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Research Paper

Characteristics of biodegradable films based on cassava starch and soy isolate protein treated by electron beam radiation

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ABSTRACT

Polymers from renewable sources can fulfill in some aspects the needs of consumers without damaging the environment, health and economy. Soy protein concentrate and cassava starch may be considered an alternative to petrochemical polymers. Ionizing radiation processing with gamma rays or electron beam is currently used for the modification of polymers and macromolecules. The widely known ability of proteins and polysaccharides to form films as a starting point for the development of new materials aimed at edible packaging for the food industry was employed. Films based on cassava starch and isolated soy proteins were prepared in two different formulations and electron beam irradiated with 0, 20 and 40 kGy. The tensile strength decreased upon irradiation and yellow color intensified. Regarding thermal properties, no significant differences were observed between irradiated and non-irradiated samples. However, regarding properties such as water vapor permeability and water absorption, the films became less permeable at higher radiation doses. Films with good resistance to water vapor and low water absorption would be considered suitable for food packaging. Radiation seems a convenient tool for the modification of this kind of biopolymeric blends and opens a huge array of possibilities of application.

Key words: Cassava starch, isolated soy protein, biopolymers, electron beam irradiation, soluble films.

INTRODUCTION

Great varieties of proteins from plant origin (for example, corn zein, wheat gluten and soy protein) received attention in the last decades for the production of biodegradable films as a result of environmental concerns (Gennadios, 2002; Vieira et al., 2011). Packaging from biobased plastics are at present been developed. New biobased materials and material combinations, for example, blending of different bioplastics such as starch-based materials create packaging solutions with completely new functionalities such as biodegradability/compostability (Giuggioli et al., 2017).

The physical and chemical properties of polymeric materials can be modified by treatment with ionizing radiation in the form of gamma rays, X-rays and electron-beam (EB) radiation (Cleland et al., 2003) mainly through the induction of cross-linking. Industrial EB accelerators with energies in the 150±300 keV range such as curing of surface coatings are in use in applications where low penetration is needed. Accelerators operating in the 1.5 MeV range are used where more penetration is needed in the cross-linking of cable insulation. High-energy commercial e- beams operating in the 10 MeV range are used for applications such as sterilization of boxes with disposable medical devices (Berejka, 1995). Electron beam treatment is similar to gamma rays processing in that, upon contact with the exposed product, electrons alter various chemical and molecular bonds (Vieira and Del Mastro, 2002). However, the study of the application of EB irradiation on food proteins is rather scarce (Kuan et al., 2013) when compared with gamma radiation.

In the present work, biodegradable films based on cassava starch and soy isolate proteins treated by EB radiation were prepared and some resulting properties also established.

MATERIALS AND METHODS

Material and irradiation

Samples of cassava starch and isolate soy protein in bulk were obtained at a local grocery store and analytical grade glycerol and deionized water used for the film preparation. For EB irradiation, an accelerator, Dynamitron II and Radiation Dynamics Inc. were employed: energy 1.202 MeV, beam current 0.62 mA and dose rate at 2.81 kGy s^{-1} room temperature with doses of 20 e 40 kGy were applied.

Film formulation and preparation

Based on preliminary tests, films were prepared in two formulations:

- From 5 g of isolate soy protein (ISP) in 200 ml water, a filtration was performed for removing particles in suspension. Thereafter, 7.5% cassava starch, 3% glycerol and 0.5% Ca propionate were incorporated.
- The filmogenic solution (FS) was prepared with 1% powder ISP, 6% cassava starch, 2.6% glycerol and 0.4% Ca propionate.

The films were prepared by casting the gelatinized starch solutions. The two FS were heated in water bath to 70°C under constant stirring for 30 min. The solution was poured into petri dishes previously covered with polyethylene film. The plates were placed in an oven with forced air circulation at 30°C for 20 h until irradiation. The films were stored (58% RH, 25°C) in a desiccator containing silica gel for 48 h before the characterization. The thickness of the films was in the range of 1.95±0.05 mm.

Film characterization

At least ten pieces of each film were employed. Tensile strength (TS) was measured according to the standard method ASTM D 882-09 (2009), with a Texture analyzer (TA.XT2, Stable Micro Systems, UK), software Texture Expert with a 5 kg load cell, a distance between the grips of 55 mm and a speed of 1 mm/s test. For these analyses, the films were cut into squares (30 × 30 mm) and conditioned at 23°C and 50% humidity for 48 h before testing.

Water vapor permeability (WVP) was measured according to ASTM E96M-10 (2010). Circular acrylic cells containing pieces of film (exposed area ~15.2 cm^2) were introduced into desiccators at ambient temperature with a relative humidity of ~50%. Weight gain was determined by the difference between weight at time zero and 24 h. The analysis was performed in triplicate and values determined by the equation:

$$WVP= w×L(1)\ A × t × Δp$$

Where w is the weight gain rate (water) (g) by the permeation cell, L is the thickness of the film (mm), A is the permeation area (m^2), t is the time of permeation (h) and Δp is the water vapor pressure difference between the two sides of the film (Pa). All assays were performed in triplicate.

Water absorption tests were carried out on (10 × 10) mm film samples according to ASTM D-7031-4 specification after 24 h immersion in distilled water at 25°C (room temperature).

Water solubility (WS) of the films were determined by drying the samples at 105°C for 24 h. The films were cut into discs with a diameter of 2 cm, weighed and placed in capsules with 30 ml of distilled water and kept under stirring in a 25°C water bath for 24 h. Subsequently, the samples were filtered using pre-weighed filter paper and then dried at 105°C for 24h. The resulting materials were weighed to determine the final dry weight (Wf). The analysis was performed in triplicate and determined using the following equation:

$$WS(\%) = Wi − Wf/Wi ×100$$

Where Wi is the initial dry weight of the sample (g) and Wf is the final dry weight of the sample (g).

Color analysis was performed on the films exposed to light at ambient temperature (25°C) measuring different points of each film using a colorimeter (Minolta®, model CR400, Japan) following the color system of the CIE-L* a* b*. The parameter L* (luminosity) ranged from black (0) to white (100), the values of the chroma a* ranged from green (−60) to red (+60) and chroma b* values ranged from blue (−60) to yellow (+60). Thermal analyses of the films were performed using a TA SDTQ600 thermogravimetric analyzer in an atmosphere of nitrogen and flow rate 20 ml min^{-1}. Samples of 5.0 ± 1.0 mg were heated from room temperature to 600°C at a heating rate of 20°C min^{-1}.

RESULTS AND DISCUSSION

Radiation technology

Published studies on the development of coating or films based on protein or starch are limited until now, however it is expected to increase. Although there are more works

Table 1: Published articles on ionizing radiation (*γ* or *EB)* and protein/starch obtained from Web of Sciences database (collected March 9th, 2017) using different tags.

Tags	Number of articles
Coating + protein + starch	446
Films + protein + starch	625
Ionizing radiation + films or coating	484.596
I. Radiation + film or coating + protein or starch	135.876
I. Radiation + protein	10.370
I. Radiation + polysaccharides or starch	84.401
EB radiation + protein	254
γ radiation + protein	5.134
EB radiation + polysaccharides or starch	84.327
γ radiation + polysaccharides or starch	84.487

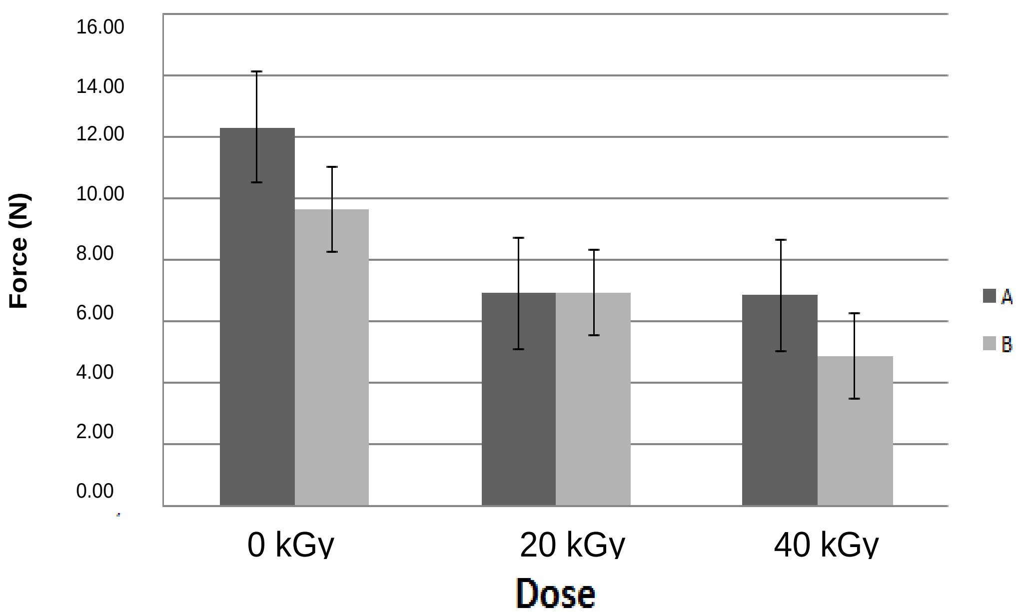

Figure 1: Tensile strength a function of EB radiation dose of two types (A and B) of cassava/isolate soy protein blend films.

employing *γ* radiation than EB for protein studies for polysaccharides or starch using any one of the sources and the number of published articles are quite similar (Table 1).

Tensile strength

Tensile properties of edible protein films are dependent on film constituents, their relative proportions and preparation conditions as was already established (Atares and Chiralt, 2016). Figure 1 shows the maximum rupture force of the cassava + isolate soy protein films measured. It is evident that a dose of 20 kGy of EB radiation was sufficient to decrease this property, although it was different for the two samples.

Water vapor permeability (WVP)

WVP is one of the most important properties of edible films since one of the main functions of food packaging is to prevent or reduce the transfer of moisture from the surrounding environment to the food. WVP can be used to predict the loss or gain of water in the food covered by the film. WVP is affected by numerous factors such as the thickness of the films, a_W, humidity and the relative proportions of the components used in their formulation. Coatings and edible films made from polysaccharides are characterized by their limited capacity to prevent the transfer of water vapor due to their hydrophilic nature

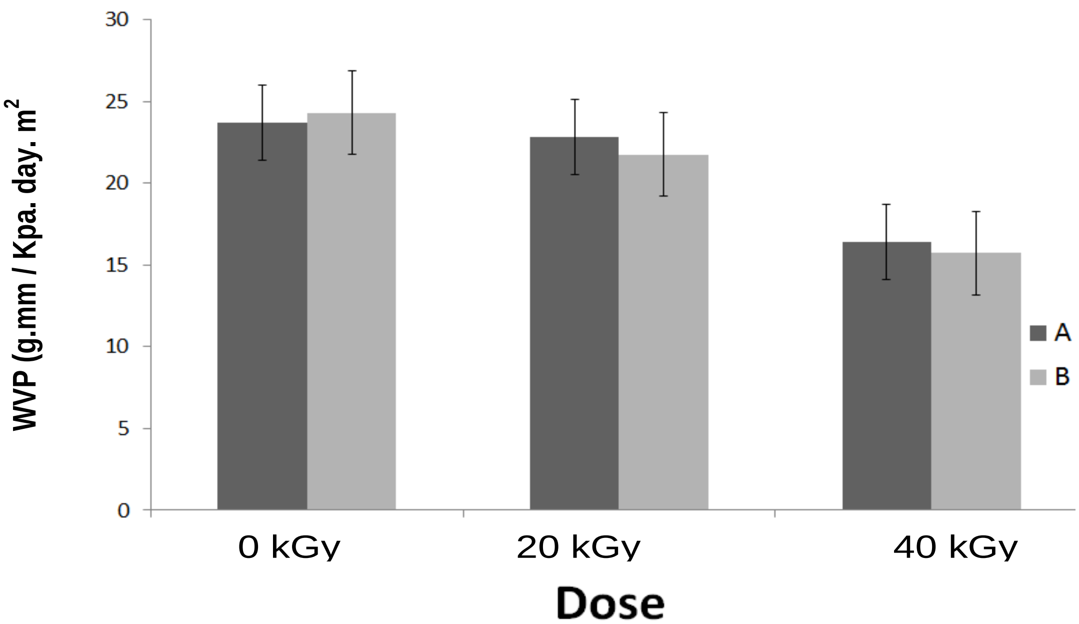

Figure 2: WVP as a function of EB radiation dose of the two blends (A and B) made of cassava starch and isolate soy protein.

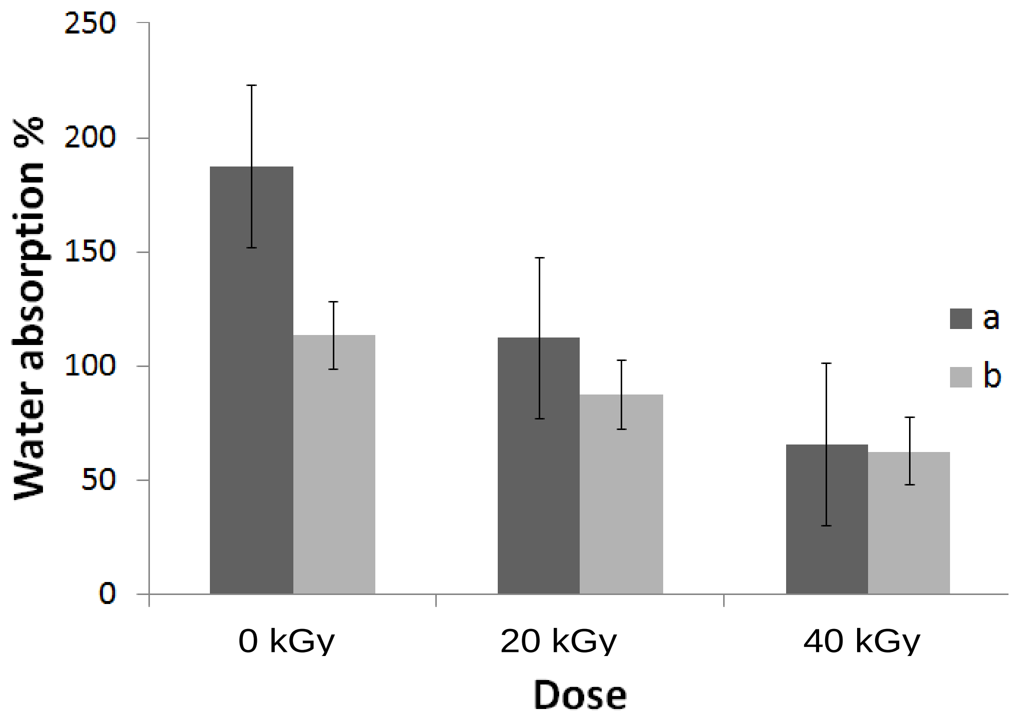

Figure 3: Water absorption as a function of EB radiation dose of two types of blends (A and B) made of cassava starch and isolate soy protein.

(Gutierrez et al., 2015). Figure 2 displays the results of WVP tests for the 2 types of blends of cassava starch and isolate soy protein. A dose of 20 kGy of EB radiation did not alter the WVP; however, the highest dose applied (40 kGy) induced a decline.

Water absorption

Figure 3 shows the results of measurement of water absorption of the two types of cassava starch/isolate soy protein blends displayed. A significant decrease as a result

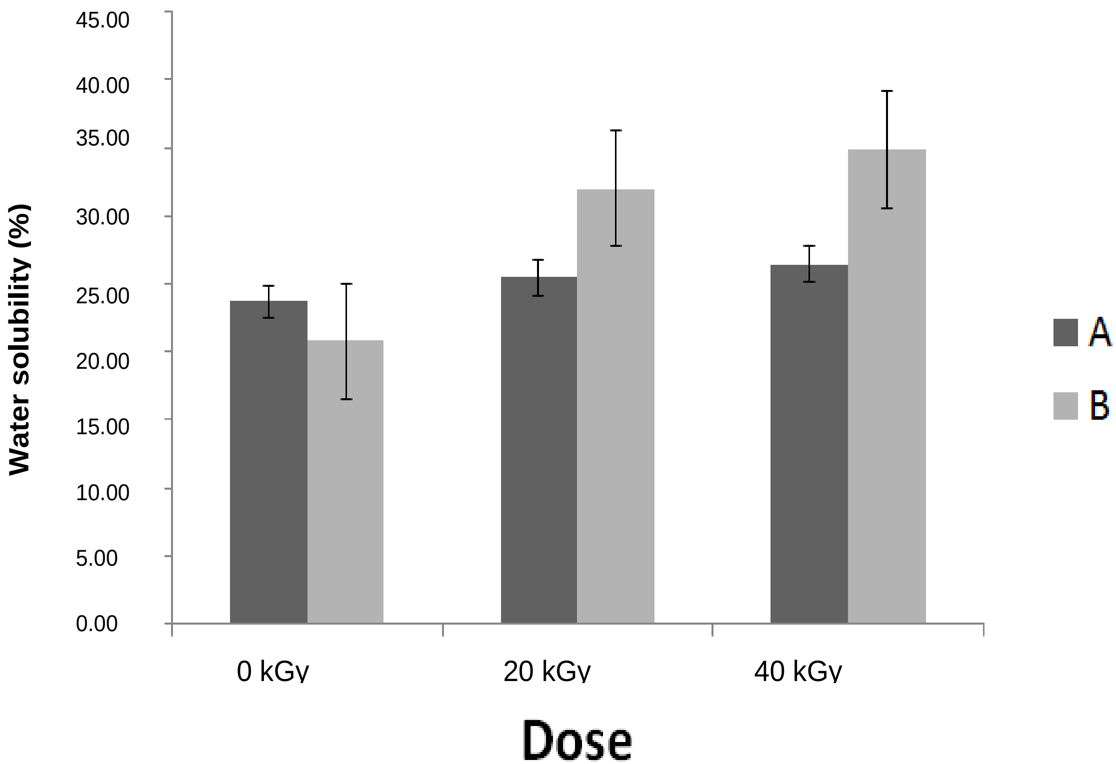

Figure 4: Water solubility as a function of EB radiation dose of A and B cassava/isolate soy protein blend films.

Table 2: Color parameters as a function of EB radiation dose of cassava/isolate soy protein blend films.

Parameter	Sample	Dose (kGy)		
		0	20	40
L*	A	93.47 ± 0.7	92.70 ± 0.3	92.52 ± 0.7
	B	84.9 ± 2.2	82.95 ± 2.2	79.31 ± 1.4
a*	A	- 1.40 ± 0.9	-1.53 ± 0.6	-1.55 ± 0.5
	B	- 0.04 ± 2.7	-0.09 ± 0.4	-1.04 ± 0.5
b*	A	10.76 ± 0.4	13.53 ± 0.5	14.5 ± 0.7
	B	12.99 ± 2.0	23.56 ± 5.4	27.83 ± 1.2
Chroma	A	10.85 ± 0.5	13.62 ± 0.3	14.62 ± 0.4
	B	12.99 ± 2.0	24.1 ± 5.5	27.87 ± 1.3
Hue angle	A	97.41 ± 0.3	96.45 ± 0.4	96.08 ± 0.6
	B	180.00 ± 1.6	179.21 ± 1.7	178.53 ± 5.3

of EB irradiation treatment is evident for both samples.

Solubility

Figure 4 shows the water solubility of the two types of cassava and isolate soy protein. As natural blends like the present ones aim at producing edible coating or packaging, an increase in solubility of nutritious components are not necessarily a limitation.

Color

Table 2 displays the parameters related to color measurements. The yellowness is notoriously intensified when samples (A and B) were irradiated.

Thermal analysis (TGA)

Thermogravimetric analysis or thermal gravimetric

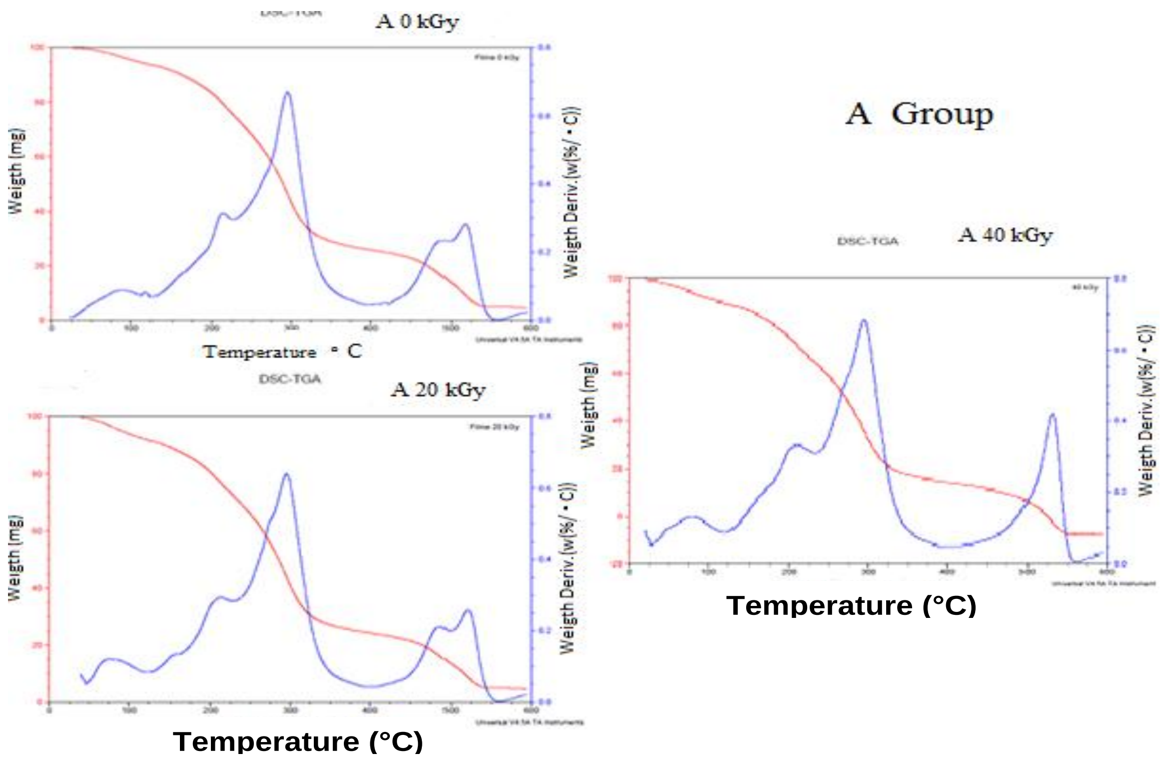

Figure 5: TGA of de biofilms of cassava/isolate soy protein blend films, samples A.

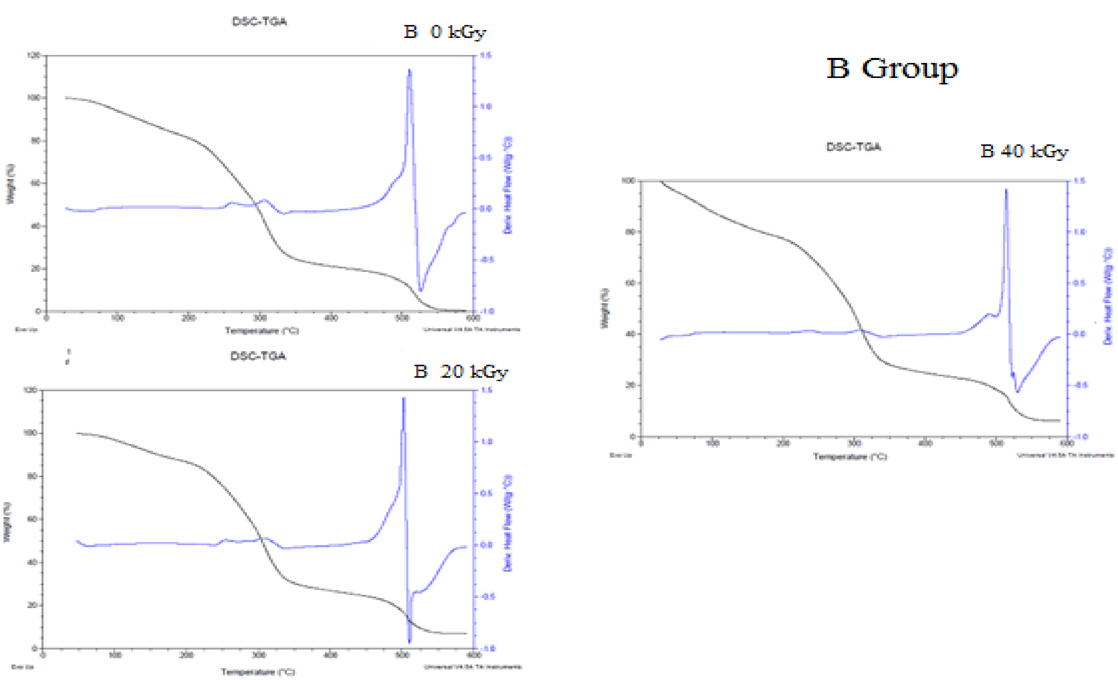

Figure 6: TGA biofilms of cassava/isolate soy protein blend films of samples B.

analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate). The characteristic decomposition patterns of sample A (Figure 5) and sample B (Figure 6) of mass loss is attributed mainly to decomposition or loss of volatiles such as moisture and are quite similar among irradiated and non - irradiated samples.

Conclusion

The present result shows a preliminary employment of EB treatment on a nutritious starch/protein based films opening a wide array of research possibilities in terms of blend composition, radiation dose or irradiation conditions.

Sustainable packaging is an important part of the food system innovation that is able to influence the purchase decision for the fresh produce. Biopolymers fulfill environmental concerns, but they also show some limitations in terms of performance, barrier and mechanical properties. In this article, examples of films prepared with a blend of two plants derived natural polymers; cassava starch and isolate soy protein were introduced with the potential to be used in food industry.

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