

Gelatin/piassava composites treated by electron beam radiation

P.Y.I. Takinami^I; K. Shimazaki^I; M.A. Colombo^{II}; E.A.B. de Moura^I; N.L. del Mastro^I

^I Instituto de Pesquisas Energéticas e Nucleares, IPEN - CNEN/SP, Av. Prof. Lineu Prestes, 2242,
CEP: 05508-000, SP, Brazil, +55 11 3133-9803

e-mail: patyoko@yahoo.com ; shimazakikleber@hotmail.com ; 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

ABSTRACT

Piassava (*Attalea funifera* Mart) fiber has been investigated as reinforcement for polymer composites with potential for practical applications. The purpose of the present work was to assess the behavior of specimens of piassava fiber and gelatin irradiated with electron beam at different doses and percentage. The piassava/gelatin specimens were made with 5 and 10% (w/w) piassava fiber, gelatin 25% (w/w), glycerin as plasticizer and acrylamide as copolymer. The samples were irradiated up to 40 kGy using an electron beam accelerator, at room temperature in presence of air. Preliminary results showed mechanical properties enhancement with the increase in radiation dose.

Keywords: Ionizing radiation, gelatin, natural fiber.

1 INTRODUCTION

Composites reinforced with natural fibers have been the subject of several publications due to technical and economic interest factors. The natural fibers have the advantages of biodegradability, use of locally available renewable resources, low cost, lightweight, possibility of environmental protection and good mechanical properties compared with traditional reinforcement material such as glass fiber [1, 2, 3]. Natural fibers offer reduced dependence on non renewable energy/material sources, induce lower pollutant and lower greenhouse gas emissions, enhance energy recovery and permit components biodegradability after use [4]. Hence, the management and recycling of plastic waste is an economic priority worldwide [5]. Consequently, recycled material meets up with many practical applications, such as fabrication of diverse composites [6]. Nowadays, composite development is one of the most viable choices to natural polymers applications in terms of physical and mechanical properties improvement [7].

Ionizing irradiation treatment of polymeric material is able to break chemical bonds introducing changes that depend mainly on the system composition and conditions where irradiation is taking place: process conditions such as type of radiation, presence of oxygen or other atmospheres, additives, solvents, crystallinity degree and uniformity of the polymer that will absorb the energy etc [8, 9].

Numerous studies have shown that the improvement of material properties induced by ionizing irradiation is the result of cross linking and scission processes, where radicals are formed randomly throughout the polymer chains. Internal crosslinks may also be produced by the combination of two radicals on the same molecule [3, 10-15].

Two primary sources provide ionizing irradiation: radioactive elements, such as cobalt 60, and electron beam. Industrial electron beam processing have the advantages of modify fibers without need of chemicals, the process can be done at room temperature, and the reactions that occur are usually nonpolluting (solvent-free) [10, 16, 17]. In recent years electron beam irradiation has been efficiently applied to modify the properties of different polymers for versatile applications [18].

Piassava is a lignocellulosic fiber extracted from the leaves of palm tree native from Brazil. The fiber content (around 48%) is the highest among the lignocellulosic fibers [2, 18, 19]. This could be responsible for its inherent flexural rigidity and water proof resistance. The main use of these fibers is for industrial and domestic brooms, industrial brushes, ropes and baskets, carpets and roofs. It is estimated that around 30% of the fiber is disposed as residue by the transformation industries, before production [19-22].

Studies with piassava (*Attalea Funifera* Mart) fiber showed that it can be used to reinforce polymer matrix composites [22-24]. It was reported that composites of recycled high-density polyethylene reinforced

with piassava fiber treated with silane showed an improvement of mechanical performance due to the increase of fiber polymer matrix interface adhesion [2].

Gelatin is a heterogeneous mixture of water-soluble proteins of high average molecular mass not found in nature but derived by hydrolytic action from collagen, a protein of mammal external protective tissues, by boiling skin, tendons, ligaments, bones, etc., with water. Swells up and absorbs 5-10 times its weight of water to form a gel in solutions below 35-40°C. Commercially gelatin is presented as a colorless or slightly yellow, transparent, brittle, practically odorless, tasteless sheets, flakes or coarse powder. Their uses include not only food (confectionery, jellies, ice cream) and pharmaceutical technology but also manufacturing of rubber substitutes, adhesives, photographic plates and films, matches and clarifying agent [25-28].

This work aims at assessing preliminarily the behavior of specimens of piassava fiber and gelatin, together with glycerin as plasticizer and acrylamide as copolymer, irradiated with electron beam at different doses.

2 EXPERIMENTAL

2.1 Material

Bovine skin gelatin was provided as a courtesy from 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). Piassava fiber samples were residues throw aside from brooms and brushes manufacturers.

2.2 Preparation and Incorporation of Piassava Fiber in Gelatin

Initially piassava fiber residues were washed in distilled water for 24 h to remove impurities. Fibers were then dried at 80 °C in the oven. The dry fiber was reduced to a fine powder, with particle sizes equal or lower than 250 µm by using a ball mill. The specimens of gelatin reinforced with 10% of piassava 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 and subsequently fiber addition under vigorously stirring for 30 minutes.

2.3 Electrom-Beam Irradiation

Samples of gelatin reinforced with piassava fiber were irradiated using an electrostatic 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 6.72m/min, being the applied doses: 20 and 40 kGy. The dosimetry was done with cellulose triacetate film dosimeters "CTA FTR 125" from Fuji Photo Film Co. Ltd.

Completed irradiation, samples were placed inside plastic bags and stored in a dry and protected from light place until the tests to avoid the influence of natural light and to consider the post irradiation effects.

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 test were measured according to ASTM D 638 99 [29] from printed plate. Mechanical tests were performed on Microcomputer Controlled Electronic Universal Testing Machine (model WDW-20 of Time Group Inc, China), using 50 mm of gage length, specimen type IV and a speed test of 5 mm/min.

Hardness test were performed on the conditioned specimens at Universal Hardness Testing Machine, Zwick, UK, by Shore type A durometer according to ASTM D 2240 00 [30], using a mass of 1 kg and indenter diameter of 0.79 ± 0.03 mm.

3 RESULTS AND DISCUSSION

The development of biodegradable barrier coatings based on radiation-curable methacrylated gelatin was already reported [31]. Also, grafting of cross linked gelatin with acrylamide in aqueous medium was investigated elsewhere [32].

The tensile strength of gelatin/piassava composites electron beam-irradiated with different doses is shown in Table 1. The tensile strength increased with the increase of the radiation dose. The tensile strength of the 40 kGy-irradiated sample was the highest among the treatments as well as the elongation at break. The samples showed also a good barrier behavior against oxygen and a high resistance against boiling water. On the other hand, the resilience was reduced with the increase of radiation dose.

Methacrylated gelatins are considered to possess good adhesion characteristics. Therefore, they were considered suited as barrier adhesives in laminates for, for instance, food packaging applications.

Table 1: Mechanical properties of gelatin composite with 10% piassava electron beam-irradiated at different doses.

Mechanical Properties	20 kGy	40 kGy
Tensile strength at yield (MPa)	12.59 ± 0.01	14.11 ± 0.01
Elongation at yield (%)	86.38 ± 0.01	88.73 ± 0.01
Resilience (J)	0.11 ± 0.01	0.06 ± 0.01

Data from the literature described that for gellan and gelatin composite films, as the gelatin proportion increased, tensile strength decreased and tensile elongation increased. Thus, gelatin seemed to act as a plasticizer, which enhanced film flexibility and decreased brittleness [33].

Gelatin/piassava composite showed increase of elongation at yield with the increase of radiation dose, (86.38±0.01)% to (88.73±0.01)%, respectively. Haroun *et al.* [34] prepared composite films based on gelatin and collagen with 40.8% of elongation at yield for gelatin/low density polyethylene (1:1) samples. They expected low stress values at yield for the composite films to confirm their brittle behavior, because of a poor adhesion between copolymerized polyethylene and gelatin or collagen (amorphous component).

Jacob *et al.* [35] studied the mechanical properties of natural rubber composites reinforced with sisal/oil palm hybrid fiber. They established that the sisal/oil palm fibers loading increased in the rubber matrix resulting in stiffer and harder composites. Then, the 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.

Figure 1 shows the results of shore A hardness testing. Gelatin/piassava composite irradiated at 20 kGy presented shore A hardness of 19. Subsequent reading, after five seconds, the same sample, performed under the same conditions, showed shore A hardness value of 14, lower than at the beginning of the test.

In recent years, those products at the low end of the scale, i.e. Shore A 30 or less have received increased attention because they can be formulated to make products with very soft tact or even liquid-like properties that find use in comfort and pressure relief applications. According to Saraswathy *et al.* [36] the ideal range of hardness of, for instance, insoles material is 18 to 22 Shore A, because the materials will deform on walking and regain its original thickness before the second step, representing a resilience property. Therefore polyurethane (15-20%) sheets can be used as insole materials where uniform pressure distribution under the foot is essential. Present preliminary research shows that the sample irradiated at 20 kGy presented promising results for application in therapeutic footwear. The composite performance and the resilience value (0.11±0.01 J) also showed better regain deformation compared with the sample irradiated at 40 kGy (0.06±0.01 J).

The increase of radiation dose to 40 kGy increased shore A hardness value to 35. However, after five seconds, the reading decreased to 26, lower when compared to time one second. Saraswathy *et al.* [36] showed that the increase in hardness is due to increase in polymer concentration and higher molecular weight when working with polyurethanes. Sheets with hardness in the range of 25–33 shore A were grouped as hard materials. Therefore, it seemed that the increase in molecular weight and polymer concentration increased the hardness of the sheets due to the decrease in the porosity of the sheets.

Ismail *et al.* [37] observed that the hardness of natural rubber composite increased with increasing of filler loading of bamboo fiber from 35 to 65 varying the filler loading (phr) from 0 and 50.

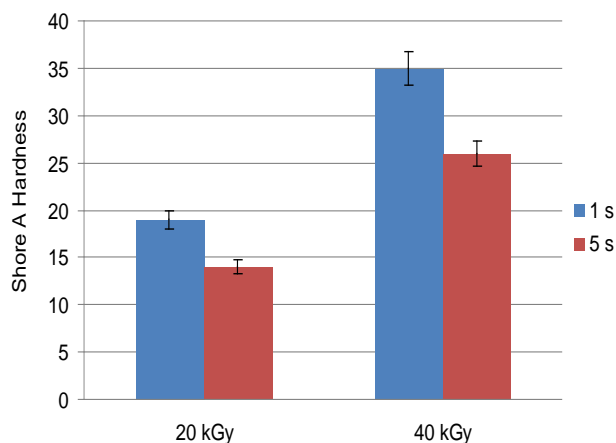


Figure 2: Hardness of composites with 10% piassava irradiated at different radiation doses.

4 CONCLUSION

This study presents preliminary results on the mechanical properties of a gelatin/acrylamide polymer reinforced with a natural fiber, piassava, prepared by electron beam irradiation. Considering the load amount, i.e. piassava fiber was constant 10% (w/w), the observed hardness increase in the composites samples with the increase of electron beam irradiation dose from 20 to 40kGy suggests the prevalence of cross-linking induced by electron beam irradiation instead of the degradation process. Such effects added to the observed gains in tensile x strain of irradiated composite (Tab. 1) indicate that electron beam irradiation would be a suitable process for the development of gelatin/acrylamide/piassava fibers composite with good mechanical properties.

5 ACKNOWLEDGEMENTS

The authors want to express their thanks to Eng. Elizabeth S.R. Somessari and Eng. Carlos Gaia da Silveira for guidance in the irradiation operation and Faculdade de Tecnologia da Zona Leste for the support provided to this work.

6 REFERENCES

- [1] MONTEIRO, S.N., AQUINO, R.C.M.P., LOPES, F.P.D., D'ALMEIDA, J.R.M., "Tenacidade ao entalhe por impacto charpy de compósitos de poliéster reforçados com fibras de piaçava", *Revista Matéria*, v. 11, n. 3, pp. 204-210, 2006.
- [2] BONELLI, C.M.C., ELZUBAIR, A., SUAREZ, J.C.M., MANO, E.B., "Comportamento térmico, mecânico e morfológico de compósitos de polietileno de alta densidade reciclado com fibra de piaçava", *Polímeros: Ciência e Tecnologia*, v. 15, n. 4, pp. 256-260, 2005.
- [3] 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, n. 5, pp. 2466-2473, 2008.
- [4] 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, n. 3, pp. 371-376, 2004.
- [5] ŻENKIEWICZ, M., KURCOK, M., "Effects of compatibilizers and electron radiation on thermomechanical properties of composites consisting of five recycled polymers", *Polymer Testing*, v. 27, n. 4, pp. 420-427, 2008.
- [6] DINTCHEVA, N.T., JILOV, N., MANTIA, F.P., "Recycling of plastics from packaging", *Polymer Degradation and Stabilization*, v. 57, n. 2, pp. 191-203, 1997.

- [7] 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”, *Portal do Biodiesel, Governo Federal*, pp. 28-33, 2006, <http://www.biodiesel.gov.br/docs/congressso2006/Co-Produtos/PreparoCompositos6.pdf> , Acessado em: 02/02/2010
- [8] CLEGG, D.W., COLLYER, A.A., *Irradiation effects on polymers*, England, Elsevier Science Publishers Ltd., pp. 68-69, 1991.
- [9] THAYER, D.W., “Food irradiation: benefits and concerns”, *Journal of Food Quality*, v. 13, n. 3, pp. 147-169, 1990.
- [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 Chemistry*, v. 47, n. 3, pp. 333-336, 1996.
- [12] MEHNERT, R., “Review of industrial applications of electron accelerators”, *Nuclear Instruments and Methods in Physics Research B*, v. 113, n. 1-4, pp. 81-87, 1996.
- [13] KHAN, F., AHMAD, S.R., KRONFLI, E., “Stability of jute fibers on exposure to ionizing radiation”, *Polymer Degradation and Stability*, v. 63, n. 1, pp. 79-84, 1999.
- [14] ROUIF, S., “Radiation cross-linked polymers: Recent developments and new applications”, *Nuclear Instruments and Methods in Physics Research B*, v. 236, n. 1-4, pp. 68-72, 2005.
- [15] KIM, H.S., KIM, H.J., “Enhanced hydrolysis resistance of biodegradable polymers and bio-composites”, *Polymer Degradation and Stability*, v. 93, n. 8, pp. 1544-1553, 2008.
- [16] 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 Protection*, v. 56, n. 11, pp. 991-997, 1993.
- [17] RATNAM, C.T., RAJU, G., YUNUS, W.Z.W., “Oil palm empty fruit bunch (OPEFB) fiber reinforced PVC/ENR blend-electron beam irradiation”, *Nuclear Instruments and Methods in Physics Research B*, v. 265, n. 2, pp. 510-514, 2007.
- [18] MOURA, E.A.B., NOGUEIRA, B.R., ORTIZ, A.V., “Changes in physicochemical, morphological and thermal properties of electron-beam irradiated ethylene-vinyl alcohol copolymer (EVOH) as a function of radiation”, In: *International Topical Meeting on Nuclear Research Applications and Utilization of Accelerators*, Vienna, Austria, 4-8 May, 2009.
- [19] 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, 2000.
- [20] 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, 2003.
- [21] NASCIMENTO, D.C.O., MOTTA, L.C., MONTEIRO, S.N., “Resistência ao impacto charpy de compósitos de matriz epóxi reforçada com fibras de piaçava”, In: *18º CBECiMat - Congresso Brasileiro de Engenharia e Ciências dos Materiais*, Porto de Galinhas, PE, 24-28, nov 2008.
- [22] D’ALMEIDA, J.R.M., AQUINO, R.C.M.P., MONTEIRO, S.N., “Tensile mechanical properties, morphological aspects and chemical characterization of piassava (*Attalea funifera*) fibers”, *Composites: Part A*, v. 37, n. 9, pp. 1473-1479, 2006.

- [23] SATYANARAYANA, K.G., GUIMARÃES, J.L., WYPYCH, F., “Studies on lignocellulosic fibers of Brazil. Part I: source, production, morphology, properties and applications”, *Composites: Part A*, v. 38, n. 7, pp. 1694–1709, 2007.
- [24] 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 Chemical and Technologies*, v. 29, pp. 705-712, 1995.
- [25] WINDHOLZ, M., *The Merck Index*, 9th Edition, Rahway, NJ, USA, Merck & Co, Inc., 1976.
- [26] ANONYMOUS, Gelatin. In: Krochwitz J.I., Howe–Grant M. editors. *Encyclopedia of Chemical Technology*, v. 11, 3rd ed. New York, John Wiley & Sons, pp. 711-721, 1980.
- [27] JONES, N.R., *Uses of gelatin in edible products*, In: Ward A.G., Courts A. editors. *The Science and Technology of Gelatin*, Academic Press, New York, pp. 365-370, 1997.
- [28] CHOI, S.S., REGENSTEIN, J.M., “Physicochemical and sensory characteristics of fish gelatin”, *Journal of Food Science*, v. 65, n. 2, pp. 194-199, 2000.
- [29] ASTM - American Society for Testing Materials. Standard Test Methods for Tensile Properties of Plastics. D 638 - 99. ASTM, 1999.
- [30] ASTM - American Society for Testing Materials, “Standard Test Methods for Rubber Property – Durometer Hardness”, D 2240 – 00, ASTM, 2000.
- [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] Chatterji, P.R., “Glutaraldehyde Crosslinked Gelatin with Polyacrylamide Grafts”, *J. Mol. Sc. Part A*, v. 27, n. 4, pp. 435-443, 1990.
- [33] Lee, K.Y., Shim, J., Lee, H.G., “Mechanical properties of gellan and gelatin composite films”, *Carbohydrate Polymers.*, v. 56, n. 2, pp. 251–254, 2004.
- [34] 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, n. 4, pp. 2083–2094, 2010.
- [35] 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.
- [36] ISMAIL, H., SHUHELMY, S., EDYHAM, M.R., “The effects of a silane coupling agent on curing characteristics and mechanical properties of bamboo fibre filled natural rubber composites”, *European Polymer Journal*, v. 38, n. 1, pp. 39-47, 2002.
- [37] 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 cushioning properties for therapeutic footwear application”, *Polymer-Plastics Technology and Engineering*, v. 48, n. 3, pp. 239-250, 2009.