Gamma radiation as a modifier of starch – Physicochemical perspective

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1. Introduction

Starch is one of the most common and abundantly found carbohydrates in cereals, roots, legumes, and some fruits. It is a tasteless, colorless, and odorless source of energy that is present in the amyloplasts of plants. Native starch comprises amylose, a linear α-glucan having α-1,4-linkage and amylopectin, a branched polysaccharide with both α-1,4-linkage and α-1,6-linkage. Due to the low solubility, high viscosity, and unstable pasting property of native starch, it has been restricted from its application in industries. Although native starch has been widely used in various industries, modification of the same by various chemical, enzymatic and physical methods have been carried out to alter its properties for better performance in several industrial aspects. Physical modification like gamma radiation is frequently used as it is rapid, penetrates deeper, less toxic, and cost-effective. Starch when irradiated with gamma rays is observed to produce free radicals, generate sugars owing to cleavage of amylopectin branches, and exhibit variation in enzymatic digestion, amylose content, morphology, crystallinity, thermal property, and chemical composition. These physicochemical properties of the starch due to gamma radiation are assessed using optical microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), and its application are discussed.

Abbreviations: Amylose Content, AC; Rapidly Digestible Starch, RDS; Slow Digestible Starch, SDS; Resistant Starch, RS; Scanning Electron Microscopy, SEM; X-Ray Diffraction, XRD; Fourier-Transform Infrared, FTIR Spectroscopy; Differential Scanning Calorimetry, DSC.

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extract starch from the native sample without processing (Lopez-Rubio et al., 2008). Starch in the industry can be modified accordingly by various methods like chemical methods using enzymes, the thermal method using heat, and physical methods using radiations for better applications in the food and health sector (Amagliani et al., 2016; Maniglia et al., 2021). Gamma radiation is the most common physical method used for modification of starch in the food industry as it is fast, independent of catalyst, and minimal sample preparation is required (Dikkala and Shirisha, 2018). It is more preferable to chemical and enzymatic modification as these techniques are complex and can induce toxic products in food samples (Dikkala and Shirisha, 2018). In addition, gamma rays can be used at a higher dose in contrast to X-rays which show a negative effect on the nutrition of food (Dikkala and Shirisha, 2018; Lee and Fong, 2021). Gamma radiation has been widely used to increase the pasting properties of potato and corn starch in many industries. It has also been used to modify gelatinization temperature, decrease moisture content and alter the structural feature of rice starches (Kumar et al., 2017; Polesi et al., 2018). According to FDA, a low dose of gamma radiation (less than 2 kGy) can be used for improving the quality of food, a medium dose of gamma radiation (2-10 kGy) can be used to increase the shelf-life of food products and higher dose of gamma radiation (more than 10 kGy) can be used for sterilization of food products (Komolprasert and Morehouse, 2004). Currently, food irradiation is permitted in more than 60 countries with an increase in the production of gamma irradiated foods and trading of such food materials has been occurring over the 10 years of gamma irradiation of food (Gani et al., 2012). Based on the gamma radiation effect on food processing, in this review, we discuss the impact of gamma irradiation on starch to physicochemical properties determined by various biophysical techniques like optical microscopy, scanning electron microscope (SEM), X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC).

2. Gamma radiation mediated changes in physicochemical properties

2.1. Functional properties of starch

As mentioned earlier, starch comprises different physicochemical properties including enzymatic digestibility, thermal property, and chemical composition. Besides physicochemical properties, starch also possesses functional properties like solubility, viscosity, swelling power, water absorption, and rheological changes. These properties can be highly influenced by starch modification procedures thereby affecting the starch quality (Zhu, 2018). Amylose, amylopectin, and phosphorous content are also some of the components of starch that are affected by gamma radiation. Amylopectin is more extensively studied compared to amylose, it is said to represent growth rings, blocklets, and double helices. These tend to split up when introduced with gamma radiation releasing the tension and producing more sugars as well as changing other physicochemical properties (Bertolt, 2017). Further, the phosphorous content in the starch correlated to swelling power. The swelling power of the starch is seen to increase with the increase in phosphorous content. In addition, the amylose/amylopectin ratio was observed to be decreased with higher phosphorous content (Noda et al., 2007).

In a study with gamma irradiated whole wheat starch with 0.5, 1, 2.5, 5, and 10 kGy, the swelling capacity increased significantly in higher dose irradiated starch samples. It was concluded due to the breakdown of the amylopectin chain that was responsible for starch swelling. A decrease in swelling property was also observed at 90 °C due to the prevention of water entering the starch matrix after gelatinization (Bashir and Haripriya, 2016). Similar results were reported for sago starch, cowpea starch, and chestnut starch. In another study with buckwheat and potato starch radiated with a similar dose of gamma radiation, the water absorption as well as oil absorption capacity was estimated (Verma et al., 2018). The water and oil absorption capacity was observed to increase from 10 kGy radiated starch samples. Due to the formation of simple sugars like glucose, maltose, etc., the water absorption capacity of irradiated starches increases as the sugar molecules have more affinity towards water molecules (Wani et al., 2015). In the case of oil absorption, it was concluded due to the unfolding of proteins and deformation of amylopectin chains (Sofi et al., 2013). Amylose content in this starch seems to differ in percentage due to starch specific crystallinity as well as the extent of amylopectin and amylose deformation (Bashir and Haripriya, 2016; Verma et al., 2018).

Solubility of starch sample mainly depends on its morphology, sugar molecules, amylose and amylpectin content, branching length, etc. Gamma irradiated potato starch presented higher solubility than native form due to mutilation of starch morphology as well as binding of water molecules to free hydroxyl group of amylopectin and amylose (Suja et al., 2015). Similar results were obtained from buckwheat starch, lentil starch, and various others (Majeed et al., 2017). Syneresis is one of the other properties of starch that plays a critical role in assessing the modification process. Syneresis is the phenomenon where gelatinized starch expels excess water content which is an undesirable property. Syneresis analysis of gamma-irradiated horse chestnut starch represented a steady decrease in starch syneresis with an increase in radiation dosage. After 120 h of storage, 15 kGy gamma treated starch depicted the lowest rate of syneresis due to crystallization, amylose deformation, and amylopectin aggregation occurring in later stages (Wani et al., 2014). In the case of potato, wheat, and buckwheat starch, syneresis of native starch was highest after storing for 120 h. Nevertheless, the percentage of syneresis decreases after the highest dose of gamma treatment (Verma et al., 2018). These properties in combination affect the quality, nutrition, and shelf life of the starch.

2.2. Enzymatic digestibility and amylose content

The SDS and RDS are partially hydrolyzed by salivary α-amylase which is then chiefly hydrolyzed by pancreatic amylase into glucose via several steps. α-Amylase catalyzes the hydrolysis of α-1,4-bonds of both amylopectin and amylose polymers followed cleavage between the third and second α-1,4-linked glucoyl residue (Singh et al., 2010). Amylose polymers are hydrolyzed into products like maltose, maltotriose, maltotetraose, maltotetrose, maltotetrose, and maltotetraose. In the case of amylopectin, α-amylase has no specificity towards α-1,6-bond hence the cleavage of α-1,4-bonds was interfered by steric hindrance. Hence, the amylopectin hydrolyzed products included branched oligosaccharides or dextrins (Magallanes-Cruz et al., 2017). Gamma radiation of the starch sample was seen to show variation in their digestion thereby producing RS in many cases which are useful for diabetic patients and in some other sources of starch, digestion decreases leading to the quick availability of sugar. Furthermore, the effect of gamma radiation on starch digestibility can be affected by intrinsic factors like the presence of trace amounts of water or extrinsic factors like chemical and enzymatic factors (Magallanes-Cruz et al., 2017; Ramadoss et al., 2019; Toutounji et al., 2019).

Two similar studies with gamma-irradiated rice endosperm starch and brown rice starch were assessed for their in vitro digestibility as well as amylose content (AC) in comparison to native starch. Rice endosperm starch and brown rice starch were irradiated by Cobalt-60 with 1, 2, and 5 kGy as well as 5, 10, 15, and 20 kGy doses of radiation. It was observed that resistant starch and AC were more in the rice endosperm starch. In the case of irradiated brown rice starch, AC decreased from 26.22% to 17.9% for 20 kGy doses which were concluded as a breakdown of amylose to oligomers (Kumar et al., 2017; Zhou et al., 2018). In another study regarding digestibility, gamma treated corn starches showed increased RDS in waxy starch and decreased SDS in both waxy as well as normal starch when treated with porcine pancreatic α-amylase (Yoon et al., 2010). Further, RS content increased in waxy starch which was assumed to be produced by converting SDS to RS, but proportion RS decreased with an increase in radiation dose from 5 to 10 kGy (Yoon et al., 2010). It was finally concluded that corn starch digestibility...
decreased with an increase in radiation dose. In the case of gamma treated kithul starch (0.5, 1, 2.5, 5, 10 kGy) and lotus starch (5, 10, 15, 20 kGy), decrease in AC with an increase in the dose of radiation was observed. The in vitro digestibility of irradiated kithul starch with porcine pancreatic α-amylase displayed increase in digestion with an increase in radiation dose (Sudheesh et al., 2019) (Fig. 1). The RDS content was increased in the irradiated starch whereas both SDS and RS were seen to decrease (Atrous et al., 2015; Punia et al., 2020). A similar study with gamma radiated Sago starch with 6, 10 and 25 kGy dose exhibited final amylose content of 27.6% in native starch whereas the irradiated starch had the lowest AC at 6 kGy and it significantly decreased to 25.3% as maximum content as the dose increased to 10 and 25 kGy (Othman et al., 2015). Gamma irradiated wheat starch (3, 5, 10, 20, 35, and 50 kGy) displayed a gradual decrease by 0.9% in AC with an increase in the radiation dose which was also seen in gamma-irradiated lentil starch (Atrous et al., 2015). It was established that a decrease in AC was due to the breakdown of macromolecules that produced short polymeric chains. Due to the production of short chains, iodine binding becomes difficult hence leading to less color production of iodine in the solution which strengthens the evidence for the breakdown of amylose (Fig. 1) (Atrous et al., 2015; Majeed et al., 2017). Another study with gamma radiated RS4 waxy maize starches when digested with porcine pancreatic α-amylase showed an increase in RS till 40 kGy and significantly decreased as the dose was increased to 100 kGy.

It was suggested that a higher dose of radiation broke down the starch which gave more access to an enzyme (Chung et al., 2010). A comparable study of gamma-irradiated potato starch with chloroprop-ham, a plant growth regulator, treated potato starch when assessed for in vitro digestibility with porcine pancreatic α-amylase represented an increase in RDS and SDS content. In addition, there was a decrease in RS observed as the radiation-induced breakage of chains benefitting the enzyme to act on the polymer very easily (Lu et al., 2012). A similar study with sorghum grain using bacterial α-amylase and bean starch with invertase, pancreatin and amyloglucosidase, observed that both showed an increase in the rate of digestion, but bean starch specifically depicted a decrease in SDS. It was reported that molecular as well as structural degradation of starch increased access for enzymatic action (Hussain et al., 2014). Hence, we can conclude that most of the starch from various sources, when exposed to gamma radiation, is shown to decrease AC with an increase in radiation dose whereas the digestibility depends on the cleavage of amylopectin molecule of starch into di-saccharides as well as oligosaccharides. Nevertheless, various other starches were seen to show increased digestibility when irradiated with gamma radiation. Gamma radiated starch is readily digestible providing a larger amount of energy in the form of sugar. Further, more studies on gamma modification starch can provide knowledge on controlling the sugar produced in the starch for health purposes.

2.3. Morphology of starch

Starch appears as a semi-crystalline granule ranging in the size from 100 nm to 100 μm with alternative crystalline and amorphous growth rings measuring from 9 to 10 nm on the surface (Amaglani et al., 2016). The morphological features of the starch are commonly assessed by SEM, transmission electron microscopy (TEM), polarization light microscopy (PLM), and atomic force microscopy (AFM). The key components that SEM can detect are the shape of the starch granules, the surface of the starch (Inkson, 2016). SEM detection of esterified chemically modified starch represented minor surface alterations with aggregation of starch acetate on the surface and surface gelatinization leading to the use of better modification techniques (Masina et al., 2017). A study on assessing the functional and structural properties of gamma-irradiated potato starch, SEM, and transmission electron microscopy (TEM) were used to display the difference between irradiated and native potato starch granules. Potato starch irradiated with 10 kGy and 30 kGy gamma rays showed depolymerization, crack on the surface and fused product of starch compared to native starch that displayed oval or round shape with a smooth surface (Sujka et al., 2015). A study with the gelatinization product prepared from radiated and native potato starch exhibited honeycomb structure with different sizes of cages and smooth borders and the surface by SEM. Once the lyophilized gels were radiated 5 kGy, the cages appear to flatten with tiny fractures, and initiation of lamellar structures could be observed. Further radiation with 10 kGy to 30 kGy showed increased porosity increases drastically with cracks accompanying them following the appearance of larger holes (Cielsa et al., 2015). Similar studies have been performed with buckwheat, potato, and kithul starch. In all these studies, irradiated starches exhibited splitting of granules, reduced smoothness, fissures and cracks (Fig. 2) (Sudheesh et al., 2019; Verma et al., 2018). Another study with gamma-irradiated wild arrowhead starch with 5, 10, and 15 kGy suggested that starch granules were seen to be oval, round, elongated with the smooth surface by SEM, and had no changes after irradiation (Wani et al., 2015). In contrast to arrowhead starch, chickpea starch with an oval shape and rice starch with the polyhedral and irregular shape when treated with gamma rays exhibited fissures on the surface, slight deformation, and a decrease in the diameter with respect to dose of radiation (Fig. 2) (Bashir and Harripriya, 2016; Gul et al., 2016).

In addition to SEM and TEM analysis of the granular structure and size of starch, various other techniques like polarization light microscopy (PLM) and atomic force microscopy (AFM) are greatly recommended. PLM works based on collecting polarized light transmitted after the sample helping to identify native starches (Ando, 2018; Gotze, 2009; Govindaraju et al., 2021; Xiao et al., 2020). A study on radiated potato and bean starch using PLM showed starch being less affected by radiation than the bean starch. There was the appearance of cracks which increased with an increase in radiation. It was concluded that bean

Fig. 1. Enzymatic hydrolysis and amylose content of starch. i. In vitro digestibility of native and irradiated kithul starch. Figure adapted with permission from Sudheesh et al. (2019). ii. Ratio of apparent amylose content (AAC) of irradiated starch (IS) to AAC of native starch (NS) vs. irradiation dose (a: wheat starch, ■: potato starch). Figure adapted with permission from Atrous et al. (2017).
starch was C-type starch which is highly susceptible to radiation than B-type potato starch as B-type starches are more crystalline compared to C-type starches that are both amorphous and crystalline (Chung and Liu, 2010). An analogous study was performed with irradiated rice by many researchers for the evaluation of morphological features of the starch using PLM. A defined malteese cross structure in the hilum was observed in the native rice starch but no changes were seen in the microstructure of these starch granules alike corn starch. However, the diameter of the granule was observed to decrease in the irradiated sample in a dose-dependent manner (Ben Bettaïeb et al., 2014; Guimarães et al., 2013; Gul et al., 2016). AFM and TEM studies were performed on gamma radiated maize starch for evaluation of structural changes. There was not much difference seen between the irradiated and non-radiated maize starch but the nanoparticles produced from these starch were shown to be less crystalline (Ocloo et al., 2019). In conclusion, it was observed that most of the irradiated starch showed deformed granular

### Table 1
Variation in physicochemical properties in different starch types.

| Properties       | Morphology (SEM) | Crystallinity (XRD) | Chemical Composition (FTIR) | Gelatinization Property (DSC) | References                   |
|------------------|------------------|---------------------|-----------------------------|------------------------------|------------------------------|
| Starch Type      |                  |                     |                             |                              |                              |
| A-Type Crystallinity (Rice) | 0 kGy | Round or polyhedral | 22.53%                      | Highly ordered structural peaks | ΔH = 11.5 J/g | (Gul et al., 2016; Kumar et al., 2017) |
|                  | 10 kGy           | Deformation and cracks | 22.06%                      | Increased intensity in some peaks | ΔH = 9.2 J/g | (Gul et al., 2016; Kumar et al., 2017) |
| B-Type Crystallinity (Potato) | 0 kGy | Smooth surface and oval | 32.8%                      | Highly ordered structural peaks | ΔH = 19.2 J/g | (Chung et al., 2010; Teixeira et al., 2018) |
|                  | 10 kGy           | Depolymerization and fused granules | 30.7% | Increased peak intensity | ΔH = 18.2 J/g | (Chung et al., 2010; Sujka et al., 2015; Teixeira et al., 2018) |
| C-Type Crystallinity (Chickpea) | 0 kGy | Smooth surface and oval to spherical fissures | 27.04% | Highly ordered structural peaks | ΔH = 8.37 J/g | (Bashir and Aggarwal, 2017; Bashir and Haripriya, 2016) |
|                  | 10 kGy           | Fixures             | 16.91%                      | Increased intensity in some peaks | ΔH = 6.26 J/g | (Bashir and Aggarwal, 2017; Bashir and Haripriya, 2016) |
morphology whereas potato starch was seen to have the least difference in its physical structure (Table 1). The changes in the morphological feature by gamma irradiation are also seen to help in easier breakdown and gelatinization of the starch which could actively help in the digestibility of starch.

2.4. Crystallinity of starch

Starch granules depict semi-crystalline form with alternate crystalline and amorphous lamellae. Starch granules can exhibit three crystalline forms based on the degree of hydrolysis and the arrangement of amylose double helices. The forms are A-type those which produce square-shaped nanocrystals consisting of left-handed double helices packed in a monoclinic unit cell, B-type those which produce round nanocrystals with high amylose content formed by six double helices in the loosely packed hexagonal unit cell, and C-type which comprises of the core as B-type crystalline structure surround by A-type crystalline starch granule crystals (Sarko and Wu, 1978; Vamadevan and Bertoft, 2015). In addition, it was reported that removal of amylose during hydrolysis increased the crystallinity of starch granules which can be detected via the XRD technique (Dome et al., 2020; Mukurumbira et al., 2017). Other modification techniques like the high hydrostatic pressure technique were also assessed by XRD but this modification had an introduction of water molecules to the starch. Besides, this modification also represented the transformation of starch from one crystallinity to the other which was not helpful (Han et al., 2020). Hence, XRD is the most common technique that is used to study the crystallinity and atomic spacing of the specimens. In a study, native wild arrowhead starches showed an A-type pattern of crystallinity with reflection angle of 15°, 17°, 18°, and 23° whereas radiated samples with the dose of 5 kGy, 10 kGy, and 15 kGy showed similar angles with decreased intensity as the dose increased (Wani et al., 2015). In another study regarding modification of poovan banana starch by gamma irradiation showed a decrease in the angle from 19.57° in native starch to 18.41° in 25 kGy gamma-irradiated starch which was concluded due to loss of amylopectin chain (Reddy et al., 2015b).

In contrast, studies on irradiated white rice starch, brown rice starch, and chickpea starch with a radiation dose of 0.5 to 20 kGy suggested no significant changes after radiation. Nevertheless, there was a relative change in crystallinity which could be due to the compact structure of A-type crystalline which was less affected by radiation with the presence of firm packing of double helices (Fig. 3) (Gul et al., 2016). In brown rice, the crystallinity decreased with increased radiation dose due to the breakage of amylopectin and double helices which was then related to decreased gelatinization enthalpy (Kumar et al., 2017). Chickpea starch displayed a C-type crystalline structure comprising more of the A-type than the B-type crystallographic pattern. However, XRD angle decreased with an increase of 4 kGy and 8 kGy of radiation but a sharp increase was observed at 12 kGy radiation dose which was assumed due to reorganization of double helices as well as a regrouping of depolymerized amylose into a firmer and compact structure (Bashir and Haripriya, 2016). Similar results were exhibited by gamma-irradiated lentil, kithul, cassava starch but potato starch mostly shows increased crystallinity as it possesses B-type crystallinity comprising 30–44 glucose units whereas A-type possess 23–29 glucose units making B-type more resistant to gamma rays (Fig. 3) (Majeed et al., 2017; Sudheesh et al., 2019; Teixeira et al., 2018). Based on these studies, it can be stated that starch possessing A-type and C-type crystallinity with core comprising of A-type

![Fig. 3. XRD results of starch.](image-url)
crystallinity is more sensitive to gamma rays compared to the B-type that appear more resistant (Table 1). Further, modifying the starch crystallinity could provide the food industry to classify the starch according to their crystallinity, breakdown, and amount of energy produced by the same.

2.5. Chemical composition of starch

Starch as mentioned is made up of two different polysaccharides with primary and secondary hydroxyl group. The primary hydroxyl group is attached to C6 and the secondary hydroxyl group is attached to C2 and C3 (Polesi et al., 2018). In addition, starch also contains carboxylate ion (COO) and CH2 group which plays a major role in the variation of the chemical composition of starch after irradiation and it can be assessed by FTIR spectroscopy. Further, starch also comprises moisture content, ash, protein, and fat contents in very small quantities (Mohamed et al., 2017). The chemical composition also gets affected by the molecular order of the starch. The non-gelatinized starch possessed long-range molecular order but when gelatinized the order disrupts for shorter cluster leading to the formation of a short-range molecular order starch structure. Hence, the effect of gamma radiation would differ from the native non-gelatinized starch to gelatinized starch depicted in a few of the starch studies (Huang et al., 2021). A study with gamma radiation and sonication of lentil starch to determine the various properties of the starch was assessed with FTIR spectroscopy to determine the chemical composition of the starch. A very distinct broad absorption band was observed at 3328 cm\(^{-1}\) for native and 3326 cm\(^{-1}\) for dual treated starch due to –OH stretching. In addition, a band at 2938 cm\(^{-1}\) was observed which was associated with CH2 deformation; however, after dual treatment of lentil starch, the absorption intensity of the starch decreases which could be due to the breakage of chemical bonds leading to unstable reactions suggesting proceedings with the most effective modifying technique only (Majeed et al., 2017). Another study with gamma-irradiated (0 kGy–20 kGy) oat starch found, absorption bands at 1500 cm\(^{-1}\), 1600 cm\(^{-1}\), 995-928 cm\(^{-1}\), and 620-527 cm\(^{-1}\) corresponded to C–O–C, carboxylate ion (COO), C–O–H bending and CH2 related modes as well as pyranose ring. The –OH absorbance peak appeared narrower in the irradiated starch compared to the native starch sample and the ratio of bands of the crystalline and amorphous region was decreased in comparison to native samples. Hence, it concludes that due to the breakage of the amylose and amylopectin chain, the ratio appears to decrease gradually once irradiated (Mukhtar et al., 2017). A similar study on two varieties of gamma radiated rice starch (0, 1, 5, and 10 kGy) as well as alkali extracted chickpea starch (0, 4, 8, and 12 kGy) confirmed a decrease in the number of double helices as well as various bonds (Fig. 4). On the other hand, the carboxyl content of irradiated rice and chickpea starch was observed to increase due to the formation of acetic, pyruvic, and formic acid. Hence, the pH of the starch was reported to decrease significantly (Bashir and Aggarwal, 2017; Bashir and Haripriya, 2016; Gul et al., 2016).

In another study, the impact of gamma radiation was assessed on the physicochemical property of kithul starch (0.5 kGy–10 kGy) and arrowroot starch (0 kGy–15 kGy). The range of wave number used for kithul starch is 500–4000 cm\(^{-1}\) whereas for the latter it is 650–4000 cm\(^{-1}\).

![Fig. 4. FTIR results of starch. i. FTIR Spectra of native and gamma irradiated chickpea starch. Figure adapted with permission from Bashir and Aggarwal (2017). ii. FTIR spectra of native and irradiated brown rice starch. Figure adapted with permission from Kumar et al. (2017). iii. FT-IR spectra of native and irradiated kithul starch. Figure adapted with permission from Sudheesh et al. (2019). iv. FTIR spectrum of gamma-irradiated elephant foot yam starches. Figure adapted with permission from Reddy et al. (2015a). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)](image-url)
1. Kithul starch when irradiated exhibited a decrease in the intensity of peak which depicts CH2 and OH group stretching vibration and C–O–H bending vibration with increasing radiation dose than the native starch (Fig. 4). The reason for this observation could be due to irradiation, the production of free radicals depolymerizes the chemical bond in the starch which leads to a decrease in the corresponding intensity of peaks (Barroso & del Mastro, 2019; Sudheesh et al., 2019). In addition, the moisture content was observed to decrease with an increase in radiation dose due to the radiolysis of water. Further, the pH also decreased due to an increase in carboxyl content (Sudheesh et al., 2019). Similar results were shown to be represented with arrowroot and yam starch whereas for potato and corn starch the absorbance intensity was increased gradually after the treatment (Teixeira et al., 2018). It can be concluded that most of the starch possess similar chemical composition but not the same concentration as it varies from species to species. Due to less change in chemical composition by gamma modification, the food industry can safely use this technique to enhance the quality of the starch as well as food containing starch without producing harmful by-products (Table 1).

2.6. Thermal property of starch

Starch granules enter glass transition before gelatinization when heated in an aqueous medium and this phase is irreversible. During this phase, starch granule loses its crystallinity and this characteristic is very important for starch in cooking. This property was analyzed by various techniques like DSC, FTIR, and NMR spectroscopy (Vamadevan and Bertoft, 2015). The difference in the energy between the native and irradiated samples can be correlated to the specific thermodynamic properties of these samples by detecting peak temperature for crystallinity, onset, and conclusion temperature determines different phases in semi-crystalline starch (Durwoju et al., 2017). DSC has a wide application in the food industry to assess specific heat, state of the water, the cation in the food industry to assess specific heat, state of the water, the cation, protein interaction and denaturation, thermal properties of lipids, and starch gelatinization (Parniakov et al., 2018).

Amorphophallus paeoniifolius also commonly known as elephant foot yam is a very rich source of starch that can be used as food thickeners when modified commercially. A study with gamma radiated (5 kGy–25 kGy) A. paeoniifolius was assessed after irradiation by DSC and it was observed that gelatinization temperature reduced in irradiated starch except with 25 kGy irradiated samples. It was also concluded that starches with higher crystallinity and longer amylopectin chain displayed higher temperature and enthalpy (Reddy et al., 2015a). Furthermore, the pasting property of the irradiated starch represented a steady decrease in the peak, hold, and final viscosity with an increase in radiation dose assessed by Rapid Visco Analyser (RVA) correlating with decreasing swelling power, repolymerization of leaked amylose, and depolymerization of amylopectin (Reddy et al., 2015a). In another study with gamma radiated (6, 10 and 25 kGy), Metroxylon sagu starch which is a very important plant source for industrial application, DSC analysis exhibited an increase in onset, peak and gelatinization temperature to 68.5 °C, 74.1 °C and 83.5 °C from the native starch having 67.6 °C, 73.3 °C and 82.8 °C temperature, respectively (Fig. 5). It was justified with the reason stating that the radiation created small molecules like monosaccharides because of degradation leading to an increase in gelatinization temperature and decreased crystallinity. Further, it was also noticed that the gelatinization enthalpy of radiated sago starch remained unaffected (Othman et al., 2015). A similar experiment with gamma-irradiated brown rice starch (5 kGy–25 kGy) and chickpea starch (0.5 kGy–10 kGy) exhibited decreased onset, peak, conclusion temperature, and gelatinization enthalpy temperature with increased radiation dose due to partial depolymerization of amylopectin chains by gamma radiation and disrupting the force between double helices. Overall, it was suggested that the change in thermal property was the result of reduced crystallinity due to the cleavage of polysaccharides (Bashir and Aggarwal, 2019; Kumar et al., 2017). Another study with gamma radiated arrowroot (0 kGy–15 kGy) and tapioca starch (0 kGy–20 kGy), it resulted in increased gelatinization temperature to 83.9 °C with increased radiation dose as well as gelatinization enthalpy (22.3 J/g) due to double-helical melting and amylose leaching in case of arrowroot. In contrast to arrowroot, irradiated tapioca starch exhibited a decrease in gelatinization enthalpy (11.99 J/g) (Barroso & del Mastro, 2019; Kanatt, 2020). Gelatinization temperature decreased from 143.21 °C to 140 °C after the radiation treatment due to exposure of hydrogen sites by breakage of intra as well as intermolecular bonds in lotus seed starch. As a result of the cleavage of such bonds, a significant difference in the molecular spatial arrangement will be observed that affects the thermal activity of starch which was also observed in corn and rice starch (Prince et al., 2020). The pasting properties of almost all starch varieties seemed to decrease with an increase in radiation with respect to its swelling power. In contrast to gamma radiation, stearic acid modification of starch leads to increasing viscosity and higher gelatinizing of starch making it difficult to assess the quality of starch (D’Silva et al., 2011). Overall, the starch gelatinization property was observed to decrease in most of the starch, making it easier for cooking. Whereas in some rare cases, starch seems to increase its gelatinization temperature after gamma irradiation, which also helps absorb less moisture (Table 1).

3. Conclusion and future prospects

The human population has been scaling up immensely in the past few decades to which the respective needs have to be met. Starch being the most crucial component of staple diet plays a major role in meeting the needs of the basic human diet. By modifying the properties of starch, different demands of different types of human populations can be met. As discussed earlier, modification by gamma radiation is one of the rapid
and effective techniques that help in incorporating required changes in the properties of starch. As summarised in this review, the higher dose of gamma irradiation of starch samples is shown to create fissures and cracks on the surface of these granules. In addition, it was also observed that the crystallinity of some starches is seen to change which further affects the thermal properties of these starch. Nevertheless, the chemical composition of starch was seen to differ the least when irradiated by gamma rays. Above mentioned specific physicochemical modifications can benefit the cooking properties of starch and the quality of these starch can be maintained. Gamma radiation also has a beneficial effect on decreasing the moisture or water capturing property of the starch. Although higher moisture content is beneficial for the biodegradability starch can be maintained. Gamma radiation also has a beneficial effect on decreasing the moisture or water capturing property of the starch. Hence, gamma radiation helps in increasing the shelf-life and decreasing the degradation of the starch by relatively decreasing moisture content. Although there is diversity in the research studies of starch, the internal structure of starch is not perfectly determined. For example, the amylopectin component has two different models namely the backbone model and the tree-like cluster model. Determining and understanding the right model to move forward with the future study seems to be very much important (Hamaker, 2021). Further, modifications of starch in the food industry have been performed by various techniques as stated in the review. Almost all seem to have similar effects, however, each has drawbacks of its own. Gamma radiation of starch is the rapid and easy process of modification, yet it cannot be stated as the most recommended. The reason behind this statement is due to its health-hazardous nature while processing, production of acids, sugars, and ions that could be a threat to human health. Nevertheless, gamma treatment of starch in the food industry is carried out in a very precautionary manner avoiding the hazard (Komolprasert and Morehouse, 2004). Further, starch modification by gamma radiation has not been identified for the production of free radicals affecting human well-being. Gamma radiation being one of the quick and powerful techniques, the production of resistant starch can also be carried out by this process as this category of starch has shown immuculate health benefits (Kaur et al., 2012). In future studies, standardization of gamma radiation dose to attain a certain quality of starch can be carried out. On the whole, the effectiveness of gamma radiation for modification of starch must be taken into consideration as it understands the approach for producing the best product for society, especially in the food industry. Modification by gamma treatment can furthermore be studied to improve the texture, color, quality, and prolong the shelf-life of the starch as well as starch products.

CRediT authorship contribution statement

Mridula Sunder: Writing – original draft. Kamalesh D. Mumbrakar: Writing – review & editing, Supervision. Nirmal Mazumder: Project administration, Conceptualization, Writing – review & editing, Funding acquisition, Supervision.

Declaration of competing interest

The authors declare that they have no competing interests reported in this paper.

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