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Plasma modification of starch

Fan Zhu

School of Chemical Sciences, University of Auckland, Private Bag 92019, Auckland 1142, New Zealand

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A B S T R A C T

Plasma is a medium of unbound negative and positive particles with the overall electrical charge being roughly zero. Non-thermal plasma processing is an emerging green technology with great potential to improve the quality and microbial safety of various food materials. Starch is a major component of many food products and is an important ingredient for food and other industries. There has been increasing interest in utilizing plasma to modify the functionalities of starch through interactions with reactive species. This mini-review summarises the impact of plasma on composition, chemical and granular structures, physicochemical properties, and uses of starch. Structure-function relationships of starch components as affected by plasma modifications are discussed. Effect of plasma on the properties of wheat flour, which is a typical example of starch based complex food systems, is also reviewed. Future research directions on how to better utilise plasma to improve the functionalities of starch are suggested.

Contents

1. Introduction

Plasma processing is a physical treatment that induces chemical changes. Non-thermal plasma is suitable for processing thermo labile materials without generating industrial waste, making it a novel green technology. It has great potential to be used in food and other industries (Mir, Shah, & Mir, 2016; Sarangapani et al., 2016; Scholtz, Pazlarova, Souskova, Khun, & Julak, 2015; Thirumdas, Sarangapani, & Annapure, 2015). A notable application of plasma is the disinfection and sterilization to ensure microbial

E-mail address: fzhu5@yahoo.com

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safety for food and medical purposes (Moreau, Orange, & Feuilloley, 2008; Scholtz et al., 2015). Compared with some traditional disinfecting methods, the plasma processing has the advantage of little affecting quality attributes of food material (Scholtz et al., 2015). Plasma based technology is now commercially available for disinfecting (Scholtz et al., 2015).

Apart from ensuring microbial safety, non-thermal plasma may influence other quality attributes of food material, which has been reviewed recently (Mir et al., 2016; Thirumdas et al., 2015). For example, a low-pressure plasma decreased the cooking time of rice while improving the eating quality; a cold argon plasma decreased the enzyme activity of peroxidase and polyphenoloxidase in a model food system; a microwave processed air plasma better retained the color of freshly cut kiwifruit; a surface discharge reactor air plasma increased the germination rate of wheat seeds; a cold atmospheric pressure argon plasma enhanced the anthocyanin concentration in sour cherry; a cold atmospheric air plasma improved the dough strength of wheat flour; and a cold oxygen plasma decreased the emulsifying and foaming capacity of whey protein isolate (Mir et al., 2016; Thirumdas et al., 2015). The above mentioned effects are due to the interactions of food components with the reactive species in the plasma. Therefore, understanding the plasma-food component interactions provides a basis for its further development of this green food processing technique.

Starch is a major component of many food products. It is widely used in diverse food and non-food industries. Starch is consisted of amylose and amylopectin molecules, which are naturally assembled in granular forms with the size ranging from 1 to 100 μm (Pérez & Bertoft, 2010). Native starch has limited functionalities and is commonly modified to expand the functional range (BeMiller & Whistler, 2009). There has been a trend of using green technology to modify the starches without generating any waste products, and plasma treatment falls into this category (Chaiwat et al., 2016). However, there is a lack of systematic knowledge on the effect of plasma processing on starch properties.

This mini-review firstly briefs the plasma generation and chemistry to provide basic background information. Then, the impacts of plasma processing on the chemical composition, chemical structure, granular and crystalline structure, physicochemical properties, and applications of starch are summarised. Structure-function relationships of starch components affected by plasma processing are discussed. The influence of plasma treatment on the functional properties of wheat flour (a typical starch based food system) is also reviewed, with an aim to illustrate the contributions from the changes of non-starch components (e.g., protein) to the overall modification of complex food systems. Lastly, research gaps are pointed out to better understand the plasma-starch interactions. The basics of starch have been well reviewed previously and are, therefore, not covered here (BeMiller & Whistler, 2009; Pérez & Bertoft, 2010). This review may stimulate further interest in utilising plasma for food ingredient processing to create novel functionalities in a green way.

2. Plasma generation

William Crookes firstly identified and described the plasma as "radiant matter" in a Crookes tube in 1879 (Crookes, 1879). The term "plasma" was introduced by Irving Langmuir in the middle 1920s (Mott-Smith, 1971). Plasma, together with gas, liquid, and solid, are the four basic states of matter. It is a medium of unbound negative and positive particles with the overall electrical charge being roughly zero (Moreau et al., 2008; Scholtz et al., 2015). The particles of plasma include electrons, photons, negative and positive ions, free radicals, atoms, and non-excited or excited molecules (Moreau et al., 2008). There are two types of plasma, namely thermal and non-thermal, based on the conditions in which they are generated. The former is generated at high pressure ($\geq 10^5$ Pa) with high power input (up to 50 MW). The temperature can be very high (up to 2×10^4 K) (Moreau et al., 2008). In contrast, non-thermal plasmas are produced at lower pressures with much less power input. The non-thermal plasmas are of interest for food processing (Thirumdas et al., 2015).

Plasma can be produced by the use of energy in various forms such as thermal, magnetic or electric fields, and microwave or radio frequencies (Thirumdas et al., 2015). The treatment increases the thermodynamic energy of the electrons and the collisions of particles, resulting in the formation of plasma (Thirumdas et al., 2015). A range of techniques have been used to obtain non-thermal plasmas. They include corona discharge, dielectric barrier discharge, microwave discharge, gliding arc, and plasma jet (Scholtz et al., 2015) (Supplementary Fig. 1). These discharges differ in the instrumental design and settings, and may have different impact on the food quality. Various plasma processing systems have been set up (e.g., Supplementary Fig. 2). Currently, plasma jet is the mostly used in practical applications because of the easy maintenance and simple design (Scholtz et al., 2015). A range of gas such as helium, nitrogen, argon, oxygen, hydrogen, air, and their mixtures, have been used to generate the plasmas. The majority of reactive species in plasmas from common sources are vibrationally and electronically excited nitrogen N_2 and oxygen O_2, reactive nitrogen species (e.g., atomic nitrogen N, nitric oxide $NO^{\cdot}$, excited nitrogen $N_2(A)$), active forms of oxygen molecules and atoms (reactive oxygen species) (e.g., ozone O_3, superoxide anion O_2^-, singlet oxygen $^1O_2$, and atomic oxygen O), and OH^- anion, H_2O^+, $OH^{\cdot}$ radical or hydrogen peroxide (H_2O_2) if moisture is present (Scholtz et al., 2015). There are other agents associated with plasmas such as UV radiation, heat, and electric field (Guo, Huang, & Wang, 2015). All these plasma components interact with food components and microbes in food products, altering food properties and ensuring food safety (Mir et al., 2016). It should be noted that the composition of these reactive agents differs greatly among various types of plasma and experimental conditions. The molecular mechanisms for the interactions of these agents with food biomolecules remain to be better studied (Guo et al., 2015; Mir et al., 2016; Scholtz et al., 2015). All the reactive species immediately disappear when the power is off (Mir et al., 2016). Therefore, plasma processing is ecologically and environmentally green.

3. Effect of plasma treatment on starch composition

The chemical composition of starch can be greatly affected by plasma treatments (Supplementary Table 1). The plasma treatment decreased the moisture content of starch (Chaiwat et al., 2016; Lii, Liao, Stobinski, & Tomasik, 2002a). For example, a low-pressure argon plasma (180 min) reduced the moisture content of cassava starch from 13.5 to 6.2% (Chaiwat et al., 2016). This is probably due to the interactions of the reactive species with the water and starch molecules surrounding the water molecules. The interactions resulted in the release of bound water molecules from the starch, and the released water was subsequently removed by the vacuum (Chaiwat et al., 2016). Amylose is a major component of starch. Plasma treatment reduced the amylose content of starch (Thirumdas, Trimukhe, Deshmukh, & Annapure, 2017). For example, a cold air plasma (60 W) decreased the apparent amylose content (quantified by iodine binding-spectrophotometry based method) of rice starch from 30 to 23% (Thirumdas et al., 2017). This may be due to the extensive degradation of the amylose as a result of interactions with the reactive species. The decreasing molecular size of starch by plasma treatment is described in the following Section 4.2. Plasma treatment reduced the pH of starch solution (Lii, Liao, Stobinski, and Tomasik, 2002b; Lii et al., 2002a;