



Investigation of degradation of polypropylene in soil using an enzymatic additive

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Abstract

Polypropylene (PP) has been widely used industrially in several sectors, mainly in the use of packaging of different products. Thus, this has been accumulated in our environment due to the incorrect disposal and its high resistance toward degradation, causing an array of environmental impacts. With this, one alternative that has been explored to minimize the problems intensified by these residues is the use of pro-degrading additives. Therefore, the aim of this work is to evaluate the degradation process of PP blends in soil using enzymatic additive. The soil degradation experiment was done for 6 months; monthly collected samples were checked for alterations on the material properties during that time. The extent of PP degradation with enzymatic additive was compared to an organic additive by techniques of FTIR, TGA, DSC, carbonyl index (CI), and crystallinity. From the obtained results it was observed that the additives influenced the degradation of PP. In addition, the enzymatic additive caused more significant changes in the CI (increase of 3693%), crystallinity (variation of 18.7%), and structural characteristics, indicating a greater influence on the degradation process in relation to the organic additive. In this way, this work has had an important role in the research and development of biodegradable materials with the aim of minimizing the effects induced by plastic waste in the environment.

Keywords Polypropylene · Pro-degradant · Additive · Degradation · Enzymatic · Organic

Introduction

In recent years, the plastic consumption has gone up exorbitantly worldwide, because of the development of new materials based on synthetic polymers. A majority of these plastic products are used for short-term application and posteriorly discarded [1, 2]. Among the several plastic classes known

in the world, the polypropylene (PP) shows a huge use due to its low cost, chemical resistance, effective water and gas barrier properties, being the second most used resin in Brazil (approximately 21.9%) [3–5]. On the other hand, PP is a petroleum-derived product, highly stable, and takes long time for degradation. Consequently, its low degradability and the incorrect disposal of its products, mainly in the packaging sector, impose the development of new technologies to provide the degradation/biodegradation of these polymers [6–8]. Currently, biodegradable polymers such as polylactic acid (PLA) [9], polyhydroxybutyrate (PHB) [10], and polycaprolactone (PCL) [11], are considered the alternatives to minimize the effects of these discarded materials. However, their use is still restricted due to several properties that are not equivalent to conventional plastics, such as low flexibility, low impact resistance, and high temperature, among others. In addition, biodegradable polymers have higher production cost compared to conventional plastics [12].

Another alternative that has been explored is the degradable polyolefin, which can be obtained with the addition of

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special additives called pro-oxidants. These additives catalyze the cleavage of the bonds with heat or light, accelerating the abiotic oxidation and increasing the polymer's degradability [13, 14]. In fact, it is known that PE, which is similar to the chemical structure of PP, receives biodegradability by the additives [15]. On the other hand, studies on the degradability in soil of PP with transition metal-free pro-degrading additives are still scarce, although this polyolefin is one of the most widely used commodity polymers today. Among the existing works, we can highlight that of Miyazaki et al. [16], where the degradation of a composite prepared from polypropylene with the addition of TiO₂-containing poly(ethylene oxide) (PEO) microcapsule was evaluated. In this paper, the authors observed that degraded PEO produced an acid and an aldehyde, capable of facilitating PP degradation. Subsequently, Fontanella et al. [17] studied the biodegradability of polypropylene films with the addition of phenolic antioxidant and pro-oxidants based on Mn, Mn/Fe, or Co. Finally, the authors concluded that the degradation was very efficient for PP samples with additives compared to no additives.

Although these biodegrading additives for polymer degradation have been studied in the literature, most studies evaluate the use of transition metal additives that can cause a passive environment due to their toxicological potential [17]. The biodegradation of oxidegradable plastics happens after their fragmentation, but the fate of plastic fragments remaining in the environment is uncertain, causes a great concern about the ingestion of these pieces by insects, birds, fishes, and others animals. In addition, other pro-degradant additive is the organic additive that induces the polymer chain to break and does not show transition metals on its composition [18].

Therefore, considering the importance of researches about the influence of additive, without transition metals in its composition, on the degradation of polyolefins to minimize the effects caused by plastic waste and at the same time aiming to preserve the plastic properties. With this, a gap has been observed in the literature and a great possibility of innovation regarding the use of enzymatic additive in the biodegradation of PP. In this way, the goal of this work is to evaluate the degradation of polypropylene in soil by the incorporation of an enzymatic additive.

Experimental

Materials

The materials used to blend the mixtures were acquired commercially and used without pre-treatment. The PP (code: CP 141) used is an isotactic polymer supplied by Braskem (density of 0.9 g/cm³). Two types of additives were used:

enzymatic, formed by 95% of low density polyethylene (LDPE) and 5% of enzymatic compounds, and organic, formed by 50% of PP and 50% of organic compounds.

The soil (mature compost) used in this work was obtained in a sorting and composting unit, administered by the Municipal Department of Urban Cleaning (DMLU) in Porto Alegre city, Rio Grande do Sul State, Brazil.

Methods

The following topics describe how the blends and their respective films were prepared, and the assembly of the degradation experiment and the characterization techniques was used to evaluate the changes of the blends after the experiment.

Blends preparation

Eight blends were prepared using two different additives (for comparison: enzymatic and organic) and the quantity of respective additives used in each blend was 2, 4, 6, and 8% (w/w). The blends were prepared in the HAAKE Rheomix mixer mark Thermo Fisher Scientific, under the following operational conditions: process temperature: 170 °C, stirring speed: 60 rpm and time of 7 min [19]. The nomenclature adopted for the prepared blends is described in Table 1.

Film preparation

The PP and its blends were transformed into films with the objective of increasing the exposure area in the degradation environment, as well as better simulate the form on which most plastic materials are discarded.

The respective films were prepared on the Marconi hydraulic press with 15 tons capacity. The films with 0.3 to 0.6 mm thickness were obtained through pressing of the

Table 1 Nomenclature of the blends

Nomenclature	Additive content (w/w %)	Additive
PP	0	–
PP-2% enzymatic	2	Enzymatic
PP-4% enzymatic	4	
PP-6% enzymatic	6	
PP-8% enzymatic	8	
PP-2% organic	2	Organic
PP-4% organic	4	
PP-6% organic	6	
PP-8% organic	8	

material with teflon-coated aluminum plates, at 110 °C and a pressure of 3 tons during 2 min.

Degradation experiment

The degradation experiments in soil were carried out using 6 g of soil/1 g of blend ratio, according to ISO 14855-1. The experiments were performed on the orbital stirrer table for soil, model MA-SOLO (Maistro), under room temperature conditions not control: 50 rpm stirring, temperature and humidity average of 25 °C and 50%, respectively. The blend samples exposure time was 6 months and every month the blends were collected for latter analysis. The experiments were carried out in duplicate (Fig. 1).

Characterization

The chemical, thermal, and morphological alterations that happened in the samples during the tests were monitored through following parameters and instrumentals techniques: Fourier transform infrared spectroscopy (FTIR), carbonyl index, differential scanning calorimetry (DSC), crystallinity degree (X_c), thermogravimetric analysis (TGA), and field emission scanning electron microscopy (FE-SEM). The soil samples were monitored through parameters: pH, moisture content, and C, H, and N. All analyses were performed in triplicate.

Fourier transform infrared spectroscopy (FTIR)

Infrared analyses were done to evaluate the chemical alterations based on the absorption bands of the chemical bonds of the samples. A PerkinElmer Instruments Spectrum One FTIR spectrometer was used in these experiments and the spectrum data acquisition was done with the universal attenuated total reflectance (UATR) sample accessory in the wave interval of 650 to 4000 cm^{-1} .

The carbonyl index (CI) was calculated according to the method described in the literature for the samples before and

after the degradation experiments [20]. The CI is calculated through the following :

$$CI = \frac{A_{1715}}{A_{2870}}, \quad (1)$$

where A_{1715} is the absorbance of the carbonyl group (CO) and A_{2870} is the absorbance of the methylene group ($-\text{CH}_2-$).

Differential scanning calorimetry (DSC)

Differential scanning calorimetry was done to determine the thermal properties of the samples, such as T_c and ΔH_m , used to calculate the crystallinity ($X\%$). The thermal behavior of the samples was analyzed through a calorimeter, from TA Instruments—model Q20, between -90 °C and 200 °C, with a rate of 10 °C/min, under nitrogen inert atmosphere and with the crystallization temperature determined after the second cycle in the cooling region. Through the DSC results, it was possible to calculate the crystallinity degree of the samples using the following:

$$X\% = \frac{\Delta H_m}{\Delta H_{m.c}} \times 100, \quad (2)$$

where ΔH_m is the fusion enthalpy and $\Delta H_{m.c}$ is the polypropylene's crystallinity enthalpy (209 J/g) [20]. For the blends the percentage of additive used was considered.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed to determine the thermal properties of the samples, as T_{10} , T_{50} , and T_{max} , as well as to obtain the TG/DTG curves to evaluate the thermal stability of the samples. Thermal degradation analysis was performed on a thermogravimetric balance, model Q600 from TA Instruments, using a heating rate of 10 °C/min, from room temperature to 600 °C under inert atmosphere.

Field emission scanning electron microscopy (FE-SEM)

Field emission scanning electron microscopy was used to verify the possible morphological changes and biofilm formation occurred in the sample after the soil degradation experiment. The images were obtained in an FEI Inspect F50 equipment on the secondary electron (SE) mode. The samples were metalized with gold.

pH measurement

The pH of soil samples was analyzed according to the ASTM D4972-01 standards, using the potentiometric measurement with a glass membrane-combined electrode inserted in the soil/water suspension. First, the soil was previously dried at

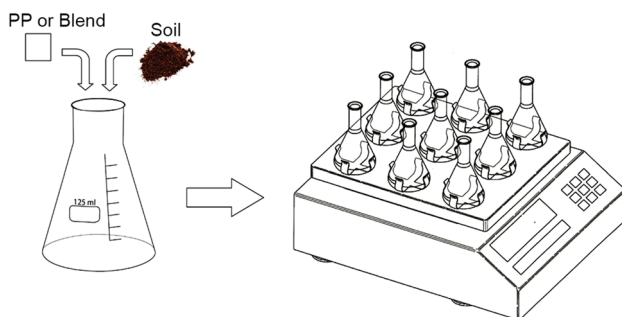


Fig. 1 PP and blends degradation experiments in soil

room temperature and sieved to 9 mesh granulometry. After, 10 g soil was mixed with 10 mL of deionized water, stirred and left for 1 h. Next, they were stirred and left to stand for a short time again, after which the pH electrode was immersed in the suspension for the pH measurement.

Moisture content

The moisture content analysis was performed according to ASTM D2216-98, using a gravimetric analysis method. 10 g (± 0.1 mg) of soil was weighed in a sample container previously cleaned and dried. The material was dried at 110 °C until constant mass (variations smaller than 0.1%) was obtained. After, the samples were kept in a desiccator until it reaches room temperature. The moisture content (dry basis) calculation was done through the following:

$$U(\%) = \frac{m_i - m_f}{m_i} \times 100, \quad (3)$$

where U , m_i , and m_f designate: moisture content, initial sample mass, and final sample mass, respectively.

Elemental analysis

The total carbon percentage (TC%) and total nitrogen percentage (TN%) were performed on a TruSpec CHN non-dispersive elemental analyzer, mark Leco, equipped with an infrared detector for carbon and hydrogen, and a thermal conductivity detector for nitrogen. For the determination, a small amount of the sample was used, which ranged from 50 mg to 100 mg (± 0.01). The samples were weighed into thin sheets of tin and taken directly to the equipment. The samples were burned under a 6.0 oxygen (99.99%) atmosphere with 10 lpm flow at 950 °C [21].

Results and discussion

Characterization of soil

First, properties of the soil used at the degradation experiments were analyzed, showing a pH of 8.0, moisture content of 37.7% and C/N ratio of 14.9. The values of these parameters are in accordance with those recommended by ISO14855-1 for the soil used in the degradation test.

Characterization of blends

Figure 2 shows the FTIR spectrum of PP blends of 2, 4, 6, 8% of each additive, enzymatic (Fig. 2a), and organic (Fig. 2b).

From the analysis of the spectrum, it is observed that the appearance of the main bands of PP at 2950, 2918,

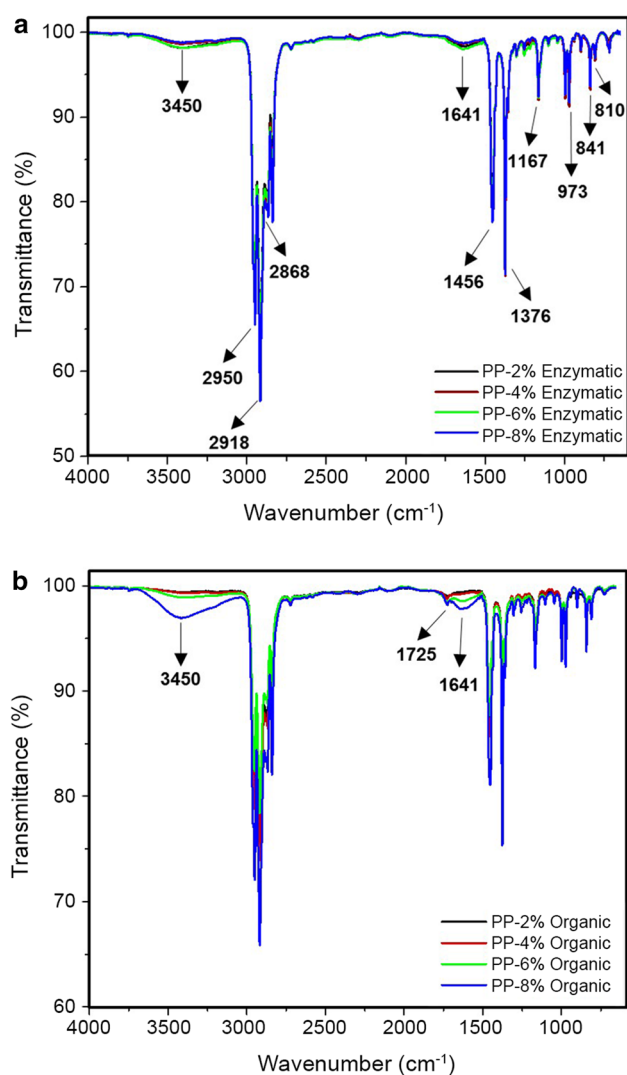


Fig. 2 FTIR spectrum of PP blends with different percentages 2, 4, 6, and 8% of each additive, enzymatic (a) and organic (b)

2868 cm^{-1} corresponding to the asymmetric and symmetrical CH elongation vibrations, 1456 cm^{-1} to the asymmetric strain CH_3 , 1376 cm^{-1} to symmetrical strain CH_3 , 1167 cm^{-1} to tertiary carbon flexural vibration, 973, 841, and 809 cm^{-1} to out-of-plane CH strain, confirming the matrix in which the active principle is dispersed [4, 22, 23]. Moreover, all dominant bands observed are characteristics of the isotactic nature of polypropylene [22, 24]. The main differences between the spectra are the absorption peaks at 1641 cm^{-1} attributed to ethylene groups, at 1725 cm^{-1} (observed only in Fig. 2b) attributed to the stretch vibration of the carbonyl groups and the band at 3450 cm^{-1} , corresponding to hydroxyl groups. This peak indicates the presence of polar groups in the sample that probably derive from the incorporated additives. In

addition, variations at band intensity between mixtures of the same additive may be related to concentrations [22].

Carbonyl index

The first step was to find out the ideal additive amount using the carbonyl index results, since this data can be used to monitor the material degradation (Table 2). The percentage of increase in CI was calculated for 30 days duration of exposure as a function of the initial value (0 days), since this was the highest value found.

According to the literature, initially, an increase in the carbonyl content is expected, since it is related to the break of the polymer chain and consequently, the oxidation of PP. This behavior can be attributed to the presence of additives in the polymer matrix, accelerating the generation of free radicals and efficiently promoting chain breakage. After some time exposure to the medium, the microorganisms consume these compounds produced, and for this reason it is expected to decrease CI [22, 25].

Analyzing the results reported in Table 2, it is possible to notice that the blends with lower percentages of the additives showed higher increases of the carbonyl content after 30 days. Although the 4% organic additive sample presented the best result among the different percentages, the 2% blend showed a good result with a lower percentage of material. Like this, the percentage of 2% of additive was chosen as the ideal in function of the results presenting and the smaller amount of additive needed. Therefore, this work will show only the results for PP-2% enzymatic and PP-2% organic blends.

Degradation of polypropylene with additives in soil

During the degradation experiment, the samples were characterized monthly, aiming to follow the degradation process closely. However, for each characterization technique (FTIR, MEV, DSC, and TGA) only the relevant results for the comparison and analysis of the material degradation are shown.

Structural characteristics

The structural characteristics of the samples, before and after the soil degradation test, were evaluated from the FTIR analysis to verify changes due to exposure to the medium. Figure 3 shows the infrared spectrum of the PP sample, in the wavenumber range of 4000 to 650 cm^{-1} , throughout the soil degradation assay. From the FTIR analysis, it was possible to evaluate the changes in the chemical structure of the polymer.

It can be seen in Fig. 3 that new bands appeared in the frequencies of 1740 cm^{-1} related to the carbonyl group (C=O) of aldehydes and/or esters and 1646 cm^{-1} due to the presence of unsaturated ethylene groups (C=C). In addition, there was the increase of bands in the region of 3353 cm^{-1} related to the axial deformation of the –OH group, at 1373 cm^{-1} the presence of alkyl groups (CH₃) and 1100–007 cm^{-1} of the C–OH bond of alcohols and at the stretching of N–O bond [26–28].

Figure 4 presents the infrared spectrum for the blends with enzymatic (PP-2% enzymatic, Fig. 4a) and organic (PP-2% organic, Fig. 4b) additives after getting exposed to the soil.

The results presented in Fig. 4 show that there are modifications that can be attributed to the degradation of the samples. In the region of 3347 cm^{-1} , the increase in the band relative to the deformation of the axial groups –OH was observed, which may be related to the hydrophilic components present in the additives. Therefore, these modifications are related to the water absorption attributed to the degradation [29]. In addition, new bands appeared at 1736 cm^{-1} , related to the carbonyl group (C=O) of aldehydes and/or esters, and at 1648 cm^{-1} , the presence of ethylene unsaturated groups (C=C). Albertsson et al. [30] concluded that carbonyl groups can be produced by oxidizing agents and that these groups are the main indicators of the onset of degradation. Moreover, according to the literature, the increase in the carbonyl groups, as well as the unsaturated ethylene group, tend to decrease hydrophobicity, facilitating accessibility to microbial degradation. In 30 days the

Table 2 Carbonyl index for all the studied blends

Blend	CI				Increase (%)
	0 days	30 days	90 days	180 days	
PP-2% enzymatic	0.031 ± 0.003	1.145 ± 0.001	0.760 ± 0.006	0.075 ± 0.007	3693
PP-4% enzymatic	0.029 ± 0.002	0.601 ± 0.005	0.427 ± 0.001	0.173 ± 0.005	2072
PP-6% enzymatic	0.048 ± 0.004	0.530 ± 0.002	0.429 ± 0.004	0.113 ± 0.001	1104
PP-8% enzymatic	0.024 ± 0.002	0.653 ± 0.002	0.258 ± 0.004	0.128 ± 0.002	2721
PP-2% organic	0.072 ± 0.003	0.686 ± 0.006	0.417 ± 0.003	0.129 ± 0.006	953
PP-4% organic	0.081 ± 0.001	0.889 ± 0.001	0.425 ± 0.002	0.176 ± 0.003	1097
PP-6% organic	0.125 ± 0.007	0.973 ± 0.003	0.585 ± 0.006	0.216 ± 0.005	778
PP-8% organic	0.099 ± 0.005	0.677 ± 0.001	0.131 ± 0.002	0.202 ± 0.002	684

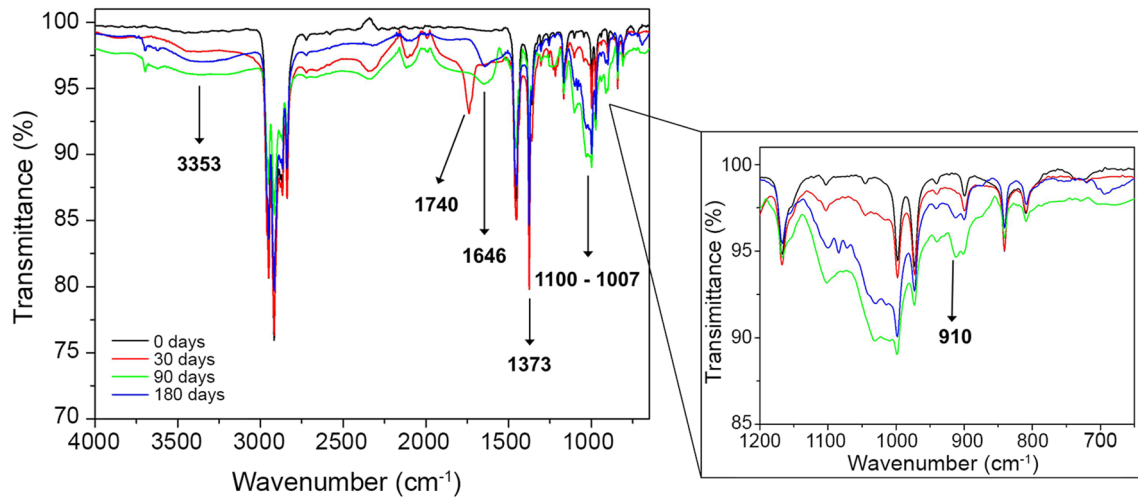


Fig. 3 Infrared spectrum of PP exposed to soil

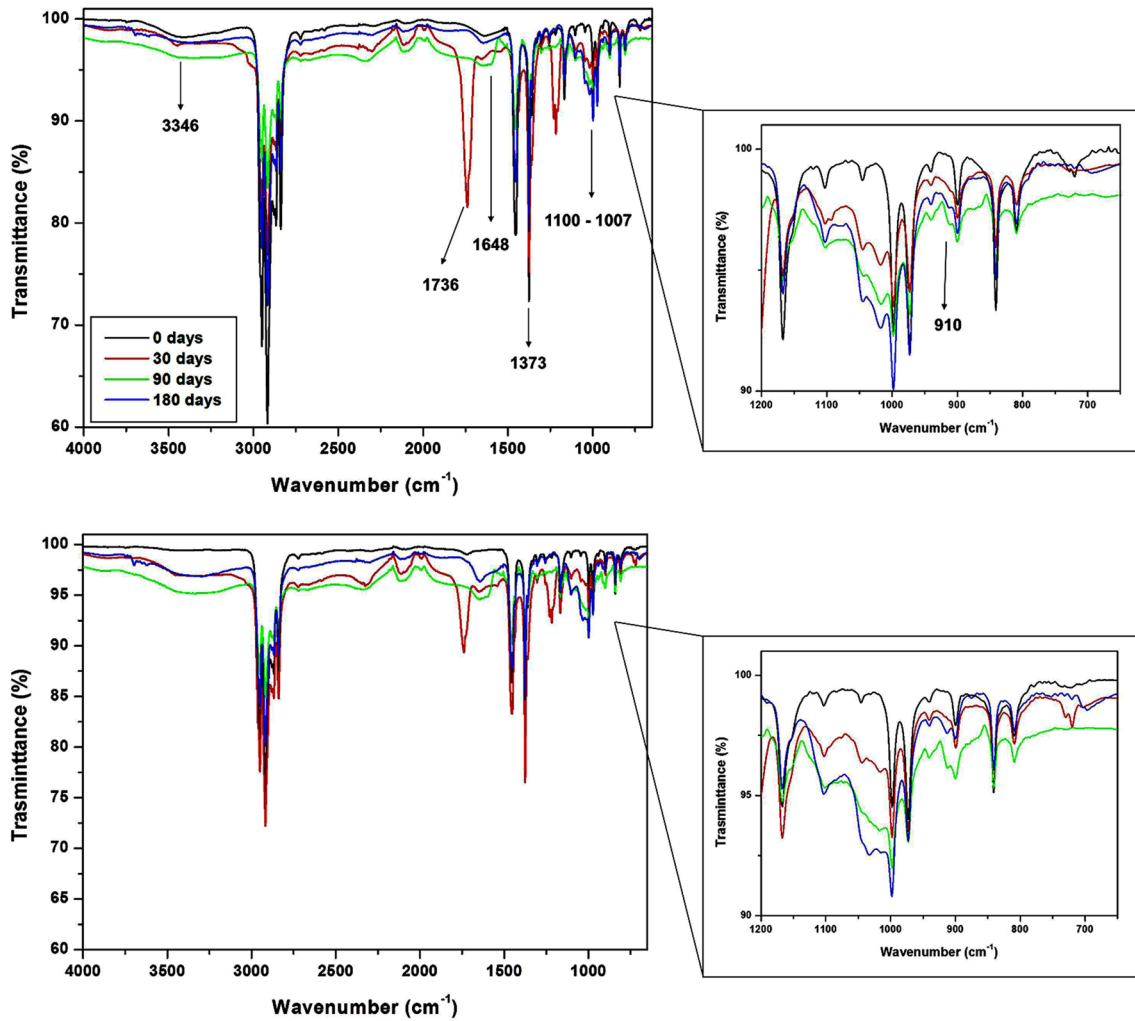


Fig. 4 Infrared spectrum for the PP-2% enzymatic (a) and PP-2% organic (b) after exposed to the soil

appearance of the band corresponding to carbonyl (C=O) of carboxylic acids was observed, indicating the beginning of the degradation. In addition, the disappearance of the carbonyl group after 30 days is related to the consumption of these compounds by the microorganisms [30]. It should be noted that these results corroborate with those of the carbonyl index presented above. Furthermore, the bands observed at 1733 cm^{-1} could be attributed to the presence of alkyl groups (CH_3), $1100\text{--}1007\text{ cm}^{-1}$ belongs to the bond of alcohols (C–O) and the stretching of N–O bond, and 910 cm^{-1} due to the presence of vinyl group ($\text{CH}=\text{CH}_2$) [26–28]. According to Das and Kumar [31], the band at 910 cm^{-1} may be linked to the depolymerization caused by microorganisms.

Comparing the PP-2% enzymatic with the PP-2% organic and the pure PP, it is possible to observe that the structural modifications were more significant in the additive samples, and PP-2% enzymatic showed the most expressive changes, mainly in the carbonyl group and ethylene bands. This behavior corroborates the values obtained for the carbonyl index of the samples, since the PP-2% enzymatic blend presents the largest increase after 30 days of experiment, as shown in Fig. 5. As already discussed, the increase and decrease of the CI are due to the formation of carbonyl at the beginning of degradation due to oxidation of the material, followed by the consumption of these compounds by microorganisms [30]. In addition, there is a greater variation in the carbonyl index for the additive samples (3693% for the enzymatic additive and 953% for the organic additive) compared to pure PP (681%).

Morphology

Figure 5 shows the MEV images for the PP samples and the blends before and after 30, 90, and 180 days exposed to the soil. At the initial time, it was observed that the samples presented uniform surfaces without the presence of

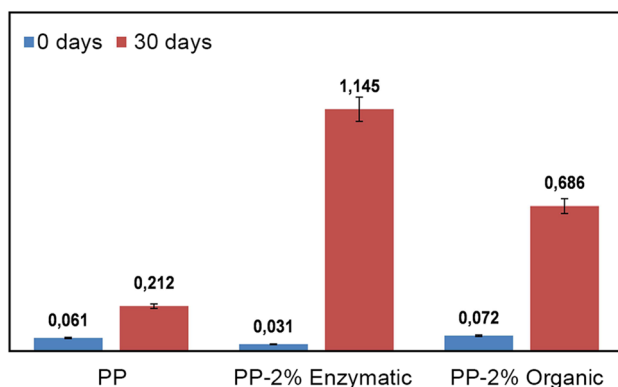


Fig. 5 Carbonyl index of samples before and after 30 days of fresh water exposure

microorganisms adhered. Using the images presented above, the formation of a biofilm in all the samples after the soil exposure is evident. Biofilm or microfouling is a process through which a complex microorganism community is built over the surface. This community is formed of microorganisms and its extracellular polysaccharides and the amount of each component is highly variable both in space and time [32–34]. Moreover, it is possible to see modifications on the sample surface, as well as the presence of bacteria, fungi and hyphae, as described before in the literature [35–37]. Biodegradation depends on the formation of biofilm on the surface of the polymer, which enables the polymer to breakdown into low molecular weight oligomers, probably due to the enzymes secreted by the microbes, and then easily being assimilated [38].

Thermal properties

The thermal behavior of the samples, before and after the degradation experiment, was analyzed by the DSC and TGA techniques to verify the possible changes in the thermal properties caused by the degradation of the material. Using the DSC curves it was possible to determine the crystallization temperature (T_c) and the crystallinity of the samples (%X) as shown on Table 3.

Pure PP and PP-2% enzymatic samples showed a decrease in T_c with increasing time. According to the literature, this behavior may be related to the reduction of polymer molar mass due to degradation [39]. At the same time, the PP-2% organic sample showed an increase in this property as a function of soil exposure time, which may be related to the additive composition.

From the values of the degree of crystallinity, an association can be made with the degradation of the polymer. As the chain breaks in the amorphous phase the crystallization

Table 3 Crystallization temperature (T_c) and crystallinity of PP, and the blends (%X) before and after the soil degradation experiment

Sample	Time (day)	T_c (°C)	X (%)
PP	0	127.3 ± 0.1	39.7 ± 0.5
	30	125.7 ± 0.6	39.5 ± 0.3
	90	122.3 ± 0.5	39.8 ± 0.2
	180	121.9 ± 0.8	39.6 ± 0.2
PP-2% enzymatic	0	125.5 ± 0.6	36.3 ± 0.7
	30	123.9 ± 0.3	43.1 ± 0.2
	90	122.4 ± 0.7	38.7 ± 0.2
	180	122.2 ± 0.6	37.1 ± 0.3
PP-2% organic	0	119.7 ± 0.1	37.6 ± 0.8
	30	120.9 ± 0.5	41.3 ± 0.2
	90	121.9 ± 0.3	39.8 ± 0.6
	180	123.3 ± 0.5	38.7 ± 0.2

process may be stimulated, an increase in the crystalline content of a semicrystalline polymer should be considered as a signal of degradation. Applying this approach, it is possible to link the crystallinity degree data with the polymer degradation. It is known from the literature that in semicrystalline polymers, the degradation starts in the amorphous phase and in the interfacial regions, leading to the increase in the number of crystals [40]. This behavior is associated with high microbial activity in the amorphous phase and in the smaller crystals. However, depending on the time when polymeric materials are exposed to the microorganisms, oxidation of the polymer chain and occurrence of chain breaks can cause the reduction in degree of crystallinity after exposure [40–42].

The crystallinity of the polymer is directly associated to a number of factors, among them we have the molecular mass and size of the molecules, therefore, the smaller the chain size and the lower the molecular mass, the higher the crystallinity of the polymer as compared to the blends before and after the degradation test [25, 43]. PP-2% enzymatic samples presented the highest crystallinity variation compared to the other samples, showing an increase of 18.7% after 30 days. This result corroborates with the CI increase shown for this sample, since, according to the literature, an increase in the CI would mean chain split and so smaller chain sizes, consequently, higher crystallinity [22, 25]. PP-2% organic sample also showed a variation in crystallinity (9.8%), however, less significant than the PP-2% enzymatic (18.7%). Moreover,

PP samples showed a linear behavior throughout the experiment, not having a change in its crystallinity.

Evaluating the crystallization temperature, it can be seen that the PP and PP-2% enzymatic samples show a slight reduction in their values. According to the literature, this result is related to the decrease in the molar mass of the polymer due to the degradation of the material [39]. In addition, the PP-2% organic sample presented a distinct behavior, where T_c increased after exposure of the sample to the medium, which has already been observed by the other authors [22, 44].

Figure 6 presents the TGA/DTG curves for the blends, before and after the degradation tests, while Table 4 shows the thermal properties obtained from TGA before and after the soil degradation tests (values for the initial degradation temperature with 10% of the mass lost, temperature with 50% weight loss and maximum degradation temperature).

Evaluating the results of Table 4, it can be noticed that the pure PP showed a reduction in T_{10} after 180 days exposed to soil, while the PP-2% enzymatic and PP-2% organic showed a small increase on this parameter as a function of exposure time. Thus, it can be deduced that the additive action made the polymer more thermally stable, since after exposure to the environment, the initial degradation temperatures were higher than the initial ones [44]. In relation to T_{50} , it was observed that PP and PP-2% organic samples showed a fall in properties as a function of the testing time, while PP-2% enzymatic sample showed a slight increase. Moreover, it is

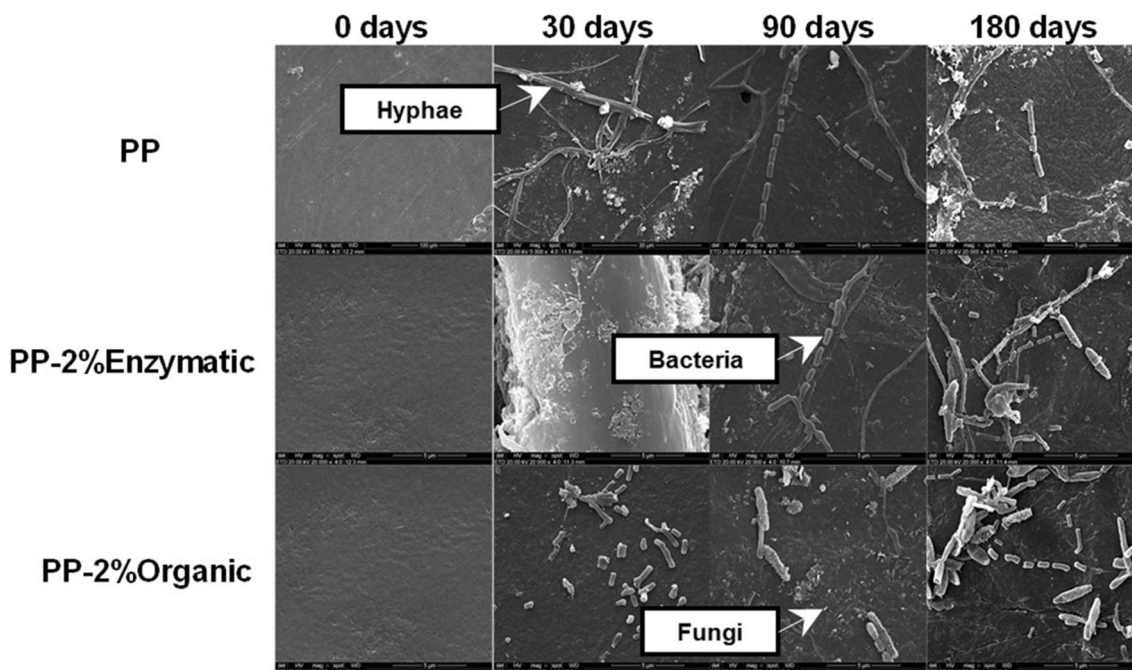


Fig. 6 MEV images of the PP and blend samples after exposure to soil

Table 4 Initial degradation temperature with 10% of mass loss (T_{10}), temperature with 50% weight loss (T_{50}), and maximum degradation temperature (T_{max}), before and after the soil degradation experiment

Sample	Time (day)	T_{10} (°C)	T_{50} (°C)	T_{max} (°C)
PP	0	439.6 ± 0.9	468.07 ± 1.52	472.8 ± 0.8
	30	435.5 ± 0.6	454.22 ± 0.02	468.5 ± 0.6
	90	427.2 ± 0.8	454.05 ± 0.35	459.2 ± 1.0
	180	425.6 ± 0.8	453.79 ± 0.47	458.6 ± 0.8
PP-2% enzymatic	0	425.9 ± 0.7	445.48 ± 0.82	459.7 ± 0.9
	30	428.2 ± 0.1	454.22 ± 0.01	459.6 ± 0.8
	90	428.9 ± 0.9	452.09 ± 0.42	460.1 ± 0.9
	180	429.0 ± 0.8	448.02 ± 0.61	459.4 ± 0.6
PP-2% organic	0	409.3 ± 0.8	465.42 ± 1.07	457.2 ± 0.8
	30	420.1 ± 0.6	453.69 ± 0.54	458.1 ± 0.4
	90	424.7 ± 1.0	451.61 ± 0.41	458.9 ± 0.9
	180	425.6 ± 0.5	448.78 ± 0.19	459.2 ± 0.7

noteworthy that by 200 °C, the samples did not show weight loss, indicating the absence of water in the samples [45].

The T_{max} property also showed different results between pure PP and the blends. While pure PP samples showed a reduction of this temperature with longer time, blends did not show any change on this parameter. Besides that, pure PP and PP-2% enzymatic showed higher thermal stability than PP-2% organic, since the PP-2% organic has an initial degradation temperature of 409.3 °C, while pure PP and PP-2% enzymatic resulted in 439.6 and 425.9 °C, respectively. This behavior had already been observed for additives of organic nature in the literature, which can be attributed to the presence of higher amount of active principle in its composition (50% of organic compounds) [22, 44]. Regarding the residue, the initial values (0 days) ranged from 2.1 to 1.8%, while the values obtained after 180 days ranged from 0.6 to 0.3%. Thus, there were no significant variations in residue percentages observed between the samples.

Using the TG/DTG curves (Fig. 7), it is possible to notice that both PP and PP-2% enzymatic samples presented only one degradation stage, while PP-2% organic showed two (as it is highlighted in Fig. 7c). According to previous works, this first stage is related to the initial degradation of pro-oxidant derivatives, while the second stage is the degradation of the polymeric matrix (PP) [22, 44]. The difference between the blends can be explained by the percentages of

active principle present in each additive, because the organic additive has 50% of organic compounds, while the enzymatic additive has 5% of the enzymatic compounds.

The behavior of PP can be explained by tacticity of the polymer, whereas CH_3 substituents in each repetitive unit, with the same configuration along the polymeric chain (isotactic polymer). Thus, this polymer exhibits a single rupture center and therefore a single degradation stage [46].

Conclusion

In this work, the degradation of pure propylene and PP-2% enzymatic and PP-2% organic was studied through a soil degradation test. The results of FTIR showed more significant structural changes for PP-2% enzymatic and PP-2% organic, compared to PP samples. Similarly, these blends showed increases in their carbonyl index, from which PP-2% enzymatic had the best result with the final CI after 30 days (3693%) higher than the initial one. At the same time, this sample presented greater variation of the carbonyl index (18.7%) after the degradation test. The thermogravimetric analysis showed that the pure PP and PP-2% enzymatic samples had a higher thermal stability after the soil exposure, since they only presented one degradation stage. On the other hand, PP-2% organic had two degradation stages, indicating that this sample was more susceptible to thermal degradation.

Therefore, by analyzing the results, it can be concluded that the additives (organic and enzymatic) had influence on the degradation of PP films with 2% of additive (low percentage), indicating that they accelerated this process. At the same time, it was observed that, in general, the enzymatic additive presented the best results, in relation to changes in the structural characteristics, carbonyl index, and crystallinity variation after the degradation test. Thus, it is suggested that the enzymatic additive was more effective for the degradation of PP in soil than the organic additive.

This work plays an important role in the research and development of biodegradable materials (without transition metals in its composition), to minimize the effects caused by plastic waste on the environment, as it proposes the use of an additive never reported in the literature (enzymatic). However, there is still a need for further studies with this additive to evaluate its behavior in other environments that can be disposed such as rivers and seas.

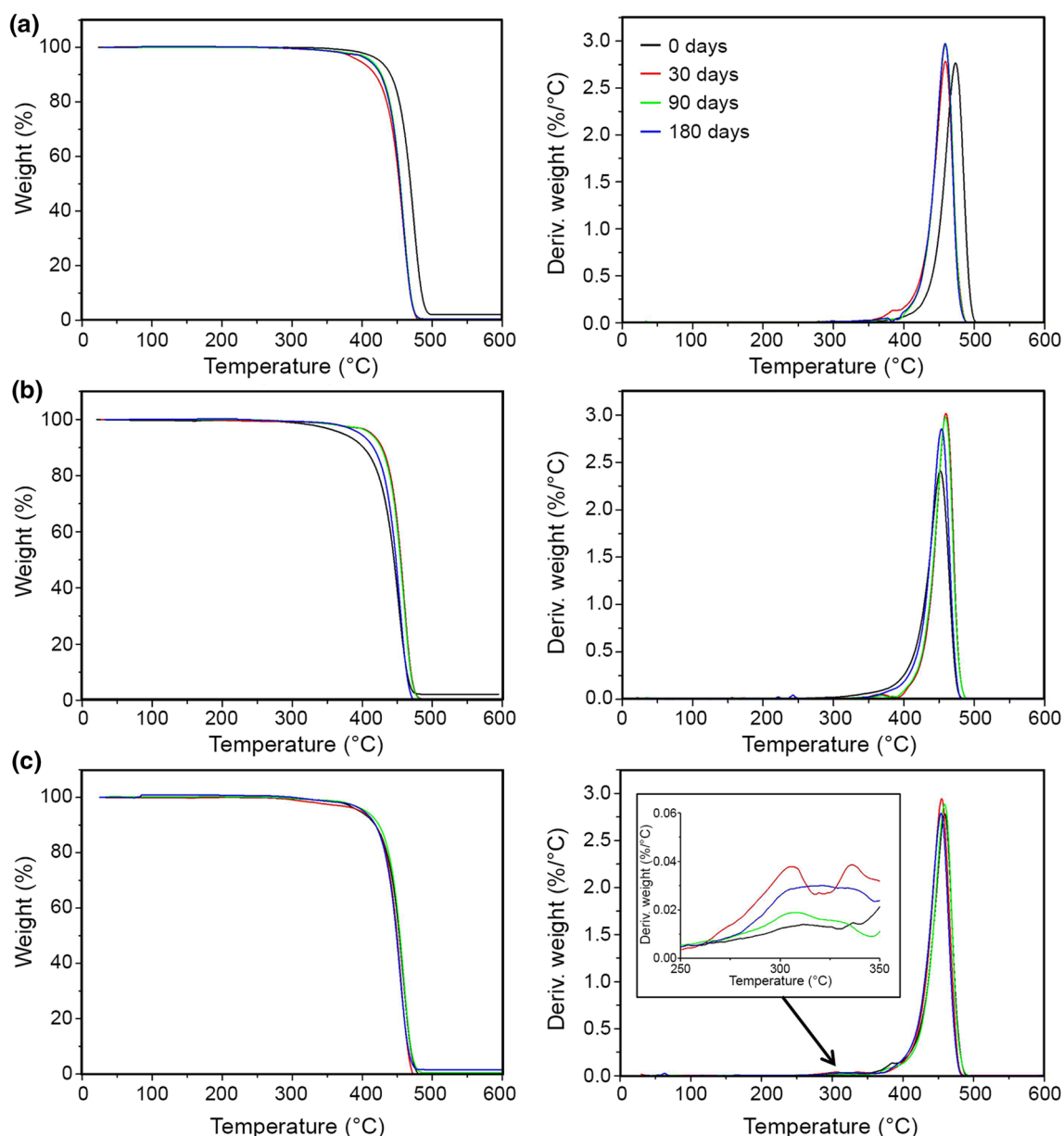


Fig. 7 TGA/DTG curves for PP (a), PP-2% enzymatic (b), and PP-2% organic (c) samples

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