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Review

High Hydrostatic Pressure (HHP)-assisted Starch Modification: Acid Hydrolysis, Hydroxypropylation, Acetylation, Cross-linking and Cationization

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Abstract: High hydrostatic pressure (HHP) processing is an attractive non-thermal technique because of its potential to achieve interesting functional effects. In spite of the rapid expansion of HHP application to food systems, limited information is available on effects of HHP on modification of starch and their structural and physicochemical properties. Therefore, functional roles of HHP in starch modification such as acid-hydrolysis, hydroxypropylation, acetylation, cross-linking and cationization of starch, as well as physicochemical properties of HHP-assisted modified starches were reviewed. HHP-assisted modified starches revealed similar or different physicochemical properties compared to conventionally modified starches, suggesting the consideration of HHP as a processing parameter for hydrolysis and modification of starch. Moreover, HHP-assisted starch modification would be an attractive technology and can be effectively used in starch industry with relatively low cost and short reaction time.

Key words: high hydrostatic pressure, starch, modification, physicochemical properties

INTRODUCTION

In high hydrostatic pressure (HHP) processing process, foods are subjected to pressures more than 100 MPa for certain time. The applications of HHP to food products can be traced back to the work of Hite (1899), who reported a significant reduction in microbial content in milk following pressurization at 680 MPa for 10 min and discovered that egg albumin was coagulated by HHP treatment.[1,2] Over the past several decades, the HHP process has been studied and applied to inactivate microorganisms and enzymes with minimal heating for the purposes of retaining the end-use qualities (*e.g.*, sensory characteristics, nutritional values) of foods and extending their self-lives. Regarding a function of HHP in HHP process, it is independent of the morphological characteristics (size and shape) of the substrate, acting instantly and homogeneously from every direction. HHP reduces the volume of the reaction mixtures in the chemical reaction, accelerating the reaction rate and increasing the reaction products.[3] HHP treatment can form or break off hydrogen bonds within or among biological macromoleculs without cleaving their covalent bonds, which ruptures and/or damages their secondary and tertiary structures.[4] Accordingly, the treatment of foods with HHP altered their physicochemical properties, including the density, viscosity, thermal conductivity, ionic dissociation, pH and freezing point.[5] Moreover, the recent researches have reported that HHP modifies the structural characteristics and reactivities of the protein-based hydrocolloids, impacting their physical and rheological functionalities. In general, an increase of pressure holding time at pressure levels above 300–400 MPa non-thermally denatures the protein structures, and subsequently, their reaggregation and refolding irreversibly occurs, resulting in gel formation. Thus, excessive HHP treatment of foods, especially in protein-rich foods, may change their appearance and texture, resulting in their improved end-use qualities and *vise versa*. Nevertheless, the pressure-induced protein gels which is observed for some proteins (*e.g.*, soybean, gluten, meat, fish and egg albumin) exhibit the smooth, glossy and soft texture with greater elasticity and maintain their natural color and flavor, compared to those of heat-induced protein gels.[5,6]

Furthermore, the investigations on the effects of HHP on the structural characteristics and physical functionalities of native starch granule have been studied with three standpoints of HHP application to native starch: the application of HHP levels not high enough to gelatinize starch,[7] the application of HHP to starch in dry state, and starch suspended in ethanol or at low moisture level,[8] and the treatment of starch suspen-

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RESEARCH ARTICLE

Freeze-thaw Stability, Glass Transition, and Retrogradation of High Hydrostatic Pressure-assisted Hydroxypropylated Corn Starch

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Abstract Effects of high hydrostatic pressure (HHP) and the propylene oxide (PO) concentration on the freeze-thaw stability, glass transition temperature (*Tg'*), and retrogradation degree of HHP-assisted hydroxypropylated corn starch were investigated. HHP-assisted hydroxypropylated corn starches were prepared using propylene oxide (4, 8, and 12%, v/w) at 25°C for 15 min under HHP (100, 200, 300, and 400 MPa). The freeze-thaw stability, *Tg'*, ice melting enthalpy (H_i), and retrogradation degree of HHP-assisted hydroxypropylated corn starches showed patterns different from native corn starch. In general, higher pressures and PO levels lowered *Tg'* and H_i values, and the retrogradation degree. The highest freeze-thaw stability was observed in HHP-assisted hydroxypropylated corn starch prepared using 12% PO at 400 MPa for 15 min. Retrogradation kinetics of hydroxypropylated corn starch gels observed from the glass transition temperature, ice melting enthalpy, and retrogradation degree revealed that recrystallization occurred with instantaneous nucleation, followed by rod-like growth of crystals.

Keywords: high hydrostatic pressure, hydroxypropylated corn starch, freeze-thaw stability, glass transition, retrogradation

Introduction

Starch is a major carbohydrate reserve in plants. Corn, wheat, potato, tapioca, and rice all contain large reserves of starch. Native starch is a good texture stabilizer and regulator in food systems (1), but the variety of applications in foods is limited due to low shear resistance, thermal decomposition, and a tendency towards retrogradation. Chemical modifications of starch bring about structural alterations and produce new functional groups that are suitable for industrial uses (2). Reactions of starch with the etherifying reagent propylene oxide (PO) introduce hydroxypropyl groups into the starch polymeric chain (3). Hydroxypropyl groups are hydrophilic and weaken internal bonding that holds granules together, resulting in slow retrogradation (4,5).

High hydrostatic pressure (HHP) affects the chemical reactivity of modified starch. HHP causes reversible hydration of the amorphous phase, followed by irreversible distortion of the crystalline region, which leads to destruction of the granular structure of starch. Refined high amylose maize treated at 650 MPa showed a small reduction in the size of the crystalline region, and some granules appeared to contain a cavity inside (6). In addition to hydroxypropylation (7), other chemical modifications have been performed via partial hydrolysis using acids (8.9), derivatization using phosphorus oxychloride (10) and acetic anhydride (11), and dual modification (12).

Many researches have focused on the physicochemical properties of HHP-assisted modified starch, but little information is available regarding HHP-assisted hydroxypropylated starch. Therefore, the objective of this study was to investigate the freeze-thaw stability, glass transition, and retrogradation of HHP-assisted hydroxypropylated corn starch.

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Materials and Methods

Materials Corn starch (9.5% moisture content on a wet basis) was provided by Daesang Co. (Incheon, Korea).