ARTICLE IN PRESS

Food Hydrocolloids xxx (2016) 1–14

Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: www.elsevier.com/locate/foodhyd

Potato starch modification using the ozone technology

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A R T I C L E I N F O

Article history:
Received 18 October 2016
Received in revised form
1 December 2016
Accepted 2 December 2016
Available online xxx

Keywords:
Starch modification
Starch oxidation
Ozone
Emerging technologies
Green technologies
Food properties

A B S T R A C T

Ozone is a very powerful oxidizing agent and it can be quickly decomposed into oxygen, leaving no residues and meeting the global demand for sustainability. The effects of the different ozonation times on the structure and properties of the potato starch were investigated. With increasing ozonation time, it was observed an increase in the carbonyl, carboxyl and reducing sugar contents, as well as a decrease in the pH, apparent amylose content and molecular size, demonstrating that the potato starch processed with ozone was modified in its molecular level. Further, X-ray diffraction showed no significant changes in the relative crystallinity, while it was possible to observe alterations in the granules morphology. All these changes directly affected the modified starch properties, resulting in significant differences in terms of pasting properties, gel texture and paste clarity, proving the effectiveness of using ozone as an efficient oxidizing agent for starch modification.

1. Introduction

Starch is an important energy source in human diet and a major component of many plants. Furthermore, it is an important component for many industrial applications, including different industries such as food (human and animal), pharmaceutical, cosmetic, chemical, petrochemical, textile, etc. Although being formed mainly by α-D-glucopyranosyl units, starch is a very complex material, being presented as a water insoluble granule with a double-helical, semi-crystalline and birefringent structure, formed by two main polysaccharides: amylose and amylopectin (Liu, 2005; Miles, Morris, Orford, & Ring, 1985). Amylopectin is a highly branched molecule composed by short chains of (1 → 4)-linked α-D-glucopyranosyl units with (1 → 6)-linked branches, with a tree-like arrangement of double helices, being the main component of the crystalline domains in the starch granule. Amylose is essentially linear, composed by (1 → 4)-linked α-D-glucopyranosyl, presenting a small amount of branches, and it is believed to be randomly mixed with other materials in the amorphous domain of the starch granule (Hizukuri, Abe, & Hanashiro, 2006; Tester, Karkalas, & Qi, 2004).

Starch has attracted much academic and industrial interest as it is an abundant, renewable, cheap and biodegradable resource, as well as generally regarded as safe and environmentally acceptable (Kochkar, Morawietz, & Hölderich, 2001; Zhang, Zhang, Wang, & Wang, 2009). On the other hand, the naturally available starches have limited properties, being necessary the modification in order to provide further properties for the different industries requirements.

The modified starches present some characteristics that the native starches does not have, thus allowing further uses from a specific source. In fact, the modified starches can bring competitive advantages to some products, with many new functional and added value properties (Kaur, Ariffin, Bhat, & Karim, 2012). The starch modification can be carried out by chemical, physical and/or enzymatic processes, as well as by genetic improvement.

Oxidation is a chemical method of starch modification, being performed by a reaction with an oxidant agent under controlled conditions (Wang & Wang, 2003). The main reagents used for starch oxidation are sodium hypochlorite and hydrogen peroxide. However, by using these chemical agents, toxic wastes are generated (Chan et al., 2011).

In contrast, if compared to other chemical oxidants, the ozone is considered a “green” and “environmentally friendly” technology, since, by being quickly decomposed to oxygen, it does not leave any residues in food or in environment (Çatal & İbanoğlu, 2014). In fact, it meets the global demand for sustainability being safer for both consumer and environment. The ozone is a very powerful oxidizing

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http://dx.doi.org/10.1016/j.foodhyd.2016.12.001
0268-005X/

Please cite this article in press as: Castanha, N., et al., Potato starch modification using the ozone technology, *Food Hydrocolloids* (2016), http://dx.doi.org/10.1016/j.foodhyd.2016.12.001

agent, with a relatively high ($E^0 = +2.075$ V) electrochemical potential (Mahapatra, Muthukumarappan, & Julson, 2005). It can be generated by the exposure of oxygen/air to a high-energy source, which convert molecules of oxygen (O_2) to ozone (O_3) (Khadre, Yousef, & Kim, 2001).

In fact, the ozone is already being used for starch modification in a wide range of starch sources, such as corn, sago, cassava, rice, wheat and potato, among others (Çatal & İbanoğlu, 2012a, 2013, 2014; An & King, 2009; Chan, Bhat, & Karim, 2009; Chan et al., 2011; Klein et al., 2014). However, it is a still fairly studied process. For example, Çatal and İbanoğlu (2012a; 2012b) studied the effects of processing starches with ozone in aqueous solution for a determined time (1 h for both studies). In their first work (2012a), corn and potato starch suspensions were processed and the effects on the structural (only the granule morphology), thermal and pasting properties were evaluated. The second study (2012b) evaluated the effect of the ozonation on the structure (only the granule morphology), physic-chemical (pH and color) and microbiological (total bacteria and mold/yeast) properties of wheat, corn, potato and rice starches. Both works discuss the functional properties of the processed starches. However, they slightly discussed the mechanisms of ozone action and how it acts over the process. In addition, the structural changes are described only through the granule morphology, without further molecular information - chemical and structural modifications of starches, i.e. the possible changes in the crystallinity of the starch granules or carbonyl and carboxyl group contents, were not demonstrated. Finally, only one experimental condition was evaluated, which limits the understanding of the involved mechanisms. This present work, therefore, aims to deeply study the potato starch modification by ozone, providing more information about the molecular and granule modification and degradation by ozone and correlating it with the resulted changes on functional and technological properties. Therefore, it proposes a better understand about the process-structure-properties relationships.

Potato (*Solanum tuberosum* L.) is a worldwide known tuber, cropped under a wide range of climatic and soil conditions, and contains an unique starch, presenting a large granule size, long amylose and amylopectin chain lengths and the presence of phosphate ester groups (Vasanthan, Bergthaller, Driedger, Yeung, & Sporns, 1999). The phosphorus content in potato starch is relatively high when compared with other sources, and seems to be contained mostly in the branched (amylopectin) fraction in the form of covalently bonded phosphate groups (Posternak, 1950), which also affect the starch properties. The industrial application of starches is directly related to their characteristics. For example, when oxidized, the potato starch may present an even more clearer paste, a higher retrogradation tendency (and, therefore, stronger gels after cooling) and lower apparent viscosity at high solids concentration (Parovuori, Hamunen, Forssell, Autio, & Poutanen, 1995), if compared to the native starch. These characteristics are important to obtain starches with good binding capacity and film forming properties, among others (Chan et al., 2012).

In order to increase the possibilities of using potato starch, as well as meeting the growing industrial demand for specific functional characteristics, considering the environmental and food security claim, this work aimed to modify potato starch using the ozone technology. In addition, some structural and functional properties of the modified starch were evaluated and described aiming to better understand the degree of the oxidation in each processing time.

2. Potato starch oxidation: general hypotheses

To subsidize the evaluation and the discussion of the results in the present work, it is important to point out some assumptions and information that explain or at least elucidate the characteristics and the structure of starches and some hypothesis about its modification by oxidation. The most important information that should be enlightened is described in the topics listed below.

1. Ozonation is an oxidation method, and it is considered a process of starch chemical modification (Kaur et al., 2012);
2. Two main reactions take place during the starch processing by an oxidizing agent: oxidation and hydrolysis. The first one consists on the oxidation of the hydroxyl groups (C–OH) of the starch molecules to carbonyl (C=O) and carboxyl (HO–C=O) groups, primarily at the carbons 2, 3 and 6. In the second reaction, the starch molecules are depolymerized by cleaving glycosidic bonds (Boruch, 1985; Forssell, Hamunen, Autio, Suortti, & Poutanen, 1995; Wurzburg, 1986a).
3. The starch granules, a highly organized structure, is composed essentially by amorphous and crystalline domains. This conformation is ruled by genetic and environmental factors, being the structure affected by intermolecular bonding between amylose and amylopectin molecules (Liu, 2005). A possible representation of the starch granule structure is shown in Fig. 1. Fig. 1 was inspired by the illustrations presented in the works of Gallant, Bouchet, and Baldwin (1997), Pérez, Baldwin, and Gallant (2009), and Tang, Mitsunaga, and Kawamura (2006), and refined by the theories and details presented in the works of Eliasson and Gudmundsson (2006), Gallant, Bouchet, Buléon, and Pérez (1992), Hizukuri et al. (2006), Liu, 2005, and Tester et al. (2004). This scheme is important to indicate the parts in the starch granule where the oxidation possibly occurred.
4. Acids and enzymes attacks initially and rapidly the amorphous region of the starch granules (Fig. 1d), which is also more susceptible to be rapidly penetrated by water (Hizukuri et al., 2006; Robyt, 2009), due to its higher accessibility. Then, if the attack is long/strong enough, a second slowly stage may occur on the more crystalline domains (Liu, 2005). Thus, it is reasonable to expect that the oxidation by ozone in aqueous solution occur in the same way. Furthermore, the amylose molecules and some of the branching points of the amylopectin molecules are believed to be mainly in the amorphous phase of the granules (Fig. 1d), and these regions, as the periphery of the crystalline rings, are supposed to be attacked first (Eliasson & Gudmundsson, 2006).
5. Potato starch, unlike starches from other sources, has a high phosphorus content in its composition, which is in the form of covalently bond phosphate groups, mainly associated with the amylopectin molecules (Takeda & Hizukuri, 1982). This phosphate groups are believed to be located far from the reducing groups and from the branching points in the potato starch molecules (Posternak, 1950). The phosphorus content can affect several properties of the starch, such as rheological, thermal and structural properties, depending, however, of an delicate balance between phosphorus and amylose contents (Lu, Donner, Yada, & Liu, 2012). This is due to the high electronegativity of the phosphate group when ionised, which is repelled by the electronegative oxygen of the starch molecules, causing a higher dispersion of the amylopectin molecules (Craig, Maningat, Seib, & Hoseney, 1989; Nutting, 1951).

3. Material and methods

The ozonation was carried out by dissolving the ozone into the starch suspension in water, by considering that the ozone in aqueous solution penetrates easier the starch than in gas form (Tiwari, Muthukumarappan, O'Donnell, Chenchaiah, & Cullen,

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