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VARIABILITY OF ELECTRON SPIN RESONANCE (ESR) SIGNAL OF γ -IRRADIATED STARCHES

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ABSTRACT

Food preservation is one of the practical applications of radiation processing of materials. Starch is an abundant and cheap nutritious biopolymer and also is the material for appropriate food systems and for technical industries. Starch granules are partially crystalline structures composed mainly of two types of starch: amylose, an essentially linear polymer, and amylopectin, with 3-44% of branch points. Electron spin resonance (ESR) spectroscopy is a very powerful and sensitive method for the characterization of the electronic structures of materials with unpaired electrons. The aim of the present work was to monitor the disappearance of the short-life and long-life free radicals formed during γ-irradiation of 3 different starches. Corn, potato and fermented cassava starches were irradiated in a ^{60}Co source Gammacell 220 with 20 kGy, dose rate around 1 kGy h-1. EPR spectra were obtained at room temperature using a Bruker EMX plus model, X band equipment. The main type of ESR signal from irradiated starch is a singlet with a g-value of about 2.0. The fading of ESR signals was followed for 350 hours, and presents differences among the different starch type reflecting differences in molecular arrangements of starch crystalline and amorphous fractions, although ESR spectra seemed to be common for all starches.

1. INTRODUCTION

Starch is the food material that is stored in plants and can be found in seeds, in roots, in tubers or in stems. It is the most important carbohydrate in the human diet. Foods rich in carbohydrates are usually the most abundant and cheapest when compared with foods high in protein and fat content. Starch granules are partially crystalline structures and are composed mainly of two types of starch: amylose, an essentially linear α (1–4)-linked glucan polymer, and amylopectin, which is also an α(1–4)-linked glucan but with 3-44% of α (1–6) branch points. Native starches contain normally 20–30 wt.% of amylose [1]. Generally, native starch granules have between 15 and 50% crystallinity [2].

Electron spin resonance (ESR) or electron paramagnetic resonance (EPR) is a spectroscopic method permitting the detection of unpaired electrons, which can appear in different situations: i) defects in semiconductors; ii) paramagnetic ions derived from transition or main group elements: these are commonly observed in foods as many enzymes functions are mediated by transition metals; iii) free radicals, included those induced by radiation [3].

As many biological macromolecules are affected by ionizing irradiation through the formation of free radicals [4], electron spin resonance (ESR) spectroscopy was employed to detect free radicals in many systems and also in irradiated food products [5-9] or for the determination of antioxidant capacity [10].

The aim of the present work was to monitor by means of ESR spectroscopy the disappearance of the short-life and long-life free radicals formed during γ-irradiation of three different starches, two native, corn and potato starches, and one modified through fermentation, cassava starch, known in Brazil as *polvilho azedo*.

2. EXPERIMENTAL

Corn, potato and fermented cassava (sour cassava) starches were acquired in bulk at local food market, edible degree, and no pure substances. According to Brazilian legislation, they contain a minimum of 80% of starch, a maximum of 14% of humidity and 0.5% of mineral residue. Irradiation was performed in a ^{60}Co source Gammacell 220 with 20 kGy, dose rate around 1 kGy h^{-1}. Electron Paramagnetic Resonance (EPR) spectra were obtained at room temperature using Bruker EMX plus model, X band, interval from 337.6 to 367.5 mT, field modulation amplitude 0.2 mT, field modulation frequency 100 kHz, microwave power 2 mW. Analyses were made to study the kinetics of the free radicals. The fading of ESR signal was followed for 350 hours. *OriginPro 8* program was used to obtain the equations of the decay curves.

3. RESULTS AND DISCUSSION

Paramagnetic or spin resonance absorption is due to the unpaired electrons associated with free radicals. Non-irradiated cornstarch exhibits no ESR signal. Sour cassava and potato starches, on the other hand, has a pre-dose signal, as is shown in Fig. 1.

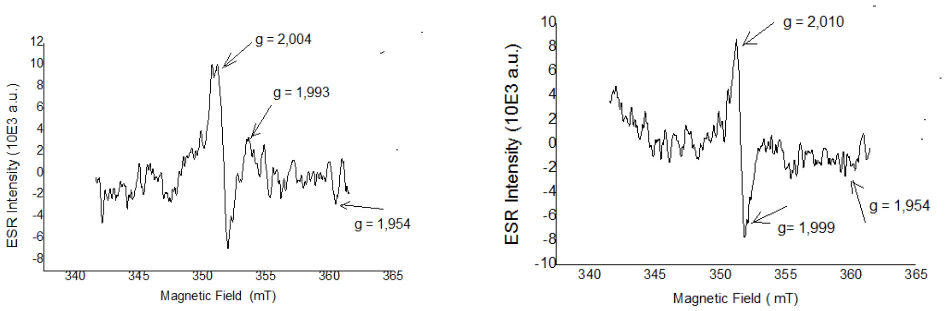
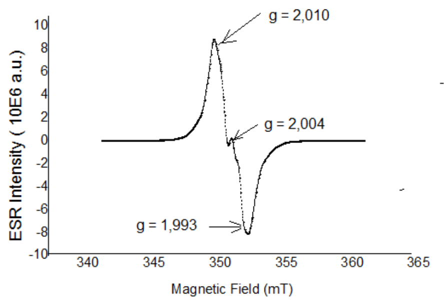


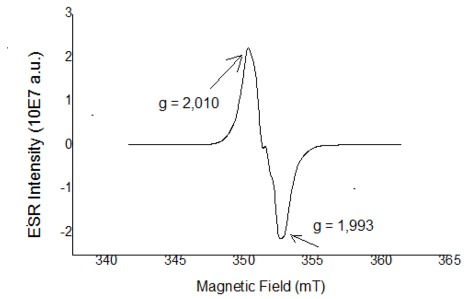
Figure 1: EPR Spectra of non-irradiated sour cassava starch (left) and potato starch (right)

EPR spectra of corn, potato and cassava starches irradiated with 20 kGy were recorded and are presented in Fig. 2. These irradiated samples exhibited an ESR singlet centered at g ≈ 2.0 that can be attributed, among other factors, to other than starch components of the samples. As can be seen, the intensity of ESR singlet peaks was strongly increased by irradiation.

a) corn starch



b) potato starch



c) cassava starch

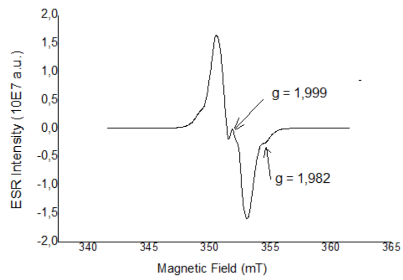
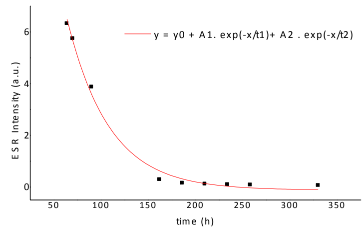


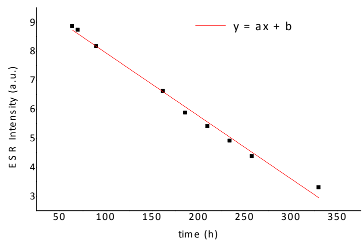
Figure 2: EPR spectra of corn (a), potato (b) and cassava (c) starches irradiated with 20 kGy, one day after irradiation

The decay kinetics of the radiation-induced free radicals of the three starches was studied by EPR spectroscopy. The radicals, highly reactive, are destroyed by reaction mainly with oxygen and water molecules leading to an exponential decrease of the radicals with time. According to Bertolini et al. [4] the kinetic constant is independent of the water content in the crystalline parts and proportional to the water content or its square in the amorphous parts. Fig. 3 presents the decay curves of the 3 starches with their equations and Table 1 displays the correspondent parameters. ESR spectra seemed to be common for all starches, but the kinetics of disappearance of ESR signal followed different patterns, reflecting differences in molecular arrangements of starch crystalline and amorphous fractions.

a) corn starch



b) potato starch



c) cassava starch

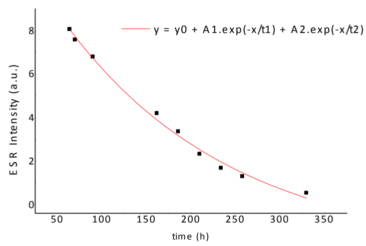


Figure 3: Decay of EPR signal intensity of corn (a), potato (b) and cassava (c) starches irradiated with 20 kGy

The decay curves of 20 kGy irradiated samples were adjusted by a kinetic function consisting of the sum of two exponentials for corn and sour cassava starches. Exceptionally, for potato starch, the best adjustment was a straight line.

Table 1: Decay curve equation parameters of the of radiation-induced RPE signal of corn, potato and starch starches

starch	correlation coefficient	Y_0	A_1	A_2	T_1	T_2
Corn	0.9894	-0.0118	1.3781	1.3781	44.86	44.86
Potato	0.9907	a=-0.002	b=1.011	-----------	-----------	----------
Sour cassava	0.9892	-0.2190	0.7183	0.7183	188.30	188.30

4. CONCLUSIONS

ESR spectra were obtained for three different types of 20 kGy irradiated starches, one a cereal (corn), one a bulb (potato) and one a root (cassava) and seemed to be similar for all starches. Pre-dose signal contribution obtained for potato and sour cassava starches had a small influence on the overall spectrum. The fading of ESR signals followed for 350 hours was different for each starch type reflecting differences in molecular arrangements of starch crystalline and amorphous fractions. The decay curves were adjusted by a kinetic function consisting of the sum of two exponentials for corn and sour cassava starches. Exceptionally, for potato starch, the best adjustment was a straight line.

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