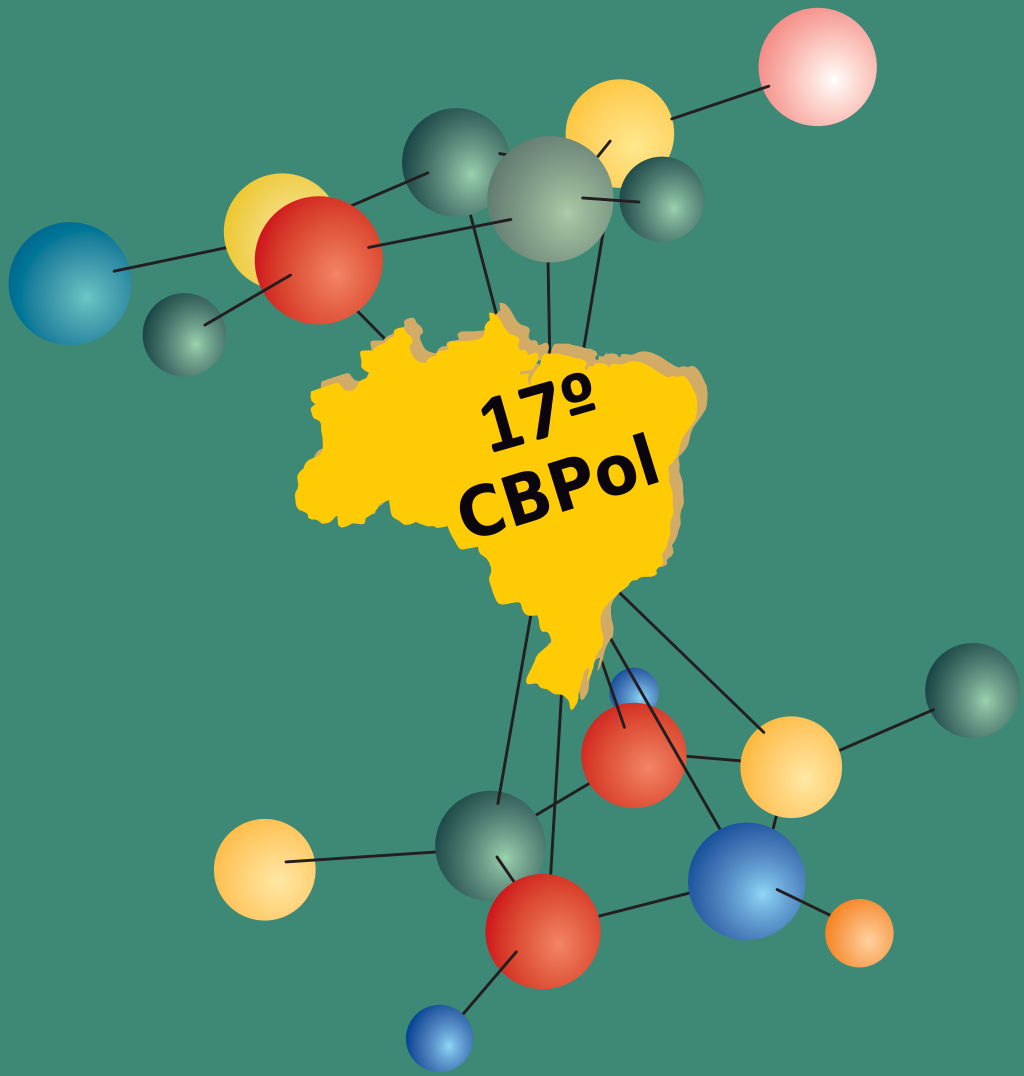


17º Congresso Brasileiro de Polímeros

29 de Outubro a 02 de Novembro de 2023

Joinville - SC

ANAIS

ABPol®
Associação Brasileira de Polímeros

Revisão textual e gramatical: Resposanbilidade dos respectivos autores.

Dados Internacionais de Catalogação na Publicação (CIP)
(Câmara Brasileira do Livro, SP, Brasil)

Congresso Brasileiro de Polímeros (17. : 29 out. - 2 nov. 2023 : Joinville, SC)
Anais do 17° Congresso Brasileiro de Polímeros [livro eletrônico] / organização Associação Brasileira de Polímeros. -- Joinville, SC : Aptor Software, 2023.

PDF

Vários colaboradores.
ISBN 978-85-63273-55-0

1. Polímeros 2. Polímeros e polimerização 3. Química - Congressos I. Título.

24-188263 CDD-540

Índices para catálogo sistemático:

1. Química : Congressos 540

Eliane de Freitas Leite - Bibliotecária - CRB 8/8415

EVALUATION OF THE DEGRADATION OF OXO-BIODEGRADABLE PP BY THE ACTION OF NATURAL WEATHERING

João A. O. Brandão[1*], Francisco Gehlen[1], Edson L. Francisquetti[2] and Ruth M. C. Santana[1]
1 –Departamento de Engenharia de Materiais, Universidade Federal do Rio Grande do Sul (UFRGS), Porto Alegre, RS, Brasil
jaobrandao@yahoo.com.br
2 – Instituto Federal do Rio Grande do Sul, Campus Farroupilha, Farroupilha, RS, Brasil

Abstract – Polypropylene (PP) is one of the most used polymers in the world, especially in packaging. As the recycling of these items is still unfeasible, an alternative to favour its decomposition is to process PP with pro-degradant additive, which will favour its abiotic and biotic degradation. In this work, benzoin was used to obtain oxo-biodegradable PP, and the properties of the injection-molded PP were evaluated before and after 30 days of natural aging. It was evidenced that the benzoin favoured the thermo-oxidation of the PP in the processing, reducing its molar mass and increasing its MFI, but with little influence on its mechanical properties, evaluated by tensile and Izod impact tests. After 30 days of aging, it was observed that benzoin favours photooxidation, with a significant reduction of the molar mass of the additived PP, accompanied by a significant increase of the MFI. The losses of mechanical properties were similar for PP with and without additive.
Keywords: PP, thermo-oxidation, photooxidation, mechanical properties, molar mass

Introduction

Benzoin proved to be effective as a promoter of the degradation by thermo-oxidation [1] and photooxidation [2] of polyethylene (PE) in previous studies, indicating that, in the future, it may be used in obtaining oxo-biodegradable PE. Considering that the mechanism of degradation by thermo-oxidation and photooxidation of PE and polypropylene (PP) are similar [3], since they are polyolefins, it is convenient to think that benzoin can also be used to obtain oxo-biodegradable PP, an alternative to solve the problem involving the accumulation of polymeric material in the environment, a result of the incorrect disposal, especially of packaging, which does not present attractive recycling. Currently, however, the pro-degradant additives are based on organic salts of transition metals [4], whose use could lead to a second problem: the accumulation of metals where, normally, their presence would not be observed. Benzoin, on the contrary, is a biodegradable and non-toxic substance (according to EC Regulation No. 1907/2006).

In this work, it was sought to obtain oxo-biodegradable PP from the addition of benzoin in the processing. Besides evaluating the acceleration of thermo-oxidation and photooxidation, the changes in the mechanical properties of PP with and without the additive were evaluated, before and after exposure to natural weathering. Injection-molded specimens were obtained, with 0, 2, 4 and 6% of masterbatch produced in PP matrix, which was characterized by dilute solution viscometry, with subsequent determination of the viscosity average molar mass; determination of MFI, to confirm the reduction of chain size due to degradation; besides the evaluation of mechanical properties by Izod impact and tensile strength tests.

Experimental

Materials

In this work, PP grade H-605, with MFI of 2.1 g/cm3 (230 ºC/2.160 kg) and density of 0.905 g/cm3, produced by Braskem Brasil; benzoin, with purity degree higher than 99%, produced by Merck KGaG, were used.

Benzoin masterbatch production in PP matrix (pro-degradant additive)

The masterbatch was obtained from the mixture of PP with benzoin in a Haake thermokinetic mixer, model RheoDrive 7, at a temperature of 190 ºC. The initial 6 minutes were to guarantee the melting of the PP. After that, the benzoin mass was added, with an effective mixing time of 4 minutes. Therefore, the total process lasted 10 minutes. A masterbatch with a mass ratio of 3:1 (PP/benzoin) was obtained. The mixture was cut with the help of pliers into granules with dimensions like those of PP pellets. Fig 1 shows the produced masterbatch.

Figure 1 – Benzoin masterbatch after cutting with pliers, with dimensions like PP pellets.

Obtaining the injection-molded specimens

Specimens with 0, 2, 4 and 6% (w/w) of benzoin masterbatch were produced and therefore were named as: PP_0%, PP_2%, PP_4% and PP_6%, respectively. All were obtained in Thermo Scientific Haake MiniJet II at 190 ºC, with injection pressure at 400 bar and withdrawal pressure at 350 bar. The mixture of the masterbatch with the virgin PP was previously done in the thermokinetic mixer, as it is a piston type injection molding machine. Besides guaranteeing a good diffusion of the additive in the PP, the process simulated the usual processing in the thermoplastic industry, in which the material would pass through a screw for later injection. Five specimens were obtained for each one of the different samples to be tested for tensile strength and Izod impact.

Natural weather ageing in Porto Alegre/RS

The specimens were naturally aged in Porto Alegre/RS. The specimens were placed on a 45º inclined stand, specifically located in front of the State Center for Research and Remote Sensoring and Meteorology (UFRGS) with their phases facing north. They were evaluated before and after 30 days of exposure. The experiment was performed from 21 November 2022 to 21 December 2022. (ASTM 1435-13). Fig 2 shows the specimens exposed to natural weathering on the first day.

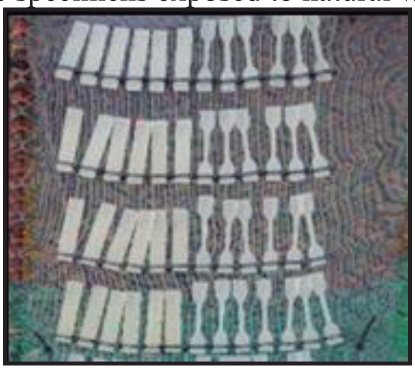


Figure 2 – PP specimens, with and without benzoin, exposed to natural weathering in Porto Alegre/RS.

Determination of the average viscosimetric molar mass of PP ($\overline{Mv}$)

The intrinsic viscosity ([η]) of PP in the samples was determined by dilute solution viscometry, for subsequent calculation of $\overline{Mv}$. Solutions with concentrations of 0.7; 0.5; 0.39; 0.32; 0.27 and 0.23 g/dL were used. The flow times of the initial solution and other dilutions were measured at a temperature of 135 ± 0.1ºC in a Cannon-Ubbelohde viscometer for diluted solutions (nº 50). From the flow times of the solutions and solvent (decalin) the relative (η_{rel}), specific (η_{esp}), and reduced specific ($n_{esp.red}$) viscosities were determined. The intrinsic viscosity ([η]) of PP was obtained from the graph of $n_{esp.red}$ versus concentration by extrapolation of the linear regression of the curve when the concentration tends to zero. Through the Mark-Howink-Sakurada equation (Eq. 1) the $\overline{Mv}$ of PP was determined. The constants α and k used for the polymer-solvent were 0.8 and 1.05 x 10^{-4} dL/g, respectively [5] (ASTM D446 and D445).

$$[\eta] = k.(\overline{Mv})^{a} \qquad (1)$$

Determination of the MFI of PP in injection-molded specimens
The melt flow indexes (MFI) of PP, with and without the additive, were obtained in a CEAST model 7026.000 modular plastomer. The conditions were: 230 ºC/ 2.160 kg, with 240 seconds of residence time (ASTM D1238).

Tensile test
Universal equipment Instron, model 4200, was used, using a load cell of 5 kN and removal speed of 25 mm/min (ASTM D638-10).

Izod impact test
Ceast equipment, model Impactor II, was used. The specimens were notched, and a 0.5 J hammer was used for impact, at room temperature (ASTM D638-10).

Results and Discussion

The PP specimens were characterized before and after exposure to natural weathering. Fig 3 presents the values determined by dilute solution viscometry. The $\overline{Mv}$ at t=0 indicates that, the higher the content of benzoin added, the higher the rate of thermos-oxidation in processing. In natural aging, it was possible to observe that the higher the benzoin content, the higher the degradation rate, mainly induced by photooxidation (caused, in turn, by the incidence of UV radiation). Such results show the pro-degradation action of benzoin, which favoured the degradation process in a similar way to the pro-degradants based on organic salts of transition metals on polyolefins [6].

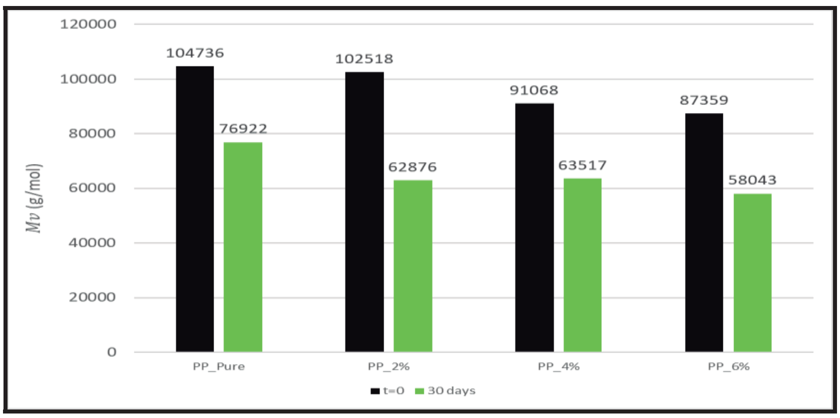


Figura 3 – $\overline{Mv}$ do PP nos corpos de prova injetados, antes e após a exposição ao intemperismo natural.

The MFI values, before and after exposure to natural weathering, are presented in Fig 4. At t=0, it was possible to observe that there was an increase in MFI, indicating greater ease of flow of the melt, possibly due to the reduction of chain size, corroborating the results obtained from $\overline{Mv}$, which strongly evidences the higher rate of thermo-oxidation for the injection-molded specimens with benzoin. After processing, the samples PP_4% and PP_6% presented an increase of 70% in MFI compared to PP_0%. The same occurred after exposure to natural weathering, and it was possible to observe that the photooxidation was more favored with the addition of benzoin, because when exposed to solar radiation, the increase in MFI was 154% for PP_6% compared to PP_0%. The increase is also consistent with the reduction in molar mass. These results are consistent with those verified in other studies in which the degradation of polyolefins processed with metallic pro-degradants and subjected to natural aging was evaluated [7].

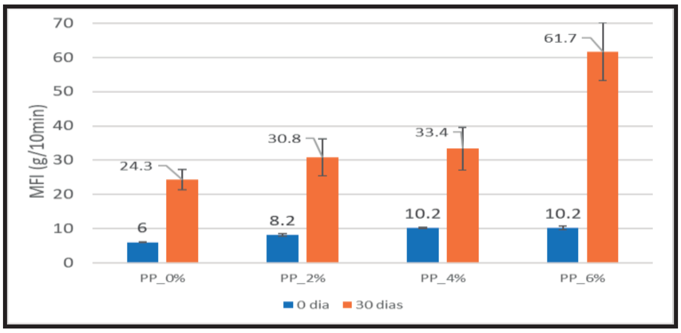


Figure 4 – MFI of the injection-molded specimens before and after exposure to natural aging.

The results of the Izod Impact test are presented in Fig 5, and it is possible to observe that, at t=0, the values found were statistically similar, allowing predicting that the addition of benzoin does little alter this mechanical property of PP. However, due to the acceleration of the photooxidative degradation process, part of this property is lost in natural aging. On average, it is possible to observe a reduction of the mechanical resistance to impact, although, considering the experimental error, the values for PP_4 and PP_6% are similar to the value found for PP_0%.

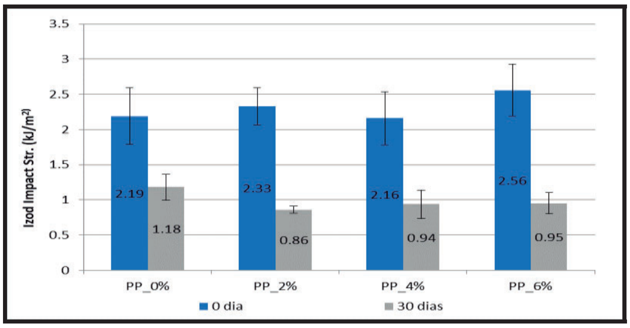
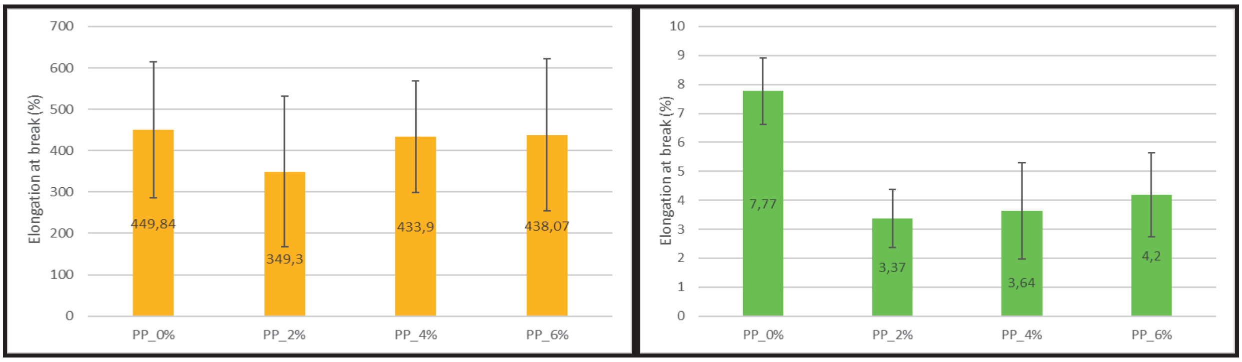


Figure 5 – Impact strength of the specimens, before and after natural aging.

Fig 6 presents the results of the tensile tests. The results of the elongation at rupture of the specimens will be discussed. At t=0, only PP_2% presents an average deformation below 430%. However, considering the experimental error, all of them have similar tensile, i.e., benzoin had little effect on this property of PP after processing, a behaviour similar to the one observed in impact strength. Regarding the elongation observed in the specimens after 30 days of aging, an accentuated reduction was observed in all samples. However, PP_2%, PP_4%, and PP_6% presented elongation values, on average, 50% lower than PP_0%. The results of this study are similar to those found in other scientific research in which the oxo-biodegradable PP, obtained from metallic organic salts, also showed reduced loss of mechanical properties compared to unadditivated polymer [8].



(a) (b)

Figure 6 – Elongation at break of the injection-molded specimens, (a) before and (b) after 30 days of aging.

Conclusions

According to the results found in this study, it was evidenced that benzoin also acts as a pro-degradant of PP, as occurs with PE, accelerating its abiotic degradation by thermo-oxidation and photooxidation. The higher the concentration of the additive, the higher the thermos-oxidation rate in injection-molding process. Similarly, the higher the concentration of the additive, the higher the photooxidation rate caused by the incidence of UV radiation from sunlight during exposure to natural weathering.

However, despite the reduction in the molar mass and increase in the MFI of the samples, the mechanical properties are weakly altered due to the addition of benzoin, indicating that, when used as a pro-degradation additive, it will little affect the quality of the items manufactured with oxo-biodegradable PP.

Acknowledgements

Thanks to Capes-Proex for the financial support.

References

1. J.A.O. Brandão; F.D.P. Morisso; E. L. Francisquetti; R.M.C. Santana. Polímeros 2021, 31, e2021029. https://doi.org/10.1590/0104-1428.20210058.
2. J.A.O. Brandão; F.D.P. Morisso; E. L. Francisquetti; R.M.C. Santana. Heliyon 2022, 8, e10217. https://doi.org/10.1016/j.heliyon.2022.e10217.
3. X. Liu; C. Gao; P. Sangwan; L. Yu; Z. Tong. Journal of Applied Polymer Science 2014, 131, 40750. https://doi.org/10.1002/app.40750.
4. A. Benitez; J.J. Sánchez; M.L. Arnal; A.J. Müller, O. Rodríguez; G. Morales. Polymer Degradation and Stability 2013, 98, p. 490-501. https://doi.org/10.1016/j.polymdegradstab.2012.12.011.
5. S. Gupta; X. Yuan; T.C.M. Chung; M. Cakmak; R.A. Polymer 2016, 107, p. 223-232. https://doi.org/10.1016/j.polymer.2016.11.027.
6. J.L. Pablos; C. Abrusci; I. Marín; J. López-Marín; F. Catalina; E. Espí; T. Corrales. Polymer Degradation and Stability 2010, 95, p. 2057 - 2064. https://doi.org/10.1016/j.polymdegradstab.2010.07.003.
7. P.K. Roy; P. Surekha; C. Rajagopal; V. Choudhary. Polymer Degradation and Stability 2006, 91, p. 1980-1988. https://doi.org/10.1016/j.polymdegradstab.2006.02.007.
8. T. Jachowicz; T. Garbacz; A. Tor-Swiatek; I. Gajdos; A. Czulak. International Journal of Polymer Analysis and Characterization 2015, 20, p.307-315 https://doi.org/10.1080/1023666X.2015.1016788.