Thesis for the Degree of Doctor of Philosophy

Freeze-thaw Stability, Glass Transition and Retrogradation Behavior of Conventionally and Ultra High Pressure-assisted Modified Corn Starches

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by

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DEDICATION

To my wife and parents for their patience and understanding.

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ABSTRACT

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Starch is a major food reserve substance in plants, and occurs in discrete granules. Starch consists of two biopolymers: an essentially linear polysaccharide called amylose and a highly branched polysaccharide called amylopectin. In foodstuffs, the use of native starch or unmodified native starch is limited by their lack of stability under processing condition such as heating, refrigeration and freezing because of their lack of stability under temperature, pH, frozen and refrigeration conditions, which commonly applied to processed food. Chemical modification of starch is being use to introduce desirable properties in starch for specific application. Perhaps ultra high pressure technology offers a new possibility of starch application in food products and chemical modification is usually carried out to overcome the unstable properties of starch and to improve its physical properties and inhibit retrogradation of starch gels. In this study, corn starch was hydroxypropylated and/ or crosslinked under ultra high pressures (UHP) using propylene oxide (PO), sodium trimetraphosphate (STMP) and sodium tripolyphosphate (STPP) and their freeze-thaw stability, glass transition temperature (Tg') and retrogradation behavior were

investigated to elucidate the effects of non-thermal hydroxypropylated and/or crosslinked corn starch gels.

Effect of ultra high pressure (100, 200, 300, and 400MPa for 15 minutes) on freeze-thaw stability, glass transition temperature (Tg'), and retrogradation behavior of hydroxypropylated corn starch with propylene oxide (4, 8, 12%, v/w) was investigated. Freeze-thaw stability, glass transition temperature (Tg'), ice melting enthalpy (ΔH_i) and retrogradation behavior of UHP-assisted hydroxypropylated cornstarch showed different pattern compared to native and conventionally hydroxypropylated cornstarches. Degree of propylene oxide and level of ultra high pressure greatly influenced freeze-thaw stability, glass transition temperature (Tg'), ice melting enthalpy (ΔH_i) and retrogradation behavior. The highest freeze-thaw stability was observed in UHP-assisted hydroxypropylated cornstarch with 12% of propylene oxide at 400 MPa for 15 minutes. Moreover, higher pressure and propylene oxide level lowered glass transition temperature (Tg'), ice melting enthalpy (ΔH_i) and retrogradation behavior.

For crosslinked corn starch was crosslinked with STMP/STPP (99:1) (4, 8, 12%, v/w) at 100, 200, 300, and 400MPa for 15 minutes and conventionally method reaction at 45 °C for 3 hr. Freeze-thaw stability, glass transition temperature (Tg'), ice melting enthalpy (ΔH_i), recrystalization and retrogradation behavior of UHP-assisted crosslinked cornstarch showed different pattern compared to native and conventionally crosslinked cornstarches. Degree of STMP/STPP showed not significant of freeze-thaw stability between 8 and 12% of STMP/STPP (99:1) mixture and levels of ultra high pressure was not influenced freeze-thaw stability, The highest freeze-thaw stability was observed in conventionally cornstarch with 12% of STMP/STPP (99:1) mixture. Moreover, higher pressure and 12% of STMP/STPP (99:1) mixture lowered glass transition temperature (Tg'), ice melting enthalpy (ΔH_i) and conventionally cornstarch with 12% of STMP/STPP (99:1) mixture showed lower recrystalization and retrogradation behavior.

In case of effect of dual modified corn starch by using ultra high pressures on freeze-thaw stability, glass transition temperature (Tg'), and retrogradation behavior of hydroxypropylated and crosslinked or crosslinked and hydroxypropylated corn starch with 12% of propylene oxide and 12% of STMP/STPP (99:1) mixture at 400 MPa for 15 minutes and conventionally method reaction at 45 °C for 20 hours and 3 hours for hydroxypropylation and crosslinking, respectively. The crosslinked and hydroxypropylated cornstarch by using ultra high pressures showed higher freeze-thaw stability and lower recrystalization and the lowest glass transition temperature (Tg'), ice melting enthalpy (ΔH_i) and retrogradation behavior was observed in conventionally-assisted hydroxypropylated and crosslinked corn starch.

Data confirmed that the ultra high pressures effect of hydroxypropylated and/or crosslinked corn starch during storage was related with the degree of reagent and ultra high pressure levels. Therefore, the freeze-thaw stability of modified starches during storage in this case was related to other changes such as amylopectin recrystally, stiffening of the amorphous domains and glass transition temperature.