Materials Research. 2019; 22(suppl1): e20190072
DOI: http://dx.doi.org/10.1590/1980-5373-MR-2019-0072

Effects of Gamma Radiation on the Properties of the Thermoplastic Starch/Poly (Butylene Adipate-*co*-Terephthalate) Blends

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Received: January 25, 2019; Revised: July 15, 2019; Accepted: August 15, 2019

The development of blends made from matrices of synthetic biodegradable polymers, and natural additives, are considered less environmentally aggressive materials. This work aimed to study the effects of gamma radiation on the properties of the thermoplastic starch (TPS)/poly(butylene adipate-co-terephthalate) (PBAT). In this work, blends of TPS/PBAT were prepared with glycerol, castor oil and TWEEN® 80, which were prepared by extrusion and then subjected to the radiation process and characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results demonstrated increased thermal degradation for the F2 (composed by OM) and F3 (composed by OM and TWEEN® 80) regarding F0 (composed by glycerol) e F1 (composed by glycerol and TWEEN® 80) blends. A good blend component chemical interaction and partial miscibility for the blends F0 and F1 was observed and compared to the others. However, F2 and F3 blends did not present co-continuous phases; being that the XRD curve patterns were not altered by the gamma radiation. The tests performed demonstrated that the irradiated and non-irradiated samples did not have their properties significantly altered. Thus, it was concluded that it is feasible to replace castor oil with glycerol in TPS/PBAT blends.

Keywords: *Gamma radiation, Blends, TPS, PBAT.*

1. Introduction

The development of blends made from matrices of synthetic biodegradable polymers, and natural additives are considered less environmentally aggressive materials; because they can be degraded by the action of microorganisms or enzymes. Among the biodegradable materials the thermoplastic starch (TPS), despite having poor mechanical resistance and low water resistance, if mixed with synthetic derivatives of co-polyesters or other biodegradable polymers, can reduce the production costs and make the biodegradable blend more competitive [1,2].

The use of radiation has been considered one of the promising techniques for modifying biodegradable polymers because it offers several advantages over other modification methods, such as an environmentally friendly process, without additives, temperature independence and low energy consumption, being widely used to modify biodegradable polymers. Thus, the irradiation process has been used to improve its final properties [1].

The PBAT, being a thermoplastic, semi-crystalline polymer and biodegradable under composting conditions and having physico-mechanical properties close to the polyethylenes family, can be used in conventional transformation processes such as: extrusion, blowing, mixing, injection molding, etc. [3]. It is also compatible with materials from renewable sources such as starch, vegetable fibers, corn and soybean meal among others.

Starch is a homopolysaccharide from belonging to the carbohydrate family, composed of amylose and amylopectin chains. The amylose is formed by glucose units linked by α (1 → 4) glycosidic bonds, giving a linear chain, although in a smaller percentage, and amylopectin is formed by α (1 → 6) glycosidic bonds, giving a branched chain [4,5]. It is responsible for influencing part of the functional properties of the starches [4]. Thus, to obtain the TPS it is necessary to break the semicrystalline structure of the granules. For this, the starch must be heated at high temperatures (90°C - 180°C) in the presence of plasticizers and under agitation, so that it acquires characteristics similar to most conventional thermoplastics [6].

Glycerol or propane-1,2,3-triol, is a polyol. In studies carried out with up to 25% of glycerol in mass, as the only plasticizer, the T_g of the starch was not below 20°C due to the low quantity, which favors the resistance to the impact of the material [5].

Castor oil is the triacylglycerol of ricinoleic acid, originating from the family *Ricinus communis*, composed of a fatty acid with chemical structure $C_{18}H_{34}O_3$, having a cis-unsaturation at carbon 9 and a hydroxyl at carbon 12. Unlike most vegetable oils, in ricinoleic acid, there are three places that can undergo chemical modifications: hydroxyl, unsaturation and carboxyl [7].

TWEEN® 80 is a commercial non-ionic surfactant stabilizer, developed by Sigma-Aldrich®, and has a relatively low average molecular weight [8].

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This work aimed to study the effects of gamma radiation on the properties of the thermoplastic starch (TPS)/ poly(butylene adipate-*co*-terephthalate) (PBAT) blends. Originating from two or more polymers with different constitutional or configurational characteristics and which have a low degree of chemical bonding between them and may be miscible or immiscible [9].

This blend is intended to improve the properties of existing polymer materials by varying their applications in various areas.

2. Experimental Procedure

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

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 the *Fisatom* 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.

The samples were extruded in the corroting screw extruder of *AX Plásticos Máquinas Técnicas Ltda.* The material was cooled by forced ventilation and passing through water. Subsequently cut into pellets and separated into individual packages for the irradiation process.

The samples were irradiated at 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 characterization of the blends was performed by using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), X-ray diffraction (XRD) and scanning electron microscopy (SEM).

3. Results and Discussion

3.1 Thermogravimetry Analysis (TGA)

In Fig. 1 and 2 it is presented the thermogravimetric curves of non-irradiated (NIR) and irradiated blends and their components. The TGA of the shows the temperature variation of non-irradiated and irradiated with 25 kGy blends, carried out at 20°C/min up to 600°C.

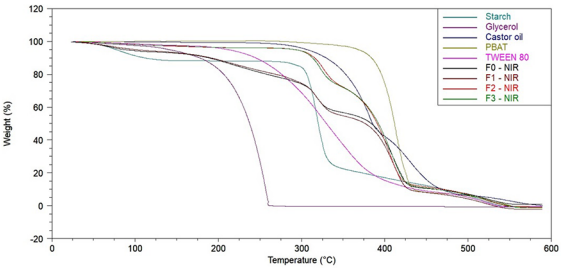

Figure 1. Thermogravimetric curve of NIR blends and their components

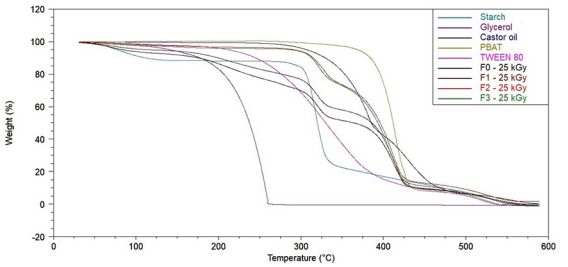

Figure 2. Thermogravimetric curve of blends irradiated at 25 kGy and their components

From the analysis of the curves of variation and loss of mass as a function of temperature in Fig. 1 and 2, it is observed that the degradation event occurred in several stages and started at room temperature in all formulations. F2 and F3 samples had higher resistance to degradation in relation to F0 and F1, due to the esterification process of castor oil used in the plasticization process of the starch in reactive extrusion. This result is in agreement with the literature [10]. It was also observed that F0 and F1 irradiated blends composed of glycerol and TWEEN® 80, were degraded in relation to the NIR blends, due to the radiation-induced

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

(γ) degradation of the amylose present in the starch, as demonstrated also in agreement with the literature [4,11].

The F2 and F3 blends had the same degradative behavior, both in NIR and irradiated blends, which is observed by the TGA curves obtained from the two graphs. Thus, it was concluded that the process of esterification and compatibilization of castor oil with the constituents can be obtained by reactive extrusion and radiation induction (γ), an advantage observed in relation to glycerol both compatibilized and not compatibilized with TWEEN® 80. The blends did not suffer loss of plasticizers over time, which favored their thermal properties.

The addition of the plasticizers and surfactant did not contribute relatively to the mass variation between the formulations F0-F1 and F2-F3. The chemical and temperature resistance differences between the formulations containing glycerol and TWEEN® 80 (F0 and F1); castor oil and TWEEN® 80 (F2 and F3) in both NIR and irradiated samples at 25 kGy, it is justified by the fact that castor oil consequently TWEEN® 80 can withstand sudden variations in temperature and pressure [7].

From the analysis of the curves shown in Fig. 3 and 4, four correlated stages of degradation of the blends and their constituents are observed:

I. The first enthalpy stage, with endothermic reaction of all samples, followed by loss of moisture present in the constituent starch in the samples and initial degradation at 150°C;

II. The second stage, consisted of the starch degradation in the samples F0 and F1 at ~ 190°C due to the insertion of the plasticizers that makes the chemical bonds weaker [5]. Followed by the sequential degradation of samples F0 and F1; and after secondary events;

III. The third stage of the degradation of all the samples started with the starch at ~ 307°C T_{onset}, PBAT, TWEEN® 80 and castor oil, respectively at ~ 330°C T_{onset}, showing the differences between oleic acids (TWEEN® 80) and ricinoleic (castor oil) [5], in relation to the samples constituted by glycerol (F0 and F1);

IV. The fourth stage of the degradation event starts at 420°C with exothermic event, and is characterized by the final degradation of the starch present in the samples and the beginning of the final thermal degradation of the PBAT at ~ 350°C, due to the disintegration of the starch [12]. The exothermics events are shown in Fig. 5 and 6.

V. In the last stage of thermal degradation with final transition around 530°C the samples are carbonized and converted into gases CO, CO_2, H_2O, among others [12].

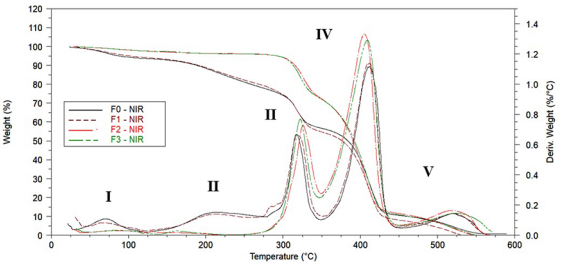

Figure 3. TGA/DTG curves of NIR blends

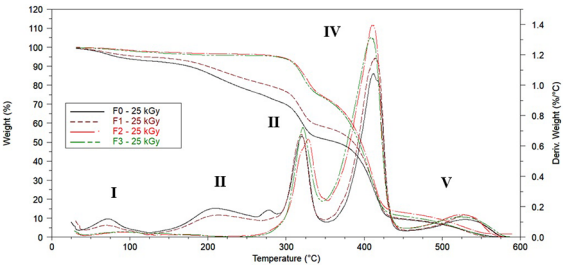

Figure 4. TGA/DTG curves of 25 kGy irradiated blends

3.2 Differential Scanning Calorimetry (DSC)

In Fig. 5 and 6, the differential heat flow scanning calorimetry curves of the non irradiated (NIR) and irradiated at 25 kGy blends are shown.

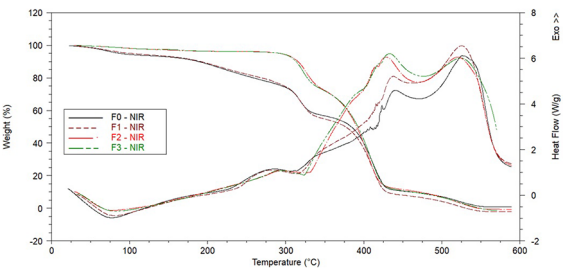

Figure 5. DSC curves of the non irradiated (NIR) blends

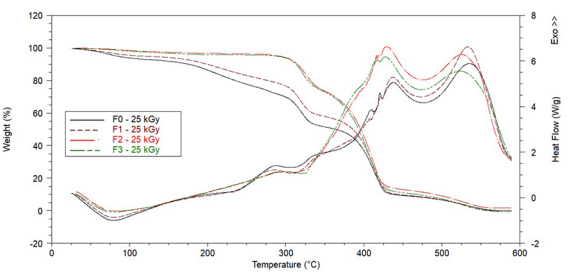

Figure 6. DSC curves of the irradiated 25 kGy blends

It was also observed from Figures 5 and 6 that the dose of gamma radiation did not significantly change the DSC curves between samples F0 (glycerol) and F1 (glycerol and TWEEN® 80); and F2 (castor oil) and F3

(castor oil and TWEEN® 80) up to 350°C, as well as degradation events of the samples. It was observed an endothermic transition due to the humidity of the starch in the samples between 20°C and 100°C [11]. Followed by a mild endothermic transition in the temperature range between 200°C and 300°C for irradiated F0 and F1 samples due to the interaction, migration and degradation of the glycerol used as plasticizer, the lower degradation temperature among the reagents and also the amount used in the plastification process of the starch [5].

The primary exothermic and asymmetric peaks of NIR and irradiated samples in the range of 350°C to 450°C and 500°C to 560°C were also observed in Figures 5 and 6, due to the different degradations of the samples [13]. In the range of 350°C to 450°C, secondary degradation peaks occurred in all samples; and the primary degradation peak in the range of 500°C to 560°C had a greater amplitude of degradation for the non-irradiated F0 and F1 samples, where NIR and irradiated samples composed of glycerol and TWEEN® 80 (F1), had the highest heat flux in the final stage of degradation.

3.4 X-Ray Diffraction (XRD)

In Fig. 7, the X-ray diffraction curves of the non-irradiated and irradiated at 25 kGy blends are shown.

The XRD curves of F0 and F1 blends (NIR and irradiated) with glycerol in its composition, showed similarities in the diffraction peaks where the interaction of the radiation (γ) in the components of the blends was not observed. The diffraction peaks coincided with those of pure PBAT and irradiated starch, and are in agreement with the literature [11,14-16], where their crystalline peaks and their transitions were observed. The curves of the F2 and F3 blends shown in, composed of castor oil/TWEEN® 80, presented similarities in the peaks 2θ, where 3 peaks were defined at 17°, 20° and 23°, which are in agreement with the literature [11,14-16]. The irradiated F3 blend, had a greater amplitude of the crystalline peaks than the non-irradiated F3 blends.

3.5 Scanning Electron Microscopy (SEM)

In Fig. 8 micrographs at 200x magnification of non-irradiated (NIR) and irradiated at 25 kGy blends are shown.

The micrographs obtained from the blends shown in Fig. 8, demonstrated a partially homogeneous surface and structure where the PBAT matrix partially plasticized with starch and glycerol was highlighted, showing remaining non-fully plasticized starch granules in F0 and F1 blends. The all samples also presented microcavities during the glass fracture process by nitrogen (dimples), because the TPS had two distinct phases: the in natura (unplasticized) starch and the plasticized phase [5]. The dimple and chemical interaction events between blends components and PBAT were also observed and studied [5,16]. However, it was observed that the blends with TWEEN® 80 (F1-F3) had a more homogeneous and smooth behavior in relation to the sample plasticized with glycerol (F0) and castor oil (F2), only and the radiation did not significantly modify the morphological properties of the blends.

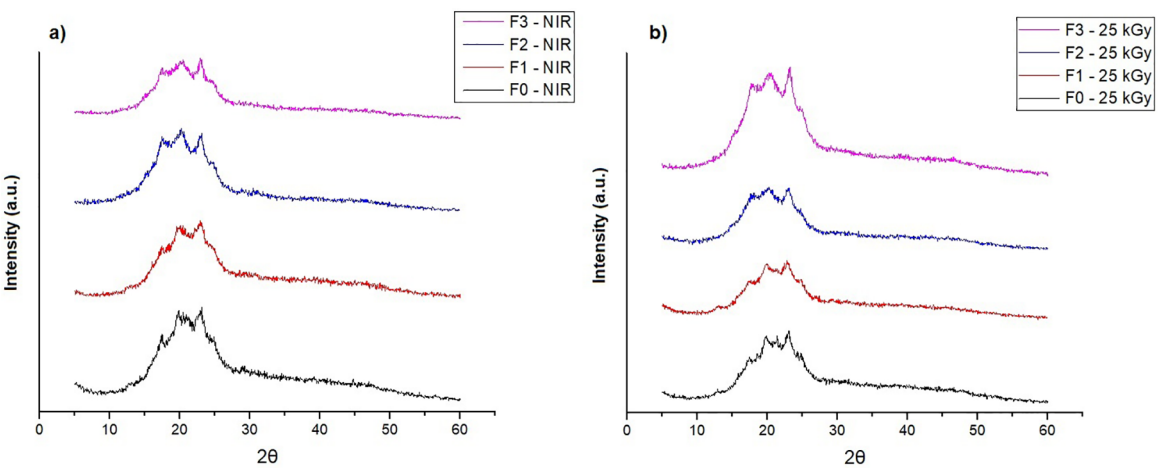

Figure 7. XRD curves a) non-irradiated (NIR); b) irradiated at 25 kGy blends

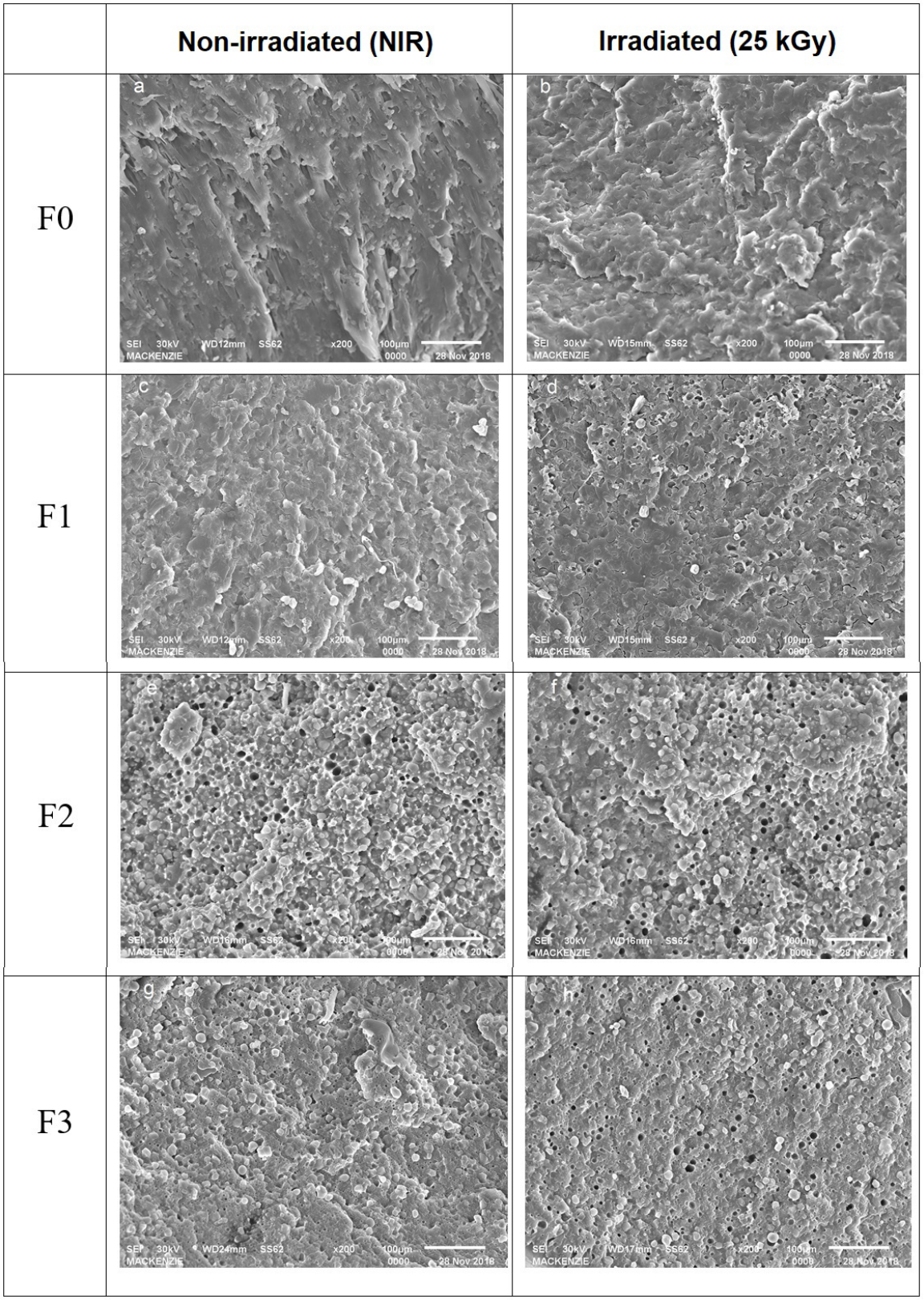

Figure 8. Micrographs of NIR and irradiated blends at 200x magnification

4. Conclusions

According to the thermal analyzes (TGA), the blends plasticized with castor oil presented better resistance to thermal degradation, in relation to those constituted by glycerol. Therefore, the addition of the plasticizers and surfactant did not contribute to the enthalpy change between the formulations F0-F1 and F2-F3 in DSC analysis, but the chemical and temperature resistance differences between the formulations containing respectively glycerol (F0) and glycerol with TWEEN® 80 (F1); castor oil (F2) and castor oil with TWEEN® 80 (F3) was observed. Also the adsorption of water by the TPS after extrusion was observed and confirmed by the endotherm reaction presented in the TGA/DSC graphs. According of XRD results, the blends had no changes in crystalline peaks and 2θ between them. The blends F2-F3 presented the best results obtained for XRD, where F3 sample with presence TWEEN® 80 presented more peak. SEM analyzes demonstrated the samples presented microcapsules resulting from the vitreous fracture by N_2, but did not have any morphological alterations among all blends. Thus, it was observed that the dose of radiation applied did not alter the properties the blends analyzed.

5. Acknowledgements

The authors are thankful to: Julio Harada from BASF S.E.; Luci Diva B. Machado by the teachings and use of the thermal analysis; Ingredion and *A. Azevedo Ind. e Comércio de Óleos* for providing the materials, *Universidade Presbiteriana Mackenzie* and *IPEN-CNEN/SP* for supporting this study.

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