COMPARATIVE STUDY OF THE EFFECT OF MARINE ENVIRONMENT SIMULATED ON FILMS OF PP MODIFIED WITH PRO-DEGRADANT ORGANIC AND COMMERCIAL

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Abstract – The consumption increasing of plastic materials over time has resulted in serious problems to the environmental. This study addresses the impact of plastic materials in marine environment, which is one of the most affected by the pollution caused by plastics bags and other artefacts usually made of polymers. Films of PP modified with pro-degradants, one free of transition metals and a commercial, were exposed under marine environment during three months aiming at a comparative study on their degradation properties. Physical and thermal properties were evaluated before and after have been submitted to marine environment, comparatively to neat PP film. The films of PP modified with organic pro-degradants showed higher weight loss during the experiment and a decreasing in the average viscometric molar mass, compared to the neat PP samples. Both modified PP films showed an increase in the PP crystallinity degree because of the molar mass decreasing of the polymer molecules.

Keywords: *Polypropylene, degradation, organic pro-degradant, marine environmental, simulated test*.

Introduction

The market of polymeric materials has been growing over time and consequently increases your disposal, causing several environmental problems for the planet. Due to the fact, the polymers are macromolecules of difficult to degrade, the discarding of improperly in the natural environment originate several problems, by being inert to attack from microorganisms carrying an average of 100 years for the degradation. This property of the polymers to be resistant to degradation, causes serious environmental impacts, because when disposed in urban centers result in environmental and visual pollution, damaging and contaminating renewable natural resources, as well as clogging of storm paths and streams, causing serious problems for society [1, 2].

In this way, with the worsening of the problem and the improper disposal of polymeric wastes, emergent ecological and governmental pressures have incentivized research and search for others biodegradable synthetic polymers for applications in products with a short shelf life. Therefore, to reduce these environmental impacts caused by the inadequate disposal of plastics, among these alternatives, there is the use of biodegradable polymers [3, 4, 5, 6].

The biodegradable polymers can be natural or synthetic. In this work, was used a polypropylene (PP), which is a synthetic polymer, and was introduced a pro-degradant additive, that serves to accelerate the degradation of the polymeric material when exposed to ideal conditions of degradation. Generally, the commercial pro-degradant present in the composition is a transition metal such as Co, Ni, Mn, Fe, among others, that in elevated amounts may cause contamination of the environment in which it is disposed [7, 8].

In the current study was investigated the influence of the marine environment in the degradation of PP films modified with two different types of pro-degradant, organic and commercial, using a simulated marine environmental test, in which the samples remained for a period of 90 days. After this time the samples were characterized by changes in physical (weight loss and viscosimetric average molar mass) and thermal properties (degree of crystallinity) and compared with samples of neat PP.

Experimental

Materials

Polypropylene homopolymer (PP) with a melt flow index of 38 g/10min (Grade: H125) and density of 0.905 g/cm^3 were kindly supplied by Braskem S.A. Benzoin (Sigma-Aldrich, purity > 98%), containing at least one 1,2-oxo-hydroxy group and free of transition metals, and potassium salt were used as received. Benzoin and potassium salt were the catalyst and co-catalyst, respectively, and comprised the organic pro-degradant additive. The commercial pro-degradant, d$_2$w®, was donated by RES Brazil.

Preparation of PP films with pro-degradant additives

The PP films with different amounts (1 and 3% w/w) of the organic and commercial pro-degradant additive were extruded in a Ciola single-screw extruder (L/D=22) at 180 ºC and 45 rpm. Modified PP was ground in liquid nitrogen and oven dried at 40ºC for 24 h for better homogenization of the samples. The ground PP particles were placed into the extruder with a temperature profile of 140, 150 and 160ºC equipped with rectangular die for planar film production. Samples of neat PP submitted to the same process were used as reference.

Degradation in simulated marine environment test

The methodology used for the polymer degradation in simulated marine environment test was adapted according to ASTM D1141-08 [9] and D7081-05 [10]. Three kinds of Stock Solutions were prepared and used for simulated marine water composition. Fig 1 shows the apparatus used in the simulated marine environment test, performed in a JarTest equipment (Model: JT-2013 Brand: Milan) under 60 rpm. Three PP film pieces of 5 x 5 cm were added into six flasks containing approximately 1 L of simulated marine water the experiment was carried out during 90 days at at room temperature. At the end, the samples were taken from the flasks and were dried at 40ºC (± 2) for 24 hours.

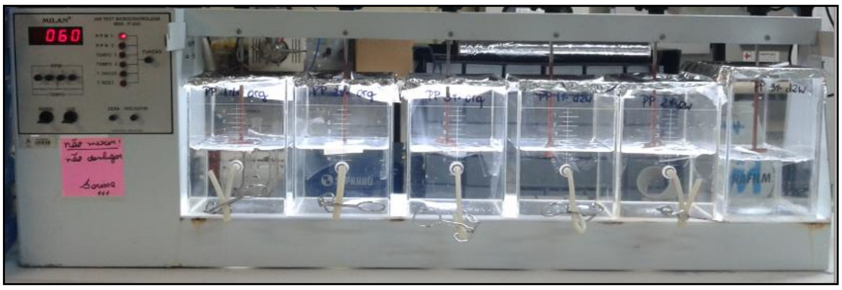

Figure 1. Biodegradation in simulated marine water test.

Weight loss

Prior to starting the experiment, the PP films were weighed in an analytical balance (Model: AY220, Marte Balances) to determine the initial weight of the samples. At the end of the experiment, the films were removed of the degradation test in marine simulated environment and placed in the oven at 40°C (± 2) for 24 hours and then weighed again to determine the final weight. The percent weight loss determined as a function of the degradation in simulated marine water test was calculated using the Eq. 1:

$$Wt.loss\,(\%) = \frac{W0 - W}{W0}\, X\, 100 \qquad (1)$$

where W_0 is the initial weight prior to the degradation test and W is the weight after exposed at de degradation in marine environmental during 90 days. This test was performed in triplicate.

Differential Scanning Calorimetry (DSC)

The degree of crystallinity (Xc) was determined according to the methodology described by Montagna. et al. [11]. DSC measurements were carried out using a DSC-Q20 calorimeter (TA Instruments). Approximately 5-6 mg of each sample was heating and cooling at a rate of 10 °C min^{-1} in nitrogen atmosphere with a gas flow of 50 ml min^{-1}. The samples were heated from 25 to 250 °C, cooled to 25 °C and re-heated to 250 °C. The thermal properties were evaluated in the first run. The crystalline content was obtained by Eq. 2 and the melting enthalpy of the 100% crystalline PP (ΔH°_{m}) used was of 209 Jg^{-1}:

$$Xc\ (\%) = \frac{\Delta H}{\Delta H°m}\ X\ 100 \qquad (2)$$

Molar mass

The determination of the molar mass was carried out according to the method described by Montagna et al. [7] and Bandrupt et al. [12]. Firstly, the specific viscosity (ηsp) was obtained and to estimate the intrinsic viscosity [η] the Huggins equation was used, Eq. 3, corresponding to the plot of the values for reduced specific viscosity vs concentration of the polymer solutions (ηsp/c) and Eq. 4 corresponding Mark-Houwink-Sakurada:

$$\frac{\eta\ sp}{c} = [\eta] + K.[\eta]^2.c \quad (3) \qquad [\eta] = k\ M^a \quad (4)$$

Results and Discussion

Figure 3 shows the percentage weight loss of the films of neat and modified PP with organic and commercial pro-degradant, before and after their exposure at simulated under marine environment simulated test. In analyzing the results, it is observed that there was weight loss for both PP films. But the samples of PP modified with organic pro-degradant presented higher percentages of weight loss when compared to neat PP films and the amounts were 97.85%, 98.26% and 98.35% for samples modified with 1, 2 and 3% of organic pro-degradant respectively. However, the samples of PP modified with 1, 2, and 3% of commercial pro-degradant showed weight loss 96.45%, 96.12% and 95.95%, respectively, when compared with the neat PP film.

The presence of pro-degradant in the films of PP may have influenced the hydrolytic degradation of both PP samples when exposed to marine water environment test. This may be associated with the two phases that occur in the hydrolytic degradation of semicrystalline polymer, which is the case of the polymer under study, the polypropylene. Firstly, the water penetrates in the sample, preferentially attacking the chemical bonds of the amorphous phase, converting long polymer chains into smaller chains, ie into smaller fragments.

Figure 4 shows that both PP films modified with pro-degradant, organic and commercial, showed high values of Xc before exposure simulated marine water test. This may be due to the presence of pro-degradants in PP films that influenced in the stage of initiation of degradation during processing in which the films were subjected to high temperatures and shear.

It was verified that the PP film without modification in the end of simulated marine environmental test had increased by approximately 1.66% on the values of Xc. This fact may be related to some contaminant or impurity present in the PP processing, which after exposure to simulated marine water test caused the scission of PP chains, increasing the percentage of crystallinity, possibly due to the more orderly packing of smaller polymeric segments that composing the polymer chain [20].

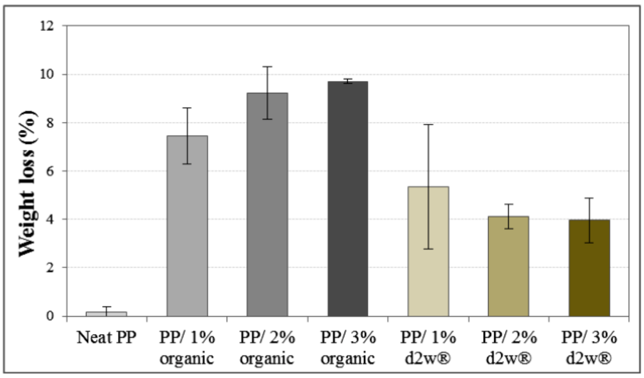

Figure 3. Weight loss (%) of neat and modified PP with organic and commercial pro-degradant before and after exposure at marine environment simulated test.

It was verified changes in the values of Xc of PP films modified after degradative process in marine environment simulated test. The results show that both modified PP films presented high values of Xc, except to PP samples with 3% of organic and commercial pro-degradant which showed a reduction. The increase in the values of Xc of modified PP films after exposure at simulated marine water test is related to the influence of both pro-degradant in a scission of molecular chains entrapped in the amorphous regions, which allowed free segments crystallize.

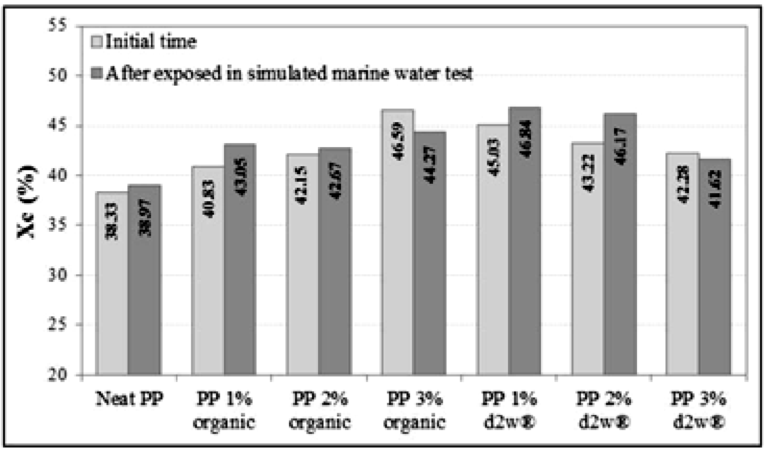

Figure 4. Degree of crystallinity (Xc) of neat and modified PP with organic and commercial pro-degradant samples, before and after exposure marine environment simulated test.

Figure 5 shows that both modified PP films showed a reduction in the values of viscosimetric molar mass, in compared to neat PP, after exposed at marine environment simulated test. After exposure at marine environment simulated test, the PP films modified with 1, 2 and 3% organic pro-degradant presented reduced in the viscosimetric molar mass of 29.62%, 43.02% and 29.33%, respectively, when compared with the values before the degradation process. Already the films modified with 1, 2 and 3% of the commercial pro-degradant were reduced by 11.00%, 2.40% and 2.22%, respectively, and these values decrease were lower when compared to the other samples modified with organic pro-degradant. By the results presented, it can be considered that the reduction in the Mv values for both modified PP films may be due to the presence of the pro-degradants in the samples, which when subjected to the condition of degradation under marine environment simulated test have influenced in degradation of the sample. This promoted the scission of the polymer chains, occurring considerable increase in the amount of crystallinity and consequently in reducing the viscosimetric molar mass. Thus, there have been more significant changes in PP films containing organic pro-degradant, which showed higher influence to degrade PP samples under conditions of biodegradation in marine environment simulated test.

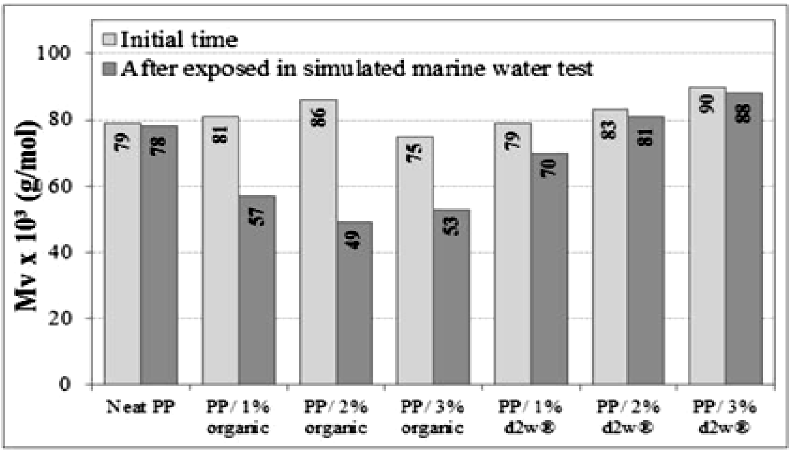

Figure 5. Average viscometric molar mass of the neat and modified PP samples with organic and commercial pro-degradant, at initial time and after been exposed at marine environment simulated test.

Conclusion

The results showed that the pro-degradant additives have changed the physical and thermal properties of the PP after exposure to degradative process under marine environment simulated test. Both modified PP samples showed an increasing in the values of the degree of crystallinity, and it was more evident in the films of PP modified with organic pro-degradant free of transition metals. The modified PP samples have showed higher weight loss and average viscometric molar mass decrease. It was found that the organic pro-degradant is efficient in the degradation of PP films in simulated environment of marine water compared to those films of PP modified with commercial pro-degradant.

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