

GAMMA IRRADIATION EFFECT ON MECHANICAL AND BARRIER PROPERTIES OF FOAMED ARTICLES BASED ON CASSAVA STARCH

Natália Naime, Patrícia Ponce and Ademar B. Lugão

Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
nnaime@usp.br

ABSTRACT

With the increasing environmental concern, replacing the traditional non-biodegradable synthetic materials for biodegradable products is the challenge for many researchers and companies. Starch is considered one of the most promising natural polymers for packaging application because of its renewability, biodegradability and low cost. However, there are some limitations in developing starch-based products due to its poor mechanical properties and high moisture sensitivity. These properties can change when subjected to any process of sterilization, especially by gamma radiation. This work aims to study the mechanical and barrier properties of cassava starch in front of gamma radiation, for cobalt-60 (^{60}Co), when subjected to doses of 3 kGy, 6 kGy, 12 kGy and 25 kGy for the development of packaging, and then it compares the results to those of conventional packaging, as the expanded polystyrene (styrofoam) and paper cards. The starch foams (packaging) were obtained by thermopressing process. After baking, the foams were conditioned for one month at 23°C and 60% relative humidity (RH) before mechanical and barrier testing. Polyethyleneglycol (PEG 300) was selected as plasticizer. The packaging in which the cassava starch was subjected to irradiation had higher resistance to compression and higher flexibility compared to that in which the starch had not been irradiated. The expanded polystyrene and paper card packages are less resistant to compression than the cassava starch packages. The styrofoam is more flexible than the paper cards, which in turn is more flexible than packages of starch. After irradiation, the barrier properties of the foams were improved.

1. INTRODUCTION

Nowadays, the largest part of materials used in packaging industries are petroleum-based synthetic plastics and are practically *undegradable* – most plastics take more than 100 years for total degradation [1,2]. For this, packaging materials for foodstuff, like any other short-term storage packaging material, represent a serious global environmental problem [3]. Efforts are being made worldwide to search for biodegradable and renewable substitutes for non-biodegradable plastics.

One of the commodities that researchers have studied extensively for packaging application is starch. Starch is a renewable polymeric material, biodegradable and also abundant at low cost, which makes it attractive and a substitute for petroleum based plastics. Starch is comprised of linear amylose and branched amylopectin where the amounts of each vary according to the source and plant type [4].

The cassava (*Manihot esculenta* crantz) is one of the most cultivated vegetables in the world, being Brazil a major producer country [5]. Starch is the most abundant constituent of the cassava roots, obtaining from it the greatest number of applications and products - the food packaging production is a good example.

Due to its physical and chemical properties, different methods are used to process starch into packaging materials: extrusion, injection molding and film blowing, thermopressing solidification [6]. Moldings, such as plates, cups, trays, etc. can be manufactured in modified wafer baking equipment. Starch foams with insulating properties similar to polystyrene foam have been industrially developed by extrusion process [7]. Glenn and Orts described a method of forming molded starch foams with a cellular structure using a compression/explosion process [8].

The thermopressing process, which was used in this work, consists of equipment with two heated steel molds where dough starch (cassava starch and water) is placed in the bottom of a mold. The mold top can be hydraulically lowered to mate with the bottom half for a set amount of time, to spread the mixture on the mold surface. With heating, the water from mixture begins to evaporate and the starch granules expand and gelatinize it – transformation process of starch granular into viscoelasticity paste [9,10,11]. The steam causes the mass expansion and the whole mold is filled, leading to material solidification and obtaining the resulting foam, which can be removed, still hot, of the machine.

The disadvantage of the resulting materials is their fragility and their high affinity for water [12]. To overcome these weaknesses, various physical methods have been developed such as an association with additives [13,14], the application of accelerated electron beams [15] and gamma radiation [16]. Among these methods, gamma irradiation has become well known as a very convenient tool for the modification of polymer materials through a crosslinking, grafting and degradation techniques [17].

A number of advantages in the sterilization technology by gamma radiation: (i) sterilization of seal pre-packaged products, which prevent subsequent microbial re-infection and insect exposure [18]; (ii) high penetration depth and rate into the most unapproachable places of plastic containers; (iii) comparatively high mechanical resistance of irradiated packaging materials; (iv) simple process control; (v) possibility of material sterilization at room temperature (no heat exposure of sensitive products) [19].

Amylose and amylopectin diminish their degree of polymerization as a consequence of γ -radiation, as was shown by the increase of reducing sugars when the radiation dose increases from 0 to 30 kGy in native waxy and cassava [20], and in corn starch with amylose content up to 70% [21].

The objective of the present work is to study the mechanical and barrier properties of cassava starch foams (packaging) when this starch was subjected to doses of 3 kGy, 6 kG, 12 kGy and 25 kGy in front of gamma radiation, for cobalt-60 (^{60}Co), and then it compares the results to those of conventional packaging, as the expanded polystyrene (styrofoam) and paper cards.

2. EXPERIMENTAL PART

2.1. Materials

- Cassava starch purchased from Flor de Liz Inc.;
- Polyethyleneglycol (PEG 300) purchased from Labsynth Produtos para Laboratórios.

2.2. Production of Cassava Starch Foams

The starch foams were obtained by thermopressing a mixture of cassava starch, gel (cassava starch suspended in water [22]) and plasticizer to about 190°C. The cassava starch was suspended in water (5:100) and heated to 80°C with constant stirring, for 45 minutes until complete gelatinization of starch [22]. Then the suspension was naturally cooled and added to starch powder and the plasticizer polyethyleneglycol (PEG 300). The cassava starch and polyethyleneglycol were added to the gel in a laboratory mixer (capacity to two pounds of weight) for 3 minutes, approximately.

The thermopressing process consists in two parallel steel plates where dough starch (cassava starch, plasticizer and gel) is processed to form the structure by rigid joint swelling, gelatinization and network formation. After baking, the foams were conditioned for one month at 23 ° C and 60% relative humidity (RH) before mechanical and barrier testing. The plasticizer has been added to foam from renewable sources to improve the strength of packaging and increasing the resistance of the same water. According Rabello, a laminating of a polymer is to add the plasticizers to change the viscosity of the system, increasing the mobility of macromolecules [23].

The irradiation of starch powder (before thermopressing process), for future acquisition of foam described above, was performed by means of gamma radiation from a source of cobalt-60 (⁶⁰Co) at room temperature, being subjected to doses of 3 kGy, 6 kGy, 12 kGy and 25 kGy. The dose rate was 5.0 kGy / h.

Five formulations of foams (ST 0, ST 3, ST 6, ST 12 and ST 25) were developed with the same concentrations of cassava starch (57%), gel (41%) and polyethyleneglycol (2%), but differed as to the irradiation dose of starch: ST 0 = 0 kGy, ST 3 = 3 kGy, ST 6 = 6 kGy, ST 12 = 12 kGy and ST 25 = 25 kGy.

2.2.1. Stability of foams formulations

The stability of cassava starch foams in different formulations, produced in the laboratory, was calculated on the total amount of foam produced and the amount of foam formed with bubbles and/or cracks, representing their loss of production. Thus, for the production of each formulation, made the following calculation:

$$\% \text{ Loss of production} = \frac{\text{defectives foams}}{\text{total foams}} \times 100 \quad (1)$$

A table was designed to better analyze the results.

2.3. Mechanical Properties of the Foams – Compression Strength and Flexibility

After production, the foams were conditioned for one month at 23°C and 60% relative humidity before mechanical testing. For the analysis of compression strength and flexibility it was used a texturometer TA.XT2i of Stable Micro Systems with cylindrical probe of 36 mm diameter and an annular support for 63 mm diameter. The compression speed was 1.00 mm/s with compression force of 25 g. The samples of cassava starch foams were cut into rectangular shape, 10 cm x 4 cm. For each formulation were used six samples, taking the average in the end. Graphics (formulations versus force (N) and formulations versus distance (mm)) were constructed to better analyze the results.

2.4. Barrier Properties of the Foams – Solubility in Water

After production, the foams were conditioned for one month at 23°C and 60% relative humidity, before barrier testing. In the barrier test (solubility in water of foams) foam samples of cassava starch (14 cm x 9 cm) were weighed and immersed in 500 mL of distilled water for 10 seconds at room temperature. After this period, the samples were dried, using a dry cloth and weighed. For each formulation were used two samples, taking the average in the end.

The amount of water absorbed by the foam was calculated by the equation:

$$\text{Water absorption (\%)} = \frac{\text{mass (u)} - \text{mass (s)}}{\text{mass (s)}} \times 100 \quad (2)$$

where: mass (u) = wet mass and mass (s) = dry mass;

A table was designed to better analyze the results.

3. RESULTS AND DISCUSSIONS

3.1. Stability of Foams Formulations

The cassava starch foams were produced every two minutes, over a period of two hours, to verify the stability of the tested formulations (with the same concentrations of plasticizer, gel and starch, but differed as to gamma radiation dose). During this period, the minimum amount of mass was added to fill the entire mold and to form foams without bubbles and cracks.

The ideal formulation is the one that produces more stable foams, it means, the one with less variation in the amount of clay to form foams without bubbles and cracks during the whole period and with a minor loss of production. According Shogren et al. [24], Lawton et al. [25] and Zitny et al. [26], the ideal mass, it means, the more stable one, is that one which has enough viscosity to expand the mass inside the mold and retain in its structure the water vapor generated during the expansion process, thereby characteristics of foam. The following table shows us the loss of production by bubbles and cracks formations in the foams of irradiated cassava starch (at doses of 3 kGy, 6 kGy, 12 kGy and 25 kGy) and non-irradiated (0 kGy) with the same type and concentrations of plasticizer (polyethyleneglycol), starch and gel.

Table 1. Production lost results of the foams with irradiated and non-irradiated starch.

| Formulations* | Loss of production (%) |
|----------------------|-------------------------------|
| ST 0 | 0.00 |
| ST 25 | 17.9 |
| ST 3 | 44.4 |
| ST 12 | 60.7 |
| ST 6 | 71.4 |

*** Irradiated (at doses of 3 kGy, 6 kGy, 12 kGy and 25 kGy) and non-irradiated (0 kGy) starch with the same type and concentration of plasticizer (polyethyleneglycol), starch and gel: ST 0 = non-irradiated starch; ST 3 = irradiated starch at 3 kGy; ST 6 = irradiated starch at 6 kGy; ST 12 = irradiated starch at 12 kGy; ST 25 = irradiated starch at 25 kGy.**

As shown in Table 1, the production losses ranged from 0.00 to 71.4%. The formulation which the starch was irradiated at 6 kGy showed the greatest loss of production. The cassava starch when irradiated (ST 3, ST 6, ST 12 and ST 25 formulations) increased the production of bubbles and/or cracks in the foams, being less stable than the foams with non-irradiated starch (ST 0).

3.2. Mechanical Properties of the Foams – Compression Strength and Flexibility

The cassava starch foams were subjected to mechanical tests for compression strength and flexibility. For comparison effect we determined the strength and flexibility of expanded polystyrene and paper card packaging. The results are shown in Fig. 1.

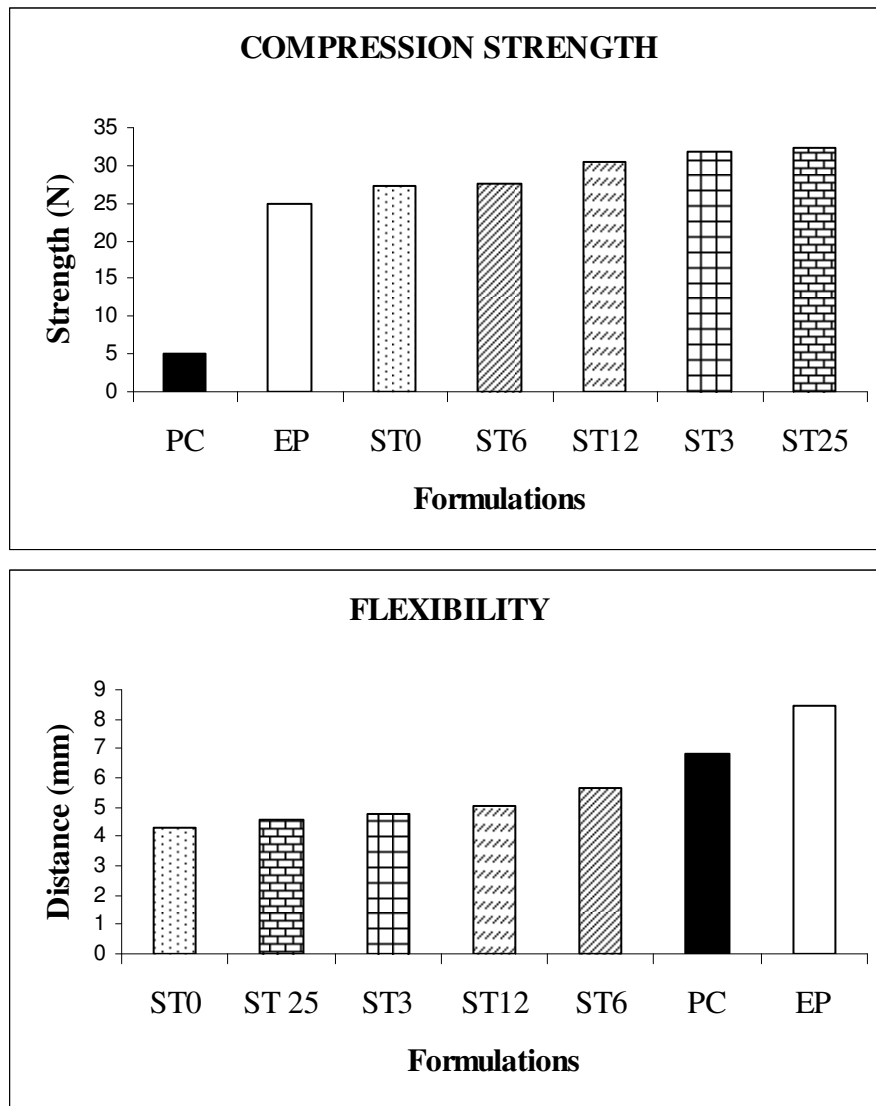


Figure 1. Compression strength and flexibility of the foams with irradiated and non irradiated starch and conventional packaging. ST 0 = non-irradiated starch; ST 3 = irradiated starch at 3 kGy; ST 6 = irradiated starch at 6 kGy; ST 12 = irradiated starch at 12 kGy; ST 25 = irradiated starch at 25 kGy; EP = expanded polystyrene; PC = paper card.

The conventional packaging were less resistant to compression than the cassava starch foams. The paper card (PC) was the less resistant packaging, corresponding to a force of 5.0 N, followed by the expanded polystyrene (EP = 25.0 N). The resistance of the foams ranged from 27.4 ± 2.29 N to 32.4 ± 2.02 N and the gamma radiation of cassava starch increased the foams resistance. The foams with non-irradiated starch (ST 0) presented a force of 27.4 ± 2.29 N while the foams of irradiated starch at 3 kGy, 6 kGy, 12 kGy and 25 kGy doses presented, respectively, forces of 31.9 ± 1.68 N, 27.6 ± 3.46 N, 30.6 ± 2.31 N and 32.4 ± 2.02 N. Therefore, it says that the higher radiation dose becomes the cassava starch foams more resistant. Zhai et al. reported that the tensile strength of dry starch-based plastic sheets increased with an increase of the irradiation dose in the dose ranges of 30-70 kGy, but when the dose was increased even more (>120 kGy), the tensile strength leveled off or decreased

slightly [27]. The authors explain that the improvement of tensile strength of starch-based plastic sheets attribute mainly to the crosslinking reaction of starch molecules [27]. Irradiation of natural polymers, carbohydrate or proteins, may improve the film strength [28]. However, the optimum target dose should be determined before an application because irradiation of natural polymers can result in both degraded and cross-linked polymers [29]. With regard to flexibility, even in Fig. 1, we found that conventional packages were more flexible than the foams of cassava starch. The expanded polystyrene and paper card presented flexibilities of 8.4 mm and 6.8 mm respectively, while the flexibility of the foams ranged from 4.27 ± 0.74 mm (ST 0), to 5.66 ± 0.79 mm (ST 6). As for the compression strength, the gamma radiation also increased the flexibility of the starch foams. The foams formulations which the starch was subjected to irradiation doses of 3 kGy (ST 3), 12 kGy (ST 12) and 25 kGy (ST 25) showed, respectively, flexibilities of 4.75 ± 0.45 mm, 5.07 ± 1.21 mm and 4.58 ± 1.43 mm. Percent elongation of starch-based plastic sheets decreased with an increase of the irradiation dose [28] – the same almost happened in this work if were not the foams with irradiated starch at 3 kGy (ST 3).

3.3. Barrier Properties of the Foams – Solubility in Water

The produced foams of cassava starch are totally soluble in water and packages of starch do not offer good quality of products in storage to remove water. As well as foams, starch films have been reported to be ineffective moisture barriers due to their hydrophilic nature [30]. Therefore, to improve the water-resistance properties of starch foams, the gamma irradiation treatment was implemented in this study.

In Table 2 are presented the results of water absorption by expanded polystyrene (EP) and by foams of irradiated (at doses of 3 kGy, 6 kGy, 12 kGy and 25 kGy) and non-irradiated cassava starch with the same type and concentrations of plasticizer (polyethyleneglycol), starch and gel.

Table 2. Results of the water absorption by expanded polystyrene and by foams with irradiated and non-irradiated starch.

| Formulations* | Water absorption (%) \pm SD |
|----------------------|---|
| EP | 3.42 ± 0.05 |
| ST 3 | 25.6 ± 1.75 |
| ST 6 | 26.2 ± 0.05 |
| ST 12 | 26.8 ± 1.05 |
| ST 25 | 27.4 ± 1.75 |
| ST 0 | 37.0 ± 0.15 |

*** Expanded polystyrene (EP) and irradiated (at doses of 3 kGy, 6 kGy, 12 kGy and 25 kGy) and non-irradiated (0 kGy) starch with the same type and concentration of plasticizer (polyethyleneglycol), starch and gel: ST 0 = non-irradiated starch; ST 3 = irradiated starch at 3 kGy; ST 6 = irradiated starch at 6 kGy; ST 12 = irradiated starch at 12 kGy; ST 25 = irradiated starch at 25 kGy.**

As shown in Table 2, the expanded polystyrene packaging (EP) has good barrier property, absorbing a very low amount of water when compared to the cassava starch packaging (ST). The foams which the starch has not been irradiated (ST 0) absorbed more water than those with irradiated starch (ST 3, ST 6, ST 12 and ST 25), and the absorbed amount of water increased with the increasing of irradiation dose of starch in the foams.

4. CONCLUSIONS

Despite the irradiation of cassava starch, using gamma radiation, at doses of 3 kGy, 6 kGy, 12 kGy and 25 kGy, have produced the least stable formulations, it improved the mechanical (resistance to compression) and barrier (solubility in water) properties of the foams when compared to foams with non-irradiated starch. The absorbed amount of water increased with the increasing of irradiation dose of starch in the foams but the same rule did not occur to the mechanical and barrier tests.

The conventional packaging were less resistant to compression and more flexible than the cassava starch packaging. The expanded polystyrene has much better barrier properties than the starch foams.

One way to increase the barrier properties of the expanded foams from cassava starch is to waterproof the trays with an also biodegradable film.

ACKNOWLEDGMENTS

The authors acknowledge the National Commission of Nuclear Energy (CNEN) for financial support, the Institute of Energy and Nuclear Research (IPEN) for offering useful equipment to the project, and suppliers of cassava starch – Flor de Liz Inc. - and reagents – Labsynth.

REFERENCES

1. S. Y. Lee; J. Choi, *Polymer Degradation and Stability*, p.387 (1998).
2. D. S. Rosa; N. T. Lotto; C. G. F. Guedes, *Polym. Test*, p.3 (2004).
3. M. J. Kinwan; J. W. Strawbridge, "Plastics in food packaging", *Food Packaging Technology*, p.174-240 (2003).
4. K. M. Dean; D. M. Do, "Key interactions in biodegradable thermoplastic starch/poly(vinyl alcohol)/montmorillonite micro and nanocomposites", *Composites Science and Technology*, **v.68**, p.1453-1462 (2008).
5. S. S. Butarelo; A. Beleia; I. C. B. Fonseca; K. C. Ito, "Hidratação de tecidos de raízes de mandioca (*Manihot esculenta* crantz) e gelatinização do amido durante a cocção", *Food Technology and Science*, **v.24** (2004).
6. T. Hofmann; L. Linke; A. Tsiapouris; A. Ziems, "Porous materials made from starch", *Chem. Eng. Technol.*, **v.21**, p.580-584 (1998).
7. P. Cinelli; E. Chiellini; J. W. Lawton; S. H. Iman, "Foamed articles based on potato starch, corn fibers and poly(vinyl alcohol)", *Polymer Degradation and Stability*, **v.91**, p.1147-1155 (2006).

8. G. M. Glenn; W. J. Orts, "Properties of starch-based foam formed by compression explosion processing", *Industrial Crops and Products*, **v.13**, p.135-143 (2001).
9. R. C. R. Souza; C. T. Andrade, *Polymers* (2000).
10. A. A. Ragheb; I. A. El-Thalouth; S. Tawfik, *Starch*, p.57 (1996).
11. A. Beleia; R. A. Miller; R. C. Hosney, *Starch*, p.259 (1996).
12. G. M. Glenn; W. J. Orts; G. A. R. Nobes, "Starch, fiber and CaCO₃ effects on the physical properties of foams made by a baking process", *Industrial Crops and Products*, **v.14**, p.201-212 (2001).
13. J. N. Coupland; N.B. Shaw; F. J. Monahan; E. D. O'riordan; M. O'sullivan, "Modeling the effect of glycerol on the moisture sorption behavior of whey protein edible films", *Journal of Food Engineering*, **v.43**, p.25-30 (2000).
14. M. A. Garcia; M. N. Martino; N. E. Zaritzki, "Lipid addition to improve barrier properties of starch-based films and coatings", *Food Chemistry and Toxicology*, **v.65**, p.941-947 (2000).
15. M. R. Nemtanu; R. Minea; K. Kahraman; H. Koksel; P. K. W. Ng; M. I. Popescu; E. Mitru, "Electron beam technology for modifying the functional properties of maize starch", *Nuclear Instruments & Methods in Physics Research*, p.795-798 (2007).
16. J. K. Kim; C. Jo; H. J. Park; M. W. Byun, "Effect of gamma irradiation on the physicochemical properties of a starch-based film", *Food Hydrocolloids*, **v.22**, p.248-254 (2008).
17. M. Lacroix; T. C. Le; B. Ouattara; H. Yu; M. Letendre; S. F. Sabato, "Use of γ -irradiation to produce films from whey, casein and soya proteins: structure and functional characteristics", *Radiation Physics and Chemistry*, **v.63**, p.827-832 (2002).
18. K. A. Riganakos; W. D. Koller; D. A. E. Ehrlmann; B. Bauer; M. G. Kontiminos, "Effects of ionizing radiation on properties of monolayer and multilayer flexible food packaging materials", *Radiat Phys Chem*, **v.54**, p.527-540 (1999).
19. P. G. Demertzis; R. Franz; F. Welle, "The effects of γ -irradiation on compositional changes in plastic packaging films", *Packag Technol Sci*, **v.12**, p.119-130 (1999).
20. J. J. Raffi; J. P. Agnel; C. J. Thieri; C. M. Fréjaville; R. L. Saint-Lève, "Study of γ irradiated starches derived from different foodstuffs: a way for extrapolating whole someness data", *J. Agric. Food Chem.*, **v.29**, p.1227-1232 (1981).
21. S. Dygert; L. H. Li; D. Florida; J. A. Thoma, "Determination of reducing sugars with improving precision", *Anal. Biochem.*, **v.13**, p.367-374 (1965).
22. P. A. Bobbio; F. O. Bobbio, "Material de embalagem", *Química de processamento de alimentos*, Campinas: Cargill Fundation, p.189-202 (1984).
23. M. Rabello, "Aditivacão de polímeros", São Paulo: Artliber Publisher (2000).
24. R. L. Shogren; J. W. Lawton; W. M. Doanne; F. K. Tiefenbach, *Polymer*, **v.39**, p.6649-6655 (1998).
25. J. W. Lawton; R. L. Shogren; K. F. Tiefenbach, *Cereal Chemistry*, **v.75**, p.682-687 (1999).
26. R. Zitny; J. Sestak; A. Tsiapouris; L. Linke, *Journal of Food Engineering*, **v.52**, p.375-385 (2002).
27. M. Zhai; F. Yoshii; T. Kume, "Radiation modification of starch-based plastic sheets", *Carbohydrate Polymers*, **v.52**, p.311-317 (2003).
28. J. K. Kim; C. Jo; H. J. Park; M. W. Byun, "Effect of gamma irradiation on the physicochemical properties of a starch-based film", *Food Hydrocolloids*, **v.22**, p.248-254 (2008).
29. T. Kume; N. Nagasawa; F. Yoshii, "Utilization of carbohydrates by radiation processing", *Radiation Physics and Chemistry*, **v.63**, p.625-627 (2002).
30. O. Martin; E. Schwach; L. Averous; Y. Coutrier, "Properties of biodegradable multilayer films based on plasticized wheat starch", *Starch/Starke*, **v.53**, p.372-380 (2001).