



BJRS

BRAZILIAN JOURNAL
OF
RADIATION SCIENCES
10-03 (2022) 01-10



Thermal degradation and spectroscopy analysis of TPS/PBAT blends irradiated by Cobalt-60 source

Castro^a D.P., Andrade e Silva^a L.G.

^a Instituto de Pesquisas Energéticas e Nucleares/Comissão Nacional de Energia Nuclear

Postal code 05508-000, São Paulo, SP, Brazil

lgasilva@ipen.br

ABSTRACT

This study aimed to prepare blends of natural polymers of TPS with PBAT by reactive extrusion that were subsequently subjected to the irradiation process and evaluated for their thermal and chemical properties. The blends were incorporated with plasticizers (glycerol, castor oil and surfactant) and submitted to the irradiation process using a Cobalt-60 source at a 25 kGy dose and then characterized by FTIR and DSC. The results obtained in the FTIR analysis, the blends did not undergo chemical changes during the irradiation process and thus, maintained their properties. In the DSC analysis, it was observed that the blends F2 (castor oil) and F3 (castor oil and TWEEN® 80) showed higher values of heat flow for degradation than the samples F0 (glycerol) and F1 (glycerol and TWEEN® 80), probably due to the chemical interaction of castor oil and its constituents. There was no thermal variation in the irradiation process between blends F0 and F1 or F2 and F3. It was concluded that it is feasible to replace castor oil with glycerol in TPS/PBAT blends, and that irradiation using a Cobalt-60 source did not change the properties analyzed and contributed to microbiological protection.

Keywords: Biodegradable polymers, blends, irradiation process.



1. INTRODUCTION

The preparation of raw chemical materials used in mixtures of various natural polymers (polysaccharides and proteins) with natural and biodegradable artificial polymers is an alternative and sustainable practice [1]. Among these removable materials are three types: biopolymers, biodegradable polymers and green polymers. Each has various applications in agriculture and are non-degradable over a period of time [1,2].

Radiation processing is considered to be one of the most promising techniques for modifying biodegradable polymers, as it offers several advantages over other modification methods, being an ecologically correct and controllable process [3,4]. Irradiation using a Cobalt-60 source is widely used for disinfection and sterilization of food products, contributing to the microbiological protection of food and increasing a product's shelf life. However, changes in its chemical and nutritional properties may occur, depending on the type of food and the dose applied in the irradiation process [5]. Several researchers and research groups have conducted studies on the use of radiation in polymers and especially in TPS and PBAT [1,3-5].

Nemtanu and Brasoveanu [6] studied the physical degradation of polysaccharides, especially amylose, that were exposed to electron beam radiation at doses between 10 kGy and 50 kGy, and a dose rate of $2.5 \text{ Gy}\cdot\text{s}^{-1}$ in the presence of oxygen. They demonstrated that the radiation dose applied to amylose directly impacted its properties, with a decrease of up to 40% of its average numerical molar mass (Mn) and 20% for the weighted average molar mass (Mw) in doses over 40 kGy.

Atrous et al. [7] conducted a study for food industry application in which the effect of gamma radiation on the physical, chemical, thermal, morphological and rheological properties of wheat starch obtained from cereals were submitted to doses of (3, 5, 10, 20, 35 and 50 kGy). The results obtained showed that the starch crystallinity was not altered with doses below 50 kGy. The gamma radiation did not interact with the starch's crystalline regions (amylose), but limited the interaction in the amorphous region (amylopectin) of the wheat starch.

Hwang et al. [3] studied the effect of electron beam radiation and its impact on the thermal and mechanical properties of PBAT. Films were made using the casting technique and then irradiated with doses from 20 kGy to 200 kGy and subjected to thermogravimetric analysis (TGA) and other

techniques. The percentage of cross-linking was dependent on the applied dose and varied from 5% to 52%, changing their final properties.

Among the sites subject to modification in castor oil (CO), ionizing radiation can act as a natural moderator in the crosslinking of CO with starch, due to reactive sites such as hydroxyl, carbonyls and ester groups present in its chemical structure [8,9]. Stabilizers are very important for emulsions, such as oils in water or in polar molecules. This stability is achieved when there is no change in the size of the drops or a change in the arrangement between them. One of these commercial non-ionic surfactant stabilizers is TWEEN® 80, developed by Sigma-Aldrich®, which has an average molar mass of 1.31 g/mol [10].

2. MATERIALS AND METHODS

Materials used in this study were corn starch containing 28% amylose and 14% maximum moisture (Amidex® 3001, Ingredion); PBAT copolyester polymer (Ecoflex® F Blend C 1200, BASF SE); nature castor oil (*A. Azevedo Ind. and Com. de Óleos*); glycerol (G9012) and non-ionic surfactant (TWEEN® 80 P1754) from Sigma-Aldrich®. The blends were processed in an *AX Plásticos Máquinas Técnicas Ltda* extruder with dual screw profile at a rotation of 75 rpm and their temperature zones (120°C - 122°C - 124°C - 126°C - 126°C - 128°C - 130°C - 132°C - 134°C) are described. The compositions of the blends are shown in **Table 1** and pellets obtained after the extrusion process are shown in **Figure 1**.

Table 1: Formulations and compositions of the TPS/PBAT blends

Formulations	TPS Composition				
	PBAT (% mass)	Starch (% mass)	Glycerol (% mass)	Castor oil (% mass)	TWEEN® 80 (% mass)
F0	51.0	27.0	22.0	-----	-----
F1	51.0	27.0	20.5	-----	1.5
F2	51.0	27.0	-----	22.0	-----
F3	51.0	27.0	-----	20.5	1.5

Figure 1: TPS/PBAT pellets

2.1. Irradiation process

The irradiation process on the blends was realized using a Gammacell 200 irradiation unit (Atomic Energy of Canada Limited) with 25 kGy dose and 0,662 kGy/h dose rate.

2.2. Fourier Transform Infrared Spectroscopy – FTIR

The blends were characterized using a Fourier Transform Infrared Spectroscopy (Spectrum One model [Perkin-Elmer, Norwalk, CT, USA]) with an ATR system (Sampling Accessory), in the range of 600-4000 cm^{-1} with a 2 cm^{-1} of resolution in transmittance mode.

2.3. Differential Scanning Calorimetry – DSC

The effect of heat treatment on the blends was determined using DSC. The thermogravimetric analyzer simultaneous TGA-DSC SDT Q600 (TA Instruments, New Castle, DE, USA) was used. The test conditions were as follows: temperature 20–600°C at a heating rate of 20°C/min, in a compressed air atmosphere (100 mL/min) in alumina crucible. In order to interpret the DSC curves, TA Universal Analysis® software was used.

3. RESULTS AND DISCUSSION

3.1. ATR-FTIR

Infrared spectra were performed in order to compare samples composed of glycerol (F0), glycerol with TWEEN® 80 (F1) (**Figure 2A and 2B**), CO (F2) and CO with TWEEN® 80 (F3)

(Figure 3A and 3B). Non-irradiated (NIR) and irradiated (25 kGy) samples were used to evaluate the effect of radiation on the chemical structure of the blend compounds and their modifications.

Figure 2: IR spectrum of the F0-F1 (NIR/25 kGy) blends in the range of 4000-2600 cm⁻¹ (A) and 2000-600 cm⁻¹ (B)

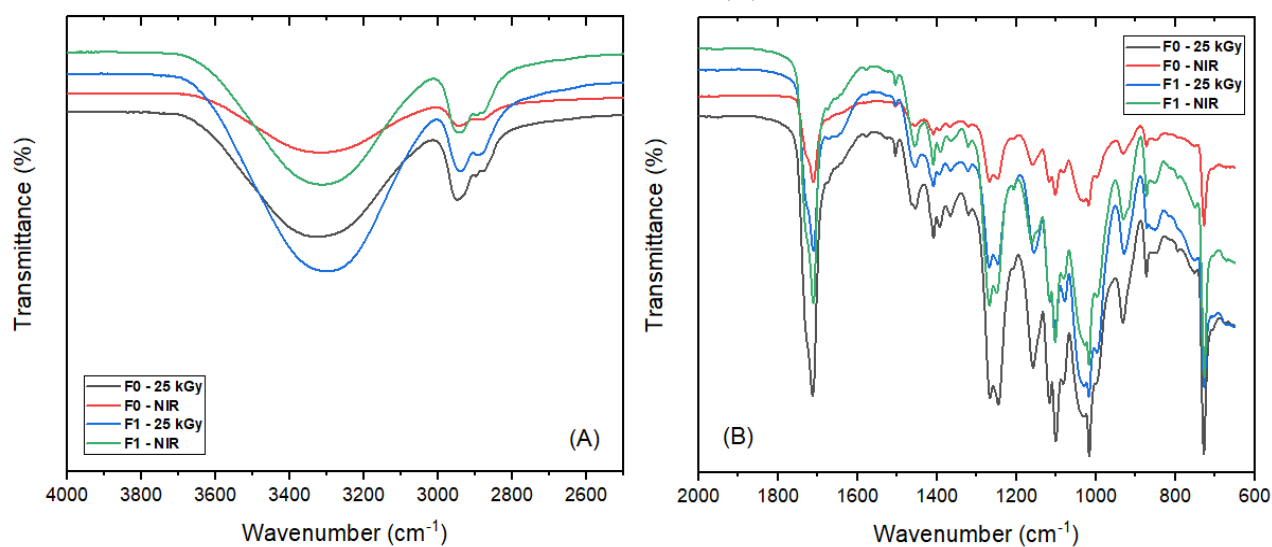
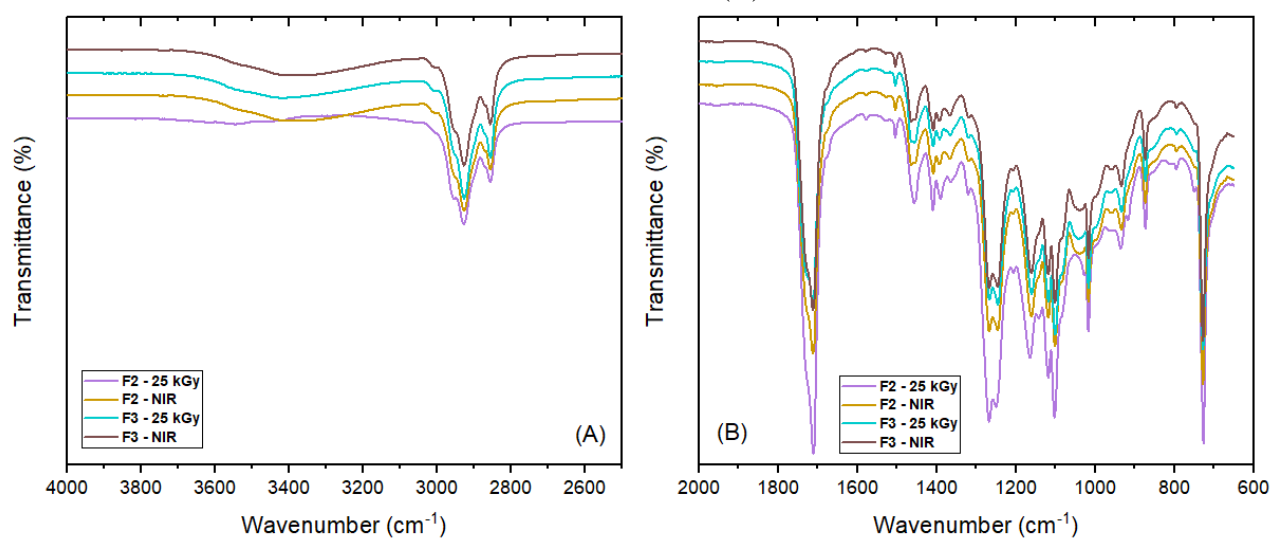


Figure 3: IR spectrum of the F2-F3 (NIR/25 kGy) blends in the range of 4000-2600 cm⁻¹ (A) and 2000-600 cm⁻¹ (B)



The bands between 3000 cm^{-1} and 3600 cm^{-1} , are attributable to -OH adsorbed water, due to the hydroxyls present in the structure of amylose in starch; and hydroxyls (-OH) present in glycerol and castor oil chemical structure respectively [6,7].

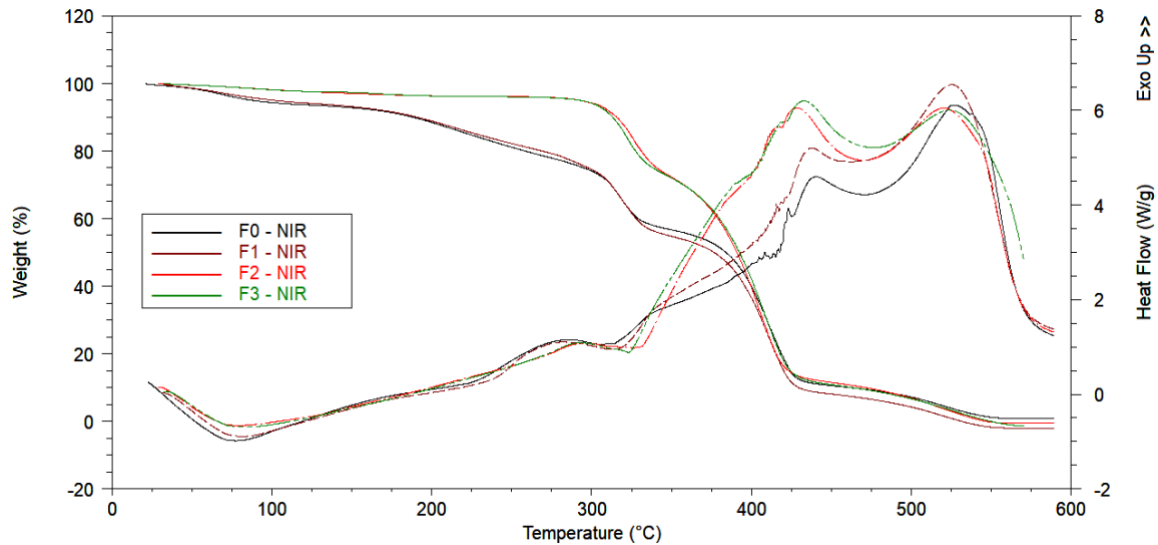
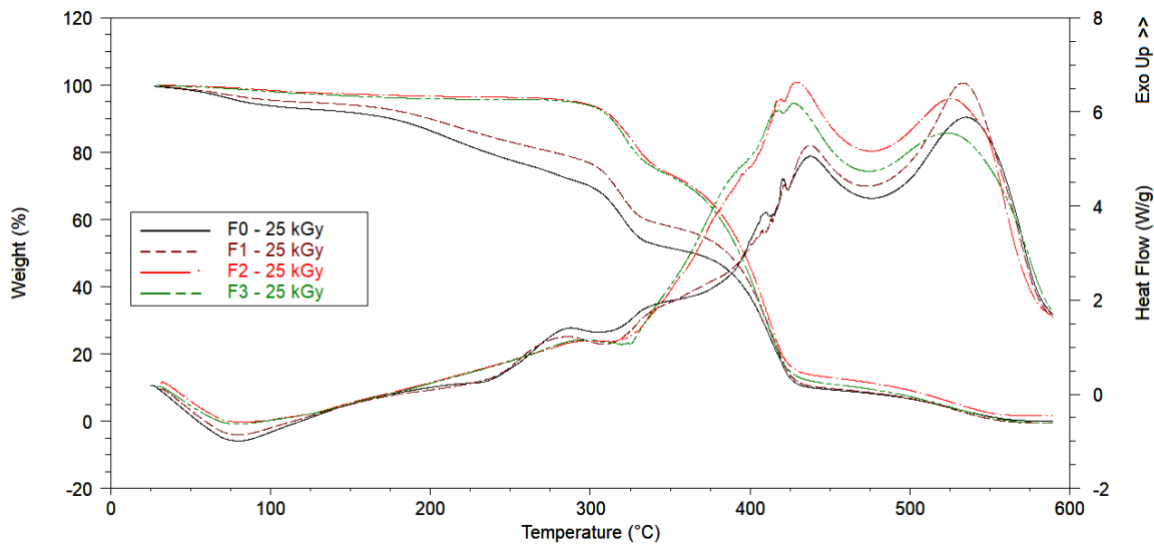
The starch and PBAT characteristic bands previously observed are present in all samples, such as those at $3000\text{-}3500\text{ cm}^{-1}$, $2800\text{-}2930\text{ cm}^{-1}$ and 1715 cm^{-1} , which are attributed to -OH bands, CH-bands of carbonyl groups of esters, from the castor oil and PBAT respectively [11].

The bands between 900 cm^{-1} and 600 cm^{-1} are attributed to the glycosidic bonds that unite the starch molecules; bands between 1000 cm^{-1} and 915 cm^{-1} are attributed to (C-OH) in the starch and the C-O-H bond, corresponding a glycosidic characteristic bands the molecules of the starch together with CH_2 - characteristic bands. And the absorption bond H-O-H in the range of 1500 cm^{-1} was attributed to water present in the starch [12]. The bands at 1025 cm^{-1} , 1110 cm^{-1} and 1270 cm^{-1} are due to the stretching of the C-O bonds present in starch, glycerol, PBAT [11].

The bands between 1400 cm^{-1} and 1550 cm^{-1} are attributed to the stretching of C=C present in the castor oil; the peaks between 2800 cm^{-1} and 2900 cm^{-1} is the C-H bonds of the methyl group of the castor oil and PBAT; and the bands between 1000 cm^{-1} and 1200 cm^{-1} are characteristic of the C-O-C ester bonds of castor oil [9].

3.2. DSC

The thermal analysis of the samples shows the variation of heat flow by temperature in relation to mass which was observed in the non-irradiated samples (NIR) (**Figure 4**) and irradiated samples at 25 kGy (**Figure 5**), performed at $20^\circ\text{C}/\text{min}$ up to 600°C .

Figure 4: DSC/TGA curves of the (NIR) F0-F3 blends**Figure 5:** DSC/TGA curves of the (25 kGy) F0-F3 blends

In Figures 4 and 5, the events start with an initial endothermic transition in temperatures ranging between 20°C and 100°C [7] with endothermic transition in temperatures ranging between 200°C and 300°C for the irradiated samples F0 and F1. This is due to the interaction, capture and degradation of the glycerol used as plasticizer, caused by a lower degradation temperature among the reagents and the quantity used in the starch plasticization process [13,14].

The primary exothermic and asymmetric peaks of the NIR samples irradiated in the range of 350°C to 450°C and 500°C to 560°C were caused by the different degradation of the samples [14,15]. In the range of 350°C to 450°C, secondary degradation peaks occurred in all samples. The primary peak of degradation in the range of 500°C to 560°C had a greater amplitude of degradation for the non-irradiated F0 and F1 (NIR) samples, whereas the NIR and irradiated samples composed of glycerol and TWEEN® 80 (F1), had the highest heat flow in the final degradation stage [14]. The use of the plasticizer contributed to the variation in enthalpy among the samples analyzed, where samples F2 and F3 had the highest values analyzed, due to the chemical resistance of castor oil [8,14].

Furthermore, it is possible to guarantee that the analyzed blends present homogenization and partial miscibility shown between 450°C and 500°C without high decrease heat flow (W/g), demonstrated in the two degradation curves shown for the starch and castor oil, and that the radiation dose of 25 kGy did not visually interfere with the thermal properties of the analyzed blends [14].

4. CONCLUSIONS

It was concluded that the low dose rate irradiation process at 25 kGy did not change the chemical properties of the blends, as analyzed by the FTIR spectra. The replacement in the plasticizers altered final thermal properties (DSC) of samples F2 and F3, composed of castor oil and TWEEN® 80, whereas the surfactant improved the thermal degradation properties, compared to the other samples analyzed. Thus, it is concluded that the radiation dose and its applied dose rate do not change the properties of the blends and contribute to microbiological protection.

ACKNOWLEDGMENTS

The authors would like to acknowledge the National Council for the Improvement of Higher Education (CAPES), National Council for Scientific and Technological Development (CNPq) and São Paulo Research Foundation (FAPESP) for their financial support.

REFERENCES

- [1] ABRAMOWSKA, A.; CIEŚLA K. A.; BUCZKOWSKI, M. J.; NOWICKI, A.; GŁUSZEWSKI, W. The influence of ionizing radiation on the properties of starch-PVA films. **Nukleonika**, v. 60, n. 3, p. 669-677, 2015.
- [2] American Society for Testing and Materials. **Labeling of Plastics Designed to be Aerobically Composted in Municipal or Industrial Facilities**, ASTM 2012. (ASTM D 6400-12).
- [3] HWANG, I. T.; CHAN-HEE, J.; IN-CHOI, K.; JAE-HAK, C.; YOUNG-CHANG, N. Electron beam-induced crosslinking of poly(butylene adipate-co-terephthalate). **Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms**, v. 268, n. 21, p. 3386-3389, 2010.
- [4] AKHAVAN, A.; KHOYLOU, F.; ATAEIVARJOVI, E. Preparation and characterization of gamma irradiated Starch/PVA/ZnO nanocomposite films. **Radiation Physics and Chemistry**, v. 138, p. 49-53, 2017.
- [5] ZHU, F. Impact of gamma-irradiation on structure, physicochemical properties, and applications of starch. **Food Hydrocolloids**, v. 52, p. 201-212, 2016.
- [6] NEMTANU, M. R.; BRASOVEANU, M. Degradation of amylose by ionizing radiation processing. **Starch-Starke**, v. 69, n. 3-4, p. 9, 2017.
- [7] ATROUS, H.; BENBETTAIEB, N.; HOSNI, F.; DANTHINE, S.; BLECKER, C.; ATTIA, H.; GHORBEL, D. Effect of gamma-radiation on free radicals formation, structural changes and functional properties of wheat starch. **International Journal of Biological Macromolecules**, v. 80, p. 64-76, 2015.
- [8] NUNES, M. R. S.; MARTINELLI, M.; PEDROSO, M. M. Epoxidação do óleo de mamona e derivados empregando o sistema catalítico VO(acac)₂/TBHP#. **Química Nova**, v. 31, n. 4, p. 818-821, 2008.
- [9] SATHISKUMAR, P. S.; MADRAS, G. Synthesis, characterization, degradation of biodegradable castor oil-based polyesters. **Polymer Degradation and Stability**, v. 96, n. 9, p. 1695-1704, 2011.
- [10] AGUILERA-MIGUEL, A.; LÓPEZ-GONZALEZ, E.; SADTLER, V.; DURAND, A.; MARCHAL, P.; CASTEL, C.; CHOPLIN, L. Hydrophobically modified dextrans as stabilizers for O/W highly concentrated emulsions. Comparison with commercial non-ionic polymeric stabilizers. **Colloids and Surfaces a-Physicochemical and Engineering Aspects**, v. 550, p. 155-166, 2018.

- [11] GARCIA, P. S.; TURBIANI, F. R. B.; BARON, A. M.; BROZOLA, G. L.; TAVARES, M. A.; YAMASHITA, F.; EIRAS D.; GROSSMANN, M. V. E. Sericin as compatibilizer in starch/polyester blown films. **Polímeros**, v. 28(5), p. 389-394, 2018.
- [12] KUMAR, P.; PRAKASH, K. S.; JAN, K.; SWER, T. L.; JAN, S.; VERMA, R.; DEPIKA, K.; DAR, M. Z. ; VERMA, K.; BASHIR, K. Effects of gamma irradiation on starch granule structure and physicochemical properties of brown rice starch. **Journal of Cereal Science**, v. 77, p. 194-200, 2017.
- [13] OLIVEIRA, C. F. de P. **Obtenção e caracterização de amido termoplástico e de suas misturas com polipropileno**. 2015. Thesis (Metallurgical and Materials Engineering) - Escola Politécnica, University of São Paulo, São Paulo, 2015.
- [14] CASTRO D. P.; SARTORI, M. N.; ANDRADE E SILVA, L. G. Effects of Gamma Radiation on the Properties of the Thermoplastic Starch/Poly (Butylene Adipate-co-Terephthalate) Blends. **Materials Research**, v. 22, e20190072, 2019.
- [15] WELLEN, R. M. R.; RABELLO, M. S.; FECHINE, G. J. M.; CANEDO, E. L. The melting behavior of poly(3-hydroxybutyrate) by DSC. Reproducibility study. **Polymer Testing**, v. 32, n. 2, p. 215-220, 2013.

This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third-party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material.

To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.