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Short Communication

Free radical formation in UV- and gamma-irradiated cassava starch

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Abstract

Cassava starch is degraded by UV irradiation, particularly when previously acidified with lactic acid. Gamma irradiation also induces starch degradation through the formation of free radicals. The aim of this work was to confirm the hypothesis that free radicals are formed in starch through UV treatment and to compare free radical formation and the extent of degradation in native or acidified starches as a result of UV and gamma irradiation. Both types of irradiation result in a decrease in starch intrinsic viscosity. Electronic spin resonance (ESR) shows that radicals formed in UV irradiated samples are similar to those produced by gamma irradiation. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Starch; Cassava; Gamma irradiation; UV irradiation; ESR; Depolymerization; Free radicals

1. Introduction

The treatment of starch by UV light, with or without a photosensitizer (Phillips & Rickards, 1969), induces changes in its functional properties: it increases water binding capacity and solubility (Gholap, Marondeze & Tomasik, 1993) and decreases hot paste viscosity (Fiedorowicz, Tomasick & Lim, 1999). The latter phenomenon can also be observed after treatment with natural sunlight, particularly with cassava starch that has been previously acidified with lactic acid (Mestres & Rouau, 1997; Fiedorowicz et al., 1999; Nunes, 1994; Plata-Oviedo & Camargo, 1998).

Sunlight or UV irradiation do not seem to alter the crystalline structure of starch; the gelatinization enthalpy remains mainly unchanged (Mestres & Rouau, 1997; Fiedorowicz et al., 1999). However, irradiation decreases the intrinsic viscosity (Merlin & Fouassier, 1981; Mestres & Rouau, 1997) and could also promote starch cross-linking under oxygen (Fiedorowicz et al., 1999). UV photodegradation of starch results in glycosidic bond cleavages, with a shortening of the amylose chain and a debranching of the amylopectin chain, through free radical formation (Merlin & Fouassier, 1981). Some studies suggest that free radicals produced by UV irradiation are identical to those produced during thermal treatments (Tomasick & Zaranyika, 1995) or to those generated by additives such as sulphite or ascorbic acid (Sriburi, Hill & Barclay, 1999). However, the starch photodegradation mechanism remains unclear.

Electronic spin resonance (ESR) experiments have made a major contribution to our understanding of the mechanism of starch degradation after gamma irradiation. It has been reported that gamma irradiation induces free radicals at the C_1 position on the glucose molecule (Raffi & Agnel, 1983; Raffi, Agnel, Boizot, Thiery & Vincent, 1985). The aim of this work was to confirm the hypothesis that free radicals are formed in starch after UV treatment and to compare free radical formation and the extent of starch degradation after UV and gamma irradiation.

2. Materials and methods

Cassava starch (*Manihot esculenta* Crantz) used was a commercial sample from Lorenz Co. (São Paulo, Brazil). Amylopectin was extracted from the starch according the method described by Banks and Greenwood (1967). Dextrin 10 derived from corn starch was obtained from Fluka BioChemika.

The cassava starch, amylopectin and dextrin were acidified with lactic acid (Sigma L1250) solution (2% w/w) for 10 min at room temperature then dried in an oven at 25°C for 24 h, giving a final water content of 12% (wb).

Acidified and non-acidified samples were exposed to UV

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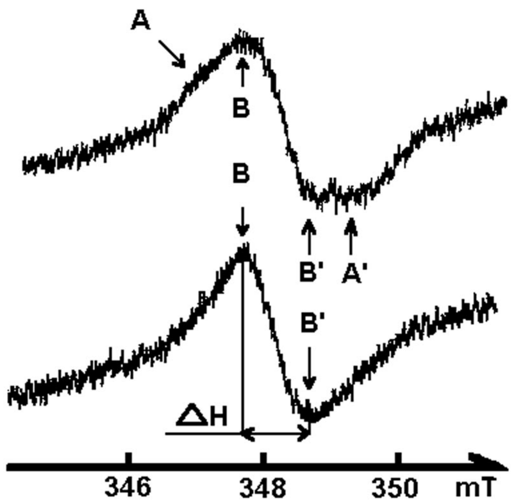

Fig. 1. ESR spectra of cassava starch one and eight days after UV irradiation, top and bottom, respectively.

light (HPK 125 W, Philips) in an air-conditioned room (25°C, 65% relative humidity). Thin layers (2 mm thickness) of the powder were exposed to 1739 J/cm^2 of total energy and 772 J/cm^2 of UV energy (<420 nm). The final water content of the samples was 9–10% (wb). Gamma irradiation was carried out at room temperature, with the Cadarache ^{60}Co γ source of 60,000 Ci supplying a dose rate of 8.1 kGy/h. The total irradiation dose was 1.0 kGy. The irradiation trials were duplicated for the acidified and non-acidified samples.

The ESR patterns were recorded at room temperature on an EMS104 Bruker spectrometer. The recording parameters were those previously used by Raffi and Agnel (1983) for irradiated starch: power 4.99 mW, sweep width 10 mT, modulation 0.802 mT, sweep time 5.24 s and number of sweeps 20.

Intrinsic viscosity was measured at 35°C in 0.2 N KOH using viscosimetric micro-Ubbelohde tubes after solubilization of the samples (50–60 mg) in 2 ml KOH 1 N solution (Mestres & Rouau, 1997). All measurements were duplicated.

3. Results and discussion

3.1. ESR

The native cassava starch did not show any ESR signal. The ESR patterns of the cassava starch samples after UV or gamma radiation (Fig. 1) showed different shapes depending on water content and storage time after irradiation. They can present two main signals, AA$'$ and BB$'$ (Table 1), according to the notation of the signals already found in gamma-irradiated starches (Raffi & Agnel, 1983), or a main BB$'$ signal; these two signals are singlets. Merlin and Fouassier (1981) also noted the presence of triplet signals in the case of UV-irradiated potato starch. The intensity of the ESR signal of the UV-irradiated starch decreased with time, with transformation of an AA$'$/BB$'$ shape to a BB$'$ shape. The kinetic constant (k_{III}) of disappearance of the BB$'$ signal was calculated as proposed by Raffi and Agnel (1983): it was $24 \times 10^{-3} \pm 8 \times 10^{-3}$ day^{-1} for UV-irradiated samples and $30 \times 10^{-3} \pm 6 \times 10^{-3}$ day^{-1} for gamma-irradiated ones. This was very close to the value ($34 \times 10^{-3} \pm 11 \times 10^{-3}$ day^{-1}) previously measured for the BB$'$ pattern of various gamma-irradiated starches (Raffi & Agnel, 1983), proving that UV and gamma irradiations of starch lead to the formation of the same final radicals.

After UV irradiation, the amylopectin ESR pattern presented an AA$'$/BB$'$ shape, with a predominant AA$'$ signal. The dextrin presented an ESR pattern equivalent to the AA$'$ signal (Table 1) observed for gamma irradiated maltotriose or crystalline dextrins (Raffi & Agnel, 1983; Thiéry, Thiéry, Agnel & Vincent, 1990) and for starch just after gamma irradiation (Raffi et al., 1985).

In the dry state and especially for irradiated crystalline glucose oligomers, the AA$'$ signal is always predominant, hiding the BB$'$ (Raffi et al., 1985). For such products, the BB$'$ becomes predominant after several months of storage or after heating at 70–80°C for several hours. The intensity of free radicals is, in fact, dependent on starch water content, irradiation dose, temperature and time of

Table 1
Characteristics of the AA$'$ and BB$'$ lines induced by UV and gamma irradiation

	Irradiation	AA$'$ line		BB$'$ line	
		g factor	Peak to peak width (mT)	*g* factor	Peak to peak width (mT)
Cassava starch	UV	2.0050	2.33	2.0051	0.90
	Gamma	2.0050	2.37	2.0056	0.84
Other starches	Gamma[a]	2.0048	2.61	2.0057	0.87
	UV	2.0056	2.03	2.0060	0.79
Amylopectin					
	Gamma[b]	2.0050	2.53	2.0050	0.84
Dextrin	UV	2.0053	1.97	–	–
Maltotriose	Gamma[b]	2.0042	2.65	2.0050	0.90

[a] Raffi and Agnel (1983).
[b] Raffi et al. (1985).

Table 2
Intrinsic viscosity (mean values of duplicates) (ml/g) of cassava starch samples

	Non-acidified samples	Acidified samples
Non-irradiated	177	139
UV irradiated	126	97
Gamma irradiated	131	108
Standard deviation of the residual	6	

storage (Raffi & Agnel, 1983). The radicals are destroyed only by reaction with water molecules leading to an exponential decrease of the radicals with time; the kinetic constant is independent of the water content in the crystalline parts and proportional to the water content (BB' line) or its square (AA' line) in the amorphous parts. This explains why the AA' lines disappear more quickly than the BB' ones in starch samples, which are partly amorphous. In addition, after irradiation, dextrin and amylopectin water contents (4–6%) were lower than starch water content (8–10%); this could also play a part in explaining the predominance of the AA' signal in the dextrin and amylopectin samples and the predominance of the BB' signal in the starch samples.

ESR shows radical formation in UV-irradiated samples. Final radicals were the same as those observed after gamma irradiation. The BB' pattern was predominant for the starch samples and the AA' pattern for the amylopectin and dextrin. Using both powder studies on starches and glucose oligomer (Raffi et al., 1985) and spin trapping studies on the same product (Thiéry et al., 1990), the AA' signal has been tentatively assigned to an $R \cdot OR$ radical at C_1 of anhydroglucose which turns into an $ROO\cdot$ radical after the breaking of the glycosidic bond and contact with atmospheric oxygen. This $ROO\cdot$ radical should then give a BB' signal (Thiéry et al., 1990). Similarly Merlin and Fouassier (1981) attributed the ESR signal of UV-irradiated potato starches to chain scission and hydrogen abstraction.

3.2. Viscosimetry

UV and gamma irradiation both significantly decreased starch intrinsic viscosity (Table 2). The depolymerization effect of UV and gamma irradiation was similar whether starch was acidified or not. In addition, the acidification also induced a starch depolymerization as already observed by Michel, Raffi and Saint-Lèbe (1980).

We can thus conclude that UV irradiation of starch results to similar phenomena than gamma irradiation i.e. formation of the same free radicals and similar extent of depolymerization.

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