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

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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-polymesters 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.4

Starch is a homopolysaccharide from belonging to the carbohydrate family, composed of amyllose and amylopectin chains. The amyllose 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.5,6 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 Tg 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 C18H34O3, 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,8 and has a relatively low average molecular weight.9
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.

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 60Co 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. 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

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

| 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                  |
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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.

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. 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.

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. 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, 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 20, where 3 peaks were defined at 17°, 20° and 23°, which are in agreement with the literature. 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. The dimple and chemical interaction events between blends components and PBAT were also observed and studied. 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](image-url)
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 20 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 N2, 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.

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6. References

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