Chapter 5

Aspects on Starches Modified by Ionizing Radiation Processing

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Additional information is available at the end of the chapter

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Abstract

Starch is one of the most studied natural polymers due to its widespread and applications as well as to the global interest regarding renewable, cheap, and easy to process resources. The native form of starch is frequently subjected to different processing methods in order to modify its structure and thus to obtain some functional properties suitable in specific industrial applications. Radiation-based method is a "green tool" for modification of natural polymers, such as starch, cellulose, pectin, and chitosan, alginate, having advantages over conventional methods that involve chemical agents associated with environmental toxicity. Radiation processing of natural polymers involves a simple, ecofriendly, and fast process that has harmless feature and provides advanced materials with unique properties. The chapter intends to be an overview of the major findings in the last decade concerning the starches modified by ionizing radiation processing. Therefore, aspects strongly related to changes in physicochemical, functional, and structural properties of starches from various botanical origins are approached. The main key points of this topic are highlighted by a critical evaluation of the mentioned aspects and future perspectives are suggested.

Keywords: starch, modification, gamma radiation, electron beam, processing

1. Introduction

Starch is one of the most widespread and used natural polymers in different applications such as food, pharmaceutical and cosmetics, paper, and textile industries. Even starch is a renewable, cheap, and easy to process resources, its use as a native form has been restricted by some limitations (high viscosity, low solubility in cold water, paste instability, etc.) in specific applications due to its structure. Therefore, starch is frequently subjected to different processing methods (chemical, physical and enzymatic treatments) in order to modify its structure resulting in functional properties suitable in specific industrial applications. The most used way to obtain modified starch is by chemical methods, which are most of the time complex, expensive, and time consuming.

Progressive methods of starch modification are generally considered the physical techniques (e.g., ionizing and non-ionizing radiation treatments, plasma treatment), which are fast, low cost, and environmentally friendly because they do not use polluting agents, do not allow the penetration of any toxic substances in the treated products, do not generate undesirable residual products, and do not require catalysts and laborious preparation of samples.

In the last decade, there is a great amount of reported studies related to the effects of ionizing radiation (gamma radiation, electron beam) on different type of starches. The studies concerning the impact of gamma radiation or electron beam (e-beam) were performed on starches extracted from various vegetal sources—cereals, tubers, legumes, and stems—as presented in **Table 1**.

The reported data showed that ionizing radiation processing generates free radicals on starch molecules that can alter their size and structure, leading to changes of functional and physicochemical properties of starch as a function of experimental processing parameters (irradiation dose, irradiation dose rate, moisture content of samples, and type of gas atmosphere).

Type of starch	Type of ionizing radiation/processing parameters	Investigated properties	Techniques of characterization	References
Cereal				
Corn	Gamma rays; 1–50 kGy, 1 kGy/h, in air	Apparent amylose content Thermal properties Pasting profile Granule morphology and crystallinity	Chemical methods, DSC, viscometry, X-ray diffraction, SEM	[1]
	Gamma rays; 3–50 kGy, 19 Gy/min, in air	Pasting behavior Thermal properties Spectral characteristics Granule morphology and crystallinity	Viscometry, DSC, FTIR, X-ray diffraction, PLM	[2]
	E-beam 6 MeV; 10–50 kGy, 2 kGy/min, in air	Apparent viscosity Pasting properties Thermal properties Colorimetric properties Molecular weight and molecular weight distribution Granule morphology Spectral characteristics	Rheology, viscography, DSC, UV-Vis spectrometry, GPC, SEM, FTIR	[3–6]
	E-beam 6 MeV; 1–10 kGy, in air	Colorimetric properties	UV-Vis spectrometry	[7]
	E-beam 6 MeV; 5–100 kGy, solid and liquid	Apparent viscosity, Molecular weight and radius of gyration Granule morphology	Viscometry, rheology, MALLS, SEM	[8]

Type of starch	Type of ionizing radiation/processing parameters	Investigated properties	Techniques of characterization	References
Wheat	Gamma rays; 0.5–10 kGy, in air, moisture content 11%	Proximate composition Color Swelling and solubility indices Light transmittance Syneresis Freeze thaw stability Total amylose content Water and oil absorption capacities Pasting parameters Spectral characteristics	Chemical and visible spectroscopic methods, viscography, FTIR	[9]
	Gamma rays; 3–50 kGy, 13.84 Gy/min, in air, moisture content 13.4%	Structural, spectral and morphological properties Thermal properties Apparent amylose content Water solubility index and swelling power Pasting behavior	EPR, FTIR, XRD, SEM, DSC Chemical methods, viscography and viscometry	[10]
	E-beam 6 MeV; 10–50 kGy, 2 kGy/min, in air	Apparent viscosity Intrinsic viscosity Thermal properties Colorimetric properties Molecular weight and molecular weight distribution	Rheology, viscometry, DSC, UV-Vis spectrometry, GPC	[4, 5, 11]
	E-beam 2 MeV; 1–4.4 kGy, relative humidity 70 ± 5%	Pasting properties Thermal properties Molecular weight distribution Microscopic characteristics	Viscography, DSC, HPSEC, SEM	[12]
	E-beam 3 MeV; 5–30 kGy	Pasting profile Swelling volume Leaching of carbohydrates and amylose	Viscography, chemical and spectroscopic methods	[13]
	E-beam/6 MeV, 1–10 kGy, in air	Colorimetric properties	UV-Vis spectrometry	[7]
Rice	Gamma rays; 1–5 kGy, 0.4 kGy/h, in air, moisture content 9%	Amylose and carboxyl contents Acidity Thermal properties Molecular weight distribution Granule morphology and crystallinity	Chemical methods, DSC, GPC, SEM, X-ray diffraction	[14]
	Gamma rays; 1–10 kGy, 0.4 kGy/h, in air, moisture content 12%	Swelling power and solubility Carboxyl content Pasting properties Thermal properties Granule morphology and crystallinity Spectral characteristics	Chemical methods, viscography, DSC, SEM, X-ray diffraction, FTIR	[15]
	E-beam 6 MeV; 10–50 kGy, 2 kGy/min, in air	Apparent viscosity Thermal properties Colorimetric properties Molecular weight and molecular weight distribution	Rheology, DSC, UV-Vis spectrometry, GPC	[4, 5]

Type of starch	Type of ionizing radiation/processing parameters	Investigated properties	Techniques of characterization	References
Tuber				
Potato	Gamma rays; 5–20 kGy, 2 kGy/h, in air, moisture content 10%	Carboxyl content Apparent amylose and amylose leaching Swelling power and solubility Syneresis Pasting properties Granule morphology and crystallinity	Chemical methods, spectroscopy, viscography, SEM, X-ray diffractometry	[16]
	Gamma rays; 10 and 50 kGy, 2 kGy/h, in air, moisture content 10%	Carboxyl content Swelling factor and amylose leaching Apparent amylose content Pasting properties Thermal properties Granule morphology and crystallinity Spectral characteristics In vitro digestibility	Chemical methods, DSC, viscography, FTIR, SEM, optical microscopy, X-ray diffraction	[17]
	E-beam 6 MeV; 10–50 kGy, 2 kGy/min, in air	Apparent viscosity Thermal properties Colorimetric properties Molecular weight and molecular weight distribution	Rheology, DSC, UV–Vis spectrometry, GPC	[4, 5]
	E-beam 6–7 MeV; 110–440 kGy, in air, moisture content 12%	Phase structure Structure morphology Dynamic viscosity Amount of carboxylic and carbonyl groups Solubility in cold water	Wide-angle X-ray diffraction, SEM, FTIR, rheology, chemical methods	[18]
Tapioca	E-beam 3 MeV; 5–30 kGy	Pasting profile Swelling volume Leaching of carbohydrates and amylose	Viscography, chemical and spectroscopic methods	[13]
Elephant foot yam (*Amorphophallus paeoniifolius*)	Gamma rays; 5–25 kGy, 2 kGy/h, in air	Color, pH Apparent amylose and carboxyl contents Swelling power and solubility Water absorption capacity Light transmittance Syneresis Pasting parameters Morphological characteristics and crystallinity Spectral characteristics Thermal analysis	Chemical and spectroscopic methods, viscography, SEM, FTIR, DSC	[19]

Type of starch	Type of ionizing radiation/processing parameters	Investigated properties	Techniques of characterization	References
Legume				
Bean	Gamma rays; 5–25 kGy, 185 Gy/h, in air	Solubility and swelling power Carboxyl content, pH Retrogradation Apparent amylose content and amylose leaching Water absorption capacity Pasting parameters Thermal properties In vitro digestability Granule morphology and crystallinity Antioxidant activity	Chemical methods, viscography, DSC, SEM, X-ray diffractometry	[20]
	Gamma rays; 5–15 kGy, 83 Gy/min	Color Apparent amylose and carboxyl contents Water and oil absorption capacities Bulk density Swelling and solubility indices Light transmittance Syneresis Freeze thaw stability Pasting properties Granule morphology and crystallinity Spectral characteristics	Chemical methods, viscography, visible spectroscopy, SEM, X-ray diffraction, FTIR	[21]
	Gamma rays; 5–20 kGy, 2 kGy/h, in air, moisture content 10%	Carboxyl content, pH Apparent amylose Swelling power and solubility Water absorption capacity Light transmittance Syneresis Pasting properties Granule morphology and crystallinity	Chemical methods, viscography, visible spectroscopy, SEM, X-ray diffractometry	[22]
	Gamma rays; 10 and 50 kGy, 2 kGy/h, in air, moisture content 10%	Carboxyl content Swelling factor and amylose leaching Apparent amylose content Pasting properties Thermal properties Granule morphology and crystallinity Spectral characteristics In vitro digestibility	Chemical methods, DSC, viscography, FTIR, SEM, optical microscopy, X-ray diffraction	[17]

Type of starch	Type of ionizing radiation/processing parameters	Investigated properties	Techniques of characterization	References
Stem				
Lotus	Gamma rays; 5–20 kGy, 2 kGy/h, in air, moisture content 12%	Apparent amylose content Carboxyl content, pH, Amylose leaching and swelling power Water absorption capacity Syneresis Pasting properties Granule morphology and crystallinity	Chemical methods, viscography, SEM, X-ray diffractometry	[23]
Sago	E-beam 3 MeV; 5–30 kGy	Pasting profile Swelling volume Leaching of carbohydrates and amylose	Viscography, chemical and spectroscopic methods	[13]

Table 1. Studies relevant to effects of ionizing radiation on various starches.

The chapter gives an overview of the major findings in the last decade concerning the starches modified by ionizing radiation processing. Therefore, aspects strongly related to changes in physicochemical, functional, and structural properties of starches from various botanical origins are approached. The main key points of this topic are highlighted by a critical evaluation of the mentioned aspects and future perspectives are suggested.

It is to be mentioned herein that in the last decade two other reviews regarding the impact of radiation processing on starch [24, 25] have been published, and the most recent one [25] has summarized only the gamma radiation influence on starches.

2. Fundamentals of radiation processing

Radiation is generally a form of energy characterized by its ability to move from one location to another, and it can be divided into non-ionizing (ultraviolet light, visible light, infrared radiation, microwaves, etc.) and ionizing (X-rays, gamma rays, electron beams, etc.) ones [26]. Ionizing radiation—mainly gamma radiation and electron beam—is the most used to modify starch macromolecules and, further, the approach will be made in context of the processing procedures using ionizing radiation. Gamma rays—electromagnetic radiation—are emitted by radionuclides such as isotopes of cobalt-60 (^{60}Co) and cesium-137 (^{137}Cs). Electron beam consists of accelerated electrons, which are charged particles generated from regular electricity using linear accelerators, and do not involve radioactive isotope sources. It is noteworthy that electron beam irradiation is similar to gamma processing with basically the same interaction with materials to be subjected to irradiation processing [27].

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2.1. Interaction of radiation with matter

Gamma rays transfer energy by the photoelectric effect, Compton effect, and pairs generating, leading to liberation of fast electrons that lose energy by the same effects as accelerated electrons of the electron beams. Later on, the energy is absorbed by matter when electrons pass through it and two distinct primary effects, *ionization* and *excitation* of atoms and molecules of the substance occur as presented synthetically in **Figure 1**.

Ionization is the primary process by which a neutral atom or molecule becomes charged, and the resulting product is called *ion*. An ion formed by the loss or capture of an electron contains an unpaired electron, being actually a *free radical*, which is highly reactive chemical specie. The ejected electron may ionize further other atoms and molecules by successive collisions and ionizations. Excitation is another primary effect occurring when a high-energy charged particle passes through atoms imparting energy to atomic electrons without ejecting them and leads to an excited atom.

The secondary effects consist in different reactions of primary species (ions, excited molecules, or free radicals) that lead to the final products. These effects could be dissociation of an excited molecule into two radicals or into two different molecules. The free radicals participate further in recombination processes between themselves (radical-radical recombination) leading either to the initial molecule or new molecules. The formed radicals can also suffer a recombination with a new molecule abstracting a hydrogen atom forming a new free radical and a new molecule.

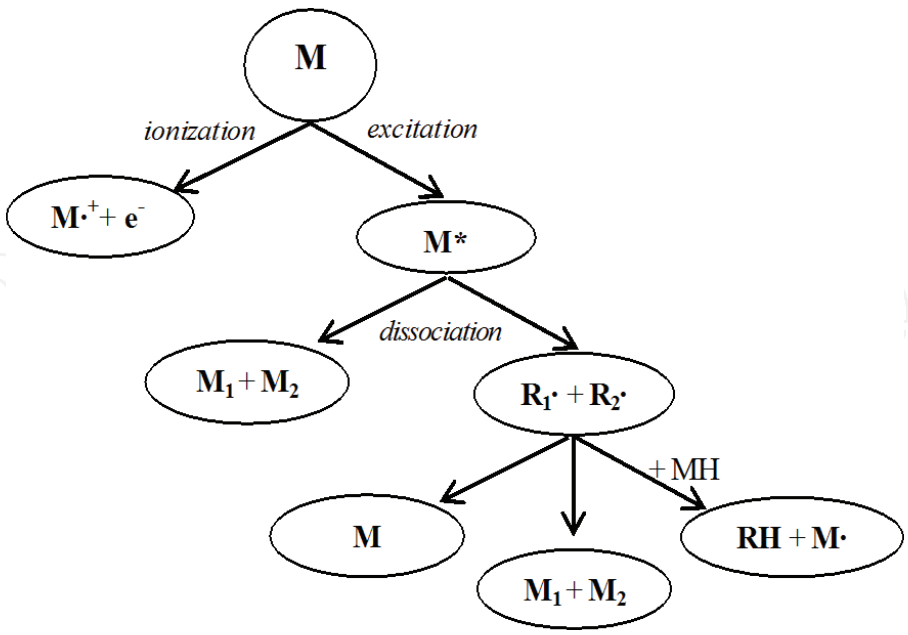

Figure 1. Fundamental processes of electrons passing through matter.

2.2. Radiation quantities

The most used dosimetric quantities and their units are the absorbed dose and the absorbed dose rate according to the International Commission on Radiation Units and Measurements (ICRU) Report no. 33 [28]. Moreover, these radiation quantities are the most important in the physical quantities used in the dosimetry field in order to optimize and control the irradiation process [29, 30].

The *absorbed dose*, *D*, is the amount of energy absorbed per unit mass of irradiated matter at a point in the region of interest [29]:

$$D = \frac{d\bar{\varepsilon}}{dm} \tag{1}$$

where $d\bar{\varepsilon}$ is the mean energy imparted by ionizing radiation to the matter in a volume element and dm is the mass of that volume element.

The SI derived unit of absorbed dose is the *gray* (Gy), which replaced the earlier unit of absorbed dose, the *rad* that is still tolerated, but less used:

$$1\,\text{Gy} = 1\ \text{J/kg} = 100\,\text{rad}$$

For this absorbed dose, the rate of change of it with time can be defined as the absorbed dose rate, $\dot{D}$:

$$\dot{D} = \frac{dD}{dt} \tag{2}$$

The SI derived unit of absorbed dose rate is the *Gy/s*.

The absorbed dose and the absorbed dose rate will be hereinafter referred as irradiation dose and irradiation dose rate, respectively.

2.3. Advantages and disadvantages of ionizing radiation processing

Ionizing radiation has many advantages in material processing, being an effective tool to induce changes in structure and functional properties of materials without environmental negative implication. Thus, it is an environmentally friendly process that involves no use of polluting agents, no generation of undesirable residual products, and no penetration of toxic substances in treated products. Despite the advantages, ionizing radiation processing is accompanied by some disadvantages as shown in **Table 2**.

Type of radiation	Advantages	Disadvantages
Gamma rays	-Cold method -High penetration depth	-Low dose rate -Long time processing (hours) -Use of radioactive source
Electron beam	-Cold method -High dose rate -Very short time processing (s) -Radiation can be turn on and off	-Low penetration depth

Table 2. Ionizing radiation processing: Advantages and disadvantages.

3. Effects of ionizing radiation on functional properties

The physicochemical and functional properties of starch in various applications are of great interest, especially for manufacturers of starch-based products. Aspects related to the ionizing radiation effects on physical, chemical, and functional characteristics of starch are onward presented.

3.1. Physicochemical properties

The moisture contents of starches extracted from various botanical sources (lotus, sago, tapioca, wheat) were insignificantly affected by gamma radiation up to 20 kGy (dose rate ≤ 9 kGy/h) and electron beam up to 30 kGy [13, 23]. On the other hand, the moisture contents of rice starches were also insignificantly affected by gamma radiation at low doses (<1.5 kGy with dose rate of 0.63 kGy/h) [31], whereas a significant reduction in moisture content occurred at irradiation doses >2 kGy (dose rate of 0.4 kGy/h) as a result of radiation energy dissipation while ionizing radiation penetrates the starch sample [15]. Also, for starch extracted from elephant foot yam, the amount of moisture decreased significantly by gamma irradiation up to 25 kGy with dose rate of 2 kGy/h [19]. According to Reddy et al. [19], the reduction in the moisture content of starch sample by radiation processing may improve the shelf life of starch by avoiding the microorganisms' development.

pH of aqueous starch solutions decreased with increase of irradiation dose regardless of the botanical origin of the starch [5, 14, 16, 19, 23, 31–33]. The descending change of solution pH after irradiation could be attributed to the formation of chemical groups with acidic character such as carboxyl, carbonyl, or peroxide groups. Moreover, this behavior is sustained due to the fact that radiation processing of starch was generally performed in the presence of oxygen, thus promoting the appearance of free radicals, compounds with carbonyl bonds (aldehydes/ketones), organic peroxides, or other polysaccharide degradation products [34] that can lead to the increase of starch acidity. Therefore, the reduction of solution pH is strongly correlated with the increase of carboxyl content by the ionizing radiation processing of starch.

The water solubility can be improved concomitantly with the reduction of swelling power of granule by ionizing radiation processing for all starches. Therefore, the solubility value increased with the increase of irradiation dose for starches extracted from various botanical sources (corn, wheat, rice, potato, bean, elephant foot yam, lotus, chickpea, and Indian horse chestnut) [5, 9, 10, 15, 16, 18, 19, 21–23, 31–33, 35, 36]. The increase in solubility was due to the increase in polarity as a result of chain scission under irradiation and the decrease in inter-chain hydrogen bonds [35]. Such behavior demonstrates clearly that the starch molecules suffered important changes as a consequence of a degradation phenomenon induced by ionizing radiation processing.

The ionizing radiation processing of all types of starches caused the reduction of **swelling power** as the increase of the irradiation dose, especially at higher doses [5, 9, 10, 15–17, 19, 21, 22, 31, 32, 36–38]. This evolution could be attributed to the fact that starch granules become sensitive being weaker and easier to break after irradiation. In addition, a consequence of starch radiation-induced degradation can be also the inhibition of granule ability to trap water and provoke the swelling explaining thus the reduction of swelling power by irradiation.

3.2. Rheological properties

Ionizing radiation processing is able to produce significant changes in the rheological properties of starch especially by decreasing its viscosity. In this way, the most studies approached the evaluation of pasting behavior of irradiated starches. Thus, a considerable decrease in the paste viscosities was noted as the irradiation dose increased (up to 500 kGy) for starches with different botanical origins [2, 3, 6, 9, 12, 13, 15–17, 19–23, 27, 31–33, 35, 38]. However, exceptions were reported for the breakdown viscosity that increased with the irradiation dose up to 10 kGy for corn or wheat starches [35, 37, 39]. In addition, a comparative study on corn starch treated with the same gamma irradiation dose (10 kGy) in the dose rate range of 0.4–2 kGy/h clearly revealed that the viscosities of the starch pasting profile decreased more at lower dose rates in comparison to native starch [37].

The level of radiation-induced changes in the pasting profile was different according to the starch variety [20, 22, 31] and may be assigned to difference in extent of polymerization of leached amylose and amylopectin molecules of each starch variety. The reduction of the peak viscosity of starch was assigned to its weaker water binding capacity, granular rigidity, and integrity due to glycosidic bond cleavage [35, 40]. Moreover, the decrease in the setback and final viscosities were attributed to the degradation or shortening of amylose and longer amylopectin branch chains by irradiation [17, 37].

A gradual decrease of the initial pasting and peak temperatures was also induced by irradiation [3, 9, 17, 19, 21, 32, 33, 35, 37]. Although the peak time was not influenced by irradiation dose rate, it depended on starch variety [31].

Likewise, the apparent viscosity of irradiated starches decreased significantly as the irradiation dose increased for different cereal and tuber starches [4, 5, 8, 10, 11]. Kamal et al. [8] demonstrated that the electron beam effect on the apparent viscosity of corn starch was greater than that of gamma radiation in the early stage of irradiation ~5 kGy. Moreover, a mathematical model was elaborated to describe the exponential decrease of the apparent viscosity against irradiation dose [4]. At the same time, it was proved that each starch is characterized by a material constant that indicates the functional sensitivity of starch to irradiation. Consequently, in technological applications, based on this model and the material constant typical for each starch, one can calculate the irradiation dose required to be applied in order obtain a certain value of the apparent viscosity.

3.3. Gelatinization

Gelatinization is one of the most important functional properties of starch. Ionizing radiation processing of starch generally leads to great modifications of gelatinization temperatures and process enthalpy due to structural reconfiguration occurring in starch macromolecule. Lately, starch gelatinization is studied and monitored by differential scanning calorimetry (DSC), which is an extremely valuable tool to provide a quantitative measure of the gelatinization enthalpy and a determination of temperature range where gelatinization occurs as well.

From the outset, it should be emphasized that the multitude of experimental data reported in a large volume of papers shows that although the gelatinization properties of starch are affected by irradiation, a pattern of alterations cannot be identified. More specifically, it can be claimed that the evolution of gelatinization temperatures and enthalpy is practically unpredictable for various irradiation conditions and types of starch.

Several investigations [1, 2, 5, 6, 35] reported the decrease of both gelatinization temperatures (onset, peak and conclusion temperatures) and enthalpy as the irradiation increasing (up to 50 kGy) for cereal starches. However, Liu et al. [35] reported that the gelatinization parameters of corn starch almost remained constant under 20 kGy, and afterwards, their significant decrease occurred for irradiation doses up to 500 kGy. Later on, certain decrease in the gelatinization temperatures was reported for corn starch with different amylose content, up to 50 kGy, but only marginal effect on enthalpy values was identified [1]. These results indicated that gamma irradiation caused the production of defective crystalline structure and an increase in the proportion of short chains in amylopectin, which caused a decrease in gelatinization temperature [17]. The decrease in enthalpy value was explained by the disruption of the crystalline domain of starch granules in addition to disruption of double helical order [2, 17].

Other investigations [10] revealed that the gelatinization temperatures and enthalpy had no statistically significant alteration after irradiation with gamma rays for wheat starch treated with irradiation doses up to 50 kGy at a dose rate of 13 Gy/min. More than that, another study [39], using a higher dose rate (1 kGy/h) in the irradiation dose range up to 9 kGy, pointed out no significant difference in gelatinization temperatures and enthalpy for wheat starch after irradiation.

The investigations on rice starch irradiated at low rate of 0.4 kGy/h, with irradiation doses up to 10 kGy [15], also showed no significant shift of gelatinization temperatures up to 5 kGy, confirming the previously reported results [14], but a decrease of gelatinization temperatures and enthalpy was observed after 10 kGy irradiation. Similar results showing no important alteration of gelatinization parameters were also reported for elephant foot yam starch treated with doses up to 25 kGy at a dose rate of 2 kGy/h [19].

An extensive study on four varieties of starch extracted from the beans [20] revealed the reduction of the gelatinization temperatures and enthalpy of bean starch by irradiation with doses up to 25 kGy at low dose rate of 185 Gy/h. Contrary, Chung et al. [17] have found that the gelatinization temperatures for bean starch remained unaffected at 10 kGy and increased slightly at 50 kGy (2 kGy/h). An increasing behavior of gelatinization temperatures has also been reported for potato starch exposed to e-beam up to 50 kGy at high dose rate (2 kGy/min) [5], while the gamma irradiation at a dose rate of 2 kGy/h caused the increase of gelatinization temperatures when irradiated at 10 kGy, but decreased at 50 kGy [17]. A significant increase in the onset and peak temperatures was reported while no important effect on the gelatinization enthalpy was noticed for sago starches under irradiation treatment with doses less than 25 kGy [36]. Increase in gelatinization temperatures in irradiated starches was correlated with decreases in the overall crystallinity resulting that among the starch crystallites containing various rigidities, the relatively weak crystalline structure could be preferentially destroyed during irradiation [17].

4. Effects of ionizing radiation on structure

The investigation of ionizing radiation effects on starch structure revealed information related to the granule morphology, crystalline structure, or structural characteristics as determined by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy and chromatography.

4.1. Crystallinity

Crystallinity and crystallinity degree of starch macromolecule can be evaluated by different analytical techniques of investigation, such as X-ray diffraction, infrared spectroscopy, or DSC. The same starch granule consists of both crystalline regions (crystalline lamellae of amylopectin) and amorphous regions (typical to amylose) without a net delimitation making the determination of its crystallinity actually difficult.

One of the most used method to analyze the crystallinity and crystallinity degree is the X-ray diffraction because it can provide the crystallographic patterns of starch granules. The crystalline lamellae show two types of polymorph structures that design different diffraction patterns: the A-type crystallinity with relatively compact structure, the B-type crystallinity with a more open structure, including a hydrated helical core, and the C-type crystallinity that is a mixture of A-type and B-type patterns [41]. The crystallinity and crystallinity degree depend on the botanical source of starch and amylose content [1] or distribution of chain length in amylose. The experimental data proved that the diffraction pattern remained generally unaffected even at very high irradiation doses up to 500 kGy [35]. However, Reddy et al. [19] reported alteration of crystallographic pattern of elephant foot yam starch by gamma radiation processing. Thus, the B-type pattern of native starch changed in the C-type in irradiated starch.

On the other hand, most investigations recorded the decrease in the crystallinity degree of starch as a result of irradiation. The reduction in crystallinity degree with the increasing irradiation dose has been explained by breaking of the crystalline regions. Conversely, some studies [2, 10] found out that the degree of crystallinity was insignificantly changed for cereal starches by gamma irradiation processing with irradiation doses up to 50 kGy and low irradiation dose rates (<19 Gy/min). In case of wheat starch, Kong et al. [39] reported that the gamma irradiation at a dose rate of 1 kGy/h moderately affected the crystallinity degree that increased continuously with irradiation dose increasing up to 7 kGy and decreased at 9 kGy. This behavior was attributed to the alterations predominantly in amorphous regions induced with irradiation dose up to 7 kGy, whereas the crystalline regions were more affected by irradiation dose of 9 kGy. Also, the irradiation at 10 kGy with dose rate of 0.4 kGy/h caused an increase of the crystallinity degree of corn starch indicating that a slower dose rate is able to induce more crystalline structure [37]. Moreover, the investigation on rice starch [14] revealed both reduction and an increase in crystallinity degree by irradiation up to 5 kGy with dose rate of 0.4 kGy/h depending on rice cultivars. Therefore, the ionizing radiation processing influenced both the crystalline region and amorphous region of starch granules, leading to the decrease or increase in crystallinity degree in accordance with the most affected region by irradiation dose. Anyway, the investigators considered even the possibility of crosslinking in the case of the increase of crystallinity degree.

Another study [17] stated that the crystallinity degree decreased more rapidly with irradiation dose increasing for bean starch (C-type pattern) than potato starch (A-type pattern), showing that the crystallographic patterns have different sensitivity to irradiation. Thus, the B-type pattern has been proven to be more sensitive to ionizing radiation processing than A-type pattern and justified the behavior of bean starch in which the B-type pattern degraded faster than A-type pattern from granule surface. It is noteworthy that recently an opposite behavior has been identified by Chung et al. [1] for corn starch with different content of amylose subjected to ionizing radiation processing, namely the high amylose corn starch showed a B-type pattern being more radiation resistant than the waxy corn starch with A-type pattern.

Several works [3, 10, 17, 21, 33, 37] have reported results on the crystallinity degree of irradiated starch, estimated by using infrared spectroscopy, which involves the analysis of the absorption bands at 1047 cm^{-1} (crystalline structure) and 1022 cm^{-1} (amorphous region), and their respective ratio indicates the degree of starch order. The experimental data revealed that the ratio of 1047/1022 decreased with an increase of gamma radiation dose up to 50 kGy, and the starch granular crystallinity was affected [17, 21, 33, 37]. However, a couple of studies [3, 10] showed that the ionizing radiation processing (up to 50 kGy) had no influence on this ratio, suggesting that larger crystalline regions might be broken into small crystallites such that the crystallinity degree was practically unaffected.

4.2. Granule morphology

Morphology of starch granule exposed to ionizing radiation can be affected depending on starch type and irradiation parameters. For instance, studies on potato and rice starches [16, 38] reported the surface cracking of granules as well as deformation of granular structure were identified to increase with increasing irradiation dose in the range of 5–20 kGy at a dose rate of 2 kGy/h. Also, the extent of change depended on starch variety. Other studies on rice starches [14, 15] at lower irradiation doses (<10 kGy) and lower dose rate (0.4 kGy/h) also showed some modifications in the values of the mean sizes of the granules depending on irradiation dose and rice cultivars even if the irradiation apparently caused no change in the granule morphology. On the contrary, Shishonok et al. [18] reported that the surface structure of potato starch suffered no damage by electron beam irradiation even at high irradiation doses (110–440 kGy).

For corn starch irradiated with gamma rays up to 50 kGy and dose rate around 1 kGy/h, an absence of notable changes on the shapes and sizes of starch granules has been noticed [1, 2]. These observations were confirmed and completed by another investigation [35], which reported that gamma irradiated corn starch retained the original shape and size without any granular cracking or roughness occurring on the surface, even for 500 kGy with a dose rate 83 Gy/min. On the other hand, other investigations found changes in corn starch morphology induced by ionizing radiation. Although the granule shape and sizes were apparently unaffected by electron beam processing, the appearance of small circular perforations on the granule surface could be observed for irradiation of 50 kGy (dose rate of 2 kGy/min) [3]. Moreover, Kamal et al. [8] showed that the shape of corn starch granule was somewhat deformed by both gamma rays and electron beams for doses up to 100 kGy. It is noteworthy that the different content of amylose in corn starch had no influence on morphological aspects of irradiated starch; the granules remained intact and visually unchanged by gamma irradiation up to 50 kGy with dose rate around 1 kGy/h [1].

Microscopic observation of bean starches indicated surface cracking of granule with irradiation in a dose-dependent manner in the irradiation dose range of 5–25 kGy (<185 Gy/h) without significant changes in granule dimensions [20, 21]. However, in an earlier study, Gani et al. [22] have found the deformation of granule increased with increasing irradiation dose in the range of 5–20 kGy (dose rate of 2 kGy/h), the extent of change depending on starch variety. Other starches extracted from different botanical sources (lotus, chickpea) also presented surface fissures induced by irradiation [23, 32], while the ionizing radiation processing had no influence on the morphological characteristics for starches from elephant foot yam, Indian horse chestnut, and sago [19, 33, 36].

Consequently, the ionizing radiation is an energetic penetrating radiation that able to produce effects in the whole volume of the samples, so that the radiation-induced changes may occur both in the central regions and in the peripheral regions of the starch granules. However, the fact that microscopic methods reveal no damage to the granule outer layer for some starches leads to the conclusion that the radiation-induced changes might occur at a more intimate level of matter in the form of structural changes depending on starch granular structure.

4.3. Spectral characteristics

Generally, the analytical evaluation of FTIR spectrum of native starch must show five different frequency regions as presented in **Table 3** [42–44]. Therefore, potential modifications induced by ionizing radiation processing of bands assigned to those frequency regions should be evaluated.

The spectral features of the irradiated starch were apparently similar to native starch and no bands of new functional groups were found in spectrograms [3, 9, 10, 15, 18, 19, 33, 35]. For instance, Liu et al. [35] found that all spectral patterns for corn starch irradiated with gamma radiation were similar to those of control sample even after 500 kGy irradiation. However, some differences related to the frequency and intensity of some bands were identified after irradiation indicating radiation-induced alteration of the macromolecule structural integrity. Thus, slight shifts of some peaks and the decrease in intensity of some bands or the increase in intensity of other bands with the irradiation dose increasing have been noticed for all types of starches. The most affected bands were especially those assigned to O─H and C─H bonds [2, 3, 8], indicating that the stability of the inter- and intramolecular hydrogen bonds of starch structure was affected by ionizing radiation processing [3]. As an example, Bettaïeb et al. [2] found intensity decrease with 38.4 and 19.6%, respectively, for corn starch after irradiation with 50 kGy at 19 Gy/min. Instead, for wheat starch [10], the absorbance intensity of the same bonds decreased dramatically about 70 and 67%, respectively, after irradiation with 50 kGy at

Frequency region [cm^{-1}]	Assignment
3000–3700	O─H stretch
2800–3000	C─H stretch
1550–1800	O─H vibrations from bound water molecules
800–1550	Fingerprint region
Below 800	Pyranose ring of the glycosidic unit

Table 3. Band region frequencies and assignments of FTIR absorption of starch.

13.84 Gy/min. These results were attributed to the breaking of chemical bonds by irradiation. Besides, the botanical source of starch and the irradiation dose rate influenced the degree of the radiation-induced changes. Also, the findings [2] showed a decrease in peak intensity of the bending mode of the glycosidic linkage (C─O─C) with 13.4% explained by a depolymerization of amylose chains of starch and/or the amylopectin double helices within the amorphous regions after irradiation due to the breaking of glycosidic linkages [2, 10]. Conversely, an increase in the intensity of the characteristic peak at 1647 cm^{-1} ascribed to carbonyl groups was also observed [8] for e-beam irradiated corn starch, suggesting that the starch degraded by free radical reaction.

At the same time, the band intensity of the bending mode of water was also affected by a decreasing trend as the irradiation dose increased [2, 10]. This change occurred by water radiolysis that involves the breakdown of the water structure under the action of ionizing energy and leads to the formation of hydroxyl and hydrogen radicals.

4.4. Molecular weight and molecular weight distribution

Molecular weight of polymers influences most of their physicochemical and functional properties, and its investigation can reveal information useful to understand the behavior of macromolecules to ionizing radiation processing. Unfortunately, one can notice the lack of interest in this subject and the existence of only a few papers [4, 5, 12, 17] that have approached the study of the influence of the electron beam or gamma radiation on the starch molecular weights. The experimental data showed the decreasing evolution of the molecular weights with the irradiation dose independently of the starch botanical source. This kind of behavior indicated the break of polymeric chain and formation of the fragments with different molecular weights, which modified the mass molecular distribution of starch. However, the radiation-induced changes were correlated with the structural organization of starch, especially the branched structure component of starch (amylopectin). Hence, for cereal starches having short chains, the molecular weight distribution was affected mainly by the formation of the fractions with higher molecular weight than the formation of the fractions with low molecular weight. Instead, for tuber starch having long chains, the molecular weight distribution was slightly modified by irradiation, namely the scissions in fractions with high molecular weight being closer to that of the fractions with low molecular weight.

5. Concluding remarks and future perspectives

The great volume of results published in the last decade indubitably proved that the ionizing radiation (gamma rays and electron beam) is able to produce changes in structural and functional properties of starch, mainly due to the degradation process.

The radiation-induced effects are related to depolymerization of starch macromolecule followed by the reduction of molecular weight as well as the alteration of the double helix in the branched regions and crystalline structure, especially in the intrusion area of the amorphous region in the crystalline structure. Consequently, irradiation induces generally reconfiguration of starch molecules which lead to the reduction of crystallinity degree, shifts and decrease of spectral bands, and changes of thermal parameters. The general trend of decreasing for viscosity and swelling power concomitantly with the increasing of water solubility by irradiation makes the irradiated starches able to meet the specific needs in different new applications.

It is important to note that a number of factors related both to starch and ionizing radiation processing plays a major role in dictating the response of granular starch to ionizing radiation (**Table 4**). Taking into account this aspect, the comparison of properties among the irradiated starches should attentively be performed due to the differences in methodologies of ionizing radiation treatments and in composition and structure of starches. In other words, the random approaches of ionizing radiation processing of starch extracted from various botanical sources can lead to various results making difficult their comparison and the identification of a typical pattern behavior of a specific starch property.

Further studies should systematically focus on the response (physicochemical and structural properties) of each type of starch having different moisture content exposed to ionizing radiation (gamma rays and/or electron beam) in a large range of irradiation dose rate and different gas atmospheres. Studies on the major starch components, amylose and amylopectin, extracted from different native starches and subsequently exposed to ionizing radiation can be useful to validate observations on starch, leading to advancements in this research area.

Another issue that must be carefully explored is related to the investigation of thermal properties by DSC since nowadays the available reports showed a large variability of results without consistent correlations with other structural investigated properties of starch.

It is also opportune to make deeper chromatographic studies on the molecular weight and mass distribution of irradiated starch, especially as the chromatographic technique has developed spectacularly in recent years. The comprehensive evaluation of the dynamics of molecular mass distribution of irradiated starch will provide new relevant knowledge, contributing to a better

Starch factors	Ionizing radiation processing
Type of starch (botanical source)	Irradiation dose
Variety of starch (cultivar)	Dose rate
Water content	Type of gas atmosphere

Table 4. Factors influencing the response of starch to ionizing radiation processing.

understanding and even to behavior prediction of specific functional characteristics of starches exposed to ionizing radiation processing.

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