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Effect of oxygen glow plasma on supramolecular and molecular structures of starch and related mechanism

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ABSTRACT

The effect of oxygen glow plasma (OGP) on the supramolecular structures (fractal, lamellar, and crystalline characteristics) and molecular characteristics (molecular weight, mean square radius of gyration) of potato and corn starches were investigated, and the related mechanism was explored. Compared with native corn starch, native potato starch possessed more compact scattering objects which however displayed a weaker resistance to OGP. For both starches, while the OGP treatment simultaneously influenced the crystalline and amorphous materials, there was a higher degree of destruction to the amorphous materials at the initial period. Both starches displayed a typical positive deviation from Porod's law. Interestingly, potato starch suffered a higher degree of destruction to both of its supramolecular and molecular characteristics (particularly, a higher degree of decrease in the molecular weight). This can be attributed to the large amount of inter-helical water molecules which could be induced by OGP, and to the fracture of the glycoside bonds in the solid starch granules which happened in a non-random way and close to the chain center.

1. Introduction

While starch is traditionally the main material for foods (Juansang, Puttanlek, Rungsardthong, Puncha-arnon, & Uttapap, 2012), it has gained much attention in recent year as a polymer resource for functional foods, and carriers for bioactive component (Pu et al., 2011). Starch is normally a mixture of two major D-glucan polymers, i.e., amylose, a mostly linear 1,4-α-D-glucan with a small number of long branches, and amylopectin, mainly 1,4-α-D-glucan but having a large number of 1,6-α linkages at the branch points (Jiang, Gao, Li, & Zhang, 2011; Liu, Halley, & Gilbert, 2010). Despite the potential of starch as mentioned above, the inherent characteristics of native starch, such as hydrophilicity and chain characteristics, may limit the application of starch-based products. In order to meet the requirements of application, various techniques of starch modification, including chemical, physical and enzymatic methods (Juansang et al., 2012; Zhang, Chen, Zhao, & Li, 2013), are widely used to improve the structures and properties of starch-based products.

Plasma, referred to as the 4th state of matter, is an important process to modify the chemical and physical properties of materials. Depending on the way of activation and the working power, plasma can possess either low or very high "temperature" and are correspondingly referred to as cold or hot plasma (Tendero, Tixier, Tristant, Desmaison, & Leprince, 2006). Glow plasma is a low-pressure cold plasma and has been extensively used in materials modification (Coburn, 1991; Liu, Vissokov, & Jang, 2002), which can produce high energy electrons and other highly active species at room temperature (Zou, Liu, & Eliasson, 2004). Thus, there are suggested applications of glow plasma for the modification of natural polymers such as starch. A previous study reported that glow plasma could induce the graft-polymerization of ethylene onto sweet potato and rice starches, while the homopolymerization of ethylene on the granules took place for cassava, potato, corn, and waxy corn starches (Lii, Liao, Stobinski, & Tomasik, 2002a). Furthermore, starch can be highly cross-linked by Argon glow plasma without the presence of conventional chemical agents, avoiding any environmental problems (Zou et al., 2004). However, it was also found that ammonia, hydrogen and oxygen glow plasmas could lead to depolymerization of starch polysaccharides and changes in the crystalline structure, and the extent of depolymerization was related to the nature of starch as well as the type of plasma used (Lii, Liao, Stobinski, & Tomasik, 2002b). Therefore, it is concluded that glow plasma can influence the supramolecular or molecular characteristics of starch.

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The supramolecular structure of starch mainly consists of the granular morphology, the nanostructure (fractal structure, and lamellar structure), and the crystalline structure, while the molecular structure is mainly related to the chain characteristics of starch molecules. The structure of native starch is organized in four length scales: the whole granular morphology (μm), the growth rings (~0.1 μm), the lamellar structure (8~9 nm), and the molecules (~0.1 nm) (Pikus, 2005). The mass fractal structure and the surface fractal structure of starch have been found using the small-angle X-ray scattering (SAXS) technique (Zhang, Li, Liu, Xie, & Chen, 2013). It is shown that the two kinds of starch polymers (amylose and amylopectin) form the amorphous and crystalline regions in starch granules (Oates, 1997). Two main types of crystalline structures have been shown by the X-ray diffraction (XRD) technique (Kim & Huber, 2010), i.e., the A-type crystalline structure of cereal starches such as wheat and rice starches, and the B-type crystalline structure of tuber, fruit and stem starches such as potato and banana starches. Additionally, the C-type crystalline structure which is actually a combination of both A- and B-type structures (Gernat, Tadosta, & Damaschun, 1990); Sarko & Wu, 1978), and the V-type crystalline structure were also detected by XRD (Buleon, Colonna, Planchot, & Ball, 1998). It is worth noting that the supramolecular structure, especially the crystalline structure, can affect the swell of starch granules in aqueous solutions and thus has a significant influence on the viscosity and rheological property of a suspension of starch granules, which is closely related to the application of starch in liquid foods. Moreover, the fractal structure, the crystalline structure (Zhang, Chen, et al., 2013), and the lengths of branches (Gidley et al., 1995) have an influence on the enzymatic resistance of starch, displaying a nutritional relevance. In addition, the molecular weight and the extent of branching also display an effect on the properties of the resulting products, such as starch-based food ingredients and bioactive component carriers. Therefore, the supramolecular and molecular structures play a key role in determining the properties and applications of starch. Nonetheless, there have been no studies on the mechanism regarding the effect of glow plasma, especially oxygen glow plasma (OGP), on the supramolecular and molecular characteristics of starch.

In this work, potato and corn starches were treated with OGP for different times, and the effect of OGP on the fractal characteristics, lamellar structure, crystalline structure, molecular weight, and mean square radius of gyration of these two starches were investigated and the related mechanism was explored. To the best of our knowledge, this is the first report regarding the detailed mechanism of the OGP effects on the structures of starch at different scale levels. The results from this study would form the basis for further investigations of the OGP-induced structural changes of starch and the related mechanism to facilitate the application of OGP to starch polymer modification and thus to widen the application of starch.

2. Materials and methods

2.1. Materials

Potato starch from Avebe (Netherlands) and corn starch from Huanglong Food Industry Co., Ltd. (China) were used in the experimental work. The moisture content of each sample was determined using a moisture analyzer (MA35, Sartorius Stedim Biotech GmbH, Germany).

2.2. Oxygen glow plasma (OGP) treatment

About 10 g of starch (dry basis) was loaded into the reactor chamber and treated with OGP for different time (30, 45, or 60 min). The OGP was realized by using an HPD-2400 plasma installation (Nanjing Suman Electronics Co., Ltd., China) with oxygen gas (2000 Pa) as the atmosphere, operated at 245 V and 1.1 A. The discharge distance applied in the present study was 10 mm and the moisture of all the samples was about 12% before the treatment. The native and modified samples treated for different times were referred to as Potato, Potato-30, Potato-45, and Potato-60 (Corn, Corn-30, Corn-45, and Corn-60).

2.3. Small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD)

SAXS measurements were performed according to our previously method (Zhang, Li, et al., 2013; Zhu, Li, Chen, & Li, 2012) with proper modification. An SAXSess system (Anton Paar, Austria), operated at 50 mA and 40 kV, using Cu Kα radiation with a wavelength of 0.1542 nm as the X-ray source, was used. Each sample was placed in a paste sample cell and was exposed at the incident X-ray monochromatic beam for 10 min. The data, recorded using an image plate, were collected by the IP Reader software program with the Perkin–Elmer Storage Phosphor System. The samples were prepared by premixing the starch granules with added water in glass vials. The vials were sealed and kept at 20 °C for 24 h before the SAXS measurements to achieve homogeneous samples. The total moisture content of each sample was 60%. All data were normalized, and the background intensity and smeared intensity were removed using the SAXSquant 3.0 software program for further analysis. The data in the region of $5 < q < 25$ nm^{-1} were used as the WAXD results. The average repeat distance of the amorphous and crystalline lamellae (semi-crystalline lamellae) of each sample was calculated by:

$$d = 2\pi/q \tag{1}$$

where d (nm) is the lamellar repeat distance and q (nm^{-1}) is the scalar of scattering vector. The relationship between q and θ can be calculated by:

$$q = (4\pi \sin\theta)/\lambda \tag{2}$$

where λ (nm) is the wavelength of the X-ray source (Suzuki, Chiha, & Yano, 1997).

Fractal geometry has been used as a natural description for disordered objects possessing dilation symmetry, meaning that they look geometrically self-similar under transformation of scale such as changing the magnification of a microscope (Schaefer, 1989). In other words, the structure of the object is independent of the characteristic length scale of observation (Teixeira, 1988), which can be seen as a middle ground between geometrical order and geometrical chaos (Martin & Hurd, 1987). The fractal structure is normally characterized by the fractal dimension D, and SAXS appears to be the most appropriate technique for the determination of D (Teixeira, 1988), which is related to the scattering power-law equation:

$$I \sim q^{-a} \tag{3}$$

where I is the SAXS intensity and α is an exponent which can be used to calculate the value of D of the surface/mass fractal structure, and it is possible to determine the value of $-\alpha$ as the slope of the linear region of the double logarithm graph. The relation between α and D follows as $D_s = 6 - \alpha$ ($3 < \alpha < 4$) representing a surface fractal, which means, if the surface is magnified, its geometric features do not change (Schaefer, 1989), and $D_m = \alpha$ ($1 < \alpha < 3$), which is classified as a mass fractal and means that the density profile of the scattering objects has a self-similar nature.