International Journal of Biological Macromolecules 44 (2009) 57–63

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: www.elsevier.com/locate/ijbiomac

Controlling degradation of low-molecular-weight natural polymer "dextrin" using gamma irradiation

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ARTICLE INFO

Article history:
Received 21 August 2008
Received in revised form
26 September 2008
Accepted 7 October 2008
Available online 18 October 2008

Keywords:
Natural polymer
Degradation
Dextrin
Radiation

ABSTRACT

Dextrin, which is widely used throughout many industries for their functional properties, was selected for studying the influences of gamma irradiation on its viscosity, physicochemical properties and dextrin granule structure. The formation of radicals during irradiation process of dextrin in air condition was investigated by electron spin resonance (ESR) showing the influence of irradiation and storage parameters on the nature and concentration of the free radicals. Two major radicals or groups of radicals are observed. The radicals show g-values varying among $g = 2.0102 \pm 0.0002$ and $g = 2.0126 \pm 0.0006$. Irradiation was observed to induce increases in the intensity of single. The material left behind after irradiation treatment was characterized using thermal analysis, TGA and DSC. A structural analysis was made using SEM and X-ray diffraction to investigate whether the partial hydrolysis had any influence on the granular structure and the crystallinity of the dextrin. The results show that dextrin undergoes oxidative degradation under the influence of gamma radiation.

1. Introduction

Functionalization of polymers has emerged as an important area of polymer science and technology. In the recent years, biodegradable polymers have been widely investigated, especially for biomedical field [1]. There has been a worldwide realization that nature-derived monosaccharides, disaccharides, oligosaccharides and polysaccharides can provide us raw materials needed for the production of numerous industrial consumer goods [2]. There is a recognized need to identify new biodegradable polymers suitable for development as drug carriers. Synthetic and natural polymers have been explored as drug carriers [3]. As there are other natural polymers or related carbohydrate groups like proteins, lignin or dextrins, which are used as constituents of polysaccharide-containing composites, their environmental impact is covered. Mixing of polysaccharide-based materials with plastics means mixing hydrophilic and hydrophobic materials, which requires energy. The goal to replace only a part of the higher cost plastics with lower cost polysaccharides is not the best strategy. The full replacement of plastics with polysaccharides for composites production is a part of the non-pollute environmental strategy [4].

Dextrin is one of the several carbohydrates having the same general formula as starch, but the structural difference between dextrin and starch is that dextrin is a smaller and less complex molecule. Dextrins have the same empirical formula ($C_{12}H_{22}O_{11}$) as starch, they have the general formula, $-[C_x(H_2O)_y)]_n-$ ($y = x - 1$), in which glucose units are joined to one another usually head-to-tail. A diagram of the dextrin structure molecule is shown in Diagram 1 [5]. It comprises two types of α-glucan, amylose and amylopectin; amylose is a relatively long linear α-glucan and amylopectin is a much larger molecule than amylose and has a heavily branched structure. Dextrins are polysaccharides and are produced as intermediate products in the hydrolysis of starch by heat, by acids, and by enzymes. Dextrin is typically characterized by the "dextrose equivalent" (DE), which refers to the total reducing power of all sugars present relative to glucose. While the DE gives the supplier and buyer a rough guide to the bulk properties of the material, the physiochemical properties of dextrins are dependent on the overall oligosaccharide profile [6]. Their nature and their chemical behavior depend to a great extent on the kind of starch from which they are derived. For example, some react with iodine to give a reddish-brown color, others a blue, and still others yield no color at all. For commercial use dextrin is prepared by heating dry starch or starch treated with acids to produce a colorless or yellowish, tasteless, odorless powder which, when mixed with water, forms a strongly adhesive paste. After an extensive acid hydrolysis, the amorphous regions of the granules are removed and leave crystalline residues, which consist of amylodextrins of linear and singly branched and multiply branched structures [7]. The oligosaccharides or dextrin hydrolysis products are consider-

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doi:10.1016/j.ijbiomac.2008.10.002

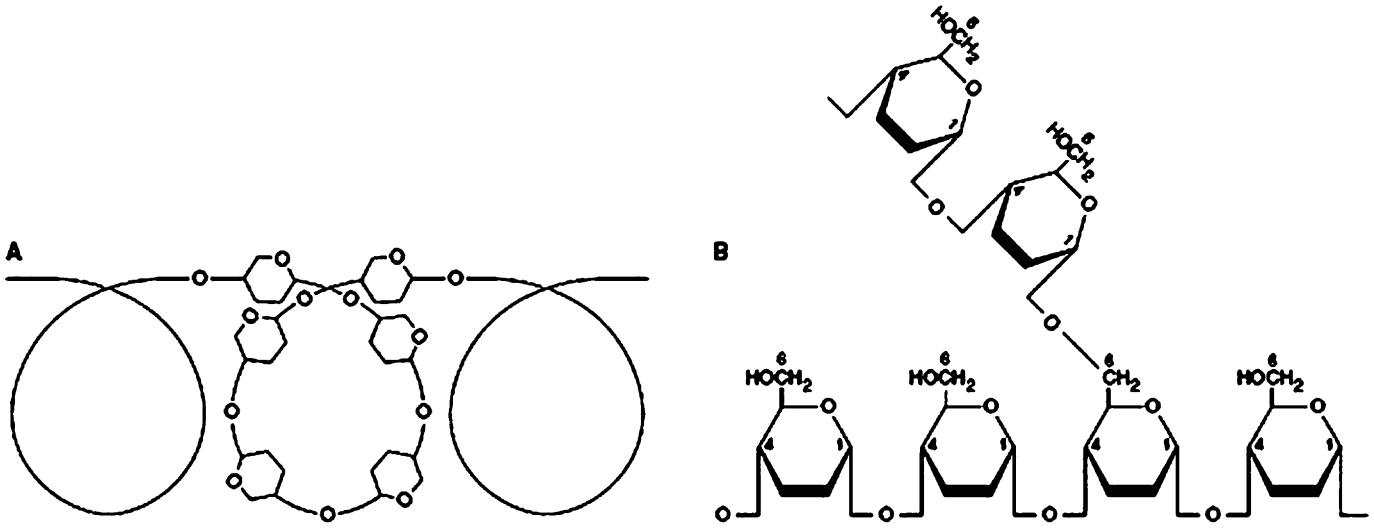

Diagram 1. Structure of starch or/dextrin. (A) Amylose, showing helical coil structure. (B) Amylopectin, showing 1 → 6 branch point [4].

ably more highly biodegradable because they would be the natural foods of bacteria present in sewage or raw river water [8]. Dextrin is a natural polymer used clinically as a dialysis solution and as a controlled drug delivery formulation. It is widely used throughout the food industry for their functional properties and adhesives, i.e., for postage stamps, envelopes, and wallpapers. Also employed in textiles, bulking agents, crystallization inhibitor, fat replacer, film formers additionally for sizing paper.

Degradation of dextrin granules represents a biochemical process, in which dextrins are easily hydrolyzed further into small fragments [9]. Irradiation is the simplest way to degrade a polysaccharide in any physical form (solid, suspension, paste, solution, etc.). The process is very efficient and can be easily controlled by choosing a proper irradiation dose. No chemicals are needed, there is no additional processing and there is no waste. Besides, at appropriate conditions sterilization may be accomplished in parallel to the reduction in molecular weight. A disadvantage that may limit the applicability of solid-state irradiation is the possibility of some radicals being trapped in crystalline regions of polymer, resulting in further degradation ('post-effect'), slow but difficult to control [10,11].

More information is available about starch degradation using irradiation [12–15] but there is less information on the dextrin. The presented paper focuses on the degradation of the dextrin using γ-irradiation as a clean and safety tool and studding the physicochemical properties and dextrin granule structure.

2. Experimental

2.1. Materials and methods

Dextrin (White) was supplied by Sisco Research Laboratories, sulphated ash maximum 0.2% and reducing sugars (as dextrose) maximum 4%, moisture 5% maximum. The molecular weight for the used dextrin is not allowed however commonly dextrin molecular weight may amplitude from 800 to 70,000. All other chemicals were of reagent grade and were used as-received.

2.2. Irradiation of samples

The dextrin specimens were packed as solid powder in polyethylene bags and were then exposed to γ-radiation from a ^{60}Co source at a dose rate of 6.316 kGy/h using a gamma cell available in NCRRT, AEA, Cairo, Egypt. The irradiation process was performed in air, at room temperature. The gamma irradiation was conducted at 5–100 kGy.

2.3. Electron spin resonance measurements

Electron spin resonance (ESR) spectra were recorded at ambient temperature with a Bruker EMX spectrometer (X-band); the cavity used was the standard Bruker ER 4102 rectangular cavity. The operating conditions for the ESR spectrometer were as follows: center field: 3480.160 G, sweep width: 200 G; resolution 1024 points, microwave frequency: 9.769 GHz; microwave power 4.024 mW; sweep time 41.943 s. For measurements, samples of dextrin (≈0.1 g) were inserted in the sample tube (3-mm internal diameter) such that the sample is adjusted at the center of the vertical dimension of the sensing zone of the ESR cavity.

The intensity of ESR signal in relative units

= Peak height/sample weight/1000

2.4. Rheological measurements

A cone-plate rheometer (Brookfield, DV III, Brookfield Engineering Laboratories, USA) was used to determine the rheological properties of the dextrin at 25 °C. The properties were measured at shear rates ranging from 10 to 100 s^{-1}. The power-law model and Bingham equation were used to describe the rheological properties of dextrin solutions [16]. The flow behavior index n and consistency index k values were obtained by plotting the shear stress vs. the shear rate values and fitting the data by the function

$$\tau = k\gamma^n$$

where τ is the shear stress (dyene/cm^2), k the consistency index (dyne s/cm^2), γ the shear rat (s^{-1}), and n is the flow index (a dimensionless value, which reflects the natural of the rheological behavior). In addition, to calculate the apparent viscosity and yield stress, the Bingham model was used to fit the data:

$$\tau = \eta\gamma + \tau_0$$

where η is the apparent viscosity (cP) and τ_0 is the yield stress (dyne s/cm^2).