



Natural freshwater degradation of polypropylene blends with additives of a distinct nature

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Abstract

Polypropylene (PP) is one of the most widely used polymers in the world, mainly due to its versatility, good properties and low cost. However, as it does not easily degrade in the natural environment, several research projects have been developed in order to increase its biodegradability. The use of pro-degrading additives has been explored, as they promote the polymer degradation process. However, few studies have evaluated the degradation of these materials in natural aqueous environments such as rivers and lakes, which contain large amounts of PP residues. Thus, the present work aims to evaluate the influence of different additives on the degradation process of PP in natural freshwater. Samples from degradation tests were evaluated for 6 months, and their structural, morphological and thermal properties (crystallinity, etc.) were monitored. From the obtained results, it was observed that the additives influenced the degradation of PP. In addition, the enzymatic additive had more promising results since it caused more significant changes in the properties analysed, especially in relation to the morphology and structural characteristics analyses (and consequently the carbonyl index), indicating a greater influence on the degradation process. Thus, the materials studied in this work are an alternative in the field of plastic packaging, reducing the effects caused by plastic waste on the environment.

Keywords Polypropylene · Additive · Degradation · Natural freshwater · Plastic · Blends

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Introduction

In the last century, polyolefins have been one of the most used polymers; the two main types are polypropylene (PP) and polyethylene (PE). They are used for a diverse range of applications, such as packaging, automotives, toys, adhesives, prosthetic implants and biomedicine, among others. Contributing to the great versatility of these materials, the properties that stand out are their good chemical resistance, low cost of raw materials production, excellent recycling capacity and mechanical properties, consequently making the world production of these polymers exceed 100 million tonnes per year [1, 2].

At the same time that technological developments and the needs of the population are progressing, environmental pollution with solid waste has been expanding as the use of polymeric materials also increases [3]. Today, most of the waste produced daily consists of plastics from packaging and the slow decomposition and often incorrect disposal of these materials after use cause serious environmental problems [4]. In recent years, interest in research related to biodegradable materials has increased due to important environmental concerns with all living things. Thus, it is crucial to increase the biodegradability of polymeric materials to make a significant contribution to environmental sustainability [5].

The accumulation of plastic waste in the environment has reached a rate of 25 million tonnes per year, and when accumulated mainly in aquatic habitats, it is estimated that 8 million tonnes of plastic enter the oceans annually [6–8]. In the aquatic environment, this waste comes from various sources, such as dumping of ships, land sources and wastewater systems, among others [9]. The improper disposal of plastic packaging in the aquatic environment leads to numerous problems, such as sewage blockage, pollution of the aquatic environment, unpleasant aesthetic appearance and a major threat to aquatic animals and birds [10]. It is important to note that plastics generally take longer to degrade in water than in soil, due to low temperatures and reduction in its exposure to ultraviolet (UV) radiation by water, causing plastic debris to persist and accumulate in aquatic environments [11, 12].

Due to problems in relation to the plastic waste that reaches rivers, lakes and other aquatic springs of the large freshwater reserve placed in Brazil, there is a need to look for alternatives to mitigate this problem. One alternative that has been explored is to obtain degradable polyolefins, which have with special additives called pro-oxidants or degraders, in order to accelerate and improve the degradability of polymers [13, 14]. Among existing additives, the most commonly used are transition metals, but there are problems related to this type of additive as they have the potential to cause negative effects after disposal [15]. These additives catalyse the decomposition of long polymer chains, making the material become brittle and fragment into smaller pieces, which may then be ingested by animals and, consequently, cause their deaths [16].

In our group's previous work [13], the soil degradation of polypropylene with a pro-degrading additive (without the presence of heavy metals) of an enzymatic nature was published, which demonstrated a higher activity when compared to

organic additives. As there are few published studies that evaluate degradation in aqueous media [17–19], this work aims to investigate the degradation behaviour of PP with commercial additives without metals (enzymatic and organic) in freshwater and compare the results with the previous work [13], due to the different characteristics between soil and water, such as luminosity and temperature.

Experimental

Materials

The materials used to make the blends were commercially purchased and used without pretreatment. The materials used included PP (code: CP 141—*isotactic polymer* supplied by Braskem with density 0.9 g/cm³) and two types of additives: enzymatic, formed by 95% of low-density polyethylene (LDPE) and 5% of enzymatic compounds; and organic, consisting of 50% PP and 50% organic compounds. The freshwater used in this work was collected from Guaiba Lake in the city of Guaiba, Rio Grande do Sul, Brazil (latitude: –30.1130, longitude: –51.3136). In addition, natural freshwater had the following parameters: pH 7.32, turbidity 55.3 NTU (ABNT MB 3227), biochemical oxygen demand (BOD) 20 mg/L (NBR 12614), chemical oxygen demand (COD) 109 mg/L (NBR 10357), 2.4×10^1 NMP/100 mL total coliforms and 2.0×10^2 NMP/100 mL faecal coliforms (APHA 20th Ed).

Methods

The following sections describe how the blends and their films were prepared, as well as the preparation of the degradation experiment and the characterisation techniques used to evaluate the samples' decomposition.

Preparation of the blends

PP blends were prepared using two types of additive (enzymatic and organic), and the amounts used were 2, 4, 6 and 8% (w/w). Mixing was performed on a HAAKE Rheomix mixer (Thermo Fisher Scientific) under the following operating conditions: 170 °C process temperature, 60 rpm and 7 min duration [20]. The nomenclature adopted for the prepared mixtures is described in Table 1.

Film preparation

After processing, blends were transformed into films in order to increase the exposure area in the degradation medium, as well as to approximate the way most plastic materials are discarded. Pure PP films and PP/additive blend films were prepared in a 15-ton capacity Marconi brand hydraulic press. Film thicknesses between 0.3 and 0.6 mm were obtained by pressing Teflon-coated aluminium plates at 110 °C with a 3 ton load for 2 min.

Table 1 PP/additive blend samples nomenclature

Nomenclature	Percentage of additive (w/w%)	Additive
PP	0	–
PP-2Enz	2	Enzymatic
PP-4Enz	4	
PP-6Enz	6	
PP-8Enz	8	
PP-2Org	2	Organic
PP-4Org	4	
PP-6Org	6	
PP-8Org	8	

Degradation test

The methodology used for the freshwater degradation test was adapted from studies described in the literature [17, 21]. The degradation experiment was performed with proof bodies (15 mm × 15 mm) of PP and blends immersed in 15 mL of freshwater in an Erlenmeyer flask (125 mL capacity). All systems were shaken (50 rpm) on a Quimis Model Q225M shaker table under uncontrolled room temperature (average temperature and humidity of 25 °C and 50%, respectively). The test time was 6 months, and monthly samples were collected for further analysis. The experiments were performed in duplicate.

Characterisation techniques

The chemical, thermal and morphological alterations occurring in the PP and blends samples after the degradation test were evaluated by the following instrumental techniques: Fourier transform infrared spectroscopy (FTIR), differential exploratory calorimetry (DSC), thermogravimetric analysis (TGA) and field-emission scanning electron microscopy (FE-SEM). All analyses were performed in triplicate.

Fourier transform infrared spectroscopy (FTIR)

Infrared analyses were done in order to evaluate chemical alterations based on the absorption bands of the chemical bounds 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 650–4000 cm^{-1} .

It was also possible to determine the carbonyl index (CI) of the samples from this analysis, which is an important parameter to evaluate the degradation process. The CI of the samples was calculated before and after the degradation experiments, according

to the method described in the literature [22]. The CI was calculated through following Eq. 1:

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

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)

DSC was performed to determine the thermal properties of the samples, such as T_c and ΔH_m , used to calculate crystallinity ($X\%$). The thermal behaviour of the samples was analysed through a calorimeter, model Q20 (TA Instruments), between -90 and 200 °C, with a heating rate of 10 °C/min, under nitrogen inert atmosphere and with the crystallisation 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 Eq. 2:

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

where ΔH_m is the fusion enthalpy and $\Delta H_{m.c}$ is the polypropylene's crystallinity enthalpy (209 J/g) [18]. 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 (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 (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)

FE-SEM was used to verify the morphological modifications and biofilm formation that had occurred in the samples after the soil degradation experiment. The images were obtained on FEI Inspect F50 equipment on the secondary electron (SE) mode. The samples were metalised with gold.

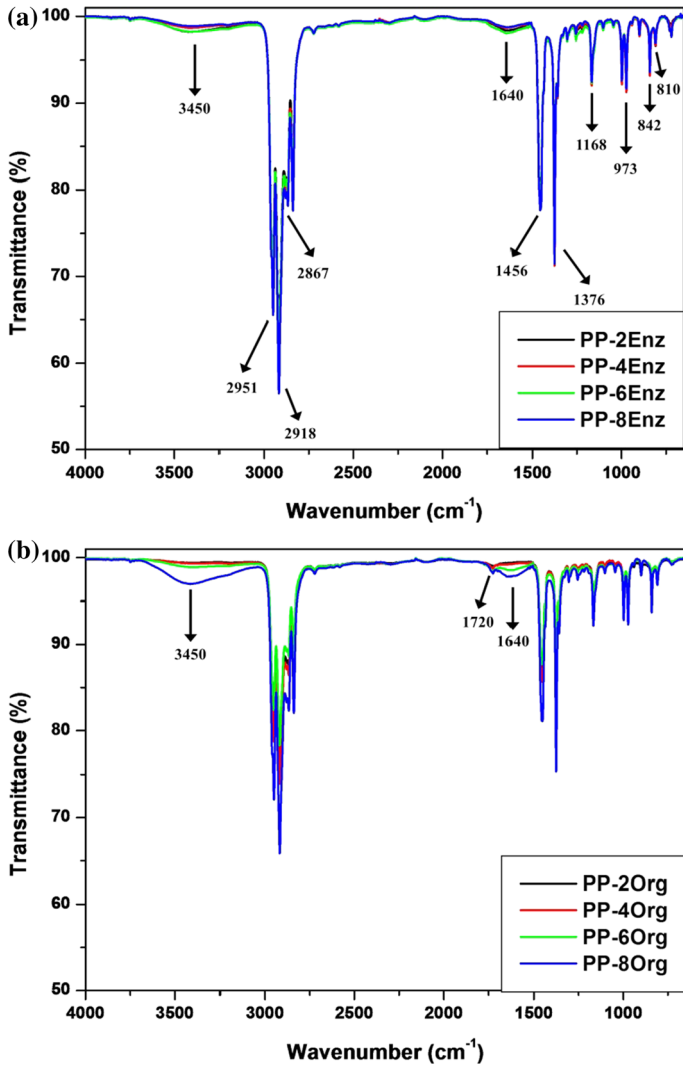


Fig. 1 FTIR spectra of PP blends with different percentages (2, 4, 6 and 8%) of each additive, enzymatic (a) and organic (b)

Results and discussion

Blends characterisation

Figure 1 shows the FTIR spectra of PP mixtures with different percentages (2, 4, 6 and 8%) of each additive: enzymatic (Fig. 1a) and organic (Fig. 1b).

Evaluating the obtained spectra, appearance of the main bands of PP is observed at: 2951, 2918 and 2867 cm^{-1} , corresponding to the asymmetric and symmetrical

CH elongation vibrations; 1456 cm^{-1} , corresponding to the asymmetric strain CH_3 ; 1376 cm^{-1} , corresponding to symmetrical strain CH_3 ; 1168 cm^{-1} , corresponding to tertiary vibration of carbon flexion; and $973, 842$ and 810 cm^{-1} , corresponding to the off plan strain of CH. Thus, one can confirm a matrix (PP) in which the active principle is dispersed [23–25]. Furthermore, all observed dominant bands are characteristic of the isotactic nature of polypropylene [26, 27].

The main differences highlighted in the spectra are the 1640-cm^{-1} absorption bands assigned to the ethylene groups, the 1720-cm^{-1} band (seen only in Fig. 1b) attributed to the elongation vibration of the carbonyl groups and the 3450-cm^{-1} band corresponding to hydroxyl groups. These peaks are related to the presence of polar groups in films, which are likely to be derived from additives. Similarly, variations in band intensity among blends of the same additive may be related to different concentrations [24].

Carbonyl index (CI)

Initially, for the development of this work, the optimal amounts of each additive were determined using the CI results, as these data can be used to monitor material degradation (Fig. 2). The percentage increase in CI was calculated for the 30 days exposure time, as this was the highest value found. According to the literature, an initial increase in carbonyl content is expected, as it is related to the breakdown of the polymeric chain and, consequently, to the oxidation of PP. After some time of exposure to the medium, microorganisms consume these produced compounds and there is therefore a decrease in the CI [18, 24]. This explains the behaviour obtained for the samples, where an increase was observed after 30 days, followed by a decrease in CI in the following periods.

Evaluating the results presented in Fig. 2, it can be seen that the incorporated blends with the highest percentages of enzymatic additive (6 and 8%) had the

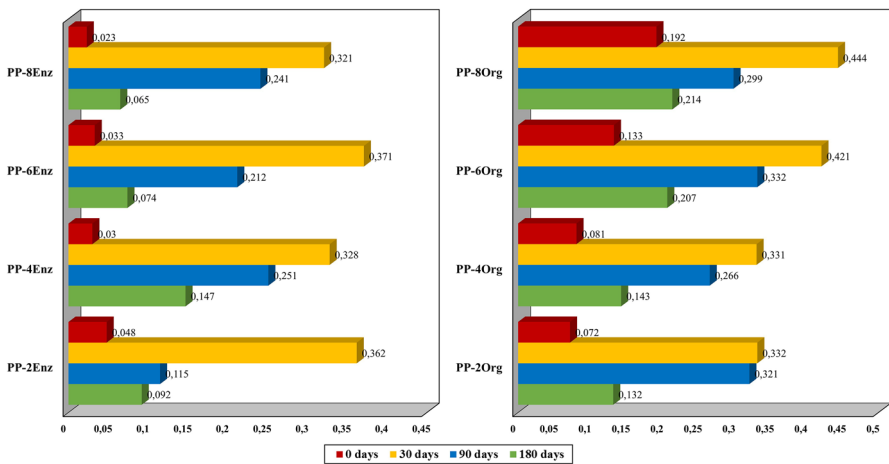


Fig. 2 Carbonyl indexes of the PP/additive blends

largest increases in CI after 30 days of exposure to the medium (1124% and 1395%, respectively). On the other hand, blends incorporated with the lowest percentages of organic additive (2 and 4%) showed the largest increases in carbonyl index (461% and 408%, respectively). Thus, the percentages of 8% enzymatic additive and 2% organic additive were chosen as ideal concentrations based on the results presented (after 30 days of exposure), so this work will only show the results for the PP-8Enz and PP-2Org.

Degradation of polypropylene blends with freshwater additives

During the degradation experiment, the samples were characterised monthly, aiming to follow the degradation process closely. However, for each characterisation 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 freshwater degradation test were evaluated by FTIR analysis to verify the changes resulting from their exposure. Figure 3 shows the infrared spectra of the PP samples (a), PP-8Enz (b) and PP-2Org (c) during the degradation test, and it is possible to evaluate changes in the chemical structure of the polymer.

From the spectra, it can be observed that there is an increase and/or appearance of absorption bands in the regions of: 3348 cm^{-1} , corresponding to the axial deformation of the OH group; 1647 cm^{-1} , attributed to the presence of the unsaturated ethylene group (C=C); 1371 cm^{-1} , corresponding to alkyl groups (CH_3); $1100\text{--}1007\text{ cm}^{-1}$, corresponding to --CO-- bonding of alcohols and stretching of NO bond, respectively; and 910 cm^{-1} , corresponding to the presence of a vinyl group (--HC=CH_2) [23, 25, 26, 28].

It is noteworthy that the band corresponding to the axial deformation of the --OH group (3348 cm^{-1}) shows a significant increase with the time of freshwater degradation, especially for the blends; this can be attributed to the absorption of water due to the presence of polar groups in the composition of the additive [24, 27].

According to Das and Kumar [29], the band at the 910 cm^{-1} region may be related to depolymerisation caused by microorganisms. In addition, the carbonyl (--C=O) of aldehyde and/or ester band appeared in the region of 1730 cm^{-1} after 30 days of testing. Chiellini et al. [30] concluded that carbonyl groups can be produced by oxidising agents and are the main factors that indicate the onset of degradation through being attacked by microorganisms that degrade the shorter segments of chains. According to the literature, the increase at the unsaturated ethylene group causes a decrease in hydrophobicity, facilitating accessibility to microbial degradation [23].

Comparing PP-8Enz with PP-2Org, it is possible to observe that the sample incorporated with the enzymatic additive presents more intense structural modifications, mainly at the bands related to the carbonyl and ethylene groups. This

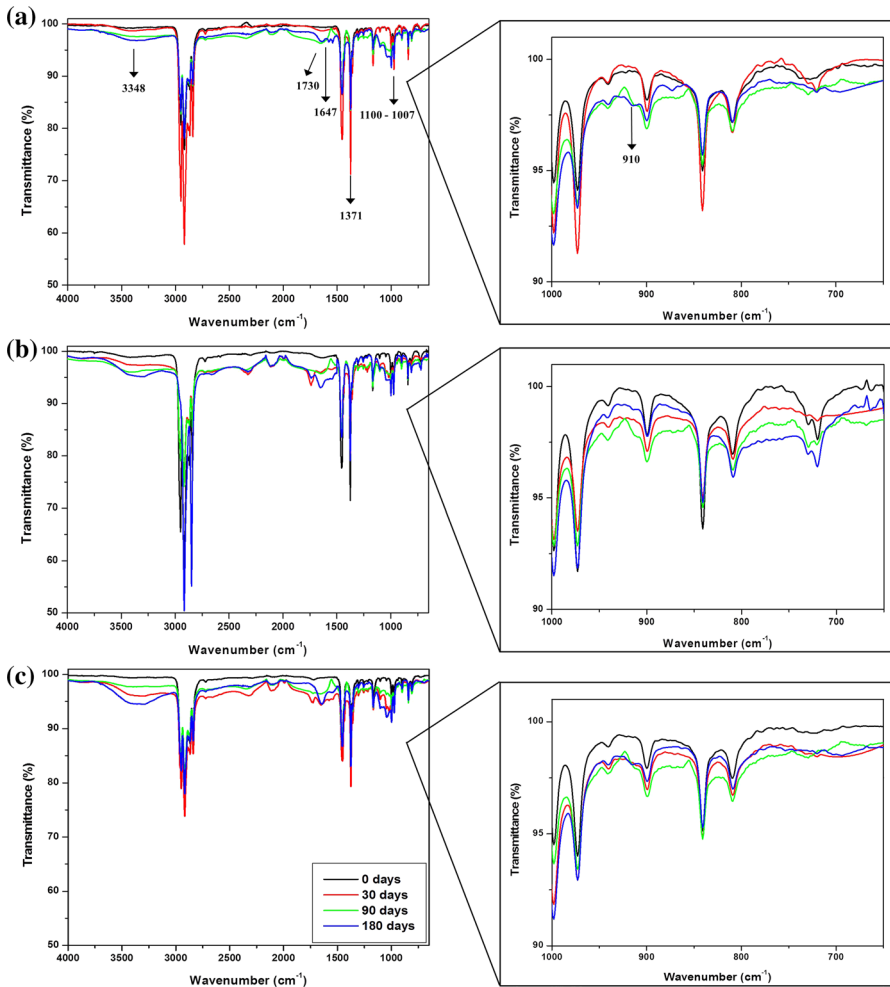


Fig. 3 Infrared spectra of PP (a), PP-8Enz (b) and PP-2Org (c) samples at different freshwater exposure times

behaviour corroborates values obtained for the CI of the samples, since the PP-8Enz blend shows the largest increase after 30 days of experiment, as shown in Fig. 4. As already discussed, the increase and decrease in the CI should be the formation of carbonyl at the beginning of the degradation due to the oxidation of the material, followed by the consumption of these compounds by microorganisms [30]. In addition, the largest variation in the CI for the additive samples is highlighted (1395% for the enzymatic additive and 461% for the organic additive) in relation to pure PP (347%).

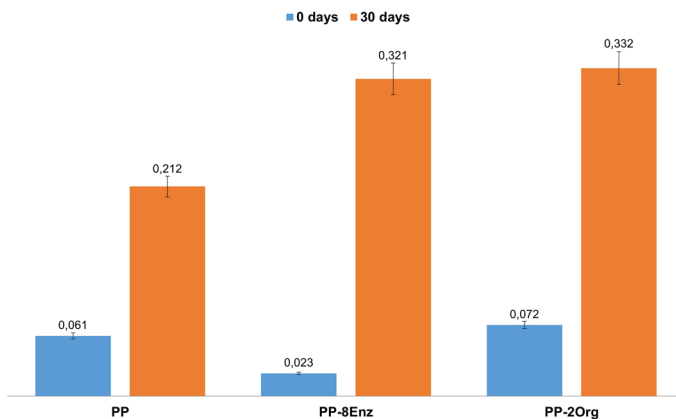


Fig. 4 Carbonyl index variation of PP, PP-8Enz and PP-2Org samples before and after 30 days of freshwater exposure

Morphology

The morphologies of the samples before and after the freshwater degradation test were analysed. Figure 5 shows SEM images for PP samples and enzymatic (PP-8Enz) and organic (PP-2Org) additive blends before freshwater degradation assay and after 30, 90 and 180 days exposure.

Modifications in the surface of all samples can be verified after exposure to fresh water, as well as the presence of some bacteria, fungi and hyphae, as already described in the literature [31–33]. However, the blends present a much larger amount of microorganisms, in relation to pure PP, mainly in the PP-8Enz sample after 180 days.

Biofilm formation is observed in all samples after exposure to the aqueous medium. Biofilm formation is a process in which a complex community of microorganisms is established on a surface, consisting of microorganisms and their extracellular polysaccharides [34]. Biodegradation depends on the formation of a biofilm, specifically a deposition layer of microorganisms and its polysaccharides secreted on the polymer surface. This is followed by the polymer breaking into low molecular weight oligomers, probably due to the enzymes secreted by the microorganisms and then easily assimilated by them [35].

Thermal analysis

The thermal behaviour of the samples before and after the degradation experiment was analysed by DSC and TGA techniques to verify possible changes in thermal properties caused by material degradation. Using the DSC curves, it is possible to determine the crystallisation temperature (T_c) and the crystallinity of the samples ($X\%$), allowing visualisation of the variation in these properties as function of time (Fig. 6).

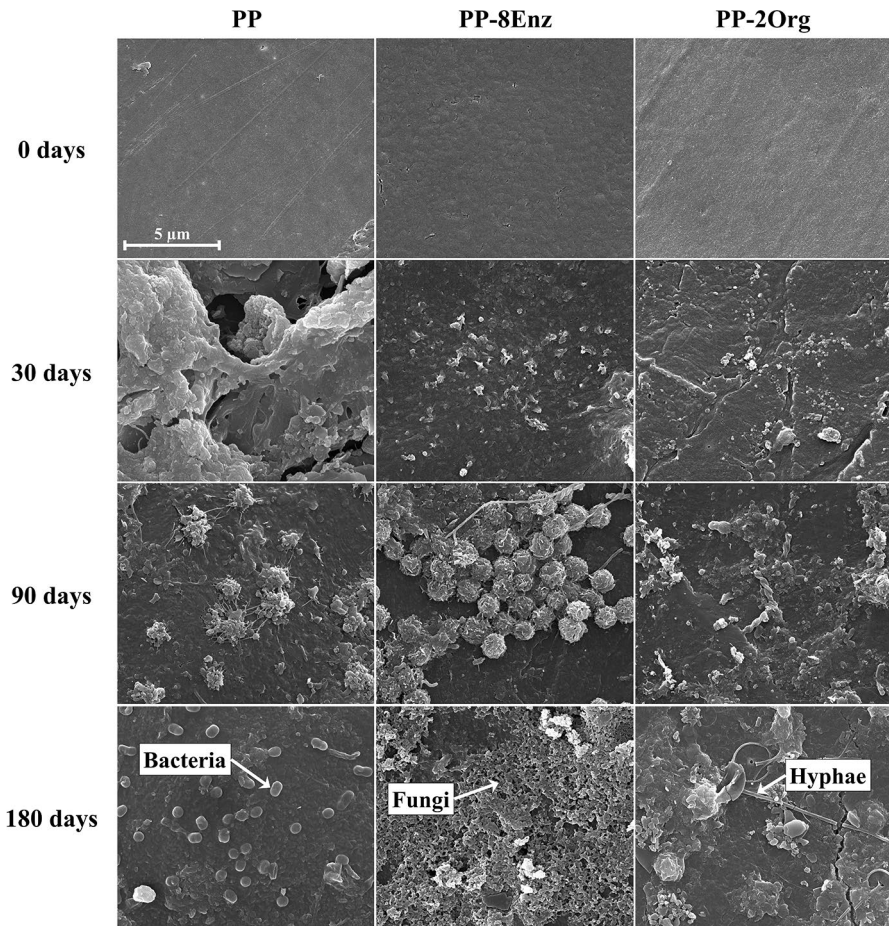


Fig. 5 SEM images for PP, PP-8Enz and PP-2Org samples exposed in freshwater

From the results expressed in Fig. 6, it is observed that there are slight variations in the properties of PP in relation to the exposure time, indicating that the test did not influence these thermal properties (T_c and $X\%$) of this material. However, it is observed that both the T_c and the initial crystallinity of the additive samples were lower compared to PP, which may be attributed to the incorporation of the additive.

The crystallisation temperature of the blends with enzymatic additives decreases with increasing time of exposure to the medium. This is related to the reduction in polymer molar mass due to degradation, according to Chawla et al. [36]. Conversely, blends with organic additives present a constant T_c after exposure to freshwater. But regarding the crystallinity, there was a slight increase in this property after the degradation test, being the values of the sample PP-2Org more expressive. The crystallinity degree values are related to the polymer degradation, since the degradation begins in the amorphous phase and in the interfacial

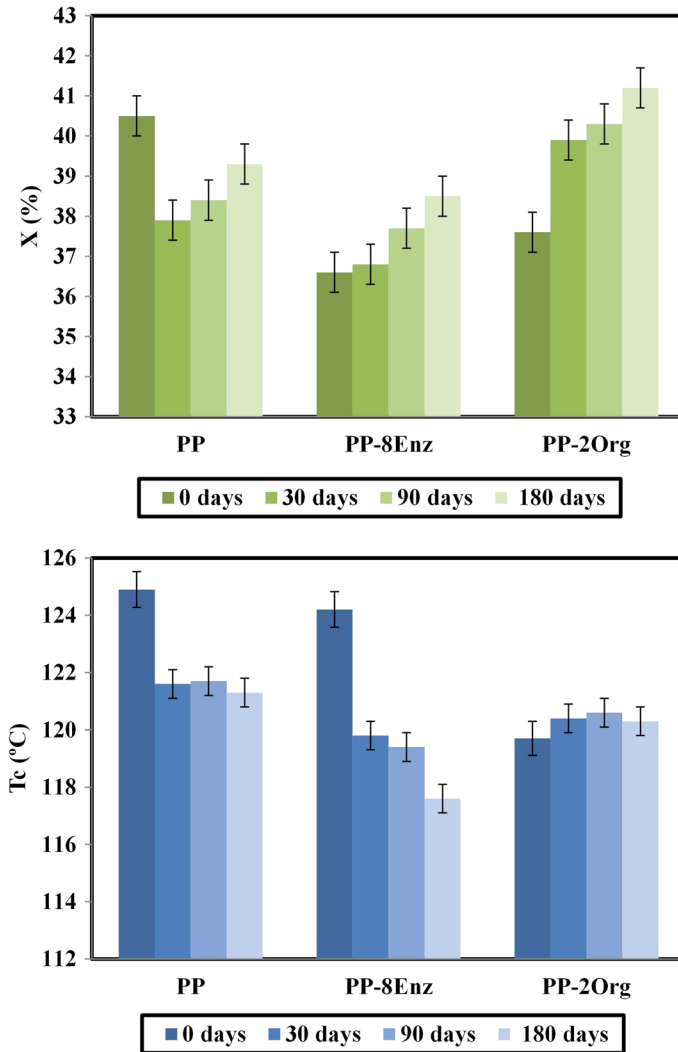


Fig. 6 Variation in crystallisation temperature (T_c) and crystallinity ($X\%$) of samples as a function of exposure time to the aqueous medium

regions in semicrystalline polymers, leading to an increase in the number of crystals. Thus, it can be shown that this behaviour is associated with high microbial activity in the amorphous phase and smaller crystals [37–39].

Figure 7 shows the TGA/DTG curves for the samples before and after the degradation experiment for PP (a), PP-8Enz (b) and PP-2Org (c), while Table 2 shows the thermal properties obtained for these samples (values of temperature with 10% mass loss [T_{10}], temperature with 50% mass loss [T_{50}] and maximum degradation temperature [T_{max}]).

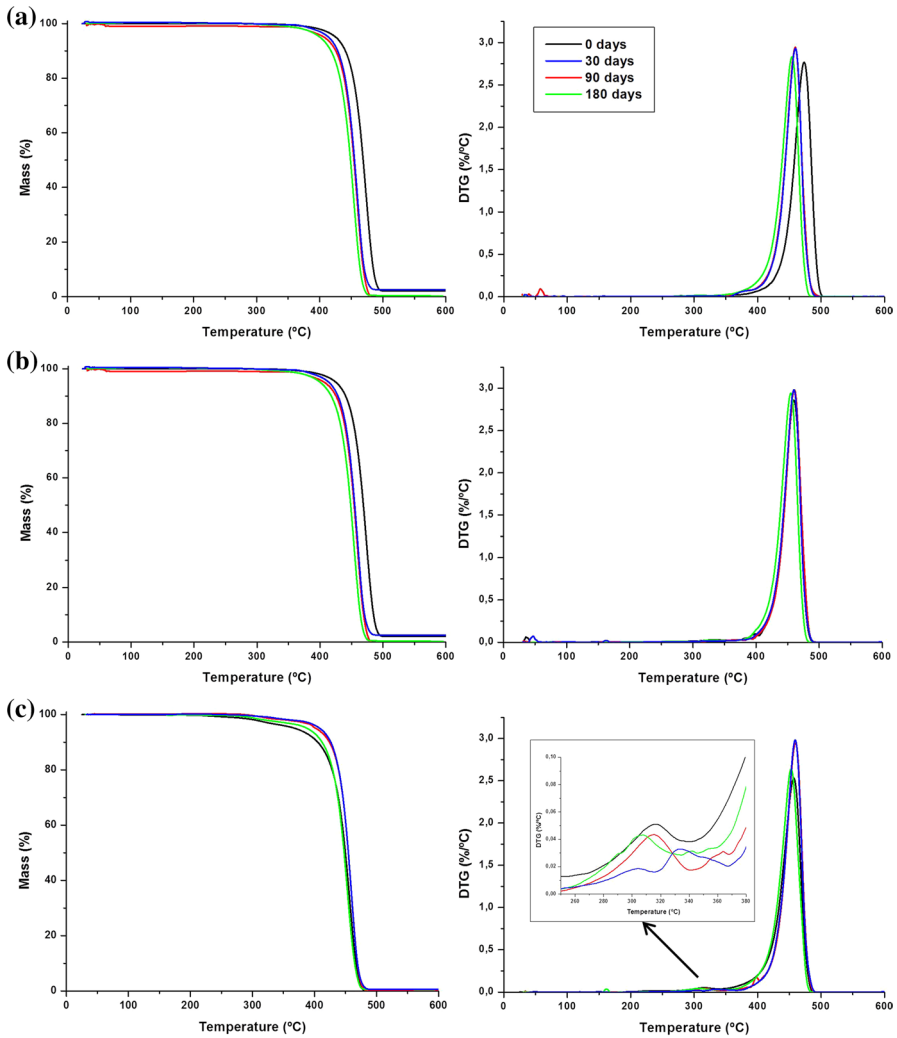


Fig. 7 TG/DTG curves for PP (a), PP-8Enz (b) and PP-2Org (c)

From the results obtained by the TGA analysis, it is possible to observe that the sample PP-2Org shows an increase of T_{10} and T_{50} up to 90 days of testing. This behaviour may be related to the incorporation of additive chains in the polymer, giving greater thermal stability to the material [40]. However, for the enzyme additive blend, these temperatures decrease after exposure to the medium. The presence of the additive in the polymeric chain leads to degradation, resulting in short chains that require less energy for degradation [24, 40, 41]. It is noteworthy that, for all samples, there is no significant weight loss up to 200 °C, indicating low water absorption in the samples [42]. Evaluating the initial degradation temperatures, it can be observed that both blends present lower thermal stability than pure PP, since

Table 2 Temperature with 10% mass loss (T_{10}), temperature with 50% mass loss (T_{50}) and maximum degradation temperature (T_{max}) before and after the freshwater degradation experiment

Sample	Time (days)	T_{10} (°C)	T_{50} (°C)	T_{max} (°C)
PP	0	439.3 ± 0.9	459.1 ± 0.3	472.6 ± 0.5
	30	428.4 ± 0.5	457.4 ± 0.2	459.5 ± 0.5
	90	425.8 ± 0.9	454.6 ± 0.8	459.5 ± 0.1
	180	418.3 ± 0.8	448.9 ± 0.6	454.6 ± 0.2
PP-8Enz	0	427.9 ± 0.5	455.5 ± 0.2	459.5 ± 0.2
	30	426.2 ± 0.6	452.1 ± 0.5	460.3 ± 0.4
	90	415.4 ± 0.8	452.8 ± 0.7	460.5 ± 0.4
	180	416.1 ± 0.5	450.1 ± 0.1	459.7 ± 0.3
PP-2Org	0	425.8 ± 0.9	448.9 ± 0.5	472.6 ± 0.5
	30	426.9 ± 0.4	450.3 ± 0.4	470.5 ± 0.7
	90	430.7 ± 0.1	451.1 ± 0.3	464.9 ± 0.5
	180	426.7 ± 0.8	448.3 ± 0.8	463.9 ± 0.4

PP presents a T_{10} of 439.3 °C, while the blends PP-8Enz and PP-2Org results are at 427.9 and 425.8 °C, respectively. When evaluating T_{max} , different behaviours are observed between the samples. PP and PP-2Org show a decrease in this parameter after the degradation test, while the PP-8Enz sample remains constant.

Regarding the DTG curves, it can be observed that the blend with enzymatic additive presents one degradation stage, while the blend with organic additive presents two stages after exposure to the medium. According to some authors, the first step corresponds to the initial degradation of the compounds derived from the pro-degradant, and the second step corresponds to the thermal degradation of the polymeric matrix (PP) [24, 41]. Although the PP-8Enz sample does not present the second stage, this fact may be related to the low percentage of additives present in the blends, as well as their composition: the organic additive has 50% organic compounds in its composition, while the enzymatic additive only has 5% enzymatic compounds.

PP also has only one degradation stage; this behaviour can be explained by the polymer tacticity, since it has CH_3 substituents with the same configuration along the polymeric chain in each repetitive unit (isotactic polymer). Thus, this polymer exhibits a single rupture center and therefore a single degradation stage [43].

Comparison between the degradation media

Comparing the results obtained in this work with the previous work [13], it can be highlighted that in both degradation media (freshwater and soil), the blends with enzymatic additive show more pronounced results after 180 days of testing. However, the use of the lowest percentage (2%) of PP with enzymatic additive shows the largest increase in CI after 30 days in soil (3693%), while blends of PP with the highest percentage of enzymatic additive (8%) show the largest CI increase in freshwater (1395%). Table 3 provides a comparison between the results obtained with

Table 3 Comparison between the results obtained for each degradation medium (freshwater and soil)

Analysis	Work	
	Freshwater (this work)	Soil [13]
CI (%)	1395	3693
Structural characteristics	–	Major changes
Morphology	–	Large amount of surface-attached microorganisms
X (%)	9.8	5.2

different degradation media for the samples with the enzymatic additive, as it presented the best results (as highlighted above).

In addition, it is noteworthy that the CI and crystallinity results obtained in the present study are better compared to another study in the literature. Montagna et al. [44] studied the degradation of PP films with pro-oxidant additives with and without transition metals. They observed an increase of about 85% of the CI, when compared to the value before the degradation process (0.01–0.02), whereas in this work we find an increase of 1345% in relation to the initial value (0.023–0.072). Regarding crystallinity, the authors found an increase of 4–5% after the degradation experiment, which was also lower than the present study, where we observe an increase of 9.8%. Thus, it is possible to verify that the soil is more effective for the degradation of the blends because, in relation to the aqueous medium, it presents more expressive results for the structural characteristics and morphology, and especially in relation to the CI (approximately three times higher). This is probably due to the contact with a larger number of microorganisms that are susceptible to PP degradation, highlighting the importance of research in different environments, particularly given the great pollution of aquatic environments.

Conclusions

This work presents evidence that the incorporation of additives improves the biodegradability of a polymeric matrix (PP), since they cause larger modifications in the evaluated properties in relation to the degradation of the pure PP. The presence of additives interferes with the structural characteristics (the appearance of oxygenated groups and double bonds that indicate the occurrence of a degradation process), the morphology (the presence of microorganisms adhered to the surface of the material) and the thermal properties (less resistant materials thermal degradation) of PP, favouring the process of material degradation. Although the organic additive blend shows good results for thermal analysis, the enzymatic additive blend has the most promising behaviour compared to the set of analyses performed, mainly due to the significant increase in CI and higher absorption band intensity, as well as the formation of biofilms with large amounts of microorganisms adhered to the surface of the material after the degradation test in natural aqueous medium. Thus, it is concluded

that the degradation of PP in freshwater is evidently favoured by the use of enzymatic additives, showing that blends will have less durability after use, which leads to environmental benefits, since it is an alternative to minimise the effects caused by plastic waste in the environment.

Regarding the comparison between the different degradation media, it can be concluded that soil is more aggressive to the degradation process of PP blends, probably due to the contact with a larger number of microorganisms that are susceptible to PP degradation. These results are proven with the highest CIs and morphological and structural characteristics.

Thus, it can be concluded that the materials studied in this work have potential for application in the field of plastic packaging, allowing for the reduction in effects caused by plastic waste in the environment.

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