

CHARACTERIZATION OF TPS/PBAT BLENDS IRRADIATED BY IONIZING RADIATION

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Abstract - The use of biodegradable polymers is an important alternative today for both the environment and industry. However, when compared to conventional polymers, biodegradables are more expensive. The development of polymeric blends using matrices of biodegradable and synthetic polymers with natural additives are less damaging to the environment and more cost efficient. This study aimed to prepare natural blends of thermoplastic starch (TPS) with poly(butylene adipate-co-terephthalate) (PBAT) by reactive extrusion. The blends were submitted to the irradiation process using a Cobalt-60 source at a 25 kGy dose and then characterized by Fourier-transform infrared spectroscopy (FTIR) and differential heat flow scanning calorimetry (DSC). According to the results obtained in the FTIR tests, the blends did not undergo chemical changes during the irradiation process and, thus, maintained their properties. In the DSC tests, it was observed that the blends F2 (composed of castor oil) and F3 (composed of castor oil and TWEEN® 80) showed higher values of heat flow for degradation than the samples F0 (composed of glycerol) and F1 (composed of 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.

Keywords: *Biodegradable polymers, blends, irradiation process.*

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.

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 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 (M_n) and 20% for the weighted average molar mass (M_w) 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.

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].

Experimental

Materials used in this study were regular corn starch containing 28% amylose, 5.5% maximum pH and 14% maximum humidity (Amidex® 3001, Ingredient); PBAT copolyester (Ecoflex® F Blend C 1200, BASF SE); castor oil (A. Azevedo Ind. and Com. de Óleos); glycerol (G9012) and surfactant (TWEEN® 80 P1754) from Sigma-Aldrich®. The blends were processed in an AX Plásticos Máquinas Técnicas Ltda extruder, and irradiated using a Cobalt-60 source at a 25 kGy dose. The composition of the blends are shown in Table 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

Results and Discussion

3.1 Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy – ATR-FTIR

FTIR analyses were performed in order to compare samples composed of glycerol (F0) and glycerol with TWEEN® 80 (F1) (Fig. 1A) and CO (F2) and CO with TWEEN® 80 (F3) (Fig. 1B). 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. The ATR-FTIR spectra are shown in Figure 1.

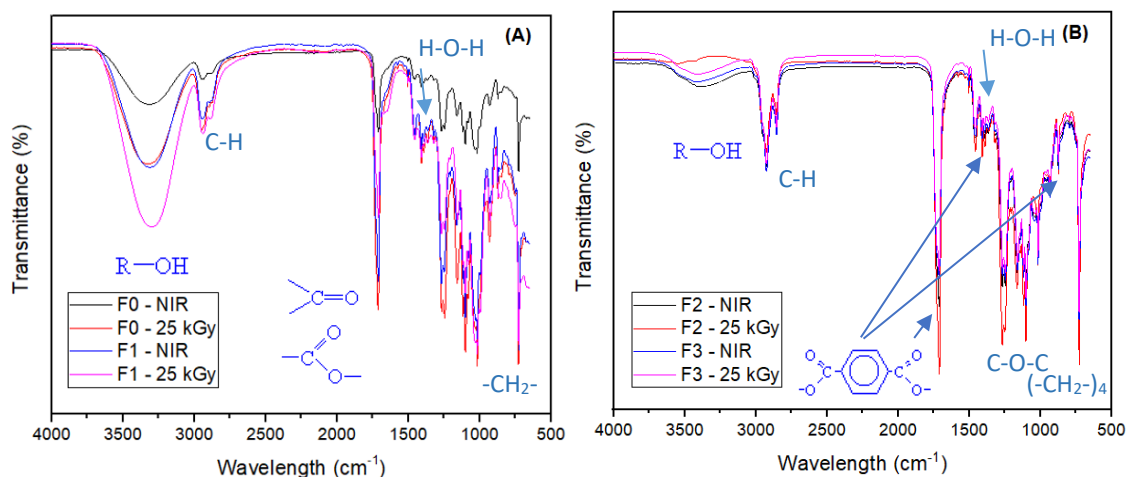


Figure 1 – ATR-FTIR spectrum of the (NIR/25 kGy) blends; (a) F0-F1; (b) F2-F3

The peaks between 3700 cm^{-1} and 3500 cm^{-1} , are attributable to O-H bonds, due to the hydroxyls present in the structure of starch, glycerol and castor oil [6,7].

Starch/PBAT characteristic bands and molecular vibrations 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- stretching, CH- stretching and absorption of carbonyl groups of esters, respectively [11].

The bonds between 900 cm^{-1} and 600 cm^{-1} are attributed to the glycosidic bonds that unite the starch molecules; peaks in the range between 1000 cm^{-1} and 915 cm^{-1} are attributed to C-OH bonds, C-O-H molecular vibrations and CH_2 - deformations; and the absorption band 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 bonds between 1400 cm^{-1} and 1550 cm^{-1} , are attributed to the stretching of C=C present in the CO; the bond represented by the peaks between 2800 cm^{-1} and 2900 cm^{-1} is the C-H bond of the methyl group CO and PBAT; and the band represented by the peaks between 1000 cm^{-1} and 1200 cm^{-1} are characteristic of the C-O-C ester bonds of castor oil [9].

3.2 Differential Heat Flow Scanning Calorimetry – DSC

The DSC analysis of the samples showed the variation of heat flow by temperature in relation to mass which was observed in the non-irradiated samples (NIR) (Fig. 2) and irradiated samples at 25 kGy (Fig. 3), performed at $20^\circ\text{C}/\text{min}$ up to 600°C .

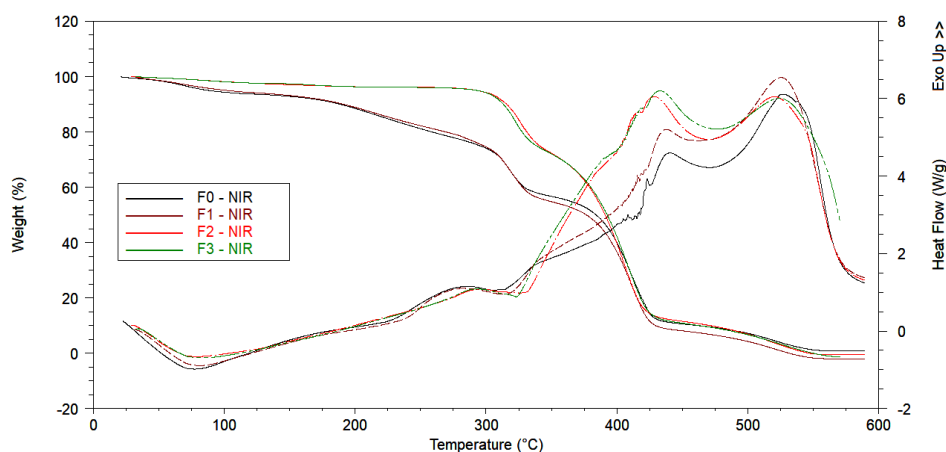


Figure 2 – TGA/DSC curves of the (NIR) F0-F3 blends

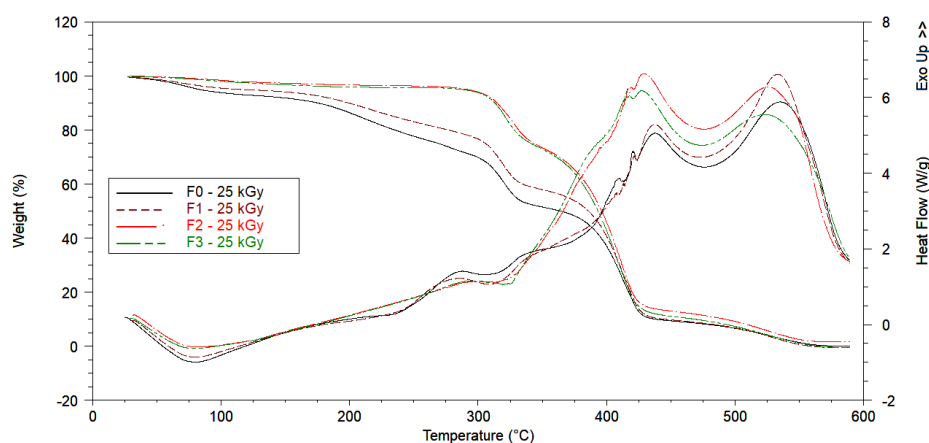


Figure 3 – TGA/DSC curves of the (25 kGy) F0-F3 blends

In Figures 2 and 3, the events start with an initial endothermic transition in the ranges 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 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].

Conclusions

It was concluded that the irradiation process doesn't change the chemical properties of the blends, as analyzed by FTIR. The replacement in the plasticizers altered final thermal properties (DSC) of samples F2 and F3, composed of castor oil and TWEEN® 80, where the surfactant improved the properties in comparison with other samples.

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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. <https://dx.doi.org/10.1515/nuka-2015-0088>.
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. <https://doi.org/10.1016/j.nimb.2010.08.010>.
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. <https://doi.org/10.1016/j.radphyschem.2017.02.057>.
5. Zhu, F. Impact of gamma-irradiation on structure, physicochemical properties, and applications of starch. *Food Hydrocolloids*, v. 52, p. 201-212, 2016. <https://doi.org/10.1016/j.foodhyd.2015.05.035>.
6. Nemtanu, M. R.; Brasoveanu, M. Degradation of amylose by ionizing radiation processing. *Starch-Starke*, v. 69, n. 3-4, p. 9, 2017. <https://doi.org/10.1002/star.201600027>.
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. <https://doi.org/10.1016/j.ijbiomac.2015.06.014>.
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. <https://dx.doi.org/10.1590/S0100-40422008000400021>.
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. <https://doi.org/10.1016/j.polymdegradstab.2011.07.002>.
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. <https://doi.org/10.1016/j.colsurfa.2018.04.022>.
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. <https://dx.doi.org/10.1590/0104-1428.05117>.
12. Kumar, P.; Prakash, K. S.; Jan, K.; Swer, T. L.; Jan, S.; Verma, R.; Deppika, 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. <https://doi.org/10.1016/j.jcs.2017.08.017>.
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. <https://dx.doi.org/10.11606/T.3.2016.tde-16062016-101007>.
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. <https://doi.org/10.1590/1980-5373-mr-2019-0072>.
15. Wellen, R. M. R.; Rabello, M. S.; Fechine, G. J. M.; Canedo, E. L. The melting behaviour of poly(3-hydroxybutyrate) by DSC. Reproducibility study. *Polymer Testing*, v. 32, n. 2, p. 215-220, 2013. <https://dx.doi.org/10.1016/j.polymeresting.2012.11.001>.