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Influence of irradiation on powder characteristics and chitosan solution

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ABSTRACT

Chitosan is a biodegradable polymer composed of β- (1,4) -D-glucosamine linkages (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). It is commercially produced by the deacetylation of chitin and in the food industries it is used as a stabilizer, thickener, in water treatment and easily processed into nanofibers, gels, nanoparticles and films. The objective of this work was to evaluate the effect of gamma irradiation on morphological, rheological and color properties of chitosan and gels. Chitosan samples were irradiated at the 5, 10 and 15 kGy doses and performed by scanning electron microscopy (SEM), color and rheology. SEM analyzes showed that the chitosan particles have a network agglomerated with irregular arrangements, and the irradiated samples presented smaller granules. It was observed that gamma radiation induces changes in the intensity of the tonality of the chitosan powder and gels, increasing the brown coloration. These changes are observed by the decreasing values of L * (luminosity) with increasing radiation dose and, consequently, an increase in the values of b * (brown tone), C * and h *, indicating a higher intensity of color. As for the rheological behavior, all the gels were characterized as Newtonian fluids and the irradiation altered their viscosity, leaving them less viscous.

Keywords: **effects, gamma radiation, chitosan solution**

1. INTRODUCTION

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Gamma radiation is a method of modifying the properties of biodegradable polymeric materials [4]. Irradiation is a physical phenomenon which there is interaction of electromagnetic waves with matter, which ionize atoms or molecules inducing chemical reactions that can disrupt cellular, organic or physiological processes and cause the desired effect [7]. Its purpose is to increase storage stability by reducing microorganisms, eliminating parasites or insects, or blocking enzyme activity [12]. They also have advantages when applied to polymers because strong bonds between macromolecules can be formed, with crosslinking of proteins by promoting improvement in mechanical and barrier properties of materials [3, 17].

Polymers have two main effects when they are irradiated: crosslinking and degradation or breaking of the polymer chain [18]. Depending on the structure of the polymer, the concentration, the dispersion of the cross-linking agent and the irradiation conditions (dose, temperature and atmosphere), one of these processes is favored [13]. These are methods that modify the material according to its possible applications, especially the reduction of the molecular weight of chitosan without losing its chemical structure [11]. This reduction in molecular weight is associated with increased antioxidant and antimicrobial activity of chitosan. [9]. The aim of this study was to evaluate the effect of irradiation on color and morphological properties of chitosan powder and color and rheological properties of the filmogenic solution.

2. MATERIALS AND METHODS

The chitosan powder was purchased from company Polymar that produces biopolymers, located in Fortaleza city, state of Ceará, Brazil, has a mean molecular weight and degree of deacetylation of 85%. The experiment was carried out at the Fruit and Vegetable Laboratory of the Federal University of Tocantins and at the Multiuser Laboratory of the Federal University of Goiás.

The chitosan powder was divided into four portions, of equal weights, packed in polyethylene bags and submitted to doses of 0 (control); 5, 10 and 15 kGy using the commercial irradiator with ^{60}Co source with irradiation rate of 0.6 kGy / hour. The irradiation was performed at the Center for Nuclear Energy in Agriculture (CENA / USP). Chitosan filmogenic solutions were prepared with concentrations of 1% and 2%. After 5 g and 10 g of chitosan were added respectively in 25 mL of glacial acetic acid and the remainder of distilled water to complete 500 mL to dissolve the chitosan. The solution was constantly stirred in the Turrax until complete dissolution. Color analyzes were performed for both the powder and the chitosan solution. The CIE system was used to calculate the parameters: brightness (L*), from black (0) to white (100) a* (intensity of color green to red) and b* (intensity of color yellow to blue). The color parameters were determined using the equipment software. In each sample, five readings were performed. The chroma index (C), considered as a quantitative color and hue (h) attribute, was also calculated, considered the qualitative color attribute.

The chitosan powders samples were placed in aluminum support or stubs with double-sided adhesive tape, then they were taken to the metallising chamber (SCO -040 Marca Balzers), to be coated with a gold foil. Scanning electron microscopy was performed using the electron microscope (JEOL - JSM 6610, Japan), using a voltage accelerator of 2.5 kV.

The rheological behavior of chitosan solutions was determined by computerized Rheometer (Anton Paar - Physica MCR101). The parameters used to characterize the fluid were constant temperature of 25ºC with the variation of the deformation rate of 1 to 500 s, with a homogeneous cone-plate system 50, to determine the flow profile, obtaining 50 points. For the confirmation of the Newtonian fluid behavior, the linear regression was applied to adjust the shear stress and strain rate data according to [2]. Statistical analysis of the results was performed using the Tukey test ($p \leq 0.05$), using the statistical program SISVAR 5.6 [8].

3. RESULTS AND DISCUSSION

It was observed that the luminosity L * decreases as the dose of radiation increases, presenting significant difference ($p < 0.05$) between the control and irradiated samples. This change in the coloration of chitosan is due to the chemical and biological changes that the molecule undergoes with the process [19]. It was observed that the powder shows no tendency to green and red color (Table 1).

The irradiation caused a significant increase in the value of the chroma C when compared to the chitosan powder without irradiation. According to [10], the higher the chroma values, the higher the color intensity of the samples. The chroma index was strongly influenced by the values b*, following the same trend as these, that is, the irradiation intensified the yellowish coloration of the powder tending to brown. The values of h ranged from 85.67 to 88.83 degrees, without irradiation and at a dose of 15 Gy, respectively, which means that the samples are yellow. The tone of the samples intensified with increasing doses of radiation, however there was no significant difference (p> 0.05) that proves the influence of irradiation in this parameter.

Table 1. Effect of gamma radiation on coloration of chitosan powder.

Parameter /cor	**0 kGy**	**5 kGy**	**10 kGy**	**15 kGy**
L*	$77.49^{a*}\pm0.06$	$65.86^{b}\pm0.08$	$64.29^{b,c}\pm0.04$	$62.55^{c}\pm0.06$
a*	$1.18^{a}\pm0.05$	$0.93^{b}\pm0.05$	$0.75^{c}\pm0.06$	$0.38^{d}\pm0.08$
b*	$15.58^{b}\pm0.03$	$18.83^{a}\pm0.05$	$18.50\pm^{a}\pm0.06$	$18.58^{a}\pm0.03$
C	$15.62^{b}0.01$	$18.85^{a}\pm0.04$	$18.51^{a}\pm0.06$	$18.58^{a}\pm0.04$
h	$85.67^{a}\pm0.02$	$87.17^{a}\pm0.03$	$87.67^{a}\pm0.03$	$88.83^{a}\pm0.01$

* Different lowercase letters indicate significant difference (p <0.05) between columns (doses).

The color parameters of the chitosan film-forming solution are presented in Table 2. There was a significant difference (p<0.05) in all parameters analyzed between radiation doses and chitosan concentrations. A great influence of the irradiation was identified in the tone of the solutions, making them darker. The sample with a dose of 15 kGy of radiation had higher values of chroma C and h, and is in agreement with the obtained values of the powder, proving that the bigger the dose of the radiation, the stronger the yellow tone of the sample. Similar results were found with [4], who worked with irradiated chitosan at doses of 30, 50, 100 and 200 kGy and observed that the tone of the solution became dark brown as the dose increased. They concluded that above 100 kGy, the pitch was no longer desirable. [14] investigated the effects of irradiation on the color change of alginate and concluded that the increase in brown tone is due to the formation of double bonds in the breakdown of the molecule chain. [17] obtained similar results, irradiated the chitosan at doses 10, 25, 50 and 100 kGy and reported an increase in the tone as the dose increased.

Table 2. Effect of gamma radiation on the color of the chitosan film-forming.

	0 kGy	**5 kGy**	**10 kGy**	**15 kGy**
L -1	29.38^{c*B**}±0.01	29.47^{bcB}±0.08	31.21^{aA}±0.03	31.21^{aA}±0.03
L-2	35.62^{aA}±0.02	34.16^{bA}±0.02	31.86^{cA}±0.03	34.31^{bA}±0.04
a-1	-0.33^{aA}±0.01	-0.40^{bA}±0.02	-0.52^{cA}±0.02	-.36^{abA}±0.03
a-2	-0.80^{bB}±0.06	-0.90^{cB}±0.01	-0.65^{aB}±0.01	-0.89^{cB}±0.02
b-1	1.19^{dA}±0.03	1.38^{cB}±0.02	1.56^{bB}±0.03	1.76^{aB}±0.05
b-2	1.83^{dB}±0.02	2.19^{cA}±0.02	2.47^{aA}±0.07	2.39^{bA}±0.02
C-1	1.28^{cA}±0.03	1.39^{bB}±0.04	1.65^{aB}±0.04	1.65^{aB}±0.05
C-2	2.02^{cB}±0.03	2.37^{bA}±0.02	2.54^{aA}±0.03	2.54^{aA}±0.02
h-1	74.54^{bA}±0.32	73.25^{bA}±0.86	71.38^{cB}±0.64	8.21^{aA}±1.25
h-2	65.27^{dB}±0.29	67.64^{cB}±0.20	74.94^{aA}±0.35	69.45^{bB}±0.28

* Different lowercase letters indicate significant difference (p <0.05) between columns (doses). ** Different upper case letters indicate significant difference (p <0.05) between the lines (concentration).

Electronic microscopy

Scanning electron microscopy (SEM) showed that the particles of chitosan powder have a network agglomerated with irregular arrangements. The irradiated powder samples differed slightly from the others, presenting smaller granules. According to [14] after irradiation, a deformation in the carbohydrate tends to occur because the irradiation causes chain breakage separating the glycosidic bonds 1-4, making them oligomers with chains with small numbers of repetitive units. These results indicate that the chitosan molecules are degraded with the application of gamma radiation because after the process, it has a heterogeneous porous surface. The porous structure of the powder is an important feature in the applications of chitosan, such as adsorption dyes [5] and active biodegradable films [1].

Rheology

The irradiated and non-irradiated samples assumed the behavior of Newtonian fluid, since the shear stress (τ) versus strain ratio (γ) ratio remained constant. The control sample presented higher values of shear stress as the shear rate increased the radiation doses 5, 10 and 15 kGy. The irradiated samples presented different behavior when compared to the curve of samples with 2% concentration of chitosan, since they did not overlap between them. The sample with the lowest radiation dose of 5 kGy showed the lowest shear viscosity, 0.01 $Pa.s^{-1}$, and the control sample that did not undergo irradiation had the highest viscosity, 0.04 $Pa.s^{-1}$, after stabilizing. Samples with radiation doses of 10 kGy and 15 kGy had, respectively, viscosities of 0.025 and 0.020 $Pa.s^{-1}$.

CONCLUSION

The irradiation caused a more intense effect on the shade of the powder and the filmogenic solution of chitosan. Electron microscopy revealed degradation of the molecule and formation of smaller granules and irregular arrays, evidencing the effect of irradiation. The solution showed Newtonian fluid behavior and the irradiation promoted a decrease in viscosity.

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