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Structural characteristics and rheological properties of plasma-treated starch

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ABSTRACT

Corn starch was treated by a dielectric barrier discharge plasma, and the changes in the granule morphology, crystalline structure, and molecular structure, as well as the rheological properties, were investigated using diverse techniques. Dielectric barrier discharge plasma could change not only the granule surface but also the internal structures of the starch granule through its pinholes. Specifically, after the plasma treatment, as the pinhole diameter increased, the relative degree of crystallinity decreased, accompanied by molecular chain oxidation, i.e., the generation of carboxyl groups, and degradation, i.e., molecular weight reduction. Therefore, the rheological behavior changed from pseudo-plastic to Newtonian with a decrease in the paste viscosity. The results indicate that dielectric barrier plasma could be used to produce modified starch with low viscosity at a high concentration for food and non-food applications.

Industrial relevance: As an eco-friendly and non-thermal physical technique, dielectric barrier discharge plasma has attracted great attention in polymer modification due to the interest in reducing generated wastes during modification and producing polymer products with high safety. Starch is traditionally a main material for foods and has been widely used in food and non-food industries. For improving the properties of starch and thus widening its industrial applications using a specific technique, it is indispensible to understand how the technique affects starch's structure and property. The present work revealed that not only was the surface of starch granules altered by the dielectric barrier discharge plasma but also the internal structure was affected, since the pinholes promoted the penetration of the plasma into granule interior. In particular, along with a reduced degree of crystallinity, molecular chain oxidation and degradation occurred, as confirmed by the generation of carboxyl groups and the molecular weight reduction. Then, the rheological behavior of starch paste changed from pseudo-plastic to non-Newtonian, together with a decreased paste viscosity. These results have demonstrated that dielectric barrier discharge plasma could be used as a new physical method to modulate the structure and rheological properties of starch, for the production of starchy food products with relatively low viscosity at a high concentration.

1. Introduction

Starch is an important food ingredient and has been widely used in different industrial fields (Juansang, Puttanlek, Rungsardthong, Puncha-arnon, & Uttapap, 2012; Tan, Zhang, Chen, Li, Li, & Xie, 2015; Zhang, Li, Liu, Xie, & Chen, 2013). Starch typically exists as semi-crystalline granules and is a mixture of two polymers, i.e., amylose, which is a linear chain of α-D-glucose units linked by α-1,4-glycosidic bonds, and highly branched amylopectin in which the α-D-glucose units are linked via α-1,4- and α-1,6-glycosidic bonds (Jiang, Gao, Li, & Zhang, 2011; Liu, Halley, & Gilbert, 2010; Zhang et al., 2015b; Zhang, Xiong, Li, Li, Xie, & Chen, 2014a). When heated in water, starch granules with molecular orders (crystallites) could be gelatinized to form starch paste, which plays a key role in the production of food products with a certain viscosity and consistent properties (Zhang, Chen, Li, Li, & Zhang, 2015a; Zhang, Zhao, Li, Li, Xie, & Chen, 2014b). In particular, the rheological property of starch paste is an important feature (Singh, Kaur, & McCarthy, 2007; Wang, Chen, Li, Xie, Liu, & Yu, 2011) since it determines the delivering, mixing, blending, processing, and energy consumption during food production. In addition, the changes in quality and texture of starchy foods during processing and storage could be predicted by the rheological properties (Saha & Bhattacharya, 2010). However, the rheological characteristics of native starch, such as low shearing resistance, hinder the applications of starch in the food industry. To improve the rheological properties, physical, chemical and biological methods have been used to modify starch to make its rheological properties suitable for industrial applications (Bemiller, 1997; Singh et al., 2007).

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The properties of starch could be improved by regulating its structure using various techniques. Plasma is known as the fourth state of matter, which can be divided into high-temperature plasma and low-temperature plasma. Low-temperature plasma is widely used in the modifications of material surface, powder, amino acids and sugars due to advantages such as waste reduction and enhanced safety (Li, Friedman, Fridman, & Ji, 2014; Li, Kojtari, Friedman, Brooks, Fridman, & Ji, 2014; Lii, Liao, Stobinski, & Tomasik, 2002a, 2002b; Zou, Liu, & Eliasson, 2004). Currently, plasma is used less often in the research of starch modification. Starch molecules could be crosslinked and degraded by plasma (Lii et al., 2002a; Zhang et al., 2015a, 2014a; Zou et al., 2004), which provides the possibility of using plasma to change the structure and thus regulate the rheological properties of starch. Dielectric barrier discharge plasma is an important starch modification technique and can be used at atmospheric pressure, in contrast to glow plasma. Thus, high-density plasma could be obtained using dielectric barrier discharge with a low requirement of accessory equipment, making dielectric barrier discharge plasma suitable for industrial applications. However, the effects of dielectric barrier discharge plasma on the rheological behaviors and the structure of starch have not been elucidated.

Corn starch is the most widely used starch product and contains a multi-scale structure with amylose and amylopectin organized on different scales in the starch granule (Pikus, 2005; Tan, Flanagan, Halley, Whittaker, & Gidley, 2007). In contrast to other types of starch such as potato starch, corn starch has a unique pinhole structure, connecting the hilum to the granule surface (Chen, Yu, Simon, Petinakis, Dean, & Chen, 2009; Huber & BeMiller, 1997; Huber & BeMiller, 2000). The modification of powder by plasma is a typical gas–solid reaction system, and the efficiency of plasma modification could be influenced by the pinhole structure of starch, which may change the mode of interaction between the plasma and starch granules. In this study, the effects of the interior pinhole structure on the structure and rheological properties of starch were investigated.

Corn starch was chosen as the raw material and was treated by dielectric barrier discharge plasma. The microstructure, surface morphology, molecular structure and molecular weight distribution of plasma-modified starch, as well as the rheological properties, were investigated. The mechanism of the effects of dielectric barrier discharge plasma on the structure and rheological properties of starch was elucidated.

2. Materials and methods

2.1. Materials

Maize starch with an amylose/amylopectin ratio of 23/77 was purchased from Huanglong Food Industry Co., Ltd. (China). A MA35 moisture analyzer from Sartorius Stedim Biotech GmbH (Germany) was used to determine the moisture content (*MC*). Sodium cyanoborohydride (reagent grade, 95.0%), 8-aminopyrene-1,3,6-trisulfonic acid trisodium salt (APTS) (reagent grade, 96.0%), and hydrochloric acid (ACS reagent, 37%), were purchased from Sigma-Aldrich (USA). Dimethyl sulfoxide (DMSO, chromatographic grade) was purchased from Honeywell (USA).

2.2. Plasma treatment

The dielectric barrier discharge plasma apparatus consisted of a reaction cell (DBD-50), a power supplier (CTP-2000 K), and a voltage-regulator (Nanjing Suman Electronics Co., Ltd., China) (See Diagram 1). The diameter of the circular electrode was 3 cm, and the thicknesses of the upper quartz medium and under quartz medium were 2.5 mm and 1 mm, respectively. The distance between the two media was 3 mm (i.e., the discharge distance was 6.5 mm). Starch (dry basis) was uniformly dispersed on the under medium and then was placed in a reactor at 40% air humidity. Air was used as the gas source and samples were obtained after plasma treatment for 1 min, 5 min or 10 min. The plasma treatment conditions were as follows: the input voltage was 50 V, and the discharge was maintained at 1.5 A by adjusting the frequency of the input current, i.e., the input power was 75 W.

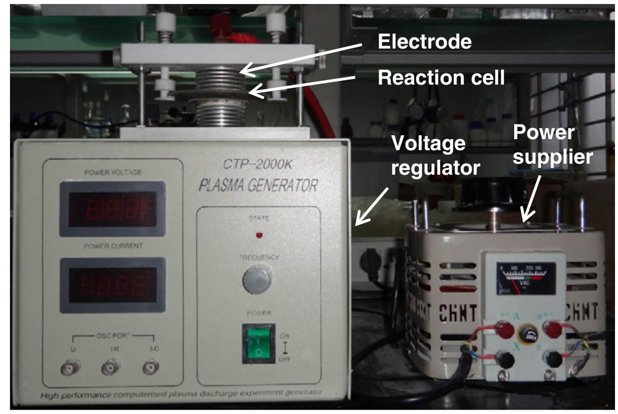

Diagram 1. Schematic diagram of dielectric barrier discharge (DBD) plasma system.

2.3. Confocal laser scanning microscopy (CLSM) 3D

Starch was stained using a method by Blennow (Blennow, Hansen, Schulz, Jørgensen, Donald, & Sanderson, 2003) and Pei (Chen et al., 2009) with proper modifications. Starch (10 mg) was mixed with 15 μL of 10 mM freshly prepared APTS acetic acid solution and 15 μL of 1 M aqueous solution of sodium cyanoborohydride, reacted at 30 °C for 15 h, and then washed 5 times with 1 mL of solvent. Then, the starch particles were suspended in 100 μL 50% (v/v) glycerol/water solution. A drop of starch suspension was transferred to the glass slide, covered with the coverslip, and then observed with a Digital Eclipse Cl Plus confocal microscope (Nikon, Japan). The internal structures of the starch granules before and after plasma treatment were observed. The lenses were HCX PL APO CS 40.0 × 1.25 OIL and HCX PL APO CS 100.0 × 1.40 OIL, and the laser emission wavelength of the Ar/Kr gas laser was 488 nm (20% capacity), accompanied by a receiving wavelength range of 500–600 nm and multi slices (thickness, 0.5 μm) of starch with an image resolution of 1024 × 1024 pixels. Pictures were superimposed using Imaris 6.1.5 software to construct a three-dimensional map of the starch granules.

2.4. Optical microscopy and polarized light microscopy (PLM)

Starch was uniformly dispersed in water, and a drop of starch suspension was placed on a glass slide and covered with a coverslip, which was then placed under an optical microscope. An Axioskop 40 Pol/40A Pol polarized light microscope (Zeiss, Germany) equipped with a Power Shot G5 camera (Canon, Japan) was used, and the magnification was set to 500 (50 × 10).

2.5. Fourier transform infrared (FTIR) spectroscopy

FTIR analysis was performed using our previous method (Pu, Chen, Li, Xie, Yu, & Li, 2011). KBr was ground and mixed with the dried starch samples at a percent of 1% w/w. The FTIR spectra were acquired using an infrared spectrometer (Bruker, Germany). The resolution was 4 cm^{-1} with 64 scans in a wavenumber range of 4000–400 cm^{-1}, and OPUS 6.5 software was used for spectrum baseline correction and normalization.

Attenuated total reflectance (ATR) FTIR was also used for evaluating the samples with the same infrared spectrometer. A certain amount of dried starch sample was placed on the ZnSe crystal and pressed. The wavenumber range was 4000–600 cm^{-1}, and the reflection spectrum was processed by OPUS 6.5 software. The Lorentz function was used for deconvolution of all of the spectra, and then the ratio ($R_{1047/1022}$)