BIODEGRADABLE FOAM TRAYS OBTAINED FROM MIXTURES OF NON-IRRADIATED AND IRRADIATED CASSAVA STARCHES

A. J. C. Brant[1,2], N. Naime[1,2], A.B. Lugão[1], P. Ponce[1,2]

[2] Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN)
Av. Professor Lineu Prestes 2242
05508-000 – São Paulo – SP, Brazil
thonybrant@gmail.com

[2]*Bio&Green Ltda.*
Rua Pelotas, 557 A
04012-002 – São Paulo – SP, Brazil
patiponce@gmail.com

ABSTRACT

Biodegradable polymers, such as starch, cellulose, PHB, PLA, and derivatives thereof, are being studied to produce innovative packaging in the most diverse shapes (films, bags, trays, bottles, etc.) to attend this current market trend. The aim of this work was to produce foam trays from cassava starch for food packaging by extrusion-thermopressing process. Their formulations were based on non-irradiated and γ-irradiated starches at diverse radiation absorbed doses (kGy) in order to evaluate the influence of the irradiated starches on the physical properties of the trays. Water absorption results showed an irregular increase with the increase of the absorbed dose: 26.32% and 39.84% for the trays based on starch 0 kGy and 1:1 (w/w) mixture of starches 0 kGy and 100.0 kGy, respectively. Other physicochemical properties were evaluated from the starches utilized and the trays obtained.

1. INTRODUTION

In the last two decades, there has been an increase of commercial and academic interest in synthesizing or developing biodegradable polymers, mainly to produce packaging from renewable resources. Biodegradable polymer is every natural or synthetic polymer that can be decomposed by microorganisms (bacteria, fungi, algae) in favorable environments in terms of temperature, aeration, humidity, and other conditions. Its total decomposition leads to release of CO_2 and H_2O molecules and formation of a biomass over a specific period of time [1]. This definition still continues a little unclear in the academic medium due to the inherent complexity of the subject, especially in relation to the conditions of biodegradation environment. Biodegradable packaging, despite having some use limits, could be at least a good alternative to lessening the environmental-impact solid waste in the planet.

Among the natural polymers from renewable resources, starch and its respective derivatives have encountered growing interest in their use as packaging. However, these polysaccharides have poor mechanical properties and are quite hydrophilic to be straightly employed as packaging in any shape (film, bottle, cup, tray, other) [2]. Development and production of starch-based trays to replace those from expanded polystyrene (EPS) for food packaging constitute an innovative subject that appears to be promising [3].Glenn et al. [4] have reported numerous advances in starch-based packaging, focusing on foams, but pointed out that the improvement of their physical properties (barrier, water absorption, elongation to rupture, others) demands incorporation of other polymers in their formulation, that is,

formation of blends. For this case, poly(vinyl alcohol), despite being a synthetic polymer, appears to be a good choice once it is compatible with starch, has higher mechanical strength than this natural polymer and is totally biodegradable. Hence, several challenges related to the trays' quality may emerge due to various chemical and physical properties inherent to native starch, for instance, its high water absorption. This implies in a poor barrier property for its straight use as packaging for foods.

Starch is a mixture of linear and branched 1,4-α-D-glucopyranose biopolymers, called amylose and amylopectin, respectively. Amylose is an essentially linear (l→4)-linked α-D-glucan, whereas amylopectin is a highly branched macromolecule consisting of short chains of (1→4)-linked α-D-glucose with (1→6)-α-linked branches [5]. This polymer originates from various renewable resources (potato, rice, corn, cassava, arrowroot, others), and its use encompasses foods, drug encapsulation, paper adhesives, textile sizing, and in many other applications. For instance, corn starch and its derivatives have been used in the development of biodegradable disposable packaging , domestic and commercial utensils in the most varied shapes — films and trays for food packaging, plastic containers, cups, tableware, etc. [6].

 Effects of ionizing radiation on polymers are a subject of increasing interest in research and development of novel polymeric materials once their chemical and physical properties are quite affected, mainly by induction of crosslinking and / or degradation reactions. Other implications, such as, crystallinity grade changes, isomerization also may occur [7]. In relation to starch, this polymer undergoes breaking of its glycosidic bonds — degradation — [8, 9], besides having possible modifications of its crystalline structure as well. Literature concerning starch films for food packaging has reported increase of their tensile strength and barrier properties after subjected to ionizing radiation exposure [10, 11].

The aim of this work was to produce, by extrusion-thermopressing process, biodegradable foam trays from cassava starch, containing in their formulations non-irradiated starch aqueous gel, non-irradiated starch, a glycol-based plasticizer, and starch γ-irradiated at diverse radiation absorbed doses. Afterwards, to evaluate the influence of the irradiated starches on some physicochemical properties of the trays, such as barrier against water, compression strength, flexibility, and other properties of the trays destined for food packaging.

2. EXPERIMENTAL

2.1.Materials

 Cassava starchpowder (Companhia Lorenz – Paraná State – Brazil); glycerol (Labsynth – São Paulo – Brazil); tapwater.

2.2. Methods

2.2.1. Starch irradiation

Cassava starch powder was irradiated at absorbed doses of 25.0, 50.0, and 100.0 kGy on a sealed ^{60}Co source of γ-rays at EMBRARAD (Cotia – SP – Brazil) with an absorbed dose rate of 5.0 kGyh^{-1} in presence of air at room temperature (ca. 25°C).

2.2.2. Batter preparation

Batches of 3.0 kg of each formulation were prepared by mixing 40% of non-irradiated starch, 40% of γ-irradiated starch, followed by addition of 19% of tap water and 1% of glycerol, being all proportions by weight. For this operation a stainless steel mixer (from MH EquipamentosLtda, Guarulhos – SP – Brazil) of 8.0 L capacity was used, equipped of a double helice, and working for 3 min at 1100 rpm and RT. As reference, only non-irradiated starch (80%, w/w) was used together with the same components of the mixtures containing the γ-irradiated starches.

2.2.3.Trays' molding

A mixture of 1:1(w/w) of each γ-irradiated starch and non-irradiated starch was prepared. Next, an aqueous starch gel prepared apart and glycerol were added to the mixture under mechanical stirring up to attainment of a consistent mass for extrusion on a single-screw extruder (built by GFC Indústria e Comércio Ltda., São Paulo - SP) equipped with 3 heating zones (60°C, 80°C, 90°C) ,working at 45 rpm. Afterwards, the extruded mass was heat-pressed — 65.00-75.00 g for the control, i.e. based on non-irradiated starch, and ca. 60.00 g for those based on the two starch types — on an appropriate teflon-coated stainless steel mold at 190-195°C and ca. 1 MPa for 80 s. Foam formation occurs during water elimination by fast evaporation from the batters and consequent expansion of these. The obtained trays were identified as Bj15 (St 0 kGy), Bj30 (St 25 kGy), Bj31 (St 50 kGy), Bj32 (St 100 kGy).

2.2.4. Compression strength–flexibility

After production, the foams formed after elimination of water by evaporation were conditioned at 23°C and 60% RH for 3 days before mechanical testing. They were cut into rectangular shapes (10 cm x 4 cm), being 6 specimens of each formulation. For this assay, a TA.XT2i texture analyzer from Stable Micro Systems was used, equipped with a cylindrical probe of 36 mm diameter and an annular support of 63 mm diameter. The compression speed was 1.00 mm/s with a trigger force of 25 g. The final results were taken as the numerical average of each six-specimen set and expressed in compression strength (N) and displacement of the probe up to the specimen rupture (mm), i.e. distance /flexibility.

2.2.5. Barrier properties of the foams – water absorption

 After production, the foam trays selected for barrier testing tests were conditioned at ca. 23°C and RH (relative humidity) of 60% for 3 days, at least. In this testing, each tray was weighed; next, 300 mL of distilled water were poured on it, and the system (tray - water) was kept for 10 s at room temperature. After this period, water was removed from the tray, and this was quickly dried by using an absorbent dry cloth, and weighed again. Two samples were used for each formulation. The amount of water absorbed by the foam was calculated by the equation

$$\text{Water absorption (\%)} = \frac{m_h - m_d}{m_h} x100 \qquad (1)$$

where: m_h = wet mass and m_d = dry mass. The final results were taken as the numerical average of the sample sets.

2.2.6. Aerobic biodegradation by mass loss

Biodegradability testing was performed based on the soil burial test. Two rectangular (5.0 cm x 7.0 cm x 0.3 cm) samples of each formulation (foams), previously weighed on a Shimazu analytical balance – model ., were separately buried in 500.0 g of a simulated soil (earth + sand + cow manure) kept inside duly identified beakers. The beakers containing the foams fully buried in the soil were stored in a closet with air circulation and temperature control (19° C to 21° C) at a an air relative humidity (RH) from 70% to 78%. After this procedure, every 7 days, the samples were dug up, cleaned, weighed on a digital scale, and usually photographed for a better control until extensive degradation of the polymer has occurred. To compensate losses of the soil moisture (ca.65%) by evaporation in this open system, 50.0 g of distilled water were added to the soil after the samples' evaluation   and for the continuity of the soil burial tests. The average mass loss (in %) of each duplicate was calculated for each foam formulation using the equation:

$$[(m_i - m_f)/m_i] \times 100 \qquad (2)$$

where m_i is the initial mass of the sample at the initial day   and m_f, the final mass of the sample measured at every 7 days.
On the 42nd day, the samples, after duly cleaned, were weighed and placed in a drying oven at $70^{o}C$ for 24 h. Thereafter, they were weighed again for calculation of their actual mass losses.

3 – RESULTS AND DISCUSSION

3.1. Processability and appearance of the trays

The processability of the batters based on starch mixtures on extrusion appeared to be easier than that of of the batter containing only non-irradiated starch, probably thanks to degradation of polymer by γ-radiation and the thermopressing process, resulting formation of parcels of low-molecular weight starch. In relation to appearance of the trays, some ruptured bubbles on their surfaces, mainly on those from starch mixtures visually were observed (Fig. 1) as well as trends in yellowing of the trays containing γ-irradiated starch. Such trends also may occur due to by-products from starch degradation reactions after chain radiolysis or oxidative reactions caused by non-inert atmosphere throughout radiolysis, enhanced with Maillard reactions [12, 13].

Figure 1. Appearance of trays molded from mixtures of non-irradiated and γ-irradiated cassava starches compared to that of a styrofoam tray from Brazilian market.

3.2. Compression strength – flexibility

Compression strength and distance run by the probe up to rupture of the sample clearly diminished under influence of γ-irradiated starch (50% by weight) with increasing radiation absorbed dose (Table 1).

Table 1: Results of compression strength (N) and flexibility/ distance (mm) of starch tray samples, measured at 23 ± 2^oC, RH (relative humidity) 60%

Tray sample	Compression strength (N)	Flexibility/distance (mm)
Bj15 (St 0 kGy)	33.01 ± 0.84	10.24 ± 0.28
Bj30 (St 25 kGy)	26.17 ± 3.34	10.35 ± 0.19
Bj31 (St 50 kGy)	19.22 ± 0.71	6.64 ± 0.08
Bj32 (St 100 kGy)	16.44 ± 2.08	5.74 ± 0.17

Such results suggest predominance of chain backbone scission and internal crystallinity changes of the polymer submitted to γ-radiation together with a partial depolymerization of starch components on the extrusion process [14].There was also a trend of diminishing the flexibility of the samples (except for Starch 25 kGy) with addition of irradiated starches, and this trend was proportional to the radiation absorbed dose.

3.5. Water absorption (%)

Results in Table 2 show a trend of an increase of water absorption with the increase of radiation absorbed dose by starch. It is an indicative of a growing presence of glycoside oligomers and other low-molecular weight products formed after the polymer having been γ-irradiated.

Table 2: Water absorption of foam trays,molded from mixtures of non-irradiated and γ-irradiated cassava starches

Tray sample	Water absorption at RT (%, w/w)
Bj15 (St 0 kGy)	26.32 ± 1.19
Bj30 (St 25 kGy)	30.83 ± 1.57
Bj31 (St 50 kGy)	44.29 ± 3.78
Bj32 (St 100 kGy)	39.84 ± 0.00

Therefore, the irradiated polymer tends to become more hydrophilic or hydrosoluble than the non-irradiated one. Moreover, along extrusion under high shear forces and subsequent thermopressing process of the starch batters, it is also possible to form such low-molecular-weight products owing to degradation [15].

3.6. Aerobic biodegradation of foam starch trays by mass loss

Fig. 2 exhibits average mass loss (in %), considered in absolute values, of starch foam samples by aerobic biodegradation throughout 42 days, time usually sufficient for 100% of pure-starch foam to be biodegraded, according to our routine experiments.
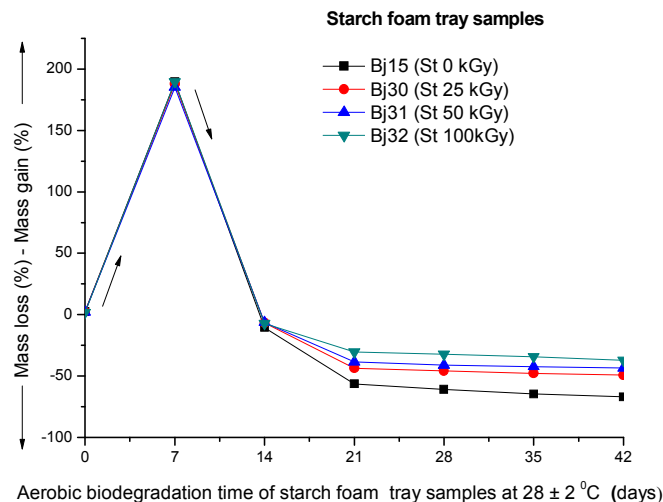

Figure 2: Aerobic biodegradation of starch foam trays evaluated by average mass loss (in %) throughout 42 days. Samples kept buried in organic soil (ca. 60% moisture) at 20 ± 1°C , and at ca. 74 ± 4% external RH.

During the first seven days, all starch samples surely has absorbed water from the humid soil gradually and swelled to a maximum, thus increasing their masses (mass gain: 189.6%, 187.9%, 185.2%, and 189.6% for Bj15 (St 0 kGy) , Bj30 (St 25 kGy), Bj31 (St 50 kGy), and BJ32 (St 100 kGy), respectively. It is due to high hydrophilicity of starch and glycerol. So, the losses registered in the graphic (Fig. 2) encompass starch together with water absorbed by each sample. On the 21st day, an abrupt mass loss of all the samples was registered, and thereafter the mass losses continued to occur, but gently up to the 42nd day in decreasing order: Bj15 (St 0 kGy)> Bj30 (St 25 kGy)> Bj31 (St 50 kGy)> BJ32 (100 kGy) in absolute values.

The average mass losses (in %) of samples formulated with γ-irradiated starches were slightly lower than those from the non-irradiated starch, diminishing with the increase of the γ-radiation absorbed doses by the polymer. Hypothetically, this fact may characterize presence of crosslinked parts in the irradiated polymer systems, which retard biodegradation [16]. The results either calculated or visually evaluated by photos (not shown) suggest that starch becomes slightly less susceptible to biodegradation after being submitted to γ-radiation. However, in the case of probable prevalence of scission reactions on the polymer chain [(Table 3, sample Bj32 (St 100 kGy)], biodegradation should occur at a higher level and a lesser time. This fact shows the complexity of interpreting such results with multiple variables acting concomitantly (enzymatic activity of microorganisms, changes of pH and humidity of soil, besides others). The average results of actual mass losses (in %) of the starch trays on the first and 42th day for each 2-specimen set are registered in Table 3.

Table 3:   Average mass loss (in %) of starch foam trays made of non- γ -irradiated starch and 1:1(w/w) mixtures of the latter with γ -irradiated starches at different radiation absorbed doses

Tray sample	Initial average mass on the first day (g)	Average mass on the 42nd day (g)	Average mass loss on the 42nd day (in %)
Bj15 (St 0 kGy)	2.4338	0.3127	87.15
Bj30 (St 25 kGy)	2.1734	0.4510	79.25
Bj31 (St 50 kGy)	2.1122	0.4993	76.36
Bj32 (St 100 kGy)	1.7618	0.3109	82.35

Note: On the 42nd day, samples were cleaned and weighed after drying at 70°C for 12 h up to constant weight.

Evaluation of the results using this methodology is not a so easy task once starch is partially soluble in water and becomes tacky in the humid soil, where it can be eroded, solubilized, and / or hydrolyzed. Moreover, the specimens were not dried after being unearthed for cleaning and weighing, except on the 42nd day (samples cleaned and weighed after drying at 70°C for 12 h up to constant weight) (Table 3). Hence, a total removal of dirty material adhered to the samples was almost impossible, what hindered us to make a precise estimate of the actual mass losses of them. Polynomial regression equations (2nd order) of data obtained from total biodegradation of the samples buried in soil forecast in these experiments: ca. 48 , ca. 53, ca. 54, and ca. 51 days for Bj15 (St 0 kGy) , Bj30 (St 25 k Gy),

Bj31 (St 50 kGy), and Bj32 (St 100 kGy), respectively. The results in Table 3 corroborate this prevision or trend.

4. CONCLUSIONS

Mixtures of γ-irradiated starch — at radiation absorbed doses of 25, 50, and 100 kGy — and non-irradiated cassava starches to mold biodegradable foam trays, in general, worsened the properties of barrier and the mechanical ones of the foamed product, displaying results of an increase of water absorption and a decrease of compression strength in comparison with those measured on trays made of only non-irradiated cassava starch. However, the processability on the extrusion of the batters containing irradiated starches showed to be better than for that containing only non-irradiated starch, probably due to the partial degradation and consequent lowering of molecular weight of the irradiated starch.

1- Aerobic biodegradation time by mass loss in soil burial increased at a little extension for the samples containing irradiated starch, and probably it is due to crosslinked polymer parcels present in them.

2- In the continuity of this work, new trays will be molded using in their formulations only non-irradiated cassava starch , a glycolic plasticizer, tap water, sugarcane bagasse and a little amount of mineral filler as reinforcing materials in order to enhance the physical properties of the foams**.** Even so, the finished product will be mechanically and chemically evaluated after sterilization by γ-radiation. However, in this case, by using radiation absorbed doses below 25 kGy , which supposedly do not compromise the structure of the polymer.

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