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ELECTRON BEAM EFFECTS ON GELATIN POLYMER

Patrícia Y. Inamura[1], Kleber Shimazaki[1], Clécia de M. Souza[1], Maria A. Colombo[2], Esperidiana A. B. Moura[1] and Nelida L. del Mastro[1]

[1] Instituto de Pesquisas Energéticas e Nucleares, IPEN - CNEN/SP
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
patyoko@yahoo.com

[2] Faculdade de Tecnologia da Zona Leste
Avenida Águia de Haia, 2633
03694-000 São Paulo, SP
mascolombo@yahoo.com.br

ABSTRACT

The main field of electron-beam radiation processing applications is the modification of polymeric material. Polymer development includes new pathways to produce natural polymers with better mechanical and barrier properties and thermal stability. The aim of this paper was to investigate the behavior of a gelatin/acrylamide polymer treated by electron-beam radiation. Gelatin is a heterogeneous mixture of water-soluble proteins of high average molecular mass derived by hydrolytic action from animal collagen, a fibrous insoluble protein, which is widely found in nature as the major constituent of skin, bones and connective tissue. Hydrolyzed collagen is composed of a unique sequence of amino acids, characterized particularly by the high content of glycine, proline and hydroxyproline. Among biomaterials, gelatin is an interesting material because is a partially crystalline polymer and has a relatively low melting point. Samples of gelatin together with glycerin as plasticizer and acrylamide as copolymer were irradiated with doses of 10 kGy and 40 kGy, using an electron beam accelerator, dose rate 22.41kGy/s, at room temperature in presence of air. After irradiation, some preliminary analyses were done like viscometry, texture analyses and colorimetry. The results of the diverse tests showed changes that can be ascribed to radiation-induced crosslinking. The electron-beam processed acrylamide-gelatin polymer using glycerin as plasticizer must be first extensively characterized before to be used for general applications.

1. INTRODUCTION

Gelatin has been used as a starting material in a variety of applications because of its biosafety verified in food and clinical fields for a long time. It is an irreversibly hydrolyzed form of collagen. Cattle bones, hides, pigskins, and fish are the principle commercial sources. As such, it may come from either agricultural or non-agricultural sources. It is also used as a fining agent in wine, and as a stabilizer, thickener, and texturizer for a range of products. Gelatin can be used as either a processing aid or an ingredient. In some cases, it will comprise

over 5% of a food. It has been commonly used in food, pharmaceutical, photography, and cosmetic manufacturing [1].

Gelatin is composed of a unique sequence of amino acids. Polymer characteristic features are the high content of the amino acids glycine, proline and hydroxyproline. Also, the protein has a mixture of single and double unfolded chains of hydrophilic character. At approximately 40 °C, 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 [2]. Gelatin films with plasticizer have sufficient stability, strength and flexibility to allow them to be used as support and packaging materials.

In our laboratory [3] the texture profile of gamma irradiated gelatin hidrogels was established, showing that the gel hardness and gel brittleness of the polymer were affected by the increase of radiation dose. Nevertheless, no further studies on the nanostructure of the resulting material were already concluded.

Radiation processing can cause a variety of modifications, all of which have found useful industrial applications. These modifications include: cross-linking, in which polymer chains are joined and a higher molecular mass network is formed. Cross-linking usually brings about an improvement in mechanical properties, chemical resistance, thermal stability and other important properties. Radiation can also induce polymeric degradation, in which the molecular mass of a polymer is reduced through chain scission. With the reduction of molecular mass, the melt flow of the polymer increases and particle size can be reduced [4].

Polymers from renewable resources (proteins, carbohydrates and lipids) have gained considerable research interest mainly for environmental concerns [5]. Among biomaterials, gelatin is an interesting material because the dehydrated gelatin is a partially crystalline polymer and has a relatively low melting point [6,7].

The inherent biodegradability of natural polymers also means that it is important to control the environment in which the polymers are used, to prevent premature degradation. For example, the water solubility of many natural polymers raises their degradability and the speed of degradation, however, this moisture sensitivity limits their application. Another limitation of many natural polymers is their lower softening temperature [8,9].

The aim of this work was to investigate the behavior of a gelatin/acrylamide polymer prepared by electron beam irradiation, analyzing some properties like viscosity, color, solubility and compression resistance.

2. MATERIAL AND METHODS

2.1. Sample preparation

Pigskin gelatin was provided as a courtesy from GELITA do Brasil Ltda, 250Bloom/8 mesh, lot: LF21806P 06. Glycerin PA ACS, cod. 15375 were provided by Casa Americana de Art. Lab. Ltda (CAAL) and Art Mono acril. H, lot: 30261003 from Aratrop Industrial. Specimens

were prepared by dissolving glycerin as plasticizer 1.5% (w/w), acrylamide as copolymer 1.5% (w/w) and gelatin 20% (w/w) in distilled water in a water bath at 80 °C under vigorously stirring for 30 minutes. All samples control and irradiated, were moisture conditioned in a 60% RH at ambient temperature (ca. 23 °C).

2.2. Irradiation

Samples of gelatin polymer were irradiated using an electrostatic accelerator (Dynamitron II, Radiation Dynamics Inc., at room temperature, in the presence of air, dose rate 22.41kGy/s, energy 1.407MeV, beam current 5.4 mA, tray speed 6.72m/min, being the applied doses: 10 and 40 kGy. Dosimetry was done with cellulose triacetate film dosimeters "CTA-FTR-125" from Fuji Photo Film Co. Ltd.

2.3. Viscosimetry

Radiation effects were measured following viscosity changes at 60 ºC using Brookfield viscometer; model LV-DVIII with small sample adapter (SSA), spindle SC4-18, with Rheocalc software and Neslab water bath model RTE-210, precision ± 0.1 °C. Viscosity measurements were performed according to the laboratory previous experience [10] and the results are the means of at least 5 readings.

2.4. Texture Analysis

The measures of compression had been carried through using Texture Analyzer Stable Micro Systems TA-XT2 with capacity of compression of 25 kg. The used accessory was stainless steel cylindrical probe with a diameter of 2 mm (P/2) for all the samples. The samples had been compressed to a speed of 1mm/s generally until 2mm of compression.

2.5. Color Measurement

A Chroma meter (CR-400 Chroma Meter, Konica Minolta Co., Osaka, Japan) was employed. Samples were placed on the surface of a white standard plate (calibration plate CR-A43, L = 95.91, a = 0.05 and b = 1.27) and 3 flashes were taken at each time.

2.6. Solubility in hot water

In order to know whether the electron beam treated gelatin could withstand hot water, samples were immersed in a water bath at 80°C for 30 min.

3. RESULTS AND DISCUSSION

The cross-linking of the gelatin-acrylamide-glycerin derivative was performed by EB irradiation that is a safe method as no initiator residue is left and for that is the preferred method for packaging applications. The viscosity of the unirradiated gelatin polymer was 0.25±0.17 Pa.s. Viscosity measurement of the samples irradiated at 10 and 40 kGy could not be performed probably due to the degree of cross-linking attained which produced changes in bulk and surface properties.

Texture analyses were done to establish compression resistance, as presented in Figure 1.

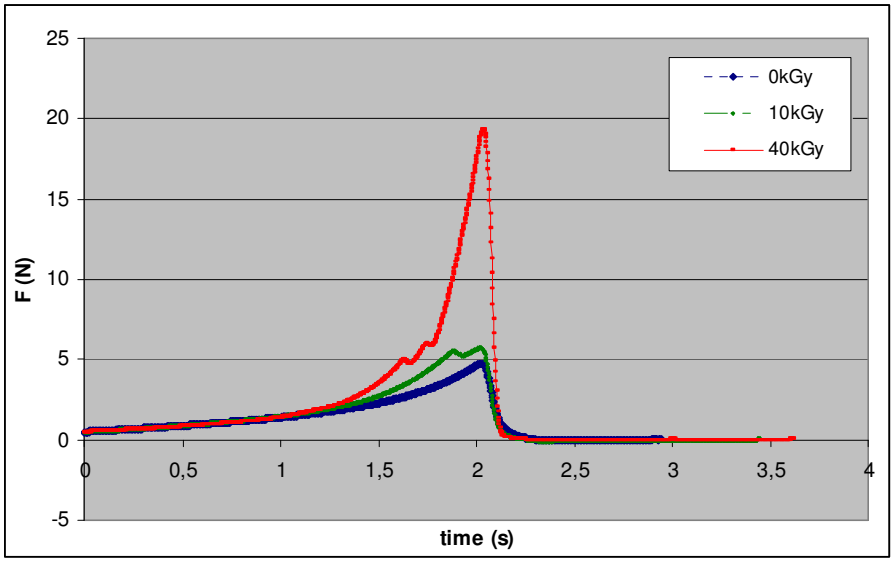

Figure 1. Compression of gelatin polymer at 10 and 40 kGy.

Samples irradiated at 40 kGy presented the highest compression resistance (19.4 N). Data from our laboratory [3] showed that the gel hardness and gel brittleness of the gelatin alone were affected by the increase of ionizing radiation dose. According to Scherzer [11] an EB radiation dose of 30-40 kGy is required for cross-linking of methaacrylated gelatin.

Assays to verify the solubility in hot water were done for all samples after irradiation, Due to the radiation-induced cross-linking, gelatin was no longer soluble in water. However, they remain slightly swellable. According to some work from the literature, cross-linked gelatin layers are also insoluble in organic solvents such as ethanol or diethylether. Additionally, they are impermeable to margarine, cooking and mineral oil among others fats [11].

The Hunter *L* (lightness) and b (yellowness) color values of polymer is presented in Table 1. The main effects on sample color values were increased *L* values (lightness) and decreased +b values (yellowness) of the sample at 10 kGy and the similar color between the control and 40 kGy. Statistical analyses were developed using ANOVA, followed by Tukey-test. Results

showed significantly difference ($p<0.05$) between all samples for yellowness (*b*) and lightness (*L*).

Table 1. Color values of gelatin polymer at 10 and 40kGy.

Doses (kGy)	*L*	*b*
0	79.74±0.62	6.51 ± 0.17^{ab}
10	81.40 ± 0.61^{ac}	4.64 ± 0.05^{ac}
40	76.15 ± 0.71^{bc}	7.14 ± 0.06^{bc}

L: Lightness, *b*: yellowness.
^{a,b,c} Means with different superscripts in a column are significantly different ($p<0.05$), n=70.

Change of color under radiation is general, but not universal. For that reason very different organic and inorganic materials are used for dosimetric purposes. Particularly with protein, is quite common a yellowness shift in the irradiated samples that is usually accounted to the disruption of the ordered structure of the protein molecules, as well as degradation, cross-linking, and aggregation of the polypeptide chains [12].

Several authors studied gelatin properties and behavior under radiation processing due to their importance for the food industry [13-15]. Cataldo et al., in 2008 [16] described that by means of radiation-induced cross-linking of collagen gelatin is possible to obtain a stable hydrogel. Canadian researchers had already reported the gamma radiation capability in inducing an improvement of barrier properties and tensile strength of proteic films through creation of a cross-linked β-structure. They found also that gels prepared using irradiated protein solutions mixed with calcium salt were stronger than gels prepared using non-irradiated solutions owing to the preferred binding of calcium ions to the cross-linked protein network [17]. Liu et al. [18] reported that they prepared porous bioceramics reinforced by gelatin coating.

The development of biodegradable barrier coatings based on radiation-curable methacrylated gelatin was reported [11]. In that study the electron beam cured gelatin layers showed a superior barrier behavior against oxygen and a high resistance against boiling water. Moreover, the methacrylated gelatins possess good adhesion characteristics. Therefore, they were considered suited as barrier adhesives in laminates for food packaging applications.

4. CONCLUSIONS

This study presents preliminary results on the behavior of a gelatin/acrylamide polymer prepared by electron beam radiation. The present paper presented some expected rheological behavior [19] similar to those obtained with ionizing radiation coming from gamma sources in terms of increase of viscosity with the radiation dose. Also, compression resistance showed its maximum level with the highest dose applied. Results showed significantly difference between all samples for yellowness (*b*) and lightness (*L*). Nevertheless, the electron beam processed acrylamide-gelatin polymer using glycerin as plasticizer must be first extensively

characterized to be used for general applications and the acceptable mechanical and barrier properties established.

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