

Study on the Accelerated Biodegradation of PP Modified with an Organic Pro-Degradant Additive

Larissa Stieven Montagna, 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

Correspondence to: R. M. C. Santana (E-mail: ruth.santana@ufrgs.br)

ABSTRACT: In order to reduce the environmental impact of the accumulation of synthetic polymer waste, especially in the case of products with a short shelf life, such as disposable diapers and sanitary napkins, this study evaluated the biodegradation of samples of polypropylene (PP) modified with an organic additive free of transition metals. The samples were prepared using a single-screw extruder, then ground with liquid nitrogen and processed by thermal compression molding into the form of plates. They were then submitted to a respirometric test involving biodegradation carried out at 58°C for 120 days. The samples were characterized according to their physical, thermal, and morphological properties. The results verified that the modified PP showed evidence of enhanced degradation through increased CO₂ generation and weight loss during incubation. The thermal analysis revealed an increase in the degree of crystallinity and a decrease in the melt temperature. SEM micrographs showed exfoliation, the appearance of holes, and surface deterioration. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41054.

KEYWORDS: biodegradable; degradation; polyolefins

Received 5 December 2013; accepted 27 May 2014

DOI: 10.1002/app.41054

INTRODUCTION

The volume of polymeric waste produced by modern society has grown exponentially over decades, leading to serious environmental problems. The availability of landfill space has decreased rapidly and the cost of the landfilling of plastic wastes has increased enormously.^{1,2} To alleviate these problems, the recycling of plastic is becoming a priority in most waste management programs, but for many products recycling is not viable and thus the development of biodegradable polymers for products with a short shelf life is a newly emerging field.^{3,4}

Biodegradation can have various definitions depending on the field of application of the polymer (e.g., the biomedical area or natural environmental).⁵ The biodegradation of this type of material (polymeric waste) occurs on exposure to environmental factors. This process is defined as the deterioration of the physical and chemical properties along with a decrease in the molecular mass accompanied by the formation of CO₂, H₂O, CH₄, and other low molecular-weight products. It is influenced by the action of microorganisms, under both aerobic and anaerobic conditions, and is aided by abiotic chemical reactions like photodegradation, oxidation, and hydrolysis.^{6,7}

Biodegradable polyolefins can be obtained using pro-degradant additives, which can be transition metal ions, notably stearate (St), copper (CuSt), silver (AgSt), cobalt (CoSt), and manganese (MnSt),

or alkaline earth metals such as magnesium (MgSt) and calcium (CaSt). The presence of these pro-degradant agents accelerates the degradation of polyolefins.^{8,9} The aim of this study was to use an organic pro-degradant additive, free of transition metals, to accelerate the degradation of polypropylene (PP). According to Jansen and Gijsman,¹⁰ benzoin is an efficient catalyst and it undergoes molecule cleavage through the action of radiation, as described by Lewis.¹¹ However, it requires, as a co-catalyst, a potassium salt, with groups derived from 1,2-oxo-hydroxy, forming an organic pro-degradant agent which is appropriate for polyolefin degradation.

In the context of the growing consumption of polyolefins worldwide and the pollution caused by their accumulation in the environmental, the purpose of this study was to evaluate and compare the degradation of samples (without prior degradation) of neat PP and PP modified with an organic pro-degradant additive, free of transition metals, submitted to 58°C for 120 days in a respirometric test. The changes in the physical, thermal, and morphological properties of the samples were monitored via the cumulative CO₂ generation, weight loss, degree of crystallinity, melt temperature, and surface morphology.

EXPERIMENTAL

Materials

Commercial PP homopolymer with a melt flow index of 38 g/10 min (Grade: H125) and a density of 0.905 g/cm³ were kindly

donated by Braskem. 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 a catalyst and a co-catalyst, respectively, and together comprised the pro-degradant additive.

Preparation of Samples of Polypropylene Containing the Additive

PP samples were extruded with the pro-degradant additive (10 g/0.1 g) 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 sample. Samples of the PP containing the pro-degradant in plate form (5 cm diameter and 2 mm thickness) were obtained using a molding press at 220°C with a 2-ton loading for 5 min. Samples of neat PP were submitted to the same treatment and used as a reference.

Biodegradation Tests Using Respirometric Test

The methodology used for the polymer biodegradation tests was based on some parameters reported by Chiellini et al.,¹² using a biometer flask adapted according to ASTM D 5338-98¹³ and D6003.¹⁴ The level of biodegradation was estimated through the mineralization of the polymer carbon atoms evolving CO₂, which was trapped in a NaOH solution.¹⁵

The biodegradation tests were carried out in sealed (air-tight) cylindrical glass biometer flask (500 mL capacity) with a multi-layer substrate comprised of a mixture of 70 g of soil and ~0.200–0.800 g of the polymer to be biodegraded (neat PP, modified PP, or cellulose). The mixture was sandwiched between two layers of 10 g 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 was connected via a glass tube with a silicone hose to an Erlenmeyer flask containing 300 mL of 0.35 mol dm⁻³ NaOH (Synth) solution, which was replaced every 4–7 days and titrated with a 0.25 mol dm⁻³ HCl (Vetec) solution.

The respirometry apparatus was kept at 58 ± 2°C and opened every 3 days for aeration and titration of the NaOH solution. Prior to the titration, 3 mL of 35 mass/vol (%) 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 without any further carbon source) during the incubation time.

Analytical Methods

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

Determination of Cumulative CO₂ Generation During the Respirometric Test. The cumulative amount of CO₂ produced during the metabolism of living organisms present in the medium was calculated according to the method described in ISO 17556/2003.¹⁶ When in contact with a basic solution

(NaOH), CO₂ reacts to form Na₂CO₃, which is precipitated with an aqueous solution of BaCl₂ forming BaCO₃, according to reactions 1 and 2.



Thus, the amount of NaOH that did not react with the product gas is reacted with the same amount of HCl in the titration of the acid solution, according to eq. (3).⁹

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

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) → 0.35M, CS is the exact concentration of the NaOH solution (mol L⁻¹) → 0.25M, 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 molarity of CO₂.

Differential Scanning Calorimetry. The polymer crystallinity was determined using a differential scanning calorimetry (DSC)-Q20 calorimeter (TA Instruments). Approximately 5–6 mg of each sample was subjected to 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, then cooled to 25°C and again heated to 250°C. The results for the thermal properties were obtained from the first heating run, and the crystallinity was calculated using eq. (4), where ΔH is the melting enthalpy and ΔH_{100} is the enthalpy of 100% crystalline PP, previously reported to be 209 J g⁻¹.¹⁷

$$X_c = \frac{\Delta H}{\Delta H_{100}} \times 100 \quad (4)$$

Weight Loss. A simple and quick way to measure the biodegradation of polymers is by determining the weight loss, which is proportional to the degradation, since a loss of polymer integrity leads to weight loss, which is proportional to the surface area since biodegradation usually begins at the surface of the polymer.² The percent weight loss determined as a function of the incubation period (number of days) was calculated using the equation:

$$\% \text{ Wt. loss} = \frac{W_0 - W}{W_0} \times 100 \quad (5)$$

where W_0 is the initial weight prior to the biodegradation test and W is the weight after 120 days.

Scanning Electron Microscopy. The morphology of the PP samples before and after being submitted to the respirometry test for 120 days was examined with a JEOL, JSM-6060 scanning electron microscope operating at 10 kV. The samples were sputter-coated with gold prior to the analysis.

RESULTS AND DISCUSSION

Figure 1 shows the cumulative CO₂ emissions detected in the test flasks after 120 days. The biodegradation test gave satisfactory

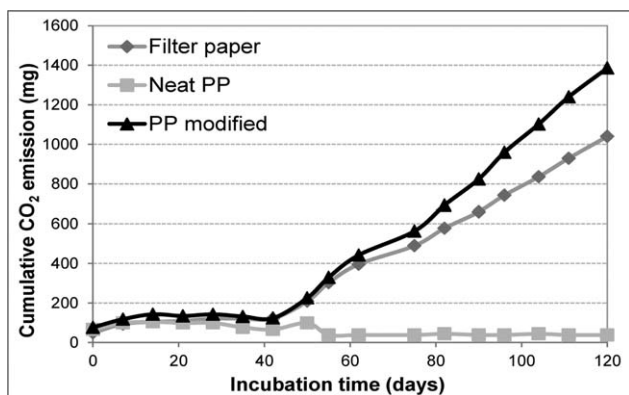


Figure 1. Cumulative CO₂ emissions observed using filter paper, neat PP and modified PP after 120 days in the accelerated biodegradation test.

results, that is, the microorganisms were in an environment conducive to their development and nutrition and, after a short time, this was confirmed by the much higher amount of CO₂ released as a metabolized product from the filter paper (positive control) compared with the test materials, indicating that the assay is reliable.¹⁸

The CO₂ generation observed for the different samples of neat PP and modified PP varied as a function of the incubation time. This may be related to the fraction of the polymer chain of the modified sample metabolized by microorganisms present in the medium. It was possible to observe the high production of CO₂ starting from the twentieth day of treatment with the standard biodegradable carbon source, indicating good conditions for the inoculum.

It can be noted that the curve for the degradation of the modified PP sample shows no tendency to stabilize. This implies that the biotic degradation of this material will continue for longer periods of incubation. However, 100% conversion of carbon to CO₂ is not expected because a fraction of the polymer chain carbon is transformed into the microorganism biomass, organic substances, and other gases.^{5,19}

For the neat PP sample, it was observed that the values for the CO₂ released remained similar over the incubation period of 120 days. On comparing the PP samples with and without modification, the influence of the organic additive present in the samples is evidenced through the continuous increase in the CO₂ production, suggesting a higher degradation rate for the samples containing the organic pro-degradant additive. The CO₂ values obtained for the modified sample can be considered

Table I. Weight Loss Observed for the Cellulose and PP Samples After 120 Days in the Biodegradation Test

Samples	W ₀ (g) ^a	W (g) ^b	Weight loss (%)
Filter paper	0.2026	0	100.00
Neat PP	0.4628	0.4624	0.09
Modified PP	0.3296	0.2966	10.00

^a Initial weight in the beginning.

^b Final weight after the biodegradation test.

to be good in comparison with the results for the neat PP and the cellulose, which showed higher CO₂ production, considering that the samples did not undergo previous oxidation. Thus, the use of organic pro-degradant additive is efficient in reducing the time required for the degradation of the PP samples during the respirometric test.

Weight loss is one of the main parameters used to determine the degradation of polymers.²⁰ The percentage of weight loss for the filter paper, neat PP, and modified PP samples after 120 days at 58°C in the respirometric test is shown in Table I.

On analyzing the results, the filter paper sample presented total mass loss (100%), because this is a biodegradable material and the conditions present in the respirometric test facilitated the complete degradation of this material, confirming the biodegradation efficiency of the test.

It was observed that there was weight loss for both PP samples, but after exposure to the biodegradation test for 120 days the modified PP samples showed greater weight loss (10.0%) when compared to the neat PP samples (0.09%). Also, after 120 days of incubation the samples with the pro-degradant additive (modified PP) had a weak and milky appearance.

In relation to these results, it should be noted that the weight loss could have been higher since, due to the humid conditions in the respirometer, the diffusion of water into the polymer may have occurred. This absorption of water by the samples is the initial step in the degradation process, and thus the true weight loss of the samples would have been higher.²¹ The period of 120 days used in this experiment is another factor that may have affected the weight loss of the samples, since a much longer time is required for microorganisms to adapt to a new substrate, or previous degradation of the polymer molecules may have left them less susceptible to microbial attack.

Figure 2(a,b) shows the degree of crystallinity and melt temperature of the neat PP and modified PP before and after being submitted to the biodegradation test for 120 days. On analyzing the results for the samples not exposed to degradation (neat PP and modified PP), slightly lower crystallinity values were observed for the modified samples compared with the unmodified samples. This may be due to the presence of the organic pro-degradant additive in the modified samples, which could increase the free volume, reducing the crystallinity.²²

The neat PP sample after the biodegradation process showed no significant changes in terms of X_c . However, the modified PP sample showed a significant increase in X_c (~18%) after being submitted to the biodegradation test in relation to the sample at the start of the test. This increase is due to polymer degradation occurring firstly in the amorphous phase (more sensitive), probably due to the presence of oxygen in the composition of the organic pro-degradant additive, and subsequently in the crystalline phase, a stage which was not reached in the study period. According to a study by Rabello and White,²³ the semi-crystalline structure of PP samples can result from non-uniform degradation due to the different degrees of oxygen permeability of the amorphous and crystalline regions. Thus, in the amorphous regions free radicals are generated, which can migrate to

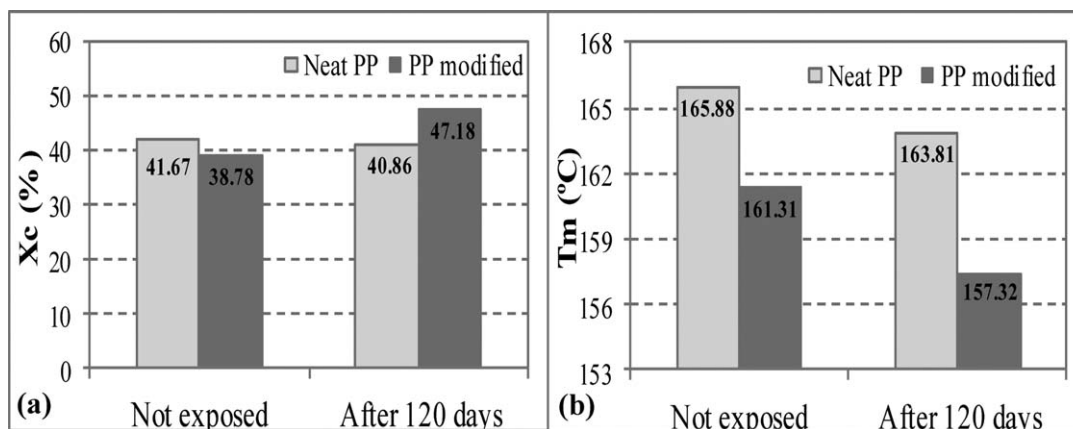


Figure 2. Values for the neat PP and modified PP before and after 120 days in the biodegradation test: (a) degree of crystallinity, (b) melt temperature.

the crystalline regions, thereby extending the degradation to the entire volume of the material.²⁴

Figure 2(b) shows the T_m values for the samples after the biodegradation test, and they are similar to those of the samples without exposure, i.e., no significant change was observed, only a slight reduction in the temperature for both samples. This result is a reflection of the chain cleavage process when the samples are subjected to the conditions of the respirometric test.

The SEM micrographs of the PP samples before and after biodegradation in the respirometric test are shown in Figure 3. Small changes in the surface of the control samples (neat PP)

were observed after 120 days of incubation, with uniform deterioration leading to small cracks and pitting on the surface. These changes could indicate that the neat PP biodegradation processes occurred slowly.²⁵

In the case of the modified PP, the distinct changes observed from the micrographs after 120 days in the respirometric test, with roughening, cavities, and disintegration of the surface, are clear evidence of degradation.¹³ After this period, more pronounced exfoliation, peeling, and holes in the plate structure was observed compared with the neat PP, indicating a greater degree of surface deterioration. This is because, with the

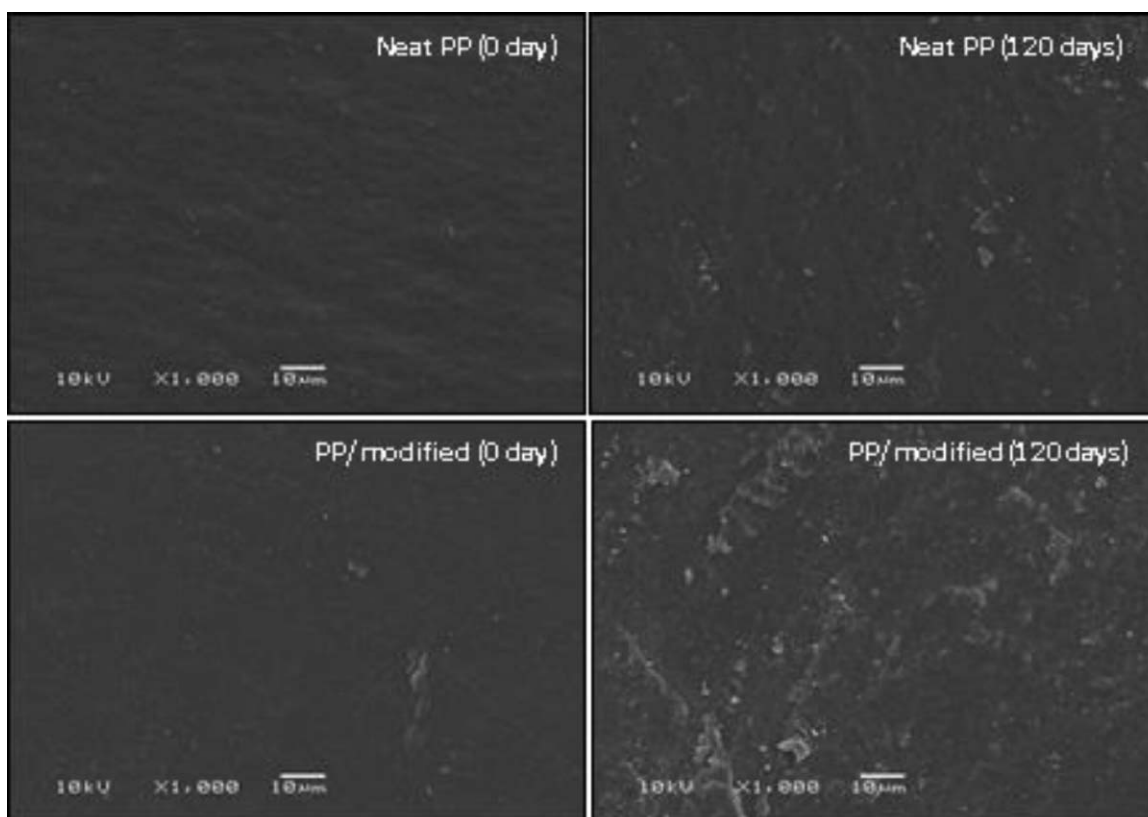


Figure 3. SEM micrographs of the neat PP and modified PP surfaces before and after 120 days under the biodegradation test conditions.

presence of the organic pro-degradant additive, this sample became more fragile during the incubation at 58°C for 120 days, which favored greater changes in the form of fractures and undulations on the surface. Mumtaz et al.²⁶ reported a study on the degradation of commercially available low density polyethylene carrier bags in natural soil during periods of up to 2 years. As in the study reported herein, the SEM images revealed signs of degradation, such as exfoliation and the formation of cracks, leading to disintegration.

CONCLUSIONS

The biodegradation behavior of neat PP and PP modified with organic pro-degradant was studied applying the respirometric test. After exposure to the accelerated biodegradation test for 120 days, the PP modified with organic pro-degradant showed higher levels of CO₂ production and weight loss compared to the neat PP. Thus, it was verified that the presence of the organic pro-degradant was effective in enhancing the biodegradation of PP samples. The thermal analysis by DSC revealed an increase in the degree of crystallinity and a slight increase in the melt temperature. With regard to the morphological properties of the sample surface, it was possible to observe the deterioration of the surface and, after being subjected to the biodegradation test for 120 days, this was more apparent in the case of the PP samples modified with the organic pro-degradant.

ACKNOWLEDGMENTS

The authors are grateful to CNPq and FAPERGS for financial support, to Braskem for providing the polymeric material and to CME for the morphological analysis.

REFERENCES

1. Abu-Sharkh, B. F.; Hamid, H. *Polym. Degrad. Stab.* **2004**, *85*, 967.
2. Singh, B.; Sharma, N. *Polym. Degrad. Stab.* **2008**, *93*, 561.
3. Khanna, N. D.; Kaur, I.; Bhalla, T. C.; Gautam, N. *J. Appl. Polym. Sci.* **2010**, *118*, 1476.
4. Khalil, H. P. S. A.; Poh, B. T.; Jawaid, M.; Ridzuan, R.; Suriana, R.; Said, M. R.; Ahmad, F.; Nik, N. A. *J. Reinf. Plast. Compos.* **2010**, *29*, 1653.
5. Sudhakar, M.; Doble, M.; Murthy, P. S.; Venkatesa, R. *Int. Biodeterior. Biodegrad.* **2008**, *61*, 203.
6. Luckachan, G. E.; Pillai, C. K. S. *J. Polym. Environ.* **2011**, *19*, 637.
7. Ammala, A.; Baterman, S.; Dean, K.; Petinakis, E.; Sangwan, P.; Wong, S.; Yuan, Q.; Yu, L.; Patrick, C.; Leong, K. H. *Prog. Polym. Sci.* **2011**, *36*, 1015.
8. Contat-Rodrigo, L. *Polym. Degrad. Stab.* **2013**, *98*, 2117.
9. Vogt, N. B.; Kleppe, E. A. *Polym. Degrad. Stab.* **2009**, *94*, 659.
10. Jansen, J. F. G. A.; Gijsman, P. WO 2008/006492 A1 (2008). Process for improving the biodegradability of a polymer.
11. Lewis, F. D.; Lauterbach, R. T.; Heine, H. G.; Hartmann, W. *J. Am. Chem. Soc.* **1975**, *97*, 1519.
12. Chiellini, E.; Corti, A.; Swift, G. *Polym. Degrad. Stab.* **2003**, *81*, 341.
13. American Society for Testing Materials, ASTM D 5338-98. Standard Test Method for Determining Aerobic Biodegradation of Plastics Materials Under Controlled Composting Conditions, Book of Standards vol. 08.03.
14. American Society for Testing Materials, ASTM D6003-96. Standard Test Method for Determining Weight Loss From Plastic Materials Exposed to Simulated Municipal Solid-Waste (MSW) Aerobic Compost Environment. ASTM International, West Conshohocken, PA, **1996**.
15. Ojeda, T. F. M.; Dalmolin, E.; Forte, M. M. C.; Jacques, R. J. S.; Bento, F. M.; Camargo, F. A. O. *Polym. Degrad. Stab.* **2009**, *94*, 965.
16. International Organization for Standardization: ISO 17556:2003. Plastics—Determination of the Ultimate Aerobic Biodegradability in Soil by Measuring the Oxygen Demand in a Respirometric or the Amount of Carbon Dioxide Evolved. International Organization for Standardization, Online Browsing Platform, **2003**.
17. Fu, Q.; Bing, N.; Wang, K.; Zhang, Q.; Du, R. *Polymer* **2005**, *46*, 3190.
18. Rudnik, E.; Briassoulis, D. *J. Polym. Environ.* **2011**, *19*, 18.
19. Chiellini, E.; Cinelli, P.; Corti, A.; Kenawy, E. R. *Polym. Degrad. Stab.* **2001**, *73*, 549.
20. Muthukumar, T.; Aravinthan, A.; Mukesh, D. *Polym. Degrad. Stab.* **2010**, *95*, 1988.
21. Gaborardi, F. *Avaliação das propriedades mecânicas, térmicas e de biodegradação de blendas de PHB e PEBD com e sem aditivos pró-degradantes*. [Master's dissertation]. Itatiba-SP: University of São Francisco; 2007.
22. Popov, A. A.; Blinov, N. N.; Krisyuk, B. E.; Zaikov, G. E. *Eur. Polym. J.* **1981**, *17*, 169.
23. Rabello, M. S.; White, J. R. *Polímeros: Ciência e Tecnologia* **1997**, *April/June*, 47.
24. Calvert, P. D.; Ryan, T. G. *Polymer* **1984**, *25*, 921.
25. Nowak, B.; Pajak, J.; Drozd-Bratkowicz, M.; Rymarz, G. *Int. Biodeterior. Biodegrad.* **2011**, *65*, 757.
26. Mumtaz, T.; Khan, M. R.; Hassan, M. A. *Micron* **2010**, *41*, 430.