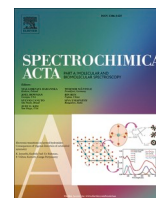




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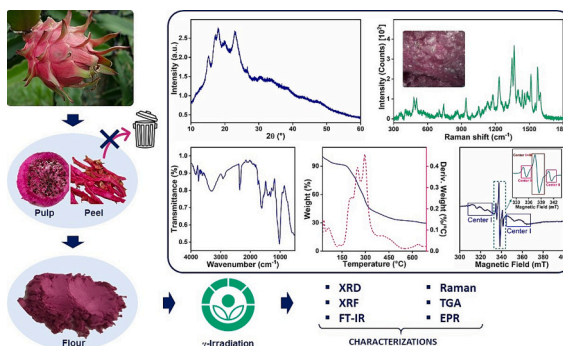
Physicochemical characterization of red pitaya (*Hylocereus* sp.) peel flour using FT-IR, Raman, and EPR spectroscopy: Effects of γ -irradiation on its intrinsic properties

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HIGHLIGHTS

- The structure, functional groups, and thermal properties of pitaya peel flours are largely preserved after irradiation.
- γ -radiation induces different paramagnetic species in red pitaya peel flours with different chemical compositions.
- The combination of spectroscopic and thermal approaches provides reliable physical markers for distinguishing irradiated pitaya flour.

GRAPHICAL ABSTRACT



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ABSTRACT

To ensure food and fruit safety, it is essential to use accurate and appropriate techniques that allow irradiated products to be identified and labelled, thereby preventing their adulteration and that of their derivatives. In this context, in this study, we evaluated the physicochemical properties of γ -irradiated red pitaya peel flour from lab-prepared (PT) and commercial (PC) samples, using X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier transform infrared (FT-IR), Raman, and electron paramagnetic resonance (EPR) spectroscopic techniques, as well as thermal analysis (TGA/DSC). The moisture content ranged from 8.01% to 16.38%, with the highest values being 16.38% for the PC sample at 3.5 kGy and 10.56% for the PT sample at 7.5 kGy. FT-IR and Raman spectroscopy revealed differences in betalain concentrations, indicating that irradiation did not significantly alter the spectral profiles. However, chemical changes were detected in the PC sample compared to the PT sample. In the PT sample, at least three distinct paramagnetic centers were identified. A six-line EPR spectrum was assigned to Mn^{2+} ions (center I). Center II arises from at least two radical species, with the dominant radical exhibiting hyperfine interaction with one α -type and two nearly equivalent β -type protons and characterized by a g-value of

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2.0023. The cellulosic component of the pitaya contributes to the formation of center III, which exhibits a g-value of 2.0027. In the PC sample, only center III was detected, with no evidence of Mn^{2+} signals.

1. Introduction

Global demand for plant-based and fruit-derived products has grown significantly, driven by an increase in the number of flexitarian consumers who aim to reduce their consumption of meat and dairy products for environmental sustainability, ecological balance, and animal welfare reasons [1]. In recent decades, economic globalization has experienced continuous growth, which has increased global demand for a wider variety of agri-food products and, therefore, increased their vulnerability to fraud and contamination during processing, as well as microbial contamination during storage and distribution [2].

The pitaya, also known as dragon fruit (*Hylocereus* sp.), is a species of cactus native to the tropical regions of Central and South America, as well as some areas of India and Malaysia [3–5]. It is considered a non-traditional tropical fruit with significant agronomic and commercial potential, and its cultivation and consumption have increased in Brazil [1], especially in the Caatinga, a biome exclusive to the northeast of the country [6]. Pitaya species are classified according to the color of their flesh and skin. *Hylocereus undatus* has white flesh and pink skin and is commonly known as white pitaya; *Hylocereus polyrhizus* has red flesh and pink skin and is commonly known as red pitaya; and *Hylocereus megalanthus* has white flesh and yellow skin and is commonly known as yellow pitaya [5,7,8].

The principal by-product of pitaya fruit, both from fresh consumption and industrial processing, is the peel, which is often discarded into the environment, contributing to ecological degradation and the loss of valuable bioactive compounds present in the waste [7,9]. Among these compounds are flavonoids [10]. The pitaya peel, which accounts for approximately 33% of the total weight of the fruit, is the main waste generated during processing and is rich in betalain-type phenolic compounds, which are classified as betaxanthins, responsible for yellow pigmentation, and betacyanins, responsible for pink or purple coloration [5,7,11,12]. In addition, pitaya peel is mainly composed of carbohydrates, which account for approximately 70% of its weight, and pectin, which constitutes between 15% and 35% of the dry weight of the primary cell walls [9].

Although consumers commonly discard the pitaya peel, researchers have increasingly focused on its comprehensive use due to its high content of bioactive compounds and nutrients [6,9,13]. The fruit is rich in vitamins B1, B2, B3, and C, as well as proteins, fats, carbohydrates, fiber, flavonoids, thiamine, niacin, pyridoxine, glucose, phenols, betacyanin, polyphenols, carotene, phosphorus, heteropolysaccharides, and iron [4,5,13–15]. Red pitaya is very rich in iron and is a good source of pectin and dietary fiber (60–80%) [5,15,16].

However, there is little research in the literature on the use of pitaya peel as a source of natural coloring for the food industry [8,12,17]. Betalains are gaining importance as natural colorants in the food industry, but they have been studied less than other plant-based pigments, such as chlorophylls, carotenoids, and anthocyanins [1,6]. In addition, betacyanin, one of its main compounds, has attracted considerable interest due to its antioxidant properties and other beneficial health effects, such as its antimicrobial, anticancer, and antilipidemic activity [13,14]. Sample preparation and the selection of appropriate extraction techniques are essential for the effective isolation, identification, and analysis of bioactive compounds from pitaya plants [6,7,14,16], as these residues, which are normally discarded, could be reused to obtain valuable by-products, such as flours [5,12,14].

Spray drying methods of pitaya-colored extracts are a common practice used for the production and stabilization of natural colorants, enhancing their shelf life and stability [5,18]. Additionally, the reduced volume facilitates easier handling [8,11,17]. Rondán-Flores et al. [11]

studied pitaya flour produced by spray drying and irradiated with γ -radiation between 500 Gy and 30 kGy. These authors did not observe significant changes in the coloration or crystalline structure of their compounds. However, γ -radiation induced two paramagnetic species that were identified by EPR spectroscopy. It is well established that EPR is a powerful and versatile technique for investigating radiation-induced effects in materials. Numerous studies have employed EPR spectroscopy to characterize defects generated by irradiation; representative examples include [19–24]. On the other hand, Santos et al. [3] analyzed the effect of γ -radiation, between 1 and 4 kGy, on the bioactive compounds of pitaya peel flour.

Accurately identifying whether a food product has been irradiated and determining the radiation dose it has received are crucial steps in ensuring its quality and safety. These measures not only guarantee compliance with regulations but also increase consumer confidence in irradiated food products. To do this, reliable and accurate analytical techniques are necessary. Several methods have proven effective in detecting irradiation and measuring absorbed dose, making them valuable tools for quality control and food safety monitoring [11,25]. In the case of products such as pitaya peel flour, it is essential to use effective preservation methods [3,8,11].

Among the various spectroscopic techniques, FT-IR [3,10,26], Raman spectroscopy [10,27,28], and EPR [11,25] stand out for their high sensitivity in detecting free radicals formed in irradiated foods and food adulteration. Other studies show that significant changes in the intensity of hydroxyl groups on the material surface, influenced by the irradiation dose range, can be detected and measured by FT-IR spectroscopy [28,29], as well as associated effects on radical recombination and other irradiation-induced processes [30–34]. Compared to the aforementioned techniques, these are relatively simple, inexpensive, and do not require extensive sample preparation or additional chemicals. Recently, FT-IR and Raman spectroscopy have also been used to identify adulteration in industrialized natural products and derivatives [2,10,27] and to assess the quality of fruit species available in common markets [27,28,35].

In this study, the impact of γ -irradiation on the physicochemical properties and quality of natural flour obtained from red pitaya peel and commercial pitaya flour was evaluated, taking into account the possibility of alterations in nutritional quality due to γ -irradiation. The physicochemical properties of both irradiated flours are expected to be similar, since the type of peel used to produce commercial flour is similar to that used in the laboratory. Thus, it seems interesting to study the physicochemical data of both flour samples to detect possible adulterations. Furthermore, there are no comparative studies in the scientific literature that allow red pitaya flour samples from different origins to be differentiated. Therefore, the objectives of this study are as follows: (i) to compare the physicochemical properties of the bioactive compounds in the control sample and the irradiated samples using X-ray fluorescence (XRF), X-ray diffraction (XRD), Raman spectroscopy, Fourier-transform infrared spectroscopy (FT-IR), and electron paramagnetic resonance (EPR) spectroscopy techniques; and (ii) to use these data to identify possible structural alterations and compare them between both samples to differentiate the flours. The data generated in this work will help to clarify the impact of irradiation on the processing of red pitaya peel and to develop comparative analysis methodologies to verify possible alterations in commercialized products.

2. Materials and methods

2.1. Preparation of pitaya flour

The red pitayas of the *Hylocereus costaricensis* variety studied in this work were grown in the interior of the State of São Paulo (Brazil) and purchased at the CEAGESP (Companhia de Entrepósitos e Armazéns Gerais de São Paulo) supply center in the city of São Paulo (Brazil). These fruits were transported to the Laboratory for Analysis and Detection of Irradiated Foods (LADAI) at the Radiation Technology Center (CETER), IPEN/CNEN.

To obtain red pitaya flour, the fruits were first washed thoroughly with water and subsequently disinfected using a sodium hypochlorite solution. The peel was then separated from the pulp, and the peels were dehydrated by freeze-drying. Once the pitaya peel was freeze-dried, it was ground using an alumina ball mill for four hours. Finally, the ground sample in the form of flour was sieved to select grains between 4 and 6 mm in diameter; this product was called the PT sample. Fig. 1 shows two red pitaya peel flours (lab-prepared PT and commercial PC sample). On the other hand, to perform a comparative analysis of the physico-chemical properties of the red pitaya flour processed in our laboratory and the commercially available flour, pre-processed red pitaya peel flour was purchased from the local market in Minas Gerais (Brazil). This pre-processed flour was designated as a PC sample.

2.2. Irradiation of the material

In order to preserve their nutritional properties, the PT and PC samples were stored at -80°C until irradiation. The irradiation of the pitaya flour samples (PT and PC) with doses in the range of 1 to 10 kGy was carried out at the Radiation Technology Center (CETER) of IPEN, using a ^{60}Co gamma cell source, model Gamma Chamber 5000 (BRIT, Maharashtra, India), with a dose rate of 9.11 kGy/h. γ -irradiation of both samples was performed at room temperature. After irradiation, all samples, both irradiated and non-irradiated, were immediately stored at -80°C for subsequent analysis.

For the irradiation process, five aliquots of approximately 10 g of PT and PC samples were prepared and placed in plastic bags. Four of the five aliquots were irradiated with doses of 1.0, 3.5, 7.5, and 10.0 kGy, respectively, under the same conditions. After irradiation, the samples from each aliquot (including the non-irradiated sample) were subdivided into four aliquots for analysis by XRD, FT-IR, Raman spectroscopy, and EPR, respectively. The same preparation and irradiation procedure was followed for both samples to ensure dose uniformity.

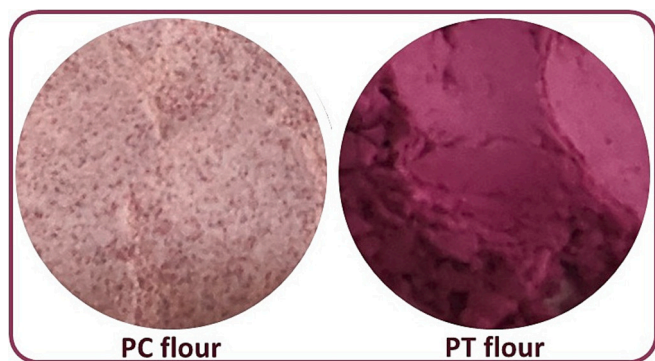


Fig. 1. Illustration of two red pitaya peel flours (laboratory-prepared PT and commercial PC samples) used in this study. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.3. Characterization techniques

2.3.1. X-ray fluorescence (XRF)

The elemental composition of the PT and PC samples was determined using a Rigaku Supermini 200 X-ray fluorescence (XRF) spectrometer equipped with an X-ray tube that uses palladium (Pd) as the anode. The operating conditions of the equipment were as follows: the X-ray tube was set to 50 kV and 4 mA, the sample chamber was kept under vacuum to improve the detection of light elements, and the detector operated with a P-10 gas flow (90% argon and 10% methane), which acts as an ionizable medium. To perform the XRF measurements, the samples, with a particle size of less than 75 μm , were placed in the cylindrical supports of the equipment and pressed lightly until a smooth and compact surface was obtained. Five measurements were performed for each sample under the same conditions.

2.3.2. X-ray diffraction (XRD)

X-ray diffraction (XRD) measurements of PT and PC samples without dose and with γ doses of 1, 3.5, 7.5, and 10 kGy were carried out using a Rigaku MiniFlex 600 XRD diffractometer (Tokyo, Japan) with $\text{CuK}\alpha$ radiation (1.54059 Å), operating at 40 kV and 25 mA. The samples were placed on a glass sample holder, leveling the surface with a glass slide. A single X-ray diffraction (XRD) spectrum was obtained for all samples (with or without dose) in the Bragg angle range 2θ from 10° to 60° , with a step size of 0.05° and a speed of $4^{\circ}/\text{min}$, at room temperature.

2.3.3. Fourier-transform infrared spectroscopy (FT-IR)

The FT-IR spectra of the PT and PC samples, both irradiated and non-irradiated, were obtained using a Bruker FT-IR spectrometer, model INVENIO™, operating in ATR transmittance mode, with the following configuration: 64 scans, a resolution of 4 cm^{-1} , and a wavenumber range of $400\text{--}4000\text{ cm}^{-1}$. To obtain the FT-IR spectra, the PC and PT samples were deposited on a diamond crystal. In order to eliminate noise from the spectrum, smoothing was applied using the Savitzky-Golay convolution method with a 10-point window and a 2-polynomial order. The analyzed spectra were averaged over five registered spectra.

2.3.4. Raman Spectroscopy

Atomic vibrational modes were determined and characterized by means of Raman Spectroscopy measurements using a Horiba® confocal microscope, model LabRAM HR Evolution™ (Villeneuve-d'Ascq, France), with a 785-nm laser module and 33.8 mW of power delivered on the sample. The microscope incorporates a $50\times$ objective lens with $4\mu\text{m}$ of working distance for the image's resolution, using a ViewSharp™ picture system. The spectra were acquired in the range of $200\text{--}3500\text{ cm}^{-1}$ with a spectral resolution of 1 cm^{-1} . Each point was recorded with an exposure time of 7 s, without signal accumulation. In order to improve signal-to-noise ratio of the data, seven scans were performed to obtain a spectrum. Wiley's KnowItAll Analytical 2024 Edition™ software was used for primary identification of the chemical compounds present in the samples.

2.3.5. Thermal analysis (TGA/DSC)

TGA analysis was performed on an SDT Q600 equipment (TA Instruments, Delaware, USA) with a sample of approximately 10 mg of pitaya flour placed in an alumina crucible. The temperature was increased from 20 to 900°C at a constant rate of $10^{\circ}\text{C}/\text{min}$ in a nitrogen atmosphere (100 ml/min). Due to the good reproducibility of the measurements, only one TGA curve was recorded for each sample. To evaluate the effects of γ -irradiation on the PT and PC samples, the data from the TGA graphs were analyzed using TA Universal Analysis™ software.

2.3.6. Electron paramagnetic resonance (EPR)

The EPR spectra of the PT and PC samples, both irradiated and non-irradiated, were recorded at room temperature using a Bruker

spectrometer operating in the X band, with a microwave frequency of 9.75 GHz. The PT and PC samples, with the same mass of 150.0 ± 0.1 mg, were placed in quartz tubes with an internal diameter of 4 mm and inserted into the EPR cavity. The same EPR spectrum acquisition parameters were used for all measurements to ensure reproducibility and to be able to compare the EPR signals: a central field of 350 mT, a modulation amplitude of 0.1 mT, a modulation frequency of 100 kHz, a microwave power of 0.2 mW, a sweep magnetic field from 300 to 400 mT, and a total of 20 scans. Diphenylpicrylhydrazyl (DPPH) was used as a reference sample to calibrate the g factors of the paramagnetic species. To calculate the EPR signal intensities, the peak-to-peak height (first derivative absorption spectrum) was used.

3. Results and discussion

3.1. X-ray fluorescence (XRF) analysis

The results of the elemental analysis of the two pitaya samples (PT and PC) using XRF are shown in Table 1. The elements are listed in descending order according to their percentage (w/w) content. Both samples contain the same elements, but in different concentrations. Among the macronutrients quantified in the PT and PC samples are K, Ca, Cl, Mg, P, and S, while the micronutrient category includes Mn, Fe, Cu, and Zn, which are necessary in minimal amounts for the proper metabolic functioning of our body [36]. Although the same elements are found in both samples, Mn and Cu are absent in the PC sample, and the concentrations of the elements are completely different between the two pitaya flour samples. A very notable difference between PT and PC is related to the amount of P and S. The non-essential elements detected include Al, Si, and Sr. Although the latter element is rarely found in plant samples, Minea et al. [37] and Penić et al. [38] also detected its presence in fruit peel samples.

3.2. X-ray diffraction (XRD) analysis

The XRD patterns of the PT and PC pitaya samples, both unirradiated and exposed to γ -radiation doses of 1, 3.5, 7.5, and 10 kGy, are shown in Fig. 2. This analysis was performed to identify crystalline and/or amorphous phases formed during the freeze-drying process and to evaluate the effect of γ -irradiation on both samples.

The PT sample (Fig. 2a) shows more intense and defined peaks than the PC sample (Fig. 2b), indicating a greater presence of crystalline structures. In the PC sample, specific diffraction peaks are observed at 17.3° and 19.6° , corresponding to retrograded starch-betanin compounds [39], as well as peaks at 15.4° , 17.2° , 18.1° , 19.8° , and 22.9° associated with starch base compounds [40,41], which is consistent with a typical pattern of type A starch crystal structure [40,42].

As for the PT sample, the peaks observed at 22.50° and 22.17°

Table 1

Elemental analysis by XRF of the main minerals in red pitaya flour from samples PT and PC.

Elements (mass%)	Sample	
	PT	PC
K	64.57 ± 0.25	31.97 ± 0.23
Ca	21.50 ± 0.36	15.57 ± 1.38
Cl	3.45 ± 0.05	7.02 ± 0.50
Al	3.11 ± 0.05	–
Mg	2.51 ± 0.25	3.69 ± 0.57
P	1.70 ± 0.02	20.57 ± 0.96
Mn	0.88 ± 0.12	–
S	1.08 ± 0.03	18.20 ± 1.20
Fe	0.48 ± 0.02	1.90 ± 0.18
Si	0.25 ± 0.02	0.69 ± 0.20
Cu	0.29 ± 0.02	–
Zn	0.13 ± 0.02	1.19 ± 0.18
Sr	0.06 ± 0.01	–

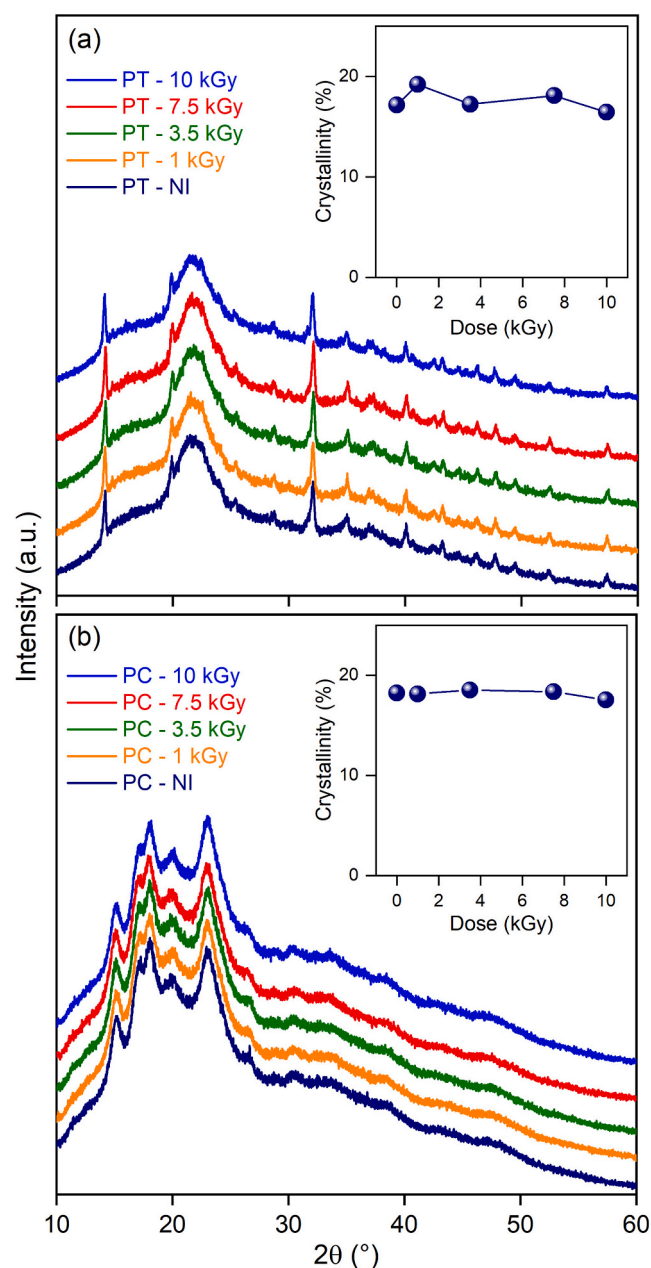


Fig. 2. XRD spectrum of samples: (a) PT and (b) PC, non-irradiated (NI) and irradiated with γ -doses of 1.0, 3.5, 7.5, and 10.0 kGy. The inset of the figure shows the behavior of the crystallinity index as a function of dose for the PT and PC samples.

indicate the presence of cellulose crystallinity, a fact that was also reported by Taharuddin et al. [43] in red pitaya peel flour of the *Hylocereus polyrhizus* variety. The additional diffraction peaks observed at 14.11° , 20.01° , 22° , and 35.05° can be attributed mainly to the crystalline structure of cellulose [11]. The peaks observed at 14.55° and 32.36° correspond to the (110) and (004) lattice planes of cellulose I [43], while the peaks observed at 19° , 24° , and 28° are due to the presence of sugars, such as D-glucose [11]. These cellulose-related peaks are absent in the PC sample. The 19.8° peak shows a significant narrowing in the PT sample compared to the PC sample, indicating that the starchy compounds modify the molecular reorganization of the PC sample and reveal structural differences between the two sample groups. The predominant presence of crystalline phases of low molecular weight sugars (sucrose, fructose, and glucose) in the PT sample is attributed to the drying process, which created conditions conducive to the nucleation and growth

of organic crystals [24]. Additional low-intensity diffraction peaks corresponding to the $\text{H}_{12}\text{MgN}_2\text{O}_{12}$, $\text{C}_{21}\text{H}_{25}\text{NO}_3\text{S}$, and SiO_2 phases [12,44] were also observed, with greater intensity in the PT sample.

The peak at 24.5° associated with long amylopectin chains [45] could not be visualized, probably due to overlapping with crystalline peaks in the PC sample, where amorphous structures predominate.

It should be noted that the shape and intensity of the XRD peaks do not show significant changes with the γ -radiation dose in any of the samples. The diffraction patterns of all irradiated samples are very similar to those of the non-irradiated samples, allowing for direct comparison of the PT and PC, as well as the irradiated groups. These results suggest that γ -radiation does not cause significant alterations in the crystalline or amorphous structure of the pitaya samples, regardless of the method used to obtain the flour.

3.3. FT-IR spectra analysis

The FT-IR spectra of the PC and PT samples non-irradiated (NI) and irradiated with doses of 1.0, 3.5, 7.5, and 10.0 kGy are shown in Fig. 3. The spectra of both samples exhibit bands whose intensity varies as the irradiation dose increases. The bands located between 3000 and 3600 cm^{-1} , between 2800 and 3000 cm^{-1} , and between 1600 and 1800 cm^{-1} are attributed, respectively, to OH stretching, CH stretching, and water bending mode [3,10]. The band at 3251 cm^{-1} corresponds to the stretching vibration of the -OH group, indicating the presence of phenolic compounds in the samples, while the band between 1405 and 1355 cm^{-1} is associated with aromatic ring stretching [24,46].

In the PC sample, bands are observed in the 900–1165 cm^{-1} region that coincide with those reported by Pozo et al. [40] for type A starch samples. According to these authors, the bands around 1157, 1105, and 982 cm^{-1} are due to C—O and C—C stretching with some contributions from C—OH, and they exhibit higher intensities in type A starch samples. Pozo et al. [40] also found a well-resolved band at 1022 cm^{-1} related to type A starches. The spectrum of the PC sample shows bands with more detailed and narrower baselines than those of the PT samples. The peaks observed at 1135, 1105, 1054, 998, and 926 cm^{-1} (see Fig. 3a) are associated with stretching and bending vibrations

characteristic of sugar molecules [26], corresponding to the bending vibrations of C—O and C—H groups of aromatic rings, as well as the C—O stretching vibration characteristic of glycosides. Peng et al. [47] also observed bands at 1100, 1082, and 1030 cm^{-1} characteristic of glycosides. The intense band at 1018 cm^{-1} corresponds to the deformation of the aromatic ring of betalains [46]. Peaks at 1362 and 1426 cm^{-1} (C—H and O—H bending) and at 1344 and 1417 cm^{-1} (C—H oscillation and O—H bending) were also identified for glucose and fructose, respectively. These peaks were more intense in the PT sample and less intense in the PC sample in the region between 800 and 1200 cm^{-1} .

The lower intensity peaks observed in the region of 1400 and 1700 cm^{-1} suggest the presence of C=O stretching vibrations associated with functional groups such as aldehydes, ketones, esters, carboxylic acids, and amides in the pitaya flour samples. The peak observed at approximately 1743 cm^{-1} corresponds to the C=O stretching vibrations of the acetyl and uronic ester groups present in polysaccharides such as pectin, lignin, and hemicellulose [43]. These bands are found in all the samples evaluated. The structures of pectin saccharides, particularly the furanose and α - and β -pyranose rings, are responsible for the bands observed at 1015 cm^{-1} and 1143 cm^{-1} [9]. The positions of all experimental FT-IR bands and their vibrational assignments are shown in Table 2.

According to the results shown in Fig. 3, exposure to γ -radiation doses does not modify the FT-IR spectral profile of the pitaya peel flour samples, although it increases the intensity of the bands at 3285, 1550, and 1338 cm^{-1} . This indicates that irradiation can induce chemical modifications in the structure of the macromolecules of both samples. Santos et al. [3] obtained similar results in a pitaya sample of the same variety as the PC sample. Furthermore, Figueroa-Enríquez et al. [46] observed a shift in the amide III band from 1242 to 1238 cm^{-1} , which they attributed to changes in hydrogen bonds caused by variations in betalain concentrations. As the concentration of betalains in the PT samples increases, the band becomes narrower and more intense, probably due to interactions between hydrogen bonds and the amino and hydroxyl groups present in the compound, compared to the PC sample spectra. Additionally, it has been reported that γ -radiation not only affects linear amylose chains but also breaks amylopectin chains in the amorphous regions of polysaccharides up to a dose of 10 kGy [45].

3.4. Raman spectra analysis

Fig. 4 shows the Raman spectra of the PT and PC samples, non-irradiated. Both samples exhibit distinct spectral features that reflect differences in their chemical composition.

In the PC samples, a Raman shift of approximately 480 cm^{-1} was observed, indicating the presence of amylose and amylopectin. The bands at 1135 cm^{-1} and 1060 cm^{-1} are associated with alterations in the crystalline structure of starch materials [41], and appeared with high intensity in these samples. The band at 1461 cm^{-1} , present in all spectra, corresponds to C—H, C—H₂, and C—OH deformation vibrations. In addition, shifts in the 1380–1400 cm^{-1} region related to untreated starch [41,48] were observed, reflecting changes in the coupling of the C—CH and C—OH deformation modes.

In the PT samples, bands with maxima at 1128 and 1082 cm^{-1} were observed (see the enlarged region of the spectrum in Fig. 4). These bands can be assigned to different modes of deformation of the C—H (bending vibration), C—O—C (asymmetric stretching vibration), and C—C (skeletal vibrations) groups present in starches and dietary fiber [48]. Bands corresponding to flavanols were observed at 1613 and 1518 cm^{-1} (carbonyl group vibrations), 1460 cm^{-1} (phenyl ring vibration), 1280 cm^{-1} (OH group deformation), 1144 cm^{-1} (C—O stretching of aromatic alcohols), and 1034 cm^{-1} (C—O—C stretching vibrations) [10]. In the PT samples, bands were also observed in the regions of 1640–1600 cm^{-1} ($\nu(\text{C}=\text{C})$ vibrations of the ring) for all flavonoid groups except flavanones, as well as bands between 1345 and 1240 cm^{-1} associated with anthocyanin compounds [10].

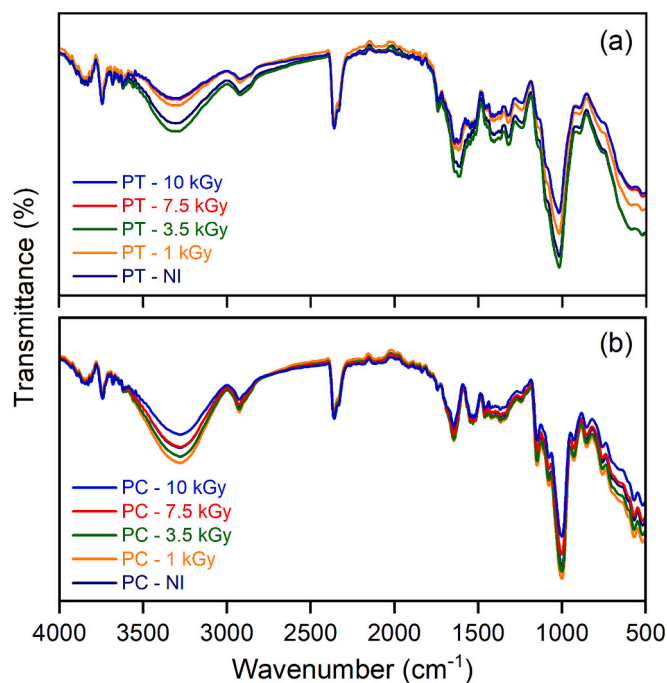


Fig. 3. FT-IR spectra for PT and PC samples non-irradiated (NI) and irradiated with different doses of γ -radiation: 1.0, 3.5, 7.5, and 10.0 kGy.

Table 2

Main experimental FT-IR and Raman shift bands' positions in wavenumbers and inelastic scattering assignments for the PT and PC samples.

FT-IR, wavenumber (cm ⁻¹)			Band assignment
PT	PC	Both	
		3000–3600	O–H stretching
		3251	O–H vibration
		2800–3000	–CH stretching
		1700–1743	C=O stretching vibrations of carbonyl-containing groups
		1600–1800	Water bending mode
1405–1355			Aromatic ring
1426			C–H bending
1417			O–H bending
1362			O–H bending
1344			C–H oscillation
1242–1238			Amide III band modifications from betalain
1200			C–O stretching vibrations
	1157		C–O–C/C–O stretching
1143			Asymmetric C–O–C stretching (α - and β -pyranose rings from pectin)
		1135	Asymmetric C–O–C stretching of glycosidic linkages β -(1 $\rightarrow$ 4)
	1105		C–OH + C–O stretching vibrations
		1100	C–OH + C–O stretching vibrations, also associated with glycosidic C–O–C linkages
		1182	C–O stretching and C–C skeletal vibrations of the carbohydrate backbone
		1054	C–O stretching of polysaccharide
		1030	C–O stretching of primary alcohol groups (–CH ₂ –OH)
1018			Aromatic ring of betalains deformation
1015			C–O stretching vibrations of pectin (furanose)
		998	C–O stretching and ring deformation modes
	982		Associated with C–O stretching and C–O–C skeletal vibrations
		926	Anomeric C–O–C vibration + ring deformation, typically attributed to β -(1 $\rightarrow$ 4) glycosidic linkages
	900–1165		Related to type A-starches (C–O–C and C–O vibrations)
800			Ring deformation and out-of-plane C–H bending
Raman shift (cm ⁻¹)			Inelastic scattering assignments
1640–1600			C=C vibration bands of the ring from anthocyanins
1613			C=C stretching vibrations of aromatic rings of flavanols
1518			Aromatic ring stretching vibrations (C=C) of flavanols
	1461		C–H, C–H ₂ , and C–OH deformation vibrations
1460			Phenyl ring vibration
	1400		C–CH deformation modes
	1380		C–OH deformation modes
1280			Deformation vibration (–OH)
1188–1183			Phenolic –OH groups of isoflavones
		1144	C–O stretching of aromatic alcohols
	1135–1128		Asymmetric C–O–C stretching vibrations in starches
		1082	C–O stretching vibrations of secondary alcohol groups (–C–OH) and C–C skeletal vibrations in starches
		1034	C–O–C stretching vibrations
	480		C–O skeletal vibrations of amylose and amylopectin

When comparing the spectra of both samples, it can be seen that the PC sample has less intense bands and a broader background due to the Raman resonance effect. This difference in signal intensity reflects their different chemical compositions; the PT sample is mainly composed of

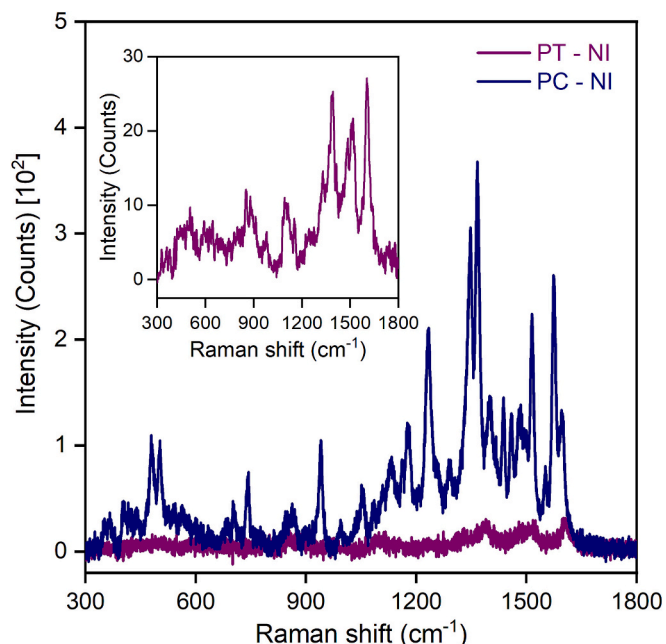


Fig. 4. Raman spectra from PT and PC samples. The inset shows the Raman spectrum of the non-irradiated PT sample (PT-NI).

phenols, polyphenols, pectin, and polysaccharides. These compositional differences also explain the different coloration of the powders observed in Figs. 1 and 5.

It should be noted that irradiation did not alter the spectral characteristics of any of the samples, indicating that the crystalline structure of the pitaya powders was not affected by exposure to γ -radiation. Table 2 shows all the positions of the Raman bands observed experimentally, together with their vibrational assignments and corresponding FT-IR assignments, as well as the chemical compositions of the PT and PC samples.

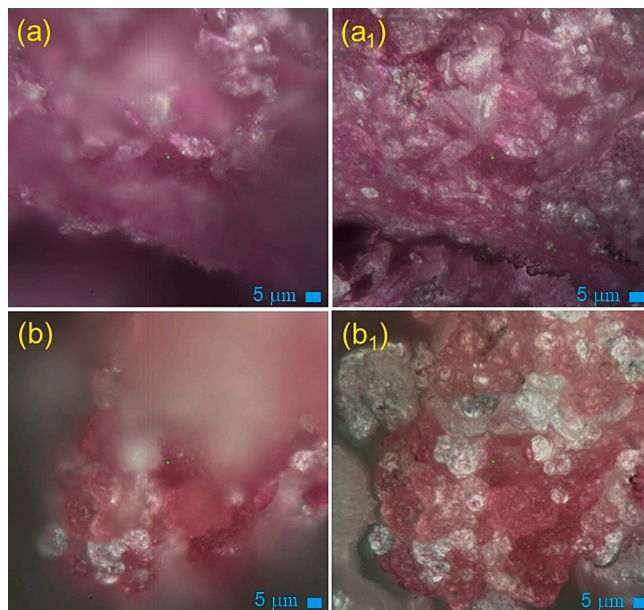


Fig. 5. Raman images of non-irradiated pitaya powder: PT (a) and PC (b) specimens, and in zoomed-in (a₁, b₁) region rendered by ViewSharp™ picture system, respectively.

3.5. TGA and DSC analyses

The thermal degradation behavior of PT and PC samples irradiated with different doses of γ -radiation was evaluated using thermogravimetric analysis (TGA). Fig. 6 shows the TGA profiles of both samples, while Table 3 summarizes the recorded thermal properties.

The PT samples showed three distinct stages of thermal decomposition. The first stage, up to approximately 170 °C, showed a weight loss between 10.51% and 11.58%, corresponding to the evaporation of water and moisture. The second stage, between 170 and 400 °C, showed a substantial weight loss ranging from 49.79% to 62.82% (Fig. 6a and c), attributed to the thermal decomposition of polysaccharides, in particular the degradation of pectin galacturonic acid, which underwent significant degradation, leading to the breakdown of glycosidic bonds [9]. The DTG curve showed three prominent peaks at ~207, ~248, and ~295 °C (Fig. 6a), indicating events of maximum weight loss. Similar thermal behavior has been reported for red pitaya flour of the *Hylocereus polyrhizus* variety [43].

In the PC samples, an initial weight loss of approximately 10% was observed below 130 °C (Fig. 6c), also associated with water evaporation. The second stage of decomposition began at around 290 °C and extended to approximately 550 °C, with a weight loss of around 50%. This behavior is consistent with the thermal decomposition of starch, similar to that observed in corn starch [45]. Analysis of the weight derivative (%/°C) of the PC samples showed patterns similar to those of starch-containing materials [45]. The peaks observed in the range of 260–330 °C (Fig. 6c and d) correspond to the main thermal degradation event of starches. Thermal decomposition between 318 °C and 480 °C is possibly due to cellulose degradation [29].

The ash content differed significantly between samples, with 27.82% for the PT sample and 14.60% for the PC sample, reflecting their different chemical compositions as detailed in the FT-IR and Raman analyses. In the PT sample, weight loss was observed below 105 °C, attributed to dehydroxylation and detachment of betalamic acid from betalains [46]. The ash content values obtained for the PC sample (14.60%) are consistent with the ranges reported for pectin films (12.58–28.69%) [9]. The moisture content observed in the PT sample is consistent with previously reported values for pitaya peel flour, which range from 9.7% to approximately 12% [16,32,43].

Regarding the effects of γ -irradiation, changes in the measured heat flow (mW) were observed in both PT and PC samples after irradiation, with the extent of these changes depending on the applied dose.

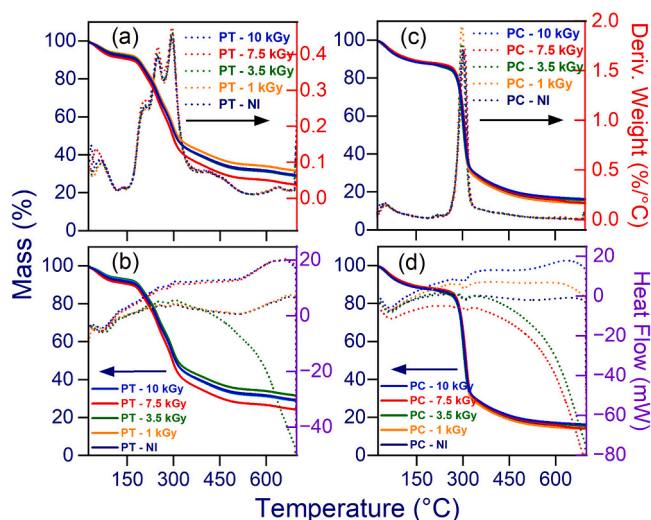


Fig. 6. (a) Thermal events and moisture content in zoomed-in registered and (b) DSC events from the PT samples. (c) Thermal events and moisture content in zoomed-in registered and (d) DSC events from the PT samples.

3.6. Electron paramagnetic resonance (EPR) analysis

The room-temperature EPR spectra of γ -irradiated red pitaya peel powder (sample PT) are shown in Fig. 7. Measurements carried out at different microwave (MW) power levels indicate that the spectrum contains contributions from at least three paramagnetic species, which are labeled in Fig. 7.

Center I is characterized by six low-intensity EPR lines. In Fig. 7, five lines are seen, and one of the lines overlaps with signals arising from other centers.

The EPR parameters of the paramagnetic centers were obtained from spectral simulations. For center I, the g -value is 2.0020, the hyperfine splitting is approximately 78 G, and the linewidth of the individual hyperfine components is about 65 G.

Several resonance lines are observed in the region around $g \approx 2.0$ (Fig. 7). These lines exhibit significantly higher intensities than those associated with center I. Among them, the set of lines assigned to center II shows similar thermal annealing behavior [11]. In the present study of the red pitaya peel flour sample (PT), center II (Fig. 7) exhibits a g -value of 2.0024. The corresponding EPR spectrum consists of a triplet with an approximate intensity ratio of 1:2:1, together with an overlapping single line that coincides with the central component of the triplet.

It should be noted that the triplet lines attributed to center II partially overlap with other weak spectral lines, as reported in earlier studies. Nevertheless, the triplet constitutes the dominant contribution to the set of lines assigned to center II.

The triplet arises from hyperfine interaction between the unpaired electron and two equivalent nuclei with nuclear spin $I = 1/2$. The hyperfine splitting is estimated to be ~30 G, and the linewidth of the individual components is approximately 7.5 G.

The overlapping single line coinciding with the central line of center II is assigned to center III. Center III is characterized by a g -value of 2.0024 and an approximate linewidth of 10 G.

The EPR lines associated with center I correspond to a single paramagnetic species. The observed g -value is close to the free-electron value (2.0023), and the signal remains observable at room temperature. The lines corresponding to center I are stable and do not exhibit any observable decay upon thermal annealing at elevated temperatures, indicating that the signal most likely originates from a transition-metal ion of the iron group. Among these, Fe^{3+} and Mn^{2+} ions are known to exhibit g -values near 2.0 and produce detectable EPR spectra at room temperature.

For Mn^{2+} ions ($S = 5/2$), the spin Hamiltonian gives rise to six spin levels, resulting in five allowed fine-structure transitions between adjacent levels. Each of these transitions is further split into six hyperfine components because the nuclear spin of Mn is $I = 5/2$ [49]. In powder samples, the fine-structure lines are usually broadened and overlap, so the spectrum typically appears as six hyperfine lines near $g \approx 2$.

Based on these spectral characteristics, the EPR lines corresponding to center I are assigned to Mn^{2+} ions. The presence of Mn^{2+} in pitaya is consistent with its natural occurrence in the fruit, where it is absorbed from the soil and contributes to photosynthetic and metabolic processes [50].

In the field of food radiochemistry, numerous investigations have been conducted on irradiated fruits such as strawberry, raspberry, apple, pear, fig, kiwi, and cherry [51,52]. These fruits typically exhibit multi-component EPR spectra arising from multiple radical species. A characteristic and commonly observed spectral pattern, referred to as a “sugar-like” signal, has been reported across different fruits [53]. The EPR spectra of irradiated D-glucose, D-fructose, and sucrose are found to be very similar to those observed in irradiated dried fruits. Since fructose and glucose are the principal sugars present in fruits, and given that pitaya also contains sugars as a constituent, the formation of similar radicals upon irradiation is expected.

The triplet observed in the present study (center II) is tentatively

Table 3Moisture content and thermal events registered for PT and PC samples irradiated at different γ -doses.

Dose (kGy)	PT							PC						
	Initial mass (mg)	Total moisture content (%)	T _{onset} (°C)	T _{max} (°C)	Total mass lost (%)	Mass lost - T _{onset} (%, min/°C)	Total ashes content (%)	Initial mass (mg)	Total moisture content (%)	T _{onset} (°C)	T _{max} (°C)	Total mass lost (%)	Mass lost - T _{onset} (%, min/ °C)	Total ashes content (%)
NI	10.67	9.36	171.47	210.16	62.01	0.6990	28.63	10.16	15.71	266.46	307.13	70.42	4.829	13.87
1.0	10.44	8.01	171.46	211.22	60.92	0.2848	31.07	10.81	15.35	265.47	301.62	70.96	4.839	13.69
3.5	11.58	8.84	173.49	211.25	62.93	0.3130	28.23	11.37	16.38	267.41	300.83	68.47	3.297	15.15
7.5	10.62	10.56	172.48	210.68	65.96	0.7906	23.48	10.18	14.26	265.42	310.20	71.47	6.803	14.27
10.0	10.51	9.24	173.46	214.60	62.53	1.7590	28.23	10.04	14.98	260.45	305.31	68.97	4.552	16.05

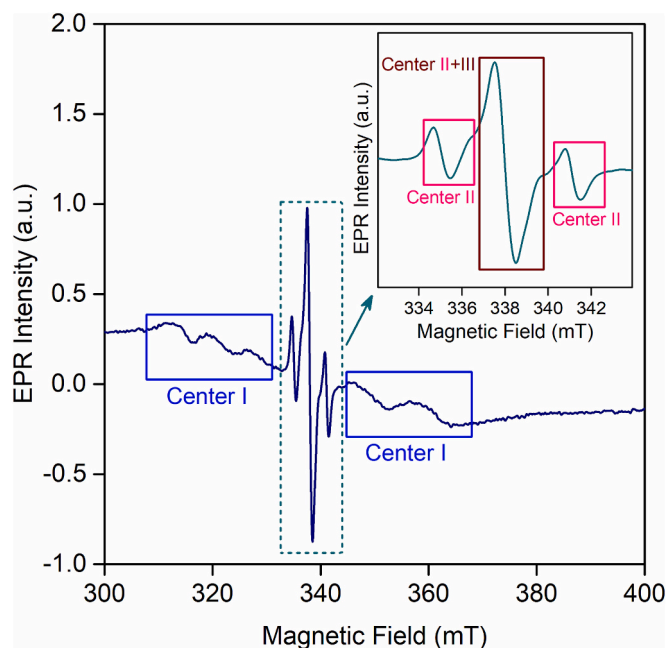


Fig. 7. Room temperature EPR spectra of the PT sample irradiated with γ -rays (dose: 10 kGy). The lines from the center I are shown by blue rectangles. These lines are from the Mn^{2+} ion. Lines of center II are attributed to the “sugar-like” spectrum observed in sugar samples. Center III is due to the radical derived from the cellulose part of the pitaya fruit. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

assigned to a radical species in which the unpaired electron interacts with two β -type protons [54]. Based on previous investigations of irradiated sucrose—particularly the work of Sagstuen et al. [54]—the spectral features of center II can be classified as “sugar-like,” with the dominant contribution arising from a radical of the type RCOCHCH_2 . It should be noted that in the present case, the hyperfine splitting due to the α -proton is relatively small and remains unresolved. Sagstuen et al. reported that the unpaired spin density is not fully localized on the carbon atom bearing the α -proton, estimating a spin density of approximately 0.53 in the $2p\pi$ orbital of the α -carbon, with about 50% delocalization onto the carbonyl oxygen. In analogy, it is proposed that in the present system, the spin density on the α -carbon is further reduced, leading to the absence of resolvable α -proton hyperfine splitting and the observation of only a triplet with an intensity ratio of 1:2:1.

In general, γ -irradiated fruits exhibit a characteristic triplet EPR spectrum arising from radicals induced in the cellulosic components of the fruit [55]. This spectrum, commonly observed in various fruits—particularly in their achenes, pips, or stones [52] is referred to as a “cellulose-like” EPR signal. It consists of an intense central singlet line

accompanied by two weak satellite lines positioned approximately 30 G to the left and right of the main line. The triplet is characterized by a g -value in the range of 2.0032–2.0044, with the satellite line separation varying between 30 and 34 G, depending on the cellulose source. The radical responsible for this triplet structure is generally attributed to dehydrogenation processes occurring along the cellulose backbone [56,57].

Considering these previous reports on irradiated fruits and the possible radicals formed in pitaya, center III in the present study is tentatively assigned to the cellulose-derived radical associated with the triplet spectrum. However, the triplet structure could not be clearly resolved due to overlap with the high-intensity lines of the center II radical. The central component of the triplet is relatively intense and can be discerned in the spectrum (Fig. 7). The satellite lines are much weaker [53].

The room-temperature EPR spectrum of γ -irradiated commercial pitaya flour (PC) powder is presented in Fig. 8. The characteristic six-line pattern corresponding to Mn^{2+} ions (center I) is absent, and no signal attributable to center II is observed. Based on the considerations discussed earlier for the PT powder sample, center III is tentatively assigned to a cellulose-derived radical. The g -value is estimated to be 2.0027, and the center has a linewidth of 12.1 G. The characteristic

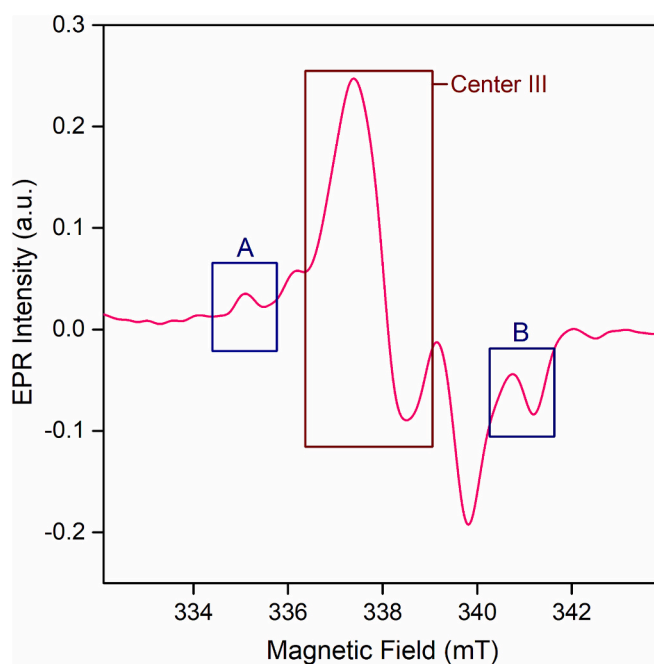


Fig. 8. Room temperature EPR spectra of γ -irradiated (dose: 10 kGy) commercial pitaya flour (PC). Only Center III is observed compared to PT flour, and this center is from the cellulose part of the fruit. Lines marked as A and B are part of the center III spectrum.

“cellulose-like” EPR signal consists of a central singlet line accompanied by two weak satellite lines symmetrically positioned on either side. The lines labelled A and B in Fig. 8 correspond to these satellites, each separated from the central line by approximately 28 G.

In addition to these features, several low-intensity lines are observed in the spectrum; however, the radicals responsible for these signals remain unidentified in the present study.

Comparison with the EPR spectrum of the PT pitaya flour indicates that the component responsible for the “sugar-like” spectral pattern is not present in the PC flour sample. In addition, the absence of Mn^{2+} resonance lines shows that manganese-related centers do not contribute to the EPR signal of the PC sample. This observation is consistent with the XRF analysis of the PC sample, which confirms the absence of Mn ions.

In addition to identifying the paramagnetic species responsible for the EPR signals in the PT and PC pitaya flour samples, we studied how these signals vary with γ -irradiation doses in the range of 1.0 to 10 kGy. According to the FAO (Food and Agriculture Organization), 10 kGy is the maximum recommended dose for food irradiation treatment. Fig. 9 shows the EPR spectra of the PT and PC pitaya flour samples non-irradiated and irradiated with γ -doses of 1.0, 3.5, 7.5, and 10 kGy. The hyperfine signals due to Mn^{2+} in the PT sample do not undergo any alteration in intensity with the irradiation dose. On the other hand, the EPR signal from center III of the PT sample is always more intense than the other EPR signals for all irradiated doses. A similar effect is observed in center III of the PC sample. Furthermore, the results indicate that more paramagnetic species are generated in the PT sample with the γ -radiation dose than in the PC sample. Therefore, we can affirm that there is a difference in the composition of both samples, since the PT sample presents EPR signals associated with sugar and cellulose molecules, while the PC sample presents only EPR signals associated with cellulose molecules. The dose dependence of the EPR signal intensities for centers II and III in the PT sample, along with the dose response of center III in the PC sample, are presented in Fig. 9.

The EPR spectra of the defect centers observed in the PT and PC samples were simulated, and the corresponding simulated spectra are presented in Fig. 10. A good agreement is observed between the experimental and simulated spectra, indicating that the chosen spectral parameters adequately reproduce the experimental features.

Table 4 shows a comparative summary of the main properties of the two samples of red pitaya peel flour, with and without γ -irradiation. Significant differences in structure, functional groups, paramagnetic centers, and thermal properties are observed between the PT and PC samples. Therefore, the combination of spectroscopic and thermal analyses allows us to distinguish between pitaya flour samples with different chemical compositions, which can be used to authenticate commercial pitaya flour and prevent possible fraud in its production. On the other hand, this work also analyzed the continuous and improved development of analytical methods that allow evaluating whether a product has been irradiated and the irradiation dose to which it has been subjected. After comparing the results in Table 4, it is concluded that the most efficient analysis technique to distinguish an irradiated pitaya flour sample is EPR spectroscopy.

4. Conclusions

After γ -irradiation, the PT pitaya powder samples exhibited no significant changes. In contrast, the FT-IR spectra of the PC pitaya powder revealed a reduction in the absorbance intensity associated with the C—O—C stretching vibration. This decrease suggests that γ -irradiation induced scission of glycosidic bonds within the starch component of the PC powder, leading to a reduction in its crystallinity. The starch incorporated was modified by γ -irradiation, but did not change the amylose to amylopectin structure, keeping the thermal properties and stability increased by γ -irradiation, and the reduction in heat flow somewhat depends on the radiation dose applied. In addition, γ -radiation did not

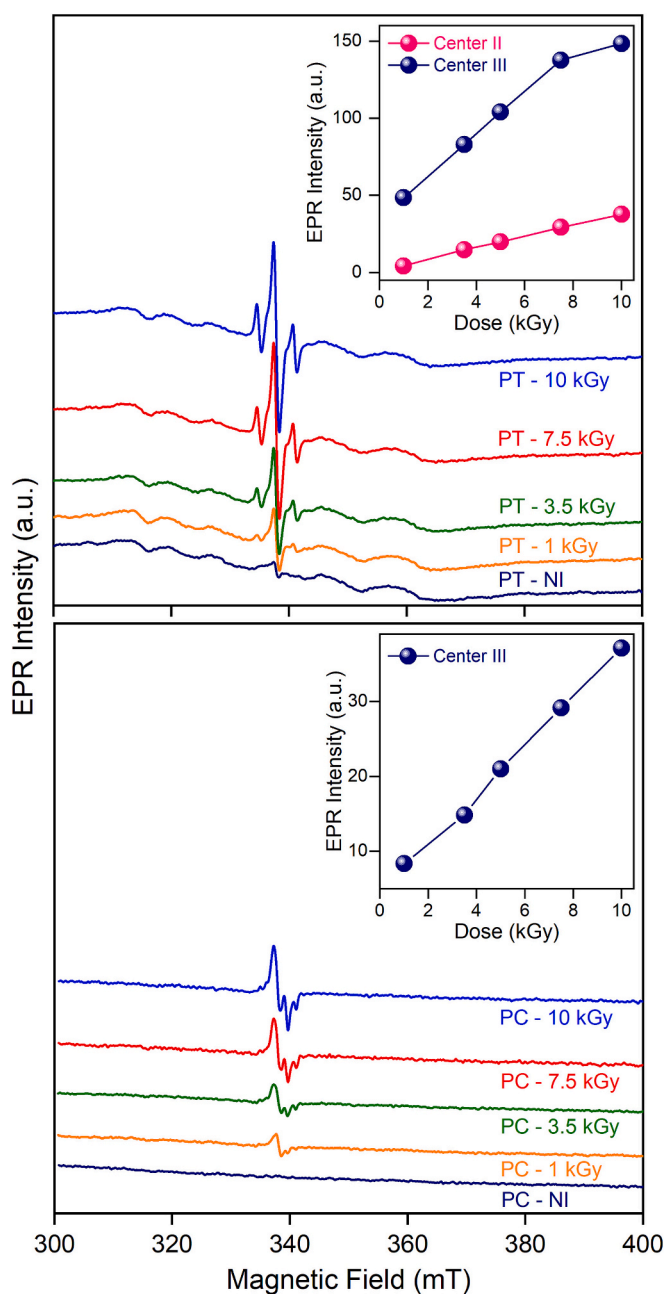


Fig. 9. The EPR spectra of the PT and PC samples irradiated to different doses between 1 and 10 kGy. The inset of the figure shows the γ -dose response of centers II and III in the PT sample (top) and center III in the PC sample (bottom).

change the XRD diffractograms and did not affect the functional groups of pitaya powders for PT and PC samples. However, the relative crystallinity of the PT sample was slightly reduced by irradiation, measured by XRD and Raman shift, in comparison with the PC sample group. γ -irradiation of the red pitaya flour (PT) results in the formation of multiple paramagnetic centers, with the corresponding EPR signals exhibiting considerable overlap. The presence of Mn^{2+} ions is confirmed in this sample. Center II is attributed to radicals originating from the sugar component of the pitaya fruit, while center III is associated with radicals derived from the cellulosic matrix. In contrast, the EPR spectrum of the commercial pitaya flour (PC) sample shows no evidence of Mn^{2+} ions, and the contribution from the sugar component is negligible. Finally, from the results obtained, we can conclude that exposure to γ -irradiation produces few changes in pitaya peel powder, except in

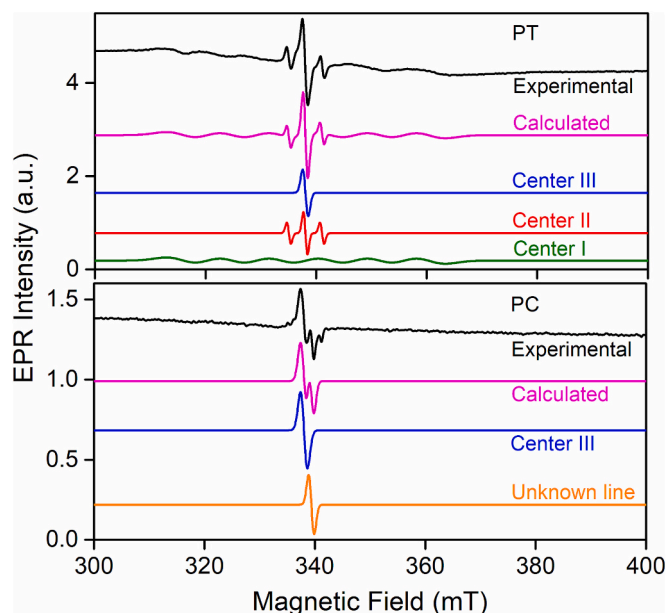


Fig. 10. The simulated EPR spectrum of (top) PT and (bottom) PC samples.

Table 4

Comparison of key properties, such as thermal parameters, crystallinity, main FT-IR bands, Raman bands, and EPR centers, before and after irradiation of PT and PC samples. To facilitate qualitative comparison, the intensities of the FT-IR, Raman, and EPR center bands are shown in parentheses.

Properties	Sample			
	PT		PC	
	Non-irradiated	Irradiated, 3.5 kGy	Non-irradiated	Irradiated, 3.5 kGy
Thermal parameters (Tonset, °C)	171.47	173.49	266.46	267.41
Crystallinity (%)	17.14	17.22	18.22	18.51
FT-IR band (cm ⁻¹) (Intensity)	1018 (0.48967)	1018 (0.46496)	1054 (0.55480)	1054 (0.52524)
	1015 (0.49166)	1015 (0.46742)	1030 (0.38830)	1030 (0.34884)
	998 (0.55183)	998 (0.52791)	998 (0.26824)	998 (0.22565)
EPR Center (Intensity)	Center I (8.29)	Center I (8.25)	–	–
	–	Center II (14.65)	–	–
	–	Center III (82.80)	–	Center III (14.84)

terms of its paramagnetic properties, since exposure to this radiation generates a progressive increase in paramagnetic species with dose. These changes in physical properties depend on the chemical composition of the pitaya flour evaluated. Of the two samples exposed to γ -radiation and analyzed, the PT sample is a natural and sustainable flour alternative.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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