

Effect of electron beam irradiation on mechanical properties of gelatin/brazil nut shell fiber composites

Patrícia Y. Inamura^I; Kleber Shimazaki^I; Maria Aparecida Colombo^{II}; Ricardo de Rosa^{III}; Esperidiana Augusta Barretos de Moura^I; Nelida L. del Mastro^I

^I Instituto de Pesquisas Energéticas e Nucleares, IPEN -CNEN/SP, Av. Prof. Lineu Prestes, 2242, CEP: 05508-000, SP, Brazil

e-mail: patyoko@yahoo.com ; shimazakikleber@hotmail.com ; eabmoura@ipen.br ; nlmastro@ipen.br

^{II} Faculdade de Tecnologia da Zona Leste, Av. Águia de Haia, 2633, 03694-000, SP, Brazil

e-mail: mascolombo@yahoo.com.br

^{III} Amazon Brazil Nuts, Rua Heliópolis, 262 B, 05318-010 SP, Brazil

e-mail: ricardo@amazonbrazilnuts.com.br

ABSTRACT

The use of natural fiber as polymeric matrix reinforcement has attracted interest, as fibers are renewable, of low cost, biodegradable and possesses non-toxic properties. In the present paper, Brazil nuts (*Bertholletia excelsa*) shell fiber (10% w/w) were mixed with gelatin (25% w/w), glycerin as plasticizer and acrylamide as copolymer to investigate the resultant mechanical properties effects upon ionizing radiation. The samples were irradiated at 40 kGy using a Dynamitron electron beam accelerator, at room temperature in the presence of air. The results showed that samples of gelatin with 10% of Brazil nuts shell fiber and irradiated at 40 kGy presented promising results for mechanical performance.

Keywords: ionizing radiation, gelatin, natural fiber.

1 INTRODUCTION

One of the most viable alternatives to natural polymers is the development of composites to improve their physical and mechanical properties improvement [1]. Superior environmental performance evidence is a potential driver of increased natural fiber composites development. A thorough comprehensive analysis of the relative environmental impacts of natural fiber composites and conventional composites, covering the entire life cycle as well as potential future uses were already approached. Also, polymeric materials like proteins, carbohydrates and lipids have gained considerable research interest in the last decades [2, 3, 4].

Ionizing irradiation (gamma rays emitted by Co-60 source or electron beam produced by electron accelerators) is an important process for modifying polymers by cross-linking and/or degradation which occur simultaneously during irradiation. Free radicals are produced which can in turn lead to the release of gases, discoloration, changes in mechanical, thermal and barrier properties. Considerable modifications caused by radiation processing have found useful industrial applications. Cross-linking usually brings about an improvement in mechanical properties, chemical resistance, thermal stability and other important properties. Radiation can also induce polymeric degradation through chain scission leading to the reduction of molecular mass that can also reduce the polymer particle sizes [5-12].

Brazil nut (*Bertholletia excelsa*) is a Brazil nut tree that grows throughout the Amazon Basin that covers parts of Bolivia, Brazil and Peru [13-15]. Brazil nuts, also the name of the tree's commercially harvested edible seed, are considered to be one of the most valuable products that can be harvested from the undisturbed rainforest. The nuts, known to Brazilians as Castanha do Pará, grow uniquely in the Amazon basin.

The fruit from *B. excelsa* is characteristically a spherical capsule, with a thick and hard surface dark brown in color. When mature, the capsule releases seeds through the lower portion. Each capsule contains between 14 and 24 seeds inside, surrounded by yellow pulp. The fruits are hazardous to collect: each hard outer shell weighs over 1 kg. Brazil nut is an angular nut with a very hard hull. A tree may produce more than

150 kg of nuts/year. The species is propagated naturally. Brazil nuts for international trade come entirely from wild collection rather than from plantations. This has been advanced as a model for generating income from a tropical forest without destroying it. The nuts are gathered by migrant workers known as castanheiros. The Brazil nut almond is very white, with dark brown tegument with a high energy content and rich in proteins of high biological values [13, 16]. The Brazil nut is one of Amazon fruits with higher socio-economic relevance. According to Aires *et al.* [15]. Brazil nuts represent among 30 million U.S. dollars annual exports. Moreover, mostly all production is exported, in shell or shelled, mainly to the United States and the United Kingdom [17]. The internal market consumption of nuts is too small, estimated in only 1% of the production [18, 19].

Although the Brazil's nuts market grows continuously the nut shell fiber residues have no further application. The search for alternative technologies is crucial for the utilization of by-products from Brazil nuts processing, with the aim of developing new products with high added value. Primary organic components of any nutshells are cellulose, hemicellulose and lignin. This sort of material could be used as reinforcement to enhance polymer mechanical properties, as other natural fibers employed with the same objective showed encouraging results [20, 22].

Gelatin is the partially renatured collagen, which consists of triple helical superstructure of extended polypeptide chains. It has been widely used as binder or coating materials in the pharmaceutical, biomedical and photographic industries. Gelatin is an interesting material because when dehydrated it is a partially crystalline polymer and has a relatively low melting point [23]. At approximately 40°C, gelatin aqueous solutions are in the sol state and form physical, thermoreversible gels on cooling. During gelation, the chains undergo a conformational disorder–order transition and tend to recover the collagen triple-helix structure [24, 25]. Gelatin films with plasticizer have sufficient stability, strength and flexibility to allow them to be used as support and packaging materials.

The aim of this work was to investigate the mechanical behavior of specimens prepared with Brazil nut shell fiber and gelatin together with glycerin as plasticizer and acrylamide as copolymer treated by electron beam radiation.

2 EXPERIMENTAL

2.1 Material

Bovine skin gelatin was kindly donated by GELITA do Brasil Ltda, 240Bloom/6 mesh, lot: LF21658 05 and Art Mono Acrylamide H, from Aratrop Industrial. Glycerin PA ACS, cod. 15375 were provided by Casa Americana de Art. Lab. Ltda (CAAL). Brazil nut shell fiber from the residues disposed by the processing industries of Brazil nuts was provided by Amazon Brazil Nuts.

2.2 Preparation and Incorporation of Brazil nut shell fiber in gelatin

Initially Brazil nut shell fiber was washed in distilled water for 24 h to remove impurities. The fiber was oven dried at 80 ± 2 C. The dry fiber was reduced to fine powder, with particle sizes equal or lower than 250 μm by using ball mill. The specimens of gelatin reinforced with 10% of Brazil nut shell fiber were prepared by dissolving glycerin as plasticizer (20 % w/w), acrylamide as copolymer (25% w/w) and gelatin (25% w/w) in distilled water in a water bath at 80 C. After homogenization, the fibers were added during stirring for 30 minutes.

2.3 Electrom-beam Irradiation

Samples of gelatin reinforced with Brazil nut shell fiber were irradiated using an electron beam accelerator (Dynamitron II, Radiation Dynamics Inc.), at room temperature, in the presence of air, dose rate 2.81 kGy/s, energy 1.202 MeV, beam current 0.62 mA, tray speed 6.72 m/min, being 40 kGy the applied dose: The dosimetry was done with cellulose triacetate film dosimeters "CTA-FTR-125" from Fuji Photo Film Co. Ltd. After irradiation, samples were kept in plastic bags and stored in a dry ambience in the dark to avoid the influence of natural light.

2.4 Mechanical Properties

The materials were compression-molded into plastic tensile bars and tested for tensile and yield strength, percentage elongation and capability of return to normal shape after stretching (resilience). Tensile strength tests were performed according to ASTM D 638-99 [26] from printed plate. Mechanical properties

were measured with a Microcomputer Controlled Electronic Universal Testing Machine (model WDW20 of Time Group Inc, China), using 50 mm of gage length, specimen type IV and a speed test of 5 mm/min.

Hardness properties were measured in a Universal Hardness Testing Machine (model ZHU 250 of Zwick Roell Testing Machines Pvt Ltd, Chennai, Tamil Nadu, India) by Shore type A durometer according to ASTM D 2240-00 [27], using a mass of 1 kg and indenter diameter of 0.79 ± 0.03 mm.

3 RESULTS AND DISCUSSION

The mechanical properties of gelatin/Brazil nut shell fiber composite (CP10%) irradiated by electron beam with 40kGy are shown in Table 1. A tensile strength at yield value of 1.18 MPa was obtained.

Table 1: Mechanical properties of the composite containing Brazil nut shell fiber 10% at 40kGy radiation dose.

Mechanical Properties	40 kGy
Tensile strength at yield (MPa)	1.18 ± 0.01
Elongation at yield (%)	61.34 ± 0.01
Resilience (J)	0.07 ± 0.01

Gelatin/Brazil nut shell fiber composite (CP10%) showed an elongation at yield of 61.34%. Haroun *et al.* [3] described composite films based on gelatin and collagen with 40.8% of elongation at yield for gelatin/low density polyethylene (1:1) samples. Furthermore, they expected low stress values at yield for composite films to confirm their brittle behavior, because of a poor adhesion between copolymerized polyethylene and gelatin or collagen (amorphous component).

The observed CP10% resilience property was 0.07 J. As comparison, data from the literature [4] show that when sisal/oil palm fibers loading increased in the rubber matrix stiffer and harder composites resulted. In that example, value of elongation at break, showed a reduction with increasing fiber loading and consequently, reduced the composite's resilience and toughness and lead to lower elongation at break.

The information about the viscoelastic behavior of polymers can be obtained by Shore A hardness test [27]. Delayed readings are more representative of not only the hardness of the material, but the resiliency. Taking as reference the time specified by ASTM D 2240 to read the Shore A hardness value, it was observed (Figure 1) that the gelatin/nut shell fiber composite presented shore A hardness of 30. After five seconds the same sample, submitted under the same conditions, showed shore A hardness values, 24, lower than at the beginning of the test.

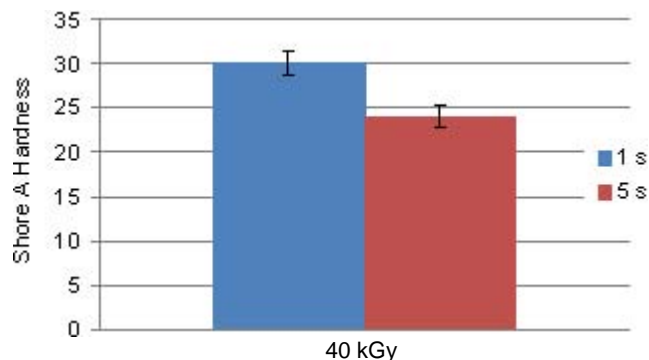


Figure 1: Shore A hardness of composite containing 10% Brazil nut shell fiber, electron beam irradiated with a dose of 40 kGy.

The hardness of a material is often one of the first criteria considered when choosing a thermoplastic elastomer. High molecular weight polyester urethanes sheets showed Shore A hardness values in the range of 25-33 which were grouped as hard materials. It was considered that the increase in hardness was due to the increase of polymer concentration and higher molecular weight of polyurethanes [28]. Ferrite– natural rubber composite exhibited a disposition to Shore hardness increase with increasing filler content from 37 to 44 varying the filler loading (phr) from 0 and 120 [29].

There are other works already published about the employment of gelatin in the fabrication of polymeric networks [30-33]. A full interpenetrating networks of polyacrylonitrile based in gelatin gave a hard biopolymer according the results of Rajvaidya *et al.* [30] published in 2007.

4 CONCLUSION

This study presents preliminary results on the mechanical properties of gelatin/Brazil nut shell fiber composite prepared by polymer reinforced with natural fiber, plasticizer and treated by electron beam radiation. The mechanical properties observed in the irradiated gelatin/Brazil nut shell fiber composite indicate that electron beam irradiation can be a potential process for gelatin/Brazil nut shell fiber composite production to be used, for instances, as elastomers substitutes.

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6 REFERENCES

- [1] GUIMARÃES, J.L., SATYANARAYANA, K.G., WYPYCH, F., RAMOS, L.P., “Preparo de compósitos biodegradáveis a partir de fibras de bananeira plastificadas com amido e glicerina bruta derivada de alcoólise de óleos vegetais”, *Biodiesel*, pp. 28-33, 2006. Biodiesel, Governo Federal. <http://www.biodiesel.gov.br/docs/congressso2006/Co-Produtos/PreparoCompositos6.pdf>. Accessed in: 02/02/2010.
- [2] JOSHI, S.V., DRZAL, L.T., MOHANTY, A.K., ARORA, S., “Are natural fiber composites environmentally superior to glass fiber reinforced composites?”, *Composites: Part A*, v. 35, pp. 371-376, 2004.
- [3] HAROUN, A.A., BEHEREI, H.H., EL-GHAFFAR, M.A.A., “Preparation, characterization, and in vitro application of composite films based on gelatin and collagen from natural resources”, *Journal of Applied Polymer Science*, v. 116, pp. 2083–2094, 2010.
- [4] JACOB, M., THOMAS, S., VARUGHESE, K.T., “Mechanical properties of sisal/oil palm hybrid fiber reinforced natural rubber composites”, *Composites Science and Technology*, v. 64, n. 7-8, pp. 955-965, 2004.
- [5] SONNTAG, C., “Trends of research in radiation chemistry”, *In: IAEA, Advanced Radiation Chemistry Research: Current Status, IAEA-TECDOC-834*, International Atomic Energy Agency, Vienna, pp. 11-41, 1995.
- [6] BUCHALLA, R., SCHÜTTLER, C., BÖGL, K.W., “Effect of ionizing radiation on plastic food packaging materials: a review. Part 1: chemical and physical changes”, *Journal of Food Protetions*, v. 56, n. 11, pp. 991-997, 1993.
- [7] KHAN, F., AHMAD, S.R., KRONFLI, E., “Stability of jute fibres on exposure to ionising radiation”, *Polymer Degradation and Stability*, v. 63, pp. 79-84, 1999.
- [8] CHOI, H.Y., HAN, S.O., LEE, J.S., “Surface morphological, mechanical and thermal characterization of electron beam irradiated fibers”, *Applied Surface Science*, v. 255, pp. 2466-2473, 2008.
- [9] NAGASAWA, N., KANEDA, A., KANAZAWA, S., YAGI, T., MITOMO, H., YOSHII, F., TAMADA, M., “Application of poly (lactic acid) modified by radiation crosslinking”, *Nuclear Instruments and Methods in Physics Research B*, v. 236, pp. 611–616, 2005.
- [10] DORSCHNER, H., LAPPAN, U., LUNKWITZ, K., “Electron beam facility in polymer research: radiation induced functionalization of polytetrafluoroethylene”, *Nuclear Instruments and Methods in Physics Research B*, v. 139, pp. 495-501, 1998.

- [11] MACHI, S., “New trends of radiation processing applications”, *Radiation Physics and Chemistry*, v. 47, n. 3, pp. 333-336, 1996.
- [12] DORSCHNER, H., LAPPAN, U., LUNKWITZ, K., “Electron beam facility in polymer research: radiation induced functionalization of polytetrafluoroethylene”, *Nuclear Instruments and Methods in Physics Research B*, v. 139, pp. 495-501, 1998.
- [13] VIANNA, P.R., “Estudo da castanha-do-Brasil”, Brasília, Ministério da Agricultura, Comissão de Financiamento da Produção, 1972.
- [14] SOUZA, M.L., MENEZES, H.C., “Processamentos de amêndoa e torta de castanha-do-Brasil e farinha de mandioca: parâmetros de qualidade”, *Ciência e Tecnologia de Alimentos*, v. 24, n. 1, pp. 120-128, 2004.
- [15] SOUZA, M.L., MENEZES, H.C., “Extrusão de misturas de castanha do Brasil com mandioca”, *Ciência e Tecnologia de Alimentos*, v. 28, n. 2, pp. 451-462, 2008.
- [16] FELBERG, I., ANTONIASSI, R., DELIZA, R., FREITAS, S.C., MODESTA, R.C.D., “Soy and Brazil nut beverage: processing, composition, sensory, and color evaluation”, *Ciência e Tecnologia de Alimentos*, v. 29, n. 3, pp. 609-617, 2009.
- [17] AIRES, J., MAGALHÃES, J.M., HESSE, S.R., SANTOS, J.C.F., “Proposta-base das diretrizes para formulação de um programa de incentivo à produção de castanha-do-Brasil (*Bertholletia excelsa* - H.B.K.)”, In: *Encontro Brasileiro de Engenheiros Florestais*, Rio de Janeiro, pp. 143-150, 1986.
- [18] RIBEIRO, M.A.A., “Aproveitamento tecnológico de castanhas do Brasil (*Bertholletia excelsa*): estudo da qualidade de conservação”, Dissertação de M.Sc., Piracicaba, pp. 117p - Escola Superior de Agricultura “Luiz de Queiroz”, Universidade de São Paulo, 1992.
- [19] RIBEIRO, M.A.A., SOLER, R.M., REGITANO-D’ARCE, M.A.B., LIMA, V.A., “Shelled Brazil nuts canned under different atmospheres”, *Ciência e Tecnologia de Alimentos*, v. 15, n. 2, pp. 105-107, Jul/Dez, 1995.
- [20] SCHUCHARDT, U., BIANCHI, M.L., GONÇALVES, A.R., CURVELO, A.A.S., BISCOLLA, F.C., PERES, L.O., “Piassava fibers (*Attalea funifera*): I. Chemical analysis, extraction and reactivity of its lignin”, *Cellulose Chemistry and Technologies*, v. 29, pp. 705-712, 1995.
- [21] AQUINO, R.C.M.P, D’ALMEIDA, J.R.M., MONTEIRO, S.N., “Propriedades de compósitos de piaçava com matriz polimérica”, In: *55º Congresso Anual da ABM*, pp. 2898, Rio de Janeiro, RJ, 2000.
- [22] BONELLI, C.M.C., ELZUBAIR, A., MARTINS, H.R., SUAREZ, J.C.M., MANO, E.B., “Utilização de fibras de piaçava como reforço em compósitos de matriz polimérica reciclada”, In: *58º Congresso Anual da ABM*, pp. 1778, Rio de Janeiro, 2000.
- [23] DAI, C.A., LIU, M.W., “The effect of crystallinity and aging enthalpy on the mechanical properties of gelatin films”, *Materials Science and Engineering A*, v. 423, pp. 121-127, 2006.
- [24] SOBRAL, P.J.A., HABITANTE, A.M.Q.B., “Phase transitions of pigskin gelatin”, *Food Hydrocolloids*, v. 15, n.4-6, pp. 377-382, 2001.
- [25] ROSS-MURPHY, S.B., “Structure and rheology of gelatin gels. Recent progress”, *Polymer*, v. 33, n. 12, pp. 2622-2627, 1992.
- [26] ASTM - American Society for Testing Materials, Standard Test Methods for Tensile Properties of Plastics, D 638 -99, ASTM, 1999.
- [27] ASTM - American Society for Testing Materials, Standard Test Methods for Rubber Property – Durometer Hardness, D 2240 -00, ASTM, 2000.

- [28] SARASWATHY, G., GOPALAKRISHNA, G., DAS, B.N., MOHAN, R., RADHAKRISHNAN, G.; PAL, S., "Development of polyurethane-based sheets by coagulation method and study of mechanical and cushion properties for therapeutic footwear applications", *Polymer-Plastics Technology and Engineering*, v. 48, n. 3, pp. 239-250, 2009.
- [29] MAKLED, M.H., MATSUI, T., TSUDA, H., MABUCHI, H., EL-MANSY, M.K., MORII, M.K., "Magnetic and dynamic mechanical properties of barium ferrite-natural rubber composite", *Journal of Materials Processing Technology*, v. 160, n. 2, 20, pp. 229-233, 2005.
- [30] RAJVAIDYA, S., BAJPAI, R., BAJPAI, A.K., "Morphological, thermal and annealed microhardness characterization of gelatin based interpenetrating networks of polyacrylonitrile: A hard biopolymer", *Bulletin of Materials Science*, v. 28, n. 6, pp. 529-534, 2007.
- [31] SCHERZER, T., "Barrier layers against oxygen transmission on the basis of electron beam cured methacrylated gelatin", *Nuclear Instruments and Methods in Physics Research B*, v. 131, pp. 382-391, 1997.
- [32] GUL-E-NOOR, F., KHAN, M.A., GHOSHAL, S., MAZID, R.A., CHOWDHURY, A.M.S., KHAN, R.A., "Grafting of 2-ethylhexyl acrylate with urea on to gelatin films by gamma radiation", *Journal of Macromolecular Science, Part A: Pure Applied Chemistry*, v. 46, pp. 615-624, 2009.
- [33] APOSTOLOV, A.A., FAKIROV, S., EVSTATIEV, M., HOFFMANN, J., FRIEDRICH, K., "Biodegradable Laminates Based on Gelatin", *Macromolecular Material and Engineering*, v. 287, n. 10, pp. 693-697, 2002.