (%), dr density of resin (g/m^3) and dg the density of starch (g/m^3).

2.4. Mechanical tests

The mechanical properties related to the materials tensile strength were analyzed according to ASTM D638 with crosshead speed of 5 mm/min in an universal testing machine (INSTRON, model 3382). The specimen dimensions were according to type V. Impact IZOD strength test was carried out as per ASTM D256 on IMPACTOR II (CEAST, Italy), using a 2.75 J hammer. The specimens were not notched and dimensions were 63.5 mm \times 12.5 mm \times 3.3 mm. It should be noted that the mechanical property results of different blends were obtained by averaging the measurement results of seven independent specimens. Results very far from the average were discarded. Hardness test was conducted according to ASTM D2240 using Shore D durometer (Mainard). Ten different measurements were carried out for a sample to obtain average values of hardness. The equipment used was the meter thick, Shore D scale, with 3 s of compression. All the mechanical property measurements were performed at room temperature at 50% relative humidity on injection molded blends.

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