

Ascorbic acid as radiation protector on polysaccharides used in food industry

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Abstract

L-Ascorbic acid or Vitamin C is a highly soluble compound that has both acidic and strong reducing properties. The natural form of the vitamin is the L-isomer; the D-isomer has about 10% of the activity of the L-isomer and is added to foods for nonvitamin purposes. Aside from its use as a vitamin, ascorbic acid or some derivatives are employed as antioxidants in foodstuffs, to prevent rancidity, browning of cut apples and other fruits and in meat curing. Radiation affects polysaccharides like carrageenan, widely used in food industry, modifying their rheological properties. In this work, ascorbic acid was used in order to verify their capability as radiation protector on irradiated polysaccharides. One percent aqueous solutions of this polysaccharide were prepared. Ascorbic acid was added to attain 5, 10, 15 and 20% (w/v) final concentrations. Co-60-irradiation was performed in a Gammacell 220 (AECL), dose rate about 5.2 kGy/h, with doses of 1.0, 2.5, 5.0 and 10.0 kGy. Radiation effects were followed by changes in the viscosity of irradiated solutions. Ascorbic acid presented a radioprotector behavior on carrageenan solutions and the radioprotective action of antioxidant Vitamin C was dependent upon their concentration.

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1. Introduction

During the last decades, increasing attention has been given to the role of free radicals in biological oxidations. Free radicals are highly reactive molecules, able to react with cellular structures and materials. For the protection against harmful free radical actions, it was suggested an increase in the dietary intake of the antioxidant vitamins, especially for diets high in polyunsaturated fats [1,2]. Free radical scavengers in the form of indigenous or added antioxidants are also necessary for the successful preservation of food [1].

Ascorbic acid and tocopherols are widely distributed in human diet and have been reported to scavenge active oxygen species and prevent cell damage [3]. There are evidences that antioxidants can scavenge or quench free radicals generated by irradiation [4]. Nutrients like ascorbic acid or vitamin C present a crucial role in the prevention or delay of the onset of degenerative diseases. These nutrients act as antiox-

idant, being responsible for the neutralization of oxidative processes generated by free radicals in animal organisms. Ascorbic acid is noted for its complex multi-functional effects. Depending on conditions ascorbic acid can act as an antioxidant, pro-oxidant, a metal chelator, a reducing agent or an oxygen scavenger. In aqueous systems containing metals, ascorbic acid can act as a pro-oxidant by reducing the metals, which become more active catalysts of oxidation in their lower valence state. In the absence of added metals, ascorbic acid is an effective antioxidant at high concentrations. In non-aqueous media, ascorbic acid and esters are not good antioxidants [5].

The interest in using natural antioxidants as additives by the food industry continues to grow because they are presumed to be safe since they occur in foods and have been used for centuries, and the question of safety of synthetic compounds can thus be avoided [5]. Antioxidants are substances that can delay the onset or slow the rate of oxidation of autoxidizable materials. Literally, hundreds of compounds, both natural and synthesized, have been reported to possess antioxidant properties. Their use in food, however,

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is limited by certain obvious requirements not the least of which is adequate proof of safety. For maximum efficiency, sometimes primary antioxidants are often used in combination with other phenolic antioxidants or with various metal sequestering agents [6].

There is an increasingly important research discipline that studies physical properties at the macromolecular and particle scale in complex food structures [7]. The sensitivity or stability against ionizing radiation of ascorbic acid present in food or in *in vitro* systems was the subject of different research [8,9]. On the other hand, the capability of ascorbic acid as radioprotector itself was established in diverse systems [10].

The aim of this work was to assess the radioprotecting capability of ascorbic acid when applied to an *in vitro* system based on carrageenan, a polysaccharide used regularly as food additive, by following the viscosity profile of the experimental mixtures.

2. Materials and methods

2.1. Materials

Kappa and iota-carrageenans distributed by Gelymar–Adicon Additives Industry and Trade Ltd., SP, Brazil, were employed. The dealer Chemical and Pharmaceutical Galena Ltd. supplied ascorbic acid kindly.

2.2. Irradiation

Irradiations were performed in a Co-60 Gammacell 220 (AECL); dose rate, 5.2 kGy/h with doses of 0, 1.0, 2.5, 5.0 and 10.0 kGy; dose uniformity factor, 1.13. For irradiation, the samples were contained in 100 ml glass tubes.

2.3. Viscosimetry

Viscosimetry techniques developed previously at the laboratory were applied [11]. A Brookfield viscometer, model LV-DVIII, with an adapter ULA and a Neslab water bath model RTE-210, precision ± 0.1 °C was employed. Carrageenan solutions were prepared at 1% (w/v) at about 100 °C. To the solutions already prepared, ascorbic acid was added to attain 0, 5, 10, 15 and 20% (w/v) final concentrations. Reported viscosity measurements were the average of at least three determinations.

2.4. pH measurement

An Analyser model pH 300 for pH measurement was employed at 25 °C.

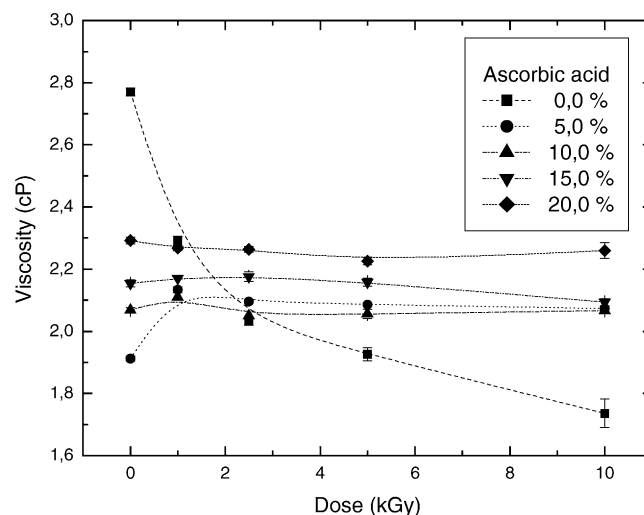


Fig. 1. Viscosity as function of the radiation dose for the carrageenan solutions (250 rpm, 60 °C).

3. Results and discussion

As previously mentioned, we wanted to examine the hypothesis of ascorbic acid been use as radioprotector in an experimental system made of a common additive used as thickener by the food industry. Fig. 1 presents the viscosity values of carrageenan solutions as a function of dose, measured at 60 °C and an angular speed of 250 rpm. The viscosity curves reflect the depolymerization action of radiation treatment characterized by a diminution on molecular weight. A progressive decrease on viscosity is verified as a function of the applied radiation dose. The viscosity reduction of carrageenan solutions due to radiation effect was of 17, 27, 31 and 37%, respectively, for 1.0, 2.5, 5.0 and 10.0 kGy.

Different radiation actions were observed depending on the percentage of ascorbic acid present in the system. When ascorbic acid was added to unirradiated carrageenan solutions, a decrease of 31, 25, 22 and 17% for the viscosity was found, for concentrations, respectively, of 5, 10, 15 and 20% (w/v), as compared to the solutions without ascorbic acid.

The decrease in viscosity was inversely proportional to the ascorbic acid concentration, showing a protective action of the antioxidant vitamin for carrageenan solutions, where greater viscosity values resulted when higher ascorbic acid concentrations were employed. As expected, the pH was inversely proportional to the ascorbic acid concentration (Table 1). As can be seen in Table 1, pH measurements remain almost unchanged whatever the gamma radiation dose applied when a certain ascorbic acid concentration was used.

It was described that carrageenan remained stable at pH values normally incurred in food systems. However, it loses viscosity in systems below pH 4.3 if held at an

Table 1
pH in different doses of gamma irradiation and ascorbic acid concentrations

Dose (kGy)	pH				
	0 ^a	5 ^a	10 ^a	15 ^a	20 ^a
0	6.96	2.56	2.28	2.13	2.00
1.0	6.99	2.55	2.26	2.09	1.94
2.5	6.90	2.55	2.29	2.13	1.96
5.0	6.70	2.56	2.28	2.12	1.97
10.0	6.38	2.55	2.30	2.13	1.98

^a Ascorbic acid (% w/v).

elevated temperature, been the gel processing time 5.0 h at 40 °C and 2 s at 120 °C [12]. The resultant hydrolysis of the carrageenan leads to a lower gel strength. Present viscosity measurement was made at 60 °C, so the influence of temperature may have also some contribution.

The protection that fruits and vegetables provides against diseases, including cancer and cardio- and cerebrovascular diseases, has been attributed to the various antioxidants contained in them [13,14]. At present, there is overwhelming evidence to indicate that free radicals cause oxidative damage to biological macromolecules. Therefore, antioxidants, which can neutralize free radicals, may be of central importance in the prevention of these disease states.

Other important actions of ascorbic acid on polysaccharides were also described elsewhere. On carrageenan and chitosan films, for instance, ascorbic acid tends to improve the resistance to the traction, to the prolongation and permeability to the steam of water [15]. As ascorbic acid is used largely in foods, their use as radioprotector [10] could easily be accepted in any food composition. Complementary studies on radiation protecting effect due to ascorbic acid on polysaccharide macromolecules are needed taking in account the increasing applications of food irradiation. In addition, research efforts must continue to explore the versatility of food hydrocolloids especially in low-fat systems for all market segments of food industry.

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References

- [1] J.K. Donnelly, D.S. Robinson, Invited review free radicals, *Foods Free Radic. Res.* 22 (1995) 147–176.
- [2] G. Block, Antioxidant vitamins and disease prevention, *Food Technol.* 48 (1994) 80–87.
- [3] M. Murakami, T. Yamaguchi, H. Takamura, T. Matoba, Effects of ascorbic acid and α -tocopherol on antioxidant activity of polyphenolic compounds, *J. Food Sci.* 68 (2003) 1622–1625.
- [4] E.J. Lee, D.U. Ahn, Effects of antioxidants on the production of off-odor volatiles and lipid oxidation in irradiated turkey breast meat and meat homogenates, *J. Food Sci.* 68 (2003) 1631–1638.
- [5] E.N. Frankel, Antioxidant in lipid foods and their impact on food quality, *Food Chem.* 57 (1996) 51–55.
- [6] S.R. Tannenbaum, V.R. Young, M.C. Archer, Vitamins and minerals in fennema, O.R., in: *Food Chemistry*, second ed., Marcel Decker Inc., New York, NY, 1985, p. 991.
- [7] H.D. Goff, Studying food structure in food research trends-2003 and beyond Neil H. Mermelstein, *Food Technol.* 56 (12) (2002) 30–59.
- [8] S.F. Sabato, N.L. Del Mastro, Spectrophotometry determination of irradiated ascorbic acid, in: *Proceedings of the 4th Meeting on Nuclear Applications*, Poços de Caldas, MG, Brazil, 1997, pp. 922–925.
- [9] X.T. Fan, D.W. Thayer, Quality of irradiated alfalfa sprouts, *J. Food Prot.* 64 (10) (2001) 1574–1578.
- [10] N. Getoff, I. Platzer, C. Winkelbauer, Transients and cooperative action of beta-carotene, Vitamin E and C in biological systems in vitro under irradiation, *Rad. Phys. Chem.* 55 (5–6) (1999) 699–704.
- [11] A.J. Aliste, Effect of gamma radiation on the viscosity of carrageenan, agar agar and alginates employed by the food industry, Master Degree Dissertation, Energy and Nuclear Research Institute (IPEN), University of São Paulo, São Paulo/SP, Brasil, 1999.
- [12] W.R. Thomas, Carrageenan in imeson, A, in: *Thickening and Gelling Agents for Food*, second ed., Chapman & Hall, London, UK, 1997, p. 320.
- [13] W. Wang, G. Cao, R.L. Prior, Total antioxidant capacity of fruits, *J. Agric. Chem.* 44 (1996) 701–705.
- [14] B.M. Ames, Dietary carcinogens and anticarcinogens: oxygen radicals and degenerative diseases, *Science* 221 (1983) 1256–1263.
- [15] S.Y. Park, B.I. Lee, S.T. Jung, H.J. Park, Biopolymer composite films based on kappa carrageenan and chitosan, *Mater. Res. Bull.* 36 (3–4) (2001) 511–519.