



# Effect of nonthermal plasma on physico-chemical, amino acid composition, pasting and protein characteristics of short and long grain rice flour



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## ABSTRACT

Nonthermal plasma (NTP) is a novel technology with potential applications in food property and functionality modification. In this study, short and long grain rice flours were exposed to different plasma intensities and resulting ozone concentrations, and their physicochemical, amino acid composition, X-ray diffraction, pasting properties and protein profile were evaluated. The  $L^*$ ,  $b^*$ , blue value,  $\lambda_{\max}$ , pH, transmittance, swelling power, and syneresis of both rice types increased with NTP treatment while  $a^*$  decreased. X-ray diffraction revealed a decrease in crystallinity with NTP treatment. Long grain rice showed higher peak viscosity, breakdown viscosity and lower pasting temperature as compared to short grain rice due to higher amylose content. Glutamic acid, asparagine, serine histidine, threonine,  $\gamma$ -aminobutyric acid, tryptophan, isoleucine, phenylalanine and proline content increased with NTP treatment in both rice types. SDS page analysis did not reveal any effect of NTP treatment on banding pattern of total protein of both rice types.

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## 1. Introduction

Plasma, often referred to as the fourth state of matter, is an ensemble of charged ions, electrons, neutral gaseous atoms and molecules with emission of photons. The developments in plasma physics and innovative designs of various plasma sources have enabled the induction of plasma at atmospheric pressure conditions in a 'cold' or ambient temperature regime, referred to as "nonthermal plasma". Nonthermal plasma (NTP) has recently drawn considerable attention of the food research community for sterilization and decontamination of foods and food processing surfaces. The applications of NTP in food processing were recently reviewed (Misra, Han, Tiwari, Bourke, & Cullen, 2014; Misra, Tiwari, Raghavarao, & Cullen, 2011). NTP in air and gaseous mixtures containing oxygen as a component yield ozone as one of the major species with a long half-life. Ozone ( $O_3$ ) is widely considered as a powerful oxidant and disinfectant in water treatment, food processing, grain preservation, pest and mycotoxin treatment in warehouses and various other environmental applications (Dhillon, Wiesenborn, Dhillon, & Wolf-Hall, 2010; McDonough et al., 2011). Several pathogenic

and spoilage microorganisms are inactivated by liquid or gaseous application of ozone during processing of fruits and vegetables. Inactivation of wide range of microorganisms including bacteria, fungi, viruses, protozoa, and bacterial fungal spores by ozone treatment is well characterized (Cullen, Tiwari, O'Donnell, & Muthukumarappan, 2009). It has been certified as Generally Recognized as Safe (GRAS) for use in food processing.

Consumer demand for chemical free grains and concerns over development of resistance in pests against insecticides have attracted the attention of grain processors for the use of ozone as an insect pest fumigant. Excessive use of ozone may promote oxidative degradation of chemical constituents, discoloration and development of undesirable odors in grains. At molecular levels, ozone oxidizes the sulfhydryl group ( $-SH$ ) of amino acids and converts polyunsaturated fatty acids to peroxides in aqueous solutions, thereby influencing the nutritional and metabolic activity of grains (Güzel-Seydim, Bever, & Greene, 2004). Ozone treatment of rice starch was reported to enhance the swelling capacity with a reduced retrogradation tendency (An & King, 2009). Therefore, ozonated starch has commercial importance. Synthetic gaseous insecticides such as methyl bromide and phosphine are widely used for infestation control of stored grain. However due to human health hazards and environmental factors, mixing of any synthetic

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insecticide in stored grain has been banned in several countries. Therefore, interest in ozone as a grain fumigant has increased in recent years. This potential consequently motivates the study of the effects of ozone in particular, and NTP in general, on grain constituents. It may be noted that a dielectric barrier discharge (DBD) set-up, as is used in this study is also a very efficient source of ozone (Moiseev et al., 2014). Furthermore, the modification of food properties under the influence of ozone and NTP could also have far more interesting consequences and potential applications in cereal products.

The electronics and polymer processing sector have employed NTP for structure modification over past few decades. NTP as a food properties and functionality modification technology is very young within the field food science, with only few recent studies. In a recent study, Misra et al. (2015) demonstrated that the secondary structure of gluten becomes more stable in atmospheric pressure cold plasma (in air) treated weak wheat flour, and corresponding changes in dough rheology also appear. An increase in water and fat binding capacities of protein rich pea flour following cold plasma treatments in air has been reported by Bußler, Steins, Ehlbeck, and Schlüter (2015). An increase in the hydrophilicity, increase in water absorption rate and decrease in cooking time of basmati rice, following radio-frequency NTP treatment have been reported recently (Thirumdas, Deshmukh, & Annapure, 2015). The effective modification of starch on exposure to oxygen glow plasma, and the multi-scale characterization of the oxidized starches have recently been reported (Zhang et al., 2013).

It is to be noted that ozone is only one of many active species of importance in atmospheric air NTP. Plasma chemistry is highly complex with physical and chemical processes occurring at drastically varying time and length scales. In fact, plasma chemistry in air is found to involve over 75 species and 500 different reactions (Gordillo-Vázquez, 2008). The NTP source used in this study has been demonstrated as an effective technology against a range of micro-organisms including bacteria, fungi, biofilms (Misra, Patil, Moiseev, Bourke, Mosnier, Keener, & Cullen, 2014; Ziuzina, Boehm, Patil, Cullen, & Bourke, 2015) spores (Patil et al., 2014), and pesticide residues (Misra, 2015; Misra, Pankaj, Walsh, O'Regan, Bourke, & Cullen, 2014). In light of this, there is also a considerable potential for inactivation of fungal and bacterial species in grains and flours. However, our core interest in the present study lies in leveraging the ozone generated from the NTP source for property modification. To the best of our knowledge there are no studies exploring the possible effects of atmospheric pressure NTP from a DBD on the properties of rice flour. Therefore, this work aims at exploring the possibility of using NTP as a means to modify the properties of rice flour. The objective of this work was to evaluate the effect of NTP treatment on physico-chemical, amino acid content, pasting properties, X-ray diffraction pattern and protein characteristics of short and long grain rice flours.

## 2. Materials and methods

### 2.1. Materials

Samples of short and long grain rice flours were obtained from Teagasc Food Research Centre, Dublin, Ireland. The samples were divided into 250 g unit portions for further experiments.

### 2.2. Ozone treatments

The NTP source comprised of a Dielectric Barrier Discharge (DBD) powered from a step-up transformer (Phenix Technologies, Inc., USA). The input voltage to the step-up transformer was regulated using a variable auto-transformer. The DBD unit includes two aluminium electrodes of circular geometry (outer diameter = 158 mm), resting over a perspex dielectric layer (10 mm thick) for driving electrode. The rice flour samples (250 ± 10 g) were placed in commercial 270 µm thick polyethylene terephthalate trays (150 mm × 150 mm × 35 mm), sealed

with a high barrier (50 µm thickness) film. The high barrier nature of the film allowed maximum retention of the reactive species, including ozone during a storage period of at least 24 h post-discharge. The atmospheric air condition at the time of treatment was 45 ± 1% relative humidity (RH) and 20 ± 2 °C, measured using a humidity-temperature probe connected to a data logger (Testo 176 T2, Testo Ltd., UK). Treatments were done in duplicates. Two discrete voltages of 60 and 70 kV were applied across the electrodes for 5 and 10 min.

### 2.2.1. Ozone concentration

The ozone concentration inside the package was measured immediately after post-treatments using short-term chemical reaction based ozone detection tubes (Product No. 18 M, Gastec Corp, Kanagawa, Japan) with ± 10% accuracy. Gas sampling was conducted using a hand-held pump (Gastec, Japan) and a needle with septum placed at the point of sampling. The tubes were pre-calibrated for specific volume of the gas and for this study 10 mL volume of the package gas was sampled.

### 2.3. Hunter color characteristics

$L^*$  (lightness),  $a^*$  (redness–greenness) and  $b^*$  (yellowness–blueness) color values of the rice flour were recorded in triplicates using an ultra-scan VIS Hunter Lab (Hunter Associates Laboratory Inc., Reston, VA, USA). Whiteness was determined by using:

$$\text{Whiteness} = 100 - \left[ (100 - L^*)^2 + a^{*2} + b^{*2} \right]^{1/2}$$

### 2.4. Blue value, $\lambda_{\text{max}}$ and pH

Rice flour (100 mg) was suspended in 1.0 mL of ethanol and 9.0 mL of 1.0 M NaOH, followed by heating in a boiling water bath for 10 min with intermittent shaking to completely dissolve the starch. The suspension pH was adjusted to 6.5 with 1.0 M HCl, and it was diluted to 100 mL with distilled water. Diluted solution (5 mL) was mixed with 1 mL of 0.2% iodine solution, and the final volume was raised to 100 mL with distilled water. The mixture was kept at room temperature for 15 min, and maximum absorbance spectra from 450 to 800 nm were scanned with a spectrophotometer (Lambda Bio 35, Perkin Elmer, Norwalk, CT, U.S.A.) to determine  $\lambda_{\text{max}}$ . Blue value was calculated with the absorbance measured at 680 nm, according to the following equation:

$$\text{BV} = 4 \times A_{680}/C.$$

The pH of rice suspensions was determined using a pH meter (Mettler Toledo). About 1 g (dry basis, d.b.) of sample was dissolved in about 10 mL of water for 10 min and then the pH was measured. Subsequently, the slurry was heated for 10 min at 80 °C, then cooled and the pH noted.

### 2.5. Transmittance

Transmittance of rice flour suspension was measured using the method described by Sodhi and Singh (2003) with a slight modification. A 2% aqueous suspension of both types of rice flours was heated in a boiling water bath for 1 h with constant stirring. The suspension was cooled to room temperature as quickly as possible, and then stored for 5 days at 4 °C in a refrigerator. Transmittance was determined after every 24 h by measuring absorbance at 640 nm against a blank using spectrophotometer (PerkinElmer Instrument, Lambda 25, UV/VIS, spectroscope).

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