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Influence of microwave parameters and water activity on radical generation in rice starch

Daming Fan [b], Yixiao Liu [b], Bo Hu [b], Lufen Lin [b], Luelue Huang [c], Liyun Wang [b], Jianxin Zhao [b], Hao Zhang [b], Wei Chen [a,b,*]

[a] State Key Laboratory of Food Science and Technology, Jiangnan University, Wuxi 214122, China
[b] School of Food Science and Technology, Jiangnan University, Wuxi 214122, China
[c] School of Applied Chemistry and Biological Technology, Shenzhen Polytechnic, 518055, China

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ABSTRACT

Radical generation in rice starch under microwave treatment as well as the related chemical bond changes were investigated by electron paramagnetic resonance (EPR) and Raman spectroscopy. Samples with water activity of 0.4 and 0.7 have been treated and analyzed. It was found that microwave power level and water content could influence the amount of radicals along with the radical components and their contribution. Raman spectra showed corresponding changes in vibrational features of chemical bonds. During storage the signal intensity started to drop after a short period of increase. Rice starch radicals were relatively stable and could exist a long time in room temperature. Through signal simulation, 3 main components were separated from the original spectra and the evolving process was investigated. The main component was the radical located on C1 position in the glucose ring.

1. Introduction

Microwave is used as heating agent for decades in both household and scientific purposes. It has the merit of fast heating and easy to operate, thus becoming more and more popular in food process and widely applied in food thawing, drying, baking, enzyme deactivation and sterilization, etc. Lots of researchers had described in their studies that certain degree of energy would start the accumulation of radicals in starch. Furthermore, both the intensity of energy and duration of treatment can affect the quantity of radicals. Thermal treatment (Ciesielski, Achremowicz, Tomasik, Baczkowicz, & Korus, 1997; Ciesielski & Tomasik, 1996, 1998; Ciesielski, Tomasik, & Baczkowicz, 1998; Dyrek et al., 2007; Labanowska, Weselucha-Birczynska, Kurdziel, & Puch, 2013; Labanowska, Weselucha-Birczynska, Kurdziel, & Sepiolo, 2013), X-ray (Tomasik et al., 2008), γ-ray (Adamić, 1968; Bertolini, Mestres, Colonna, & Raffi, 2001), UV irradiation (Kameya, Nakamura, Ukai, & Shimoyama, 2011) as well as microwave irradiation (Dyrek et al., 2007) could induce radicals in starch from different origins.

Radical is a product of chemical reactions and a middle agent in reactions. For example, thermal degradation in starch leads to the production of radicals and intramolecular or intermolecular dehydration, hence producing furan, aldehyde, ketones and CO_2, CO, H_2O, etc. (Liu, 2011). It also has been reported that long-term radicals in polysaccharides can be considered as traps for free electrons, neutralizing in this way the dangerous reactive species (Labanowska, Weselucha-Birczynska, Kurdziel, & Puch, 2013). Therefore, deciphering starch radical generation process and the influence of different factors during process may be essential for food safety and quality control.

So far there have been several researches on the aspect of microwave impact on starch, e.g., granule properties, gelatinization and swelling properties, thermal dynamics and dielectric properties of the starch, etc. Evidence showed microwave irradiation brought inevitable changes to starch granules and even to their molecule structures. However, the field of microwave induced starch radicals has merely been explored. The present discussions were about the identification of radicals and the determination of the attenuation characteristics during storage. The radical generation progress was yet to be investigated, with regard to the changes of microwave power, duration of treatment and properties of starch.

This study was focused on the forming of radicals in rice starch with low water activity, as well as the corresponding changes in

* Corresponding author at: State Key Laboratory of Food Science and Technology, Jiangnan University, Wuxi 214122, China.
E-mail address: chenwei66@jiangnan.edu.cn (W. Chen).

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chemical bonds during microwave treatment. The microwave frequency used in this study was 2450 MHz which is commonly applied in domestic and industrial ovens. In our present work, the electron paramagnetic resonance (EPR) spectroscopy was used to determine the nature of radicals, their content and relative quantities. Information collected by Raman spectroscopy was used to analyze the bond changes occurring in carbohydrate polymers and confirm the corresponding radical evolution process. The influence of microwave parameters and water activities of starch on radicals and chemical bond will be discussed.

2. Materials and methods

2.1. Materials

Native rice starch purchased from Golden Agriculture biotech Co., Ltd., was used for the investigation. The purity of the starch was up to 95%. The amylose content of the starch was equal to 30.8% (dry mass) determined according to GB/T 15683-2008 iodine colorimetry. AACC Method 46-10 (Improved Kjeldahl method) was applied to determine the protein content of the starch, which was equal to 0.37% (dry mass).

To adjust the water content in the starch sample, two kinds of saturated solution (K_2CO_3 and K_2SO_4) were prepared and kept in two separate air-tight containers each with a porous china plate in the middle of the container. The saturated solution was kept underneath the plate. Beakers containing starch were kept on the plate for 2 weeks to balance the water content. The water activity of the starch detected by a FA-st lab water activity meter (GBX, Romans sur Isere, France) was about 0.4 (K_2CO_3 solution) and 0.7 (K_2SO_4 solution).

For EPR measurements, 60 mg of each starch samples were put in a special glass tube (inner diameter = 3 mm) with a plastic lid, which showed no signal during EPR measurements.

For determination of LF-NMR, 0.8 g of each starch samples were put in a glass tube (inner diameter = 15 mm). The temperature of the samples was adjusted to 35 °C before LF-NMR measurements.

2.2. Methods

2.2.1. Irradiation with microwaves

2.0 g of starch sample was uniformly distributed in a glass Petri dish (inner diameter = 6 mm) without its lid. The average thickness of the sample in each dish was 1.5 ± 0.1 mm. 5 Petri dishes containing starch sample were placed in the center of the microwave chamber to form a circle. The samples were irradiated with microwave at 800 W (80 W/g) or 1600 W (160 W/g) for 1–5 min using a custom made microwave station (XO-SM400 Xian Ou, China) at 2450 MHz frequency. After microwave irradiation, samples in 5 Petri dishes were mixed for later analysis. A fiber optic temperature sensor (Fiso, Canada) was used to detect the temperature of the sample. The temperature sensor was connected to a computer station which could display the temperature in real time. Each experiment was conducted three times.

2.2.2. EPR measurements

The EPR measurements of the starch sample before and after microwave treatment were performed with a Bruker EMX-8/2.7 B spectrometer (Karlsruhe, Germany) operating in X band (9.85 GHz) with the modulation frequency of 100 kHz. The EPR spectra were recorded at room temperature with modulation amplitude = 0.6 mT, microwave power = 20 mW and receiver gain = 3.17 * 10^5.

g value was measured using a standard mark (Bruker, g_s = 1.9800). $H_{s(x)}$ is a value of magnetic resonance field for the standard and the sample, respectively. g_x could be calculated using the formula below:

$$h\nu = g_s\beta H_s = g_x\beta H_x$$

$$g_x = g_s H_s / H_x$$

In the equations, h stands for Planck constant ($h = 6.626 \times 10^{-34}$ J s); β stands for Bohr magneton; ν stands for the frequency of the microwave added perpendicular to the magnetic field.

Peak to peak height of each spectra was calculated as the signal intensity. The EPR acquisition and processing was conducted by WinEPR (Bruker, Germany). The signal simulations were conducted using the program EasySpin 4.5.3 (Stoll, 2013; Stoll & Britt, 2009; Stoll & Schweiger, 2006, 2007) running on Matlab R2013a (The MathWorks, Inc., US). The parameters determined by EasySpin had an accuracy of ±0.0005 for g value and ±0.1 mT for hyperfine splitting constant A.

2.2.3. Raman spectra

All the Raman spectra were recorded with a Multi-purpose Laser Raman System Raman Tracer-200-WF-B (Opto Trace Technologies, Inc., US). Samples were excited with 785 nm laser line. Registrations were repeated three times for each sample. Layer thickness and spot laser size were the same for all samples.

2.2.4. LF-NMR relaxometry

The low-field nuclear magnetic resonance (LF-NMR) relaxation measurements were performed on a NM20 NMR analyzer (Niumag, China) with a magnetic field strength of 0.28 T corresponding to a resonance frequency for protons of 21 MHz.

The temperature of the NMR instrument was set to 35 °C. The transverse relaxation time constant, T_2, was measured using the sequence based on Carr–Purcell–Meiboom–Gill (CPMG) (Carr & Purcell, 1954; Meiboom & Gill, 2004). The T_2 measurements were performed with a τ value of 50 μs (time between 90° and 180° pulses). The 90° and 180° pulses were 10 μs and 20 μs, respectively. Data from 500 echoes were acquired; they were obtained as a 32 scan repetition, with 1 dummy scan in front to ensure that a spin system is in a steady state before data are collected.

2.2.5. Infrared thermal imaging

After each period of microwave irradiation, the samples were immediately removed from the cavity and photographed using an infrared thermal camera (IRI4010, Northants NN4 9BG, UK). The photographs were then processed using the software (IRISYS 4000 Series Imager).

2.2.6. Statistical analysis

Spectra analysis and statistic calculations were performed using OriginPro 8 SR1 (OriginLab Corporation, USA) and Microsoft® Office Excel 2007 software. Raman spectra were analyzed using OMNIC v6.2 software (Thermo Nicolet, US).

3. Results and discussion

3.1. Radical generation during microwave irradiation

3.1.1. Identification

The native rice starch did not show an obvious EPR signal (Fig. 1a – insert). EPR signals of starch after microwave treatment were presented in Fig. 1. Different settings of parameters resulted in similar g factors of EPR signals. The signal shapes detected in our