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Anomalous Rheological Behaviour of Gelatin-Carrageenan-Water System Induced by Ionizing Radiation

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Polysaccharide biodegradable hydrogels had been developed to be used for the controlled delivery of pharmaceutically active protein. Also, food hydrogels having biodegradability are used to prepare new materials required for packaging by the food industry. In this paper two common food hydrogels were submitted to ionizing radiation. Gelatin and carrageenan solutions alone as well as ternary water-gelatin-carrageenan systems (97.5:1.0:1.5) were ^{60}Co-irradiated with different radiation doses (0–20 kGy). The comparison of viscosity versus dose patterns of previous and irradiated resulting systems showed an anomalous rheological behavior produced by radiation suggesting the formation of a protein–polysaccharide complex.

Keywords: biopolymers; carrageenan; gelatin; ionizing radiation

INTRODUCTION

An alternate approach to non-biodegradable synthetic plastics is packaging films based on hydrocolloids and their derivatives. They are available in plenty forms from highly renewable natural resources and their total biodegradability makes them ecofriendly. Blending as well as graft copolymerization of synthetic monomers onto natural polymers offer additional means of preparing biodegradable packaging films [1]. Among plastic materials for the food industry and

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pharmaceutical coatings under development, blends or polymers complexes of edible polymers appears as very promising. There are many different examples of biodegradable polymers prepared for drug delivery or as carriers of active agents [2,3].

The ability of biopolymers and other molecules to self-assemble forms the basis of any "living entity". The complementary application of both chemical and biochemical synthetic methods provides access to a diverse array of biopolymers. Among them, the focus turns to biopolymers conjugated with complex carbohydrates. In light of the growing recognition of the importance of glycol-protein conjugates in numerous aspects of chemical biology, a critical research objective in this area includes understanding how to exploit both chemical and biochemical synthetic approaches for the preparation of homogeneous samples of material for biological and biophysical studies. One important point is how some biopolymers conjugate with complex carbohydrates and how to exploit both chemical and biochemical synthesis approaches for the preparation of homogeneous samples of material for biological and biophysical studies [4].

As the World Health Organization has established, irradiation using good irradiation practices of any food commodity presents no special nutritional or microbiological problem [5,6]. Being so, ionizing radiation is increasingly being applied in food industry to prevent food-borne diseases and as a quarantine treatment [7].

This article presents the preliminary results of a novel method for the fabrication of biopolymer complexes using edible polymers. The polysaccharide chosen for the study was carrageenan and gelatin was taken as the proteic component of the possible complex because its gelation and water holding abilities. Instead of using electrochemical synthesis to prepared a glycoconjugate as was described before [8] we applied ionizing radiation to induce complex formation.

MATERIALS AND METHODS

Materials

Five grams cellophane packaged samples of commercial edible bovine powder gelatin was employed (1%). Commercial kappa carrageenan samples (Carragel NM Adicon) were employed. Adequate solutions of both substances (1% gelatin and 1.5% carrageenan) were prepared by dissolution in hot (80°C) water according our previous experiences [9,10]. Gelatin and carrageenan solutions alone as well as ternary water-gelatin-carrageenan systems (97.5:1.0:1.5) were irradiated with ionizing radiation, doses of 0, 2.5, 5.0, 15, and

20 kGy by means of a ^{60}Co γ source Gammacell 220 (AECL), dose rate about 5 kGy/h.

Viscosimetry

The radiation effects were measured following viscosity changes at 50°C using a Brookfield viscometer; model DVIII, spindle SC4-18, with Rheocalc software. Viscosity measurements were performed according to our previous experience [9] and the results are the means of at least 3 experiments.

RESULTS AND DISCUSSION

Ionizing radiation coming from a ^{60}Co source is able to produce chemical reactive species to result in substantially modified or novel chemical, physical or biological properties in the irradiated material [11]. Water is the most important solvent, dispersion medium, and plasticizer in biological and food systems. Since proteins and polysaccharides are the main construction materials of food, their interactions with water and with each other in the water medium govern structure-property relationships in foodstuffs [12].

In irradiated dilute aqueous solution, the solvent absorbs practically all the radiation energy and the water radicals generated by

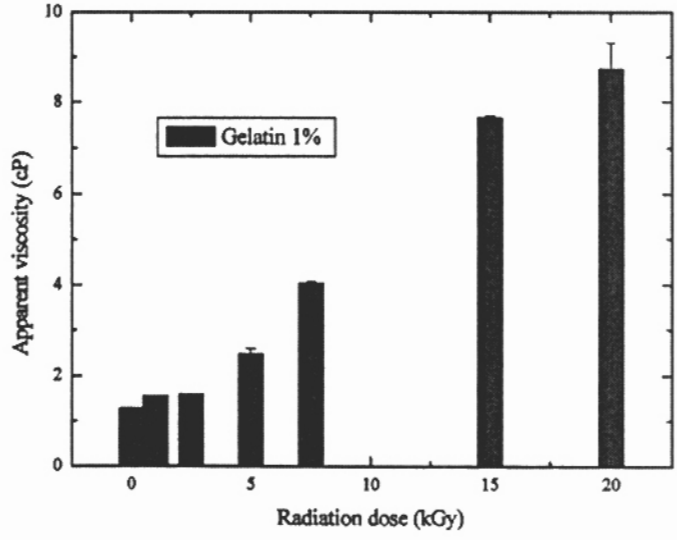

FIGURE 1 Apparent viscosity vs. γ-radiation dose of 1% gelatin solution.

the absorption of ionizing radiation interact with the solute. Then, radiation effects are caused by the water radicals HO°, e_{aq} and H° [13]. Only a fraction of the amino acid subunits of large proteins are exposed to the aqueous environment, and it is these amino acid subunits, which are most likely attacked. Zagorski [14] used aqueous solution of gelatin as a medium to perform pulse radiolysis studies. His aim was the study of the relation between the macro-viscosity, reaching very often the stage of quasi-solid state and the micro-viscosity of the medium at the molecular level. He noted that there was no relation between gelatin concentration and the diffusion of small species. He concluded that particular amino acid residues decide about the rate constant in spite of low participation in the polymer. He realized also that there were some priorities of the attack of HO· radicals on gelatin molecule.

In the present work the viscosity of the aqueous solutions from irradiated and non-irradiated bovine powder gelatin and carrageenan was compared with that of the ternary water-gelatin-carrageenan systems (97.5:1.0:1.5).

Figure 1 presents viscosity values versus dose of irradiated 1% gelatin solutions, when the applied doses were 0, 1, 2.5, 5, 7.5, 15,

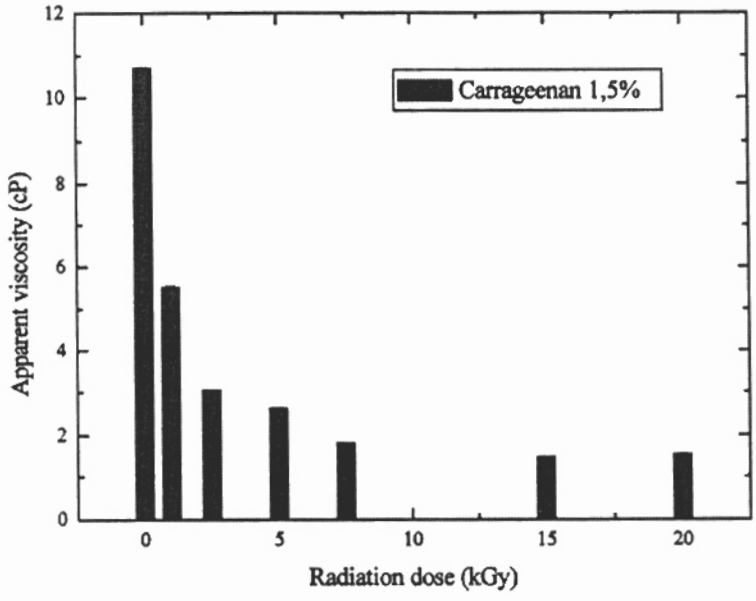

FIGURE 2 Apparent viscosity of 1.5% carrageenan solution as a function of γ-radiation dose.

and 20 kGy for viscosity measurement performed within 24 h after irradiation. It is possible to see an increase in the viscosity values with the increasing applied dose for dose values starting at 5.0 kGy.

In previous work [10] we had shown that when gelatin was irradiated as a powder, instead as in aqueous solution as in the present paper, a decrease in the viscosity of the solutions prepared afterward was obtained as the dose increased. In that case, a diminution of viscosity with dose was a clear indication that the radiation chemical transformation conducted to the production of stable end products of smaller molecular mass. In the present case, however, exactly the contrary was true: when aqueous gelatin gels were irradiated there was a viscosity increase for higher dose indicating a radiation polymerization, e.g., production of collagen like structures.

Figure 2 shows the viscosity changes performed by carrageenan solutions when irradiated with different radiation doses. A notorious reduction of viscosity was obtained with increasing dose being the viscosity reduced almost exponentially up to 7.5 kGy remaining practically constant afterwards. Like other polysaccharides, carrageenan displayed a similar rheological behavior after irradiation whether irradiated as a powder or in aqueous solution [9]. It seems that radiation-induced degradation occurred in both cases and was the predominant phenomenon.

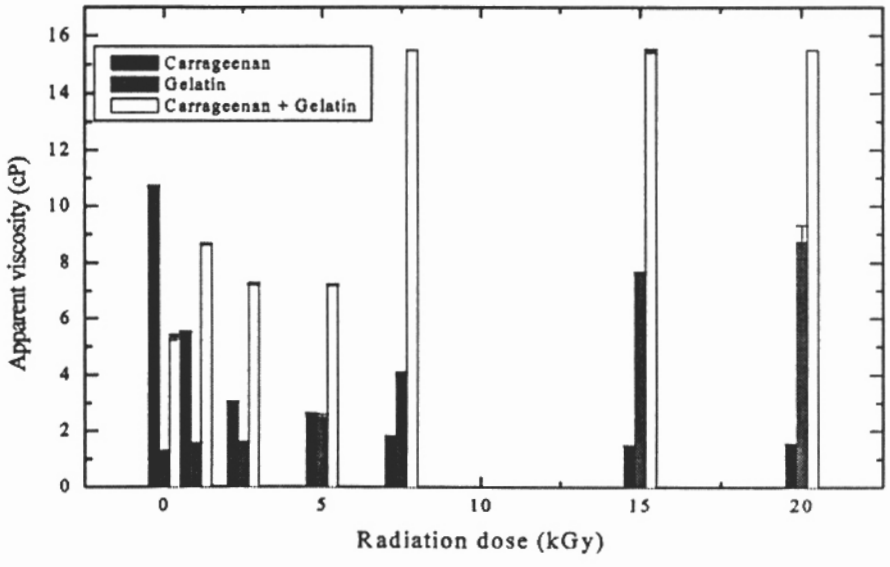

FIGURE 3 Apparent viscosity of the Carrageenan, gelatin and mixture of gelatin-carrageenan solution as a function of γ-radiation dose.

Figure 3 presents the results of the irradiation of the ternary water-gelatin-carrageenan systems (97.5:1.0:1.5). The viscosity variation of the irradiated ternary system did not correspond to neither the component alone nor to the sum of both of them. Although a mutual protection is commonly exerted when different substances are irradiated together [15], the different viscosity versus dose patterns obtained supports that a new protein-polysaccharide complex has been formed and a different balance among radiation degradation and radiation polymerization phenomena prevailed.

Polymeric biomacromolecules can be degraded by three common means either independently or in combination: (i) enzymatically, (ii) by light or high-energy radiation or (iii) by heat. In some instances rather high ionizing radiation doses (25–500 kGy) are needed [16]. In the present case, the two biopolymers alone present quite opposite behavior against radiation treatment making unpredictable the viscosity pattern of a complex made from their mixture.

These preliminary results must be confirmed by further calorimetry, thermogravimetry, infrared spectroscopy, mechanical properties and sample composition analyses.

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