ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR – ABEN
2019 International Nuclear Atlantic Conference - INAC 2019
Santos, SP, Brazil, October 21-25, 2019

Agência Brasileira do ISBN
ISBN 978-85-99141-08-3
9 788599 141083

XRD CHARACTERIZATION THERMOPLASTIC STARCH/POLY(BUTYLENE ADIPATE-*CO*-TEREPHTHALATE) (TPS/PBAT) BLENDS IRRADIATED BY GAMMA RAYS

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ABSTRACT

The aim of this research was to check the changes in the structure and crystallinity of non-irradiated and irradiated thermoplastic starch blends (TPS)/poly (butylene adipate-*co*-terephthalate) - PBAT and also to evaluate the behavior of castor oil in place of glycerol. In this work, the characterization was performed by X-ray diffraction (XRD), in which the crystallinity index (IC) of non-irradiated and irradiated blends of TPS/PBAT was calculated. For plastification of the TPS, glycerol, castor oil and TWEEN® 80 were used to verify the compatibility and compare the blends with each other. The samples were prepared by extrusion and irradiated at 25 kGy with gamma rays from a ^{60}Co source. However, the crystallinity indexes of the blends were altered according to the plasticizer used and the use of TWEEN® 80. Thus, it been concluded that glycerol substitution by castor oil is feasible in TPS/PBAT blends.

1. INTRODUCTION

Biodegradable products based on polysaccharides are widely available in nature and constitute an important class of biopolymers. Among them, starch is a renewable carbohydrate polymer, available from great variety at low cost. It possesses various application in packages, biomedical devices and industrial composting [1,2]. Amid them, some aliphatic and aliphatic aromatic biodegradable polyesters are widely used in packaging applications such as poly (lactic acid) - PLA and poly (butylene adipate-*co*-terephthalate) – PBAT, because of their favorable mechanical properties, improving the final properties of blends with other materials [2]. TPS/PBAT blends also have low cost and good chemical properties, which are suitable for various applications.

Radiation processing is considered one of the most promising techniques for modifying biodegradable polymers, as it offers several advantages over other modification methods, being an environmentally friendly, controllable process with no additives, temperature and low energy consumption. Thus, this technique has been extensively exploited to modify several biodegradable polymers [3,4].

In this article, the study is mainly focused on XRD curves behavior and crystallinity index of TPS/PBAT blends.

1. MATERIALS AND METHODS

Amidex® 3001 starch from Ingredion, biodegradable PBAT copolyester, Ecoflex® F Blend C 1200 from BASF SE, Sigma-Aldrich® Glycerol G9012, castor oil from *A. Azevedo Ind*., and surfactant TWEEN® 80 P1754 from Sigma-Aldrich® were used in the experiments. Table 1 demonstrates the formulations used for this study.

Table 1: Formulations of TPS/PBAT blends and other components.

		TPS Composition			
Formulation	**PBAT (% in mass)**	**Starch (% in mass)**	**Glycerol (% in mass)**	**Castor Oil (% in mass)**	**TWEEN® 80 (% in 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

In addition to corn starch, plasticizers were used in the preparation of the blends: glycerol, castor oil and TWEEN® 80, according to the formulations shown in Table 1. They were weighed together with the PBAT pellets in triplicate and solubilized partially with the aid of a mechanical stirrer, at 400 rpm, for 2 minutes, until obtaining consistency and homogeneity, and concluded with manual mixing due to the plasticity and swelling of the formulations during the insertion of plasticizers into the starch and PBAT.

Samples were extruded in the corroting screw extruder of *AX Plásticos Máquinas Técnicas Ltda*. The material was cooled by forced ventilation and water passage. Subsequently, samples were cut into pellets and separated into individual packages for the irradiation process with 25 kGy in the ^{60}Co irradiator, *Gammacell 200*, at a dose rate of 0.662 kGy/h at room temperature in the presence of air. The later characterization of the blends was performed by using X-ray diffraction (XRD), carried out on the equipment *Multiflex* model from *Rigaku*, using monochromatic radiation CuKα (λ = 1,541 Å) radiation under a voltage of 40 kV and 20 mA current, diffraction angle between 5-60°, and scanning speed of 4 s. and 0.06° step.

The CI in the blends was calculated from Equation 1 [1]:

$$CI\ \% = (CA/TA)*100 \quad (1)$$

where: CI = crystallinity index; CA= crystallinity area; TA = total area.

2. RESULTS AND DISCUSSION

3.1. X-Ray Diffraction (XRD)

The X-ray diffraction curves of F0 blends (NIR - 25 kGy) composed of glycerol in its composition (Figure 1) showed similarities with the other blends.

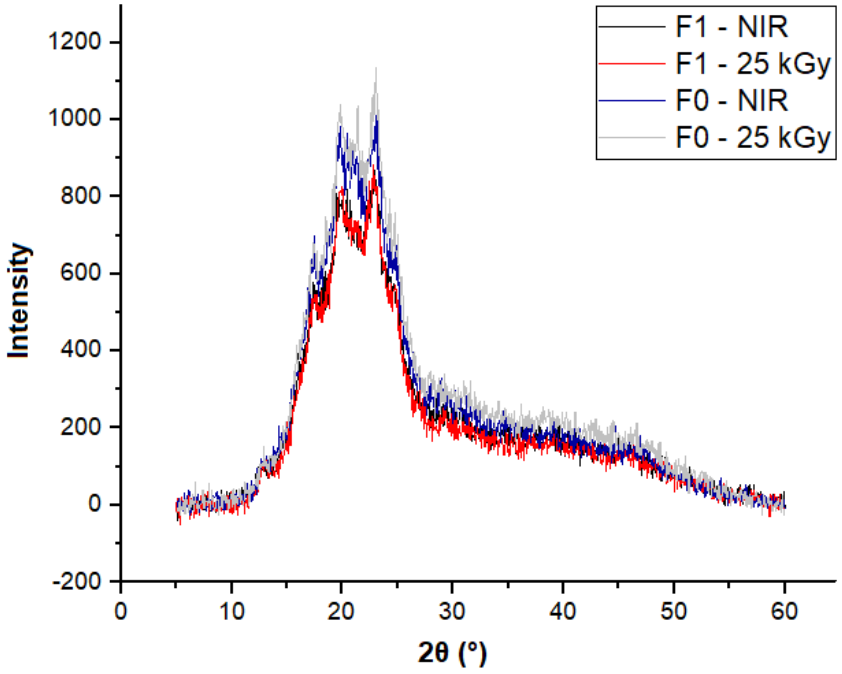

Figure 1: XRD curves: non-irradiated (NIR) and irradiated at 25 kGy blends composed by glycerol and TWEEN® 80.

In Figure 1, the XRD diffractograms of F1 blends (NIR - 25 kGy), composed of glycerol and TWEEN® 80, are shown. No noticeable differences among the diffractograms could be noticed. The 2θ peak located at 25° of the blend with TWEEN® 80, had a slight change in relation to the NIR blend. The behavior of the peaks of blends located between 20° and 23° coincided with the results obtained from the PBAT and starch at 20 kGy shown in the studies performed by researches [1,2,6,7].

The diffraction peaks coincided with those of pure PBAT and irradiated starch, and are in agreement with the results obtained by several researchers in the literature [1,2,5-7], which observed 5 crystalline peaks and their transitions.

The X-ray diffractograms of blends F2 and F3 are shown in Figure 2, composed of Castor oil (OM) / TWEEN® 80, presented similarities.

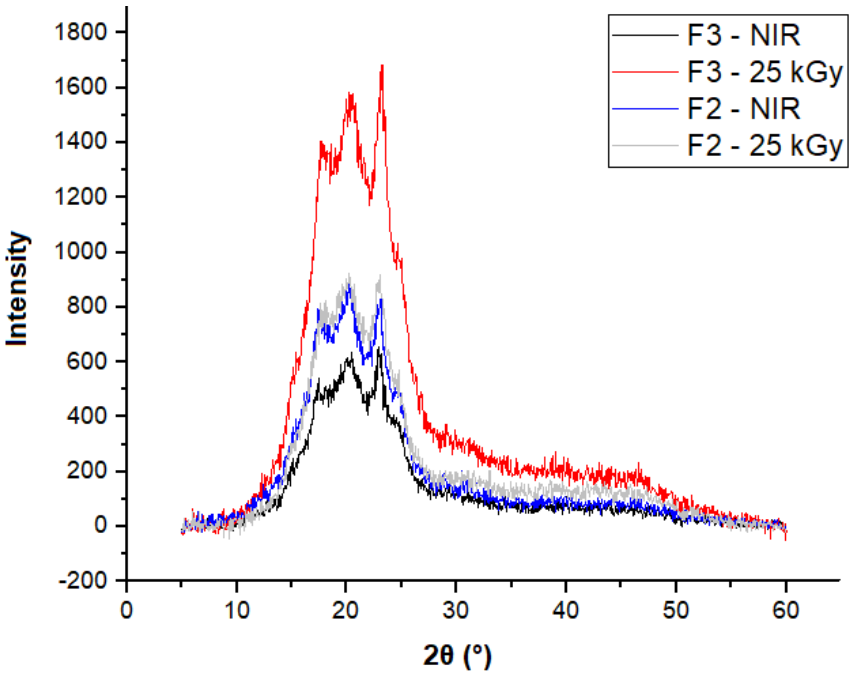

Figure 2: XRD curves: non irradiated (NIR) and irradiated at 25 kGy blends composed by castor oil (OM) and TWEEN® 80.

The peaks defined at 17°, 20° and 23°, are in agreement with the studies performed [1,2,5-7]. Concerning the irradiated F3 blends, the crystalline peaks had greater amplitude than in the non-irradiated F3 blends (NIR) composed of OM and TWEEN® 80.

3.2. Crystallinity Index (CI)

The calculated values of Crystallinity Index (CI) from the diffractograms of Figure 3 are shown in Table 2.

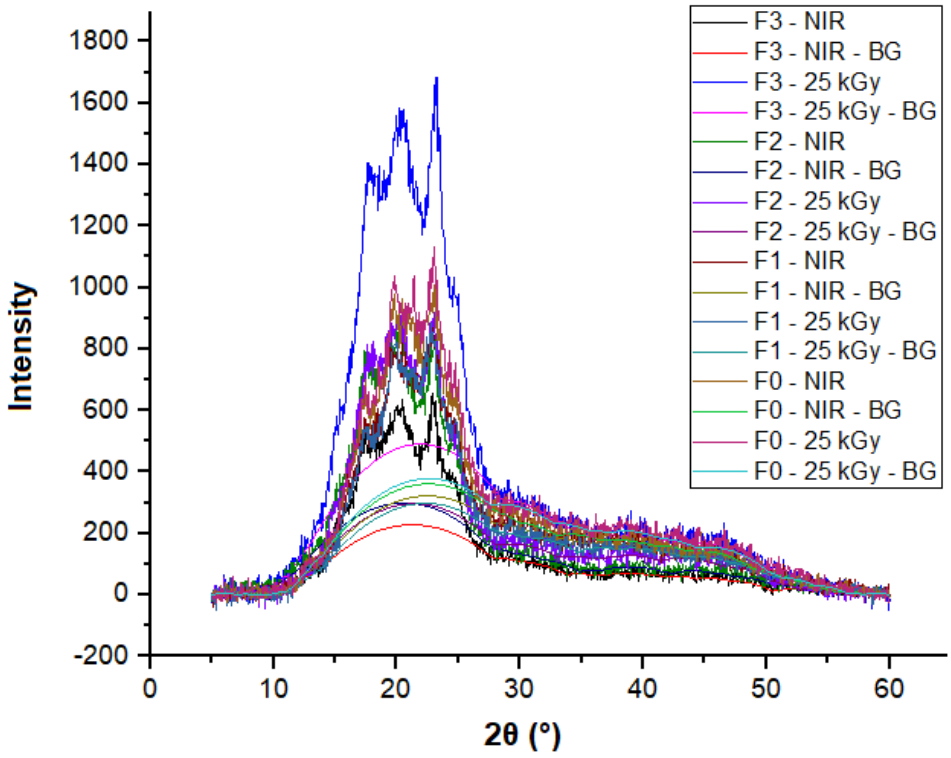

Figure 3: XRD curves: non irradiated (NIR) and irradiated at 25 kGy blends for calculation Crystallinity Index (CI).

Table 2: Crystallinity Index (CI) values calculated from the XRD data.

Blends	XRD Curves (Total area)	Crystallinity Area (CA)	Crystallinity Index (CI) %	Variation in Crystallinity (NIR/25 kGy) %
F0 - NIR	11.847	4.262	36.0	0.1
F0 - 25 kGy	13.007	4.668	35.9	
F1 - NIR	10.430	3.546	34.0	3.5
F1 - 25 kGy	9.825	3.687	37.5	
F2 - NIR	9.156	4.016	43.9	1.5
F2 - 25 kGy	10.265	4.657	45.4	
F3 - NIR	6.762	2.844	42.1	3.7
F3 - 25 kGy	18.316	8.394	45.8	

According to the data presented in Table 2, the F0 blends had no meaningful changes in the percentage of crystallinity (0.1%) after irradiation. The F1 blends had change in crystallinity; in the non-irradiated and irradiated sample (3.5%) and with TWEEN® 80. Regarding sample

F0 without surfactant obtaining the crystallinity difference of 3.4% was obtained (3.5% - 0.1%), the largest among NIR samples showing the chemical interaction of TWEEN® 80 in the analyzed blends.

In the irradiated F1 blend, a higher percentage of crystallinity was obtained comparing to the F0 - NIR sample, showing the interaction of TWEEN® 80 in the analyzed blend.

The CI of the blends may increase through the effects of radiation, possibly due to preferential degradation of the amorphous regions of amylopectin [6,7].

The chemical interaction of oleic acid, which is also present in the composition of TWEEN® 80 as plasticizer favored a better thermal resistance and stability for the starch relative to the glycerol, in addition to the plasticization process having occurred more efficiently which is agreement with the studies carried out by Schlemmer [8].

The F2 blends showed higher average values of crystallinity in relation to samples F0 and F1 and between their respective irradiated and non-irradiated compositions (1.5%), both obtaining the highest individual crystallinity value calculated among all formulations. The chemical interaction between the components of the blend and OM by esterification was observed and studied by other researchers [2,9].

The F3 blends with OM and F3 with TWEEN® 80 had significant changes in CI (3.7%) after irradiation. The F3 blend with TWEEN® 80 had the highest individual crystallinity index value (45.8%) among all analyzed samples.

3. CONCLUSIONS

It was observed that the samples did not show significant changes caused by the gamma radiation in their X-ray diffraction patterns. From the results of crystallinity index (CI), it was observed that there was a change in crystallinity according to the type of plasticizer used and the use of TWEEN® 80. A difference in crystallinity was noticed between samples F1 – NIR and F1 – 25 kGy (3.5%) with the incorporation of TWEEN® 80. The F2-F3 blends obtained higher CI's, and the rise in crystallinity after irradiation demonstrated the chemical interaction between components and the possible radiation induced crystallization process with OM/TWEEN® 80 and starch/PBAT, after the plasticization and reactive extrusion process.

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