

Biodegradation of PP films modified with organic pro-degradant: Natural ageing and biodegradation in soil in respirometric test

Larissa Stieven Montagna*, André Luis Catto, Maria Madalena de Camargo Forte, Ruth Marlene Campomanes Santana

Laboratory of Polymeric Materials, Lapol, Federal University of Rio Grande do Sul – UFRGS, Avenida Bento Gonçalves 9500, Porto Alegre, Brasil.

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ABSTRACT

In this study, PP films were modified with an organic pro-degradant in different concentrations (1, 2 and 3 wt.%), exposed in the first step of degradation to natural ageing for 100 days followed by biodegradation in simulated soil in the respirometric test for 100 days. At the end of the combined degradation process the PP samples were characterized according to their morphological and physical properties and the CO₂ generated during the biodegradation in soil was monitored. The CO₂ production by the PP films modified with the organic pro-degradant was proportional to the oxidation rate and weight loss of the samples. The reduction in the average viscosimetric molecular weight could be attributed to chain scission due to the weathering conditions to which the samples were exposed (natural ageing followed by biodegradation in soil). Scanning electron microscopy (SEM) of the PP films revealed surface deterioration of the films with the organic pro-degradant after the combined degradation process.

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Keywords: polypropylene; organic pro-degradant; natural ageing; biodegradation in soil; respirometric test

INTRODUCTION

In relation to the production and consumption of polymers there has been an increase in the scientific and industrial interest in environmentally-degradable polymers in the past decade [1]. The polymer wastes deposited in, for instance, dumps, landfills, rivers and the sea, have led to their accumulation in the environment. Thus, the use of biodegradable polymers is a potential approach to reducing the presence of this type of waste in the environment [2,3].

The obtainment of new completely biodegradable polymers requires new technologies, which may

make the final product more expensive, reducing the potential for industrial use. In this regard, one of the solutions reported in the literature is to produce partially biodegradable polymeric materials, that is, accelerated-degradation agents can be mixed with different polymers, causing them to behave in a similar manner to a biodegradable polymer [4,5]. These accelerated-degradation additives, known as pro-degradants, can be oxo-biodegradable, being composed of various complexes of transition metal salts, especially Fe³⁺, Co²⁺ and Mn²⁺, or organic compounds (free of transition metals), as in the case of this study [6].

* Corresponding Author - E-mail: larissambiental@yahoo.com.br

The organic pro-degradant (free of transition metals) used in this study is composed of a potassium salt with groups derived from *1,2-oxo*-hydroxy groups as the co-catalyst and benzoin as the catalyst. According to Gijsman and Jansen [7], benzoin is an efficient catalyst and it undergoes molecular cleavage through the action of radiation, as described by Lewis [8].

The biodegradability of polymeric materials is defined as a process in which all fragments of the material are consumed by micro-organisms as a source of food and energy. The period of time required for biodegradation is dependent on the disposal system, which can be landfill, aerobic composting, anaerobic digestion or the marine environment [6,9]. Essential considerations in relation to biodegradability are the material to be used as a source of food or energy for the micro-organisms and the period of time required for the complete biodegradation, since the material should be completely consumed in the environment [4,10].

The degradation reaction of polymeric materials can be classified as abiotic, occurring through thermal degradation, mechanical and chemical processes (photodegradation, thermo-oxidation, photo-oxidation) or biotic, that is, via biological degradation [11,12,13]. Abiotic degradation mechanisms can be investigated using several techniques, notably natural and accelerated weathering tests. In this study, the samples were submitted to natural ageing, being exposed to solar radiation, wind, ambient temperatures, rain and other natural factors, leading to the formation of free radicals, which can combine with oxygen at the surface and form peroxides and hydroperoxides via known oxidative degradation reactions [14,15,16].

Biotic degradation is a process related to the degradation of a material under the action of microorganisms, such as bacteria, fungi and algae. As a result of this degradation, water, carbon dioxide, methane, microbial cell components, salts and biomass are formed [17,18]. Biodegradation is a natural process that can occur especially in soils or water under aerobic (in the presence of oxygen) or anaerobic (without oxygen present) conditions [19]. In the study reported herein the biotic test used was the technique of biodegradation in soil, wherein during the experiment the CO₂ generated by the PP samples was quantified [3,11].

Besides the degradation processes mentioned above, the degradation of a polymeric material

can be associated with a combination of different factors, resulting from the processing conditions or environmental effects [20]. Certain characteristics may influence the degradation process, such as the chemical structure of the polymers and the packing of chains, which affects the rate of degradation [21]. The atmospheric oxygen and the incidence of UV radiation are factors associated with the weathering process to which the polymeric material is most sensitive [22]. During this process, the chemical reactions involved can be accelerated by solar heating or the presence of stresses which are externally applied or residual from the process [23].

This study aimed to assess the abiotic (natural ageing) and biotic (biodegradation in simulated soil using a respirometric test) degradability of PP films modified with 1, 2 and 3 wt% of organic pro-degradant. The physical and morphological properties and the CO₂ generation during the biodegradation in soil were also determined for a sample of neat PP.

EXPERIMENTAL

Materials and preparation of samples of PP films containing the organic pro-degradant

A commercial-grade polypropylene (PP) homopolymer (Grade: H125) manufactured by Braskem, with a melt flow index of 38 g/10 min and a density of 0.905 g/cm³, was used in this study and test samples were extruded-molded in film form. The PP films were extruded with different concentrations (1, 2 and 3 wt%) of organic pro-degradant additive, which consisted of benzoin (Sigma-Aldrich, purity > 98%), containing at least one *1,2-oxo*-hydroxy group and free of transition metals, and potassium salt, used as a catalyst and a co-catalyst, respectively.

The PP samples were extruded with the organic pro-degradant in a Ciola single-screw extruder (L/D=22) at 200 °C and 45 rpm, and then pelletized. The PP with additive in pellet form was ground in liquid nitrogen and oven dried at 40 °C for 24 h. This method was used to better homogenize the samples. The granulates obtained were pressed into the extruder with a film mold at temperatures of 140, 150 and 160 °C. Samples of neat PP were submitted to the same treatment and used as references.

Exposure to natural ageing

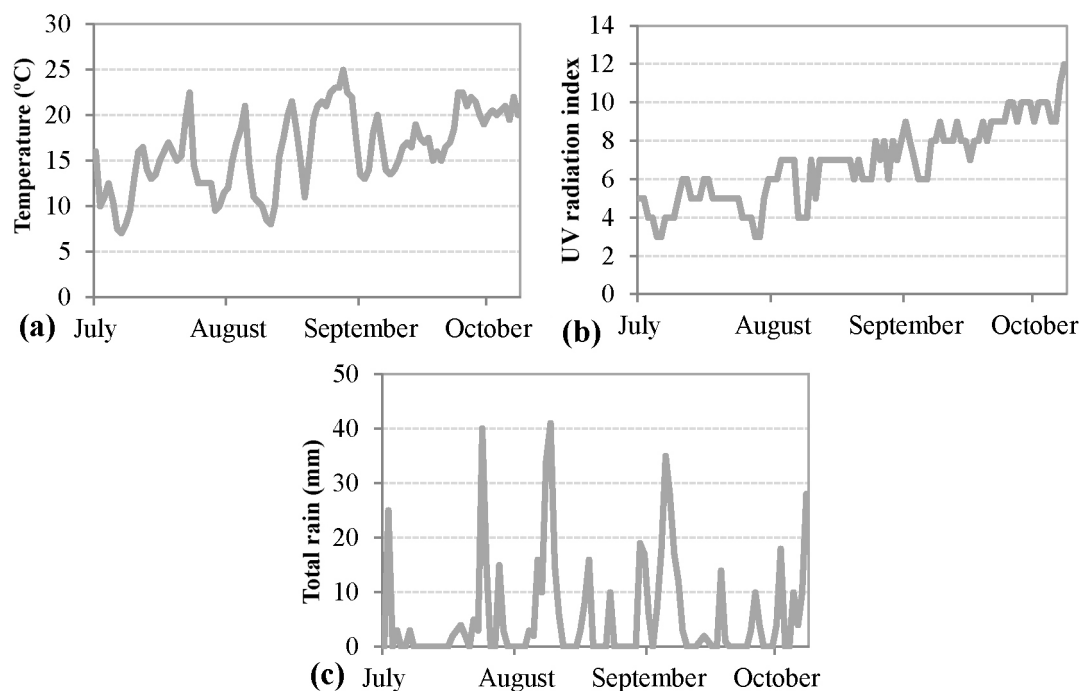


Figure 1. Weather conditions during the natural ageing for 100 days in the period of July to October of 2013: (a) temperature (°C), (b) UV radiation index and (c) total rain (mm).

This test was carried out according to the ASTM 1435-05 [24] and ASTM D5272 [25] standard methods. The PP samples were exposed to natural sunlight outdoors, facing north, at a 45° inclination, at the geographical location: latitude (30° 05' South); longitude (51° 11' West) and at an altitude of 174 meters, allowing normal incidence of solar radiation over the entire surface of the films, for 100 days during the winter and spring months (July to October of 2013) in Porto Alegre, in the south of Brazil.

During the natural ageing test the weather conditions in the city were monitored, including the average of UV radiation index, temperature and rainfall. Data were provided by the CPTED-INPE (Center for Weather and Climate Studies - National Institute for Space Research – Brazil) and are shown in Figure 1. The minimum and maximum temperatures recorded on a daily basis throughout the test period were approximately 7 °C and 25 °C, respectively.

Biodegradation tests using respirometric test in simulated soil

The methodology used for the polymer biodegradation tests was based on some parameters reported by Chiellini et al. [1] and Montagna et al. [26], using a Biometer flask adapted according to ASTM D 5338-98 [27] and D6003 [28]. In Figure 2, the system of biodegradation in the simulated soil used in this study

can be observed. The level of biodegradation was estimated through the mineralization of the polymer carbon atoms evolving CO₂, which was trapped in a NaOH solution [14].

The biodegradation test was carried out in sealed (air-tight) cylindrical glass Biometer flasks (500 mL capacity) with a multilayer substrate comprised of a mixture of 70 g of soil and approximately 0.100 – 0.200 g of the polymer to be biodegraded (neat PP, modified PP or cellulose). The mixture was sandwiched

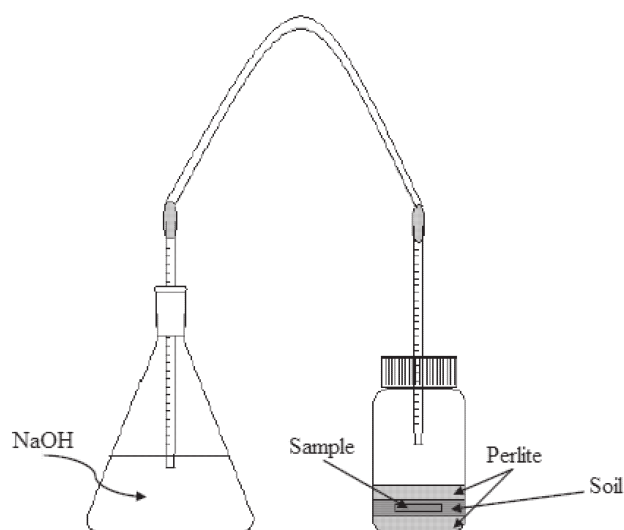


Figure 2. Schematic representation of respirometric biodegradation in simulated soil.

between two layers of 10 g of perlite wetted with 30 mL of distilled water. For the evaluation of the biodegradation capacity, through the quantification of the CO₂ produced during the biodegradation, the Biometer flask was connected via a glass tube with a silicone hose to an Erlenmeyer flask containing 300 mL of 0.35 M NaOH (Synth) solution, which was replaced every 4-7 days and titrated with 0.25 M of HCl (Vetec) solution.

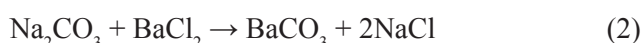
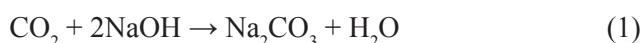
The respirometric apparatus was kept at 58 ± 2 °C and opened every 4-7 days for aeration and titration of the NaOH solution. Prior to the titration, 3 mL of 35 m/v (%) BaCl₂ (Synth) solution was added to the NaOH (30 mL) used for the titration. The amount of carbon dioxide produced during the incubation period was determined as a percentage of the theoretical quantity of CO₂ produced in the blanks (soil mixtures with no further carbon source) during the incubation time.

Analytical methods

The physical and morphological changes which took place during the sample biodegradation test were monitored through the determination of the CO₂ generation, weight loss, molecular weight and surface morphology by scanning electron microscopy (SEM).

Determination of cumulative CO₂ generation during the respirometric test

The cumulative amount of carbon dioxide produced during the metabolism of the living organisms present in the medium was calculated indirectly according to the method described in ISO 17556/2003 [29] and was based on some parameters reported by Montagna et al. [26]. In contact with a basic solution of sodium hydroxyl (NaOH), CO₂ reacts to form Na₂CO₃, which is precipitated with an aqueous solution of BaCl₂ forming a white powder, corresponding to BaCO₃, according to reactions 1 and 2.



Thus, the amount of NaOH that does not react with the product gas (CO₂) is reacted with the same amount of HCl in the titration of the acid solution, according to Equation 3 [29].

$$m = \left(\frac{(2CS \times VSO)}{CA} - \frac{(VA \times VST)}{VSZ} \right) \times CS \times 22 \quad (3)$$

where, m is the mass of CO₂ released in the biodegradation test (mg), CA is the exact concentration of the HCl solution (mol L⁻¹) → 0.25 M, CS is the exact concentration of the NaOH solution (mol L⁻¹) → 0.35 M, VSO is the volume of NaOH solution at the beginning of the test (300 mL), VST is the volume of NaOH solution before the titration (300 mL), VSZ is the volume of the aliquot of NaOH solution used in the titration (30 mL), VA is the volume of HCl solution used for the titration (mL) and 22 is half the molecular weight of CO₂.

Weight loss

The percent weight loss was determined in duplicate, as a function of the incubation period (number of days), and was calculated using Eq. 4:

$$\% \text{Wt. loss} = \frac{W_0 - W}{W_0} \times 100 \quad (4)$$

where, W_0 is the initial weight prior to the biodegradation test in soil and W is the weight after 100 days.

Molecular Weight

It is possible to ascertain the degradation of the polymer occurred through cleavage of the molecular chain using the determination of the molecular weight before and after the degradation processes. The methodology used to determine the molecular weight of the PP films was viscosimetry, based on the parameters reported by Montagna et al. [30]. The viscosimetric average molecular weight (M_v) was determined from the intrinsic viscosity $[\eta]$ of the samples, using the Mark-Houwink-Sakurada relationship $[\eta] = kM^\alpha$. The PP films were dissolved in decaline (Vetec) at 135 °C, under stirring, and then analyzed at four different concentrations (0.2, 0.4, 0.6 and 0.8 g/dL). Viscosity measurements were carried out using an Ubbelohde-type capillary viscometer at a temperature of 135 °C (±0.01 °C), which was controlled by a circulating silicone bath (SOLAB, model 159 SL), maintaining the viscometer immersed in the bath, and for each concentration measurements were performed at three flow rates [31].

Firstly, the specific viscosity (η_{sp}) was obtained and to estimate the intrinsic viscosity $[\eta]$ the Huggins

equation (Eq. 5) was used, corresponding to the plot of the values for reduced specific viscosity vs concentration of the polymer solutions (η_{sp}/c):

$$\frac{\eta_{sp}}{c} = [\eta] + k[\eta]^2 c \quad (5)$$

where, η_{sp} is the specific viscosity, η_{sp}/c is the reduced specific viscosity, $[\eta]$ is the intrinsic viscosity, k is the Huggins coefficient and c is the concentration of polymeric solution (g/dL).

The intrinsic viscosity was determined from the plot of (η_{sp}/c) vs (c), by extrapolation of the line obtained for the linear regression when $c = 0$, according to the Huggins equation. The M_v value for the samples was determined using the Mark-Houwink-Sakurada equation, which relates the average intrinsic viscosity to the viscosimetric molecular weight of the polymer, as shown in Eq. (6):

$$[\eta] = kM^\alpha \quad (6)$$

where, k and α are the constants for the polymer-solvent system, which are dependent on the polymer, solvent and temperature, as described in the literature [31], where $k = 11 \times 10^{-5} \text{ dL} \cdot \text{g}^{-1}$ and $\alpha = 0.80$ for polypropylene in a solvent system consisting of decaline at a temperature of 135 °C.

Scanning Electron Microscopy (SEM)

The changes in the surface morphology of the polymers after natural ageing for 100 days followed by biodegradation in soil for 100 days were examined with a JEOL JSM-6060 scanning electron microscope operating at 10 kV. The samples were sputter-coated with gold prior to the analysis.

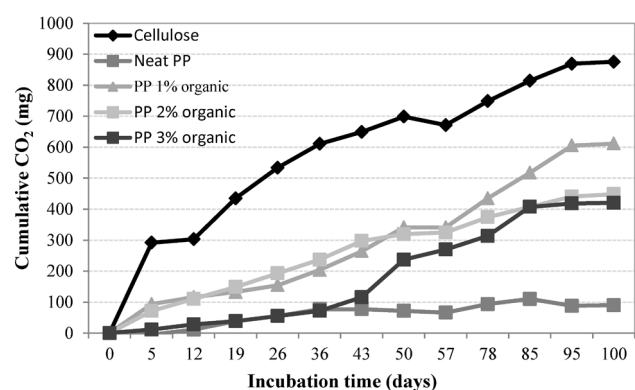


Figure 3. Cumulative CO₂ emissions for cellulose, neat PP and modified PP with 1, 2 and 3% of organic pro-degradant during incubation in the biodegradation test in simulated soil.

RESULTS AND DISCUSSION

Figure 3 shows the results for the generation of carbon dioxide in the biodegradation test with simulated soil conducted over 100 days. The biodegradation test was found to be an appropriate procedure, providing the microorganisms with a suitable environment for their nutrition and development in a short time. This was confirmed by the much higher amount of CO₂ released as a metabolized product of cellulose used as a positive standard, which verified the reliability of the test. The films of the neat PP and the PP modified with organic pro-degradant differed in terms of the CO₂ generation as a function of the incubation time. This finding may be related to the fraction of the polymer chain of the modified films metabolized by the microorganisms present in the medium. On comparing the PP films modified with organic pro-degradant, the influence of different concentrations of the pro-degradant can be observed, although the modified films all showed a continuous increase in CO₂ generation. However, a faster rate of degradation was observed for the films containing 1% of organic pro-degradant, which may be the optimal concentration and this increase could be due to the generation of a reaction product. The values for the CO₂ generation for the modified PP films can be considered satisfactory when compared with the results for the neat PP and also for cellulose, which has a high CO₂ production curve. Thus, the use of organic pro-degradant was effective for accelerating the degradation of PP films after being submitted to degradation by natural ageing.

Figure 4 shows the percentage of total weight loss for the PP films after being submitted to natural weathering for 100 days followed by biodegradation

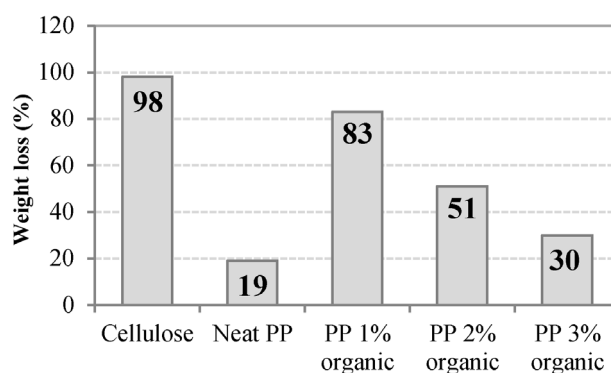


Figure 4. Weight loss (%) for cellulose, neat PP and PP modified with 1, 2 and 3% of organic pro-degradant after 100 days of biodegradation in simulated soil.

in soil for 100 days. From the results obtained it can be observed that there was weight loss for both types of PP film. The cellulose sample showed high weight loss (approximately 98%), this being a biodegradable material, and the conditions of the respirometric test facilitated the complete degradation, verifying the efficiency of this system in the respirometric biodegradation test in soil.

The film of neat PP after biodegradation in soil showed weight loss of 19%, while the PP films with modified 1, 2, and 3% of organic pro-degradant showed weight losses of 83%, 51% and 30%, respectively. It can be observed that the weight loss results are consistent with the values for the generation of CO₂ shown in Figure 3. The PP film modified with 1% organic pro-degradant showed the highest CO₂ generation and consequently the greatest weight loss and the sample containing 3% organic pro-degrading showed the lowest CO₂ generation and consequently the smallest weight loss, when compared with the other samples.

Therefore, the results show that the lowest concentration (1%) of organic pro-degradant in the PP films was sufficient to initiate the PP degradation, and increasing the concentration of the organic pro-degradant in PP films led to a reduction in these parameters.

Table 1 shows the values for the intrinsic viscosity of the modified PP samples at the initial time and after exposure to the combined degradation process, where it can be observed that the viscosity is lower compared to that of the pure PP. In the environmental process (first stage of degradation) the samples showed a faster decrease compared with the second stage, the most pronounced reduction being observed for the samples modified with the organic pro-degradant, indicating the efficiency of this additive in accelerating the sample embrittlement process. The intrinsic viscosity values

show a tendency toward a reduction in the average viscosimetric molecular weight of the PP films after degradation, confirming a reduction in the size of the molecular chains due to scission. In other words, the environmental degradation process influenced the decrease in the intrinsic viscosity, which is directly proportional to the molecular weight. During the first stage the degradation occurred predominantly by oxidation (thermal and photochemical) and in the second stage by hydrolysis, because the samples already had a higher functionalization due to the presence of carbonyl and hydroxyl groups favoring hydrolysis.

Montagna et al. [30] investigated the influence of abiotic (natural ageing) and biotic (simulated soil) degradation processes separately, using samples of PP modified with pro-degradant additive in plate form and it was observed that the samples exposed to natural ageing showed a decrease in the intrinsic viscosity and consequently lower average viscosimetric molecular weight. The authors explained that the factors involved in natural ageing, such as solar radiation, acid rain, wind and other factors, influenced the decrease in these values compared with those for the same samples exposed to simulated soil for the same period.

Therefore, in this study, it was observed that the combination of the two degradation processes and the presence of organic pro-degradant led to an even greater reduction in the intrinsic viscosity values, consequently reducing the average viscosimetric molecular weight of the PP films.

Similarly, the average M_v values for the neat PP and PP modified with 1, 2 and 3% of organic pro-degradant before and after the combined degradation process are shown in Figure 5. It can be observed that both types of film showed a reduction in the average M_v values after the combined degradation process. This is due to the processing conditions, because the polymeric

Table 1. Intrinsic viscosity of neat PP and PP modified with 1, 2 and 3% of organic pro-degradant before and after natural ageing followed by biodegradation in soil.

Samples	Initial time	First degradative process: Natural ageing (100 days)	After degradation combined processes
	[η] dL g ⁻¹	[η] dL g ⁻¹	[η] dL g ⁻¹
Neat PP	0.9180	0.8926	0.8406
PP 1% organic	0.9363	0.5426	0.4476
PP 2% organic	0.9814	0.4922	0.4540
PP 3% organic	0.8758	0.5373	0.5008

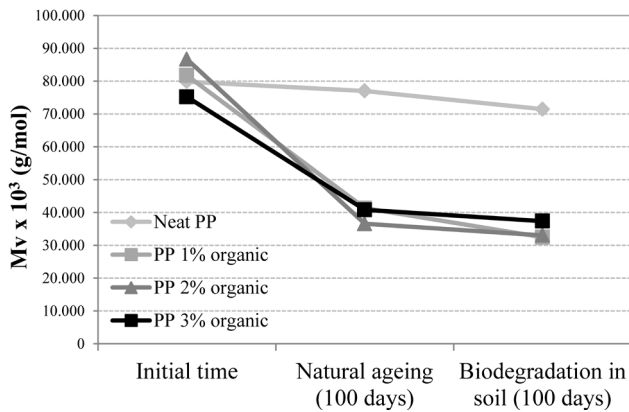


Figure 5. Average viscosimetric molecular weight of neat PP and PP films modified with 1, 2 and 3% of organic pro-degradant at the initial time, after natural ageing and after the combined degradation process.

materials are exposed to heat and shear which initiate the degradation reactions [32,33]. Thus, this finding can be related to thermomechanical degradation of the samples during the initial processing of the films, in which fission of the chains may have occurred due to the stress imposed on the chain elements and the temperature. The organic pro-degradant in the PP films may also have influenced the thermodegradation, decreasing the viscosimetric molecular weight [34].

After being submitted to the combined degradation process, the neat PP samples presented a 10% reduction in the average M_v value in relation to the same sample at the initial time, which could have been influenced by the initial degradation of the pure PP specimen during processing.

The PP films modified with 1, 2, and 3% of organic pro-degradant showed a considerable reduction in the average M_v value after the combined degradation process. The PP modified with 1% of organic pro-degradant showed a reduction from 81.763 g/mol to 41.338 g/mol, (60.25%) and the PP film modified with 2% of organic pro-degradant decreased from 86.715 g/mol to 36.596 g/mol (61.84%), that is, close to the value obtained for the sample containing the lowest percentage of organic pro-degradant. The PP film containing the highest concentration of the organic pro-degradant (3%) had the smallest reduction in the viscosimetric molecular weight (75.208 g/mol to 40.834 g/mol or 50.27%).

It was observed that after the first step of degradation (natural ageing) the PP film showed a greater reduction in the average M_v value when compared to the results for the same samples after the combined degradation

processes (natural ageing followed by biodegradation in soil), and the greatest reductions were observed for the PP films modified with organic pro-degradant. This indicates the efficiency of the natural conditions, especially the influence of UV radiation, on the modification of the physical structure of the polymer.

The M_v results obtained demonstrate that after the degradation processes (natural ageing followed by biodegradation in soil) there was a significant reduction in the molecular weight, which can be attributed to chain scission due to the exposure to weather conditions (UV, wind, rain and other factors) and the presence of the organic pro-degradant additive.

According Fechine et al. [35], the presence of a pro-degradant agent in the polymeric materials induces oxidation, leading to decreased molecular weight. Thus, the first stage of degradation (natural aging) is responsible for the molecular weight reduction and oxidation of polymers while during the second stage of degradation (biodegradation in soil) the biodegradation of the polymeric material occur, wherein the chain carbons act as nutrients for the microorganisms.

Figure 6 shows the micrographs of the PP films at the initial time and after 100 days of natural ageing followed by biodegradation in soil for 100 days, with a magnification of 1000x. On analyzing the micrographs the modification of both surfaces of the PP films after the combined degradation process can be observed.

After the combined degradation process the neat PP film had grooves, a slight roughness and cracks on the surface of the sample, which were not present at the initial time.

On the micrographs of the surface of the PP films modified with 1, 2, and 3% of organic pro-degradant it was observed that there was a significant modification of the surface compared with the same samples at the initial time. The samples after the combined degradation process showed an eroded region and several fragments were present on the surface of the sample due to the effect of oxidation. The PP films submitted to the combined degradation process showed the deterioration of the sample surface with relief and ripples along the entire length and the samples modified with the pro-degradant showed greater degrees of change and surface wear than the neat PP sample.

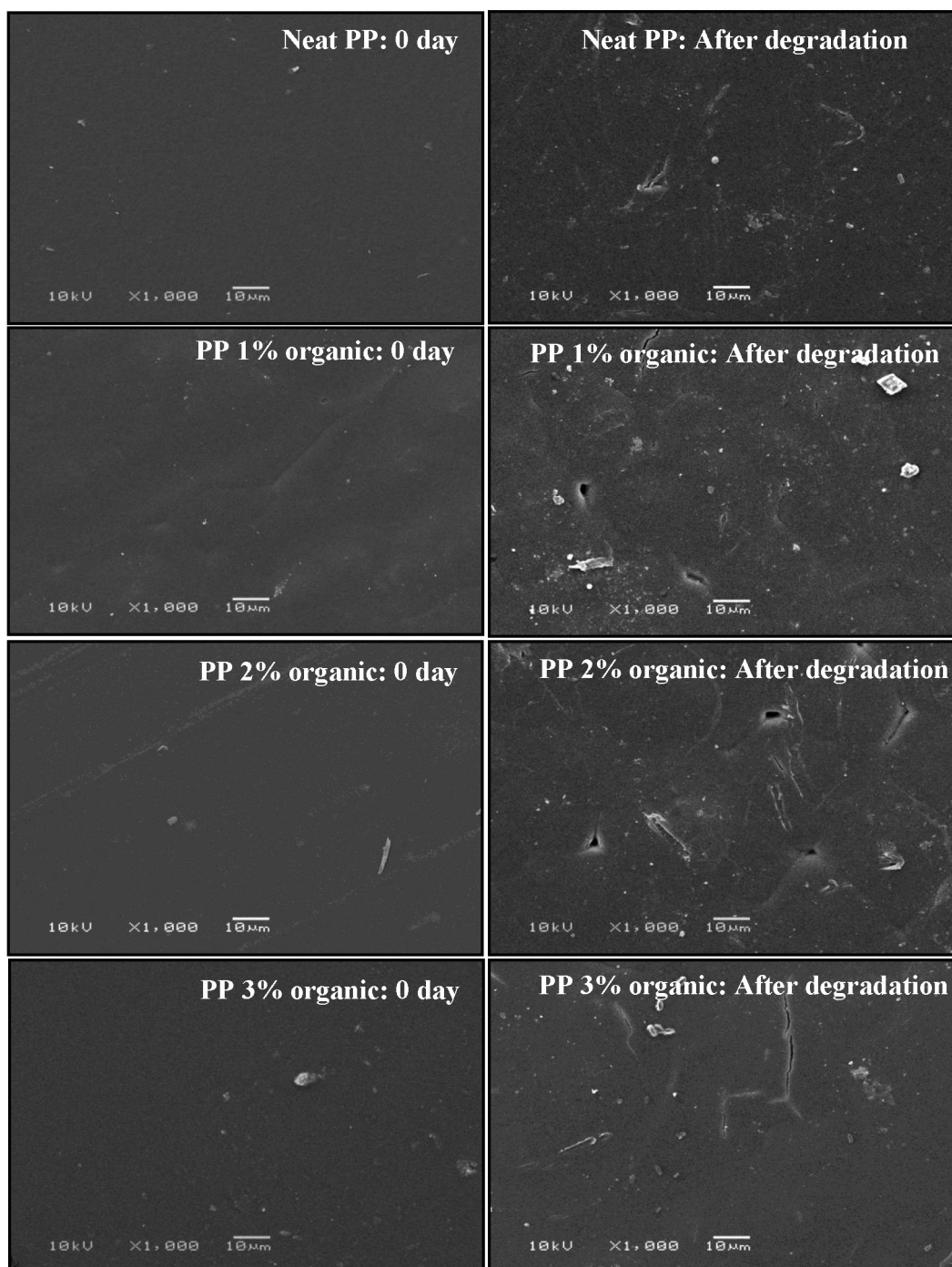


Figure 6. Scanning electron micrographs for neat PP and PP modified with 1, 2 and 3% of organic pro-degradant before and after the combined degradation process.

CONCLUSION

The neat PP samples and those modified with organic pro-degradant investigated in this study were degraded initially by natural ageing and then by biodegradation in soil using a respirometric test. At the end of the degradation processes the samples were characterized according to their physical and morphological properties and the CO₂ accumulated

during the period of biodegradation in soil was measured. The biodegradation results showed that the PP samples modified with organic pro-degradant presented higher levels of CO₂ production, and consequently these samples showed greater weight loss when compared with the neat PP. The values for the average viscosimetric molecular weight were lower for both types of PP sample after the application of the combined degradation processes. However, the

PP samples modified with the organic pro-degradant showed a greater reduction in this value, this being most evident in the first stage of degradation (natural ageing) and for the sample containing the lowest concentration of organic pro-degradant.

The morphology of the PP samples showed changes over the entire surface area analyzed, these being most evident for the samples modified with different concentrations of organic pro-degradant which, after the combined degradation process, showed surface deterioration and the presence of fragments.

The results confirmed that based on the observed changes in the physical and morphological properties investigated, the lowest concentration of organic pro-degradant was effective in relation to the biodegradation of PP samples.

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