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# Effect of γ-radiation on free radicals formation, structural changes and functional properties of wheat starch

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ABSTRACT

Wheat starch was treated by different γ-radiation doses (3, 5, 10, 20, 35 and 50 kGy). The effects of γ-radiation on structural, thermal, physicochemical, morphological and rheological properties of wheat starch were studied. The presence of free radicals after γ-radiation treatment, which number decreased with time was confirmed. Structural analysis revealed decreases in the intensities of the O—H and C—H stretches and glycosidic linkages indicating the depolymerization of amylose and probably amylopectin into shorter chain molecules, but showed that γ-radiation treatment did not affect the crystalline structure. Differential scanning calorimetric (DSC) thermograms showed the absence of significant differences in the gelatinization temperatures, as well as the corresponding transition enthalpies since the DSC parameters are related to the crystalline ordering within the granules. Apparent amylose content decreased linearly with increasing irradiation dose leading to an increase in water solubility index. An increase in the swelling power was observed after irradiation treatment until 20 kGy, followed by a rapid decrease at higher doses. Microscopic observations showed that the effect of γ-radiation was more visible on starch pastes than on starch granules. Rheological properties of the starch pastes decreased with increasing irradiation dose as a result of glycosidic bond cleavage.



## 1. Introduction

Starch is the main storage carbohydrate of plants. It is biosynthesized as semi crystalline granules [1]. Approximately, 60 million tones are extracted annually worldwide from various cereal, tuber and root crops, of which roughly 60% are used in foods and 40% in pharmaceuticals and non-edible purposes [2]. Wheat starch is widely used in many food products and chemical engineering industries. It contributes greatly to improve structure, texture and rheological properties of various foods. Wheat starch is characterized by a high gelatinization temperature, a low viscosity and a short texture. It exhibits the typical A-type X-ray pattern characteristic of most cereal starches [2]. Wheat starch is used as a gelling agent in many applications: custard, short textured sauce, sausages and cured. But, limitations such as low solubility, low shear and thermal resistance, thermal decomposition and high affinity for retrogradation limit starches use in some food and non-food systems [3,4]. Therefore, starch may need to be modified for improving these physicochemical and functional characteristics.

Gamma radiation has been considered as a useful method for the production of modified starch rapidly and conveniently [5,6]. Irradiated foods are confirmed to be nutritionally adequate and safe for human consumption even with dose above 10 kGy [7]. The basic advantages of degradation of polymers by radiation include the ability to promote changes reproducibly and quantitatively without the introduction of chemical reagents and without the need for special equipment/setup to control temperature, environment and additives [8]. Besides food industry applications, the water-binding capacity and increased solubility/reduced viscosity of radiolyzed starch may be useful in applications for building, paper and textiles materials [6]. After irradiation, many reactions occur leading to progressive changes in starch macromolecules. Changes in carbohydrates are reported to be brought about either

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through a release of ionizing energy directly upon the target molecule or through indirect action of secondary intermediates such as free radicals [9]. Starch modification by gamma radiation may change the physicochemical and rheological properties of irradiated starch-rich products, resulting in decreased swelling power [10] and decreased viscosity and consistency of starch paste [11]. A proper understanding of starch properties and its interactions with other constituents particularly water and lipids are of interest to the industrial processing operations. Thus, studies on isolated starch may provide a better understanding of the mechanisms involved in irradiation-induced modifications of starch [12].

It was stated before that the starches physicochemical properties, which are a direct result of their structure, depend mainly on the botanical origin of native starches, since the diversities in macromolecular constituents and form of starch granules influence starch functionalities [2]. Researches had been reported on irradiation of corn starch [4,6,13–15], rice starch [16–18], and potato starch [3,13,19,20], but limited studies were published on the irradiation of wheat starch [9,21]. Therefore, it appears essential to carry out more studies dealing with gamma radiation effects on the different properties of wheat starch, since firstly it may be in some cases necessary to irradiate wheat flours [22], where the starch content is between 75% and 85% (dry basis) and secondly the mechanism of wheat starch degradation remains unclear.

It has been reported that gamma radiation induces free radicals responsible for starch chain depolymerization [23,24]. However, knowledge on the formation and kinetic evolution of free radicals after radiation treatment is lacking. Thus, the purpose of the present work was to confirm and to follow the formation of free radicals in wheat starch after gamma radiation (3, 5, 10, 20 and 50 kGy), and to determine the changes induced on the structural, the thermal, the morphological and the functional (rheological, pasting and textural) properties of wheat starch.

## 2. Materials and methods

### 2.1. Materials

Commercial wheat Potato and wheat starch were purchased from Roquette (Lestrem, France). The moisture content determined according to ISO 712 (1998) was 13.4%. Samples (were packed in polyethylene bags of 200 g, with a secondary paperboard cardboard packing. Prior to irradiation, samples were grouped in batches of two bags each. They were stored in a dry and ventilated medium to avoid any humidification.

### 2.2. Gamma radiation treatment

Gamma radiation treatments were carried out using a semi-industrial cobalt-60 irradiator at an ambient temperature of 25 °C (±0.5 °C) in the National Center for Nuclear Sciences and Technology (CNSTN, Technopole of Sidi Thabet, Tunisia). The irradiation doses applied in this study were 3, 5, 10, 20, 35 and 50 kGy, with a dose rate of 13.84 Gy/min. Non-irradiated (control) and irradiated samples were stored at room temperature. Dosimetry was performed using Amber Perspex dosimeters (Harwell dosimeters). The dosimeters were calibrated against an international standard set by the Aerial Laboratory.

Apart EPR study, all structural, thermal and functional analyses were achieved on stabilized irradiated samples (minimum 1 month after irradiation treatment was accomplished).

### 2.3. Electron paramagnetic resonance (EPR) spectrometry

Approximately 0.1 g of starch sample was placed in thin-wall quartz EPR tube (5-mm internal diameter, 250-mm length, and about 0.1-mm wall thickness) sealed with a firm plastic. The sample was then inserted into a standard TE102 (ER 4102 ST) rectangular cavity of an EMX X-band EPR spectrometer (Brucker EMX EPR, Germany) with 100 kHz magnetic field modulator. EPR spectrum was recorded at room temperature under the following conditions: power, 0.5 mW; sweep width, 59.53 G; modulation width, 3 G; sweep time, 42 s; time constant, 40.96 ms and number of scan, 5.

Wheat starch irradiated at 10 kGy was subjected to the monitoring of the free radical formation by means of the EPR test on the day of irradiation, after 2 days, 4 days and 18 days. During the analysis, the peak to peak height (PPH) was measured. Besides that, all irradiated samples were analyzed 15 days after irradiation in order to compare their spectra with the non-irradiated one. EPR spectra were obtained in duplicate for each irradiation dose.

### 2.4. Fourier transform infrared (FTIR) spectrometry

Absorbance spectra from non-irradiated and irradiated starches were recorded using a spectrometer (IFS 66v/S, Brucker, EQUINOX 55, France) equipped with a deuterated tryglycine sulphate (DTGS) detector operated in the Miracle attenuated total reflectance (ATR) accessory. A few milligrams of starch sample were deposited directly on a plate crossed by an infrared beam. Each spectrum, obtained at a resolution of 4 $cm^{-1}$, was an average of 32 scans, recorded against an empty cell as background, and was subtracted from the spectrum of water. The spectra were recorded within the range 400–4000 $cm^{-1}$. Spectra of transmittance against wave number were collected and used in order to analyze the changes induced by gamma radiation on wheat starch. FTIR spectra were carried out in duplicate for each radiation dose.

### 2.5. X-ray diffraction (XRD)

X-ray diffractograms of starch granules were obtained with a Panalytical powder X-ray diffractometer (X'Pert PRO.MPD, Rigaku sales, USA) equipped with Cu $K\alpha_1$ radiation, with a wavelength of 1.54 nm. The radiation was generated at 8.047 eV and 30 mA. The samples were initially prepared at a cylindrical shape pastille before being tested and then scanned from 5° to 60° using a scanning rate of 0.016°/s. The d001 spacing was calculated by first determining $2\theta$ for the scattering peak using the X'Pert Data Viewer software and then substituting the $2\theta$ value into Bragg's law. A scintillation compteur (X'Celerator) was used to measure the intensity of the X-ray diffracted. This intensity was then reported against the angle of diffraction. Treatment of the diffractograms was carried out using the software based on the cards data of JCPDS (Joint committee on powder diffraction standards) with a data PDF (Powder Diffraction File) basis. X-ray diffractograms were carried out in duplicate for each irradiation dose.

### 2.6. Differential scanning calorimetry (DSC)

Thermal properties of starches were studied using a Differential Scanning Calorimeter Q1000 (TA Instruments, New Castle, DE, USA). 3.0 mg of starch corrected by dry matter were loaded into an hermetic aluminum pan (TA Instruments, New Castle, DE, USA) and distilled water was added using a microsyringe to achieve a starch-water suspension of 10 mg, containing 70% (g/g) water. Samples were hermetically sealed and allowed to stand for 1 h at room temperature before heating in DSC. The DSC analyzer was calibrated using indium and an empty aluminum pan was used as reference. Sample pans were heated at a rate of 10 °C/min from 30 to 100 °C. The onset (TOnset) temperature was taken at the intersection of the baseline with the tangents to the left side of the gelatinization peak. The peak temperature (TP) was taken at the maximum