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PAPER

Structure-properties correlation in PP/thermoplastic starch blends containing sustainable compatibilizer agent

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Abstract

It was studied the effect of different sustainable compatibilizer agents (myristic and stearic acid), at varied content (0% to 10%), on the properties of polypropylene (PP)/thermoplastic starch (TPS) blends. The performance was evaluated by impact resistance, scanning electron microscopy (SEM), melt flow index (MFI), colorimetric analysis and biodegradability. In addition, the influence of two PP grades—Low-Flow and High-Flow Index—was evaluated. Impact strength of uncompatibilized blends did not show PP melt flow index influence. Compatibilized blends were positively influenced by acid addition. The optimum acid content for 30% of thermoplastic starch was 6.5%. For each polypropylene there was a preferential acid. At higher contents (10%), the acids appear to act as plasticizers as well. Scanning electron microscopy images showed improvements in the components interphase. PP with high melt flow had its rheology more affected by acid insertion, while PP with low flow index had its biodegradability more affect.

1. Introduction

Due to the environmental impact caused by incorrect disposal of synthetic polymers and its non-biodegradability, the industrial sector of disposable products pursues alternative sources of raw materials, especially natural and renewable solutions. Although natural polymers are cheaper and found in large quantities, their properties are far from the polymer commodities. In contrast to the development of new polymeric materials and new routes of polymer synthesis, the mixture of natural polymers with synthetic polymers is relatively inexpensive and faster [1].

Native starch is a polysaccharide widely found in tubers and cereals and is known to be fully biodegradable. Starch insertion into synthetic polymer matrix promotes the biodegradability of these materials [2]. However, native starch presents major problems related to its processability and dependences on temperature, making it difficult to use in common polymer processing equipment such as extrusion and injection. Thus, plasticized starch, known as thermoplastic starch (TPS), is obtained by mixing the native starch with a plasticizer such as water, glycerol, sorbitol, and others [3]. The mixture of PP and TPS is extensively studied by researchers worldwide [4–7].

Synthetic plastics such as polypropylene (PP) are used widely in daily life, food industry, biomedical fields, and agriculture. This implies the availability of the same resin with different characteristics, so new grades continuously keep coming out on the market. Different grades are usually defined by its melt flow index (MFI) values. The MFI is a common analytical method and is widely used as rheological property [8]. Polymers MFI depends on its molecular characteristics, primarily, the average of its molecular weight, molecular weight distribution (MWD), and branching characteristics [9, 10]. Consequently, flow properties are important product characteristics that affect not only processability but physical properties as well [11, 12]. To our knowledge until now there is no study about the influence of PP flow characteristics on PP/TPS blends.

The main obstacle to use PP/TPS blends is the incompatibility between the hydrophilic TPS and the hydrophobic PP, which results in mechanical properties loss and increased water absorption. An alternative to

this is the use of modified synthetic polymers, such as maleic anhydride-grafted polypropylene (PPgMA), obtained from chemical modification or reactive processing [13, 14]. The purpose of this modification is the insertion of polar clusters in the main chain of the PP, making it able to establish physical and/or chemical interactions with other materials. Several authors have studied the use of synthetic compatibilizers in TPS blends [15–17].

Although synthetic compatibilizer agents are effective, they are difficult to obtain from non-renewable sources and decrease the blends biodegradability [18]. Thus, the performance of starch-based products may be improved by starch functionalization such as hydrophobic starches [19]. With the specific objective of compatibilization in the work of the authors Khanoonkon, Yoksan, and Ogale (2016a, 2016b) [20, 21], stearic acid was graphitized to cassava starch. To obtain this compound, other reagents and several stages of synthesis and purification were used, increasing the energetic cost involved, besides increasing the chemical residues. However, incorporating 1% and 3% of this compound into LLDPE/TPS (60/40) blends, the films showed higher tensile strength, secant stiffness and extensibility compared to the LLDPE/TPS blend film without the addition. In addition, there was a reduction in the TPS phase size and the higher TPS phase dispersion in the polymer matrix.

Even both starch and polymer modification were efficient, they require a synthesis system, generating waste and energy costs. Thus, literature [22, 23] has shown the positive effect of the simple incorporation of carboxylic acids, as a substitute for commercial compatibilizing agents, on the properties of PP/TPS and LLDPE/TPS blends.

This work aims to evaluate the combined effect of: (i) different sustainable compatibilizer agents; (ii) compatibilizer agent content; (iii) distinct PP grades; on polypropylene (PP)/thermoplastic starch (TPS) blends properties. The new information helps target the most suitable end-use applications of such materials.

2. Matherials and methods

2.1. Materials
The cornstarch used was food grade and was purchased at a local store in the city of Porto Alegre, RS, Brazil. The organic acid used was: myristic (C14) and stearic (C18). Two commercial polypropylene resins were studied: (1) PP-LF (Polypropylene with Low-Flow Index) with a MFI of 3.3 g/10 min, designed for disposable packaging, obtained by injection molding and thermoforming; (2) PP-HF (Polypropylene with High-Flow Index) with a MFI of 40 g/10 min, additive for general use, indicated for injection molding.

To obtain the thermoplastic starch (TPS), corn starch and glycerol were first mixed manually, in a ratio of 70 and 30%, respectively. The components were mixed at room temperature, after sieving and conditioned at 60 °C for 24 h.

The PP/TPS blends were obtained by processing in a Thermo Scientific Haake Rheomix OS internal mixer with a constant speed of 60 rpm and a temperature of 165 °C. The total processing time was 6 min, where PP was first inserted into the chamber and after 1 min the other components (TPS and/or acids) were inserted.

Torque curves were recorded during processing time to evaluate behavior during mixing. The area under the curve is related to the energy absorbed by the material during processing. The specific mechanical energy (SME) [24, 25] required for the processing of each sample was calculated according to equation (1).

$$SME = \frac{2\pi N}{m} \int C(t) \, dt \qquad (1)$$

Where N is the rotational speed (rpm), m is the total sample mass (g), t is the processing time (min) and C(t) is the total torque produced during the processing time (Nm). The SME was expressed in kJ/kg.

Table 1 shows the formulations of each of the blends developed. The amount of compatibilizing agent added to the blends ranged from 0 to 10% relative to the mass of PP and TPS. The ratio of 70/30, PP/TPS, was held constant.

After mixing, samples were ground in a RETSCH mill using a 1 mm sieve. The material was then oven dried at 60 °C for 24 h and molded by a Thermo Scientific MiniJet II injector at a temperature of 190 °C, mold heated at 50 °C and pressure of 500 bar for the preparation of the specimens.

2.1.1. Mechanical tests
The mechanical properties related to impact strength were performed according to ASTM D256, using the CEAST brand IMPACTOR II equipment and the 2.75 J hammer. The samples had no notch and the dimensions were 63.5 mm × 12.5 mm × 3.3 mm. Seven measurements were made for each sample and the result obtained corresponds to the mean of the values.

Table 1. Composition of the PP/TPS blends with and without acid (WAC).

Sample	PP grade	PP (%)	TPS (%)	Acid	Acid (%)
PP-HF/TPS/WAC	PP-HF	70	30	—	0
PP-HF/TPS/3C14	PP-HF	70	30	C14	3
PP-HF/TPS/6.5C14	PP-HF	70	30	C14	6.5
PP-HF/TPS/10C14	PP-HF	70	30	C14	10
PP-HF/TPS/3C18	PP-HF	70	30	C18	3
PP-HF/TPS/6.5C18	PP-HF	70	30	C18	6.5
PP-HF/TPS/10C18	PP-HF	70	30	C18	10
PP-LF/TPS/WAC	PP-LF	70	30	—	0
PP-LF/TPS/3C14	PP-LF	70	30	C14	3
PP-LH/TPS/6.5C14	PP-LF	70	30	C14	6.5
PP-LF/TPS/10C14	PP-LF	70	30	C14	10
PP-LF/TPS/3C18	PP-LF	70	30	C18	3
PP-LF/TPS/6.5C18	PP-LF	70	30	C18	6.5
PP-LF/TPS/10C18	PP-LF	70	30	C18	10

2.1.2. Melt flow index (MFI)

The melt flow index tests of the pure polymer and the blends were performed on the CEAST Modular MeltFlow Model 7026.000 equipment, according to Method A of ASTM D1238. The conditions used were based on polypropylene 230 °C/2.16 kg, with residence time of 4 min.

2.1.3. Scanning electron microscopy (SEM) analysis

The fracture surfaces, after the impact test, were studied using a JSM 6060 (JEOL). The voltage used was 3 and 10 kV, and the samples were plating with gold. Selected formulations, the dispersed phase (thermoplastic starch) were extracted by immersion for 2 h in 6N HCl solution, and then washed with water and dried [14, 26].

2.1.4. Colorimetric analysis

A Spectro-Guide spectrophotometer (BYK, Germain) was used to measure color by using the CIELAB color system (L^*, a^*, and b^*) based on a D65 light source. Lightness (L^*) and two chromaticity coordinates (a^* and b^*) were measured at three different positions on each. Also, it was measured of the gloss (G) of the samples.

2.1.5. Biodegradability of blends

The polymer blends in a form of thin films, 800 μm thickness, were thermo-compression molding. The biodegradation of the film samples was followed during soil burial for 120 days at 60 °C. Samples were placed into Erlenmeyer flasks containing 1 part of soil placed between two layers of expanded perlite, it provides aeration and optimum moisture retention and helps prevent soil compaction. Cellulose was used as positive control and the two polypropylene used in the study were used as negative control. The rate of biodegradation was followed by measuring the percentage weight loss, as described by [27, 28].

2.1.6. Statistical analysis

The data were analyzed using commercial statistic software with analysis of variance (ANOVA) and the Fisher test at a 5% significance level.

3. Results and discussion

3.1. Mechanical properties

Table 2 shows the impact strength results for PP with high melt flow rate (PP-HF), PP low melt flow rate (PP-LF) and its blends PP/TPS (70/30). The higher value was found for PP-HF (743 J m^{-1}), as expected. For both studied PPs, TPS incorporation had a strong negative effect on impact strength, where the resistance went from 514 J m^{-1} to 87 J m^{-1}, representing a reduction of about 80%, for PP-HF/TPS/WAC without acid addition. And this same behavior happened to PP-LF, whose impact strength was 743 J m^{-1} and decreased to 153 J m^{-1} for PP-LF/TPS/WAC, representing a reduction of 80% as well.

Such results demonstrated that melt flow index did not have an influence on the non-compatibilized blends impact strength. Perhaps, it had occurred due to the lack of affinity, where either PPs were not enabled to support impact strength transfer and starch acted as a filler increasing the areas of tension concentration, leading to fracture with lower energy absorption. Many studies have showed a decrease on mechanical properties after TPS incorporation into a synthetic polymer phase [5, 14, 29].
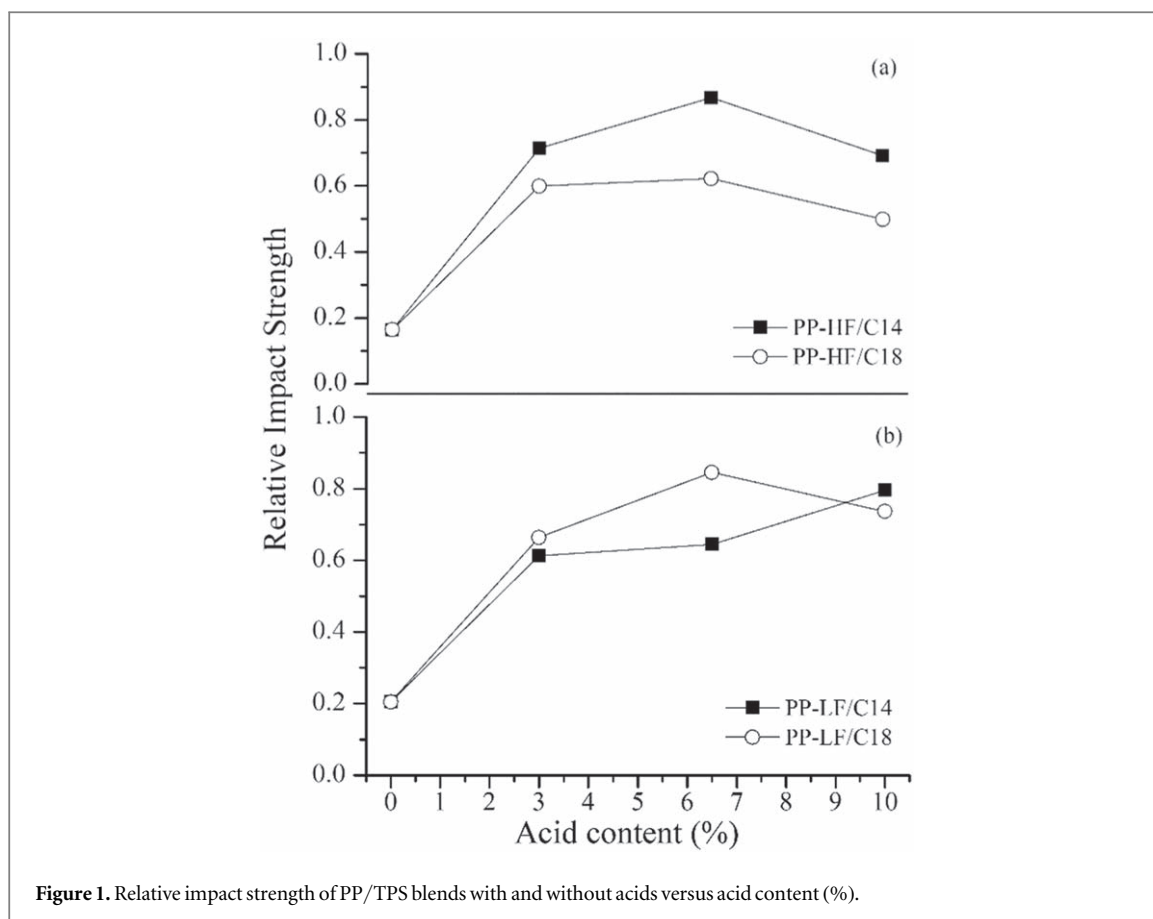
Figure 1. Relative impact strength of PP/TPS blends with and without acids versus acid content (%).

Table 2. Impact strength results for neat PP and PP/TPS blends.

Sample	Impact strength (J m^{-1})	Sample	Impact strength (J m^{-1})
Neat PP-HF	514.4^e ± 27.1	Neat PP-LF	742.6^e ± 56.4
PP-HF/TPS/WAC	86.7^a ± 5.0	PP-LF/TPS/WAC	153.4^a ± 5.2
PP-HF/TPS/3C14	358.3^d ± 46.2	PP-LF/TPS/3C14	456.8^b ± 40.8
PP-HF/TPS/6.5C14	471.5^e ± 39.2	PP-LH/TPS/6.5C14	498.0^{bc} ± 37.0
PP-HF/TPS/10C14	364.3^d ± 17.7	PP-LF/TPS/10C14	635.1^{de} ± 52.7
PP-HF/TPS/3C18	312.1^c ± 14.2	PP-LF/TPS/3C18	481.6^b ± 41.4
PP-HF/TPS/6.5C18	330.8^{cd} ± 11.9	PP-LF/TPS/6.5C18	644.9^e ± 47.4
PP-HF/TPS/10C18	262.6^b ± 14.0	PP-LF/TPS/10C18	562.0^{cd} ± 39.8

*Values in the same column containing the same superscript are not significantly different from each other (Fisher test, $p < 0.05$).

For a better understanding of mechanical properties changes, the relative values were plotted in figure 1. Where, the values have been reported in a dimensionless form—value at a given acid load divided by the value for neat polypropylene (table 2).

From figure 1, it can be seen that acid incorporation significantly improved the performance of the blends. Acid insertion promotes the interfacial adhesion, acid groups (–COOH) are highly polar, and they can establish strong interactions with hydroxyl groups in thermoplastic starch. On the other hand, its carbon chain can interact with PP chains [20–23]. For this reason, C14 and C18 act as a link between the two immiscible components, thus allowing to reduce the stress concentration effect of dispersed immiscible TPS phase, leading to better impact strength, compared to the acid-free blends.

It was possible to note that, for PP/TPS compatibilized blends, PP grade affected the impact strength. PP-HF/TPS compatibilized with C14 showed better results than blends with C18. For PP-LF, blends with C18 were more promising. However, there is an acid content (6.5%) that provides the optimum impact strength to the blends, independently of PP grade.

The main difference between the used PPs was their melt index. This property can be used as an indirect evaluation of the molar mass of the polymer, once the higher the melt flow index is, the lower is its viscosity and
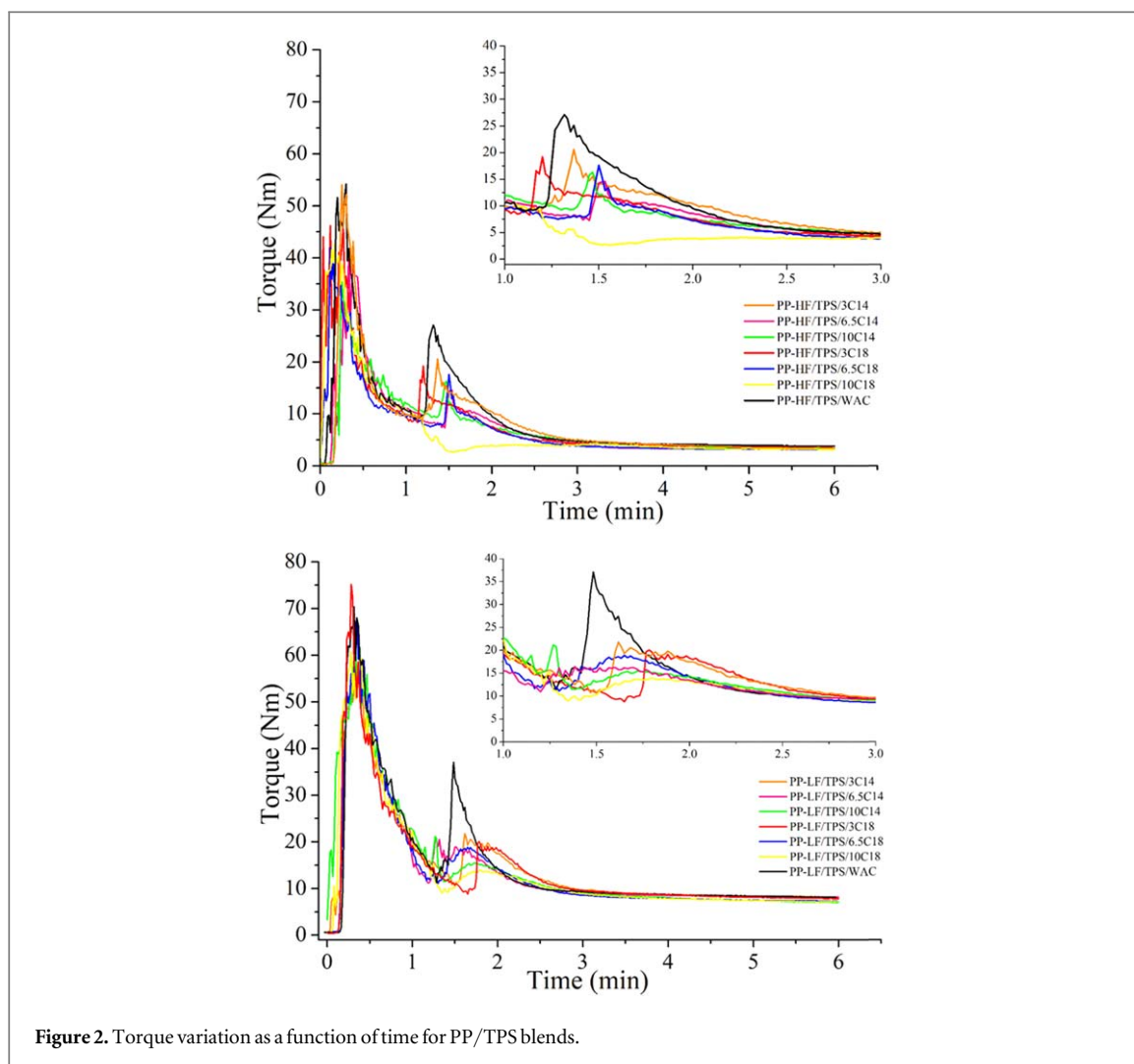
Figure 2. Torque variation as a function of time for PP/TPS blends.

consequently the lower is its molar mass. PP-HF has higher melt flow rate, consequently, lower molar mass, and shorter chains. While, PP-LF has lower melt flow rate, with higher molar mass and longer chains. So, to PP-HF the preferential acid was the one with a small chain (C14) and, to PP-LF, it was C18. This behavior shows that for each type of polypropylene there was a preferential acid but a same optimum concentration: 6.5% for the 30% content of TPS.

On the other hand, as already discussed in Martins and Santana [22], PP/TPS/3C14 blends presented an endothermic peak that could indicate an excess of this acid. Thus, sufficient acid content is necessary for the compatibilization but excess quantity will cause an extreme plasticize effect, damaging the starch molecules, leading to decrease in impact strength. An optimum impact strength at about 10% C14 were also reported for PP-LF/TPS. Although higher content may be suitable, if lower content is used, it is more preferable to have smaller quantity for large-scale processing, due to economic reasons.

3.1.1. Rheologic properties

Since torque is related to material viscosity during processing, as usual, PP-LF/TPS showed higher maximum torque values (figure 2). As TPS was incorporated into the mixture after 1 min of processing, there are two torque maximums: T1max is the torque maximum for neat PP and T2max is the torque maximum for the entire mixture. Since starch is less resistant to flow, it was expected a reduction of the T2max. However, even though PP-LF has more viscosity, a reduction of 50% on T2max, for un-compatibilized blends, was observed for both PPs.

It is seen that, for PP-HF compatibilized blends, the torque maximum ranged between 10.9–20.6 Nm, while for PP-LF compatibilized blends it ranged between 18.3–20.1 Nm. When 3% of acid was used, all blends presented similar torque maximum values, even for PP-LF blends. However, for higher acids contents, PP-HF seems to be more affected by acid incorporation, showing the lowest value to PP-HF/TPS/10C18 (10.9 Nm), while PP-LF/TPS/10C18 was 18.3 Nm.
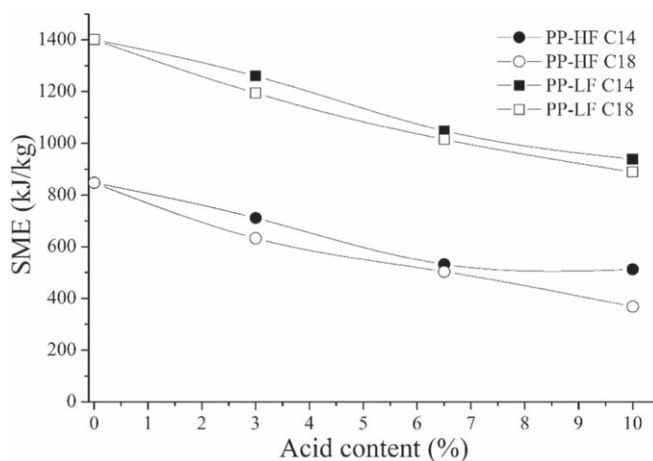
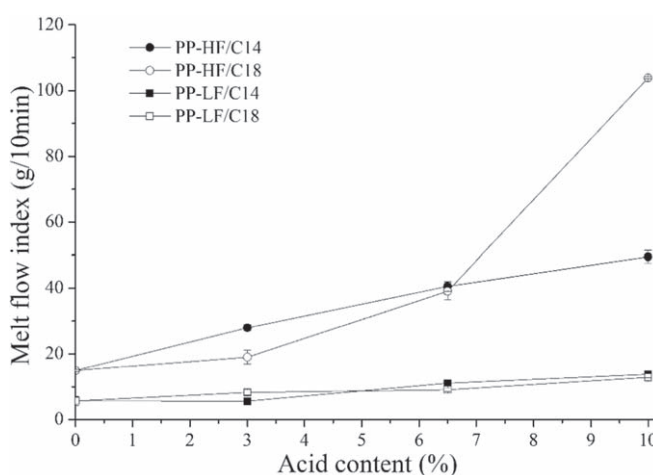**Figure 3.** Specific mechanical energy (SME) as function of type and content of acid and type of PP.

Figure 4. Melt Flow index of PP/TPS blends containing different acid concentrations.

Since PP-HF has lower molar mass, it is presumably more accessible for acid molecules to spread through their chains (intermolecular) and therefore is more susceptible to variations in their viscosity. PP-LF has higher molar mass, so has more molecular entanglements, making it difficult for the acid to penetrate and diffuse through its chains (intermolecular).

In general, acids addition favored the processing since the blends with this third component presented smaller torques (figure 2). The acid insertion probably (i) had favored starch breakage (ii) had increased slippage and molecular mobility by the plasticizing effect, and (iii) had led to an over-lubrication [30]. All these factors occasioned a lower viscosity, offering less resistance to rotors and torque decrease.

The specific mechanical energy (SME) is a good parameter for characterizing processing conditions and can be defined as the energy transmitted to the material during processing. Figure 3 shows that the highest SME values were obtained for PP-LF blends without acids and that there is an inverse relationship between the acid content and the SME, regardless acid used or PP. Blends presented lower specific energy, indicating better processability by the addition of acids. Also, this indicates a shear reduction due to a possible plasticizing or lubricating effect of the acid. These results were similar to ones find on Silva *et al* [31] study, they demonstrated that the plasticizer content effect is related to the energy dissipated during the processing. When high levels of plasticizer were used, interaction forces between starch chains were lower, resulting in high molecular mobility.

As already discussed, these acids, besides acting as compatibilizers, can act as plasticizers and their insertion may lead to an increase in the melt flow index (MFI) of the blends, as shown in figure 4. As seem from figure 4, there is a greater influence of the acids on PP-HF blends, compared to PP-LF, as already discussed. Among the acids, a further increase in C18 content substantially increases the melt flow index of the PP-HF blends, which was not found for PP-LF blends.

Thus, depending on the concentration used, the acids can also act reducing the friction between the polymer mass and the walls of the equipment, similarly to the external lubricants. As reported on Julinová *et al* [32] study, a mixture of stearic acid and palmitic acid under the commercial name *Stearin III* (used for pharmaceutical purposes), was used in order to avoid adhesion of the melt PVA (polyvinyl alcohol) and TPS to the processing equipment, reducing the shear stress. And in the work of Prachayawarakorn *et al* [33] stearic acid was used as a processing aid in the preparation of blends of rice starch and low density polyethylene.

3.1.2. Morphology analysis

The morphology study of an immiscible blend is essential for understanding its properties, since the shape, size and spatial distribution of the dispersed phase result from a complex relationship between the viscosity and elasticity of the phases, the interfacial properties, the composition of the blend and the processing conditions. In this way, figures 5(A) and (B) show the scanning electron microscopy (SEM) images of the fracture surface of PP-HF/TPS and PP-LF/TPS blends, respectively, with different myristic acid (C14) and stearic acid (C18) contents.

Although the disruption of a starch granular structure is related to its plastification, through the SEM images, it was not possible to verify this effect by acid addition. As already discussed in Taguet's, Huneault and Favis [34] work, even though glycerol is added in order to plasticize the starch, it was not in sufficient concentration to plasticize the starch. Indeed, on figures 5((A), (a)) and ((B), (a)), for PP/TPS without acid, it was possible to observe the starch granular structure.

A large quantity of flake-like crystals was noticeable on the fracture surface of PP/TPS with acid (figures 5 and 6). These structures had appeared with greater incidence in the formulations with greater acid contents. These crystals were well dispersed and also firmly adhered to the matrix, indicating a good compatibilization to it. Furthermore, when C14 (left) was used the crystals were larger and thicker, and when C18 (right) was used it was smaller and thinner (needle-shaped). The authors DU *et al* [35] observed the formation of flake-like stearic acid crystals on the fracture surface of polyolefin elastomer/stearic acid composite (50:50, respectively). Figures 5((A)(c), (e), (g)) and ((B)(c), (e), (g)) show the formation of a similar structure, which those authors called the house of cards.

The crystals observed in the images can be explained by the sweating out effect of the plasticizer, which when excess can migrate to the surface. In addition, between the PPs, there is a higher crystals presence on PP-HF blends, probably due to less entanglement of the chains, which would facilitate the acidy passage.

In order to study the dispersed phase domains, the fracture surfaces of PP-LF/TPS/C18 blends were washed down with hydrochloric acid, to remove TPS disperse phase. It was possible to distinguish spherical voids corresponding to the removed TPS particles (figure 6). However, for formulations with 6.5 and 10% C18, the compatibilization effect can be clearly observed through a reduction of the particle size and/or void diameter, as well a better dispersion of TPS domains, corroborating with the results of impact strength. This behavior is consistent with the observations for PE-TPS system compatibilized with PE-g-MA [26], with zeolites [36], and with stearic acid-grafted starch [20].
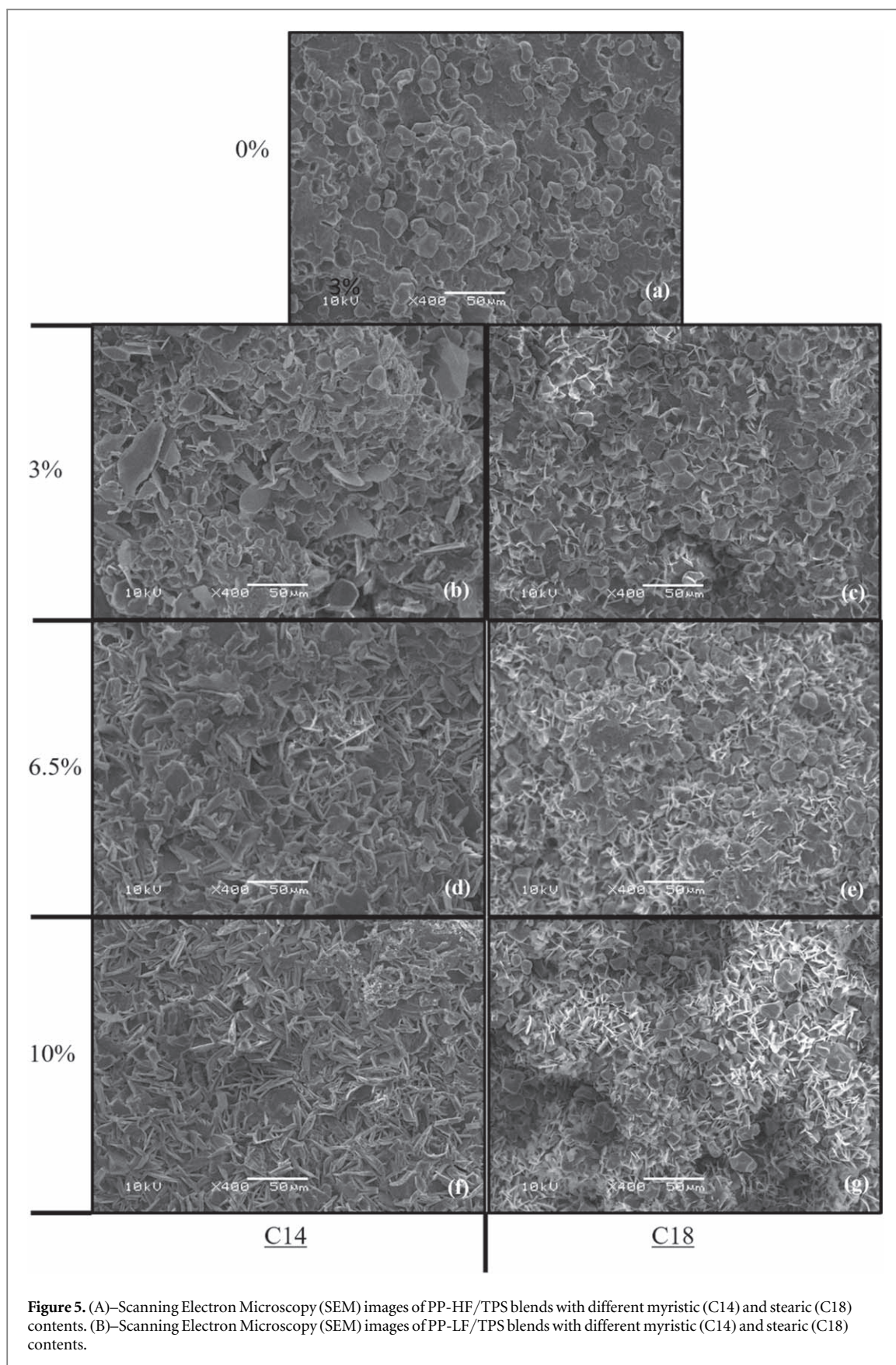
3.1.3. Colorimetric analysis

The attributes related to colouring are important since they are directly related to consumer acceptance. Tables 3(A) and (B) present the properties related to the colour parameters (L^*, a^*, b^* and Brightness). As can be seen from the above tables, the lightness (L^*), which ranges from 0 (black) to 100 (white), increases when the acid content increases. Therefore, the formulations with sustainable compatibilizer agents prevented the staining and firing of the starch, giving rise to lighter materials with less evidence of thermo-mechanical degradation. Acid incorporation has reduced significantly the brightness. Among acids, C14 was responsible for higher brightness reduction. Previously, Khanoonkon *et al* [21] also observed a reduction in gloss by the addition of stearic acid to TPS/PE blends, where the formulations with this acid gave rise to opaque materials, compared to PE matrix. The observed yellowish/reddish coloration (positive b^* and a^* values) can occur due to the non-enzymatic degradation of sugars that make up the starch. When starch is heated at high temperatures a series of reactions take place, giving rise to brown pigments associated with caramelization [37]. Furthermore, as previously discussed, the acids appear to act as plasticizers, which would decrease the melt shear with the walls of the equipment, avoiding temperature rise and starch degradation, influencing the coloration.

Also, it is possible to notice that blends with C14 presented smaller values of a^*, in relation to the blends with C18. These findings corroborated with the mechanical and morphological results, whom can be explained by the better compatibilization, where the starch granules are protected by the polymer matrix, avoiding their degradation, and consequently giving rise to less reddish blends (a^*).

3.1.4. Biodegradation results

After 120 days of soil burial, examples were dug out and cleaned to ensure removal of soil/mud. The effects of biotic agents on PP samples (negative control) were not observable (0%). However, on cellulose samples

Figure 5. (A)–Scanning Electron Microscopy (SEM) images of PP-HF/TPS blends with different myristic (C14) and stearic (C18) contents. (B)–Scanning Electron Microscopy (SEM) images of PP-LF/TPS blends with different myristic (C14) and stearic (C18) contents.

(positive control) the samples were completely degraded (100%) and it was not possible measure its weight loss. The percentage of weight loss of PP/TPS blends after degradation is presented in figure 7. As expected, TPS addition was able to increase blends biodegradation, since TPS and cellulose are biodegradable and can be metabolized by many organisms [38].

Figure 5. (Continued.)
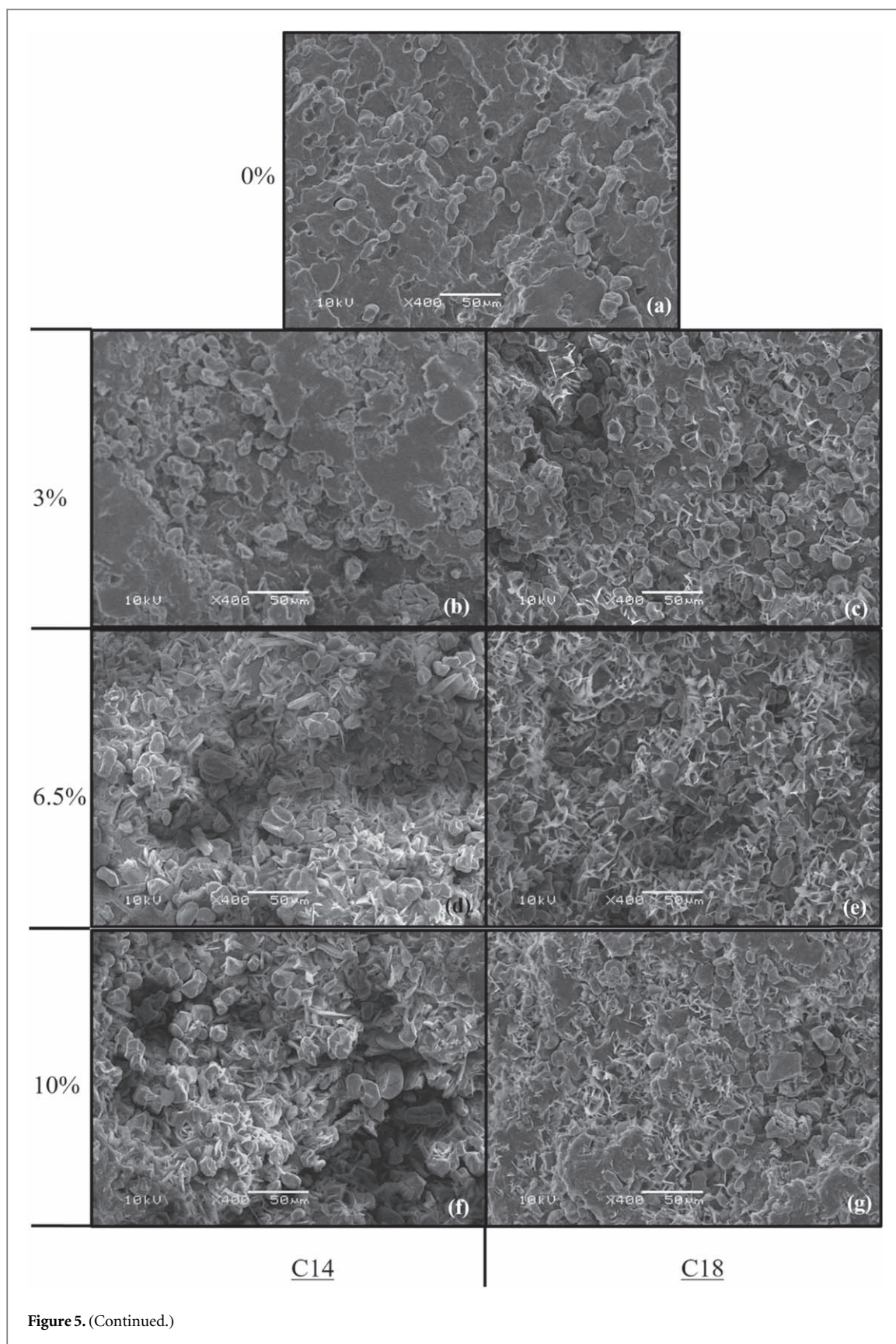
It was observed that PP grade affected the weight loss. PP-LF has higher chains, which reduces the starch mobility among PP molecules and its dispersion capacity. For this reason, PP-LF blends presented lower weight loss compared to PP-HF blends. As can be seen for PP/TPS without acid (black bars): blends with PP-HF showed greater weight loss than PP-LF, 28%, and 17.5%, respectively. In this case, a 30% of weight loss was
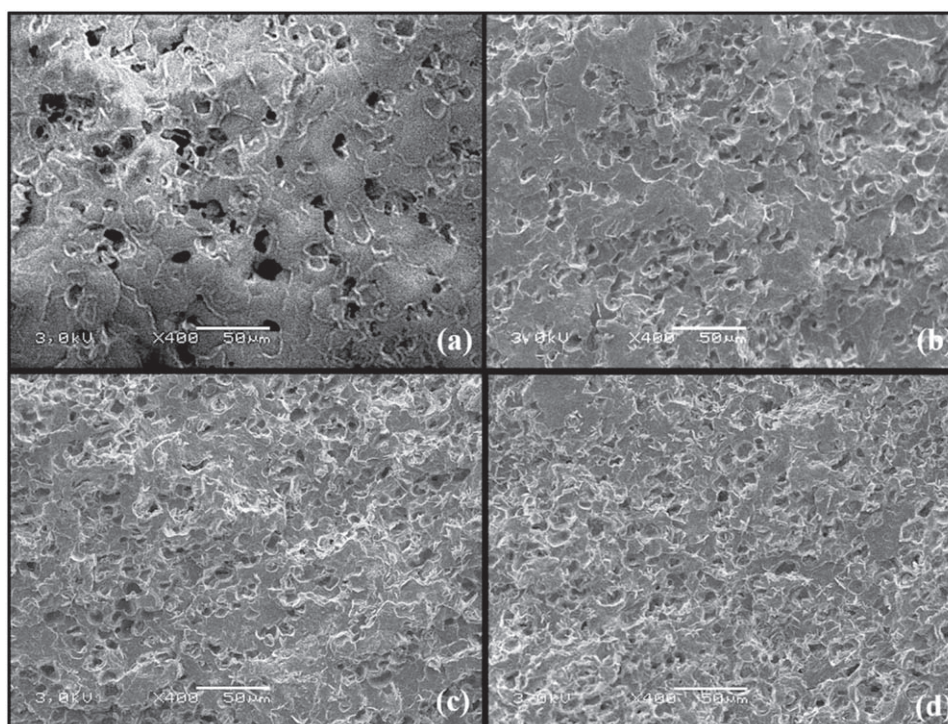
Figure 6. Scanning electron microscopy (SEM) of the PP-LF/ TPS blends with different levels of stearic acid (C18) after extraction: (a) 0%, (b) 3%, (c) 6.5% and (d) 10%.

Table 3. (A)–Values obtained of colorimetric analysis (Lightness L^*, redness a^*, yellowness b^*, and brightness) for PP-HF/TPS blends. (B) Values obtained of colorimetric analysis (Lightness L^*, redness a^*, yellowness b^*, and brightness) for PP-LF/TPS blends.

Samples	L^*	a^*	b^*	Brightness
(A)				
PP-HF/TPS/WAC	55.7 ± 0.2^{bc}	2.0 ± 0.1^{b}	16.1 ± 0.2^{a}	19.5 ± 1.1^{d}
PP-HF/TPS/3C14	53.7 ± 1.1^{a}	2.8 ± 0.1^{c}	18.5 ± 0.8^{c}	6.3 ± 2.8^{ab}
PP-HF/TPS/6.5C14	57.6 ± 0.7^{de}	1.5 ± 0.2^{a}	17.1 ± 0.9^{ab}	8.1 ± 1.9^{b}
PP-HF/TPS/10C14	58.4 ± 0.6^{e}	1.2 ± 0.2^{a}	16.2 ± 1.1^{ab}	3.5 ± 0.9^{a}
PP-HF/TPS/3C18	54.7 ± 0.8^{ab}	2.0 ± 0.1^{b}	15.7 ± 0.1^{a}	17.0 ± 2.6^{d}
PP-HF/TPS/6.5C18	53.9 ± 0.8^{a}	3.0 ± 0.3^{c}	17.7 ± 0.4^{bc}	12.2 ± 2.5^{c}
PP-HF/TPS/10C18	56.6 ± 0.2^{cd}	2.1 ± 0.4^{b}	16.3 ± 1.3^{ab}	8.0 ± 2.7^{b}
(B)				
PP-LF/TPS/WAC	49.6 ± 0.1^{a}	3.6 ± 0.1^{d}	17.9 ± 0.3^{bc}	20.6 ± 2.0^{d}
PP-LF/TPS/3C14	49.7 ± 0.4^{a}	2.3 ± 0.2^{b}	14.8 ± 0.3^{a}	5.0 ± 0.9^{a}
PP-LF/TPS/6.5C14	57.3 ± 0.6^{d}	1.4 ± 0.2^{a}	14.7 ± 0.6^{a}	4.3 ± 1.0^{a}
PP-LF/TPS/10C14	55.1 ± 1.3^{bc}	1.7 ± 0.1^{a}	14.6 ± 0.9^{a}	2.7 ± 1.6^{a}
PP-LF/TPS/3C18	53.8 ± 0.4^{b}	3.0 ± 0.1^{c}	18.2 ± 0.3^{c}	13.3 ± 3.1^{bc}
PP-LF/TPS/6.5C18	55.3 ± 0.7^{c}	2.9 ± 0.2^{c}	17.5 ± 0.7^{bc}	17.9 ± 5.0^{cd}
PP-LF/TPS/10C18	55.4 ± 1.3^{c}	2.8 ± 0.5^{c}	17.1 ± 0.7^{b}	12.2 ± 3.2^{b}

*Values in the same column containing the same superscript are not significantly different from each other (Fisher test, $p < 0.05$).

expect but it may be not achieved due to: (i) the incompatibility between phases, who can contribute to the agglomeration and, consequently, to a bad dispersion, since the granules of the starch tend to group with each other, due to the lack of affinity with the matrix. So, this factor leads to a smaller area for the microorganism's attack. (ii) Microbial invasion mechanism, who take place from the top and bottom surface of the material. Chandra and Rustgi [39] reported that, in LLDPE/starch blends containing 10%–30% starch content, less than 10% of the starch was degraded after 180 days.

On the other hand, it was found that acid incorporating led to a biodegradation increase only for PP-LF blends. For PP-LF/TPS/3C18, for example, increased blends weight loss in 70%, compared to PP-LF/TPS
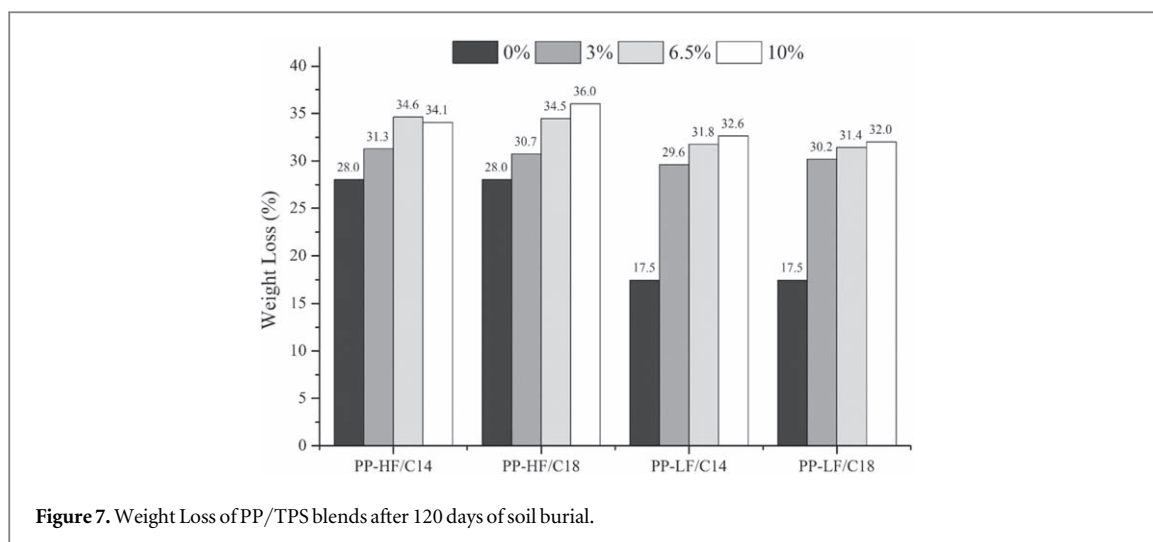
Figure 7. Weight Loss of PP/TPS blends after 120 days of soil burial.

without acid. As shown on SEM images (figures 6(b)–(d)), blends with acids presented a better dispersion with smaller starch particles, so the contact area available to the microbial action was higher. Huang and co-authors [18] found that smaller size of the starch phase gives better biodegradation. Comparing with previous literature [40], authors found 9.45% of weight loss for PE/cassava starch/PEgMA (35/40/5 w/w) after 5 months of compost soil burial. Native tapioca starch/PP (50/50 w/w) blends had a weight loss of 35% after 6 months of indoor soil burial test [41].

For PP-HF/TPS blends a small increase was observed, and it could be related to an increase on the biodegradable fraction by acid insertion. Since there was no significant difference between blends with C14 and C18, it was possible to conclude that acid nature did not affect blends biodegradability.

4. Conclusion

Between polypropylenes, acid incorporation acted differently. PP with high melt flow had its rheology behavior more affected by acid insertion, while PP with low flow index had its biodegradability more affect. Monitoring the degradation behavior of PP/TPS (70/30) for 120 days in soil burial test revealed that acid addition exhibit potential to increase the weight loss for blends with PP with low flow index.

Also, higher acid concentration (6.5%–10%) provides an effective increase in PP/TPS properties were proved. The impact resistance of PP/TPS without acid was low compared to neat polypropylene, although it was positively influenced by acid addition. In addition, according to the torque and specific mechanical energy measurements, there was an increase in the elasticity of the blends, with the increase in acid content. Scanning electron microscopy images showed improvements in the interphase between the two components, where there was a reduction in the size of the starch granules, increase of the dispersion and adhesion between the phases. From the results showed above, it was found that the optimum acid content for 30% of thermoplastic starch is 6.5%.

Among the acids, it was concluded that for each polypropylene used, there was a preferential acid. The myristic acid was preferred to blends with high melt flow polypropylene and stearic acid for low melt flow polypropylene blends. At higher acid contents (10%), the acids appear to act as plasticizers either, as could be verified by the reduction of the flow resistance and an increase of the tenacity. This behavior was also verified in relation to the flow index that varied proportionally to the acid content.

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