EFFECTS OF GENOTYPE AND ENVIRONMENT ON THE COMPOSITION AND STARCH
FUNCTIONALITY OF PEA AND FABABEAN AND THE PRESENCE OF OTHER
STARCHES OR HYDROCOLLOIDS ON THE FUNCTIONALITY OF PEA STARCH

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ABSTRACT

The effects of genotype and environment on the concentrations of starch and protein in, and the amylose concentrations and thermal and pasting properties of starch from, pea and fababean were not well known. The effect of genotype was significant for protein and starch concentration in pea and fababean, for pasting, trough, cooling and final viscosities of starch from pea and fababean, and the onset and peak temperatures of gelatinization of starch from fababean. Pea grown in locations with higher mean temperatures and lower levels of precipitation was higher in protein, and its starch exhibited a higher peak temperature of gelatinization. The starch concentration in pea and fababean, and the pasting, trough, cooling and final viscosities of pea and fababean starch, were highly heritable. Genotype and environment had minor effects on the concentration of amylose in, and the physicochemical characteristics of, starch from pea and fababean. The effects of genotype and environment on the physicochemical characteristics of starch from pea and fababean would likely not be of practical significance.

Native, heat-moisture-treated and pregelatinized blends of pea starch and starch from corn, waxy corn, high-amylose corn or potato exhibited a variety of functionalities due to differences in the functionalities of the constituent starches and to the effects of heat-moisture treatment and pregelatinization. Blends of pea starch and corn starch or waxy corn starch exhibited pasting viscosities and freeze-thaw stabilities that were higher than corresponding weighted average values calculated for the blends. Generally, heat-moisture-treated blends of pea starch and corn starch, high-amylose corn starch or potato starch exhibited viscosities that were

lower than corresponding weighted averages calculated for the blends. Pregelatinized blends of pea starch and waxy corn starch exhibited water solubilities that were lower than their respective weighted average values.

Compared to pea starch, combinations of pea starch and guar gum exhibited lower degrees of syneresis and higher viscosities, combinations of pea starch and locust bean gum exhibited higher viscosities, combinations of pea starch and xanthan gum exhibited higher pasting and trough viscosities, and combinations of pea starch and carboxymethyl cellulose exhibited higher pasting, trough and final viscosities at lower inclusion levels, and lower pasting, trough and final viscosities at higher inclusion levels.

It was concluded that some blends of pea starch and starches from corn, waxy corn, high-amylose corn or potato, and some combinations of pea starch and hydrocolloids, might offer functionality that would be of practical use.

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LIST OF ABBREVIATIONS

ΔH Endothermic enthalpy of gelatinization

CDC   Crop Development Centre

CMC   Carboxymethyl cellulose

CS   Corn starch

CV   Cooling viscosity

db   dry basis

DP   Degree of polymerization

exp   Experimental value

FT   Freeze-thaw cycle (FT1 = freeze-thaw cycle 1, etc.)

FV   Final viscosity

Ge   Genotype

GG   Guar gum

HACS   High-amylose corn starch

HMT   Heat-moisture treatment

HPMC   Hydroxypropylmethyl cellulose

LBG   Locust bean gum

Loc   Location

MC   Methyl cellulose

PG   Pregelatinized

PoS   Potato starch

PS   Pea starch

PT   Pasting temperature

PV   Pasting viscosity

RS   Resistant starch

SCFA   Short chain fatty acids

SDS   Slowly digestible starch

SP   Swelling power

SS   Shear stability

T_c Completion temperature of gelatinization

T_o Onset temperature of gelatinization

T_p Peak temperature of gelatinization

TV   Trough viscosity

WBC   Water binding capacity

WCS   Waxy corn starch

WSI   Water solubility index

wt ave   Weighted average value

XG   Xanthan gum

1. INTRODUCTION

1.1 Rationale

Starch is a major constituent of most cereal grains, roots, tubers and grain legumes, and is important in human nutrition and in a wide variety of food and industrial applications. Interest in fractionation of legumes, particularly pea and fababean, is growing due to the substantial protein and lysine concentrations. Currently, there is relatively little information available on the utilization of legume starches in the food industry when compared to other starches on the market. To increase the knowledge of pea and fababean starches, new food and industrial uses that take advantage of the unique functional characteristics of these starches must be developed.

Research has shown that starches from different genotypes of wheat (Wootton & Mahdar, 1993), rye (Gudmundsson & Eliasson, 1991), maize (Yun & Matheson, 1993), millet (Yanez et al., 1991), cassava (Asaoka et al., 1991) and lentil (Hoover & Manuel, 1995) differ in functionality. However, a study of four pea genotypes did not detect significant differences in starch functionality (Ratnayake et al., 2001). A subsequent study of genetic markers in pea genotypes (Tar'an et al., 2005) found that the genotypes used by Ratnayake et al. (2001) were closely related. A study on the effects of genotype and the environment, and their interactions, on starch functionality in pea and fababean would provide valuable information to pea and fababean breeders and the starch industry. No reports have been published on genotypic or environmental effects on the functionality of starch isolated from fababean.

Relatively little research has been undertaken to modify the functionality of, or identify unique applications for, legume starches. Instead, the usual practice is to attempt to replace cereal or tuber starches with pea or other legume starch in applications that usually employ cereal or tuber starches. Legume starches may have a place in food processing due to the need for strong gelation capacity (Vose, 1977), shear stability (Gernat et al., 1990), acid stability (Gernat et al., 1990) and enzyme resistance (Ratnayake et al., 2001).

Previous research on starch blends has provided insight into the functional modification of starch without the application of chemical or physical treatments. Blending and thermal modification are attractive due to their relatively low cost and the "naturalness" of the resulting starch product. In an effort to increase the use of legume starches in food, the functionality of pea starch in blends with corn starch, waxy corn starch, high-amylose corn starch or potato starch, and combinations of pea starch and guar gum, locust bean gum, xanthan gum or carboxymethyl cellulose, were investigated.

1.2 Hypothesis and Objectives

The primary objectives of this research were: i) to determine differences among pea and fababean genotypes with respect to the starch and protein concentrations in the seed and amylose concentrations in, and the thermal and pasting properties of starch from, pea and fababean; ii) to determine the impact of growth environment on the starch and protein concentrations in the seed and on the amylose concentrations in, and the thermal and pasting properties of, starch from pea and fababean; iii) to characterize the functionality of blends of pea starch with corn starch, waxy corn starch, high-amylose corn starch or potato starch; iv) to evaluate the functionality of, and to determine the resistant starch concentrations in, heat-moisture-treated and pregelatinized blends of pea starch with corn starch, waxy corn starch, high amylose corn starch or potato starch; and v)

to evaluate the functionality of combinations of pea starch and guar gum, locust bean gum, xanthan gum or carboxymethyl cellulose.

It was hypothesized that: i) differences in starch and protein concentrations in the seed and amylose concentrations in, and the thermal and pasting properties of, starch from pea and fababean would be detected among pea and fababean genotypes; ii) the environmental conditions during the growing season would significantly affect the functionality of pea and fababean starch; iii) native, heat-moisture-treated, or pregelatinized blends of pea starch with corn starch, waxy corn starch, high-amylose corn starch or potato starch would exhibit unique functionalities; and iv) combinations of pea starch with guar gum, xanthan gum, locust bean or carboxymethyl cellulose would exhibit improved functionality including higher viscosities and lower levels of syneresis after freezing than does pea starch.

2. LITERATURE REVIEW

2.1 Composition and Fractionation of Pea and Fababean

Field pea (*Pisum sativum* L.) and fababean (*Vicia faba* L.) belong to the Leguminosae family and the Vicieae tribe (Sathe, 1986). The composition of field pea and fababean is shown in Table 2.1.

Grain legume fractionation can be accomplished by dry or wet methods. Dry fractionation involves impact milling followed by air classification, leading to starch- and protein-rich fractions (Tyler et al., 1981). Air classification is an effective method for fractionation of grain legumes such as pea, due to its relative ease of millability and large difference in size between starch granules and protein particles. A double pass method (impact mill, air classify, impact mill, air classify) is optimal for separating starch from protein. Wet fractionation involves preparation of an alkaline, wet-milled slurry, separating the solubles (protein extract) from the insolubles (starch and cell wall fibre) by sieving and centrifugation, alteration of the pH of the protein extract to precipitate the protein (~pH 4.5), recovery of the protein by centrifugation, recovery of the starch by centrifugation and washing, and subsequent drying and grinding of the starch, protein and cell wall fibre products (Wright, 1985). Typically, dry-milled starch possesses higher concentrations of damaged starch than does wet-milled starch (Suksomboon & Naivikul, 2006). Dry-milled starch and protein fractions are of lower purity but are typically more economical to produce when compared to wet-milled starch and protein products.

Table 2.1 Composition (%, dry basis, except where noted) of field pea[a] and fababean[b,c]

	Field Pea		Fababean	
	Mean	Range	Mean	Range
Starch	45.5	41.6-49.0	41.4	30.0-42.3
Amylose[d]	25.6	20.7-33.7	32.5[e]	
Protein (N x 6.25)	23.7	20.2-27.4	32.5	
Fat	1.3	1.0-1.7	1.6	
Ash	2.8	2.3-3.4	3.5	

[a] Wang & Daun (2004b)
[b] Hill-Cottingham (1983)
[c] Cerning et al. (1975)
[d] Starch basis
[e] Biliaderis et al. (1979)

With the development of new, more-round, smaller-seeded fababean varieties, legume dehullers, millers and fractionators may have greater interest in fababean, due to reductions in seed costs and improved dehulling efficiency.

2.2 Pea and Fababean Starch

Starch is an homogeneous glucose polymer. Glucose residues are linked via α-1, 4 and α-1, 6 bonds, with α-1, 6 bonds forming branch points in the starch molecule. Amylose is mostly linear with minimal branching, whereas amylopectin is highly branched. Branch points of amylopectin are primarily located in the amorphous regions of B-type starches and distributed in both the amorphous and crystalline regions in A-type starches (Jane et al., 1997). Amorphous regions separate the crystalline lamellae, creating a semi-crystalline starch granule (Ball et al., 1998). The amorphous regions comprise approximately 70% of the starch granule (Oostergetel & van Bruggen, 1993).

Starch is the major constituent of pea and fababean, ranging in concentration from 41-49% (moisture-free basis) for pea (Wang & Daun, 2004b) and 30-42% (moisture-free basis) for fababean (Cerning et al., 1975; Hill-Cottingham, 1983). Starch concentration increases with a decrease in seed protein concentration (Cerning et al., 1975).

2.2.1 Morphology and Composition of Pea and Fababean Starch

Pea starch granules are oval, spherical or irregularly shaped (Gujska et al., 1994) and size ranges in width from 14-32 μm and in length from 15-37 μm (Hoover & Ratnayake, 2002). Fababean starch granules also are oval, spherical or irregularly shaped (Lineback & Ke, 1975). Typically, starch from smooth pea and fababean exhibit intermediate amylose concentrations of

32-35% (Biliaderis et al., 1979). Colonna et al. (1981) reported that the structures of pea and fababean starches were similar, leading to the possibility of interchanging pea and fababean starches in various applications.

During amylose-lipid complexation, the amylose conformation changes from random coil to helix, and free fatty acids or monoacylglycerols occupy the interior of the α-helix of amylose. The helical structure of amylose facilitates lipid complexation, resulting in a partially crystalline configuration referred to as V-amylose (Biliaderis & Galloway, 1989). Hoover & Manuel (1996b) and Hoover & Ratnayake (2002), respectively, reported that the amylose in native pea starch contained 7.8 and 8.1% of amylose-lipid complexes. Amylose-lipid complexes are also formed during thermal treatment (Tufvesson et al., 2003).

2.2.2 Amylose

Biliaderis et al. (1979) reported pea and fababean starch exhibited intermediate amylose concentrations of 32-35%. Davydova et al. (1995) reported that starch from five pea genotypes grown in Russia in the same year and location contained 30-43% amylose. Potato starch (Kim et al., 1995; Wiesenborn et al., 1994), normal corn starch (Biliaderis et al., 1979; Morrison et al., 1984), waxy corn starch (Morrison et al., 1984) and high-amylose corn starch (Morrison et al., 1984) contained 20.1-32.5, 22.4-32.5, 1.4-2.7 and 42.6-67.8% amylose, respectively. Ratnayake et al. (2001) reported that the degree of polymerization (DP) of amylose in pea starches ranged from 1300 to 1350. Amylose concentration and average chain length of amylose influence crystallinity in maize starches (Cheetham & Tao, 1997). Noda et al. (1998) reported that the amylose concentration of sweet potato and buckwheat starches did not affect their thermal properties. In maize starches, as amylose concentration increased, the double helical content of

amylopectin decreased (Cheetham & Tao, 1997). This phenomenon was also observed in sweet potato starch, where amylose-free starch exhibited a higher content of amylopectin long chains, higher gelatinization temperature, higher gelatinization enthalpy and less setback than was exhibited by normal sweet potato starch (Noda et al., 2002).

2.2.3 Amylopectin

Jane et al. (1999) found that shorter amylopectin chain lengths were associated with lower gelatinization temperatures. The DP of amylopectin affected gelatinization and pasting properties of yellow pea, cowpea and chickpea starches (Huang et al., 2007). Average amylopectin DP in starches from four pea genotypes (Carneval, Carrera, Grande and Keoma) ranged from 22.9 to 24.2 (Ratnayake et al., 2001). Although the variation in average amylopectin chain length in this study was significant, no significant difference in thermal and pasting properties were detected, possibly due to the close genetic relationship of the four genotypes, the similar growing conditions and the relative closeness of the average amylopectin DP of the starches. The short chain to long chain ratio of amylopectin influences crystallinity in maize starches (Cheetham & Tao, 1997). Biliaderis et al. (1981) reported that the molar ratio of short:long chains of amylopectin in legume starches (pea, fababean, chickpea, red kidney bean, lentil, navy bean and mung bean) ranged from 7.2:1 to 9.6:1. Typically, a higher proportion of longer amylopectin chains results in a higher gelatinization temperature, a higher pasting peak and improved stability of the starch gel, particularly during freeze-thaw cycles. These properties were observed in cowpea, chickpea and yellow pea starches (Huang et al., 2007).

Cooke & Gidley (1992) investigated maize starch, waxy maize starch, wheat starch, potato starch and tapioca starch, and reported that the endothermic enthalpy of gelatinization was a result of the "loss of double helical order", not crystallinity. They concluded that the packing

efficiency of the amylopectin double helices would influence gelatinization temperature and enthalpy, in that more efficient packing would lead to a higher gelatinization temperature and enthalpy. Noda et al. (1998) reported that a higher proportion of short chain amylopectin molecules resulted in poor packing in the crystalline lamellae, thus reducing the gelatinization temperature and endothermic enthalpy of starches from sweet potato and buckwheat. The DP of amylopectin also influences pasting properties. The proportions of amylopectin chains with a DP of 13-24 and greater than 37 (Han & Hamaker, 2001) play a role in the viscosity of starches. Rice starches possessing longer chains of amylopectin exhibited less breakdown during pasting (Han & Hamaker, 2001).

2.3.4 X-Ray Diffraction

Legume starches possess a C-type X-ray diffraction pattern, which is a combination of the A-type diffraction pattern of cereals and the B-type diffraction pattern of tubers. A-type and B-type polymorphs differ in water content and the packing of parallel double helices. B-type crystallinity contains more intrahelical water (Imberty & Perez, 1988; Imberty et al., 1988). Crystallinity type and amount affects starch functionality, including swelling power, solubility, gelatinization temperature, peak viscosity and freeze-thaw behaviour. In C-type polymorphs, A-type and B-type polymorphs are present in the same granule, with B-type polymorphs positioned near the centre of the granule and A-type polymorphs positioned near the outer areas of the granule (Bogracheva et al., 1998). Amylopectins containing a greater proportion of short chains typically form A-type crystallites and amylopectins containing a greater proportion of long chains typically form B-type crystallites (Hizukuri, 1986; Hizukuri et al., 1983). Factors that may affect the type of crystallite include temperature during starch formation and the presence of other constituents, such as lipid (Hizukuri et al., 1983). A-type polymorphs exhibit higher levels of

relative crystallinity than B-type polymorphs in soft wheat (Kim & Huber, 2010), wheat (Chiotelli & Le Meste, 2002), mutant corn starches (Gérard et al., 2001) and synthesized starch (Buléon et al., 1997). Typically, cooler temperatures during starch formation lead to more B-type crystalline units, and the presence of lipids may lead to the formation of more A-type crystalline units. Additionally, higher amylose concentrations reduce crystallinity, potentially leading to more B-type crystalline structures.

The proportion of B-type polymorph varies in legume starches (Hoover & Ratnayake, 2002; Sarko & Wu, 1978). Pea starch has been reported to contain 38.6% B-type and 61.4% A-type polymorphs (Gernat et al., 1990) and 44% B-type and 56% A-type polymorphs (Cairns et al., 1997). Fababean starch contained 17% B-type and 83% A-type polymorphs as reported by Gernat et al. (1990). Neither study reported the genotype of pea or fababean used, but it may be postulated that there is potential variability in the proportion of B- and A- type polymorphs in pea and fababean starches. Additionally, Ratnayake et al. (2001) found that the pea cultivar, Keoma, possessed a higher B-type polymorph content and a longer average chain length than did Carneval, Carrera or Grande, but did not display any difference in gelatinization temperature, possibly due to the genetic closeness of cultivars. Davydova et al. (1995) determined that the pea genotypes Smaract, Ovlorchanin, Orpella, Vyatich and Sprout contained 33%, 26%, 44%, 40% and 49% B-polymorph, respectively, and detected higher gelatinization temperatures for pea genotypes with lower percentages of the B-polymorph. This was in agreement with a study by Cooke & Gidley (1992) where debranched, A-type glycogen possessed a higher gelatinization temperature 15°C higher than that of debranched, B-type glycogen, and A-type corn starch had a gelatinization temperature 11°C higher than that of B-type potato starch.

Cheetham & Tao (1998) reported that in maize starches, as amylose concentration increases, crystallinity decreases. These authors also reported that as amylose concentration increases, crystallinity type changes from A-type for maize starches of low amylose concentration to C-type at intermediate amylose concentrations to B-type in high-amylose maize starches. Cheetham & Tao (1998) also reported that corn starches containing 0% or 28% amylose possessed A-type polymorphs, those with 40% amylose, C-type polymorphs, and those with 56%, 65% or 84% amylose, B-type polymorphs. Another example, the corn mutant *ae du,* containing 50% amylose, possessed a diffraction pattern similar to that of C-type polymorphs (Matveev et al., 2001).

2.4 Genotypic Differences in Starch Functionality

The functionality of wheat (Wootton & Mahdar, 1993), rye (Gudmundsson & Eliasson, 1991), maize (Yun & Matheson, 1993), millet (Yanez et al., 1991) and cassava (Asaoka et al., 1991) starches varies with genotype. Wootton & Mahdar (1993) reported differences among wheat genotypes in starch gelatinization characteristics, granule crystallinity and molecular weight. Enthalpies of gelatinization of twenty-one Australian wheat genotypes were significantly different and correlated with amylopectin content and wheat hardness (Wootton & Mahdar, 1993). Additionally, soft wheat genotypes exhibited variation in gene expression of granule-bound starch synthase I (GBSSI) and, accordingly, influenced amylose concentration, proportion of A-type and B-type granules and pasting properties (Geera et al., 2006b). Millet genotypes exhibited different amylose concentrations, thermal properties and pasting properties (Yanez et al., 1991). The temperature of onset of gelatinization for these four samples of millet ranged from 64.0-69.0°C as measured by differential scanning calorimetry. Two genotypes, Cope and Dawn,

pasted at 93.0°C, whereas the other two genotypes analyzed, Minco and Cerise, did not peak before 95°C. Depending on the crop species, there may be a large range in genotypic differences with respect to starch functionality.

2.4.1 Genotypic Differences among Legume Starches

Tulbek & Simsek (2007) analyzed the starch concentration of pea genotypes (Miami, Nitouche, DS Admiral, Eclipse, Majoret, Cruiser and CDC Mozart) grown in North Dakota and found that the starch concentration was significantly different among genotypes. Miami had the highest starch concentration at 43.9%, Nitouche contained 43.7% starch and Majoret had the lowest starch concentration at 40.9%. Simsek & Tulbek (2007) reported significant differences in enthalpy of retrogradation among genotypes, and each genotype produced a different pasting profile. Frimpong et al. (2009) reported genotype by environment interactions for starch concentration in the seed, and for amylose concentration in the starch, of chickpea.

Starches from three black bean genotypes exhibited different onset (T_o) and peak gelatinization (T_p) temperature, and endothermic enthalpies of gelatinization (ΔH) (Hoover & Ratnayake, 2002). The To values in the two genotypes of pea and lentil and the ΔH values in the genotypes of pea, chickpea and pinto bean examined by Hoover and Ratnayake (2002) were significantly different. The T_o, T_c (temperature of complete gelatinization) and ΔH were greater in Laird lentil (large, green) starch than in CDC Gold (small, yellow) lentil starch (Hoover & Manuel, 1995). However, Ratnayake et al. (2001) reported no significant differences in thermal properties among starches from four pea genotypes (Carneval, Carrera, Grande, Keoma). Czuchajowska et al. (1998) investigated two pea genotypes, Latah and SS Alaska, and reported no significant differences in T_o, T_p or ΔH.

Pasting properties of CDC Gold and Laird lentil were significantly different in that CDC Gold exhibited a higher pasting temperature (PT) than did Laird (Hoover & Manuel, 1995). Laird exhibited higher pasting viscosity (PV) than did CDC Gold. Two genotypes of grass pea (*Lathyrus sativus*), NC8A97 and Lath 96, exhibited different pasting properties, including peak viscosity and setback (Jayakody et al., 2007). However the pea genotypes, Carneval, Carrera, Grande and Keoma, exhibited pasting properties that were not significantly different (Ratnayake et al., 2001).

Hoover & Ratnayake (2002) investigated starch from three black bean genotypes and reported significant differences in swelling factor (determined by a colourimetric method using blue dextran) and amylose leaching. These authors also reported genotypic differences in swelling factor in both chickpea and pea genotypes. Starch from CDC Gold lentil exhibited a higher swelling factor than did starch from Laird lentil (Hoover & Manuel, 1995). Two genotypes of grass pea (*Lathyrus sativus*), NC8A97 and Lath 96, varied in swelling and amylose leaching (Jayakody et al., 2007). Additionally, the pea genotypes, Latah and SS Alaska exhibited swelling powers (a gravimetric method) that were not significantly different (Czuchajowska et al., 1998). Ratnayake et al. (2001) reported no significant differences among starches from four pea genotypes (Carneval, Carrera, Grande, Keoma) in swelling factor or amylose leaching, despite variations in B-type polymorph content and amylopectin branching. This may be attributed to the relatively small variabilities of methodologies used for analysis of crystallinity and amylopectin branching compared to the variabilities of methodologies used to test functional characteristics of starches, such as swelling factor and amylose leaching. Additionally, the genotypes, Carneval, Carrera, Grande and Keoma, possess similar genetic markers and are closely related as compared to other pea genotypes available (Tar'an et al., 2005).

2.5 Environmental Impacts on Starch Concentration and Functionality

Environmental conditions during the growing season may influence starch concentration and amylose concentration in starch. As a result, the functionality of starch may also be influenced by environmental conditions during the growing season. Environmental conditions influenced starch concentrations and proportion of A-type granules in soft wheat resulting in different pasting properties (Geera et al., 2006a). Four genotypes of cassava grown and harvested under different conditions exhibited significant differences in the texture of starch gels among genotypes, as well as within one genotype (Asaoka et al., 1991). These authors reported no significant differences in the crystallinity of the cassava starch granule due to genotype or time of harvest. Cottrell et al. (1995) investigated potato starch grown under three conditions, namely field, unheated glasshouse and heated glasshouse. These authors reported that warmer growing conditions increased the gelatinization temperature, amylose concentration and alpha-amylase resistance of potato starch.

Nikolopoulou et al. (2007) reported that the starch concentrations of three pea genotypes, grown in three locations over two years, were significantly different. These authors also reported that pea genotypes grown under conditions of less rainfall possessed lower starch and higher protein concentrations, and reported significance for location and the location by year interaction for differences in starch concentration.

2.6 Starch Functionality

2.6.1 Thermal Properties

Gelatinization occurs when native starch granules are heated in an excess of water and an order-disorder transformation occurs. The gelatinization temperature depends on the botanical source of the starch, granule structure and proportion of amylopectin double helices. The thermal

properties of common starches are presented in Table 2.2. Two methods for determining gelatinization characteristics are differential scanning calorimetry (DSC) and monitoring the loss of birefringence. Cooke & Gidley (1992) studied DSC traces of starch from maize, waxy maize, wheat, potato and tapioca and concluded that the ΔH was a result of the loss of double helices, not crystalline structure. Legume starches are known to have higher gelatinization temperatures than cereal or tuber starches, due to differences in starch granule structure. Tester (1997) postulated that the thermal properties of starch reflect crystalline perfection, since thermal properties are partially controlled by starch composition (amylose-amylopectin ratio, other constituents such as phosphorus), amylopectin structure (chain length, molecular weight) and granule architecture (crystalline:amorphous ratio). Peak gelatinization temperature would indicate the quality of the crystallite, reflecting the length of amylopectin chains (Tester & Morrison, 1990b). Enthalpy of gelatinization offers information regarding the quality and quantity of crystallinity, and indicates loss of molecular order during gelatinization (Cooke & Gidley, 1992; Hoover & Vasanthan, 1994a; Tester & Morrison, 1990a). Generally, due to the role of amylopectin in starch granule crystallinity, an increase in amylose concentration lowered the melting point of the crystalline region (Flipse et al., 1996). However, starches with high amylose concentrations and those that possess long chain lengths may have elevated gelatinization temperatures (Jane et al., 1999).

Differential scanning calorimetry traces of air-classified, starch-rich pea fractions displayed wider transitions than did purified pea starches (Al-Abbas et al., 2006). Sosulski et al. (1985) reported DSC results for air-classified, starch-rich fractions from pea. The starch fraction from the second air-classification of pea contained 81.5% starch and 6.2% protein, and exhibited a gelatinization temperature of 63°C and an ΔH of 15.9 J/g. Ratnayake et al. (2001) reported that pea starches (Carneval, Carrera, Grande and Keoma) exhibited T_o, T_p and T_c values of 61.0-61.4,

Table 2.2 Onset temperature of gelatinization (T_o), first and second peak temperatures of gelatinization (T_{p1} and T_{p2}), melting point temperature (T_m) and enthalpy of gelatinization (ΔH) of various starches

	T_o (°C)	T_{p1} (°C)	T_{p2} (°C)	T_m (°C)	ΔH (J/g)
Pea[a]	56	64	87	101	14.6
Fababean[a]	56	65	83	97	13.8
Potato - commercial[a]	55	60	68	85	18.4
Corn - commercial[a]	60	67	78	89	13.8
Waxy corn - commercial[a]	64	71	88	97	16.7
HACS - commercial[a*]	64	71	88	97	17.6
Potato[b]	60-66	63-70	67		12.5-17.9
Corn[c]	64	69	75		12.3
Waxy Corn[c]	64	69	75		15.5

[a] Biliaderis et al. (1979)
[b] Kim et al. (1995)
[c] Jane et al. (1999)
*Where HACS is high-amylose corn starch

66.8-67.5 and 75.0-76.0°C, respectively. The ΔH range for these pea starches was 11.2-11.5 J/g (Ratnayake et al., 2001).

2.6.2 Pasting Properties

Viscosity increases as water migrates into the granule, promoting swelling and movement of glucan molecules, particularly amylose, due to the linearity of the molecule (BeMiller & Whistler, 1996). Miller et al. (1973) reported that the viscosity continued to increase in wheat starch pastes after granule swelling was complete. The viscosity increase was attributed to leaching of glucans from the granule, forming a network. Subsequently, viscosity decreased due to solubilization and fragmentation of the starch molecules. During the 95°C hold, the starch is subjected to continual shear, and during this time many starches display a breakdown in viscosity (BeMiller & Whistler, 1996). Following the 95°C hold in viscoamylography, the starch mixture is cooled to 50°C and then held for 30 minutes. Setback is the change in viscosity between 95°C and 50°C and indicates the level of retrogradation (Tipples et al., 1980). The final viscosity of the starch indicates the ability of the starch to form a gel upon cooling. Jane et al. (1999) found that increasing the amylose, lipid or phospholipid concentration increased the pasting temperature, decreased the peak viscosity, and increased the setback viscosity and the shear stability. Upon cooling, the paste will begin to retrograde. Retrogradation is the realignment of glucans, particularly amylose, causing an increase in paste viscosity known as setback (Tipples et al., 1980). High setback is correlated with syneresis, which is defined as water exudation from starch gels, especially during freeze-thaw cycles, indicating that starches exhibiting high setback are not good candidates for freeze-thaw applications such as in batters, breadings, stabilizers or thickeners in frozen or refrigerated food products. Gel clarity and texture are affected by the extent of retrogradation.

Gujska et al. (1994) reported that pea starch exhibited a pasting temperature of 73°C and viscosities at 95°C and 50°C of 370 and 800 BU, respectively. Typically, legume starches do not exhibit much of a breakdown at this stage indicating a degree of shear stability. Scanning electron micrographs of native pea starch revealed swollen granules and incomplete granule degradation at 95°C (Yook et al., 1994), indicating that pea starch may require a higher temperature to gelatinize completely.

2.6.3 Swelling Power and Water Solubility

Heating starch in an excess of water disrupts the molecular order within the starch granule. Hydrogen bonds are formed between water molecules and the free hydroxyl groups of amylose and amylopectin, causing granule swelling and increased granule solubility (Ratnayake et al., 2002). Swelling power and water solubility are measurements that indicate the extent of the ability of the starch granules to swell and solubilize. Swelling power and solubility indicate the extent of interaction of chains within the amorphous and crystalline lamellae (Ratnayake et al., 2002; Tester et al., 1993) and the extent of amylose-lipid complexation (Tester et al., 1993; Tester & Morrison, 1990a; Vasanthan & Hoover, 1992). Tester & Morrison (1993) reported that variation in swelling power of barley starch was related to the presence of lipid-complexed amylose, where as lipid-complexed amylose increased, swelling decreased. However, Sasaki & Matsuki (1998) reported no correlation between starch-lipid content and swelling power, and a negative correlation between amylose concentration and swelling power in twelve wheat starch samples. Higher swelling powers were observed for wheat starches possessing longer amylopectin chains (Sasaki & Matsuki, 1998).

Legume starches, such as pea, exhibit restricted swelling properties (Vose, 1977) as indicated by an increase in viscosity during the 95°C hold period of a viscoamylographic plot (Czuchajowska et al., 1998). The restricted swelling properties of legume starches could be caused by the intermediate amylose concentration, strong associations between amorphous and crystalline lamellae or may also be due to the arrangement of A- and B-type polymorphs in the granule. Bogracheva et al. (1998) reported B-type polymorphs near the centre of the pea starch granule and A-type polymorphs near the periphery of the pea starch granule, and that the B-type polymorphs melted at a lower temperature than did A-type polymorphs, possibly leading to a disruption in swelling. As the temperature was increased from 50 to 95°C, the swelling factor of pea starch increased from 4.1 g/g to 26.7 g/g (Ratnayake et al., 2001). The swelling power of starch from several genotypes of corn ranged from 13.7-20.7 g/g at 90°C (Sandhu & Singh, 2007). Waxy corn starches possessed higher swelling power, ranging from 30.2-39.0 g/g at 90°C (Singh et al., 2006).

2.6.4 Freeze-Thaw Stability

The extent to which a starch gel will lose water (syneresis) after freezing and thawing reflects the tendency of the starch molecules to retrograde. Retrogradation is the phenomenon of molecular re-association between starch chains, particularly the linear chains of amylose (Morris, 1990), which causes water to exude from the molecular structure of a frozen-thawed (or refrigerated) starch gel. In addition, upon freezing, water forms ice crystals which can damage the structure and the water holding capacity of a starch gel, thereby contributing to syneresis. Crystallization during retrogradation and freeze-thaw is a three-step process: nucleation, crystal growth and maturation (perfection). Nucleation typically begins with the formation of a 'junction

zone' where glucans may associate via non-covalent interactions (primarily hydrogen bonding), increasing gel strength (Charoenrein & Udomrati, 2007). As the junction zone enlarges, glucans crystallize and exude water. Retrogradation can be accelerated during freeze-thaw cycles by increasing the rate and size of ice crystal formation, as their physical presence will force leached glucans together, increasing associations. Retrogradation and syneresis can be controlled somewhat by the inclusion of agents that promote (e.g. certain sugars such as fructose) or reduce (e.g. certain hydrocolloids) the formation of junction zones. Additionally, chemically-modified starches, particularly substituted starches, typically inhibit the formation of junction zones, reducing syneresis in food systems. The addition of hydrocolloids may reduce junction zone formation and, thereby, reduce syneresis associated with freeze-thaw cycles. Ferrero et al. (1994) postulated that the addition of xanthan gum to corn starch reduced interactions between amylose molecules. The proposed mechanism is discussed in Section 2.11.4.

2.6.5 Water Binding Capacity

Water binding capacity refers to the ability of a material to retain water during the application of a specific centrifugal force. The water binding capacity of several corn starches ranged from 82.3-97.7% (Sandhu & Singh, 2007). Kereliuk & Sosulski (1996) reported that the water binding capacity of three corn starches ranged from 104.3-107.1%; the water binding capacity of potato starch in this study was 93.8%. These authors postulated that the water binding capacity of potato starch was restricted due to its content of phosphate cross-linkages. Water binding capacity reflects the ability of starch to absorb water into the granule and to bind water to the granule surface (Medcalf & Gilles, 1965). An increased amylose concentration increases hydrogen bonding opportunities between and within amylose molecules. Hydrogen bonding site

availability varies based on granule arrangement, amorphous to crystalline ratio and amylose to amylopectin ratio.

2.7 Resistant Starch

Starch can be classified as rapidly digestible starch, slowly digestible starch (SDS) or resistant starch (RS). Resistant starch is defined as starch able to withstand enzymatic attack and absorption in the small intestine of a healthy individual (Englyst et al., 1992). Resistant starch exists in four forms: RS_1, physically entrapped starch; RS_2, native ungelatinized starch granules; RS_3, retrograded starch; and RS_4, chemically-modified starch (Haralampu, 2000). Baghurst et al. (1996) recommended that individuals consume 20 g of RS per day, indicating that the majority of the dietary fibre consumed should be RS.

Consumption of resistant starch is associated with numerous health benefits. Resistant starch increases fecal bulk and colonic fermentation, positively affecting colonic health (Jenkins et al., 1998). Colonic fermentation of RS produces short-chain fatty acids (SCFAs) including butyrate, propionate and acetate. Short chain fatty acids, particularly butyrate and propionate, are important to the maintenance of a healthy colon and may reduce the risk of inflammation and colorectal cancer (Ahmed et al., 2000; Brouns et al., 2002). Feeding rats *Phaseolus vulgaris* flours high in RS promoted the production of butyrate (Henningsson et al., 2001). The extent of butyrate production from resistant starches varies based on the botanical source of the starch. Native and gelatinized wheat, potato and pea starches were able to be used by various *Bifidobacterium* strains (Soral-Smietana et al., 2005). These authors reported 0-2.6%, 42.4-62.9% and 66.8-72.2% utilization of the resistant fraction in native starches from wheat, potato and pea, respectively, by *B. pseudolongum, B. animalis* and *B. breve* KN14 indicating that pea starch may be a suitable candidate for healthy gut flora.

The addition of RS to wheat bran benefited fecal bulking, transit time and colonic fermentation in humans to a greater extent than did wheat bran alone (Muir et al., 2004). Psyllium and HACS had a synergistic effect, increasing fecal butyrate concentrations in rats when compared to HACS alone or low-amylose corn starch with psyllium (Morita et al., 1999). Additionally, RS alters bacterial metabolism and fecal concentrations of neutral sterols, potentially reducing the risk of colon cancer (Hylla et al., 1998).

Increasing RS consumption appears to increase postprandial insulin sensitivity in healthy humans, thus possibly improving glucose tolerance in individuals with Type 2 diabetes (Axelsen et al., 1999; Robertson et al., 2003).

Resistant starch decreased the anti-nutritional effects of phytic acid (e.g. negative mineral balance) in a rat model (Lopez et al., 1998). RS increased mineral absorption in the colon of rats (Lopez et al., 2000; Lopez et al., 2001; Younes et al., 2001). This phenomenon may be a result of colonic fermentation causing a hypertrophy of the intestinal wall and intestinal acidification, thus increasing mineral absorption, particularly of calcium, magnesium, iron, zinc and copper (Lopez et al., 1998; Lopez et al., 2000).

A shortage of low glycemic index food products has been reported (Bjorck et al., 2002). Legumes elicit muted blood glucose responses (Foster-Powell & Brand Miller, 1995; Jenkins et al., 1981), possibly due to their higher concentration of total dietary fibre, RS and SDS compared to cereals (Bednar et al., 2001). Resistant starch concentration is influenced by amylose concentration (Hoover & Sosulski, 1985), proportion of B-type polymorphs (Hoover & Sosulski, 1985), interactions between glucans (Zhou et al., 2004), amount of amylose-lipid complexation (Guraya et al., 1997; Holm et al., 1983; Hoover & Manuel, 1995; Tufvesson et al., 2001), starch granule size (Snow & O'Dea, 1981), surface porosity (Huber & BeMiller, 1997; Kong et al.,

2003), and the presence of antinutritional factors such as lectins (Thompson & Gabon, 1987) and alpha-amylase inhibitors.

An investigation into the hydrolysis rates of starches from pea, lentil, pinto and black bean showed that the interaction between starch chains in the amorphous region of the granule and interactions between hydrolyzed amylose chains during the hydrolysis reaction influenced the hydrolysis rate and the amount of starch hydrolyzed by alpha-amylase (Zhou et al., 2004). Pinto bean exhibited a lower initial velocity of hydrolysis than did smooth pea, black bean, lentil and wrinkled pea, indicating that pinto bean may have stronger interactions between the amorphous and crystalline regions than do smooth pea, black bean, lentil and wrinkled pea.

Heat-moisture treatment (HMT) of high-amylose corn starch (HACS) (70% amylose) increased the RS concentration from 30% to 65% as determined by a rat model (Ito et al., 1999). The HMT-HACS was not fermented in the rat caecum and was excreted in the feces, whereas the untreated HACS was not digested or absorbed in the small intestine but was fermented in the caecum (Ito et al., 1999). Even with the increased dietary fibre concentration of the HMT-HACS, normal physiological benefits (fecal neural sterol excretion, SCFA production and enhanced mineral absorptions) were not observed in rats (Kishida et al., 2001) as the HMT-HACS passed through the rat gastrointestinal tract without being fermented. Heat-moisture or any other treatment or processing of starch that alters the amylose concentration, proportion of B-type polymorphs, interactions between glucans, amount of amylose-lipid complexation, surface porosity or the presence of anti-nutritional factors may affect its resistant starch concentration.

2.8 Functionality of Starch Blends

Numerous studies on the functional properties of blends of starches with flours, proteins, fibres, hydrocolloids and fats have been published, but few studies on blending legume starches with other starches exist.

The DSC traces of blends of wheat and rice starches at 30% were effectively the 'sums' of their constituent starches (Liu & Lelièvre, 1992). However, the DSC traces of the blends were non-additive for 50% suspensions, due to competition for water at higher starch concentrations (Liu & Lelièvre, 1992). Blends of corn starch and potato starch (75:25; w/w), wheat starch and tapioca starch (85:15; w/w), rice starch and potato starch (50:50; w/w) and Polar-Gel 18 (stabilized waxy corn starch) and Hylon V (75:25; w/w) exhibited single peaks in the DSC traces whereas the blend of 50:50 wheat starch and rice starch (w/w) exhibited two peaks (Obanni & BeMiller, 1997). Blends of lima bean starch and cassava starch possessed single endotherm transitions (Novelo-Cen & Betancur-Anacona, 2005). Most DSC traces of blends of amaranth starch and potato starch displayed two peaks corresponding to those of the individual starches, indicating independent gelatinization (Gunarathe & Corke, 2007).

Blends of yam starch with cassava starch, corn starch or both starches exhibited lower onset temperatures of gelatinization (T_o) than did yam starch (Karam et al., 2006). Blends of wheat flour with starches from potato, sweet potato, yam or cassava exhibited higher peak temperatures of gelatinization (T_p) than did wheat flour (Zaidul et al., 2008). Blending of starches with widely different gelatinization temperatures can result in restricted gelatinization of the starch with the higher gelatinization temperature due to competition for available water (Karam et al., 2006). Blends of yam starch with cassava starch, corn starch or both starches exhibited lower *ΔH* values than the constituent starches (Karam et al., 2006). Blends of corn starch with yam starch, cassava starch or both starches exhibited higher ΔH values (Karam et al., 2006).

The pasting curves of blended corn and waxy corn starch differed from those of the individual starches (Obanni & BeMiller, 1997). The curve for the 1:1 (w/w) blend of corn starch and waxy corn starch exhibited two viscosity peaks. The first viscosity peak was attributed to the pasting peak of waxy corn starch at 72°C, and the second viscosity peak to the corn starch pasting peak at 92°C. A 3:1 (w/w) blend of modified (stabilized) waxy corn starch and HACS produced an amylogram with no peak viscosity and less setback than was observed in the modified waxy corn starch pasting curve. The pasting curve of this blend resembled that of a cross-linked corn starch. Further investigation by Obanni & BeMiller (1997) revealed amylose was entrapped or bound by the granule ghosts of modified waxy corn, indicating the possibility of interactions between glucan molecules and granule structures. Granule ghosts may be defined as the remnants of starch granules remaining after heating and the release of starch molecules (Han & Hamaker, 2002). Furthermore, granule ghosts may be formed when starches swell slowly, allowing for cross-linking and stabilization of glucan molecules (Debet & Gidley, 2007). Surface proteins, such as granule-bound starch synthase (GBSS), may provide stability to the granule ghost (Han & Hamaker, 2002).

A 1:3 (w/w) blend of lima bean starch and cassava starch displayed no retrogradation, high viscosity and heat-cool cycle stability (Novelo-Cen & Betancur-Anacona, 2005). Blends of amaranth starch and potato starch exhibited two viscosity peaks; the authors postulated that the two viscosity peaks were due to the large differences in pasting temperature, swelling and amylose leaching between the two starches (Gunarathe & Corke, 2007). These researchers indicated that the blends of amaranth starch and potato starches behaved in a non-additive manner and increased the stability of the hot paste viscosity. Blends of HMT potato starch and

native amaranth starch exhibited lower peak viscosities than did potato starch and produced a very soft gel.

Blends of cassava starch and lima bean starch exhibited increased SP, water absorption and gel clarity as compared to lima bean starch, beneficially altering the functionality of both starches (Novelo-Cen & Betancur-Anacona, 2005). Blends of potato starch and rice starch exhibited SPs and water solubility indices (WSIs) that were intermediate to the SPs of the constituent starches (Sandhu et al., 2010).

Blending cassava, yam and corn starches minimized the negative characteristics of each starch, improving the functionality of the blend compared to the individual starches (Karam et al., 2005). A 2:3 (w/w) blend of cassava starch and yam starch exhibited decreased exudate production when compared to the yam starch when stored at 4°C (Karam et al., 2005).

Blending pea starch with corn starch for use in puddings has been patented (Stute & Kern, 1994). The inventors claim that blends of pea starch and corn starch in ratios between 8:2 and 4:6 (w/w) reduced the syneresis of pea starch and performed well as a gelling or texturizing agent in puddings. Blending of the corn starch mutants *duh* and *ae du* has been patented, as the behaviour of the blended starch was similar to that of chemically cross-linked starches (Friedman et al., 1988a, Friedman et al., 1988b). The corn starch mutant *ae du* contains 50% amylose and possesses a C-type diffraction pattern (Matveev et al., 2001), indicating that blending starches with C-type diffraction patterns with A- or B-type starches may produce starches with novel characteristics.

2.9 Functionality of Heat-Moisture-Treated Starches

Annealing and heat-moisture treatment (HMT) are common hydrothermal methods for modifying the physicochemical properties of starch. Annealing involves elevating the moisture

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content of starch to intermediate (40-55%) or high (> 60%) levels and heating to temperatures in excess of the glass transition temperature but below the gelatinization temperature. Heat-moisture treatment of starches involves heating starch above its glass transition temperature with a moisture concentration of less than 35%, typically 18-27%. Heat-moisture-treatement is a common pre-treatment of starches used in infant foods and baked products to modify potato starch such that it behaves more like corn starch, especially with respect to its baking characteristics (Collado & Corke, 1999; Lorenz & Kulp, 1981).

Tuber starches are more susceptible to HMT than are cereal or legume starches (Hoover & Vasanthan, 1994b; Jacobs & Delcour, 1998), due to the B-type double helical arrangement of amylopectin within the potato starch granule. Heat-moisture treatment altered the diffraction pattern of potato and true yam (*Dioscorea alata*) starch from B-type to A-type plus B-type (Gunaratne & Hoover, 2002) and from C-type to A-type in sweet potato starch (Shin et al., 2005). Heat-moisture treatment decreased the apparent amylose concentration in amylomaize V and normal maize starches (Hoover & Manuel, 1996a) and in wheat, oat and lentil starches (Hoover & Vasanthan,1994b).

Heat-moisture treatment increased the gelatinization temperature of starches from sweet potato (Collado & Corke, 1999), potato (Donovan et al., 1983, Gunaratne & Hoover, 2002), true yam (Gunaratne & Hoover, 2002), new cocoyam (Gunaratne & Hoover, 2002), cassava (Gunaratne & Hoover, 2002), taro (Gunaratne & Hoover, 2002), wheat (Donovan et al., 1983), amylomaize V and normal maize (Hoover & Manuel, 1996a) and black bean, pinto bean, pea and lentil (Hoover & Manuel, 1996b). Heat-moisture treatment also broadened the gelatinization temperature range in starches from amylomaize V and normal maize (Hoover & Manuel, 1996a) and in starches from potato and wheat (Donovan et al., 1983). Heat-moisture treatment did not affect the gelatinization temperature of waxy maize starch (Hoover & Manuel, 1996a) nor did it

affect ΔH in starches from amylomaize V, normal maize, waxy maize and dull waxy maize (Hoover & Manuel, 1996a) or black bean, pinto bean, pea or lentil (Hoover & Manuel, 1996b), indicating that glucan double helices were not disrupted during the HMT process utilized by these researchers. Hoover & Vasanthan (1994b) reported no change in ΔH due to HMT in starches from wheat, oat or lentil, and a reduction in ΔH of potato starch and yam starches. Heat-moisture treatment decreased ΔH in starches from potato, true yam, cassava, taro and new cocoyam, possibly due to double helices being disrupted during thermal treatment (Gunaratne & Hoover, 2002). All DSC traces of blends of potato starch and amaranth starch displayed two peaks corresponding to those of the individual starches (Gunaratne & Corke, 2007).

Heat-moisture treatment decreased the pasting viscocities of amylomaize V and normal maize starches (Hoover & Manuel, 1996a) and of sweet potato starches (Collado & Corke, 1999). Blends of HMT potato starch and native amaranth starch exhibited lower peak viscosites than did potato starch (Gunaratne & Corke, 2007). Blends of HMT potato starch and HMT amaranth starch exhibited lower peak viscosities than those of either HMT potato starch or HMT amaranth starch, indicating the potential of non-additive behaviour of blending heat-moisture-treated starches. Similar effects were obtained for both hot paste viscosity and cold paste viscosity. Gunaratne & Corke (2007) also found that blends of HMT potato starch and HMT amaranth starch exhibited less breakdown than did HMT amaranth starch when blended up to 1:1 (w/w), but as the concentration of HMT amaranth starch increased to 70% or 90%, breakdown during pasting occurred. Setbacks of all blends of HMT potato starch and HMT amaranth starch were lower than for either HMT starch individually. These two starches underwent HMT separately.

Heat-moisture treatment decreased SP in starches from sweet potato (Collado & Corke, 1999), wheat and potato (Kulp & Lorenz, 1981), potato, cassava and taro (Gunaratne & Hoover,

2002), amylomaize V, normal maize, waxy maize and dull waxy maize (Hoover & Manuel, 1996a), and green arrow pea, black bean, pinto bean, pea and lentil (Hoover & Manuel, 1996b). Heat-moisture treatment decreased syneresis in starches from amylomaize V, normal maize, waxy maize and dull waxy maize during freeze-thaw cycles (Hoover & Manuel, 1996a).

2.10 Functionality of Pregelatinized Starches

Pregelatinized starches are important in food manufacturing as these starches are cold water soluble and thickening (Doublier et al., 1986). This functional characteristic is important in instant food products. Pregelatinization is achieved using drum, roll or spray drying or by extrusion processing. By altering the parameters of the pregelatinization process, the functional characteristics of the pregelled starch may be varied and can be adapted to many food applications. Typically, pregelatinized starches exhibit lower pasting viscosities than do native starches (BeMiller & Whistler, 1996). No reports exist on the functionality of blends of pregelatinized starches.

2.11 Functionality of Pea Starch and Non-Starch Hydrocolloid Blends

Non-starch hydrocolloids (referred to hereafter as hydrocolloids), such as guar gum, locust bean gum, xanthan gum and carboxymethyl cellulose, are used to modify the structure and texture of both food and non-food systems. Guar gum is a neutral galactomannan consisting of a β-1, 4-D-mannose backbone with galactose residues linked to it. Locust bean gum is a neutral galactomannan, similar to guar gum, except that it contains fewer galactose side units and the galactose side chains are unevenly distributed along the mannose backbone. Due to the differences in galactose substitution on the mannan backbone, guar gum completely hydrates in cold water, whereas locust bean gum does not hydrate completely in cold water and typically

requires heating to about 60°C to solubilize completely (Hoefler, 2004). Xanthan gum is an anionic heterogeneous polymer consisting of a β-linked glucose backbone and side chains of a single unit of glucuronic acid and two units of mannose (Hoefler, 2004). Carboxymethyl cellulose is an anionic, synthetic gum derived from cellulose by reacting cellulose with sodium hydroxide and monochloroacetic acid to derivitize hydroxyl groups to carboxymethyl ether groups. Carboxymethyl cellulose exhibits thinning when heated and is easily solubilized (Hoefler, 2004). Typical commercial usage levels of guar gum, locust bean gum, xanthan gum are 0.35-2.0% (BeMiller, 2007), 0.15-0.8% (BeMiller, 2007) and 0.1-0.5% (Chantaro & Pongsawatmanit, 2010), respectively.

2.11.1 Thermal Properties

Several researchers have demonstrated modifications to starch functionality with the addition of hydrocolloids. It has been reported that the addition of hydrocolloids to starch enhanced its gelatinization, pasting and retrogradation properties (Alloncle & Doublier, 1991; Alloncle et al., 1989; Christianson et al., 1981; Fanta & Christianson, 1996; Funami et al., 2005; Gudmundsson et al., 1991; Kim & D'Appolonia, 1977).

Single endotherm peaks in DSC traces were observed with yam, taro, sweet potato and yam bean with guar gum or locust bean gum (Huang, 2009) as well as with tapioca starch and xanthan gum (Chantaro & Pongsawatmanit, 2010). The addition of 0.3% acacia gum to water chestnut starch increased the gelatinization temperature (Lutfi & Hasnain, 2009). Blends of starches with hydrocolloids exhibited lower ΔHs than did the constituent starch (Chiaswang & Suphanthanka, 2006; Huang, 2009; Viturawong et al., 2008). However, the addition of 1.0% of ß-glucan, arabinoxylan, guar gum or xanthan gum increased the ΔH and temperature range of gelatinization of wheat starch and waxy corn starch (Biliaderis et al., 1997).

2.11.2 Pasting Properties

Lower pasting temperatures (PTs) were observed for pea starch with locust bean gum or yellow mustard mucilage (Liu & Eskin, 1998), starches from yam, taro, sweet potato and yam bean with guar gum or locust bean gum (Huang, 2009), waxy corn starch with xanthan gum or guar gum (Achayuthakan et al., 2008), tapioca starch with xanthan gum (Chantaro & Pongsawatmanit, 2010; Pongsawatmanit & Srijunthongsiri, 2008) and rice starch with guar gum, hydroxypropyl methylcellulose or xanthan gum (Rosell et al., 2011). Alloncle et al. (1989) postulated that the PTs of mixtures of starch and hydrocolloids were lower than when compared to PTs of the respective starches may be due to an increase in the effective concentration of hydrocolloid and/or starch, resulting in higher viscosities earlier and, thus, a lower PT. The effective concentration of one component of a mixture changes as the amount of another component in the mixture changes. During pasting, the effective concentration of the hydrocolloid increases as glucan molecules leach from the starch molecule into the continuous phase. Another mechanism to explain the lower pasting temperatures of starch-hydrocolloid mixtures may involve hydrocolloids disrupting starch granule integrity (Liu et al., 2003) or by interactions with leached glucans (Shi & BeMiller, 2002). This increase in effective concentration along with interactions between molecularly-similar compounds may play a role in earlier viscosity generation of a starch-hydrocolloid mixture. However, not all starch-hydrocolloid blends exhibit lower PTs. The addition of xanthan gum or locust bean gum did not alter pasting temperature but did increase peak viscosity, of corn starch, potato starch and rice starch (Arocus et al., 2009).

Typically, blends of starch and hydrocolloids have higher viscosities than their respective starches. Water chestnut starch with 0.1-0.3% xanthan or guar gum or 0.3% acacia gum exhibited a higher peak viscosity than did water chestnut starch (Lutfi & Hasnain, 2009). Shi & BeMiller

(2002) found that mung bean starch with 0.4% of carboxymethyl cellulose or xanthan gum exhibited a higher viscosity than did mung bean starch. Rice starch with guar gum or xanthan gum exhibited a higher pasting viscosity than did rice starch or rice starch with hydroxypropyl methylcellulose (Rosell et al., 2011). Rice starch with guar gum, hydroxypropyl methylcellulose or xanthan gum exhibited a higher final viscosity than did rice starch (Rosell et al., 2011). Normal rice starch with methyl cellulose, ι-carrageenan or λ-carrageenan exhibited a higher peak viscosity than did normal rice starch or normal rice starch with carboxymethyl cellulose or κ-carrageenan (Techawipharat et al., 2008). Additionally, waxy rice starch with methyl cellulose, κ-carrageenan or λ-carrageenan exhibited a higher peak viscosity than did waxy rice starch or waxy rice starch with carboxymethyl cellulose or ι-carrageenan (Techawipharat et al., 2008). The concentration of the hydrocolloid increases as the starch swells leading to a synergistic viscosity increase (Alloncle et al., 1989). The addition of 0.3% acacia gum to water chestnut starch reduced setback (Lutfi & Hasnain, 2009). Rice starch with guar gum exhibited higher breakdown than did rice starch or rice starch with HPMC or xanthan gum (Rosell et al., 2011). Guar gum increased the setback of tapioca starch, whereas xanthan gum reduced setback indicating that xanthan gum may reduce retrogradation of tapioca starch (Chaisawang & Suphansarika, 2006). Furthermore, corn starch, waxy corn starch, potato starch or rice starch with xanthan gum exhibited lower setback than did their respective individual starches (Arocus et al., 2009). Rosell et al. (2011) suggested that the synergistic effect of the addition of hydrocolloids to starches may be due to "entrapment of water molecules by starch granule aggregates bound by hydrocolloid molecules". Shear forces exerted on starch granules and leached glucans are greater with hydrocolloids present in the continuous phase (Christianson et al., 1981). This increase in shear may increase the concentration of leached glucans present in the continuous phase, increasing viscosity.

2.11.3 Swelling Power and Water Solubility

Previous research indicated that starch with hydrocolloids exhibited lower SPs and water solubilities than did the corresponding starch due to increased hydrogen bonding between hydrocolloids and leached glucans (Christianson, 1981; Huang, 2009; Liu et al., 2006) possibly due to a decrease in starch granule integrity due to shear from the hydrocolloid, increased water uptake, and leaching of glucans (Christianson et al., 1981; Techawipharat et al., 2008). The effect of each hydrocolloid will vary based on possible interactions with leached glucans as each hydrocolloid differs in molecular composition and/or structure. However, the effect on SP differs with the type of hydrocolloid in the mixture. For example, rice starch with guar gum exhibited lower SPs than did rice starch, rice starch with xanthan gum exhibited higher SP than did rice starch, and rice starch with hydroxypropyl methylcellulose exhibited SPs that were not significantly different than that of rice starch (Rosell et al., 2011). Waxy rice starch with methyl cellulose exhibited lower SPs than did waxy rice starch or waxy rice starch with hydroxypropyl methylcellulose, carboxymethyl cellulose, ι-carrageenan, λ-carrageenan or κ-carrageenan (Techawipharat et al., 2008). Achayutakan et al. (2006) found that waxy corn starch or cross-linked waxy corn starch with xanthan gum possessed larger swollen granule size than was the case without xanthan gum present. Normal rice starch and carboxymethyl cellulose exhibited higher SPs and WSIs than did normal rice starch (Techawipharat et al., 2008). Normal rice starch with carboxymethyl cellulose, methyl cellulose, hydroxypropyl methylcellulose or carrageenans (ι, κ, λ) exhibited higher WSIs than did normal rice starch (Techawipharat et al., 2008). Waxy rice starch with carboxymethyl or ι-carrageenan exhibited higher SPs than did waxy rice starch (Techawipharat et al., 2008).

2.11.4 Freeze-Thaw Stability

Typically, the addition of hydrocolloids reduced syneresis during freeze-thaw cycles by reducing junction zone formation. Retrogradation is the crystallization of leached glucans, primarily amylose, in a process that includes nucleation, crystal growth and maturation. Glucans associate via non-covalent interactions and overlap, creating a junction zone (nucleation point) for crystal growth. Xanthan gum improved the freeze-thaw stability of tapioca starch (Pongsawatmanit & Srijonthongsiri, 2008). Starch from corn, waxy corn, potato or rice with 0.15% of locust bean gum or xanthan gum exhibited lower syneresis than did their respective constituent starches after one freeze-thaw cycle (Arocus et al., 2009). The addition of alginate, guar gum or xanthan gum to sweet potato starch improved the freeze-thaw stability of sweet potato starch, where xanthan gum was more effective than guar gum and both guar gum and xanthan gum were more effective than alginate (Lee et al., 2002). Muadklay & Charoenrein (2008) reported that tapioca starch with 0.25% or 0.50% xanthan gum exhibited lower syneresis after freezing and thawing than did tapioca starch. These authors also reported that blends of tapioca starch and xanthan gum exhibited lower syneresis values than did blends of tapioca starch and locust bean gum. Tapioca starch with guar gum exhibited synersis values that were not significantly different than those of tapioca starch (Muadklay & Charoerein, 2008). Starch from corn, waxy corn, potato or rice and 0.15% of xanthan or locust bean gum exhibited lower syneresis than did their repsective consituent starches after one freeze-thaw cycle (Arocus et al., 2009). Ferrero et al. (1994) postulated that the addition of hydrocolloids increased the glass transition temperature of the starch by reducing the amount of water available for starch mobility and, consequently, molecular associations. The addition of an anionic gum such as xanthan gum to corn starch may reduce interactions as the presence of an anion may promote dissociation of the hydroxyl group (Funami, 2009). With the diffusion of hydrogen ions away from the glucan

polymer, a net negative charge is associated with the glucan polymer, resulting in glucans repelling anionic hydrocolloid molecules (Funami, 2009).

2.11.5 Shear Stability

The addition of hydrocolloids to starches may promote or reduce shear stability depending on the interactions between the hydrocolloid and starch. Tye (1988) reported that corn starch with 0.2% κ-carrageenan did not recover to preshear viscosity, but that blends of corn starch with 0.2% or 0.5% ι-carrageenan or 0.5% κ-carrageenan did recover to preshear levels. Tye (1988) indicated also that hydrocolloids may protect starch against shear, and Mandala et al. (2004) postulated that hydrocolloids participate in entangling with starch increasing its shear stability.

2.11.6 Resistant Starch

Gularte & Rosell (2011) reported that corn starch with hydrocolloids exhibited higher rapidly digestible starch concentrations, with no significant difference in RS concentrations, for blends of corn starch and 2% methoxylated pectin, guar gum or carboxymethyl cellulose, and RS concentrations were lower for blends of corn starch with 2% xanthan gum or hydroxypropyl methylcellulose. Additionally, Gularte & Rosell (2011) reported that blends of potato starch and 2% methoxylated pectin, guar gum, xanthan gum or carboxymethyl cellulose exhibited higher RS values than did potato starch. The authors postulated that the resistant starch concentration and hydrolysis kinetics may be influenced by alterations in swelling and viscosity of the starches, potentially due to inclusion of hydrocolloids.

3. EFFECT OF GENOTYPE AND ENVIRONMENT ON THE CONCENTRATIONS OF STARCH AND PROTEIN IN, AND THE PHYSICOCHEMICAL PROPERTIES OF STARCH FROM, FIELD PEA AND FABABEAN*

3.1 Abstract

The effects of genotype and environment, and their interaction, on the concentrations of starch and protein in, and the amylose concentrations and thermal and pasting properties of starch from, pea and fababean were not well known.

Differences due to genotype were observed in the concentrations of starch and protein in pea and fababean, in the onset temperature (T_o) and peak temperature (T_p) of gelatinization of fababean starch, and in the pasting, trough, cooling and final viscosities of pea starch and fababean starch. Significant two-way interactions (location x genotype) were observed for the concentration of starch in fababean and the amylose concentration, To, endothermic enthalpy of gelatinization (ΔH) and trough viscosity of fababean starch. Significant three-way interactions (location x year x genotype) were observed for the concentration of starch in pea and the pasting, trough, cooling and final viscosities of pea starch.

Differences observed in the concentrations of starch and protein in pea and fababean are sufficient to be of practical significance to end-users, but the relatively small differences in amylose concentration and physicochemical characteristics of starch from pea and fababean likely are not.

3.2 Introduction

Pea (*Pisum sativum* L.) and fababean (*Vicia faba* L.) belong to the Leguminosae family. Pea and fababean are considered pulses due to the starchy nature of the cotyledon. Starch is a homogeneous glucose polymer where glucose residues are linked via α-1, 4 and α-1, 6 bonds, with α-1, 6 bonds forming branch points in the starch molecule. Amylose is mostly linear with minimal branching, whereas amylopectin is highly branched. Branch points of amylopectin are primarily located in the amorphous regions of B-type starches and distributed in both the amorphous and crystalline regions in A-type starches (Jane et al., 1997). Typically, pea and fababean starch exhibits an intermediate amylose concentration of 32.0-35.0 % (Biliaderis et al., 1979). Storage compounds of seeds are affected by environment and genetics (Hucl & Chibbar, 1996; Morris, 2004). Amylose-amylopectin ratio, granule size and starch granule arrangement affects the functional behaviour of starches. Pulse starches tend to have high pasting temperatures, no peak viscosity and high set-back (Hoover et al., 2010).

Starches from different genotypes of wheat (Wootton & Mahdar, 1993), rye (Gudmundsson et al., 1991), maize (Yun et al., 1993), millet (Yanez et al., 1991), cassava (Asaoka et al., 1991) and lentil (Hoover & Manual, 1995) differ in functionality. No significant differences among starches from four pea genotypes (Carneval, Carrera, Grande and Keoma) in swelling factor, pasting temperature, freeze-thaw characteristics, or the rate of acid or enzyme hydrolysis were detected despite variations in B-polymorph concentration and amylopectin branching (Ratnayake et al., 2001). Carneval had a slightly higher onset temperature (T_o) of gelatinization (61.4°C) than did Carrera, Grande and Keoma (61.0°C). Grande had a slightly higher peak temperature (T_p) of gelatinization than did Carneval, Carrera and Keoma (67.5°C versus 67.0, 66.8 and 67.0°C), respectively. Carrera had a lower completion temperature (T_c) of

gelatinization (75.0°C) than did Carneval, Grande and Keoma (76.0°C). The range in enthalpy of gelatinization (ΔH) for these four genotypes was 11.2-11.5 J/g. The four genotypes contained similar genetic markers and are closely related genetically when compared to other pea genotypes available (Tar'an et al., 2005). Pea genotypes Latah and SS Alaska exhibited no differences in T_o, T_p, ΔH, swelling power (determined by a gravimetric method), gel hardness at 22°C, gel cohesiveness or gel springiness (Czuchajowska et al., 1998).

Four genotypes of cassava grown and harvested under different conditions exhibited significant differences among genotypes in the texture of starch gels, as well as within one genotype grown under different conditions (conditions not specified by authors) (Asaoka et al., 1991). Cottrell et al. (1995) reported that warmer growing conditions increased the gelatinization temperature, amylose concentration and alpha-amylase resistance of potato starch. Nikolopoulou et al. (2007) reported that the starch concentrations of three pea genotypes, grown in three locations over two years, were significantly different. These authors also reported that pea genotypes grown under conditions of less rainfall possessed lower starch and higher protein concentrations, and reported significance for location and the location by year interaction for differences in starch concentration. A significant genotype by environment interaction was found for starch concentration in chickpea and amylose concentration in chickpea starch (Frimpong et al., 2009). No studies have been published regarding the effect of genotype or environment on the composition of fababean or fababean starch functionality.

A broader study on the effects of genotype and the environment on the composition of pea and fababean, and on the physicochemical characteristics of starch isolated from pea and fababean, might provide valuable information to both breeders and processors, including insight into the heritability of these traits. The primary objectives of this study were to determine the

effect of genotype and the environment, and their interaction, on the concentrations of starch and protein in pea and fababean, and on the amylose concentrations in, and the thermal and pasting properties of, starch isolated from pea and fababean.

3.3 Materials and Methods

3.3.1 Samples

Two samples of each of ten field pea genotypes (Bluebird, CanStar, CDC Striker, CDC Tucker, Cooper, Cutlass, Fusion, Reward, SW Marquee and Tamora) grown in four locations in Saskatchewan, Canada [Elrose, Hodgeville, Melfort and Saskatoon (Sutherland)] in each of 2006 and 2007 were provided by the Crop Development Centre, University of Saskatchewan. Two samples from each of eleven fababean genotypes (CDC Fatima, Disco, Dixie, Florent, Gloria, Imposa, NPZ4-7460, NPZ4-7540, NPZ5-7530, Snowbird and SSNS-1) grown in three locations in Saskatchewan in 2006 [Melfort, Saskatoon (Sutherland) and Saskatoon (SPG)] and two locations in Saskatchewan [Outlook and Saskatoon (Sutherland)] and one location in Manitoba, Canada (Roblin) in 2007 also were provided by the Crop Development Centre, University of Saskatchewan. Due to crop loss or lack of sufficient seed for starch isolation, some fababean samples were unavailable, i.e. both replications from the Saskatoon (Sutherland) location, year 2006, genotype Imposa; the Saskatoon (SPG) location, year 2006, genotypes Disco and Dixie; and one replication from the Saskatoon (SPG) location, year 2006, genotype Florent.

The pedigrees of the pea and fababean genotypes are presented in Table 3.1. The soil type and meteorological characteristics for each location are presented in Table 3.2. Genotypes and locations were selected on the basis of diversity in pedigree, soil and meteorological characteristics, respectively, and availability of seed. With the exception of a few genotypes not

Table 3.1 Description of pea and fababean genotypes used in the study

Pea	Breeding institution	Pedigree
Bluebird	Limagrain	91527 x CEB 1136
CanStar	Agriculture and Agri-Food Canada	DS Stalwarth/Aladin
CDC Striker	Crop Development Centre	Majoret/P28RS-281
CDC Tucker	Crop Development Centre	CDC9708/184-3-Y//CDC9706/Canis///CDC Handel
Cooper	Limagrain	Baccara/92585
Cutlass	Alberta Agriculture and Crop Development Centre	Carneval///Miranda/Carrera//Montana/CDC Winfield
Fusion	Limagrain	Maribu x Agadir
Reward	Agriculture and Agri-Food Canada	DS Stalwarth/MP1491
SW Marquee	Svalof Weibull	Highlight x SW C 38114
Tamora	Limagrain	Baccara/92585
Fababean		
CDC Fatima	Crop Development Centre	Outlook x Chinese Broad Bean
Disco	INRA	Unknown
Dixie	INRA	Unknown
Florent	NPZ Lembke	Unknown
Gloria	Saatzucht Gleisdorf	Unknown
Imposa	Limagrain	94012 x Pistache
NPZ4-7460	NPZ Lembke	Unknown
NPZ4-7540	NPZ Lembke	Unknown
NPZ5-7530	NPZ Lembke	Unknown
Snowbird	Limagrain	Unknown
SSNS-1	Crop Development Centre	Mass selection from Ackerperle

Table 3.2 Soil zone, monthly and total precipitation, and monthly and mean temperatures during the growing season at trial locations[1]

Location	Soil Zone	Year	Temp/Precip	May	June	July	Aug	Mean
Elrose (Rosetown)	Dark Brown	2006	°C	11.6	15.8	19.4	18.0	16.2
			mm	56.4	70.0	31.6	56.6	215
		2007	°C	10.2	15.1	20.6	15.8	15.4
			mm	38.2	121.4	33.4	40.4	233
Hodgeville (Swift Current)	Brown	2006	°C	12.3	16.2	21.0	19.1	17.2
			mm	34.9	96.8	30.6	20.6	183
		2007	°C	11.4	15.7	22.6	17.7	16.9
			mm	37.1	56.0	9.8	19.0	122
Melfort (Melfort)	Black	2006	°C	11.1	16.7	18.3	17.1	15.8
			mm	63.0	73.6	38.6	45.4	221
		2007	°C	9.6	14.4	20.1	14.7	14.7
			mm	54.0	119.0	46.8	39.2	259
Outlook (Outlook)	Brown	2007	°C	10.8	15.1	21.2	15.8	15.7
			mm	31.7	64.4	38.4	36.4	171
Roblin (Roblin)	Black	2007	°C	9.3	14.7	19.5	15.1	14.7
			mm	75.4	125.6	55.4	58.2	315
Saskatoon (Saskatoon)	Dark Brown	2006	°C	11.7	16.2	20.0	18.0	16.5
			mm	39.8	108.0	32.0	30.0	210
		2007	°C	11.2	15.0	21.0	15.8	15.8
			mm	46.0	131.0	22.0	17.5	217

[1] Meteorological data was obtained from the nearest Environment Canada weather station, which is shown in round brackets after the location (Environment Canada, 2011).

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being available, genotypes were grown in all locations and in each location, under similar conditions, allowing for greater detection of genotypic differences across locations.

Starch and protein concentrations were determined on flour samples ground using a cyclone mill (UDY Corp., Fort Collins, CO) to pass a 0.5-mm screen.

3.3.2 Laboratory Analyses

The starch and protein concentrations in seed and the amylose concentration in starch were determined according to Holm et al. (1986), method 46-30 of the AACC (2000) and Demeke et al. (1999), respectively.

Thermal properties were determined by differential scanning calorimetry (DSC) according to Ratnayake et al. (2001) utilizing a Q2000 modulated DSC (TA Instruments, New Castle, DE) using a sample size of 2.0 mg (db) and 70% total moisture (approximately 7.3 µL of deionized water added depending on the moisture content of the starch sample). A Rapid Visco Analyzer (Newport Scientific Ltd., Warriewood, Australia) was used to determine the pasting properties of starch according to standard method #2 with an 8% (w/v) slurry and a pH of 7.0 (Anonymous, 1998). Analyses were repeated a minimum of two times per biological replication.

The procedure used to isolate starch from pea and fababean began with soaking 100 g of seed overnight in 500 mL of water containing 0.5% (v/v) of ethanol (to inhibit microbial growth). The seed was then drained, rinsed and ground using a blender at low speed for 2 minutes. The puree was screened through 60- and 200-mesh sieves. The unders from the 200-mesh sieve were centrifuged at 15,000 x *g* for 10 minutes, the supernatant was decanted and the dark-coloured residue was scraped off the starch pellet, which was then reslurried in 0.05 N sodium hydroxide, mixed for 60 minutes and filtered through Whatman #4 filter paper. This filter cake was reslurried in deionized water, the pH was adjusted to 7.0 using 0.5 M HCl and the slurry was

filtered. This filter cake was reslurried in 50% (v/v) aqueous ethanol. The slurry was mixed for 5 minutes and then filtered. This filter cake was rinsed with 95% ethanol and dried overnight at room temperature.

3.3.3 Statistical Analysis

SAS PROC MIXED (SAS Institute Inc, Cary, NC) was used to detect differences among genotypes and environments in the starch and protein concentrations in, and in the amylose concentrations in and the thermal and pasting properties of starch isolated from, pea and fababean. Genotype was considered a fixed effect and year, location and replications within year by location were considered random effects. F-values were approximated (Satterthwaite, 1946; Cochran & Cox, 1992). Means were differentiated using Least Significant Differences.

Broad sense heritability (h^2) was calculated from the Type 3 sum of squares from the ANOVA generated utilizing PROC GLM (SAS Institute Inc, Cary, NC) using the following equation:

$$h^2 = \sigma^2_g / (\sigma^2_g + \sigma^2_{ge}/E + \sigma^2\varepsilon/ER) \tag{3.1}$$

where σ^2_g, σ^2_{ge} and $\sigma^2\varepsilon$ are variances for genotype, environment and ε (error), and E and R are the number of environments and replicates, respectively (Marwede et al., 2004).

3.4 Results and Discussion

For both pea and fababean, the dependent variables tested were the concentrations of protein and starch, the concentration of amylose in starch, onset temperature (T_o), peak temperature (T_p) and completion temperature (T_c) of starch gelatinization, endothermic enthalpy of starch gelatinization (ΔH), starch pasting temperature (PT), and pasting (PV), trough (TV), cooling (CV) and final viscosity (FV). The residual term (error term) was significant for all

dependent variables tested, thus there were factors that had significant effects on the variables tested but were not investigated in this study. A number of covariance parameters were found to be zero, indicating that these parameters did not influence the dependent variables.

3.4.1 Pea

The concentrations of protein and starch in pea ranged from 24.4-27.5% and 44.0-46.2% (dry basis), respectively (Table 3.3). Similar values have been reported by others for the concentration of protein in several pea genotypes grown in different locations (Wang & Daun, 2004a; Bing et al., 2006; Bing et al., 2007). Similar concentrations of starch (41.6-47.5%) were reported for four pea genotypes (Wang & Daun, 2004a). The concentration of amylose in pea starch ranged from 29.8-31.6% (Table 3.3). Both higher and lower values (ranging from 20.7-49.6%) have been reported for the amylose concentration in pea starch (Biliaderis et al., 1979; Gujska et al., 1994; Ratnayake et al., 2001; Wang & Daun, 2004a; Wang & Daun, 2004b) reflecting, in part, differences in the methodologies used for amylose determination, i.e. gel chromatography of debranched samples in the current study vs. iodine binding in most others. Genotype had a significant effect on protein and starch concentrations in pea, but not on the amylose concentration in pea starch (Table 3.4). CDC Striker and CDC Tucker were higher in protein than all other pea genotypes, and lower in starch than six of the genotypes analyzed. Cooper and Tamora share the same pedigree and exhibited protein, starch and amylose concentrations that were not significantly different. Additionally, Reward and CanStar exhibited protein, starch and amylose concentrations that were not significantly different (Table 3.3). This may be attributed to DS Stalwarth making up half of their pedigree (Table 3.1). A significant interaction between location and genotype was detected for protein concentration in pea. The location by year by genotype interaction for starch concentration in pea also was significant.

Table 3.3 Mean values for protein and starch concentrations (%, dry basis) in, and amylose concentrations (%) in starch isolated from, ten pea genotypes grown in four locations in Saskatchewan in each of 2006 and 2007*

Genotype	Protein	Starch	Amylose
Bluebird	25.0 ± 1.2b	45.5 ± 2.4a	31.5 ± 1.7a
CanStar	24.2 ± 1.2b	46.0 ± 1.5a	30.5 ± 1.0a
CDC Striker	27.5 ± 1.0a	44.0 ± 1.4b	31.1 ± 1.0a
CDC Tucker	27.1 ± 1.1a	44.1 ± 1.4b	30.6 ± 1.4a
Cooper	25.5 ± 1.4b	45.2 ± 1.7a	31.6 ± 1.6a
Cutlass	25.0 ± 1.8b	45.0 ± 0.7ab	30.9 ± 1.5a
Fusion	24.4 ± 1.1b	45.2 ± 1.3a	29.8 ± 1.4a
Reward	25.5 ± 1.5b	46.2 ± 1.7a	30.9 ± 1.9a
SW Marquee	25.3 ± 1.3b	45.7 ± 1.2a	30.3 ± 1.0a
Tamora	25.3 ± 1.7b	44.9 ± 1.6ab	31.6 ± 1.1a

*Means (± standard deviation) in the same column followed by the same letter are not significantly different ($p < 0.05$) as determined by Least Significant Differences.

Table 3.4 Analysis of variance for protein and starch concentrations in, and amylose concentrations in
starch isolated from, ten pea genotypes grown in four locations in Saskatchewan in each of
2006 and 2007

	Covariance Parameter Estimates		
Covariance Parameter	Protein	Starch	Amylose
Loc[a]	0.7914	0.4644	0.0000
Year	0.3066	0.4311	0.0000
Rep (Loc*Year)	0.0025	0.0000	0.0000
Loc*Year	0.6251	0.4735	0.2184
Loc*Ge[a]	0.1566*	0.0000	0.1247
Year*Ge	0.1514	0.0000	0.1383
Loc*Year*Ge	0.0694	0.6615*	0.0117
Residual	0.3643**	1.1410**	0.8067**

Type 3 Tests of Fixed Effects (Genotype)

Analysis	NumDF[b]	DenDF[c]	F-Value	Pr>F
Protein	9	14.3	7.70	0.0004**
Starch	9	63	3.36	0.0020*
Amylose	9	12.1	2.17	0.1048

* $p < 0.05$; **$p < 0.001$
[a] Loc = location and Ge = genotype, [b] NumDF = numerator degrees of freedom, [c] DenDF = denominator
degrees of freedom

Pea samples grown at Hodgeville and Elrose exhibited higher protein concentrations than did samples grown at Melfort and Saskatoon (Sutherland). Hodgeville and Elrose are in the Brown soil zone and more southerly located than are Melfort and Saskatoon (Sutherland), which are in the Black and Dark Brown soil zones, respectively. Hodgeville received lower levels of precipitation and had higher mean temperatures during the growing season of May to August in 2006 and 2007 than did the other locations used in this study (Environment Canada, 2011). Nikolopoulou et al. (2007) reported that the starch concentrations in three pea genotypes, grown in three locations over two years, differed significantly. These authors also reported that pea genotypes grown under conditions of less rainfall had lower starch and higher protein concentrations, and reported a significant effect of location on starch concentration and a significant location by year interaction for starch concentration.

Values for T_o, T_p, T_c, T_c-T_o and ΔH of pea starch ranged from 61.7-64.1°C, 68.6-69.7°C, 87.0-88.0°C, 23.2-24.7°C and 14.1-14.9 J/g, respectively (Table 3.5). A significant location by genotype interaction was detected for T_p (Table 3.6). The pea genotypes, Cooper and Tamora, had similar pedigrees and exhibited T_o, T_p, T_c, T_c-T_o and ΔHs that were not significantly different. Pea genotypes, CanStar and Reward, share half of their pedigree and also exhibited T_o, T_p, T_c, T_c-T_o and ΔHs that were not significantly different. Higher temperature during crop growth increased the gelatinization temperature and ΔH in rice (Asaoka et al., 1984), wheat (Shi et al., 1994) and potato starch (Tester et al., 1999). The slight effects of environment on the thermal properties of starch from pea in this study may be attributed to the small differences in temperature during crop growth in 2006 and 2007. Starch from pea grown at Hodgeville exhibited a higher T_p than did starch from pea grown at Elrose, Melfort or Saskatoon (Sutherland). Starch from pea grown at Melfort exhibited a lower T_p than did starch from pea grown at Elrose, Hodgeville or Saskatoon (Sutherland). Hodgeville is in the Brown soil zone,

Table 3.5 Mean values for onset temperature (T_o), peak temperature (T_p) and completion temperature (T_c) of gelatinization, the difference between T_c and T_o (T_c - T_o), and endothermic enthalpy (ΔH) of starch isolated from ten pea genotypes grown in four locations in Saskatchewan in each of 2006 and 2007*

Genotype	T_o (°C)	T_p (°C)	T_c (°C)	T_c - T_o (°C)	ΔH (J/g)
Bluebird	63.2 ± 2.2a	68.9 ± 1.6a	87.0 ± 2.4a	23.8 ± 2.4a	14.4 ± 1.3a
CanStar	64.1 ± 2.2a	69.7 ± 1.7a	87.9 ± 2.6a	23.8 ± 2.6a	14.3 ± 1.3a
CDC Striker	63.7 ± 2.4a	69.1 ± 1.7a	87.2 ± 3.0a	23.5 ± 3.0a	14.3 ± 1.3a
CDC Tucker	63.5 ± 3.0a	69.0 ± 2.2a	88.0 ± 3.4a	24.5 ± 3.4a	14.8 ± 1.3a
Cooper	64.0 ± 3.2a	69.3 ± 2.4a	87.2 ± 3.5a	23.2 ± 3.5a	14.1 ± 1.3a
Cutlass	61.7 ± 2.3a	69.2 ± 1.5a	87.4 ± 2.5a	23.9 ± 2.5a	14.4 ± 1.3a
Fusion	63.2 ± 2.7a	68.9 ± 1.8a	87.4 ± 3.0a	24.2 ± 3.0a	14.9 ± 1.3a
Reward	62.8 ± 2.5a	68.6 ± 1.8a	87.5 ± 2.4a	24.7 ± 2.4a	14.9 ± 1.3a
SW Marquee	63.9 ± 2.4a	69.3 ± 1.6a	87.7 ± 2.9a	23.8 ± 2.9a	14.1 ± 1.3a
Tamora	63.8 ± 3.1a	69.2 ± 2.2a	87.8 ± 3.2a	24.0 ± 3.2a	14.3 ± 1.3a

* Means (± standard deviation) in the same column followed by the same letter are not significantly different ($p < 0.05$) as determined by Least Significant Differences.

Table 3.6 Analysis of variance for onset temperature (T_o), peak temperature (T_p) and completion temperature (T_c) of gelatinization, the difference between T_c and T_o (T_c-T_o), and endothermic enthalpy (ΔH) of starch isolated from ten pea genotypes grown in four locations in Saskatchewan in each of 2006 and 2007

		Covariance Parameter Estimates			
Covariance Parameter	T_o	T_p	T_c	T_c - T_o	ΔH
Location	3.6789	2.1927	0.0633	2.5322	0.8982
Year	1.0690	0.3661	0.0000	0.2309	0.0280
Rep(Loc*Year)[a]	0.0000	0.0000	0.0000	0.0000	0.0000
Loc*Year	2.8967	1.1227	0.0000	3.7928	0.0081
Loc*Ge[a]	0.4578	0.2583*	0.0000	0.9688	0.1253
Year*Ge	0.0000	0.0052	0.0000	0.0000	0.0383
Loc*Year*Ge	2.55E-18	0.0913	0.0000	0.0000	0.2303
Residual	5.2699**	0.2269**	10.7231**	6.2185**	0.6628**

Type 3 Tests of Fixed Effects (Genotype)

Analysis	NumDF[b]	DenDF[c]	F-Value	Pr>F
T_o	9	27	1.17	0.3539
T_p	9	20.8	0.94	0.5134
T_c	9	147	1.10	0.3669
T_c - T_o	9	27	0.81	0.6094
ΔH	9	10	0.74	0.6705

* $p < 0.05$; **$p < 0.001$
[a] Loc = location and Ge = genotype, [b] NumDF = numerator degrees of freedom, [c] DenDF = denominator degrees of freedom

had higher mean temperatures and received lower levels of precipitation in the 2006 and 2007 growing seasons (May-August), whereas Melfort is in the Black soil zone, had lower mean temperatures and received higher levels of precipitation during the growing season in 2006 and 2007 (Environment Canada, 2011). Ratnayake et al. (2001) determined somewhat lower values for the To, Tp and Tc of pea starch (61.0-61.4°C, 66.8-67.5°C and 75.0-76.0°C, respectively). Starches from five pea genotypes grown in central Russia in the same location and same year exhibited ΔHs of 14.1-17.0 J/g (Davydova et al., 1995). Pea starches possessing more B-polymorphs than A-polymorphs had higher ΔHs, which might reflect differences in the packing of B- and A-polymorphs (Noda et al., 1998). Pea starches with higher gelatinization temperatures tend to be those containing more A-polymorphs than B-polymorphs (Ratnayake et al., 2002). Asaoka et al. (1984) reported higher T_o, T_p, T_c and ΔH and longer amylopectin B-chains and a reduction in shorter chains of amylopectin at higher growing temperatures (25°C versus 30°C) for rice starch. Cottrell et al. (1995) investigated potato starch grown under three conditions (field, unheated glasshouse and heated glasshouse) and reported that warmer growing conditions increased the gelatinization temperature, amylose concentration and α-amylase resistance of potato starch. Lower T_o, T_p, T_c and ΔH were indicative of a greater proportion of short amylopectin chains than long chains of amylopectin in sweet potato and buckwheat starches (Asaoka et al., 1984).

Values for the PT of pea starches ranged from 74.1-75.1°C (Table 3.7). Ratnayake et al. (2001) reported that the PTs of starch from four pea genotypes ranged from 79.0-79.5°C. PT values of 73.0°C and 65.0°C (approximately) were reported for pea starch by Gujska et al. (1994) and Davydova et al. (1995), respectively. Genotype did not affect PT, nor did location or year, but a significant location by genotype interaction was detected (Table 3.8). Values for PV, TV, CV and FV ranged from 1100-1350 cP, 1050-1230 cP, 1700-1990 cP and 1900-2110 cP,

Table 3.7 Mean values for pasting temperature (PT), pasting viscosity (PV), trough viscosity (TV), cooling viscosity (CV) and final viscosity (FV) of starch isolated from ten pea genotypes grown in four locations in Saskatchewan in each of 2006 and 2007*

Genotype	PT (°C)	PV (cP)	TV (cP)	CV (cP)	FV (cP)
Bluebird	74.8 ± 1.1a	1180 ± 50b	1050 ± 50c	1700 ± 90c	1900 ± 110b
CanStar	75.1 ± 1.3a	1350 ±170a	1230 ± 170a	1990 ± 210a	2100 ± 230a
CDC Striker	74.2 ± 1.0a	1130 ± 90b	1080 ± 80c	1870 ± 150b	2110 ± 190a
CDC Tucker	74.8 ± 1.1a	1170 ± 80b	1100 ± 90c	1790 ± 90bc	1960 ± 120b
Cooper	74.1 ± 1.6a	1140 ± 110b	1050 ± 60c	1770 ± 170c	1970 ± 200b
Cutlass	74.4 ± 1.2a	1160 ± 110b	1080 ± 60c	1840 ± 140b	2080 ± 180a
Fusion	74.1 ± 1.1a	1140 ± 140b	1070 ± 120c	1810 ± 140b	2030 ± 170b
Reward	74.6 ± 1.2a	1170 ± 80b	1150 ± 90b	1870 ± 160b	2040 ± 230b
SW Marquee	74.4 ± 1.2a	1200 ± 110b	1090 ± 110c	1810 ± 140b	2020 ± 180b
Tamora	74.9 ± 1.5a	1100 ± 70b	1080 ± 70c	1750 ± 110c	1960 ± 140b

* Means (± standard deviation) in the same column followed by the same letter are not significantly different (p < 0.05) as determined by Least Significant Differences.

Table 3.8 Analysis of variance for pasting temperature, pasting viscosity, trough viscosity, cooling viscosity and final viscosity of starch isolated from ten pea genotypes grown in four locations in Saskatchewan in each of 2006 and 2007

	Covariance Parameter Estimate				
Covariance Parameter	PT[b]	PV	TV	CV	FV
Loc	0.9430	957.84	343.34	10723	17558
Year	0.1847	0	992.77	0	0
Rep (Loc*Year)[a]	0.0000	55.7040	45.2764	0	0
Loc*Year	0.4375	4427.79	2235.01	808.41	1733.25
Loc*Ge[a]	0.2852*	995.75	0	68.1328	1564.06
Year*Ge	0.0000	0	0	0	0
Loc*Year*Ge	0.0000	4051.47**	3007.69	6970.42**	9913.57**
Residual	0.9886**	1802.07**	2178.35**	3717.83**	4715.16**

Type 3 Tests of Fixed Effects (Genotype)

Analysis	NumDF[c]	DenDF[d]	F-Value	Pr>F
PT	9	27	0.98	0.4759
PV	9	27	6.23	<0.0001**
TV	9	63	6.09	<0.0001**
CV	9	27	5.52	0.0003**
FV	9	27	3.90	0.0028**

* $p < 0.05$; **$p < 0.001$
[a] Loc = location and Ge = genotype, [b] PT = pasting temperature, PV = pasting viscosity, TV = trough viscosity, CV = cooling viscosity and FV = final viscosity, [c] NumDF = numerator degrees of freedom
[d] DenDF = denominator degrees of freedom

respectively (Table 3.7). Genotype had a significant effect on PV, TV, CV and FV, and a significant location by year by genotype interaction was detected for PV, CV and FV (Table 3.8). CanStar exhibited higher PV, TV, CV and FV than did the other genotypes tested. Although, CanStar and Reward share half of their pedigree, Reward exhibited lower viscosities. Cooper and Tamora exhibited PT, PV, TV, CV and FVs that were not significantly different as they share similar pedigrees. Starch from pea grown at Hodgeville exhibited a higher PT than did starch from pea grown at Elrose, Melfort or Saskatoon (Sutherland). Starch from pea grown at Melfort exhibited higher CV and FV than did starch from pea grown at Hodgeville, Melfort or Saskatoon. The Melfort location received more precipitation and had lower mean temperatures during the growing season (Environment Canada, 2011). Starch from pea grown at Elrose or Hodgeville exhibited lower CV and FV than did starch from pea grown at either Melfort or Saskatoon (Sutherland). Genotypic differences in the pasting properties of pea starch have been reported by others (Biliaderis et al., 1979; Ratnayake et al., 2001).

Differences between the pasting properties of pea starch observed in the current study and values reported by others were attributed, in part, to differences in the analytical methodology employed (viscoamylograph with a starch slurry concentration of 9% (w/v) and pH 5.5 in Ratnayake et al. (2001) vs. viscoamylograph with a starch slurry of 5.6% (w/v) in Davydova et al. (1995) vs. RVA with a starch slurry concentration of 8% w/v and pH 7.0 in the current study) since increasing the starch concentration decreased pasting temperature and increased viscosities at 95°C, after the 95°C hold and at 50°C (Abbas et al., 1984). Variations in starch behaviour among pea genotypes, as observed in the current study and as described by Ratnayake et al. (2001) are relatively small compared, for example, to variations observed among twenty-one

Australian wheat genotypes where PV, T_o, T_p, T_c and ΔH ranged from 280-768 Brabender units, 46-53°C, 57-62°C, 64-78°C and 4.6-13.8 J/g (Wootton & Mahdar, 1993), respectively.

3.4.2 Fababean

Concentrations of protein and starch in fababean ranged from 27.5-32.4% and 41.1-47.5%, respectively (Table 3.9). The concentration of amylose in fababean starch ranged from 28.8-30.0 %, respectively. Values of 32.5% and 41.4% for the concentration of protein and starch, respectively, in fababean have been reported by others (Hill-Cottingham, 1983). Both higher (32.5%) and lower (24.0%) values for the concentration of amylose in fababean starch have been reported by Biliaderis et al. (1979) and Naivikul & D'Appolonia (1979), respectively. Mean values for protein concentration were several percentage units higher for fababean than for pea (Tables 3.3 and 3.9), whereas starch concentrations and amylose concentrations in starch were not significantly different for both crops. Genotype had a significant effect on starch and protein concentrations in fababean, but not on the amylose concentration in fababean starch (Table 3.9). Similar results were obtained for pea (Table 3.3). The genotype Gloria was the highest in protein, and Snowbird was the highest in starch (Table 3.9). The location by genotype interaction was significant for the concentration of starch in fababean and the concentration of amylose in fababean starch (Table 3.10). Fababean grown at Saskatoon (Sutherland) in 2006 exhibited the highest starch concentration, and fababean grown at Saskatoon (Sutherland) in 2007 the lowest. Starch from fababean grown at Saskatoon (Sutherland) in 2007 was lower in amylose than was starch from fababean grown at other locations. Interestingly, starch from fababean grown at Saskatoon (Sutherland) in 2006 had the highest amylose concentration. Total rainfall for the Saskatoon (Sutherland) location was similar in 2006 and 2007 (210 and 217 mm,

Table 3.9 Mean values for protein and starch concentrations (%, dry basis) in, and amylose concentrations (%) in starch isolated from, eleven fababean genotypes grown in three locations in western Canada in each of 2006 and 2007*

Genotype	Protein	Starch	Amylose
CDC Fatima	30.7 ± 1.5b	41.1 ± 2.3c	29.3 ± 1.4a
Disco	28.5 ± 1.3c	45.2 ± 3.0b	29.5 ± 1.0a
Dixie	29.7 ± 1.9c	43.8 ± 2.2b	28.8 ± 1.0a
Florent	28.2 ± 0.9d	43.2 ± 2.6b	29.3 ± 1.0a
Gloria	32.4 ± 1.4a	44.1 ± 4.8b	28.9 ± 1.0a
Imposa	27.5 ± 1.5d	45.3 ± 1.7b	29.6 ± 1.4a
NPZ4-7460	28.3 ± 1.4d	45.3 ± 1.4b	29.1 ± 0.9a
NPZ4-7540	29.7 ± 1.4bc	42.8 ± 1.6bc	29.3 ± 1.2a
NPZ5-7530	28.7 ± 1.1c	45.2 ± 1.9b	29.4 ± 1.1a
Snowbird	28.4 ± 1.7c	47.5 ± 3.4a	29.0 ± 0.9a
SSNS-1	30.2 ± 0.8b	42.5 ± 2.5c	30.0 ± 1.1a

* Means (± standard deviation) in the same column followed by the same letter are not significantly different, ($p < 0.05$) as determined by Least Significant Differences.

Table 3.10 Analysis of variance for protein and starch concentrations in, and amylose concentrations in
starch isolated from, eleven fababean genotypes grown in three locations in western Canada in
each of 2006 and 2007

	Covariance Parameter Estimates		
Covariance Parameter	Protein	Starch	Amylose
Loc[a]	1.0908	2.3225	0.5520
Rep(loc)	0.0000	0.1009	0.0000
Loc*Ge[a]	0.1011	2.2478**	0.1772*
Residual	0.7408**	2.5151**	0.4932**

Type 3 Tests of Fixed Effects (Genotype)

Analysis	NumDF[b]	DenDF[c]	F-Value	Pr>F
Protein	10	47.3	22.14	<0.0001**
Starch	10	47.3	5.22	<0.0001**
Amylose	10	47.3	1.46	0.1863

* $p < 0.05$; **$p < 0.001$
[a] Loc = location and Ge = genotype, [b] NumDF = numerator degrees of freedom, [c] DenDF = denominator
degrees of freedom

respectively). However, the timing of the rainfall differed as more rain fell in July and August in 2006 than in 2007. Rainfall late in the growing season may prolong seed fill, leading to higher starch and amylose concentrations. The pre-amylopectin trimming model of starch biosynthesis in plants postulates that amylose is synthesized after amylopectin from pre-amylose using granule-bound starch synthase (Båga et al., 1999). This may explain the higher starch and amylose concentrations in starch from fababean grown at Saskatoon (Sutherland) in 2006 than 2007, as the late rainfall may have delayed maturity and provided more opportunity for amylose synthesis from pre-amylose.

Values for T_o, T_p, T_c, T_c-T_o and ΔH and ranged from 59.5-61.7°C, 65.8-67.6°C, 86.6-87.5°C, 25.1-27.1°C and 16.7-18.0 J/g, respectively (Table 3.11). Lower values for T_o, T_p, T_c and ΔH (56°C, 65°C, 83°C and 13.75 J/g, respectively) have been reported by others for fababean starch (Biliaderis et al., 1979). Starches isolated from pea and fababean exhibited similar thermal properties, with starches from fababean exhibiting slightly higher ΔH values (Tables 3.3 and 3.9). Genotype affected T_o and T_p but not T_c, T_c-T_o or ΔH (Table 3.11). The interaction between genotype and location was significant for T_o and ΔH (Table 3.12). Starch from fababean grown at Outlook exhibited a higher ΔH than did starch from fababean grown at other locations, whereas starch from fababean grown at Saskatoon (Sutherland) in 2006 and 2007 exhibited a lower ΔH. The enthalpy of starch gelatinization is a function of the crystallinity of the starch, which reflects the microstructure of amylopectin, which is influenced by the chain length of double helices and number of helices per amylopectin cluster (Hoover et al., 2010; Noda et al., 1996).

Values for PT of fababean starch ranged from 71.9-73.3°C (Table 3.13). PTs of 66.0°C and 72°C have been reported for fababean starch (Biliaderis et al., 1979; Naivikul & D'Appolonia, 1979). Values for PV, TV, CV and FV of fababean starch ranged from 1020-1250

Table 3.11 Mean values for onset temperature (T_o), peak temperature (T_p) and completion temperature (T_c) of gelatinization, the difference between T_c and T_o (T_c-T_o), and endothermic enthalpy (ΔH) of starch isolated from eleven fababean genotypes grown in three locations in western Canada in each of 2006 and 2007*

Genotype	T_o (°C)	T_p (°C)	T_c (°C)	T_c-T_o (°C)	ΔH (J/g)
CDC Fatima	61.3 ± 2.6a	67.2 ± 2.6ab	87.2 ± 1.0a	25.9 ± 2.3a	16.7 ± 1.7a
Disco	60.8 ± 2.1a	66.9 ± 2.3ab	86.8 ± 1.3a	26.0 ± 1.5a	18.0 ± 1.7a
Dixie	61.7 ± 2.7a	67.6 ± 2.5a	86.8 ± 1.1a	25.1 ± 2.5a	16.9 ± 1.8a
Florent	60.9 ± 3.1a	67.1 ± 2.7ab	87.5 ± 1.3a	26.6 ± 2.6a	17.0 ± 1.9a
Gloria	61.0 ± 3.0a	66.9 ± 2.9ab	87.1 ± 1.0a	26.1 ± 2.3a	16.7 ± 2.0a
Imposa	59.5 ± 2.6b	65.8 ± 2.8c	86.6 ± 1.1a	27.1 ± 1.9a	17.1 ± 1.8a
NPZ4-7460	60.8 ± 2.4a	66.9 ± 2.5ab	86.9 ± 1.6a	26.1 ± 2.1a	16.7 ± 1.8a
NPZ4-7540	61.2 ± 3.1a	66.6 ± 2.7b	86.7 ± 1.3a	25.5 ± 2.5a	17.1 ± 1.7a
NPZ5-7530	60.8 ± 2.6a	66.7 ± 2.6ab	86.6 ± 1.5a	25.8 ± 2.0a	16.9 ± 1.6a
Snowbird	61.4 ± 2.8a	66.9 ± 2.6ab	87.1 ± 1.3a	25.7 ± 2.0a	16.7 ± 1.5a
SSNS-1	61.2 ± 2.5a	66.8 ± 2.5ab	86.8 ± 1.5a	25.7 ± 1.8a	16.8 ± 1.3a

* Means (± standard deviation) in the same column followed by the same letter are not significantly different ($p < 0.05$) as determined by Least Significant Differences.

Table 3.12 Analysis of variance for onset temperature (T_o), peak temperature (T_p) and completion temperature (T_c) of gelatinization, the difference between T_c and T_o (T_o-T_c), and endothermic enthalpy (ΔH) of starch isolated from eleven fababean genotypes grown in three locations in western Canada in each of 2006 and 2007

Covariance Parameter	T_o	T_p	T_c	T_c - T_o	ΔH
Loc[a]	6.6118	6.3712	0.7105	3.1345	1.9388
Rep(loc)	0	0.0081	0.0504	0.0275	0.0442
Loc*Ge[a]	0.1972**	0.0794	0	0.2803	0.4460*
Residual	0.2431**	0.2520**	0.9248**	1.2541**	0.4905**

Type 3 Tests of Fixed Effects (Genotype)

Analysis	NumDF[b]	DenDF[c]	F-Value	Pr>F
T_o	10	47.2	5.22	<0.0001**
T_p	10	46.6	4.93	<0.0001**
T_c	10	103	1.01	0.4377
T_c - T_o	10	47.2	1.93	0.0642
ΔH	10	45.4	1.09	0.3902

* $p < 0.05$; **$p < 0.001$
[a] Loc = location and Ge = genotype, [b] NumDF = numerator degrees of freedom, [c] DenDF = denominator degrees of freedom

cP, 1020-1230 cP, 1780-2290 cP and 1920-2660 cP, respectively (Table 3.13). Starches isolated from pea had somewhat lower PT values and, in general, slightly lower viscosity values than did fababean starches (Table 3.7 and 3.13). Genotype had a significant effect on all viscosity parameters for fababean starch, but not on PT (Tables 3.13 and 3.14). Genotype SSNS-1 exhibited lower viscosities than did most of the genotypes tested (Table 3.13), whereas genotype Florent exhibited higher viscosities. The interaction between location and genotype was significant for TV (Table 3.14). Starch from fababean grown at Outlook or Roblin exhibited higher TVs than did starch from fababean grown at other locations. Outlook is the southernmost location examined in this study and is in the Brown soil zone. Amylose-amylopectin ratio, amylose-lipid complexation, glucan interactions and chain length of amylose and amylopectin play a role in the pasting properties of starches (Hoover et al., 2010). As was the case for starches isolated from the pea genotypes, variations in the thermal and pasting properties among starches from the fababean genotypes were small compared to those observed in starches from twenty-one Australian wheat genotypes (Wootton & Mahdar, 1993).

3.4.3 Heritability

Table 3.15 illustrates the relatively high heritability of starch concentration in pea and starch and protein concentration in fababean, along with the relatively low heritability of protein concentration in pea and the concentration of amylose in starch from pea and fababean. Heritabilities were low for all thermal properties and the pasting temperatures of starches isolated from pea and fababean, but were relatively high for the pasting, trough, cooling and final viscosities of pea and fababean starch. Heritabilities of corresponding dependent variables were similar in pea and fababean, with the exception of the lower heritability of protein concentration in pea (Table 3.15). Breeding efforts would have little impact on parameters exhibiting low broad

Table 3.13 Mean values for the pasting temperature (PT), pasting viscosity (PV), trough viscosity (TV), cooling viscosity (CV) and final viscosity (FV) of starch isolated from eleven fababean genotypes grown in three locations in western Canada in each of 2006 and 2007*

Genotype	PT (°C)	PV (cP)	TV (cP)	CV (cP)	FV (cP)
CDC Fatima	71.9 ± 3.3a	1130 ± 110b	1110 ± 100b	2010 ± 210cd	2330 ± 260bc
Disco	73.0 ± 1.4a	1250 ± 100a	1220 ± 100a	2290 ± 220a	2660 ± 270a
Dixie	72.7 ± 1.5a	1250 ± 140a	1210 ± 140a	2060 ± 220cd	2350 ± 270bc
Florent	72.6 ± 1.9a	1160 ± 140b	1160 ± 140ab	2190 ± 350b	2540 ± 430ab
Gloria	73.3 ± 2.0a	1040 ± 120c	1020 ± 110c	1690 ± 230e	1920 ± 280d
Imposa	72.0 ± 3.0a	1160 ± 140b	1160 ± 140ab	2190 ± 350b	2540 ± 430ab
NPZ4-7460	72.7 ± 1.5a	1230 ± 120a	1230 ± 130a	2130 ± 260bc	2440 ± 320b
NPZ4-7540	72.6 ± 1.7a	1250 ± 100a	1220 ± 100ab	2230 ± 260ab	2560 ± 330ab
NPZ5-7530	72.5 ± 1.6a	1140 ± 170b	1180 ± 120ab	2090 ± 240d	2450 ± 330b
Snowbird	72.9 ± 2.6a	1170 ± 190b	1150 ± 180ab	1950 ± 440cd	2230 ± 520c
SSNS-1	72.8 ± 2.7a	1020 ± 110c	1020 ± 110c	1780 ± 200e	2060 ± 260c

* Means (± standard deviation) in the same column followed by the same letter are not significantly different (p < 0.05) as determined by Least Significant Differences.

Table 3.14 Analysis of variance for pasting temperature, pasting viscosity, trough viscosity, cooling viscosity and final viscosity of starch isolated from eleven fababean genotypes grown in three locations in western Canada in each of 2006 and 2007

Covariance Parameter Estimates					
Covariance Parameter	PT[b]	PV	TV	CV	FV
Loc[a]	2.8880	9420.4	9391.8	52409	83059
Rep(Loc)	0	0	219.9	0	0
Loc*Ge[a]	0	1571.5	2322.8*	10567	14509
Residual	1.8327**	7176.5**	3928.8**	16791**	24972**

Type 3 Tests of Fixed Effects (Genotype)				
Analysis	NumDF[c]	DenDF[d]	F-Value	Pr>F
PT	10	109	0.97	0.4774
PV	10	46.6	8.26	<0.0001**
TV	10	47	7.86	<0.0001**
CV	10	46.4	12.76	<0.0001**
FV	10	46.5	13.33	<0.0001**

* $p < 0.05$; **$p < 0.001$
[a] Loc = location and Ge = genotype, [b] PT = pasting temperature, PV = pasting viscosity, TV = trough viscosity, CV = cooling viscosity and FV = final viscosity, [c] NumDF = numerator degrees of freedom
[d] DenDF = denominator degrees of freedom

Table 3.15 Heritability (h^2) of the concentration of protein and starch in pea and fababean and the amylose concentration, onset temperature (T_o), peak temperature (T_p) and completion temperature (T_c) of gelatinization, the difference between T_c and T_o (T_c - T_o), endothermic enthalpy (ΔH), pasting temperature (PT), pasting viscosity (PV), trough viscosity (TV), cooling viscosity (CV) and final viscosity (FV) of starch isolated from pea and fababean

	Pea	Fababean
Protein	0.55	0.86
Starch	0.77	0.90
Amylose	0.34	0.49
T_o	0.34	0.21
T_p	0.14	0.15
T_c	0.22	0.34
T_c-T_o	0.00	0.35
ΔH	0.34	0.27
PT	0.00	0.22
PV	0.79	0.81
TV	0.74	0.78
CV	0.79	0.83
FV	0.72	0.82

sense heritability values. Significant narrow sense heritability was found for the T_p, T_c and ΔH of rice starch (Bao et al., 2002). Pasting properties of rice starch were found to be controlled by genetics where allelic variation contributed the largest effect on pasting properties (Bao et al., 1999). Broad sense heritability includes allelic variation, dominance, and maternal and paternal effects, whereas narrow sense heritability includes only allelic variation.

3.5 Conclusions

Conclusive evidence of correlations between pulse starch molecular structure and thermal and/or pasting properties cannot be extended at this time due to limited research in this area (Hoover et al., 2010). However, the results from this study indicate that genotype and environment affect protein and starch concentrations in pea, and the concentration of starch and amylose in fababean seed and starch, respectively.

A primary objective of this study was to provide information to pulse crop breeders and processors on the effects of genotype and the environment, and their interaction, on the starch and protein concentrations in, and the functionality of starch from, pea and fababean. On the basis of the results obtained for the genotypes and environments included in this study, it may be concluded that:

1. The effect of genotype on the concentrations of starch and protein in pea and fababean was sufficient to be of practical significance to end-users due to the economic impacts of differences in starch and protein concentration.

2. Environment did not have a substantial effect on the concentrations of starch and protein in pea and fababean. This was in marked contrast to previous results where concentrations of starch and protein in 198 Saskatchewan producers' samples of a single genotype of pea ranged from 49.7 to 59.8% and 13.3-27.1% (dry, dehulled seed basis), respectively (Reichert

et al., 1982). However, the pea genotypes and agricultural management practices used in the Reichert et al. (1982) study were less developed than those employed in this study. The concentration of protein in western Canadian pea (green and yellow) in 2008 ranged from 18.7-29.1%, with an average of 23.2% (Canadian Grain Commission, 2010). The average in 2007 was 24.5 % (Canadian Grain Commission, 2010). These apparent differences between protein concentrations from this study and others were likely due to more uniform agronomic practices from which the samples in this study were obtained.

3. Genotype and environment had minor effects on the concentration of amylose in, and the physicochemical characteristics of, starch from pea and fababean. These effects would likely not be of practical significance.

4. The significant interactions detected namely location by genotype for protein concentration in pea and starch concentration in fababean, and location by year by genotype for starch concentration in pea, would complicate the manipulation through breeding of the concentrations of protein and starch in pea and fababean.

3.6 Connection to Subsequent Chapters

For Saskatchewan-grown pea and fababean, the lack of significant variation in the functional properties of starch may allow processors increased flexibility in seed selection for milling and fractionation or isolation of starch and protein. It would be challenging to rely on environmental conditions (location, temperature and precipitation) to create consistent starch functionality in each growing season. It would be worthwhile to investigate natural methods to modify the functionality of pea starch such as in blends with commercial starches, with or without heat-moisture treatment or pregelatinization, or in combination with commercial

hydrocolloids. Fababean starch was not used in the following studies due to the lack of commercial availability of seed and starch.

4. FUNCTIONAL PROPERTIES OF PEA STARCH AND BLENDS OF PEA STARCH AND CORN STARCH, WAXY CORN STARCH, HIGH-AMYLOSE CORN STARCH OR POTATO STARCH

4.1 Abstract

Thermal and pasting properties, swelling power, water solubility, freeze-thaw stability, shear stability, water binding capacity and resistant starch concentration were determined for native, heat-moisture-treated and pregelatinized pea starch (PS), corn starch (CS), waxy corn starch (WCS), high-amylose corn starch (HACS) and potato starch (PoS), and native, heat-moisture-treated and pregelatinized blends of PS and CS, WCS, HACS or PoS.

Several blends of native starches exhibited functionalities that were significantly different than their respective calculated, weighted average values, notably: i) blends of PS and CS exhibited lower degrees of syneresis; ii) blends of PS and WCS exhibited higher degrees of syneresis; iii) blends of PS and HACS exhibited lower pasting viscosities, trough viscosities and final viscosities; and iv) blends of PS and PoS exhibited lower water solubilities at lower temperatures.

Heat-moisture treatment of starch blends had variable effects on their functionality. Heat-moisture treatment reduced pasting viscosities, swelling power, and syneresis of gels after freezing and thawing, and increased the resistant starch concentration, compared to corresponding native starch blends. Several heat-moisture-treated starch blends exhibited functionalities that were significantly different than their respective calculated, weighted average values, notably: i) heat-moisture-treated blends of PS and CS exhibited lower pasting, trough and

final viscosities; ii) heat-moisture-treated blends of PS and WCS exhibited lower water solubilities; iii) heat-moisture-treated blends of PS and HACS exhibited lower pasting, trough and final viscosities and higher degrees of syneresis; and iv) heat-moisture-treated blends of PS and PoS exhibited lower pasting, trough, and final viscosities and degrees of syneresis.

Pregelatinization of the starch blends increased swelling powers at lower temperatures (65°C and 75°C) and reduced resistant starch concentrations. Several pregelatinized starch blends exhibited functionalities that were significantly different than their respective calculated, weighted average values, notably: i) pregelatinized blends of PS and WCS exhibited lower water solubilities; and ii) pregelatinized blends of PS and PoS exhibited higher swelling powers.

Some native, heat-moisture-treated and pregelatinized blends of PS and CS, WCS, HACS or PoS exhibited functionalities that might be useful in food or non-food applications.

4.2 Introduction

Starch is an homogeneous polymer of glucose that exists as a combination of two molecular types, amylose and amylopectin. It has been reported that PS exhibits strong gelation capacity (Vose, 1977), shear stability (Gernat et al., 1990), acid stability (Gernat et al., 1990) and enzyme resistance (Ratnayake et al., 2001). However, PS also exhibits a relatively high degree of syneresis, high cooking temperature (Yook et al., 1994) and a low pasting viscosity (Ratnayake et al., 2001). Due in part to these properties, PS has seen limited commercial application, particularly as a food ingredient.

Legume starches possess a C-type polymorph, which is a combination of the A-type polymorph of cereals and the B-type polymorph of tubers. In C-type polymorphs, A- and B-type polymorphs are present in the same granule, with B-type polymorphs positioned near the centre

of the granule and A-type polymorphs positioned nearer the periphery of the granule (Bogracheva et al., 1998). The proportion of B-type crystalline units varies among legume starches (Hoover & Ratnayake, 2002; Sarko & Wu, 1978).

Blending of PS and CS for use in puddings has been patented (Stute & Kern, 1994). The inventors claim that blends of PS and CS at ratios between 8:2 and 4:6 exhibited reduced syneresis compared to PS alone, and performed well as gelling or texturizing agents in puddings. Blending of the CS mutants *duh* (dull, horny) and *ae du* (amylose extender, dull) has also been patented, as the behaviour of the blended starch was similar to that of chemically cross-linked starches (Friedman et al., 1988a; Friedman et al., 1988b). The CS mutant, *ae du,* contained 50% amylose and possessed a C-type polymorph (Matveev et al., 2001). Blending other C-type starches, such as PS, with A- or B-type starches might produce starch products with unique characteristics. A 1:3 blend of lima bean starch with cassava starch exhibited no retrogradation, high viscosity and heat-cool cycle stability, and exhibited increased water absorption, swelling power and gel clarity compared to the lima bean starch gel (Novelo-Cen & Betancur-Anacona, 2005). The behaviour of blends of legume starches may vary based on the botanical source of the constituent starches and the molecular similarity of the glucans (Funami, 2009).

It is apparent that blends of legume starches and non-legume starches may exhibit functionality superior to that of PS alone, and may offer new, natural functionality for food and non-food applications.

4.3 Materials and Methods

Refined PS, prepared from air-classified PS by aqueous washing, was provided by Parrheim Foods (Saskatoon, SK). Corn starch, WCS, HACS (Hylon 7, 70% amylose) and PoS) were provided by National Starch Food Innovation (Bridgewater, NJ). The protein concentrations

in PS, CS, WCS, HACS and PoS were 0.48, 0.15, 0.33, 0.36 and 0.14%, respectively, as analyzed by method 46-30 of the AACC (2000). The lipid concentrations of PS, CS, WCS, HACS and PoS were 0.20, 0.12, 0.15, 0.33 and 0.18%, respectively, as analyzed by method B-20 of the Analytical Methods of the Member Companies of the Corn Refiners Association, Inc. for fat analysis of starch (Corn Refiners Association, 2011). Pea starch was blended, in duplicate, with CS, WCS, HACS or PoS in the following proportions: 3:1, 1:1 and 1:3 (w/w) by mixing the powders by inverting for 60 seconds (powder-based mixtures). Each starch or blend was mixed again prior to weighing for each experiment using a weighing spatula. These native blends and their constituent starches were analyzed for their functionality. In addition, these blends and their constituent starches were heat-moisture-treated or pregelatinized and then analyzed for their functionality. The starches were heat-moisture-treated by equilibrating their moisture contents to 30% for 48 hours at room temperature in sealed plastic containers, followed by heating for 8 hours at 100°C in a forced air-oven in a metal pan covered with perforated metal foil. The starches were pregelatinized and dried by drum drying 45% (w/v) slurries at 120°C (drum surface temperature) and ground using a UDY cyclone mill (UDY Corporation, Fort Collins, CO) to pass a 1-mm screen.

Thermal properties were determined by differential scanning calorimetry (DSC) according to Ratnayake et al. (2001) utilizing a Q2000 modulated DSC (TA Instruments, New Castle, DE) using a sample size of 2.0 mg (db) and 70% total moisture (approximately 7.3 μL of water added depending on the moisture content of the sample). Samples were allowed to equilibrate overnight. A Rapid Viscoanalyzer (Newport Scientific Ltd., Warriewood, NSW, Australia) was used to determine pasting properties using Standard method #2 with 8% starch slurries at pH 7.0 (Anonymous, 1998). The pH was adjusted with a dilute solution NaOH.

Swelling powers and water solubility indices were determined according to Li & Yeh (2001). Freeze-thaw stability was determined according to Muadklay & Charoenrein (2008) where a 6% starch slurry was heated at 95°C for 30 minutes with continuous agitation. The heated paste was cooled to room temperature in a 10°C water bath for 30 minutes to aid nucleation. The sample was then frozen at -18°C for 20 hours. The frozen paste was thawed for 2 hours at 30°C in a water bath, vortexed for 15 seconds and centrifuged at 1000 x g for 20 minutes. The supernatant was decanted and percent syneresis was calculated using:

% syneresis = (weight of water removed/weight of starch paste) x 100 (4.1)

Freeze-thaw stabilities were cumulative, meaning that the samples were frozen, thawed, centrifuged, decanted and returned to the freezer for the next cycle. Shear stabilities was performed according to Praznik et al. (1999) and calculated using:

Shear stability = $\eta_{after}/\eta_{before}$ x 100 (4.2)

Water binding capacities were determined by the method of Medcalf & Gilles (1965) at room temperature (approximately 22°C). Resistant starch concentrations were determined according to method 32-40 of the AACC (2000) using a resistant starch kit purchased from Megazyme International (Wicklow, Ireland).

In an effort to determine if synergies where observed in any of the functional properties of the starch blends, weighted averages were calculated. The concept of weighted average values was based on a linear model where the anticipated results would be calculated from values of the constituent starches. If values for two or more blends were outside the mean plus or minus two standard deviations, the functionality of the blend was considered to be non-additive, i.e. exhibited synergy. Weighted average values were calculated for each dependent variable and blend using the following equations:

Weighted ave 3:1 = (0.75 x value for PS) + (0.25 x value for other starch) (4.3)

Weighted ave 1:1 = (0.50 x value for PS) + (0.50 x value for other starch)   (4.4)

Weighted ave 1:3 = (0.25 x value for PS) + (0.75 x value for other starch)   (4.5)

where other starch is either CS, WCS, HACS or PoS. Graphs displaying the experimental values compared to the calculated weighted averages were produced using Microsoft Excel and are presented in Appendix A, B and C for native, heat-moisture-treated and pregelatinized starch blends, respectively.

Data were analyzed using PROC GLM (α = 0.05, n =4) and differences between means were determined by Least Significant Differences using SAS (SAS Institute Inc., Cary, NC). Commercial, chemically-modified starches were analyzed using the above methodologies and the results were compared to values for the starches and starch blends in this study by PROC TTEST using SAS (SAS Institute Inc., Cary, NC) where α = 0.05.

4.4 Results

4.4.1 Functional Properties of Native Pea Starch (PS), Corn Starch (CS), Waxy Corn Starch (WCS), High-Amylose Corn Starch (HACS) and Potato Starch (PoS) and Combinations of PS with Native CS, WCS, HACS or PoS

The concept of weighted average values is based on a linear model where the anticipated results from the blends would be the sum of the constituent starches. If the experimental value and the weighted average value were not significantly different, the experimental value was comparable to sum of the constituent starches. For the purpose of this study, if two or more blends were outside of the mean plus or minus two standard deviations, it was considered to deviate from the sum of the constituent starches and to be significantly different than the weighted average values.

Compared to PS: i) native blends of PS and CS exhibited lower ΔHs, higher PVs, higher SPs at 85°C and 95°C, less syneresis during freeze-thaw cycles and higher shear stabilities; ii)

blends of PS and WCS exhibited lower ΔHs, higher PVs and less syneresis during freeze-thaw cycles; iii) blends of PS and HACS exhibited lower PVs and greater syneresis during freeze-thaw cycles and; iv) blends of PS and PoS exhibited higher PVs and higher RS concentrations than did PS.

4.4.1.1 Thermal Properties

Gelatinization of starch is a phenomenon that occurs when starch is heated in an excess of water (BeMiller & Whistler, 1996). Starch granules undergo an order-disorder transition that requires energy. This energy and the temperatures at which the order-disorder transformation occurs can be measured using differential scanning calorimetry (DSC). Thermal properties of PS, CS, WCS, HACS and PoS, and their respective blends, are presented in Table 4.1. The T_o of CS (68.7°C) was higher than previously reported values of 60°C (Biliaderis et al., 1979; Jane et al., 1999) and that of WCS (65.1°C) was higher than previously reported values of 64°C and 64.2°C (Biliaderis et al., 1979; Jane et al., 1999). No endotherm was observed for HACS, due to its high-amylose content and the high gelatinization temperature of HACS. The T_o of PoS (55°C) was similar to the value (55°C) reported by Biliaderis et al. (1979), but lower than values (59.7-66.2°C) reported by Kim et al. (1995). Potato starch typically exhibits a lower gelatinization temperature, due to weakening of its starch granule structure by phosphate monoesters, the type of amylopectin crystallinity (B-type), and amylose co-crystallized with amylopectin (Hoover & Vasanthan, 1994b; Saibene et al., 2008).

In general, blends of PS and CS, WCS or PoS exhibited T_o, T_p and ΔH values that were significantly different than corresponding weighted average values (Table 4.1; Appendix A), with the exception of the T_p for blends of PS and WCS. The 1:3 PS:HACS blend did not exhibit a

Table 4.1 Thermal properties of pea starch (PS), corn starch (CS), waxy corn starch (WCS), high-amylose corn starch (HACS) and potato starch (PoS) and blends of PS and CS, WCS, HACS or PoS*

	T_o (°C)	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
PS		59.1 ± 0.1c	65.2 ± 0.6b	86.7 ± 0.7a	14.2 ± 0.3a
3:1 PS:CS		59.3 ± 0.2c (61.5)	69.3 ±0.1ab (66.9)	84.0 ± 1.0b (85.1)	9.9 ± 1.3bc (13.4)
1:1 PS:CS	59.0 ± 0.6	69.3 ± 0.2a (63.9)	72.6 ± 0.1a (68.6)	83.7 ± 1.0b (83.4)	9.9 ± 1.4bc (12.7)
1:3 PS:CS		69.2 ± 0.2a (66.3)	72.3 ± 0.2a (70.3)	81.2 ± 2.4c (81.8)	9.2 ± 1.5c (12.0)
CS		68.7 ± 0.2b	72.0 ±0.3a	80.1 ± 0.6c	11.2 ± 0.6b
PS		59.1 ± 0.1c	65.2 ± 0.6a	86.7 ± 0.7a	14.2 ± 0.3a
3:1 PS:WCS		59.4 ± 0.1c (60.7)	67.6 ± 0.2b (66.8)	85.5 ± 1.2a (85.3)	11.2 ± 0.8b (13.7)
1:1 PS:WCS		60.4 ± 0.3b (62.2)	74.4 ± 0.1d (68.4)	85.5 ± 2.4a (83.9)	9.6 ± 1.1c (13.2)
1:3 PS:WCS		65.1 ± 0.3a (63.8)	73.8 ± 0.6c (70.1)	79.6 ± 1.0b (82.5)	7.1 ± 0.4d (12.6)
WCS		65.1 ± 0.5a	72.1 ± 0.5c	81.1 ± 1.0b	12.1 ± 0.7b
PS		59.1 ± 0.1c	65.2 ± 0.6c	86.7 ± 0.7 a	14.2 ± 0.3a
3:1 PS:HACS		59.6 ± 0.3b	66.3 ± 0.6b	84.0 ± 0.2b	9.2 ± 0.6b
1:1 PS:HACS		60.4 ± 0.1a	67.4 ± 0.2a	80.2 ± 1.8c	3.0 ± 0.7c
1:3 PS:HACS		No To	No Tp	No Tc	No ΔH
HACS		No To	No Tp	No Tc	No ΔH
PS		59.1 ± 0.1b	65.2 ± 0.6a	86.7 ± 0.7a	14.2 ± 0.3bc
3:1 PS:PoS		59.7 ± 0.5a (59.3)	64.6 ± 0.3ab (64.8)	85.3 ± 0.8a (83.4)	13.4 ± 0.5cd (14.4)
1:1 PS:PoS		59.6 ± 0.3a (59.5)	64.4 ± 0.3bc (64.2)	79.2 ± 2.4b (80.1)	12.9 ± 0.9d (14.6)
1:3 PS:PoS		59.6 ± 0.2a (59.7)	64.0 ± 0.4bc (63.9)	79.6 ± 0.3b (76.8)	15.5 ± 0.7ab (14.8)
PoS		59.9 ± 0.2a	63.7 ± 0.1c	73.5 ± 1.6c	15.0 ± 0.6a
Low DS CL CS		65.7 ± 0.3	72.1 ± 0.1	85.3 ± 0.4	13.4 ± 0.1
Low DS CL WCS		61.5 ± 0.3	68.0 ± 0.0	79.9 ± 0.1	12.0 ± 0.1
High DS CL WCS		64.5 ± 0.1	70.4 ± 0.1	79.6 ± 0.1	8.9 ± 0.2
Low DS AC WCS		65.7 ± 0.3	72.1 ± 0.1	85.3 ± 0.4	13.4 ± 0.1

* Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different ($p < 0.05$) by Least Significant Differences. Values enclosed in parentheses are the weighted average values associated with the treatment. Where T_o = temperature of onset of gelatinization; T_p = temperature of peak gelatinization; T_c = temperature of complete gelatinization; ΔH = endothermic enthalpy of gelatinization; DS = degree of substitution; CL = cross-linked and AC = acetylated

gelatinization peak, which reflected the behaviour of HACS (Table 4.1), due to the small proportion of PS requiring a negligible amount of energy for gelatinization. Weighted average values were not calculated for blends of PS:HACS due to the lack of values for thermal properties for HACS. Peaks from DSC were observed when HACS was gelatinized at a 5°C/min heating rate up to 200°C (Liu et al. 2005). Blends that did not exhibit weighted average values included: i) blends of PS:CS, which exhibited higher T_o and T_p values and lower ΔHs; ii) blends of PS:WCS, which exhibited lower, and then higher, T_o values (as the proportion of WCS increased) and lower ΔHs; and iii) blends of PS:PoS, which exhibited higher T_c values.

Two peaks were observed in the endotherm for the 1:1 PS:CS and 1:1 PS:WCS blends (Table 4.1, Fig. 4.1 and 4.2). Other than these combinations, the endotherms of all native starch blends (Table 4.1) exhibited single peaks. Single peak endotherms for starch blends also were reported by Obanni & BeMiller (1997) with various blends of CS, WCS, HACS, PoS, wheat starch, rice starch and tapioca starch, Novelo-Cen & Betancur-Anacona (2005) with blends of lima bean starch and cassava starch, and Karam et al. (2006) with blends of CS, cassava starch and yam starch.

Gelatinization temperatures for most blends fell between those of the individual starches suggesting, as previously reported by Obanni &BeMiller (1997), that molecular interactions between the two starches occurred instead of each individual starch gelatinizing individually. However, not all blends exhibited single endotherms. Notably, 1:1 wheat starch and tapioca starch mixture exhibited two endotherms (Obanni & BeMiller, 1997; Liu & Leliévre, 1992) indicating that the two starches may have gelatinized individually. As mentioned above, the1:1 PS:CS and PS:WCS blends also appear to have gelatinized individually.

The thermal properties of blends of PS and CS, WCS, HACS or PoS and were compared to those of commercial, chemically-modified starches (Table 4.1). The T_p of 1:3 PS:CS (72.3°C)
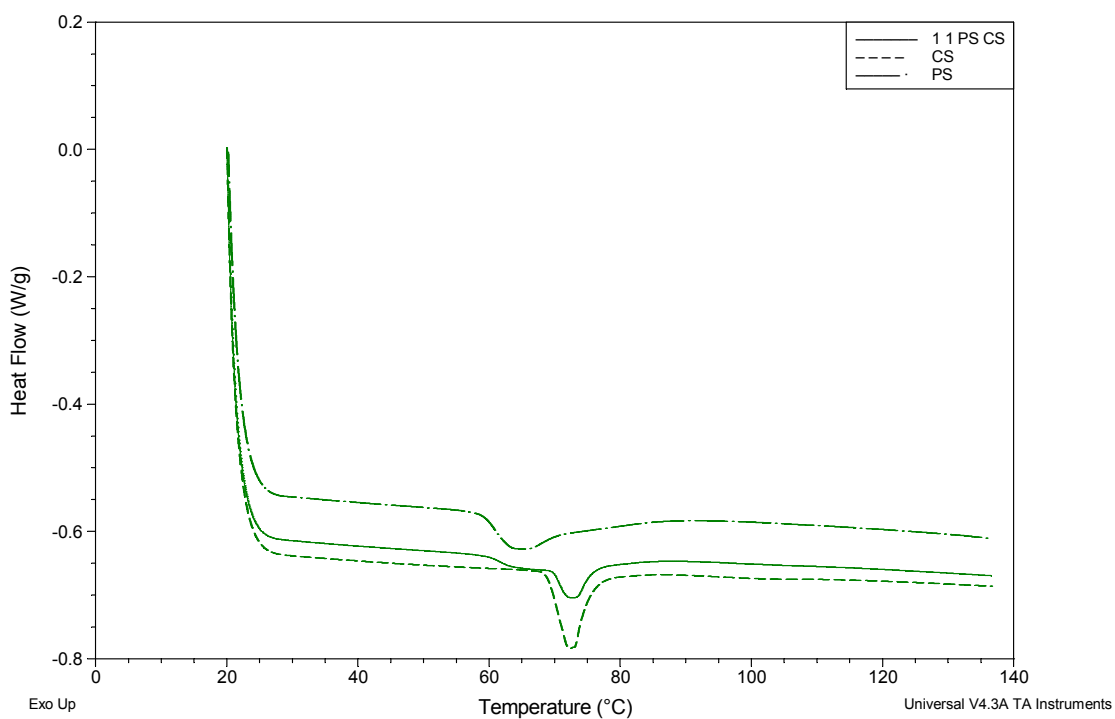
Fig. 4.1. Differential scanning calorimetry (DSC) thermograms of pea starch (PS), corn starch (CS) and 1:1 PS:CS
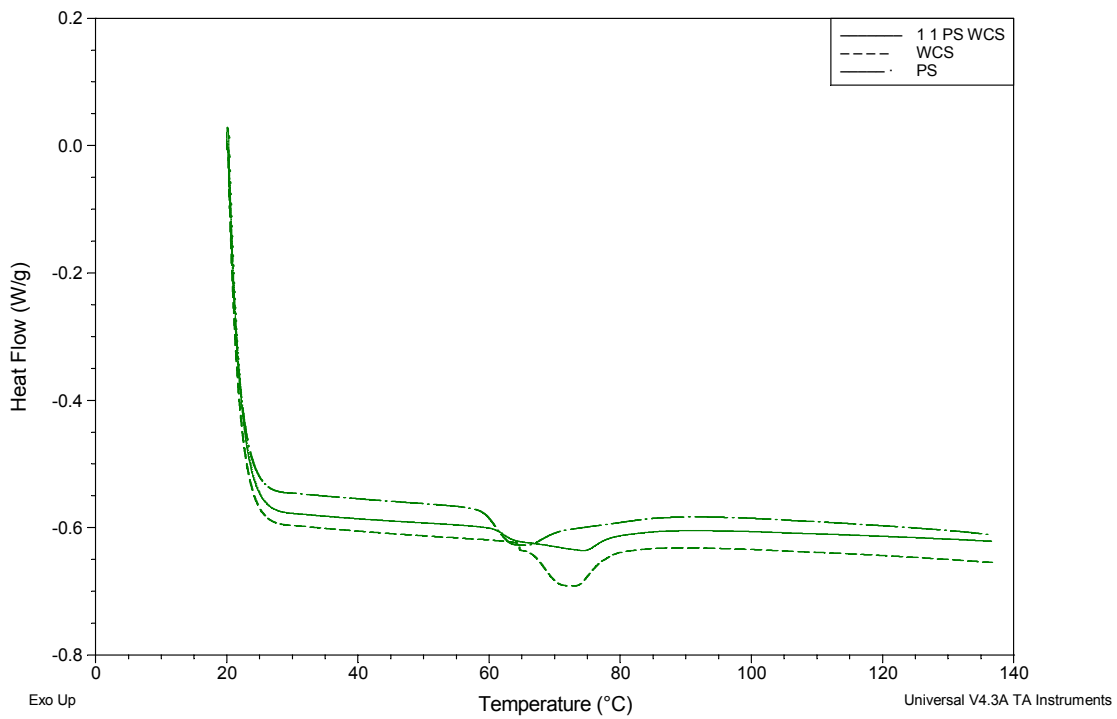
Fig. 4.2. Differential scanning calorimetry (DSC) thermograms of pea starch (PS), waxy corn starch (WCS) and 1:1 PS:WCS

was not significantly different than the T_p of a low degree of substitution (DS), cross-linked (CL) WCS, or that of a low DS, acetylated (AC) WCS (72.1°C). The ΔHs of 1:3 PS:CS, 1:1 PS:WCS and 3:1 PS:HACS (9.2, 9.6 and 9.2 J/g, respectively) were not significantly different than the ΔH of a high DS, CL WCS (8.9 J/g).

4.4.1.2 Pasting Properties

Pasting involves heating of an aqueous starch system with shear and, typically, promotes water migration into the granule, granule swelling and leaching of glucans into the continuous phase of the system (BeMiller & Whistler, 1996). Pea starch, CS, WCS, HACS and PoS exhibited pasting properties characteristic of these starches (Table 4.2). The highest viscosities were observed for potato starch, which is a high swelling starch due to its weakened granule structure, which is likely a function of phosphate monoesters, crystal structure and amylose co-crystallized with amylopectin (Hoover & Vasanthan, 1994b; Saibene et al., 2008). Waxy corn starch and HACS exhibited high and low viscosities due to their low and high amylose concentrations, respectively.

Generally, the pasting temperatures of blends of PS and WCS or PoS were lower than their respective weighted average values (Table 4.2; Appendix A). High-amylose corn starch and 1:1 and 1:3 PS:HACS blends did not exhibit pasting temperatures, due to the low viscosities achieved during pasting. As a result, weighted average values were not calculated for PTs of PS:HACS blends. Blends that did not exhibit weighted average values included: i) PS:WCS blends, which exhibited lower PTs and FVs; ii) PS:HACS blends, which exhibited lower PVs, TVs and FVs; and iii) PS:PoS blends, which exhibited lower PTs and higher TVs and FVs. The 1:3 PS:WCS blend exhibited a shoulder possibly indicated delayed breakdown (Figure 4.3).

Table 4.2 Pasting properties of pea starch (PS), corn starch (CS), waxy corn starch (WCS), high-amylose corn starch (HACS) and potato starch (PoS) and blends of PS and CS, WCS, HACS or PoS*

	PT (°C)	PV (cP)	TV (cP)	FV (cP)
PS	73.8 ± 0.2a	1350 ± 93a	1025 ± 93a	2157 ± 126a
3:1 PS:CS	73.2 ± 1.8a (76.2)	1438 ± 92a (1387)	1269 ± 257ab (1055)	1970 ± 90a (2103)
1:1 PS:CS	75.5 ± 3.1a (78.5)	1339 ± 74a (1425)	1159 ± 68ab (1086)	2015 ± 131a (2049)
1:3 PS:CS	83.1 ± 0.5b (80.9)	1534 ± 33a (1463)	1373 ± 81b (1116)	1996 ± 37a (1994)
CS	83.2 ± 1.1b	1500 ± 33a	1146 ± 162ab	1940 ± 190a
PS	73.8 ± 0.2a	1350 ± 93a	1025 ± 93a	2157 ± 126a
3:1 PS:WCS	72.5 ± 0.2a (73.7)	1573 ± 7b (1619)	1063 ± 44a (990)	1670 ± 9b (1913)
1:1 PS:WCS	68.5 ± 5.8a (73.5)	1881 ± 20c (1889)	972 ± 32a (955)	1444 ± 18bc (1668)
1:3 PS:WCS	70.0 ± 1.4a (73.4)	2200 ± 6d (2159)	957 ± 9a (919)	1349 ± 5cd (1423)
WCS	73.2 ± 0.9a	2428 ± 96e	884 ± 17a	1178 ± 111d
PS	73.8 ± 0.2a	1350 ± 93a	1025 ± 93a	2157 ± 126a
3:1 PS:HACS	77.7 ± 0.3b	693 ± 39b (1025)	699 ± 75b (774)	968 ± 110b (1621)
1:1 PS:HACS	None	260 ± 23c (700)	269 ± 11c (524)	370 ± 21c (1085)
1:3 PS:HACS	None	53 ± 4d (375)	54 ± 2d (273)	66 ± 4d (548)
HACS	None	50 ± 4d	22 ± 3d	12 ± 3e
PS	73.8 ± 0.2a	1350 ± 93a	1025 ± 93a	2157 ± 126a
3:1 PS:PoS	67.2 ± 0.3b (71.4)	3128 ± 157b (3061)	1503 ± 76b (1161)	3016 ± 174b (2170)
1:1 PS:PoS	64.7 ± 0.0c (68.9)	4351 ± 117c (4772)	1789 ± 26c (1296)	2778 ± 18c (2184)
1:3 PS:PoS	63.5 ± 0.2d (66.5)	6398 ± 112d (6483)	1956 ± 17c (1432)	2690 ± 17c (2197)
PoS	64.0 ± 0.0d	8194 ± 121e	1567 ± 100c	2210 ± 15d
Low DS CL CS	81.9 ± 0.1	1772 ± 5	1219 ± 5	2111 ± 14
Low DS CL WCS	59.5 ± 0.0	5412 ± 17	2969 ± 10	4547 ± 21
High DS CL WCS	64.0 ± 0.0	3093 ± 9	2649 ± 11	4981 ± 10
Low DS AC WCS	65.7 ± 0.3	5130 ± 10	3644 ± 14	5438 ± 25

* Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different ($p < 0.05$) by Least Significant Differences. Values enclosed in parentheses are the weighted average values associated with the treatment. Where PT = pasting temperature; PV = pasting viscosity; TV = trough viscosity; CV – cooling viscosity; FV = final viscosity; DS = degree of substitution; CL = cross-linked and AC = acetylated

Figure 4.3 Pasting properties of a 1:3 pea starch:waxy corn starch blend

The pasting properties of blends of PS and CS, WCS, HACS or PoS and were compared to those of commercial, chemically-modified starches (Table 4.2). The TV of the 3:1 PS:CS blend (1269 cP) was not significantly different than that of a low DS, CL CS (1219 cP). Cross-linked starches are used as binders in batters, coatings and meat products, and as viscosity and texture modifiers in soups, sauces, bakery and dairy applications (Thomas & Atwell, 1997).

4.4.1.3 Swelling Power and Water Solubility

As starch granules are heated in an excess of water, water migrates into the granule and the granule swells. As the granule swells and loses crystallinity, glucans are leached into the continuous phase and the solubility of the granule increases. Swelling power (SP) is influenced by amylose-lipid complexes (Hoover & Manual, 1996b; Tester & Morrison, 1990a) and amylopectin structure (Tester et al., 1993), which affect the swelling of starch granules. The SPs and water solubility indices (WSIs) of PS, CS, WCS, HACS and PoS and blends of PS and CS, WCS, HACS or PoS are presented in Tables 4.3 and 4.4, respectively. Corn starch, WCS and PoS exhibited higher SPs than did PS, due in part to the restricted swelling properties of PS, as A-type polymorphs are located near the exterior of C-type granules (Vose, 1977; Bogracheva et al., 1998). High amylose corn starch exhibited the lowest SP due to its high amylose content, which reduced swelling and increased the ability of HACS to withstand thermal treatment.

A number of blends exhibited SPs that were not similar to their weighted average values (Table 4.3; Appendix A). Blends that did not exhibit weighted average values included: i) blends of PS:CS exhibited higher SPs at 65°C and lower SPs at 85°C; ii) blends of PS:WCS exhibited higher SPs at 65°C and 95°C, and lower SPs at 85°C; iii) blends of PS:HACS exhibited higher

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Table 4.3 Swelling powers (SPs) of pea starch (PS), corn starch (CS), waxy corn starch (WCS), high-amylose corn starch (HACS) and potato
　　　　starch (PoS) and blends of PS and CS, WCS, HACS or PoS*

	65°C	75°C	85°C	95°C
PS	6.1 ± 0.0c	10.6 ± 1.0a	12.5 ± 0.2a	15.3 ± 1.3b
3:1 PS:CS	7.1 ± 0.0b (6.2)	11.3 ± 0.6a (10.6)	13.8 ± 0.3a (13.6)	16.4 ± 0.1b (16.2)
1:1 PS:CS	8.3 ± 0.5a (6.3)	11.4 ± 1.2a (10.6)	12.2 ± 0.0a (13.2)	17.0 ± 0.4ab (17.1)
1:3 PS:CS	8.2 ± 0.0a (6.4)	10.0 ± 0.3a (10.5)	12.2 ± 0.0a (12.7)	18.4 ± 0.8a (17.9)
CS	6.5 ± 0.1ab	10.5 ± 1.5a	12.7 ± 0.2a	18.8 ± 1.1a
PS	6.1 ± 0.0b	10.6 ± 1.0c	12.5 ± 0.2a	15.3 ± 1.3b
3:1 PS:WCS	5.8 ± 0.0c (6.2)	12.4 ± 0.2c (13.4)	11.1 ± 0.2a (13.0)	15.8 ± 0.0b (15.7)
1:1 PS:WCS	5.6 ± 0.2c (6.4)	17.0 ± 0.1b (16.1)	12.0 ± 0.6a (13.5)	19.1 ± 0.4a (16.1)
1:3 PS:WCS	6.2 ± 0.0a (6.5)	18.9 ± 0.6ab (18.9)	15.0 ± 0.6b (14.0)	19.4 ± 0.0a (16.4)
WCS	6.6 ± 0.0a	21.6 ± 0.3a	14.5 ± 0.0b	16.8 ± 0.4b
PS	6.1 ± 0.0a	10.6 ± 1.0a	12.5 ± 0.2a	15.3 ± 1.3a
3:1 PS:HACS	5.9 ± 0.0a (5.4)	8.8 ± 0.1b (8.9)	10.2 ± 0.6b (11.8)	12.4 ± 0.2b (13.2)
1:1 PS:HACS	5.2 ± 0.1b (4.6)	7.6 ± 0.1b (7.2)	8.0 ± 0.0c (9.5)	10.1 ± 0.0c (11.1)
1:3 PS:HACS	4.2 ± 0.1c (3.9)	5.4 ± 0.0c (5.5)	6.4 ± 0.3cd (7.1)	8.4 ± 0.1d (8.9)
HACS	3.1 ± 0.0d	3.8 ± 0.1d	4.8 ± 0.0cd	6.8 ± 0.5d
PS	6.1 ± 0.0b	10.6 ± 1.0a	12.5 ± 0.2ab	15.3 ± 1.3a
3:1 PS:PoS	9.1 ± 0.1a (6.9)	11.9 ± 0.1a (10.8)	13.7 ± 0.1a (13.3)	14.5 ± 0.1a (13.9)
1:1 PS:PoS	9.4 ± 0.5a (7.7)	11.9 ± 0.9a (11.0)	13.1 ± 1.0a (12.5)	12.4 ± 0.2b (12.5)
1:3 PS:PoS	9.7 ± 0.4a (8.4)	11.2 ± 0.2a (11.1)	12.2 ± 0.5b (11.6)	11.6 ± 0.0b (11.1)
PoS	9.2 ± 0.5a	11.3 ± 1.4a	10.8 ± 1.1b	9.7 ± 0.5c
Low DS CL CS	7.8 ± 0.2	9.9 ± 0.0	13.0 ± 0.1	19.7 ± 1.4
Low DS CL WCS	20.6 ± 0.4	21.1 ± 0.0	22.2 ± 0.2	22.8 ± 0.1
High DS CL WCS	13.4 ± 0.0	13.0 ± 0.2	14.7 ± 0.1	13.8 ± 0.1
Low DS AC WCS	12.6 ± 0.7	15.0 ± 0.2	16.7 ± 0.0	17.8 ± 0.3

* Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different (p < 0.05) by Least Significant Differences. Values enclosed in parentheses are the weighted average values associated with the treatment. Where DS = degree of substitution; CL = cross-linked and AC = acetylated

Table 4.4 Water solubility indices (WSIs) of pea starch (PS), corn starch (CS), waxy corn starch (WCS), high-amylose corn starch (HACS) and potato starch (PoS) and blends of PS and CS, WCS, HACS or PoS*

	65°C	75°C	85°C	95°C
PS	3.4 ± 0.5a	5.4 ± 0.3a	8.7 ± 1.5a	14.2 ± 0.2a
3:1 PS:CS	4.3 ± 0.1a (3.1)	8.1 ± 0.3b (5.7)	12.4 ± 0.3a (9.4)	18.3 ± 0.4b (15.3)
1:1 PS:CS	3.4 ± 0.3a (2.8)	7.0 ± 0.5ab (6.0)	10.9 ± 0.5a (10.1)	18.7 ± 0.3b (16.4)
1:3 PS:CS	1.3 ± 0.3b (2.5)	5.2 ± 0.3a (6.2)	9.7 ± 0.5a (10.7)	18.4 ± 1.4b (17.4)
CS	2.2 ± 0.4b	6.5 ± 1.3ab	11.4 ± 0.2a	18.5 ± 0.7b
PS	3.4 ± 0.5a	5.4 ± 0.3d	8.7 ± 1.5e	14.2 ± 0.2e
3:1 PS:WCS	3.3 ± 0.1a (3.1)	5.3 ± 0.1d (12.7)	13.6 ± 0.2d (22.2)	15.3 ± 0.1d (27.9)
1:1 PS:WCS	2.7 ± 0.3ab (2.7)	11.6 ± 0.2c (20.1)	25.5 ± 0.0c (35.7)	31.5 ± 0.5c (41.5)
1:3 PS:WCS	1.6 ± 0.1c (2.4)	22.4 ± 0.1b (27.4)	44.9 ± 0.1b (49.1)	46.6 ± 0.2b (55.2)
WCS	2.0 ± 0.4b	34.7 ± 0.0a	62.6 ± 3.0a	68.8 ± 0.1a
PS	3.4 ± 0.5a	5.4 ± 0.3a	8.7 ± 1.5a	14.2 ± 0.2a
3:1 PS:HACS	2.5 ± 0.1b (2.8)	6.4 ± 0.2b (4.5)	9.5 ± 0.4a (7.3)	16.1 ± 0.2b (13.5)
1:1 PS:HACS	2.0 ± 0.1bc (2.2)	4.9 ± 0.2c (3.5)	5.7 ± 0.6ab (6.0)	14.4 ± 0.2a (12.8)
1:3 PS:HACS	1.4 ± 0.2cd (1.5)	3.1 ± 0.1d (2.6)	3.6 ± 0.1b (4.6)	11.8 ± 0.0c (12.0)
HACS	0.9 ± 0.4d	1.6 ± 0.1e	3.2 ± 1.0b	11.3 ± 1.1c
PS	3.4 ± 0.5d	5.4 ± 0.3e	8.7 ± 1.5c	14.2 ± 0.2c
3:1 PS:PoS	6.4 ± 0.4c (7.3)	7.5 ± 0.2d (9.5)	12.5 ± 0.5b (11.5)	15.6 ± 0.1b (15.6)
1:1 PS:PoS	9.9 ± 0.6c (11.1)	8.0 ± 0.8c (13.1)	13.9 ± 0.5b (14.3)	15.6 ± 0.9b (17.1)
1:3 PS:PoS	9.7 ± 0.1c (15.0)	11.3 ± 0.2b (17.0)	21.0 ± 0.8a (17.0)	9.0 ± 0.8d (18.5)
PoS	18.8 ± 0.4a	20.8 ± 0.0a	19.8 ± 0.9a	19.9 ± 0.0a
Low DS CL CS	1.2 ± 0.3	3.3 ± 0.1	7.7 ± 0.1	17.5 ± 1.1
Low DS CL WCS	1.5 ± 0.4	1.1 ± 0.3	1.6 ± 0.1	1.8 ± 0.3
High DS CL WCS	2.5 ± 0.9	0.5 ± 0.0	1.1 ± 0.1	1.4 ± 0.1
Low DS AC WCS	1.3 ± 0.4	0.6 ± 0.0	1.1 ± 0.1	1.8 ± 0.3

* Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different (p < 0.05) by Least Significant Values enclosed in parentheses are the weighted average values associated with the treatment. Differences.Where DS = degree of substitution; CL = cross-linked and AC = acetylated

SPs at 65°C and 75°C, and lower SPs at 85°C and 95°C; and iv) blends of PS:PoS exhibited higher SPs at 95°C.

A number of blends exhibited WSIs that were not similar to their weighted average values (Table 4.4; Appendix A). Botanical sources of starches exhibit different SP and WSI behaviours. For example, WCS and PoS may exhibit lower SP with high WSI (Li & Yeh, 2001) whereas CS, HACS and PS may exhibit high SP and high WSI. Blends that did not exhibit weighted average values included: i) blends of PS:CS exhibited higher WSIs at 65°C, 75°C and 95°C; ii) blends of PS:WCS exhibited lower WSIs at 75°C, 85°C and 95°C; iii) blends of PS:HACS exhibited higher WSIs at 75°C and 95°C; and iv) blends of PS:PoS exhibited lower WSIs at 65°C and 75°C.

The SPs of blends of PS and CS, WCS, HACS or PoS were compared to those of commercial, chemically-modified starches (Table 4.3). At 65°C, the SPs of the 3:1 and 1:1 PS:CS blends (8.3 and 8.2%, respectively) were not significantly different than that of a low DS, CL CS (7.8%). At 75°C, the SP of the 1:3 PS:CS blend (10.0%) was not significantly different than that of a low DS, CL CS (9.9%). At 85°C, the SP of the 1:1 PS:PoS blend (13.1%) was not significantly different than that of a low DS, CL CS (13.0%). At 95°C, the SP of the 1:3 PS:WCS blend (19.4%) was not significantly different than that of a low DS, CL CS (19.7%).

The WSIs of blends of PS and CS, WCS, HACS or PoS were compared to those of commercial, chemically-modified starches (Table 4.4). At 65°C, the WSIs of the 1:3 PS:CS, 1:3 PS:WCS and 1:3 PS:HACS blends (1.3, 1.6 and 1.4%, respectively) were not significantly different than that of a low DS, CL CS (1.2%,), a low DS, CL WCS (1.6%) or a low DS, AC WCS (1.3%). At 75°C, the WSI of the 1:3 PS:HACS blend (3.1%) was not significantly different than that of a low DS, CL CS (3.3%).

4.4.1.4 Freeze-Thaw Stability

The freeze-thaw stability of starch is a function of retrogradation, which releases water when recrystallization of leached glucan molecules occurs upon cooling and storage (Yuan & Thompson, 1998). Freeze-thaw stabilities are affected by the extent of retrogradation and the rate of freezing. Freeze thaw stabilities for PS, CS, WCS, HACS and PoS and blends of PS and CS, WCS, HACS and PoS are presented in Table 4.5. All pure starches and blends exhibited increasing water loss with increasing numbers of freeze-thaw cycles.

A number of blends exhibited degrees of syneresis that were significantly different than their respective weighted average values (Table 4.5; Appendix A). Values that were not essentially weighted average values of those of the constituent starches were obtained for: i) blends of PS:CS (observed values were lower than expected); ii) PS:WCS blends (observed values were higher than expected); iii) PS:HACS (observed values were higher than expected except after the second freeze-thaw cycle); and iv) PS:PoS blends (observed values were somewhat higher than expected after four cycles and lower after one, two and five cycles).

4.4.1.5 Shear Stability

The ability of starch to withstand mechanical breakdown (shear) after gelatinization is a beneficial attribute in food processing and is a function of the ability of the glucans to entangle, which is influenced by amylose concentration (Jane et al., 1999; Lindeboom et al., 2005). Shear stabilities of PS, CS, WCS, HACS and PoS and blends of PS and CS, WCS, HACS or PoS are presented in Table 4.6. In every case, with the exception of HACS, the starch gels did not recover to their pre-shear values, i.e. shear stabilities were less than 100%. The post-shear value of HACS exceeded the pre-shear value.

Table 4.5 Freeze-thaw stabilities (% syneresis) of pea starch (PS), corn starch (CS), waxy corn starch (WCS), high-amylose corn starch (HACS) and potato starch (PoS) and blends of PS and CS, WCS, HACS or PoS*

	Freeze-Thaw Cycles				
	1	2	3	4	5
PS	25.9 ± 2.1a	28.0 ± 2.0a	30.0 ± 2.2a	32.0 ± 2.9a	46.5 ± 0.7a
3:1 PS:CS	8.6 ± 0.2b (21.2)	9.8 ± 0.2bc (22.8)	12.1 ± 0.1c (25.0)	14.4 ± 0.9b (26.5)	42.0 ± 1.9b (37.5)
1:1 PS:CS	8.7 ± 0.0b (16.5)	11.4 ± 0.3b (17.6)	12.1 ± 0.2c (19.9)	16.6 ± 1.2b (21.1)	20.3 ± 0.8c (28.5)
1:3 PS:CS	8.7 ± 0.4b (11.8)	8.7 ± 0.3cd (12.4)	8.9 ± 0.8b (14.9)	9.2 ± 0.1c (15.6)	9.1 ± 0.6d (19.5)
CS	7.1 ± 0.3b	7.2 ± 0.3d	9.8 ± 0.8bc	10.1 ± 1.1c	10.5 ± 0.5d
PS	25.9 ± 2.1a	28.0 ± 2.0a	30.0 ± 2.2a	32.0 ± 2.9ab	46.5 ± 0.7a
3:1 PS:WCS	24.9 ± 0.1a (20.2)	26.2 ± 0.5a (21.9)	27.1 ±1.6ab (24.0)	27.2 ± 1.4c (31.0)	27.5 ± 2.2a (43.9)
1:1 PS:WCS	21.2 ± 1.6b (14.5)	26.7 ± 1.1a (15.9)	23.3 ± 0.7b (18.0)	32.9 ± 2.5a (30.0)	33.1 ± 2.8a (41.3)
1:3 PS:WCS	8.5 ± 0.2c (8.7)	14.9 ± 1.0b (9.8)	16.4 ± 0.7c (12.0)	25.5 ± 0.8c (28.9)	36.1 ± 1.4a (38.7)
WCS	3.0 ± 0.5d	3.7 ± 0.4c	6.0 ± 1.9d	27.9 ± 0.6bc	36.1 ± 2.3a
PS	25.9 ± 2.1d	28.0 ± 2.0d	30.0 ± 2.2c	32.0 ± 2.9e	46.5 ± 0.7d
3:1 PS:HACS	27.4 ± 0.4d (35.9)	30.8 ± 0.4d (37.9)	33.1 ± 1.4c (40.5)	38.0 ± 0.3d (42.3)	59.4 ± 0.4c (53.4)
1:1 PS:HACS	44.1 ± 0.4c (45.8)	43.2 ± 2.8c (47.9)	58.3 ± 2.1b (50.9)	62.0 ± 0.0b (52.6)	62.6 ± 0.6b (60.3)
1:3 PS:HACS	56.3 ± 1.3b (55.8)	57.9 ± 0.3b (57.8)	58.0 ± 0.4b (31.4)	58.8 ± 0.4c (62.8)	60.3 ± 2.4b (67.1)
HACS	65.7 ± 0.1a	67.7 ± 1.1a	71.8 ± 1.1a	73.1 ± 1.0a	74.0 ± 2.1a
PS	25.9 ± 2.1c	28.0 ± 2.0c	30.0 ± 2.2c	32.0 ± 2.9c	46.5 ± 0.7c
3:1 PS:PoS	23.0 ± 1.6c (30.4)	26.2 ± 1.1c (32.1)	41.1 ± 2.9b (35.3)	46.5 ± 0.6b (37.4)	47.1 ± 1.6b (48.3)
1:1 PS:PoS	37.1 ± 0.5b (34.9)	37.5 ± 2.3b (36.2)	47.3 ± 1.1b (40.7)	48.2 ± 0.9b (42.8)	48.1 ± 0.7b (50.0)
1:3 PS:PoS	37.8 ± 1.0b (39.4)	37.9 ± 1.0b (40.2)	47.9 ± 1.0b (46.0)	48.9 ± 0.0b (48.1)	49.0 ± 0.1b (51.8)
PoS	43.9 ± 2.6a	44.3 ± 2.7a	51.3 ± 0.3a	53.5 ± 3.1a	53.5 ± 3.0a
Low DS CL CS	1.7 ± 0.4	2.0 ± 0.5	2.0 ± 0.5	2.7 ± 0.2	6.6 ± 0.8
Low DS CL WCS	2.0 ± 0.1	2.0 ± 0.1	2.0 ± 0.1	2.3 ± 0.6	2.3 ± 0.6
High DS CL WCS	20.3 ± 0.7	20.4 ± 0.7	20.4 ± 0.7	20.6 ± 0.6	20.7 ± 0.7
Low DS AC WCS	10.6 ± 0.2	10.6 ± 0.2	10.7 ± 0.2	10.8 ± 0.3	11.3 ± 0.4

* Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different (p < 0.05) by Least Significant Differences. Values enclosed in parentheses are the weighted average values associated with the treatment. Where DS = degree of substitution; CL = cross-linked and AC = acetylated

Table 4.6 Shear stabilities of pea starch (PS), corn starch (CS), waxy corn starch (WCS), high-amylose corn starch (HACS) and potato starch (PoS) and blends of PS and CS, WCS, HACS or PoS*

	Shear stability (%)
PS	$80 \pm 2c$
3:1 PS:CS	$80 \pm 1c$ (84)
1:1 PS:CS	$82 \pm 1c$ (88)
1:3 PS:CS	$91 \pm 1b$ (92)
CS	$96 \pm 1a$
PS	$80 \pm 2a$
3:1 PS:WCS	$74 \pm 1b$ (81)
1:1 PS:WCS	$75 \pm 2b$ (82)
1:3 PS:WCS	$73 \pm 1b$ (83)
WCS	$84 \pm 1a$
PS	$80 \pm 2c$
3:1 PS:HACS	$82 \pm 1c$ (87)
1:1 PS:HACS	$86 \pm 2c$ (94)
1:3 PS:HACS	$99 \pm 2b$ (101)
HACS	$108 \pm 2a$
PS	$80 \pm 2a$
3:1 PS:PoS	$83 \pm 3a$ (81)
1:1 PS:PoS	$81 \pm 2a$ (81)
1:3 PS:PoS	$81 \pm 1a$ (81)
PoS	$82 \pm 1a$
Low DS CL CS	89 ± 1
Low DS CL WCS	72 ± 1
High DS CL WCS	91 ± 1
Low DS AC WCS	91 ± 1

* Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different ($p < 0.05$) by Least Significant Differences. Values enclosed in parentheses are the weighted average values associated with the treatment. Where DS = degree of substitution; CL = cross-linked and AC = acetylated

Shear stabilities for blends that were not essentially weighted average values of those of the constituent starches, were observed for blends of PS:CS, PS:WCS and PS:HACS (lower than weighted average value).

The shear stabilities of blends of PS and CS, WCS, HACS or PoS were compared to those of commercial, chemically-modified starches (Table 4.6). The shear stability of the 1:3 PS:CS blend (91%) was not significantly different than that of a high DS, CL WCS (92%) or a low DS, AC WCS (91%).

4.4.1.6 Water Binding Capacity

Water binding capacity (WBC) is a function of the ability of starch in its native state to form hydrogen bonds with water. Water binding capacities of PS, CS, WCS, HACS and PoS and blends of PS and CS, WCS, HACS or PoS are presented in Table 4.7. Blends of PS and CS exhibited WBCs that were lower than the corresponding weighted average values. High amylose corn starch and PoS, respectively, exhibited relatively high and low WBCs. However, in all cases, WBCs of blends of PS and CS, WCS, HACS, or PoS were lower than corresponding weighted average values.

4.4.1.7 Resistant Starch Concentration

Resistant starch (RS) is not hydrolyzed during digestion in the small intestine of healthy individuals and passes more or less intact into the large intestine (Englyst et al., 1992). Numerous health benefits are associated with the consumption of RS including regulation of blood glucose and improving colonic health (Axelsen et al., 1999; Jenkins et al., 1998; Jenkins et al., 1981). PS, CS, WCS, HACS and PoS contained 6.4, 1.3, 1.7, 43.7 and 54.0% RS, respectively (Table 4.8).

Table 4.7 Water binding capacities (WBCs) of pea starch (PS), corn starch (CS), waxy corn starch (WCS), high-amylose corn starch (HACS) and potato starch (PoS) and blends of PS and CS, WCS, HACS or PoS*

	WBC (%)
PS	102.2 ± 0.6a
3:1 PS:CS	85.3 ± 0.4b (94.7)
1:1 PS:CS	81.3 ± 0.7c (87.2)
1:3 PS:CS	75.0 ± 0.6d (79.7)
CS	72.2 ± 0.1e
PS	102.2 ± 0.6a
3:1 PS:WCS	90.9 ± 0.6b (98.9)
1:1 PS:WCS	87.8 ± 0.4d (95.6)
1:3 PS:WCS	85.6 ± 0.2e (92.3)
WCS	89.0 ± 0.1c
PS	102.2 ± 0.6b
3:1 PS:HACS	98.1 ± 0.2c (102.7)
1:1 PS:HACS	95.1 ± 0.4d (103.3)
1:3 PS:HACS	98.2 ± 0.6c (103.8)
HACS	104.3 ± 0.1a
PS	102.2 ± 0.6a
3:1 PS:PoS	89.0 ± 0.6b (92.6)
1:1 PS:PoS	81.1 ± 1.0c (83.0)
1:3 PS:PoS	71.5 ± 0.0d (73.4)
PoS	63.8 ± 0.9e
Low DS CL CS	72.9 ± 1.0
Low DS CL WCS	104.6 ± 0.5
High DS CL WCS	92.6 ± 0.2
Low DS AC WCS	84.1 ± 0.2

* Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different ($p < 0.05$) by Least Significant Differences. Values enclosed in parentheses are the weighted average values associated with the treatment. Where DS = degree of substitution; CL = cross-linked and AC = acetylated

Table 4.8 Resistant starch concentrations (dry basis) of pea starch (PS), corn starch (CS), waxy corn starch (WCS), high-amylose corn starch (HACS) and potato starch (PoS) and blends of PS and CS, WCS, HACS or PoS*

	Resistant starch (%)
PS	6.4 ± 0.4b
3:1 PS:CS	7.9 ± 0.1a (5.1)
1:1 PS:CS	5.0 ± 0.0c (3.9)
1:3 PS:CS	3.1 ± 0.0d (2.6)
CS	1.3 ± 0.0e
PS	6.4 ± 0.4a
3:1 PS:WCS	4.2 ± 0.1b (5.2)
1:1 PS:WCS	3.3 ± 0.2c (4.1)
1:3 PS:WCS	2.6 ± 0.2d (2.9)
WCS	1.7 ± 0.1e
PS	6.4 ± 0.4e
3:1 PS:HACS	16.1 ± 0.3d (15.7)
1:1 PS:HACS	27.1 ± 1.9c (25.5)
1:3 PS:HACS	35.8 ± 0.8b (34.4)
HACS	43.7 ± 0.3a
PS	6.4 ± 0.4e
3:1 PS:PoS	20.1 ± 1.7d (18.3)
1:1 PS:PoS	31.5 ± 1.3c (25.1)
1:3 PS:PoS	45.9 ± 1.0b (34.4)
PoS	54.0 ± 1.6a
Low DS CL CS	2.5 ± 0.1
Low DS CL WCS	16.7 ± 0.4
High DS CL WCS	11.1 ± 0.2
Low DS AC WCS	1.1 ± 0.2

*Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different ($p < 0.05$) by Least Significant Differences. Values enclosed in parentheses are the weighted average values associated with the treatment. Where DS = degree of substitution; CL = cross-linked and AC = acetylated

Concentrations of RS in the starch blends differed significantly from corresponding calculated weighted average values, with the exception of PS:HACS. Resistant starch concentrations for blends that were not essentially weighted average values of those of the constituent starches were observed for i) PS:CS blends, which exhibited higher RS concentrations, ii) PS:WCS blends, which exhibited lower RS concentrations; and iii) PS:PoS blends, which exhibited higher RS concentrations.

4.4.2 Functional Properties of Heat-Moisture-Treated Pea Starch (PS), Corn Starch (CS), Waxy Corn Starch (WCS), High-Amylose Corn Starch (HACS) and Potato Starch (PoS) and Heat-Moisture-Treated Combinations of PS and CS, WCS, HACS or PoS

Compared to HMT PS: i) HMT blends of PS and CS exhibited higher T_o values, ΔHs, PTs, PVs, WSIs at 65°C and 95°C, and shear stabilities and lower TVs, FVs, WBCs, and RS concentrations; ii) HMT blends of PS and WCS exhibited higher T_o values, ΔHs, PVs, SPs and WSIs at 75°C, 85°C and 95°C, and WBCs and lower PTs, degrees of syneresis, shear stabilities, and lower RS concentrations; iii) HMT blends of PS and HACS higher degrees of syneresis, shear stabilities, and RS concentrations and lower PVs, TVs, FVs, SPs at 65°C, 75°C, 85°C and 95°C, WSIs at 75°C, 85°C and 95°C, and WBCs; and iv) HMT blends of PS and PoS exhibited higher ΔHs, PVs, TVs, FVs, SPs at 65°C, 85°C and 95°C, WSIs at 85°C and 95°C, and RS concentrations and lower PTs, degrees of syneresis, shear stabilities, and WBCs.

4.4.2.1 Thermal Properties

Comparing the thermal properties of the pure starches after heat-moisture treatment (HMT) (Table 4.9) with those of the corresponding native starches (Table 4.1) revealed that, in general: i) T_o was higher for HMT PS and WCS, and unchanged for HMT CS and PoS; ii) T_p was higher for HMT PS, WCS and PoS, and unchanged for HMT CS; iii) T_c was higher for HMT

Table 4.9 Thermal properties of heat-moisture-treated pea starch (PS), corn starch (CS), waxy corn starch (WCS), high-amylose corn starch (HACS) or potato starch (PoS) and heat-moisture-treated blends of PS with CS, WCS, HACS or PoS*

	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
PS	65.0 ± 1.3b	74.1 ± 1.6a	88.3 ± 0.9a	9.0 ± 1.2d
3:1 PS:CS	66.3 ± 0.6b (66.0)	74.1 ± 0.4a (73.7)	87.6 ± 2.3a (87.4)	10.9 ± 0.5cd (10.4)
1:1 PS:CS	69.7 ± 0.6a (66.9)	73.6 ± 0.7ab (73.2)	88.0 ± 1.6a (86.5)	11.3 ± 0.5bc (11.9)
1:3 PS:CS	69.0 ± 0.6a (67.9)	71.3 ± 2.3b (72.8)	86.8 ± 2.0a (85.5)	13.4 ± 0.7a (13.3)
CS	68.8 ± 0.4a	72.3 ± 0.3ab	84.6 ± 3.2a	12.7 ± 1.5ab
PS	65.0 ± 1.3ab	74.1 ± 1.6a	88.3 ± 0.9a	9.0 ± 1.2c
3:1 PS:WCS	62.5 ± 0.9bc (65.6)	74.7 ± 0.2a (73.9)	87.6 ± 0.5a (88.4)	9.3 ± 1.1bc (10.6)
1:1 PS:WCS	61.5 ± 1.2c (66.1)	74.6 ± 1.2a (73.8)	88.8 ± 3.1a (88.5)	10.1 ± 1.3b (12.2)
1:3 PS:WCS	67.1 ± 0.3a (66.7)	74.0 ± 1.0a (73.6)	88.4 ± 1.6a (88.5)	12.4 ± 1.6a (13.8)
WCS	67.2 ± 0.4a	73.4 ± 0.7a	88.6 ± 3.3a	12.6 ± 0.5a
PS	65.0 ± 1.3a	74.1 ± 1.6a	88.3 ± 0.9a	9.0 ± 1.2a
3:1 PS:HACS	64.5 ± 0.4a	74.2 ± 0.6a	88.9 ± 4.2a	5.1 ± 2.1b
1:1 PS:HACS	No To	No Tp	No Tc	No ΔH
1:3 PS:HACS	No To	No Tp	No Tc	No ΔH
HACS	No To	No Tp	No Tc	No ΔH
PS	65.0 ± 1.3a	74.1 ± 1.6ab	88.3 ± 0.9a	9.0 ± 1.2c
3:1 PS:PoS	66.6 ± 0.3a (63.6)	77.8 ± 0.9a (72.3)	88.3 ± 0.2a (87.5)	6.0 ± 0.7c (11.5)
1:1 PS:PoS	64.7 ± 0.3a (62.3)	71.3 ± 1.8bc (70.4)	87.5 ± 1.4a (86.7)	10.0 ± 0.5bc (14.0)
1:3 PS:PoS	60.0 ± 0.2b (60.9)	66.0 ± 1.4c (68.6)	87.1 ± 0.9a (85.8)	10.9 ± 0.6ab (16.4)
PoS	59.5 ± 0.6b	66.7 ± 3.2c	85.0 ± 0.3a	11.8 ± 3.2a
Low DS CL CS	65.7 ± 0.3	72.1 ± 0.1	85.3 ± 0.4	13.4 ± 0.1
Low DS CL WCS	61.5 ± 0.3	68.0 ± 0.0	79.9 ± 0.1	12.0 ± 0.1
High DS CL WCS	64.5 ± 0.1	70.4 ± 0.1	79.6 ± 0.1	8.9 ± 0.2
Low DS AC WCS	65.7 ± 0.3	72.1 ± 0.1	85.3 ± 0.4	13.4 ± 0.1

* Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different ($p < 0.05$) by Least Signficant Differences. Values enclosed in parentheses are the weighted average values associated with the treatment. Where T_o = temperature of onset of gelatinization; T_p = temperature of peak gelatinization; T_c = temperature of complete gelatinization; ΔH = endothermic enthalpy of gelatinization; DS = degree of substitution; CL = cross-linked and AC = acetylated

PS, CS, WCS and PoS; and iv) ΔH was lower for HMT PS and PoS, and unchanged for HMT CS and WCS. As previously reported, HMT increased gelatinization temperatures and decreased gelatinization enthalpy in yam and potato starches (Hoover & Vasanthan, 1994b). The lower ΔH of PS in this study compared to that reported by Hoover & Manual (1996b) may be attributed to the smaller amount of starch utilized to perform the DSC analysis and/or the method of grinding and isolation. The starch used in this study produced using dry milling methods, possibly leading to higher starch damage (Suksomboon & Naivikul, 2006), possibly increasing susceptibility to hydrothermal treatments such as HMT. Reduction in ΔH indicates a disruption of the double helices of amylopectin in the crystalline and amorphous regions (Gunaratne & Hoover, 2002) or partial gelatinization during hydrothermal treatment reducing granule stability (Hossen et al., 2011).

A number of blends exhibited thermal properties that were significantly different than their respective, weighted average values (Table 4.9; Appendix B). Blends that did not exhibit weighted average values include: i) HMT blends of PS:CS exhibited higher T_o values; ii) HMT blends of PS:WCS exhibited lower T_o values; and iii) HMT blends of PS:PoS exhibited higher To values and lower ΔH values. Similar to what was observed for the thermal properties of the native starch blends of PS and HACS (Table 4.1), no gelatinization peak was observed for HACS or 1:1 or 1:3 PS:HACS blends. All HMT starches and starch blends exhibited single endotherms (Table 4.9), which was the case for the native starches and native starch blends in this study (Table 4.1) with the exception of the 1:1 PS:CS and PS:WCS blends (Figure 4.1 and 4.2). Gunarathe & Corke (2007) observed two endotherms in blends of HMT PoS and native amaranth starch, due to the large difference in the gelatinization temperatures of the two starches. Obanni & BeMiller (1997) reported that thermal and pasting properties would be unique to the starches involved and

the ratio. These authors and Liu & Leliévre (1992) found that 1:1 blends of wheat/rice starches exhibited two endotherms whereas other starch blends did not.

Comparisons were made between the thermal properties of HMT blends of PS and CS, WCS, HACS or PoS and commercial, chemically-modified starches (Table 4.9). The T_o of the HMT 1:1 PS:WCS blend (61.5°C) was not significantly different than that of a low DS, CL WCS (61.5°C). The enthalpy of gelatinization of the HMT 1:3 PS:CS blend (13.4 J/g) was not significantly different than the ΔH value of that of a low DS, CL CS (13.4 J/g) or a low DS, AC WCS (13.4 J/g).

4.4.2.2 Pasting Properties

HMT had a variable effect of the starches due to the variability in the susceptibility of each starch to hydrothermal treatment, in part due to, to the type of crystallinity. The pasting properties of HMT starches and HMT starch blends are presented in Table 4.10. HMT increased the PTs of PS and PoS, reduced the PT of WCS, and had little effect on the PT of CS (Table 4.10) when compared to their corresponding native starches (see Table 4.2). As was the case for native HACS, no pasting peak was observed for HMT HACS.

HMT reduced the PVs and TVs of the constituent starches, markedly in the case of PoS. HMT reduced the FVs of PS, CS and HACS but increased the FVs of WCS and PoS. HMT reduced the PVs and TVs of the starch blends, markedly in the case of PS:PoS blends. HMT reduced the FVs of PS:CS, PS:WCS and PS:HACS blends, but increased the FVs of the PS:PoS blends. Blends that did not exhibit weighted average values include: i) HMT blends of PS and CS exhibited higher PTs and lower PVs, TVs and FVs; ii) HMT blends of PS and WCS exhibited lower PTs and FVs; iii) HMT blends of PS and HACS exhibited lower PVs, TVs and FVs; and

Table 4.10 Pasting properties of heat-moisture-treated pea starch (PS), corn starch (CS), waxy corn starch (WCS), high-amylose corn starch (HACS) or potato starch (PoS) and heat-moisture-treated blends of PS with CS, WCS, HACS or PoS*

	PT (°C)	PV (cP)	TV (cP)	FV (cP)
PS	80.5 ± 1.1c	966 ± 78b	1121 ± 101a	1557 ± 50a
3:1 PS:CS	92.2 ± 0.6a (81.3)	698 ± 23c (1040)	729 ± 15c (1087)	1030 ± 14b (1581)
1:1 PS:CS	84.2 ± 0.8b (82.2)	739 ± 21c (1114)	742 ± 23c (1054)	1147 ± 39b (1606)
1:3 PS:CS	83.8 ± 0.7b (83.0)	1032 ± 46b (1187)	953 ± 48b (1020)	1545 ± 120a (1630)
CS	83.8 ± 0.7b	1261 ± 119a	986 ± 52b	1654 ± 56a
PS	80.5 ± 1.1a	966 ± 78c	1121 ± 101ab	1557 ± 50a
3:1 PS:WCS	74.2 ± 0.4b (78.4)	1097 ± 35c (1283)	1286 ± 23a (1105)	1031 ± 23b (1502)
1:1 PS:WCS	71.7 ± 1.1b (76.3)	1648 ± 74b (1599)	1084 ± 118ab (1089)	1355 ± 34a (1448)
1:3 PS:WCS	72.4 ± 0.2b (74.1)	1805 ± 86b (1920)	1030 ± 32b (1073)	1357 ± 14a (1393)
WCS	72.0 ± 0.3b	2232 ± 58a	1056 ± 35b	1338 ± 5a
PS	80.5 ± 1.1a	966 ± 78a	1121 ± 101a	1557 ± 50a
3:1 PS:HACS	None	184 ± 7b (728)	279 ± 29b (846)	387 ± 33b (1174)
1:1 PS:HACS	None	53 ± 6bc (490)	52± 8c (570)	67 ± 8c (791)
1:3 PS:HACS	None	23 ± 3c (252)	15 ± 2c (293)	21 ± 3c (407)
HACS	None	14 ± 2c	19 ± 8c	24 ± 6c
PS	80.5 ± 1.1a	966 ± 78c	1121 ± 101d	1557 ± 50c
3:1 PS:PoS	77.3 ± 0.3ab (77.6)	1253 ± 78c (1722)	1183 ± 32d (1776)	2294 ± 45c (2608)
1:1 PS:PoS	75.4 ± 0.2b (74.7)	1804 ± 46b (2477)	1724 ± 68c (2431)	3941 ± 68b (3659)
1:3 PS:PoS	74.2 ± 0.5b (71.7)	2089 ± 93b (3233)	2085 ± 59b (3087)	5087 ± 59a (4710)
PoS	68.8 ± 0.4b	3988 ± 38a	3742 ± 14a	5761 ± 32a
Low DS CL CS	81.9 ± 0.1	1772 ± 5	1219 ± 5	2111 ± 14
Low DS CL WCS	59.5 ± 0.0	5412 ± 17	2969 ± 10	4547 ± 21
High DS CL WCS	64.0 ± 0.0	3093 ± 9	2649 ± 11	4981 ± 10
Low DS AC WCS	65.7 ± 0.3	5130 ± 10	3644 ± 14	5438 ± 25

* Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different ($p < 0.05$) by Least Significant Differences. Values enclosed in parentheses are the weighted average values associated with the treatment. Where PT = pasting temperature; PV = pasting viscosity; TV = trough viscosity; CV – cooling viscosity; FV = final viscosity; DS = degree of substitution; CL = cross-linked and AC = acetylated

iv) HMT blends of PS and PoS exhibited lower PTs, PVs, TVs and FVs than their respective weighted average values.

4.4.2.3 Swelling Power and Water Solubility

Swelling power (SP) for HMT PS, CS, WCS, HACS and PoS, and HMT PS:CS, PS:WCS, PS:HACS and PS:PoS blends, at 65, 75, 85 and 95°C are presented in Table 4.11. In general, HMT tended to reduce slightly the SP of pure starches and starch blends, with the exception of HMT PoS and PS:PoS blends which exhibited higher SP at 85 and 95°C (Tables 4.3 and 4.11). HMT tended to have little effect on the WSI of pure starches and starch blends (Tables 4.4 and 4.12).

A number of blends exhibited SPs that were significantly different than their respective, weighted average values. Blends that exhibited SPs that were HMT blends of PS:CS and PS:HACS exhibited lower SP than their respective weighted average values.

Generally, all HMT blends exhibited WSIs that were not essentially weighted average values, with the exception of HMT PS:CS at 75 and 85°C, HMT PS:HACS at 65°C and 75°C and PS:PoS at 95°C. Most blends of HMT PS:CS exhibited higher WSI at 65°C and 95°C. At 65°C, WSIs of HMT blends of PS:PoS were lower than their respective weighted average values (Appendix B).

Comparisons were made between SPs and WSIs of blends of PS and CS, WCS, HACS or PoS and commercial, chemically-modified starches (Tables 4.11 and 4.12). At 85°C, the SP of the 1:3 HMT PS:WCS blend (13.2%) was not significantly different than the SP of a low DS, CL CS (13.0%). At 85°C, the SP of the 1:1 HMT PS:PoS (14.7%) blend was not significantly

Table 4.11 Swelling powers (SPs) of heat-moisture-treated pea starch (PS), corn starch (CS), waxy corn starch (WCS), high-amylose corn starch (HACS) or potato starch (PoS) and heat-moisture-treated blends of PS with CS, WCS, HACS or PoS*

	65°C	75°C	85°C	95°C
PS	5.1 ± 0.4a	7.6 ± 0.5b	8.9 ± 0.7b	11.2 ± 0.9c
3:1 PS:CS	4.0 ± 0.2ab (4.9)	7.5 ± 0.1b (8.0)	9.6 ± 0.1ab (9.3)	11.2 ± 0.1c (12.5)
1:1 PS:CS	3.4 ± 0.1b (4.8)	7.9 ± 0.1ab (8.4)	9.4 ± 0.1ab (9.7)	12.5 ± 0.1c (13.9)
1:3 PS:CS	3.8 ± 0.8a (4.6)	8.7 ± 0.2ab (8.8)	9.9 ± 0.6ab (10.0)	14.6 ± 0.8b (15.2)
CS	4.4 ± 0.1ab	9.2 ± 0.3a	10.4 ± 0.7a	16.8 ± 1.2a
PS	5.1 ± 0.4a	7.6 ± 0.5b	8.9 ± 0.7c	11.2 ± 0.9d
3:1 PS:WCS	4.9 ± 0.0ab (4.8)	11.2 ± 0.1a (8.4)	12.5 ± 0.3b (10.0)	14.3 ± 0.7c (13.4)
1:1 PS:WCS	4.7 ± 0.4ab (4.5)	11.8 ± 0.5a (9.2)	14.9 ± 1.1a (11.1)	17.6 ± 0.1b (15.6)
1:3 PS:WCS	4.1 ± 0.6b (4.2)	10.6 ± 1.1a (9.9)	13.2 ± 0.9ab (12.2)	17.8 ± 1.1b (17.7)
WCS	3.9 ± 0.0b	10.7 ± 0.1a	13.3 ± 0.4ab	19.9 ± 1.1a
PS	5.1 ± 0.4a	7.6 ± 0.5a	8.9 ± 0.7a	11.2 ± 0.9a
3:1 PS:HACS	3.6 ± 0.1b (4.6)	5.9 ± 0.1b (6.5)	7.4 ± 0.1b (7.8)	8.8 ± 0.1b (9.8)
1:1 PS:HACS	3.5 ± 0.0bc (4.1)	4.9 ± 0.1c (5.4)	6.2 ± 0.0c (6.7)	7.6 ± 0.1c (8.3)
1:3 PS:HACS	3.1 ± 0.3bc (3.5)	4.0 ± 0.1d (4.3)	4.9 ± 0.0d (5.6)	6.5 ± 0.1d (6.9)
HACS	3.0 ± 0.0c	3.2 ± 0.1e	4.5 ± 0.0d	5.4 ± 0.1d
PS	5.1 ± 0.4d	7.6 ± 0.5a	8.9 ± 0.7c	11.2 ± 0.9d
3:1 PS:PoS	5.2 ± 0.5d (8.6)	7.5 ± 0.9a (8.1)	11.5 ± 1.1b (10.5)	13.5 ± 0.0c (14.3)
1:1 PS:PoS	7.6 ± 0.2c (12.2)	9.1 ± 0.8a (8.6)	14.7 ± 0.4a (12.1)	20.5 ± 0.7b (17.5)
1:3 PS:PoS	10.0 ± 0.4b (15.7)	8.8 ± 1.1a (9.6)	15.3 ± 0.4a (13.6)	22.9 ± 0.1a (20.6)
PoS	19.2 ± 0.5a	9.6 ± 0.3a	15.2 ± 0.1a	23.7 ± 0.2a
Low DS CL CS	7.8 ± 0.2	9.9 ± 0.0	13.0 ± 0.1	19.7 ± 1.4
Low DS CL WCS	20.6 ± 0.4	21.1 ± 0.0	22.2 ± 0.2	22.8 ± 0.1
High DS CL WCS	13.4 ± 0.0	13.0 ± 0.2	14.7 ± 0.1	13.8 ± 0.1
Low DS AC WCS	12.6 ± 0.7	15.0 ± 0.2	16.7 ± 0.0	17.8 ± 0.3

* Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different (p < 0.05) by Least Significant Differences. Values enclosed in parentheses are the weighted average values associated with the treatment. Where SP = swelling power; DS = degree of substitution; CL = cross-linked and AC = acetylated

Table 4.12 Water solubility indices (WSIs) of heat-moisture-treated pea starch (PS), corn starch (CS), waxy corn starch (WCS), high-amylose corn starch (HACS) or potato starch (PoS) and heat-moisture-treated blends of PS with CS, WCS, HACS or PoS*

	65°C	75°C	85°C	95°C
PS	3.1 ± 0.6c	5.3 ± 0.8b	7.8 ± 0.9a	11.7 ± 0.8c
3:1 PS:CS	3.5 ± 0.8c (3.1)	5.5 ± 0.0ab (5.5)	8.1 ± 0.3a (7.9)	10.6 ± 0.1c (13.6)
1:1 PS:CS	6.1 ± 0.6b (3.1)	5.5 ± 0.3ab (5.8)	8.0 ± 0.2a (8.1)	17.4 ± 0.2b (15.6)
1:3 PS:CS	9.5 ± 0.2a (3.1)	6.8 ± 0.2a (6.0)	8.0 ± 1.0a (8.2)	19.8 ± 0.1a (17.5)
CS	3.0 ± 0.1c	6.2 ± 1.0a	8.3 ± 0.1a	19.4 ± 0.7a
PS	3.1 ± 0.6b	5.3 ± 0.8d	7.8 ± 0.9e	11.7 ± 0.8e
3:1 PS:WCS	4.1 ± 0.4a (5.5)	8.2 ± 0.1c (9.7)	11.4 ± 0.3d (18.8)	22.0 ± 0.1d (26.6)
1:1 PS:WCS	3.7 ± 0.5a (7.9)	14.8 ± 0.6b (14.0)	28.5 ± 1.1c (29.7)	36.2 ± 0.6c (41.4)
1:3 PS:WCS	2.8 ± 0.0bc (10.3)	16.2 ± 0.8b (18.4)	32.8 ± 0.1b (40.7)	49.1 ± 0.7b (56.3)
WCS	2.7 ± 0.2c	22.7 ± 0.9a	51.6 ± 0.9a	71.1 ± 0.6a
PS	3.1 ± 0.6a	5.3 ± 0.8a	7.8 ± 0.9a	11.7 ± 0.8a
3:1 PS:HACS	1.5 ± 0.3c (2.8)	2.1 ± 0.3b (4.1)	5.6 ± 0.4b (6.2)	10.9 ± 0.1a (10.6)
1:1 PS:HACS	2.7 ± 0.2ab (2.5)	3.1 ± 0.2b (2.8)	4.0 ± 0.1c (4.7)	10.8 ± 0.1a (9.6)
1:3 PS:HACS	2.4 ± 0.5abc (2.2)	1.9 ± 0.8b (1.6)	2.7 ± 0.0d (3.1)	8.3 ± 0.2b (8.5)
HACS	1.9 ± 0.1bc	0.3 ± 0.2c	1.5 ± 0.2e	7.4 ± 0.2b
PS	3.1 ± 0.6c	5.3 ± 0.8b	7.8 ± 0.9c	11.7 ± 0.8d
3:1 PS:PoS	1.5 ± 0.1d (15.1)	6.2 ± 0.0b (9.7)	8.5 ± 0.5c (9.7)	11.1 ± 0.5d (16.3)
1:1 PS:PoS	2.7 ± 0.1c (27.1)	6.5 ± 0.1b (11.7)	12.5 ± 0.1b (11.7)	20.2 ± 0.9c (20.8)
1:3 PS:PoS	19.1 ± 0.2b (39.1)	15.8 ± 0.1a (12.4)	11.7 ± 0.8b (13.6)	25.6 ± 0.4b (25.4)
PoS	51.1 ± 0.6a	14.7 ± 0.8a	15.5 ± 0.2a	29.9 ± 0.2a
Low DS CL CS	1.2 ± 0.3	3.3 ± 0.1	7.7 ± 0.1	17.5 ± 1.1
Low DS CL WCS	1.5 ± 0.4	1.1 ± 0.3	1.6 ± 0.1	1.8 ± 0.3
High DS CL WCS	2.5 ± 0.9	0.5 ± 0.0	1.1 ± 0.1	1.4 ± 0.1
Low DS AC WCS	1.3 ± 0.4	0.6 ± 0.0	1.1 ± 0.1	1.8 ± 0.3

*Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different (p < 0.05) by Least Significant Differences. Values enclosed in parentheses are the weighted average values associated with the treatment. Where DS = degree of substitution; CL = cross-linked and AC = acetylated

different than the high DS, CL WCS (14.7%). At 65°C, the WSIs of the 1:3 HMT PS:WCS blend (2.8%), 1:1 HMT PS:HACS (2.7%), 1:3 HMT PS:HACS (2.4%) and 1:1 HMT PS:PoS (2.7%) were not significantly different than the WSI of a high DS, CL WCS (2.5%). At 65°C, the WSIs of the 1:3 HMT PS:HACS and HMT PS:PoS blends were not significantly different than that of a low DS, CL WCS (1.5%).

4.4.2.4 Freeze-Thaw Stability

Freeze-thaw stabilities for HMT PS, CS, WCS, HACS and PoS and HMT blends of PS:CS, PS:WCS, PS:HACS and PS:PoS are presented in Table 4.13. HMT improved freeze-thaw stabilities of all starches except CS (see Table 4.5). PoS exhibited the greatest improvement in freeze-thaw stability after HMT. Hoover et al. (1993) reported that starch from pigeion pea exhibited lower syneresis durirng freeze-thaw cycles after HMT. HMT may reduce retrogradation due to the increased strength of molecular associations, reducing swelling and reducing glucan leaching.

Generally, all of the HMT blends of PS and CS, WCS, HACS and PoS exhibited freeze-thaw stabilities that were not essentially weighted average values except for PS:CS blends after 2 and 3 freeze-thaw cycles and PS:WCS blends after 2 and 4 freeze-thaw cycles (Appendix B).

4.4.2.5 Shear Stability

Shear stabilities for HMT PS, CS, WCS, HACS and PoS and HMT blends of PS:CS, PS:WCS, PS:HACS and PS:PoS are presented in Table 4.14. Native blends of PS:CS, PS:WCS and PS:PoS exhibited higher shear stabilities than their corresponding HMT blends. The reduction in shear stability in HMT starches compared to native starches may be attributed to a

Table 4.13 Freeze-thaw stabilities (% syneresis) of heat-moisture-treated of pea starch (PS), corn starch (CS), waxy corn starch (WCS), high-amylose corn starch (HACS) and potato starch (PoS) and heat-moisture-treated blends of PS and CS, WCS HACS or PoS*

	Freeze-Thaw Cycles				
	1	2	3	4	5
PS	17.6 ± 1.6a	18.4 ± 1.0b	18.6 ± 0.8b	20.2 ± 0.2a	23.3 ± 2.1a
3:1 PS:CS	19.3 ± 1.5a (14.5)	21.9 ± 2.1a (19.3)	21.9 ± 2.2a (19.4)	22.0 ± 2.4a (20.8)	22.1 ± 2.1a (23.4)
1:1 PS:CS	10.4 ± 0.5b (11.4)	17.0 ± 0.1b (20.2)	17.2 ± 0.1b (20.3)	19.2 ± 1.1a (21.4)	20.3 ± 0.4a (23.6)
1:3 PS:CS	5.7 ± 0.7c (8.3)	18.7 ± 1.2b (21.0)	18.8 ± 1.6b (21.1)	18.8 ± 1.1a (21.9)	19.1 ± 0.6a (23.7)
CS	5.2 ± 0.2c	21.9 ± 0.4a	21.9 ± 0.3a	22.5 ± 1.0a	23.8 ± 2.8a
PS	17.6 ± 1.6a	18.4 ± 1.0a	18.6 ± 0.8a	20.2 ± 0.2a	23.3 ± 2.1b
3:1 PS:WCS	12.2 ± 0.4b (14.2)	13.3 ± 0.9b (15.4)	17.7 ± 0.5a (15.6)	18.0 ± 0.6b (18.9)	21.9 ± 0.7b (25.4)
1:1 PS:WCS	12.0 ± 0.3b (10.7)	13.1 ± 1.1b (12.5)	13.2 ± 0.0b (12.6)	14.4 ± 0.4b (17.7)	23.0 ± 0.4b (27.6)
1:3 PS:WCS	9.2 ± 1.4c (7.3)	10.0 ± 0.8c (9.5)	10.1 ± 0.2c (9.6)	17.3 ± 0.6b (16.4)	27.9 ± 0.6a (29.7)
WCS	3.8 ± 0.4d	6.6 ± 1.3d	6.6 ± 1.4d	15.1 ± 2.5b	31.9 ± 2.4a
PS	17.6 ± 1.6e	18.4 ± 1.0e	18.6 ± 0.8e	20.2 ± 0.2e	23.3 ± 2.1e
3:1 PS:HACS	35.6 ± 3.8d (27.7)	38.9 ± 3.9d (30.5)	39.0 ± 3.3d (30.7)	41.5 ± 2.4d (32.7)	43.1 ± 0.8d (35.4)
1:1 PS:HACS	45.2 ± 0.5c (37.8)	47.6 ± 0.1c (42.6)	47.6 ± 0.6c (42.8)	52.8± 1.3c (45.1)	54.7 ± 0.2c (47.4)
1:3 PS:HACS	51.5 ± 1.9b (47.9)	58.8 ± 0.1b (54.7)	59.0 ± 0.4b (54.8)	62.4 ± 0.9b (57.6)	62.9 ± 1.7b (59.5)
HACS	58.0 ± 2.7a	66.9 ± 1.7a	67.0 ± 1.7a	70.0 ± 1.0a	71.5 ± 1.3a
PS	17.6 ± 1.6a	18.4 ± 1.0a	18.6 ± 0.8a	20.2 ± 0.2a	23.3 ± 2.1a
3:1 PS:PoS	13.3 ± 0.3b (14.2)	13.7 ± 0.2b (15.9)	14.7 ± 0.1b (16.1)	15.3 ± 0.1c (19.9)	16.7 ± 0.9b (22.3)
1:1 PS:PoS	9.2 ± 0.3c (10.9)	10.5 ± 0.8c (13.4)	11.6 ± 0.9bc (13.6)	16.5 ± 0.7bc (19.6)	16.7 ± 1.0b (21.3)
1:3 PS:PoS	5.7 ± 0.5d (7.5)	6.5 ± 0.3d (10.9)	9.5 ± 0.3cd (11.1)	18.5 ± 2.0ab (19.2)	19.5 ± 0.1b (20.3)
PoS	4.1 ± 1.0d	8.4 ± 2.2cd	8.6 ± 1.1d	18.9 ± 1.5ab	19.3 ± 1.9b
Low DS CL CS	1.7 ± 0.4	2.0 ± 0.5	2.0 ± 0.5	2.7 ± 0.2	6.6 ± 0.8
Low DS CL WCS	2.0 ± 0.1	2.0 ± 0.1	2.0 ± 0.1	2.3 ± 0.6	2.3 ± 0.6
High DS CL WCS	20.3 ± 0.7	20.4 ± 0.7	20.4 ± 0.7	20.6 ± 0.6	20.7 ± 0.7
Low DS AC WCS	10.6 ± 0.2	10.6 ± 0.2	10.7 ± 0.2	10.8 ± 0.3	11.3 ± 0.4

*Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different ($p < 0.05$) by Least Significant Differences. Values enclosed in parentheses are the weighted average values associated with the treatment. Where DS = degree of substitution; CL = cross-linked and AC = acetylated

Table 4.14 Shear stabilities of heat-moisture-treated of pea starch (PS), corn starch (CS), waxy corn starch (WCS), high amylose corn starch (HACS) and potato starch (PoS) and heat-moisture-treated blends of PS and CS, WCS HACS or PoS *

	Shear stability (%)
PS	78 ± 1c
3:1 PS:CS	74 ± 1d (81)
1:1 PS:CS	79 ± 1c (84)
1:3 PS:CS	86 ± 1b (87)
CS	90 ± 2a
PS	78 ± 1b
3:1 PS:WCS	67 ± 3d (80)
1:1 PS:WCS	67 ± 1d (81)
1:3 PS:WCS	73 ± 1c (83)
WCS	84 ± 1a
PS	78 ± 1b
3:1 PS:HACS	80 ± 3b (83)
1:1 PS:HACS	93 ± 2a (87)
1:3 PS:HACS	97 ± 1a (92)
HACS	96 ± 3a
PS	78 ± 1b
3:1 PS:PoS	74 ± 1c (81)
1:1 PS:PoS	71± 1c (85)
1:3 PS:PoS	71 ± 1c (88)
PoS	91 ± 3a
Low DS CL CS	89 ± 1
Low DS CL WCS	72 ± 1
High DS CL WCS	91 ± 1
Low DS AC WCS	91 ± 1

*Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different ($p < 0.05$) by Least Significant Differences. Values enclosed in parentheses are the weighted average values associated with the treatment. Where DS = degree of substitution; CL = cross-linked and AC = acetylated

reduction in glucan entanglement or associations after pasting leading to more exposed glucans to be susceptible to shear.

Unexpected results, i.e. values that were not essentially weighted average values of those of the constituent starches, were observed for all HMT blends. Blends of HMT PS:CS, HMT PS:WCS and HMT PS:PoS exhibited shear stabilities that were lower, and HMT PS:HACS exhibited shear stabilities that were higher than their respective weighted average values (Table 4.14; Appendix B).

Comparisons were made between the shear stabilities of blends of PS and CS, WCS, HACS or PoS and commercial, chemically-modified starches (Table 4.14). The shear stabilities of HMT 3:1 PS:CS (74%), HMT 1:3 PS:WCS (73%) and HMT 3:1 PS:PoS (74%) were not significantly different than that of a low DS, CL WCS (72%). The shear stability of the HMT 1:1 PS:HACS blend (93%) was not significantly different than the shear stability of a high DS, CL WCS or a low DS, AC WCS (91 and 91%, respectively).

4.4.2.6 Water Binding Capacity

Water binding capacities for HMT PS, CS, WCS, HACS and PoS and HMT blends of PS:CS, PS:WCS, PS:HACS and PS:PoS are presented in Table 4.15. HMT reduced the WBC of PS, blends of PS:CS, HACS, blends of PS:HACS and PoS and increased the WBC of WCS and blends of PS:WCS (see Table 4.7 and 4.15). PoS exhibited the largest increase in WBC. Typically, potato starches are more susceptible to HMT due to their weak structure and B-type polymorph structure allowing for shifts in amylopectin crystallinity structure from B-type to A-type. The reduction of WBC in PS of PS:CS, HACS, blends of PS:HACS and PoS with HMT may be attributed to a loss of water binding sites by reduced availability of hydroxyl groups due

Table 4.15 Water binding capacities (WBCs) of heat-moisture-treated of pea starch (PS), corn starch (CS), waxy corn starch (WCS), high-amylose corn starch (HACS) and potato starch (PoS) and heat-moisture-treated blends of PS and CS, WCS HACS or PoS*

	WBC (%)
PS	96.8 ± 0.1a
3:1 PS:CS	86.4 ± 0.4b (91.8)
1:1 PS:CS	76.7 ± 0.3c (86.8)
1:3 PS:CS	71.8 ± 0.7d (83.0)
CS	76.8 ± 0.2c
PS	96.8 ± 0.1c
3:1 PS:WCS	106.0 ± 0.8a (78.4)
1:1 PS:WCS	101.8 ± 1.1b (94.2)
1:3 PS:WCS	96.5 ± 0.9c (92.8)
WCS	91.5 ± 0.6d
PS	96.8 ± 0.1a
3:1 PS:HACS	93.6 ± 0.2b (96.6)
1:1 PS:HACS	77.5 ± 0.7d (96.4)
1:3 PS:HACS	89.4 ± 0.8c (96.1)
HACS	95.9 ± 0.3a
PS	96.8 ± 0.1a
3:1 PS:PoS	92.4 ± 0.9a (92.5)
1:1 PS:PoS	83.7 ± 0.9b (88.2)
1:3 PS:PoS	84.4 ± 0.9b (83.9)
PoS	79.6 ± 0.3c
Low DS CL CS	72.9 ± 1.0
Low DS CL WCS	104.6 ± 0.5
High DS CL WCS	92.6 ± 0.2
Low DS acetylated CS	84.1 ± 0.2

*Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different ($p < 0.05$) by Least Significant Differences. Values enclosed in parentheses are the weighted average values associated with the treatment. Where DS = degree of substitution; CL = cross-linked and AC = acetylated

to the compactness of granule. Hydrogen bonding site availability varies based on granule arrangement and amorphous:crystalline ratio (Hoover, 2010).

Unexpected results, i.e. values that were not essentially weighted averages of the WBCs of the constituent starches, were observed for the i) WBCs of HMT blends of PS:CS (lower than the weighted average); ii) PS:WCS (higher than the weighted average); and iii) PS:HACS (lower than the weighted average) (Appendix B).

Comparisons were made between the WBCs of HMT blends of PS and CS, WCS, HACS or PoS and commercial, chemically-modified starches (Table 4.15). The WBC of the HMT 1:3 PS:CS blend (71.8%) was not significantly different than the WBC of the low DS, CL CS (72.9%). The WBC of the HMT 3:1 PS:PoS (92.4%) was not significantly different than the WBC of a high DS, CL WCS (92.6%).

4.4.2.7 Resistant Starch Concentration

The RS concentrations for HMT PS, CS, WCS, HACS and PoS and HMT blends of PS:CS, PS:WCS, PS:HACS and PS:PoS are presented in Table 4.16. HMT starches and blends exhibited higher RS concentrations than native or pregelatinized starches or native or pregelatinized starch blends. Chung et al. (2009) postulated that interactions between amylose molecules formed during HMT may create a barrier to enzymatic hydrolysis. HMT or other treatment/processing of starch that alters the amylose concentration, proportion of B-type crystallites, glucan interactions with glucans or other components (e.g. lipids) may affect RS concentration.

Table 4.16 Resistant starch concentrations of heat-moisture-treated of pea starch (PS), corn starch (CS), waxy corn starch (WCS), high-amylose corn starch (HACS) and potato starch (PoS) and heat-moisture-treated blends of PS and CS, WCS, HACS or PoS*

	Resistant starch (%)
PS	6.4 ± 0.5a
3:1 PS:CS	6.7 ± 0.1a (5.2)
1:1 PS:CS	4.8 ± 0.4b (4.0)
1:3 PS:CS	3.5 ± 0.1c (2.7)
CS	1.5 ± 0.1d
PS	6.4 ± 0.5a
3:1 PS:WCS	5.0 ± 0.1b (4.9)
1:1 PS:WCS	3.7 ± 0.2c (3.4)
1:3 PS:WCS	3.2 ± 0.3c (1.9)
WCS	0.4 ± 0.0d
PS	6.4 ± 0.5e
3:1 PS:HACS	17.5 ± 1.3d (17.1)
1:1 PS:HACS	28.9 ± 1.1c (27.8)
1:3 PS:HACS	39.7 ± 1.1b (38.5)
HACS	49.2 ± 0.7a
PS	6.4 ± 0.5e
3:1 PS:PoS	15.7 ± 0.8d (18.3)
1:1 PS:PoS	24.7 ± 0.2c (30.2)
1:3 PS:PoS	38.5 ± 2.7b (42.0)
PoS	53.9 ± 2.5a
Low DS CL CS	2.5 ± 0.1
Low DS CL WCS	16.7 ± 0.4
High DS CL WCS	11.1 ± 0.2
Low DS AC WCS	1.1 ± 0.2

*Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different (p < 0.05) by Least Significant Differences. Values enclosed in parentheses are the weighted average values associated with the treatment. Where DS = degree of substitution; CL = cross-linked and AC = acetylated

Generally, blends of PS and CS or PoS exhibited RS concentrations that were not essentially weighted average values of the constituent starches except blends of PS:WCS and PS:HACS. Blends of HMT PS:CS exhibited RS concentrations that were higher than the weighted average value and blends of HMT PS:PoS exhibited RS concentrations that were lower than the weighted average values (Appendix B).

4.4.3 Functional Properties of Pregelatinized Pea Starch (PS), Corn Starch (CS), Waxy Corn Starch (WCS), High-Amylose Corn Starch (HACS) and Potato Starch (PoS) and Pregelatinized Combinations of PS and CS, WCS, HACS or PoS

Compared to PG pea starch: i) PG blends of PS and CS exhibited higher WSIs at 65°C and 75°C; ii) PG blends of PS and WCS exhibited higher SPs at all temperatures, higher WSIs at 65°C, 85°C and 95°C and lower RS concentrations; iii) PG blends of PS and HACS exhibited lower SPs and WSIs; and iv) blends of PS and PoS exhibited higher SPs at all temperatures and WSIs at 65°C, 85°C and 95°C and lower RS concentration.

4.4.3.1 Thermal Properties

To confirm that the pregelatinized starches were indeed gelatinized, DSCs on PG PS, CS, WCS, HACS and PoS was performed (Figure 4.4). In all cases, with the exception of PG HACS, the DSC traces displayed no peaks. In the case of PG HACS, it was anticipated that the starch would not be completely gelatinized. The drum-drying step may have disturbed a few starch granules reducing the gelatinization temperature of a portion of the HACS granules allowing for those granules to gelatinize at temperatures used during DSC analysis.
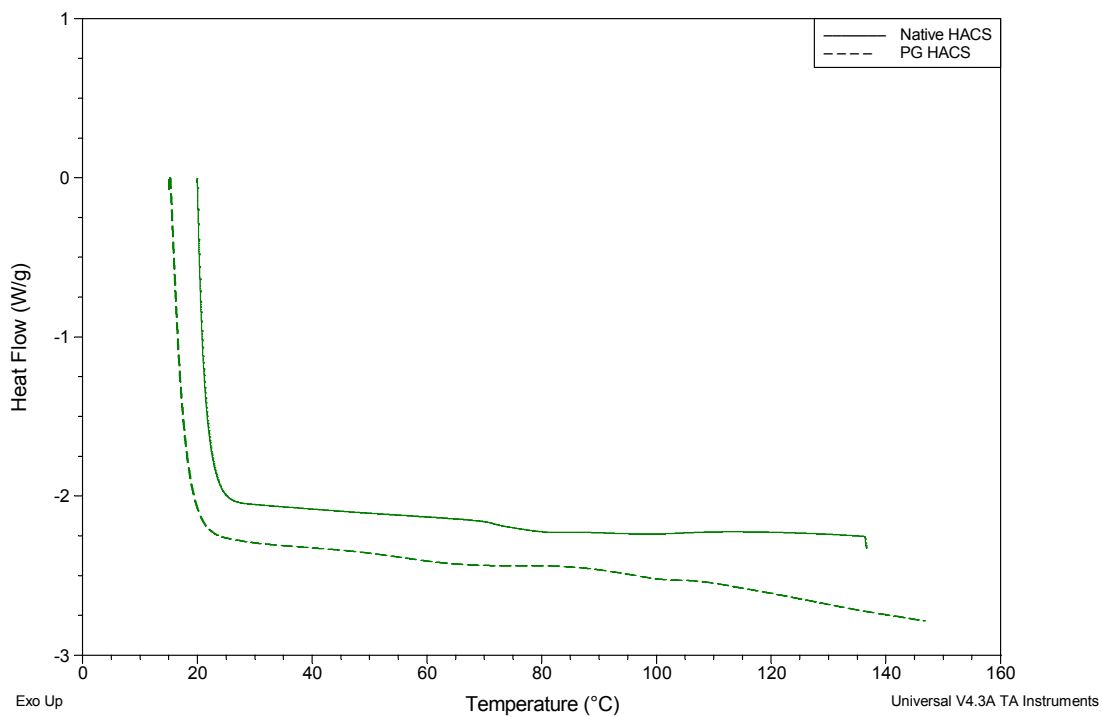
Figure 4.4   Differential scanning calorimetry (DSC) thermogram of native high-amylose corn
starch (HACS) and pregelatinized (PG) HACS

4.4.3.2 Swelling Power and Water Solubility

Swelling power analysis of pregelatinized starch indicates the ability of the pregelatinized starch to rehydrate and retain water at specified temperatures. Swelling powers of pregelatinized (PG) PS, CS, WCS, HACS and PoS and PG blends of PS:CS, PS:WCS, PS:HACS and PS:PoS are presented in Table 4.17. Generally, pregelatinization increased swelling powers of the starches and starch blends at lower temperatures when compared to native and heat-moisture-treated blends or constituent starches. WCS and HACS exhibited high and low SPs. The high and low values, respectively, for WCS and HACS reflected the low and high amylose concentrations of these starches.

Generally, combinations of PS and CS or PoS exhibited SPs that were not essentially weighted average values of the constituent starches, with the exception of SP at 75°C for PS:CS. Blends that did not exhibit weighted average values include: i) PG blends of PS and CS exhibited SPs that were higher at 65°C, 85°C and 95°C; ii) PG blends of PS and WCS exhibited SPs that were lower at 85°C and 95°C; iii) PG blends of PS and HACS exhibited SPs that were higher at 65°C and lower at 75°C; and iv) PG blends of PS and PoS exhibited SPs that were higher at 75°C, 85°C and 95°C than their respective weighted average values (Appendix C).

Water solubility indices (WSIs) of pregelatinized blends of PS with CS, WCS, HACS or PoS are presented in Table 4.18. Most dramatically, blends of PG PS:PoS exhibited WSIs that were higher than the weighted average values at 65°C and lower at 75 and 95°C. Blends that did not exhibit weighted average values include: i) blends of PG PS:CS exhibited WSIs higher at 95°C; ii) blends of PG PS:WCS exhibited lower WSIs; iii) blends of PG PS:HACS exhibited WSIs that were lower at 95°C; and iv) blends of PG PS:PoS exhibited WSIs that were higher at 65°C and lower at 75 and 95°C than their respective weighted average values (Appendix C).

Table 4.17 Swelling powers (SPs) of pregelatinized pea starch (PS), corn starch (CS), waxy corn starch (WCS), high-amylose corn starch (HACS) and potato starch (PoS) and pregelatinized blends of PS and CS, WCS, HACS or PoS*

	65°C	75°C	85°C	95°C
PS	10.5 ± 0.5b	12.6 ± 0.4a	13.1 ± 0.1a	14.2 ± 0.8a
3:1 PS:CS	10.6 ± 0.8b (10.6)	12.7 ± 0.9a (12.0)	13.3 ± 0.1a (12.7)	15.1 ± 0.4a (14.4)
1:1 PS:CS	11.1 ± 0.1b (10.6)	12.2 ± 0.5a (11.3)	13.1 ± 0.5a (12.4)	15.1 ± 0.1a (14.6)
1:3 PS:CS	12.9 ± 0.1a (10.7)	11.9 ± 0.3a (10.7)	12.7 ±0.2ab (12.0)	15.7 ± 0.1a (14.8)
CS	10.7 ± 0.5b	10.0 ± 0.9a	11.6 ± 0.2b	15.0 ± 1.1a
PS	10.5 ± 0.5d	12.6 ± 0.4c	13.1 ± 0.1e	14.2 ± 0.8d
3:1 PS:WCS	16.4 ± 2.1c (16.8)	17.7 ± 0.1b (14.8)	18.2 ± 0.5d (17.6)	21.6 ± 0.1c (19.7)
1:1 PS:WCS	23.9 ± 1.1b (23.1)	19.0 ± 1.4ab (16.9)	19.9 ± 0.4c (22.0)	23.2 ± 0.3c (25.2)
1:3 PS:WCS	24.5 ± 0.0b (29.3)	19.6 ± 1.1ab (19.1)	20.4 ± 0.1b (26.5)	19.2 ± 0.1b (30.7)
WCS	35.6 ± 0.5a	21.2 ±1.9a	30.9 ± 0.3a	36.2 ± 1.5a
PS	10.5 ± 0.5a	12.6 ± 0.4a	13.1 ± 0.1a	14.2 ± 0.8a
3:1 PS:HACS	11.2 ± 0.3a (9.2)	10.3 ± 0.3b (10.9)	12.6 ± 0.1ab (12.8)	11.9 ± 0.6b (12.4)
1:1 PS:HACS	8.8 ± 0.2b (8.0)	8.4 ± 0.3c (9.1)	12.1 ± 0.2bc (12.5)	9.2 ± 0.2c (10.5)
1:3 PS:HACS	6.7 ± 0.3c (6.7)	6.8 ± 0.2d (7.4)	12.3 ± 0.3bc (12.1)	8.6 ± 0.6c (8.7)
HACS	5.4 ± 0.1d	5.6 ± 0.1e	11.8 ± 0.4c	6.8 ± 0.0d
PS	10.5 ± 0.5e	12.6 ± 0.4e	13.1 ± 0.1d	14.2 ± 0.8d
3:1 PS:PoS	21.0 ± 1.5d (20.3)	24.2 ± 1.5d (19.6)	29.2 ± 3.5c (18.9)	28.6 ± 1.4b (16.0)
1:1 PS:PoS	37.7 ± 0.9c (30.1)	34.0 ± 2.9c (26.6)	44.2 ± 1.4a (24.7)	42.6 ± 4.1a (17.7)
1:3 PS:PoS	43.0 ± 2.5b (39.8)	49.9 ± 0.0b (33.5)	36.1 ± 4.6b (30.5)	19.3 ± 1.0c (19.5)
PoS	49.6 ± 0.9a	40.5 ± 1.7a	36.3 ± 0.9b	20.2 ± 1.6c

* Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different (p < 0.05) by Least Significant Differences. Values enclosed in parentheses are the weighted average values associated with the treatment.

Table 4.18 Water solubility indices (WSIs) of pregelatinized pea starch (PS), corn starch (CS), waxy corn starch (WCS), high-amylose corn starch (HACS) and potato starch (PoS) and pregelatinized blends of PS and CS, WCS, HACS or PoS*

	65°C	75°C	85°C	95°C
PS	7.4 ± 1.8c	12.8 ± 0.6a	13.9 ± 0.3a	16.0 ± 0.1c
3:1 PS:CS	8.2 ± 1.3b (9.8)	14.8 ± 2.8a (12.4)	16.0 ± 0.2a (13.2)	21.2 ± 0.3b (17.9)
1:1 PS:CS	11.6 ± 1.0b (12.3)	12.8 ± 0.4a (12.1)	12.5 ± 0.9a (12.5)	21.6 ± 0.5b (19.7)
1:3 PS:CS	12.9 ± 0.8a (14.7)	9.4 ± 0.2a (11.7)	12.0 ± 0.3a (11.8)	22.3 ± 0.3b (21.6)
CS	17.1 ± 2.0a	11.3 ± 0.2a	11.5 ± 1.8a	23.4 ± 0.7a
PS	7.4 ± 1.8d	12.8 ± 0.6c	13.9 ± 0.3d	16.0 ± 0.1c
3:1 PS:WCS	13.7 ± 0.1cd (14.3)	12.3 ± 1.4c (18.4)	12.7 ± 0.9c (20.2)	18.3 ± 1.9c (21.8)
1:1 PS:WCS	15.9 ± 2.4b (21.2)	13.1 ± 0.1c (24.1)	10.1 ± 0.1c (26.5)	25.2 ± 0.3b (27.5)
1:3 PS:WCS	22.9 ± 1.7b (28.1)	22.2 ± 1.5b (29.7)	39.3 ± 0.9b (32.7)	28.4 ± 1.4b (33.3)
WCS	35.3 ± 1.8a	35.3 ± 3.9a	43.7 ±1.0a	39.4 ± 0.0a
PS	7.4 ± 1.8a	12.8 ± 0.6a	13.9 ± 0.3a	16.0 ± 0.1b
3:1 PS:HACS	7.9 ± 0.6a (6.7)	9.8 ± 1.1b (10.2)	12.1 ± 0.9a (11.4)	18.4 ± 0.7a (14.7)
1:1 PS:HACS	5.4 ± 1.0b (6.0)	5.0 ± 0.2c (7.6)	7.5 ± 0.4b (8.9)	15.8 ± 0.5b (13.4)
1:3 PS:HACS	5.1 ± 1.0b (5.3)	4.2 ± 0.1c (5.0)	5.8 ± 1.4bc (6.3)	15.4 ± 0.7b (12.1)
HACS	4.6 ± 0.6b	2.4 ± 0.4d	3.8 ± 0.4c	10.8 ± 1.4c
PS	7.4 ± 1.8c	12.8 ± 0.6b	13.9 ± 0.3b	16.0 ± 0.1d
3:1 PS:PoS	16.8 ± 2.6b (9.5)	14.0 ± 0.1b (24.8)	22.6 ± 2.9b (24.8)	19.0 ± 0.3d (28.4)
1:1 PS:PoS	17.0 ± 0.9b (11.6)	11.6 ± 0.7b (36.9)	16.9 ± 1.7b (35.8)	26.3 ± 1.5c (40.8)
1:3 PS:PoS	17.6 ± 2.0a (13.7)	13.4 ± 2.4b (48.9)	58.2 ± 3.9a (46.7)	46.2 ± 2.9b (53.1)
PoS	15.8 ± 0.3b	60.9 ± 1.8a	57.6 ± 1.0a	65.5 ± 0.4a

*Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different ($p < 0.05$) by Least Significant Differences. Values enclosed in parentheses are the weighted average values associated with the treatment.

4.4.3.3 Resistant Starch Concentration

Resistant starch concentrations of PG PS, CS, WCS, HACS and PoS and PG blends of PS:CS, PS:WCS, PS:HACS and PS:PoS are presented in Table 4.19. Resistant starch concentrations of PG starches were lower than their respective native and HMT starches. Typically, gelatinization reduces resistant starch concentration by solubilizing glucans and increasing susceptibility to enzymatic attack. Resistant starch concentration of PoS exhibited the largest reduction in RS concentration from the native state. Additionally, HACS exhibited the smallest reduction in RS concentration from the native state likely due to HACS granules not completely gelatinizing during drum drying. Generally, PG blends of PS:WCS and PoS exhibited RS concentrations that were lower than their respective weighted average values (Appendix C).

4.5 Discussion

4.5.1 Effect of Heat-Moisture Treatment on Starch Functionality

The effect of HMT of starches from different botanical sources is determined primarily by the polymorphic structure of the crystalline lamellae. Corn starch and WCS are A-type polymorphs, HACS (Hylon VII) and PoS are B-type polymorphs, and PS is a C-type polymorph. A-type polymorphs form face-centered, monoclinic unit cells, whereas B-type polymorphs form hexagonal unit cells (Gidley & Bociek, 1985). A- and B-type polymorphs also vary in the number of water molecules associated with the unit cell, where A-type polymorphs contain four water molecules, and B-type polymorphs 36 water molecules, between the helices in one unit cell. Starches containing B-type polymorphs tend to shift to contain both A- and B-type polymorphs during HMT, significantly altering the functional properties of the starch (Hoover, 2010). The crystallinity in C-type starches did not change (pigeon pea, Hoover et al., 1993) or increased in

Table 4.19   Resistant starch concentrations (dry basis) of pregelatinized pea starch (PS), corn starch (CS), waxy corn starch (WCS), high-amylose corn starch (HACS) and potato starch (PoS) and pregelatinized blends of PS and CS, WCS, HACS or PoS*

	Resistant starch (%)
PS	$4.3 \pm 0.1a$
3:1 PS:CS	$3.2 \pm 0.3b$ (3.6)
1:1 PS:CS	$2.4 \pm 0.0c$ (2.9)
1:3 PS:CS	$2.0 \pm 0.1d$ (2.1)
CS	$1.4 \pm 0.0e$
PS	$4.3 \pm 0.1a$
3:1 PS:WCS	$2.7 \pm 0.2b$ (3.3)
1:1 PS:WCS	$1.3 \pm 0.0c$ (2.3)
1:3 PS:WCS	$0.5 \pm 0.0d$ (1.2)
WCS	$0.2 \pm 0.0e$
PS	$4.3 \pm 0.1e$
3:1 PS:HACS	$8.7 \pm 0.1d$ (8.3)
1:1 PS:HACS	$12.1 \pm 0.1c$ (12.2)
1:3 PS:HACS	$15.4 \pm 0.3b$ (16.2)
HACS	$20.1 \pm 0.2a$
PS	$4.3 \pm 0.1a$
3:1 PS:PoS	$2.9 \pm 0.3b$ (3.4)
1:1 PS:PoS	$2.2 \pm 0.0c$ (2.6)
1:3 PS:PoS	$1.3 \pm 0.0d$ (1.7)
PoS	$0.8 \pm 0.0e$

*Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different ($p < 0.05$) by Least Significant Differences. Values enclosed in parentheses are the weighted average values associated with the treatment.

intensity (lentil, Hoover & Vasanthan, 1994b). Hoover & Manual (1996b) postulated that the difference in effects of HMT of C-type starches might be attributed to the difference in proportions of A- and B-type polymorphs in C-type starches.

Varatharajan et al. (2010) postulated that HMT increased To, Tp and Tc of PoS due to the creation of new A-type polymorphs and interactions between glucan molecules. However, in normal maize, waxy maize, dull waxy maize and amylomaize V starches (Hoover & Manual, 1996a) and black bean, pinto bean, field pea and lentil starches (Hoover & Manual, 1996b), HMT did not alter ΔH values. The effect of HMT on starch varies depending on the botanical source of the starch and the degree of HMT treatment (moisture content, temperature, time). The increases in To, Tp and Tc are likely due to an increase in amylose-amylose, amylose-amylopectin and amylose-lipid interactions, thus reducing the glucan mobility of the amorphous regions (Gunaratne & Hoover, 2002; Hoover et al., 1993; Hoover & Manual, 1996a; Hoover & Manual, 1996b; Hoover & Vasanthan, 1994a). Reduced mobility of glucans in the amorphous regions typically results in higher temperatures for gelatinization and pasting, as swelling and water uptake may be reduced or slower (Hoover, 2010). A reduction in ΔH indicates a disruption of the double helices of amylopectin in the crystalline and amorphous regions (Gunaratne & Hoover, 2002) or partial gelatinization during HMT, reducing granule stability (Hossen et al., 2011). The potential for the formation of amylose-lipid complexes during HMT may have increased the To of blends of HMT PS:CS.

HMT tends to reduce granule swelling and glucan leaching by increasing granule crystallinity, increasing interactions of glucan molecules, and shifting granule crystallinity polymorph type from B to A plus B in the case of B-type polymorphs (Hoover & Manual, 1996a, Hoover & Manual, 1996b; Hoover & Vasanthan, 1994a). Additionally, there may be a shift in the A-type to B-type polymorph ratio in C-type polymorphs. Chung et al. (2009) reported a loss of

birefringence at the centre of the granule after HMT of PS (100°C and 120°C). Pea starch exhibits a C-type polymorph structure where the centre of the granule is B-type, and the exterior portion of the granule is A-type. Several factors may influence the reduction in SP and WSI due to HMT, including increased amylose-amylose and amylose-amylopectin interactions reducing the amount of hydroxyl groups available for formation of hydrogen bonding with water (Varatharajan et al., 2010) and, more specifically, the formation of amylose-lipid complexes. Amylose-lipid complexes are formed when amylose and a monoglycerides or fatty acids are heated together (Kugimiya et al., 1980; Tufvesson et al., 2003).

4.5.2 Effect of Pregelatinization on Starch Functionality

Pregelatinization of starch is useful in certain applications where convenience is required (institutions, co-packing, retail), or in low-moisture food processing conditions, salad dressings, baked goods (reduces spread of cookies, maintains crumb texture in bread, improves machinability of pastry doughs) and dry mixes (Mason, 2009). Typically, pregelatinized starches exhibit lower viscosities than do corresponding native starches owing to the loss of granule structure, which reduces the volume fraction of the dispersed phase and irreversible retrogradation during drying. The solubility of pregelatinized starches can be manipulated by increasing dextrinization (higher temperatures, more shear) or altering particle size or temperature of rehydration (Colonna et al., 1984). Drum-dried wheat starch exhibited lower iodine binding than did native wheat starch (Colonna et al., 1984), possibly due to the formation of amylose-lipid complexes. This may also contribute to lower viscosities.

4.5.3 Effect of Blending on Starch Functionality

Factors that may affect the functionality of starch blends or starch gels may include one or a combination of the following: i) the volume fraction of the discontinuous phase; ii) the effective concentration of system components; iii) the rigidity of the dispersed phase; and iv) interactions between the continuous phase and dispersed phase.

The *volume fraction of the dispersed phase* fluctuates during heating and cooling of a starch-water system. As a mixture of starch and water is heated and the granules swell, the volume fraction of the dispersed phase increases. As the granule breaks down and solubilizes, the volume fraction of the dispersed phase decreases, and then increases as amylose begins phase separation during gelation and retrogradation.

The *effective concentration* of components in the system is a function of the solubilized constituents in the system and the water uptake of starch granules. The constituents and viscosity of the continuous phase will change as amylose and amylopectin solubilize and amylose precipitates/crystallizes during heating and cooling. In systems containing PoS, where amylose is co-crystallized with amylopectin (Hoover & Vasanthan, 1994b; Saibene et al., 2008), amylose may also co-solubilize with amylopectin (Gudmundsson & Eliasson, 1990; Steeneken, 1989), thus, influencing the properties of the continuous phase and possibly contributing to a lack of gelation. In a blend, the effective concentration of the components in the continuous phase may change as the starch with the lower gelatinization or pasting temperature imbibes water, swells and crystallites melt, potentially affecting the amount of water available to plasticize and melt the remaining starch granules or crystalline units.

The *rigidity of the dispersed phase* may be affected by the presence or absence of granule ghosts, stabilization of granule ghosts by granule-associated proteins, the degree of crystallization of the dispersed phase (primarily precipitated amylose molecules), or the presence of other starch

particulates remaining after thermal treatment (e.g. ungelatinized starch granules) (Biliaderis, 2009). The rigidity of the dispersed phase increases upon cooling, as amylose undergoes phase separation (precipitation) and crystallization. In addition, amylose-lipid complexes may crystallize and alter the rigidity of the dispersed phase.

Interactions between the continuous phase and dispersed phase may include incompatibility between amylose and amylopectin causing phase separation of amylose, hydrogen-bonding between glucans from the starches, complexation of amylose and lipid and interactions of solubilized glucans and granule ghosts (Biliaderis, 2009).

4.5.3.1 Components of Starch

Amylose-amylopectin ratio, degree of polymerization of amylose and amylopectin, and granule crystallinity (type, stability) influence starch functionality. Amylose-amylopectin ratio influences starch functionality as waxy (low amylose) starches tend to exhibit higher swelling and paste viscosities (Tester & Morisson, 1990a) and lower levels of syneresis (Swinkles, 1985) than starches containing higher amylose concentrations. The amylose to amylopectin ratio may influence the distribution of starch components in the continuous and dispersed phases. As amylopectin and amylose are not soluble together in solution, amylopectin may induce phase separation of amylose (German et al., 1992). In CS, as amylose concentration increased, the double helical content of amylopectin decreased (Cheetham & Tao, 1997). Typically, longer amylopectin chain lengths were associated with higher gelatinization temperatures (Jane et al., 1999). In PoS, it has been demonstrated that amylose and amylopectin are co-crystallized, whereas in cereal starches they are not (Hoover & Vasanthan, 1994b; Saibene et al., 2008). Legume starches possess a C-type X-ray diffraction pattern, which is a combination of the A-type diffraction pattern of cereals and the B-type diffraction pattern of tubers. A-type and B-type

polymorphs differ in water content and the packing of parallel double helices. B-type crystallinity contains more intrahelical water (Imberty & Perez, 1988; Imberty et al., 1988). In C-type polymorphs, A-type and B-type polymorphs are present in the same granule, with B-type polymorphs positioned near the centre of the granule and A-type polymorphs positioned near the outer areas of the granule (Bogracheva et al., 1998). The proportion of B-type polymorph varies in legume starches (Hoover & Ratnayake, 2002; Sarko & Wu, 1978).

The protein concentrations in PS, CS, WCS, HACS and PoS were 0.48, 0.15, 0.33, 0.36 and 0.14%, respectively. Protein contamination of starch fractions can be located at either the surface of the granule or in the interior of the granule. Granule-bound starch synthase (GBSS) is a key enzyme in the biosynthesis of amylose and is considered the primary protein associated with starch granules, and accordingly is the protein associated with remnants of starch granules after pasting (Han & Hamaker, 2002). These proteins may influence the rigidity of the dispersed phase by assisting in the formation of granule ghosts.

The lipid concentrations of PS, CS, WCS, HACS and PoS were 0.20, 0.12, 0.15, 0.33 and 0.18%, respectively. The location of the lipid varies among botanical sources. In cereal starches, such as CS, the lipid is typically located in the granule, whereas in PoS much of the lipid resides on the surface of the granule (BeMiller, 2007). Lipids associated with PoS are largely phosphate monoesters (BeMiller & Whistler, 1996) and may create barriers to interactions among glucans due to their anionic nature, possibly increasing swelling and viscosity. Lipids associated with cereal starches are mainly free fatty acids and phospholipids, which have a tendency to complex with amylose (Thomas & Atwell, 1999). Of note, it has been postulated that amylose-lipid complexation occurs during heating, e.g. gelatinization/pasting (Biliaderis et al., 1986; Kugimiya et al., 1980). Amylose-lipid complexes may reduce granule swelling, water solubility and retrogradation (Biliaderis et al., 1986) by reducing the volume fraction of the phases and

increasing the rigidity of the dispersed phase. Pea seeds contain primarily neutral lipids and phospholipids where the majority of the neutral lipids are comprised primarily of triacylglycerols, sterols and sterol esters and monoacylglycerols, diacylglycerols and free fatty acids are minor components (Pattee et al., 1984). Monoglycerides, diglycerides and fatty acids are able to complex with amylose. The two types of amylose-lipid complexes differ in degree of order and X-ray diffraction pattern. Form II is highly ordered, crystalline and exhibits a V-type diffraction pattern and Form I is less ordered, amorphous and does not exhibit a V-type diffraction pattern (Biliaderis et al., 1990; Tufvesson et al., 2003). Amylose-lipid complexation may be more likely to occur in blends of PS and CS due to the concentration of amylose and monoglycerides, diglycerides and fatty acids in the system when compared to WCS or PoS. Amylose-lipid complexation may also occur in blends of PS and HACS if amylose and lipids are mobilized with a sufficient amount of thermal energy.

4.5.3.2 Thermal Properties

Typically, the crystallites that are the least stable will melt first and absorb more water, reducing the amount of water available for melting of the remaining crystallites (Evans & Haisman, 1980). Pea starch granules contain both A-type and B-type polymorphs and, typically, B-type polymorphs melt at lower temperatures than do A-type polymorphs. As PS granules begin to melt/gelatinize, there would be less water available for melting of the CS or WCS granules, which may explain the higher than weighted average T_o values for blends of PS and CS or WCS. This may also explain the higher than weighted average values for the T_o of blends of HMT PS:CS and HMT PS:PoS. Due to the relatively high gelatinization temperature of PS (Yook et al., 1994), the PS granules in the blend would have contributed to higher T_c values for PS:PoS blends. As CS, WCS and PoS gelatinize, the volume fraction of the dispersed phase changes as

granules swell and glucans solubilize, possibly influencing the amount of water available for the remaining, ungelatinized PS granules (Liu & Lelièvre, 1992; Obanni & BeMiller, 1997). As the proportion of CS or WCS increased, the To also increased (Table 4.1), possibly due to the smaller granule size of CS or WCS compared to PS. Smaller granules tend to gelatinize at higher temperatures (Novelo-Cen & Betancur-Ancona, 2005) due to their more stable, tightly packed granule organization (Eliasson & Karlsson, 1983). The reduction in ΔHs of PS:WCS blends and HMT PS:PoS blends may be due to molecular interactions between leached glucans and ungelatinized starch granules. These interactions between the continuous phase and the dispersed phase may enhance the mobility of the glucans from the amorphous regions and disrupt crystalline regions of the ungelatinized granule, reducing the energy required to gelatinize these starch blends (Hoover, 2010). Alternatively, if the concentration of water is too low for gelatinization of the remaining PS granules, the lower ΔH may reflect partial gelatinization of the crystalline lamellae as melting of crystallites requires higher temperatures at lower moisture contents (Biliaderis et al., 1986; Svensson & Eliasson, 1995).

4.5.3.3 Pasting Properties

The lower PTs of the blends of PS:WCS, PS:PoS, HMT PS:WCS and HMT PS:PoS may be attributed to WCS, PoS, HMT WCS and HMT PoS developing viscosity sooner than did PS or HMT PS. This may increase friction on the granules of PS, leading to earlier viscosity development. The pasting curve of the 1:3 PS:WCS blend exhibited a shoulder at the end of the 95°C hold period (Figure 4.3). This is consistent with results obtained for a 1:1 CS:WCS blend by Obanni & BeMiller (1997). These authors reported that CS granules were embedded in a matrix of completely pasted starch molecules from WCS, leading to reduced breakdown of the CS.

Blends of PS:WCS (FV), PS:HACS (TV, FV), HMT PS:CS (PV, TV, FV), HMT PS:WCS (FV) HMT PS:HACS (TV, FV) and HMT PS:PoS (PV, TV, FV) exhibited viscosities lower than their corresponding weighed average values. Viscosities lower than weighted average values are likely due to less granule swelling, resulting in a lower amount of leached glucans in the continuous phase of the system (lower effective concentration of the glucans), lower volume fraction of the dispersed phase, and increased rigidity of the dispersed phase. In the case of PS:HACS or HMT PS:HACS. This may be attributed to less friction as HACS was not gelatinizing or contributing to friction, reducing PS granule degradation, possibly reducing viscosities of the PS:HACS blends to values lower than their weighted aveage values. However, blends of PS:PoS exhibited TVs and FVs higher than their corresponding weighted average values. The mechanism for these changes for viscosity needs to be investigated further.

4.5.3.4 Swelling Power and Water Solubility

Swelling power is a function of the volume fraction (and weight, as the methodology weighed the starch-water system after removal of the soluble fraction) of the dispersed phase. Swelling power and solubility indicate the extent of interaction of chains within the amorphous and crystalline lamellae (Tester et al., 1993) and the extent of amylose-lipid complexation (Tester et al., 1993; Tester & Morrison, 1990a; Vasanthan & Hoover, 1992). Blends of PS and CS or HACS exhibited relatively low SPs at all temperatures, as the higher amylose content of PS may have inhibited swelling (Tester & Morrison, 1990; Cheng et al., 1996). Swelling power of HMT PS:WCS blends were higher than weighted average values, possibly due to more water available for HMT WCS to swell as the HMT PS:WCS blends and HMT WCS pasted at a significantly lower temperature than did HMT PS. The presence of other components in the continuous phase (leached glucans) may influence interactions between the amorphous and crystalline lamellae.

Water solubilities for PS:WCS and HMT PS:WCS blends were lower than corresponding weighted averages, possibly due to the higher amount of starch polymers in the dispersed phase. This may be attributed to the higher concentration of amylopectin (from WCS) initiating phase separation of amylose (from PS) to a greater degree than PS alone, increasing volume fraction of the dispersed phase. However, other starches (e.g. CS and HACS) possess different proportions of amylose and amylopectin, thus potentially altering the interactions of the starch molecules in the dispersed and continuous phases.

4.5.3.5 Freeze-Thaw Stability

PS exhibited relatively low freeze-thaw stabilities due to a high degree of retrogradation of amylose. Of the pure starches, CS exhibited the least syneresis after four and five freeze-thaw cycles. Syneresis of WCS was lower than that of CS after one, two or three freeze-thaw cycles, but was substantially higher after four or five cycles. High amylose corn starch exhibited the highest degrees of syneresis regardless of the number of freeze-thaw cycles, due to a lack of gelatinization/pasting due to the higher gelatinization temperature of high-amylose corn starch (Jane et al., 1999).

During freeze-thaw cycles, one predominant outcome was that PS:CS and PS:WCS blends exhibited degrees of syneresis significantly lower and higher, respectively, than corresponding weighted average values. Blends of PS and CS may have formed amylose-lipid complexes, slowing retrogradation and reducing the degree of syneresis. In addition, amylose-lipid complexes may have decreased the interactions required for formation of junction zones as they exhibit a relatively lower "binding force" (Swinkles, 1985) or may impede water movement by creating a hydrophobic barrier (Eliasson & Gudmundsson, 2006). The higher degrees of syneresis of blends of PS and WCS may be explained by a combination of a number of factors,

including amylopectin will likely force phase separation of amylose due to incompatibility of the starch molecules, increasing the volume fraction and the rigidity of the dispersed phase (German et al., 1992). Due to the high amount of amylopectin in WCS, it is likely that amylose from PS may more effectively precipitate, reduce physical proximity to other amylose molecules, and allow more interactions and, thus, increased retrogradation and syneresis. The interplay of amylose-lipid complexation on both the volume fraction of the dispersed phase and the rigidity of the dispersed phase influences the degrees of syneresis of blends of PS and CS. HMT PS:PoS blends exhibited degrees of syneresis lower than corresponding weighted average values, due to the restructuring of PoS during HMT. As amylose is co-crystallized with amylopectin, this may reduce the ability of amylose to form of junction zones, reducing retrogradation and syneresis of the HMT PS:PoS blends. However, HMT PS:HACS blends exhibited degrees of syneresis that were higher than corresponding weighted average values, likely due to the high amount of amylose, partially disturbed granules due to HMT, increasing amylose solubilization and, thus, retrogradation and syneresis. The mechanism of the relationship between the blends and the effect on freeze-thaw stability needs to be investigated further with studies into the amount and rate of ice formation and uniformity of junction zones.

4.5.3.6 Shear Stability

Shear stabilities of CS and HACS were higher than those of PS, WCS or PoS due to their granule morphologies and amylose concentrations. Waxy corn starch and PoS exhibited lower shear stabilities, perhaps due to the low amylose concentration of WCS and weaker granular structures, and amylose co-crystallized with amylopectin and the presence of phosphate monoesters in the case of PoS. One might have expected PS to have exhibited higher shear stability in light of its restricted swelling properties (Vose, 1977), amylose concentration and

incomplete granule degradation at 95°C (Yook et al., 1994). The low shear stability of PS might be explained by the level of starch damage in this sample of pea starch due to the refining procedures used. The PS used in this study was prepared from dry-milled starch, which may have a higher concentration of damaged starch granules than wet-milled starch (Suksomboon & Naivikul, 2006). The high shear stability of HACS is speculated to be due to the large portion of HACS granules that remained ungelatinized. Typically, starch granules that are not gelatinized exhibit shear thickening behaviour (dilatency) and, possibly, will also exhibit increased viscosity after a high shear event. However, this mechanism needs to be confirmed.

Typically, higher amylose concentrations lead to higher shear stability as amylose tends to reduce hydration and swelling, thus lowering susceptibility to shear (Jane et al., 1999; Lindeboom et al., 2005). Of note, blends of PS:CS, PS:WCS, PS:HACS, HMT PS:CS, HMT PS:WCS and HMT PS:PoS exhibited shear stabilities that were lower than their respective weighted averages. Shear stability would be influenced by the interaction between the dispersed and continuous phase. Shear stabilities lower than the calculated weighted averages may indicate that associations or entanglements between the leached glucans did not occur and/or protected glucans from shear. Blends of PS and WCS may exhibit lower interactions between the continuous and dispersed phases due to the incompatibility of amylose and amylopectin. However, blends of PS and HACS may exhibit lower interactions between the continuous phase and dispersed phase due to the amount of ungelatinized granules (dense, low volume fraction of the dispersed phase) and a lack of solubilization for interactions. Due to the high level of ungelatinized starch granules of the HMT PS:HACS blends, the level of shear stability is correspondingly higher than the weighted average values.

4.5.3.7 Water Binding Capacity

The high and low amylose concentrations of HACS and WCS, respectively, likely influenced their WBC characteristics, as WBC reflects the ability of starch to absorb and bind water in the granule and onto the granule surface (Medcalf & Gilles, 1965). As amylose content increases, the degree of crystallinity decreases (Cheetam & Tao, 1998). The lower WBCs may be attributed to new hydrogen bonding between glucans and surface bound molecules, possibly reducing bonding sites available for water. It may be possible that the high degree of damaged starch from the PS was able to form hydrogen bonds with CS, WCS, HACS, PoS, HMT CS or HMT HACS and reduce the WBCs of the corresponding blends. A reduction in WBC may be attributed to new hydrogen bonding between the glucans and surface molecules reducing bonding sites available for water. Further investigation into the mechanism of the lower WBCs is required to fully explain this phenomenon.

4.5.3.8 Resistant Starch Concentration

These values reflect their respective amylose contents, with the exception of PoS. Ungelatinized PoS granules have been reported to be resistant to digestion in the small intestine (Englyst et al., 1992). Blends of PS:CS and HMT PS:CS may have formed amylose-lipid complexes, slowing retrogradation, and decreasing susceptibility to enzymatic attack (Holm et al. 1983). HMT PS:PoS blends exhibited lower RS concentrations than their respective weighted averages, likely due to glucans remaining in the continuous phase and not complexed or forming junction zones, increasing susceptibility for enzymatic attack.

Generally, PG blends of PS:WCS and HACS exhibited RS concentrations that were lower than their respective weighted average values, which may be attributed gelatinization/pasting

occuring during drum-drying that would increase the glucan molecules susceptibility to enzymatic attack.

4.6 Conclusions

A number of blends exhibited non-additive (different than the calculated weighted average) starch functionality. There is a need for more systematic examination of the mechanisms behind the synergies observed in this study. It is recommended that the following blends be evaluated to determine the molecular mechanism for synergies: PS:CS, HMT PS:CS, HMT PS:HACS and HMT PS:PoS. This examination may include an investigation into behaviour during thermal treatments (gelatinization, pasting, cooling, freezing) coupled with other techniques (e.g. microscopy, near infrared, nuclear magnetic resonance analysis) of the individual starch components and blends before and after thermal treatment. It may be possible that this non-additive behaviour may be manipulated to generate unique starch functionality as consumer demand for food products with clean label declarations continues to increase. Such knowledge may enable food manufacturers and researchers to better predict functionality of starch blends.

4.7 Connection to Subsequent Chapters

In addition to blending starches from various botanical sources to generate new starch functionality, another common method that has been investigated is the addition of hydrocolloids to starch. The next study describes the functionality of combinations of pea starch and hydrocolloids, specifically guar gum, locust bean gum, xanthan gum and carboxymethyl cellulose.

5. FUNCTIONAL PROPERTIES OF PEA STARCH AND COMBINATIONS OF PEA STARCH AND GUAR GUM, LOCUST BEAN GUM, XANTHAN GUM OR CARBOXYMETHYL CELLULOSE

5.1   Abstract

Starch molecules interact with non-starch hydrocolloid molecules, which may alter the functionality of the starch during gelatinization, pasting, and/or gel formation and storage. Pea starch and combinations of pea starch and guar gum, locust bean gum, xanthan gum or carboxymethyl cellulose were evaluated for their thermal properties, pasting properties, swelling power, water solubility, freeze-thaw stability, shear stability, water binding capacity and resistant starch concentration.

Compared to pea starch: i) combinations of pea starch and guar gum exhibited lower pasting temperatures and degrees of syneresis during freeze-thaw cycles and higher pasting viscosities, trough viscosities, final viscosities and shear stabilities; ii) combinations of pea starch and locust bean gum exhibited lower pasting temperatures and higher pasting viscosities, trough viscosities, final viscosities, swelling powers at 65°C, shear stabilities and resistant starch concentrations; iii) combinations of pea starch and xanthan gum exhibited lower pasting temperatures and higher pasting viscosities, trough viscosities and swelling powers and; iv) combinations of pea starch and carboxymethyl cellulose exhibited higher pasting, trough and final viscosities at lower inclusion levels, and lower pasting, trough and final viscosities at higher inclusion levels, and higher swelling powers.

The physicochemical properties of the combinations of starch and hydrocolloids were compared to those of some commercial, chemically-modified starches. It was concluded that some pea starch-hydrocolloid combinations could mimic some of the functionalities of chemically-modified starches and have the potential for application in food.

5.2   Introduction

Starch is an homogeneous polymer of glucose comprised of two types of molecules, namely amylose (primarily linear or straight-chain starch) and amylopectin (branched-chain starch). The physicochemical properties of starches are largely determined by the ratio of these two molecular types and their degree of branching and molecular weights. Pea starch, like other pulse starches, has an intermediate amylose concentration (30-35%). Pea starch has been reported to exhibit strong gelation capacity (Vose, 1977), shear stability (Gernat et al., 1990), acid stability (Gernat et al., 1990) and enzyme resistance (Ratnayake et al., 2001). However, pea starch also exhibits high syneresis (Ratnayake et al., 2001), a relatively high cooking temperature (Yook et al., 1994) and a low pasting viscosity (Ratnayake et al., 2001). Due in part to these properties, pea starch has seen limited success in food applications.

Non-starch hydrocolloids (referred to hereafter as hydrocolloids), such as guar gum, locust bean gum, xanthan gum and carboxymethyl cellulose, are used to modify the structure and texture of both food and non-food systems. Guar gum is a neutral galactomannan consisting of a β-1,4-D-mannose backbone with galactose residues linked to it. It hydrates completely in cold water (Hoefler, 2004). Locust bean gum is a neutral galactomannan, similar to guar gum, except that it contains fewer galactose side units and the galactose side chains are unevenly distributed along the mannose backbone. It does not hydrate completely in cold water and typically requires heating to about 60°C to solubilize completely (Hoefler, 2004). Xanthan gum is an anionic

heterogeneous polymer consisting of a β-linked glucose backbone and side chains of a single unit of glucuronic acid and two units of mannose (Hoefler, 2004). Carboxymethyl cellulose is an anionic, synthetic gum derived from cellulose by reacting cellulose with sodium hydroxide and monochloroacetic acid to derivitize hydroxyl groups to carboxymethyl ether groups. It exhibits thinning when heated and is easily solubilized (Hoefler, 2004). Typical commercial usage levels of guar gum and locust bean gum are 0.35-2.0% and 0.15-0.8%, respectively (BeMiller, 2007). Typical commercial usage levels of xanthan gum range from 0.1% to 0.5% (Chantaro & Pongsawatmanit, 2010). Starches and hydrocolloids, both independently and in combination, thicken, stabilize, and provide texture and viscosity to food products. Some of the negative characteristics of starches (e.g. syneresis, retrogradation) can be altered by chemical modification. Alternatively, combinations of starch and hydrocolloids might replace chemically-modified starches in a natural, chemical-free manner.

There have been a number of studies investigating the physicochemical effects of the addition of hydrocolloids to tapioca, corn and wheat starches. It has been reported that the addition of hydrocolloids to starch (wheat, corn, waxy corn starches) enhanced its gelatinization, pasting and retrogradation properties (Alloncle & Doublier, 1991; Alloncle et al., 1989; Christianson et al., 1981; Fanta & Christianson, 1996; Funami et al., 2005; Gudmundsson et al., 1991; Kim & D'Appolonia, 1977). The thermal and pasting properties of combinations of hydrocolloids (yellow mustard mucilage, locust bean gum and gelatin) and pea starch have been studied (Liu & Eskin, 1998; Liu et al., 2006). The addition of yellow mustard mucilage to pea starch increased the peak viscosity and the enthalpy of gelatinization, and decreased the swelling power and solubility of pea starch (Liu et al., 2006). The addition of alginate, guar gum or xanthan gum to sweet potato starch improved its freeze-thaw stability. Xanthan gum was more effective than guar gum, and both guar gum and xanthan gum were more effective than alginate

(Lee et al., 2002). Muadklay & Charoenrein (2008) reported that tapioca starch with 0.25% or 0.50% (w/w) xanthan gum exhibited lower syneresis after freezing and thawing than did tapioca starch. Tapioca starch with xanthan gum exhibited lower syneresis values than did tapioca starch with locust bean gum, and tapioca starch with guar gum exhibited synersis values that were not significantly different than those of tapioca starch.

Guar gum and xanthan gum were selected for this study due to the synergies of these gums when added to other starches at levels up to 0.8% (Achayuthakan et al., 2006; Chantaro & Pongsawatmanit, 2010; Huang, 2009; Lee et al., 2002; Pongsawatmanit & Srijunthongsiri, 2008). Locust bean gum was selected for this study to aid in understanding possible interactions with starch molecules. Locust bean gum, like guar gum, is a galactomannan; however, guar gum consists of evenly spaced galactose units, whereas locust bean gum consists of unevenly-spaced galactose side units on the mannose backbone (Hoefler, 2004). The uneven distribution of galactose side units alters the functionality of locust bean gum as compared to guar gum, as the regions of the mannan backbone without galactose substituion may interact with different molecules, or may interact differently, and alter the solubility of locust bean gum at lower temperatures (Hoefler, 2004). Carboxymethyl cellulose was selected for use in the current study as it is one of the most common hydrocolloids used in the food industry and is typically more soluble than other non-starch hydrocolloids (Hoefler, 2004). The majority of studies investigating the addition of hydrocolloids to native starches used levels under 1% (w/w). This study utlized levels of 0.33%, 0.66% and 1.00% (w/w). A successful outcome of this project would be to identify combinations of pea starch and hydrocolloids having unique, commercially-relevant, functional characteristics and the potential to replace modified starches in food and non-food applications. Hence, the overall objective of this project was to evaluate the functional behaviour of combinations of pea starch and hydrocolloids.

5.3 Materials and Methods

Pea starch (PS), prepared from air-classified pea starch via aqueous washing, was provided by Parrheim Foods, Saskatoon, SK (Canada) and had a protein concentration of 0.48%, as analyzed by method 46-30 of the AACC (2000). Hydrocolloids were commercially available and food-grade. Guar gum and locust bean gum contained a minimum of 78% galactomannan. The commercial starches evaluated were low degree of substitution, cross-linked corn and waxy corn starches, a high degree of substitution, cross-linked waxy corn starch, and a low degree of substitution, acetylated waxy corn starch were obtained from National Starch Food Innovation (Bridgewater, NJ). Hydrocolloids [guar gum (GG), locust bean gum (LBG), xanthan gum (XG), and carboxymethyl cellulose (CMC)] were incorporated into PS at concentrations of 0.33%, 0.66% and 1.00% (w/w) by mixing (by repeated inverting) duplicate samples of the mixtures for 60 seconds. Each starch or blend was mixed again prior to weighing for each experiment using a weighing spatula. Pea starch and combinations of PS and hydrocolloids were evaluated for their thermal properties, pasting properties, swelling power, water solubility index, water binding capacity, freeze-thaw stability, shear stability, and resistant starch concentration.

Thermal properties were determined by differential scanning calorimetry (DSC) according to Ratnayake et al. (2001) utilizing a Q2000 modulated DSC (TA Instruments, New Castle, DE) using a sample size of 2.0 mg (db) and 70% total moisture (approximately 7.3 μL of deionized water added depending on the moisture content of the starch sample). A Rapid Viscoanalyzer (Newport Scientific Ltd., Warriewood, NSW, Australia) was used to determine pasting properties using Standard method #2 with an 8% starch slurry at pH 7.0 (Anonymous, 1998). Swelling powers and water solubility indices were determined according to Li & Yeh (2001). Freeze-thaw stabilities were determined according to Muadklay & Charoenrein (2008) where 6% starch slurries were heated at 95°C for 30 minutes with continuous agitation. The heated paste was

cooled to room temperature in a 10°C water bath for 30 minutes to aid nucleation. The samples were then frozen at -18°C for 20 hours. The frozen paste was thawed for 2 hours at 30°C in a water bath, vortexed for 15 seconds and centrifuged at 1000 x g for 20 minutes. The supernatant was decanted and percent syneresis was calculated using:

$$\% \text{ syneresis} = (\text{weight of water removed/weight of starch paste}) \times 100 \qquad (5.1)$$

Freeze-thaw stabilities were determined cumulatively, meaning that the samples were frozen, thawed, centrifuged, decanted and then placed back in the freezer for the next cycle. Shear stabilities were performed according to Praznik et al. (1999) and calculated using:

$$\text{Shear stability} = \eta_{after}/ \eta_{before} \times 100 \qquad (5.2)$$

Water binding capacities were determined by the method of Medcalf & Gilles (1965) at room temperature (approximately 22°C). Resistant starch concentrations were determined according to method 32-40 of AACC (2000) using the resistant starch kit purchased from Megazyme International (Wicklow, Ireland). Resistant starch concentrations on cooked samples were determined after thermal treatment at 95°C for 30 minutes.

Data were analyzed using PROC GLM ($\alpha = 0.05$, n =4) and differences between means were determined by Least Significant Differences using SAS (SAS Institute Inc., Cary, NC). Differences between PS-hydrocolloid combinations were analyzed using PROC GLM and Least Significant Differences using SAS. Comparison of specific data to commercially chemically-modified starches was performed using PROC TTEST using SAS ($\alpha = 0.05$).

5.4   Results

5.4.1   Thermal Properties of Pea Starch and Combinations of Pea Starch and Guar Gum, Locust Bean Gum, Xanthan Gum or Carboxymethyl Cellulose

Gelatinization is a phenomenon whereby starch granules undergo an order-disorder transformation when thermal energy is applied and excess water is available (Ratnayake et al., 2002). As water migrates into the granule, the granule swells, intermolecular associations among starch granules are disrupted, amylose leaches into the continuous phase, and the crystallinity of the granule is lost (BeMiller & Whistler, 1996).

The thermal properties of pea starch (PS) and combinations of PS and guar gum (GG), locust bean gum (LBG), xanthan gum (XG) or carboxymethyl cellulose (CMC) are presented in Table 5.1. DSC plots of PS and of all of the PS-hydrocolloid combinations exhibited single endotherm peaks. Similarly, single endotherm peaks were observed for starch from yam, taro, sweet potato or yam bean when combined with GG or LBG (Huang, 2009) and for tapioca starch when combined with XG (Chantaro & Pongsawatmanit, 2010). Addition of any of the hydrocolloids to PS at any of the concentrations tested did not have a significant effect on the onset temperature of gelatinization (T_o), peak temperature of gelatinization (T_p) or completion temperature of gelatinization (T_c) of PS. Liu et al. (2006) reported that the T_p values of combinations of PS and 0.2-0.8% yellow mustard mucilage were not significantly different than the Tp of PS. Combinations of PS and GG, LBG, XG or CMC exhibited lower ΔHs than did PS.

The thermal properties of PS and combinations of PS and GG, LBG, XG or CMC were compared to those of commercial, chemically-modified starches (Table 5.1). The T_o values (61.3-62.0°C) of combinations of PS and hydrocolloids, with the exception of PS and 0.33% GG or 0.66% CMC, were not significantly different than that of a low degree of substitution, cross-linked WCS (low DS, CL WCS) with a T_o of 61.5°C. The T_p values (67.2-68.4°C) of

Table 5.1 Thermal properties of pea starch (PS) and combinations of PS and guar gum (GG), locust bean gum (LBG), xanthan gum (XG) or carboxymethyl cellulose (CMC)*

	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
PS	61.1 ± 0.7ab	67.5 ± 0.2a	85.5 ± 0.5a	14.2 ± 0.3a
PS + 0.33% GG	60.1 ± 1.0b	66.5 ± 1.6a	84.9 ± 1.6a	8.3 ± 1.1b
PS + 0.66% GG	61.4 ± 0.2ab	68.0 ± 0.5a	86.3 ± 0.1a	8.1 ± 0.9b
PS + 1.0% GG	62.0 ± 0.0a	68.4 ± 0.0a	85.1 ± 1.0a	7.1 ± 1.2b
PS + 0.33% LBG	61.7 ± 0.5ab	68.1 ± 0.4a	84.7 ± 0.5a	8.1 ± 0.9b
PS + 0.66% LBG	61.1 ± 0.5ab	68.1 ± 0.1a	86.7 ± 0.3b	8.1 ± 1.1b
PS + 1.0% LBG	60.7 ± 0.2ab	68.0 ± 0.2a	86.6 ± 0.8b	8.0 ± 0.6b
PS + 0.33% XG	60.6 ± 0.4ab	67.9 ± 0.4a	86.8 ± 0.7a	7.4 ± 0.3b
PS + 0.66% XG	60.4 ± 0.5ab	67.9 ± 0.1a	86.5 ± 0.7a	7.4 ± 1.1b
PS + 1.0% XG	60.8 ± 0.2ab	68.1 ± 0.0a	86.7 ± 0.5a	7.4 ± 1.0b
PS + 0.33% CMC	60.7 ± 0.4ab	68.1 ± 0.2a	87.0 ± 0.1a	8.2 ± 0.9b
PS + 0.66% CMC	60.1 ± 0.7b	67.2 ± 0.3a	85.7 ± 1.8a	8.0 ± 0.9b
PS + 1.0% CMC	60.3 ± 0.0ab	67.8 ± 0.2a	85.2 ± 0.5a	8.0 ± 0.8b
Low DS CL CS	65.7 ± 0.3	72.1 ± 0.1	85.3 ± 0.4	13.4 ± 0.1
Low DS CL WCS	61.5 ± 0.3	68.0 ± 0.0	79.9 ± 0.1	12.0 ± 0.1
High DS CL WCS	64.5 ± 0.1	70.4 ± 0.1	79.6 ± 0.1	8.9 ± 0.2
Low DS AC WCS	65.7 ± 0.3	72.1 ± 0.1	85.3 ± 0.4	13.4 ± 0.1

* Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different ($p < 0.05$) by Least Significant Differences. Where T_o = temperature of onset of gelatinization; T_p = temperature of peak gelatinization; T_c = temperature of complete gelatinization; ΔH = endothermic enthalpy of gelatinization; DS = degree of substitution; CL = cross-linked; AC = acetylated; CS = corn starch and WCS = waxy corn starch

combinations of PS and hydrocolloids, with the exception of PS and 0.33% GG, were not significantly different than that of a low DS, CL WCS with a T_p of 68.0°C.

5.4.2 Pasting Properties of Pea Starch and Combinations of Pea Starch and Guar Gum, Locust Bean Gum, Xanthan Gum or Carboxymethyl Cellulose

Pasting is the heating of a starch mixture in the presence of shear where starch granules swell and exhibit leaching of glucans, causing an increase in viscosity (BeMiller & Whistler, 1996). With continued heating and shearing, the granules disintegrate and both amylose and amylopectin become dispersed in the continuous, aqueous phase. Viscosity may be influenced by amylopectin chain length and molecular size of amylose (Jane & Chen, 1992).

The pasting properties of PS and combinations of PS and GG, LBG, XG or CMC are presented in Table 5.2. Generally, combinations of PS and hydrocolloids exhibited reduced pasting temperatures (PTs) and increased peak viscosities (PVs) and final viscosities (FVs) as compared to PS. Noteworthy exceptions were observed with CMC, where the combination of PS and 0.66% CMC exhibited PT, PV, trough viscosity (TV) and FV that were not significantly different than those of PS, and PS with 1.0% CMC, which exhibited higher PT and lower PV, TV and FV compared to PS. The addition of GG, LBG or XG, at all concentrations tested, resulted in a reduction in the PT of PS (from 73.8°C to 72.3-72.8°C). Lower PTs also were observed for PS with LBG or yellow mustard mucilage (Liu & Eskin, 1998), starch from yam, taro, sweet potato or yam bean with GG or LBG (Huang, 2009), waxy corn starch with XG or GG (Achayuthakan et al., 2006) and tapioca starch with XG (Pongsawatmanit & Srijunthongsiri, 2008; Chantaro & Pongsawatmanit, 2010) than for the respective, individual starches without the hydrocolloid.

The viscosity of a particular PS-hydrocolloid combination was dependent on the hydrocolloid utilized. All combinations of PS and GG or LBG exhibited higher viscosities than

Table 5.2 Pasting properties of pea starch (PS) and combinations of PS and guar gum (GG), locust bean gum (LBG), xanthan gum (XG) or carboxymethyl cellulose (CMC)*

	PT (°C)	PV (cP)	TV (cP)	FV (cP)
PS	73.8 ± 0.2b	1334 ± 93e	1025 ± 93ef	2157 ± 126ef
PS + 0.33% GG	72.5 ± 0.3d	1748 ± 47cd	1331 ± 107ab	2620 ± 105bc
PS + 0.66% GG	72.3 ± 0.3d	1898 ± 70ab	1332 ± 41ab	2716 ± 129ab
PS + 1.0% GG	72.4 ± 0.3d	1953 ± 40a	1369 ± 63a	2764 ± 49ab
PS + 0.33% LBG	72.4 ± 0.3d	1713 ± 44cd	1201 ± 60cd	2568 ± 56bc
PS + 0.66% LBG	72.3 ± 0.2d	1823 ± 20abc	1313 ± 35ab	2783 ± 29ab
PS + 1.0% LBG	72.4 ± 0.0d	1888 ± 32a	1315 ± 15ab	2760 ± 41a
PS + 0.33% XG	72.6 ± 0.2d	1666 ± 35d	1142 ± 54cd	2409 ± 96cd
PS + 0.66% XG	72.7 ± 0.2cd	1652 ± 54d	1154 ± 38cd	2350 ± 88de
PS + 1.0% XG	72.8 ± 0.6c	1503 ± 157e	1123 ± 67de	2210 ± 53ef
PS + 0.33% CMC	72.2 ± 0.4d	1755 ± 38bcd	1234 ± 39bc	2500 ± 51cd
PS + 0.66% CMC	73.8 ± 0.2b	1413 ± 82e	1118 ± 85de	2035 ± 130g
PS + 1.0% CMC	74.7 ± 0.5a	1172 ± 120f	953 ± 73f	1553 ± 80h
Low DS CL CS	81.9 ± 0.1	1772 ± 5	1219 ± 5	2111 ± 14
Low DS CL WCS	59.5 ± 0.0	5412 ± 17	2969 ± 10	4547 ± 21
High DS CL WCS	64.0 ± 0.0	3093 ± 9	2649 ± 11	4981 ± 10
Low DS AC WCS	65.7 ± 0.3	5130 ± 10	3644 ± 14	5438 ± 25

*Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different ($p < 0.05$) by Least Significant Differences. PT = pasting temperature, PV = pasting viscosity, TV = trough viscosity, FV = final viscosity, DS = degree of substitution; CL = cross-linked; AC = acetylated; CS = corn starch and WCS = waxy corn starch

did PS. Combinations of PS and XG exhibited viscosities higher than PS at inclusion rates of 0.33% and 0.66%. However, combinations of PS and CMC exhibited higher viscosities than did PS at lower inclusion levels of CMC, but lower viscosities at higher inclusion levels. Chaisawang & Suphantharika (2006) reported that the PVs of combinations of tapioca starch and 0.35% of GG or XG were higher than that of tapioca starch. When 0.35% of GG or XG alone was subjected to the same pasting procedure as used for the tapioca starch-hydrocolloid combinations, the resulting curves exhibited viscosities of approximately 120 cP throughout the treatment regime (Chaisawang & Suphantharika, 2006).

The pasting properties of PS and combinations of PS and GG, LBG, XG or CMC were compared to those of commercial, chemically-modified starches (Table 5.2). The PV and TV of PS and 0.33% GG (1748 and 1331 cP, respectively), 0.33% LBG (1713 and 1201 cP, respectively) or 0.33% CMC (1755 and 1234 cP, respectively) were not significantly different than those of a low degree of substitution, cross-linked corn starch (low DS, CL CS), for which PV and TV were 1769 and 1216 cP, respectively. In addition, values for the pasting properties of PS and combinations of PS and hydrocolloids were compared to literature values for chemically-modified starches. The PVs of PS and 0.33% GG, 0.33% LBG or 0.33% CMC (1748, 1713 and 1755 cP, respectively) were comparable to that of a cross-linked taro starch (1728 cP) and the PVs of PS and 0.33% or 0.66% XG (1666 and 1652 cP, respectively) were comparable to that of a cross-linked lotus starch (1632 cP) (Gunaratne & Corke, 2007). The FV of PS and 0.66% CMC (2035 cP) was comparable to that of an acetylated (AC) waxy rice starch (1872 cP), and the FVs of PS and 0.33% or 0.66% XG (2409 and 2350 cP, respectively) were comparable to that of an AC normal rice starch (2400 cP) (Liu et al., 1999).

5.4.3 Swelling Power and Water Solubility of Pea Starch and Combinations of Pea Starch and Guar Gum, Locust Bean Gum, Xanthan Gum or Carboxymethyl Cellulose

As starch granules are heated in an excess of water, water migrates into the granule and the granule swells. As the granule swells and loses crystallinity, glucans are leached into the continuous phase and the solubility of the granule increases. Swelling power (SP) is influenced by amylose-lipid complexes (Hoover & Manual, 1996b; Tester & Morrison, 1990a) and amylopectin structure (Tester et al., 1993), which affect the swelling of starch granules. The swelling power of pure starch indicates the strength of starch molecular interactions, where high swelling powers indicate weak molecular interactions.

Swelling powers (SPs) and water solubility indices (WSIs) for PS and combinations of PS and GG, LBG, XG or CMC are presented in Tables 5.3 and 5.4, respectively. Generally, combinations of PS and hydrocolloids exhibited SPs only slightly higher than that of PS. SPs of combinations of PS and the anionic hydrocolloids, XG and CMC, were slightly higher than those of combinations of PS and GG or LBG.

The SPs of PS and combinations of PS and GG, LBG, XG or CMC were compared to those of commercial, chemically-modified starches (Table 5.3). At 65°C, the SPs of PS with 0.33%, 0.66% or 1% LBG (7.7, 7.8 and 7.9%, respectively), and 0.33% or 0.66% XG (7.9 and 7.8%, respectively) were not significantly different than those of a low DS, CL CS (7.8%), or a low DS, AC WCS (7.8%). At 95°C, the SPs of PS and 0.66% or 1% GG (17.6 and 18.0%, respectively), PS and 0.66% LBG (17.5%) and PS and 0.33% XG (17.8%) were not significantly different than that of a low DS, AC WCS (17.8%).

Combinations of PS and the anionic hydrocolloids XG or CMC exhibited higher WSIs than did combinations of PS with non-ionic hydrocolloids (galactomannans) (Table 5.4). At 65

Table 5.3 Swelling powers (SPs) of pea starch (PS) and combinations of PS and guar gum (GG), locust bean gum (LBG), xanthan gum (XG) or carboxymethyl cellulose (CMC)*

	65°C	75°C	85°C	95°C
PS	7.1 ± 0.1g	11.9 ± 0.9bcde	13.6 ± 1.0d	17.1 ± 0.8c
PS + 0.33% GG	7.3 ± 0.2efg	11.1 ± 0.1e	13.7 ± 0.5d	17.3 ± 0.7bc
PS + 0.66% GG	7.4 ± 0.1efg	11.9 ± 0.0bcde	13.8 ± 0.3d	17.6 ± 0.8abc
PS + 1.0% GG	7.6 ± 0.0def	11.3 ± 0.6de	14.4 ± 0.2bcd	18.0 ± 0.9abc
PS + 0.33% LBG	7.7 ± 0.3def	12.0 ± 0.5bcde	13.9 ± 0.3d	17.2 ± 0.9bc
PS + 0.66% LBG	7.8 ± 0.0d	12.1 ± 0.5bcde	13.9 ± 0.8d	17.5 ± 0.1bc
PS + 1.0% LBG	7.9 ± 0.1cd	11.5 ± 0.2cde	14.1 ± 0.4d	18.7 ± 0.6ab
PS + 0.33% XG	7.9 ± 0.4cd	11.6 ± 0.3cde	14.4 ± 0.0bcd	17.8 ± 0.3ab
PS + 0.66% XG	7.8 ± 0.2d	12.7 ± 0.3bc	14.2 ± 0.2cd	18.4 ± 0.4ab
PS + 1.0% XG	8.5 ± 0.4b	13.0 ± 0.1ab	15.3 ± 0.0b	18.6 ± 0.4ab
PS + 0.33% CMC	8.0 ± 0.1cd	12.4 ± 0.3bcd	14.3 ± 0.2cd	18.2 ± 0.2abc
PS + 0.66% CMC	8.3 ± 0.2bc	12.7 ± 0.3abc	15.2 ± 0.2bc	18.4 ± 0.4ab
PS + 1.0% CMC	9.1 ± 0.2a	13.9 ± 1.4a	17.0 ± 0.4a	19.1 ± 0.5a
Low DS CL CS	7.8 ± 0.2	9.9 ± 0.0	13.0 ± 0.1	19.7 ± 1.4
Low DS CL WCS	20.6 ± 0.4	21.1 ± 0.0	22.2 ± 0.2	22.8 ± 0.1
High DS CL WCS	13.4 ± 0.0	13.0 ± 0.2	14.7 ± 0.1	13.8 ± 0.1
Low DS AC WCS	12.6 ± 0.7	15.0 ± 0.2	16.7 ± 0.0	17.8 ± 0.3

*Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different ($p < 0.05$) by Least Significant Differences. Where DS = degree of substitution; CL = cross-linked; AC = acetylated; CS = corn starch and WCS = waxy corn starch

Table 5.4 Water solubility indices (WSIs) of pea starch (PS) and combinations of PS and guar gum (GG), locust bean gum (LBG), xanthan gum (XG) or carboxymethyl cellulose (CMC)*

	65°C	75°C	85°C	95°C
PS	1.6 ± 0.3d	4.7 ± 0.5e	7.6 ± 0.2f	14.4 ± 0.4f
PS + 0.33% GG	1.9 ± 0.2cd	5.0 ± 0.1e	8.5 ± 0.8def	15.4 ± 0.2ef
PS + 0.66% GG	2.0 ± 0.4cd	5.3 ± 0.6de	8.3 ± 0.6ef	16.1 ± 0.4de
PS + 1.0% GG	2.3 ± 0.2cd	5.8 ± 0.5de	9.8 ± 0.1cd	16.6 ± 0.2de
PS + 0.33% LBG	2.3 ± 0.2cd	5.1 ± 0.0de	8.1 ± 0.1ef	15.8 ± 0.1de
PS + 0.66% LBG	2.3 ± 0.1cd	5.5 ± 0.3de	8.0 ± 0.5f	15.7 ± 0.5def
PS + 1.0% LBG	2.4 ± 0.1cd	4.8 ± 0.1e	8.9 ± 0.6cde	17.9 ± 0.9bc
PS + 0.33% XG	2.6 ± 0.1cd	7.1 ± 0.7cd	10.3 ± 0.3c	17.8 ± 0.5bc
PS + 0.66% XG	3.0 ± 0.8bc	8.8 ± 0.2bc	10.7 ± 0.3c	16.8 ± 0.3cd
PS + 1.0% XG	4.3 ± 0.9b	10.0 ± 0.5b	12.7 ± 0.9b	19.5 ± 0.2a
PS + 0.33% CMC	3.1 ± 0.4bc	7.8 ± 0.7c	10.0 ± 1.3cd	16.0 ± 0.8de
PS + 0.66% CMC	4.3 ± 1.8b	10.3 ± 1.4b	12.9 ± 0.7b	18.1 ± 0.2bc
PS + 1.0% CMC	6.2 ± 0.1a	13.4 ± 2.1a	16.0 ± 0.9a	18.7 ± 0.1ab
Low DS CL CS	1.2 ± 0.3	3.3 ± 0.1	7.7 ± 0.1	17.5 ± 1.1
Low DS CL WCS	1.5 ± 0.4	1.1 ± 0.3	1.6 ± 0.1	1.8 ± 0.3
High DS CL WCS	2.5 ± 0.9	0.5 ± 0.0	1.1 ± 0.1	1.4 ± 0.1
Low DS AC WCS	1.3 ± 0.4	0.6 ± 0.0	1.1 ± 0.1	1.8 ± 0.3

*Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different (p < 0.05) by Least Significant Differences. Where DS = degree of substitution; CL = cross-linked; AC = acetylated; CS = corn starch and WCS = waxy corn starch

and 75°C, combinations of PS and GG or LBG, at all concentrations tested, exhibited WSIs that were not significantly different than that of PS. At all temperatures examined, the addition of 0.66% or 1% XG to PS increased the WSI of PS, as did the addition of 0.66% or 1% CMC at 75°C and the addition of CMC, at all concentrations tested, at 85°C. Combinations of PS and XG or CMC exhibited higher WSIs than did combinations of PS and GG or LBG. Assuming that the hydrocolloids added would remain in the continuous phase and would be measured as soluble material in the measurement of WSI, combinations of PS and XG or CMC exhibited WSIs higher than the combined contribution of the soluble materials added, and higher WSIs than the corresponding combinations of PS and GG or LBG.

5.4.4 Freeze-Thaw Stabilities of Pea Starch and Combinations of Pea Starch and Guar Gum, Locust Bean Gum, Xanthan Gum or Carboxymethyl Cellulose

The ability of a starch gel to withstand freezing and thawing without releasing water (syneresis) is a function of the degree of starch retrogradation. Crystallization during retrogradation and freeze-thaw involves nucleation, crystal growth and maturation (perfection). Nucleation typically begins with the formation of a "junction zone" where glucans associate via non-covalent interactions (Charoenrein & Udomrati, 2007). As the junction zone increases in size, glucans crystallize and exude water. The process of syneresis can be controlled somewhat by altering the rate of freezing or the volume of solvent (typically water), the inclusion of agents that promote (e.g. sugars) or reduce (e.g. hydrocolloids) the formation of junction zones, or by using modified starches that reduce the formation of junction zones. The addition of hydrocolloids may reduce junction zone formation and reduce the syneresis associated with freeze-thaw cycles. Ferrero et al. (1994) postulated that the addition of hydrocolloids increased

the glass transition temperature of starch by reducing the amount of water available for starch mobility and, consequently, molecular associations.

Freeze-thaw stabilities for PS and combinations of PS and GG, LBG, XG or CMC are presented in Table 5.5. In most cases, combinations of PS and hydrocolloids exhibited lower degrees of syneresis than did PS. Guar gum and XG were more effective in reducing the syneresis of PS gels than were LBG or CMC. Combinations of PS and GG, at all concentrations tested, exhibited lower degrees of syneresis than did PS after one, two, three or four freeze-thaw cycles. The freeze-thaw stabilities of combinations of PS and LBG were not significantly different than that of PS, except that after two freeze-thaw cycles, PS and 1% LBG, and after four freeze-thaw cycles, all concentrations of PS and LBG, exhibited higher degrees of syneresis. The combination of PS and 1% XG exhibited lower degrees of syneresis than did PS or combinations of PS and 0.33% or 0.66% XG after one, two, three or four freeze-thaw cycles. Combinations of PS and CMC exhibited lower degrees of syneresis than did PS after one, two or three freeze-thaw cycles, and degrees of syneresis that were not significantly different than those of PS after four and five freeze-thaw cycles. Starch gels have been stabilized using hydrocolloids, e.g. tapioca starch and 0.5% or 1% XG (Pongsawatmanit & Srijunthongsiri, 2008), sweet potato starch and 0.3% or 0.6% alginate, GG or XG (Lee et al., 2002) and pea or buckwheat starch and 0.2%, 0.5% or 0.8% yellow mustard mucilage (Liu et al., 2006).

The degrees of syneresis of PS and combinations of PS and GG, LBG, XG or CMC were compared to those of commercial, chemically-modified starches (Table 5.5). After the first freeze-thaw cycle, the degrees of syneresis of PS and 1% GG (20.2%) or 1% XG (20.8%) were not significantly different than that of a low DS, AC WCS (20.3%). The freeze-thaw stabilities of PS and combinations of PS and hydrocolloids were compared to literature values for chemically-modified starches. Freeze-thaw stabilities of combinations of PS and hydrocolloids were

Table 5.5 Freeze-thaw stabilities of pea starch (PS) and combinations of PS and guar gum (GG), locust bean gum (LBG), xanthan gum (XG) or carboxymethyl cellulose (CMC) after 1, 2, 3, 4 and 5 freeze-thaw cycles*

	Freeze-Thaw Cycles (% syneresis)				
	1	2	3	4	5
PS	26.6 ± 2.1ab	29.1 ± 2.0ab	31.3 ± 2.0a	32.5 ± 2.0bc	46.8 ± 1.5cd
PS + 0.33% GG	24.1 ± 0.0cd	24.7 ± 0.0cd	26.9 ± 0.0cd	30.1 ± 0.0de	46.5 ± 1.7cd
PS + 0.66% GG	23.5 ± 0.7cd	24.1 ± 0.7cd	26.3 ± 0.7cd	29.5 ± 0.5e	49.6 ± 2.9ab
PS + 1.0% GG	20.2 ± 1.0f	22.8 ± 1.0f	25.1 ± 1.0f	26.2 ± 1.2g	47.5 ± 2.1c
PS + 0.33% LBG	27.7 ± 1.5a	30.2 ± 0.8a	32.4 ± 1.3a	35.5 ± 1.2a	49.9 ± 2.5ab
PS + 0.66% LBG	26.8 ± 0.7a	29.3 ± 0.3a	31.5 ± 0.1a	33.4 ± 0.1ab	50.0 ± 2.7ab
PS + 1.0% LBG	28.5 ± 1.8a	30.9 ± 2.0a	33.1 ± 2.1a	34.9 ± 1.4a	48.0 ± 1.4bc
PS + 0.33% XG	26.5 ± 0.3ab	29.0 ± 0.4a	31.2 ± 0.3a	33.7 ± 1.8ab	47.8 ± 1.9c
PS + 0.66% XG	26.4 ± 0.2ab	28.9 ± 0.1a	31.1 ± 0.6ab	32.4 ± 0.1bcd	45.3 ± 1.1d
PS + 1.0% XG	20.8 ± 0.3ef	23.2 ± 0.2b	25.4 ± 0.2ef	27.2 ± 0.5f	45.3 ± 1.5d
PS + 0.33% CMC	22.1 ± 0.2def	24.6 ± 0.3b	26.8 ± 0.5def	28.8 ± 0.6ef	51.0 ± 1.3ab
PS + 0.66% CMC	24.4 ± 0.3bc	26.8 ± 0.2ab	29.0 ± 0.6bc	30.6 ± 0.2cde	36.6 ± 2.5e
PS + 1.0% CMC	22.7 ± 0.9cde	25.1 ± 1.0b	27.4 ± 0.7cde	29.2 ± 0.5e	34.6 ± 2.1e
Low DS CL CS	1.7 ± 0.4	2.0 ± 0.5	2.0 ± 0.5	2.7 ± 0.2	6.6 ± 0.8
Low DS CL WCS	2.0 ± 0.1	2.0 ± 0.1	2.0 ± 0.1	2.3 ± 0.6	2.3 ± 0.6
High DS CL WCS	20.3 ± 0.7	20.4 ± 0.7	20.4 ± 0.7	20.6 ± 0.6	20.7 ± 0.7
Low DS AC WCS	10.6 ± 0.2	10.6 ± 0.2	10.7 ± 0.2	10.8 ± 0.3	11.3 ± 0.4

*Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different ($p < 0.05$) by Least Significant Differences. Where DS = degree of substitution; CL = cross-linked; AC = acetylated; CS = corn starch and WCS = waxy corn starch

comparable to those of a cross-linked normal rice starch (% syneresis ranging from 20-30% for one to five freeze-thaw cycles) (Liu et al., 1999).

5.4.5   Shear Stability of Pea Starch and Combinations of Pea Starch and Guar Gum, Locust Bean Gum, Xanthan Gum or Carboxymethyl Cellulose

Shear stability reflects the resistance of a starch paste to mechanical breakdown (due to shear). Shear stability is a function of the ability of starch polymers to entangle. Hydrocolloids may promote shear stability by protecting the granule and starch molecules from damage or may inhibit shear stability by increasing friction (Tye, 1988).

Shear stabilities of gels from PS and combinations of PS with GG, XG, LBG or CMC are presented in Table 5.6. Generally, combinations of PS and hydrocolloids exhibited either higher shear stabilities or shear stabilities that were not significantly different than that of PS. In all cases, the viscosity of the sheared starch or starch-hydrocolloid combination did not recover to the pre-shear value, since all shear stabilities were less than 100%. The addition of GG or LBG increased the shear stability of PS from 80% to 90-91% and 85-90%, respectively. The addition of 1% CMC to PS increased the shear stability of PS from 80% to 90%, whereas the addition of XG resulted in shear stabilities that were not significantly different than that of PS. Tye (1988) reported that corn starch with 0.2% κ-carrageenan did not recover to its pre-shear viscosity, but that corn starch with 0.2% or 0.5% ι-carrageenan or 0.5% κ-carrageenan did so.

The shear stabilities of PS and combinations of PS and GG, LBG, XG or CMC were compared to those of commercial, chemically-modified starches (Table 5.6). The shear stabilities of PS and GG (90-91%) and PS and 1% LBG (90%) were not significantly different than that of a low DS, AC WCS with a shear stability of 91% or a high DS, CL WCS with a shear stability of

Table 5.6 Shear stabilities of pea starch (PS) and combinations of PS and guar gum (GG), locust bean gum (LBG), xanthan gum (XG) or carboxymethyl cellulose (CMC)*

	Shear stability (%)
PS	80 ± 2fg
PS + 0.33% GG	91 ± 2a
PS + 0.66% GG	90 ± 2a
PS + 1.0% GG	91 ± 2a
PS + 0.33% LBG	85 ± 2d
PS + 0.66% LBG	87 ± 1cd
PS + 1.0% LBG	90 ± 1a
PS + 0.33% XG	79 ± 1g
PS + 0.66% XG	80 ± 1fg
PS + 1.0% XG	80 ± 1fg
PS + 0.33% CMC	81 ± 1efg
PS + 0.66% CMC	83 ± 1e
PS + 1.0% CMC	88 ± 1bc
Low DS CL CS	89 ± 1
Low DS CL WCS	72 ± 1
High DS CL WCS	91 ± 1
Low DS AC WCS	91 ± 1

*Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different (p < 0.05) by Least Significant Differences. Where DS = degree of substitution; CL = cross-linked; AC = acetylated; CS = corn starch and WCS = waxy corn starch

91%. The shear stabilities of PS and 0.66% LBG (87%) and PS and 1% CMC (88%) were not significantly different than that of a low DS, CL CS (88%).

5.4.6 Water Binding Capacity of Pea Starch and Combinations of Pea Starch and Guar Gum, Locust Bean Gum, Xanthan Gum or Carboxymethyl Cellulose

Water binding capacity is the amount of water that a starch can retain at room temperature without gelatinization and is a function of the ability of a starch to form hydrogen bonds with water. Water binding capacities (WBCs) of PS and combinations of PS and GG, LBG, XG or CMC are presented in Table 5.7. Generally, combinations of PS and GG or XG exhibited higher WBCs than did combinations of PS and LBG or CMC. The WBCs of PS and 0.66% XG or 1% GG or 1% XG were higher than that of PS. Combinations of PS and CMC, at all concentrations, exhibited lower WBCs than did PS.

The WBCs of PS and combinations of PS and GG, LBG, XG or CMC were compared to those of commercial, chemically-modified starches (Table 5.7). The WBC of PS and 0.66% GG (103.6%) was not significantly different than that of a low DS, CL WCS (104.6%).

5.4.7 Resistant Starch Concentrations of Native and Cooked Pea Starch and Native and Cooked Combinations of Pea Starch and Guar Gum, Locust Bean Gum, Xanthan Gum or Carboxymethyl Cellulose

Resistant starch (RS) is starch not hydrolyzed during digestion in the gastrointestinal system of a healthy human (Englyst et al., 1992). Resistant starch offers numerous potential health benefits. It increases fecal bulk and colonic fermentation, positively affecting colonic health (Jenkins et al., 1998), increases postprandial insulin sensitivity in healthy humans (Axelsen et al., 1999; Robertson et al., 2003), and lowers glycemic index, eliciting lower blood glucose responses (Foster-Powell & Brand Miller, 1995; Jenkins et al., 1981). Legumes tend to be high in RS (Bednar et al., 2001).

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Table 5.7 Water binding capacities (WBCs) of pea starch (PS) and combinations of PS and guar gum (GG), locust bean gum (LBG), xanthan gum (XG) or carboxymethyl cellulose (CMC)*

	WBC (%)
PS	102.2 ± 0.6c
PS + 0.33% GG	101.1 ± 0.3c
PS + 0.66% GG	103.6 ± 0.9c
PS + 1.0% GG	108.4 ± 0.4b
PS + 0.33% LBG	97.9 ± 0.4de
PS + 0.66% LBG	98.2 ± 0.2d
PS + 1.0% LBG	101.1 ± 1.5c
PS + 0.33% XG	101.3 ± 1.2c
PS + 0.66% XG	106.8 ± 0.8b
PS + 1.0% XG	111.4 ± 3.1a
PS + 0.33% CMC	95.2 ± 0.3e
PS + 0.66% CMC	96.6 ± 0.8de
PS + 1.0% CMC	98.1 ± 0.4d
Low DS CL CS	72.9 ± 1.0
Low DS CL WCS	104.6 ± 0.5
Med DS CL WCS	85.5 ± 1.2
High DS CL WCS	92.6 ± 0.2
Low DS AC WCS	84.1 ± 0.2

*Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different ($p < 0.05$) by Least Significant Differences. Where DS = degree of substitution; CL = cross-linked; AC = acetylated; CS = corn starch and WCS = waxy corn starch

Resistant starch concentrations in native and cooked PS and combinations of PS and GG, LBG, XG or CMC are presented in Table 5.8. In most cases, RS concentrations of native combinations of PS and GG, LBG, XG and CMC were not significantly different than that of native PS, with the exception of combinations of PS and 0.66% or 1% GG or 1% CMC. Cooked PS and cooked combinations of PS and hydrocolloids exhibited lower RS concentrations than did their native counterparts. In most cases, RS concentrations of cooked PS and cooked combinations of PS and GG, LBG, XG or CMC were not significantly different than that of PS, with the exception of combinations of PS and 1% GG, 1% LBG or 0.33%, 0.66% or 1% XG.

5.5   Discussion

It was hypothesized that combinations of PS and GG, LBG, XG or CMC would exhibit higher viscosities during pasting, and lower degrees of syneresis after freezing and thawing, than would PS. Higher viscosities were observed for combinations of PS and GG, LBG or XG and, at lower inclusion rates, CMC. Lower degrees of syneresis were observed for PS and GG (with the exceptions of PS and 0.33% or 0.66% GG after the fifth freeze-thaw cycle), PS and 1% XG, and PS and CMC after one, three and four freeze-thaw cycles. In addition, compared to PS, combinations of PS and 1% GG, PS or LBG, and of PS and 0.33%, 0.66% or 1% XG, exhibited lower ΔH values, combinations of PS and XG or CMC exhibited higher SPs, and combinations of PS and GG or LBG exhibited higher shear stabilities.

Table 5.8 Resistant starch (RS) concentrations of pea starch (PS) and combinations of PS and guar gum (GG), locust bean gum (LBG), xanthan gum (XG) or carboxymethyl cellulose (CMC)*

	RS (%) Native	RS (%) Cooked
PS	6.6 ± 0.4cd	3.8 ± 0.2c
PS + 0.33% GG	7.4 ± 0.2abc	4.2 ± 0.4bc
PS + 0.66% GG	7.9 ± 0.5a	4.4 ± 0.5bc
PS + 1.0% GG	7.8 ± 0.8ab	4.5 ± 0.7bc
PS + 0.33% LBG	7.1 ± 0.3bc	4.4 ± 0.3bc
PS + 0.66% LBG	7.4 ± 0.6abc	4.4 ± 0.4bc
PS + 1.0% LBG	7.0 ± 0.2c	4.7 ± 0.4b
PS + 0.33% XG	6.3 ± 0.1de	5.2 ± 0.5a
PS + 0.66% XG	6.0 ± 0.0de	5.2 ± 0.4a
PS + 1.0% XG	6.1 ± 0.1de	5.4 ± 0.7a
PS + 0.33% CMC	5.5 ± 0.1de	4.0 ± 0.4c
PS + 0.66% CMC	5.5 ± 0.3ef	3.9 ± 0.3c
PS + 1.0% CMC	5.2 ± 0.1f	3.8 ± 0.6c
Low DS CL CS	2.5 ± 0.1	
Low DS CL WCS	16.7 ± 0.4	
High DS CL WCS	11.1 ± 0.2	
Low DS AC WCS	1.1 ± 0.2	

*Means (± standard deviation) followed by the same letter in each column for each blend are not significantly different ($p < 0.05$) by Least Significant Differences. Where DS = degree of substitution; CL = cross-linked; AC = acetylated; CS = corn starch and WCS = waxy corn starch

Possible mechanisms for this alteration in the functionality of PS may include, or may be a combination of, the following:

1. Competition for water, effective concentration of components in the system and volume fraction of the dispersed phase

As starch granules swell in an aqueous, continuous phase containing a hydrocolloid, the volume of water available for the hydrocolloid decreases, effectively increasing the concentration of the hydrocolloid and influencing functional parameters such as pasting properties and, possibly, ΔH. Increasing the effective concentration of the soluble components in the system, may reduce the water available for melting of crystallites, potentially allowing only partial gelatinization of the starch, which would reduce ΔH (Biliaderis et al., 1979; Kim & Yoo, 2011). Increasing the effective concentration of components in the continuous phase may reduce PTs and increase viscosity. In addition, as starch molecules leach from the granule during pasting, the effective concentration of hydrocolloids in the continuous phase increases. This may promote interactions between starch molecules and molecules of non-starch hydrocolloids, and may contribute to the higher viscosities of pastes of combinations of starch and hydrocolloids as compared to the viscosities of pastes of PS alone.

The volume fraction of the dispersed phase is continuously fluctuating as starch-water systems are heated. The presence of hydrocolloids in the continuous phase may induce phase separation of glucans (particularly amylose) from the continuous phase into the dispersed phase (Alloncle et al., 1989) as these components are not soluble together in the continuous phase, altering the volume fraction of the dispersed phase.

Two-phase mixtures may generate phase-separated gel networks, where starch granules may be trapped in a network of galactomannans. Such a network may increase the viscosity of starch-hydrocolloid gels (Sikora & Kowalski, 2007). As starch undergoes pasting, glucans

(primarily amylose) leach from the granule and solubilize, the continuous phase is altered in composition to include both the hydrocolloid and leached glucans, and the dispersed phase would include precipitated glucans, non-soluble glucans, granule ghosts and ungelatinized starch granules. Two-phase mixtures involve interactions between the dispersed and continuous phases (Eliasson, 1986). The amount and type of soluble material and possible molecular entanglements (amylose-amylose, amylose-amylopectin, amylopectin-amylopectin, amylose-hydrocolloid, amylopectin-hydrocolloid, and hydrocolloid-hydrocolloid) would affect the properties of the continuous phase. Additionally, interactions between the dispersed phase and continuous phase may affect network properties (granule-granule, granule-leached glucans, and granule-hydrocolloid). Peressini et al. (2011) demonstrated that starch granules in a gluten-free batter were "glued together" and "enveloped in a coating" when in combination with XG.

2. Interactions between glucans and galactomannans

Earlier viscosity development, and thus a lower PT, may be due to molecular interactions between hydrocolloid molecules already present in the continuous phase and leached glucans (Chaisawang & Suphantharika, 2006; Christianson et al., 1981; Shi & BeMiller, 2002). The lower ΔHs (PS and GG or LBG), increased viscosities (PS and GG or LBG), increased shear stabilities (PS and GG or LBG) and increased RS concentrations (PS and 1% GG or 1% LBG) observed for some starch-hydrocolloid combinations may be attributed to molecular associations between leached glucans and galactomannan molecules. When molecules are similar in linearity and composition, they tend to concentrate together (Funami, 2009). Although glucans will tend to interact with other glucans in the presence of galactomannans, glucans may interact with the mannan backbone as well. The role of the galactose moieties of a galactomannan molecule in molecular associations with starch molecules is not understood, but they may provide flexibility to the mannose backbone or interact with starch molecules (Funami, 2009).

Molecular interactions between hydrocolloid molecules and leached glucans may reduce retrogradation and, therefore, decrease syneresis of starch gels (Christianson et al., 1981; Shi & BeMiller, 2002). In addition, hydrocolloids bind water contributing to availability of water for gelatinization, pasting and ice crystal formation. Controlling the amount of water available for ice crystal formation will also affect freeze-thaw stability, as demonstrated by Yoshimara et al. (1998). The mechanism for the effect of hydrocolloids on the freeze-thaw stability of PS needs to be investigated further, with studies conducted on the amount and rate of ice formation and the uniformity of junction zone size and distribution. The higher shear stabilities of PS with GG or LBG were likely due to hydrocolloid molecules entangling with leached glucans (Mandala et al., 2004).

The significant differences between the functional properties of combinations of PS and GG or LBG indicate that differences in the distribution of galactose side chains along the mannose backbone, mass per unit length and ratio of galactose to mannose may alter the interactions of galactomannans and glucans. Both GG and LBG exist in random coil formation and the galactose side chains increase the solubility of GG when compared to LBG, due to "steric and entropic hindrance to packing" of GG (Picout et al., 2002). The segments of unsubstituted mannose (~25 units) in LBG may form entanglements due to strong hydrogen bonding, thus influencing the ability of LBG to interact with glucans from starch (Mathur, 2011). The even distribution of galactose along the mannan backbone increases solubility of GG. The ability of LBG molecules to entangle may have reduced the ability of LBG to interact with glucans from PS and reduce junction zone formation during freeze-thaw cycles, protect glucans from shear and enzymatic attack, and bind water, as compared to GG.

3. Interactions between glucan and anionic hydrocolloids

Shi & BeMiller (2002) reported that CMC interacted with amylose during the heating of maize starch. When a blend of maize starch and 0.4% CMC was heated at 65°C for three hours, amylose was distributed throughout the slurry, whereas when maize starch was heated using the same conditions as above without CMC, the amylose was located at the granule surface or close to the granule. This phenomenon is interesting as the total proportion of amylose in the slurry was comparable for maize starch and the blend of maize starch and 0.4% CMC, suggesting that interactions between amylose and CMC may have led to earlier development of viscosity (Shi & BeMiller, 2002).

The addition of XG or CMC to PS was not as effective as the addition of GG or LBG with respect to increasing viscosity during pasting, and as the concentration of XG or CMC increased, viscosity decreased. Similar results for other anionic hydrocolloids [e.g. gum arabic and soybean-soluble polysaccharide (water soluble by-product from soy protein isolation)] have been reported (Funami, 2009). Furthermore, the addition of CMC at lower concentrations increased viscosity, but at the highest level of CMC (1%) the viscosity was less than that of PS alone. The increase in viscosity at lower concentrations of CMC may be due to CMC increasing the effective concentration of PS in the system. The decrease in viscosity at higher concentrations of CMC may be attributed to the lack of molecular associations between glucans and CMC due to the dissimilarity of the anionic hydrocolloids and glucans in molecular charge, shape and composition. Shi & BeMiller (2002) reported that the viscosity of a starch paste was lower in the presence of anions. In the presence of anions, hydrogen bonds between glucans may be disrupted, allowing the hydroxyl groups to dissociate more readily and leading to a higher concentration of hydrogen ions surrounding the starch chains. As the hydrogen ions diffuse, glucans exhibit a net

negative charge, repelling the anionic gum, thus reducing interactions between glucans and the anionic hydrocolloid (Funami, 2009).

The addition of anionic hydrocolloids may influence the solubility of glucans from PS granules. Funami (2009) reported that "starch granule ghosts were observed less frequently in the presence" of anionic hydrocolloids (gum arabic and soybean-soluble polysaccharide). Granule ghosts are defined as remnants of starch granules remaining after thermal treatment. Debet & Gidley (2007) reported that granule ghosts might be formed when starches swell slowly, allowing time for glucans to cross-link and stabilize. Anionic hydrocolloids may influence the rate of granule swelling or reduce the cross-linking that occurs, reducing the formation of granule ghosts. Due to anions (XG and CMC) promoting gelatinization by disrupting hydrogen bonds, glucans may not be as able to form cross-links and generate granule ghosts, thus increasing the solubility of starch molecules. This also may account for the lower ΔH values for combinations of PS and XG or CMC when compared to PS. Although CMC solubilizes easily in water at room temperature, combinations of PS and CMC exhibited lower WBCs than did PS, possibly by blocking the water binding sites of PS and limiting hydrogen bond formation between glucans and water.

Combinations of PS and XG exhibited higher viscosities than did PS, with the exception of the FV for combinations of PS and 0.66% XG and the PV, TV and FV for combinations of PS and 1% XG where their viscosities were not significantly different than PS. The combination of PS and 0.33% CMC exhibited higher viscosities than did PS, whereas the combination of PS and 0.66% CMC exhibited viscosities that were not significantly different then, and the combination of PS and 1% CMC exhibited viscosities that were lower than, that of PS. A reduction in viscosity also was observed for combinations of potato starch and XG (Sikora & Kowalski, 2007). Viscosities generated by starch molecules during pasting are influenced by friction

between molecules in the system. As the concentration of XG or CMC increases, the distance between the starch molecules and the hydrocolloid may increase due to a higher concentration of anions in the system, reducing molecular friction and, as a result, reducing viscosity.

5.6 Conclusions

The thermal properties, pasting properties, swelling powers, water solubility indices, freeze-thaw capacities, shear stabilities, water binding capacities and resistant starch concentrations of PS and combinations of PS and GG, LBG, XG or CMC were investigated. The effects of the hydrocolloids on the functionality of PS were slight at the concentrations used in this study. Some combinations of PS and hydrocolloids exhibited reduced pasting temperatures, increased paste viscosities, increased water solubilities and improved freeze-thaw stabilities compared to PS. Pasting properties indicated that hydrocolloids may interact with leached glucans from PS and either increase (GG or LBG) or increase or decrease (XG or CMC), depending on concentration, the viscosities of PS pastes. The presence of both galactomannans and glucans increases the effective concentration of the constituents of the continuous phase, increasing the viscosity of the system. Anionic hydrocolloids may disrupt hydrogen bonding between and within glucan molecules, reducing friction and as a result, reducing viscosity. It also appears that anionic hydrocolloids increased the water solubility of leached PS molecules, possibly by increasing the net negative charge on the glucans and enhancing their dispersion.

Comparison of the functional properties of combinations of PS and GG, LBG, XG or CMC to those of commercial, chemically-modified starches indicated that certain combinations of PS and hydrocolloid mimicked some of the functionalities of the chemically-modified starches. However, none of the PS-hydrocolloid combinations mimicked all of the functionalities of any of the chemically-modified starches examined. The PV and TV of combinations of PS and 0.33%

GG, 0.33% LBG or 0.33% CMC, the SP at 65°C of combinations of PS and 0.33% or 0.66% LBG or 0.66% XG or 1% LBG, and shear stabilities of combinations of PS and 0.66% LBG or 1% CMC were not significantly different than corresponding values for a low DS, CL CS. However, no combination of PS and hydrocolloid exhibited the functionality of a commercial, chemically-modified starch in all functional properties examined in this study.

6. GENERAL DISCUSSION

In an effort to determine if natural methods have the potential to alter usefully the functionality of PS, studies on the effects of genotype, growing environment, and the presence of other starches or hydrocolloids on the functionality of PS were performed. In addition, due to increasing interest in fababean in western Canada, the effects of genotype and growing environment on the functionality of fababean starch were investigated.

Differences due to genotype were detected in the concentrations of starch and protein in pea and fababean seed. In addition, differences due to genotype were observed for the T_o and T_p of starch from fababean and the PV, TV, CV and FV of starch from pea and fababean. However, these differences were small and failed to reveal a particular genotype that might exhibit unique starch functionality sufficient to be exploited commercially. Alternatively, the small variation observed may be advantageous for processors using pea or fababean from western Canada. Pea grown in hotter, dryer conditions exhibited higher protein concentrations, higher T_p, and lower CV and FV than pea grown in cooler, wetter conditions. Fababean grown in locations where more precipitation fell in the later stages of seed development would have experienced prolonged seed fill, increasing the starch concentration in the seed and the amylose concentration in the starch, compared to fababean grown in locations where precipitation was more evenly distributed. However, it would be challenging to rely on environmental conditions to produce specific starch functionalities year after year. Further investigations into the functionality of combinations of PS and other starches or hydrocolloids were carried out.

Several of the native, HMT or PG blends of PS and CS, WCS, HACS or PoS exhibited functional properties that were significantly different than their respective calculated weighted average values. These differences indicate that several blends exhibited synergies that might be exploited in food manufacturing. For example, blends of PS and HACS exhibited higher viscosities, additive syneresis and acceptable shear stabilities. In addition, blends of PS and CS exhibited additive pasting viscosities, acceptable syneresis for native starch applications, and low shear stabilities. However, blends of PS and WCS or PoS are unlikely candidates for use in food manufacturing.

Several combinations of PS and GG, LBG, XG or CMC exhibited functional properties that were significantly different than those of PS. Combinations of pea starch and galactomannans exhibited higher viscosities, lower degrees of syneresis (GG only) and higher shear stabilities than did PS. Combinations of pea starch and XG or CMC exhibited higher viscosities at low inclusion rates and lower degrees of syneresis than did PS. Starch-hydrocolloid-water systems are two-phase systems where the continuous phase contains the hydrocolloid and solubilized glucans and the dispersed phase contains granule ghosts, ungelatinized starch granules or portions thereof, and insoluble or precipitated glucans. The presence of the hydrocolloid influences the effective concentration of the components in the system and may influence the phase separation of glucans due to incompatibilities between polysaccharides. In addition, interactions between glucans and the galactomannan or anionic hydrocolloid molecules, and the degree of solubilization of the hydrocolloids may influence the functional properties of the system. The interactions between glucans and hydrocolloid molecules will vary based on the chemical and ionic nature of the hydrocolloid.

Current food processing practices tend to involve high shear, heat and/or acid, and may reduce the ability of a native starch to function in the system. Food manufacturers need to create

optimal texture, mouthfeel, flavour and stability in a complex system with various concentrations of moisture, protein, fat and carbohydrate. In addition, food manufacturers must consider consumer handling (e.g. food may be frozen or stored longer). Applications that use native starches may include: meat (CS or wheat starch), snacks (CS, HACS, PoS or wheat starch), fill-viscosity starches in retort applications (typically PoS or WCS), confectionary (high-amylose starches), batters (high-amylose starches) and minimally processed foods (starch type is processor dependent). The following blends are recommended for further applications testing:

1. Blends of 1:3 PS:HACS in confectionary and batter/breading/coating applications due to relatively small differences in thermal and pasting properties, possibly replacing or complementing other high-amylose starches.

2. Blends of PS:HACS in glaze applications in baked goods, snacks or breakfast cereals, possibly replacing other high-amylose starches, chemically-modified starches or hydrocolloids.

3. Blends of PS:CS or PS:HACS in ready-to-eat breakfast cereals may provide texture, stability and longer bowl-life in puffed, flaked and shredded cereals, possibly replacing CS, HACS, wheat starch or chemically-modified starches.

4. Blends of PS:CS in retorted semi-moist pet foods to provide gelation, possibly replacing CS or WCS.

5. Combinations of PS and GG in glaze applications in baked goods, snacks or breakfast cereals, possibly replacing high-amylose starches, modified starches or hydrocolloids.

The development of "clean-label" food products using native starches may be restricted to using low-shear processing techniques (e.g. kettle cookers instead of plate exchangers for heating). The blends of pea starch with starches and hydrocolloids remain exposed to breakdown via shear, acid and heat as the structure of the granules is stabilized by relatively weak hydrogen

bonds as opposed to the covalent bonds of chemically-modified starches. As a result, to maintain clean-label ingredient declarations, food manufactures may need to use equipment with low shear forces and highly controlled temperature mechanisms to prevent over and undercooking of the starches in the systems. New technologies in starch manufacture continue to be developed to maintain the processability of modified food starches within a clean label definition. It may be possible to apply these new technologies to PS or PS blends.

The functional properties of a number of the starch blends and starch-hydrocolloid combinations were determined not to differ significantly from the few commercial, chemically-modified starches examined. However, no blend or combination exhibited the functionality of a commercial, chemically-modified starch in all functional properties examined. Nevertheless, demand for clean labels (ingredient declarations) and natural ingredients is increasing and being able to replace chemically-modified starches with a natural ingredient would be valuable in certain market sectors.

7. GENERAL CONCLUSIONS

It was hypothesized that: i) differences in starch and protein concentrations in the seed and differences in amylose concentrations in, and the thermal and pasting properties of, starch from pea and fababean would be detected among pea and fababean genotypes; ii) the environmental conditions during the growing season would significantly affect the composition and functionality of pea and fababean starch; iii) native, heat-moisture-treated or pregelatinized blends of pea starch and corn starch, waxy corn starch, high-amylose corn starch or potato starch would exhibit unique functionalities; and iv) combinations of pea starch and guar gum, xanthan gum, locust bean or carboxymethyl cellulose would exhibit improved functionality including higher viscosities and lower levels of syneresis after freezing than does pea starch.

Differences due to genotype were observed in the concentrations of starch and protein in pea and fababean, in the T_o and T_p of fababean starch, and in the PV, TV, CV and FV of pea starch and fababean starch. The effect of genotype on the concentrations of starch and protein in pea and fababean was sufficient to be of practical significance to end-users due to the economic impacts of differences in starch and protein concentration.

Starch from pea grown in locations that were hotter and drier exhibited higher protein concentrations and lower cooling and final viscosities. Distribution of moisture throughout the growing season influenced the concentration of amylose in the starch from fababean. High heritabilities were observed for starch concentration in pea and of starch and protein concentration in fababean and relatively low heritabilities were observed for protein

concentration in pea and the concentration of amylose in starch from pea and fababean. Breeding efforts would have little impact on parameters exhibiting low broad sense heritability values.

The key functionalities that food manufacturers consider in evaluating a food starch include pasting properties and the degree of syneresis upon cooling. The use of native starches in food manufacturing is limited due to their low shear stability and high syneresis upon cooling. The use of chemically-modified starches overcomes these negative aspects of native starches. However, food manufacturers are interested in developing products with clean labels due to consumer demand for natural food products. In addition, consumers are becoming increasingly aware that consuming resistant starch has health benefits. Native blends of PS and CS exhibited lower degrees of syneresis than did PS and higher RS concentrations than did corn starch. A blend of PS and CS may be used to increase the RS concentration in a product without compromising viscosity or freeze-thaw stability in applications with rigid texture and opaque gel clarity, such as in creams, custards, puddings and sauces (as patented by Stute & Kern, 1994) or in systems with low moisture contents, such as in extruded or fried snacks to provide crispness while retaining expansion or, at low concentrations of PS, in breadings to increase crispness (Mason, 2009).

The effect of heat-moisture treatment varied depending on the botanical source of the starch. Heat-moisture treatment reduced PVs, reduced SPs, reduced syneresis during freeze-thaw cycles and increased RS concentration compared to corresponding native starch blends. Some of the HMT blends exhibited unique functionalities. Pregelatinization of the starch blends increased SPs at lower temperatures (65°C and 75°C) and reduced resistant starch concentrations. Blends of PS and PoS exhibited SPs higher than weighted average values.

The most interesting functionalities generated in this study included the 1:3 PS:CS blend, which exhibited T_p, WSI at 65°C and shear stability that were not significantly different from

those of a low DS, AC WCS, and blends of PS and PoS which exhibited degrees of syneresis lower than weighted average values. In addition, the 1:3 PS:PoS blend exhibited lower degrees of syneresis than a low DS, AC WCS after three freeze-thaw cycles. These blends may be useful in dry mixes.

The effects of hydrocolloids on PS were slight at the concentrations used in this study and higher concentrations of hydrocolloids should be investigated. Combinations of PS with hydrocolloids exhibited reduced pasting temperatures, increased viscosities, increased water solubilities and improved freeze-thaw stabilities than did PS. Pasting properties indicated that hydrocolloids may interact with leached glucans from PS and increase (GG or LBG) or increase, and then decrease, the viscosity of PS (XG or CMC). Combinations of PS and GG, LBG or CMC may be useful in applications such as in soups, sauces and baked goods.

Novel contributions from this study include information on: i) the starch functionality of gentotypes of pea and fababean commonly grown in western Canada across several locations; ii) the impact of hydrothermal and physical starch modifications on blends of starches; and iii) the functionality of pea starch in the presence of common, commercially-available starches and hydrocolloids.

Future studies might include examination of the effect of dry heat on the functionality of starch blends, investigations into mechanisms for synergies observed in the functionality of starch blends and starch-hydrocolloid combinations, and applications testing. A few of the blends examined exhibited potentially useful functionality and applications have been suggested. A number of blends or combinations of starch and hydrocolloids exhibited synergistic functionality. There is a need for more systematic examination of the molecular mechanisms behind the synergies observed in this study. This examination may include an investigation into behaviour during thermal treatments (gelatinization, pasting, cooling, freezing) coupled with

analysis (e.g. microscopy, near infrared spectroscopy, nuclear magnetic resonance spectrometry) of the individual starch components and blends, before and after thermal treatment. To be more specific with respect to potential applications of starch blends and starch-hydrocolloid combinations, inclusion rates, and how blends behave in more complicated food systems, applications-based testing will be required.

8. REFERENCES

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APPENDIX A

List of Abbreviations

exp   Experimental value

ΔH   Endothermic enthalpy of gelatinization

FT   Freeze-thaw cycle (FT1 = freeze-thaw cycle 1, etc.)

FV   Final viscosity

PS   Pea starch

PT   Pasting temperature

PV   Pasting viscosity

RS   Resistant starch

SP   Swelling power

SS   Shear stability

T_c Completion temperature of gelatinization

T_o Onset temperature of gelatinization

T_p Peak temperature of gelatinization

TV   Trough viscosity

WBC   Water binding capacity

WSI   Water solubility index

wt ave   Weighted average value

T$_o$: pea starch and corn starch

T$_o$: pea starch and waxy corn starch

T$_o$: pea starch and high-amylose corn starch

T$_o$: pea starch and potato starch

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T$_p$: pea starch and corn starch

T$_p$: pea starch and waxy corn starch
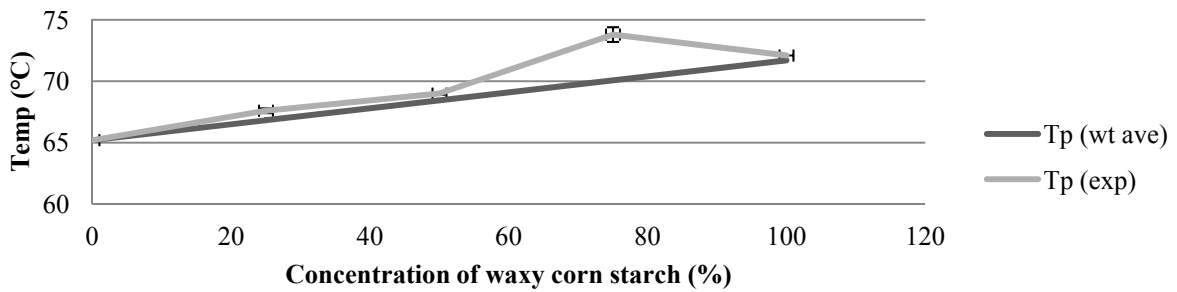
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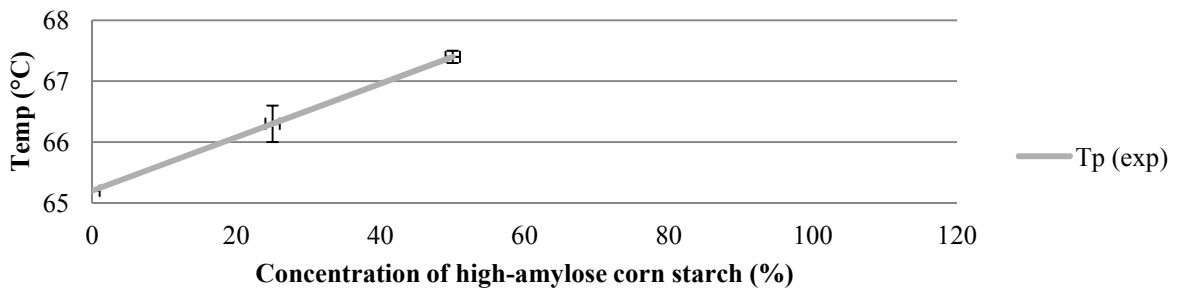
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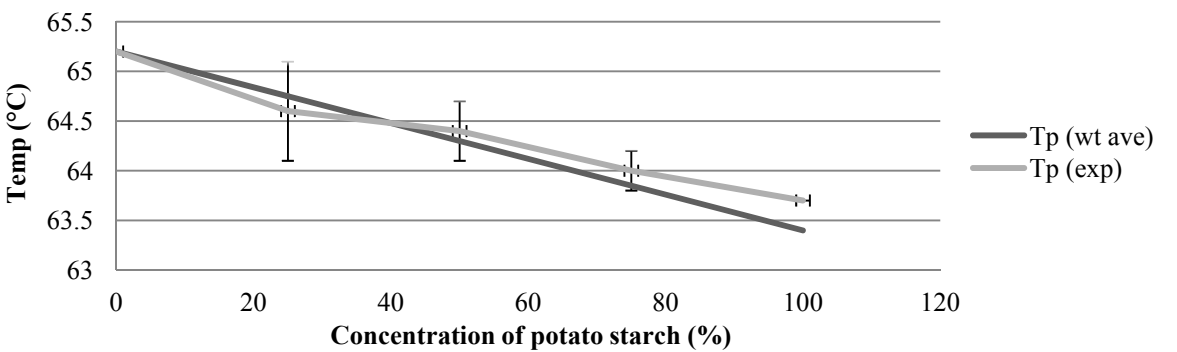
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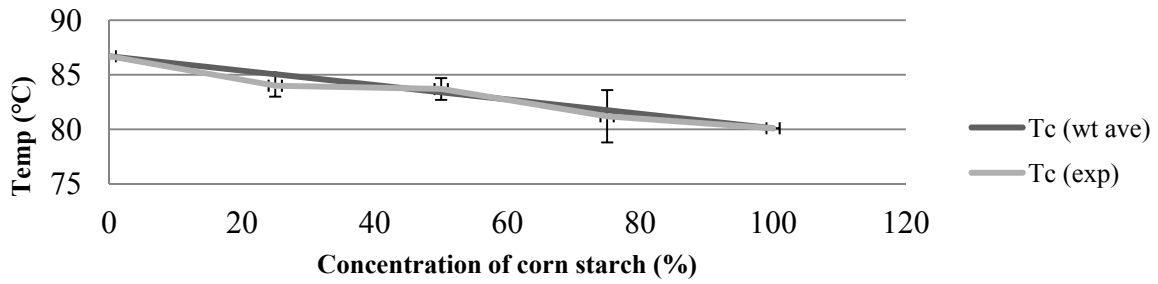
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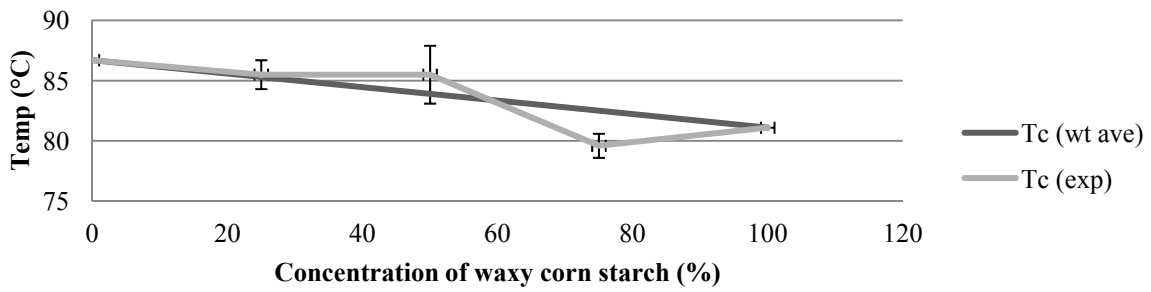
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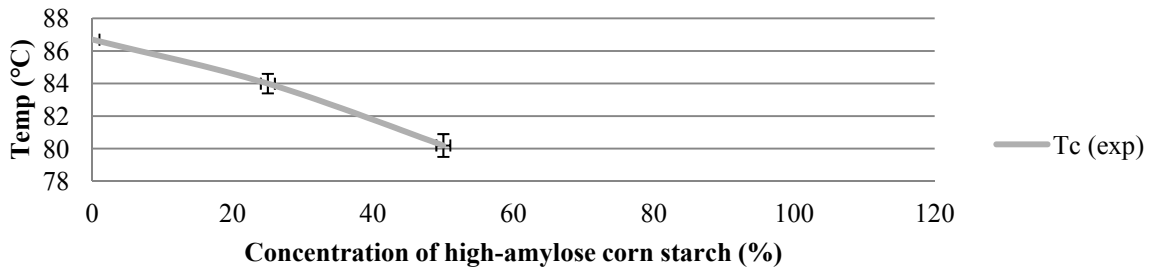
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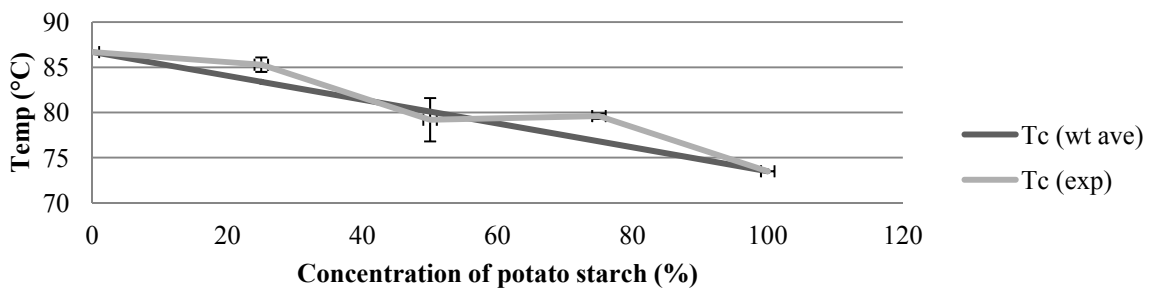
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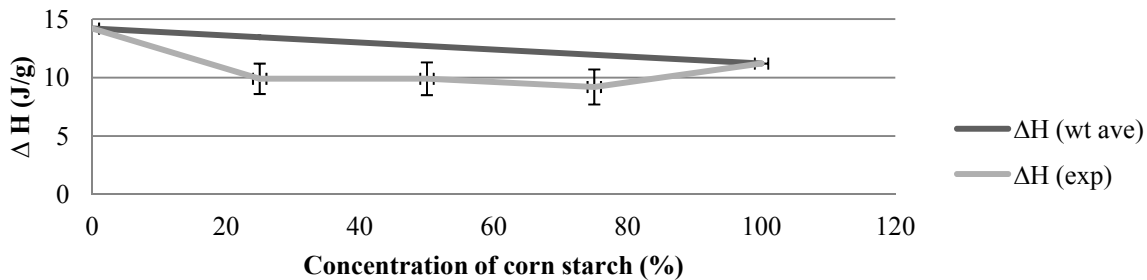
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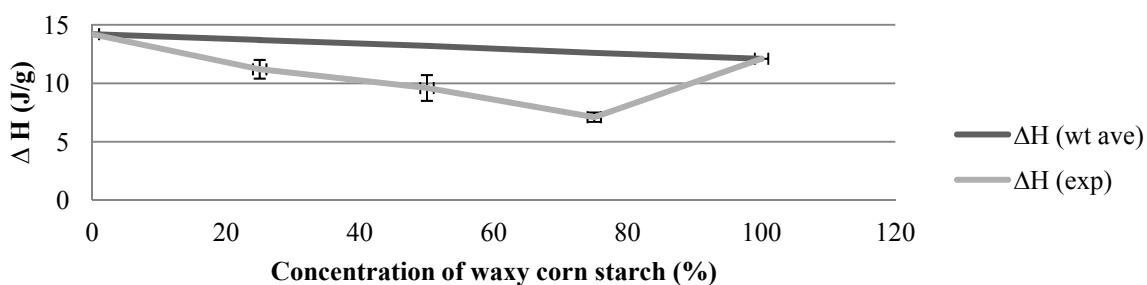
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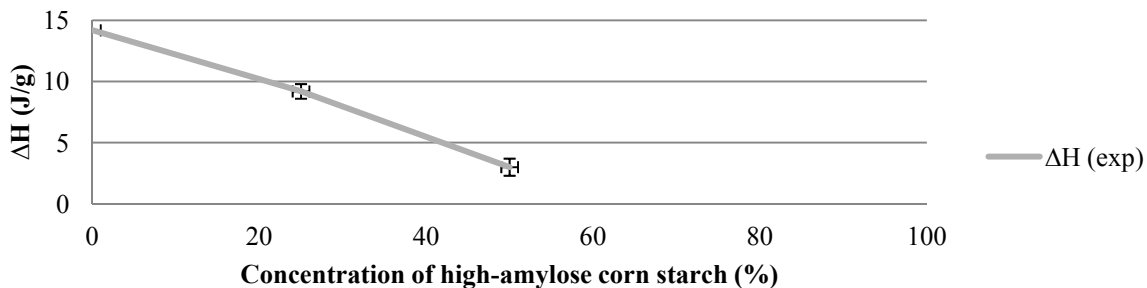
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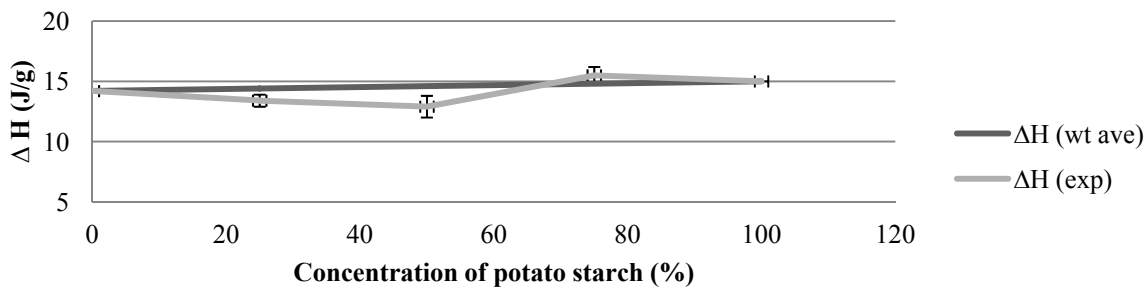
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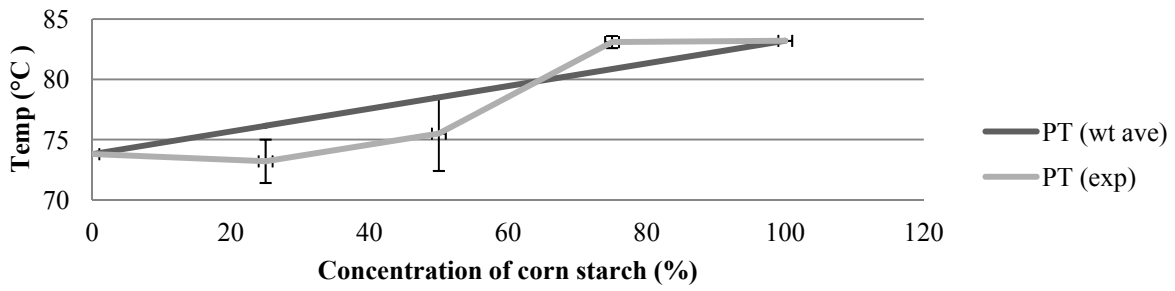
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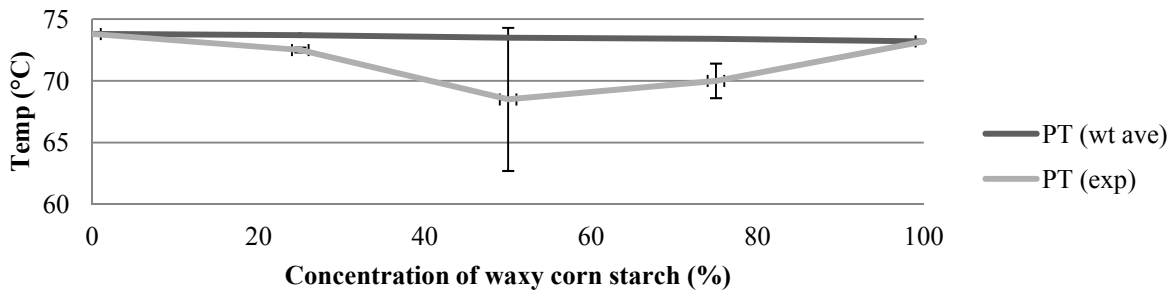
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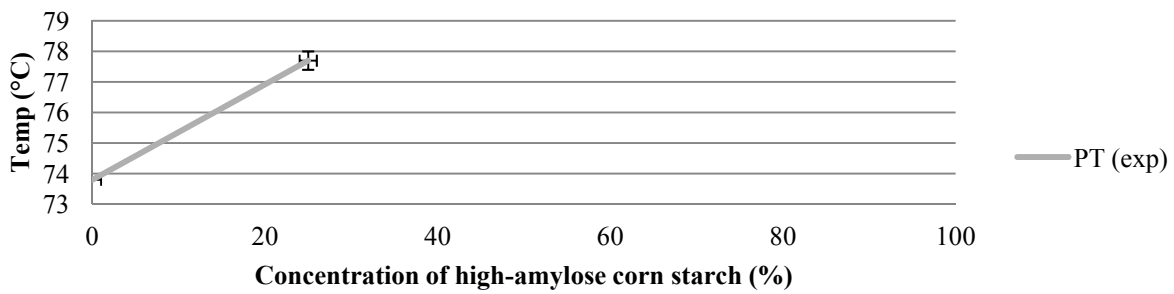
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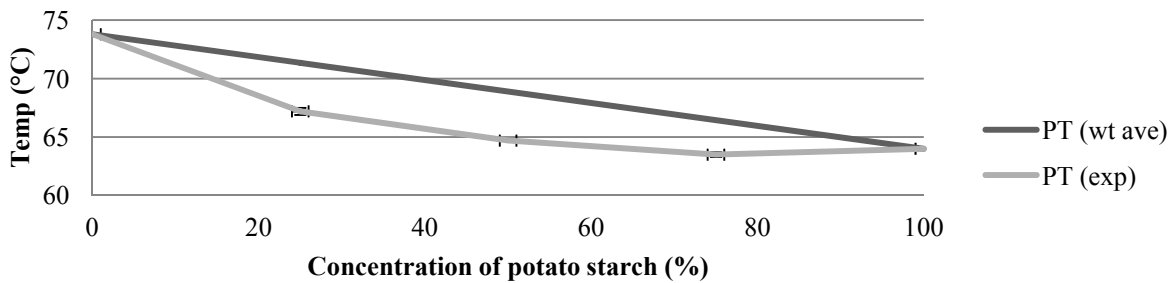
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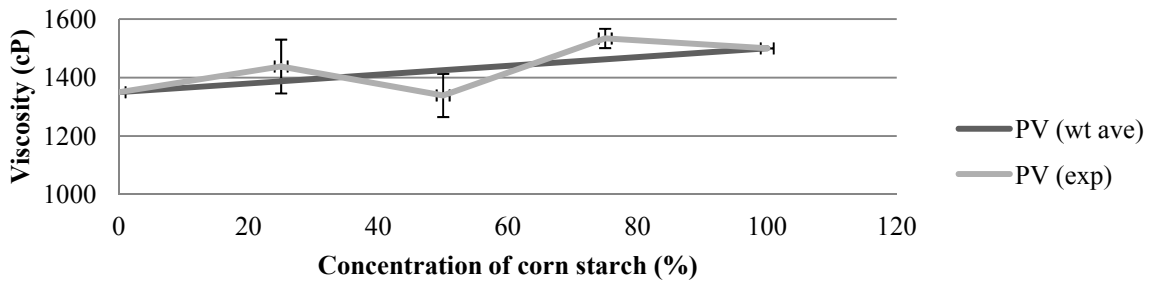
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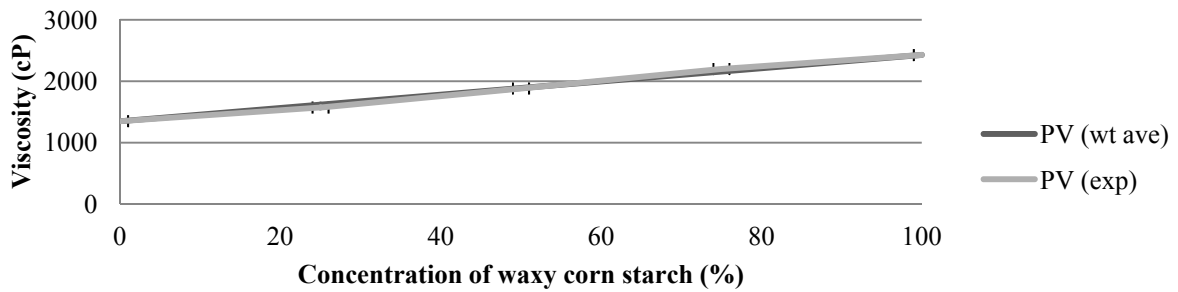
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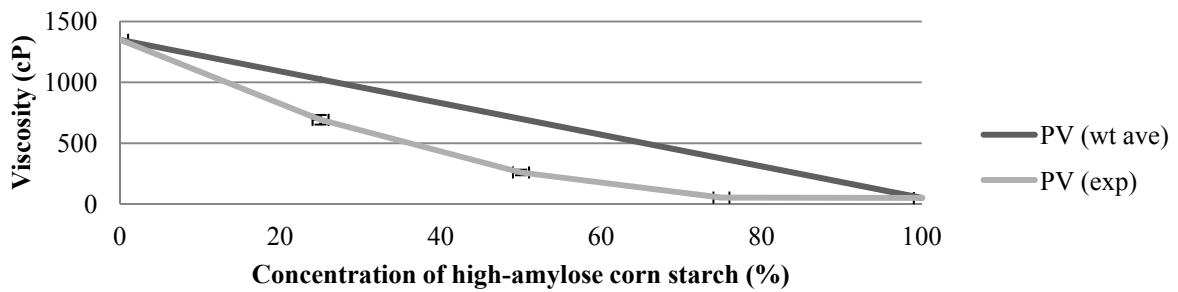
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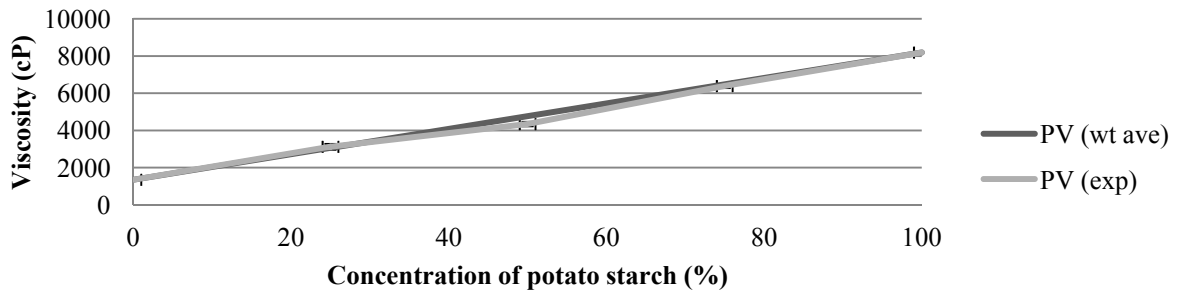
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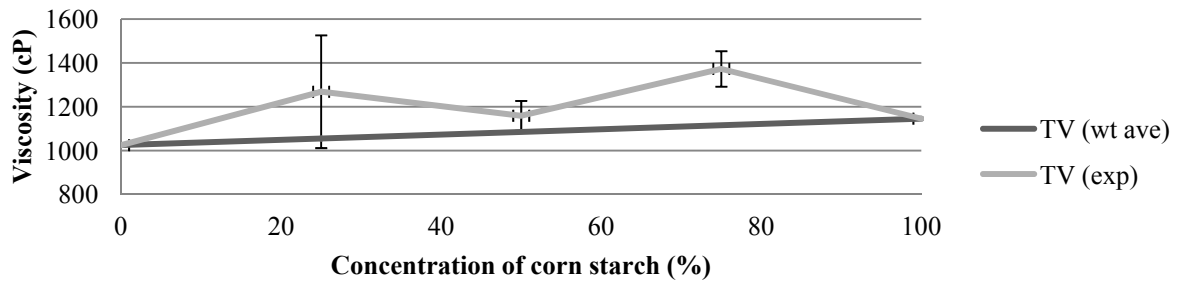
TV: pea starch and waxy corn starch
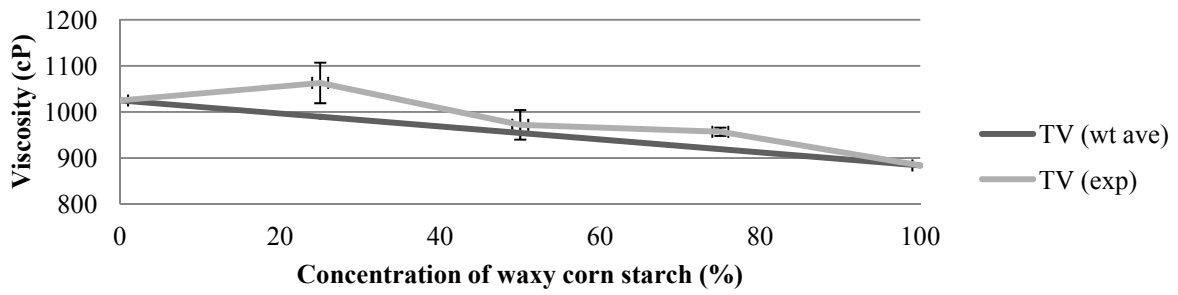
TV: pea starch and high-amylose corn starch
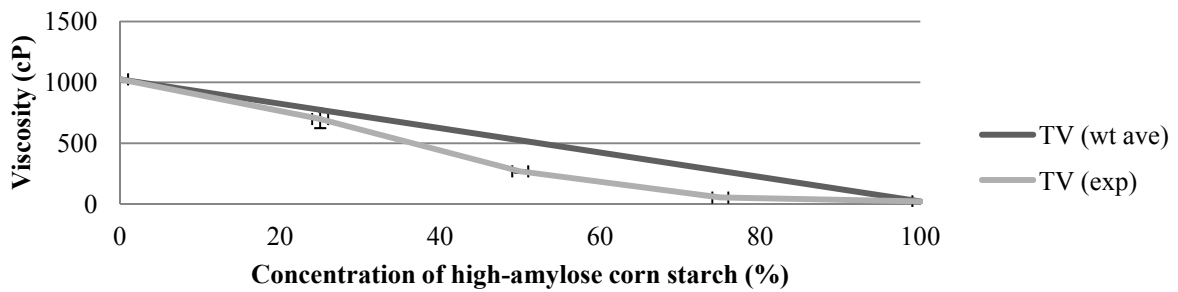
TV: pea starch and potato starch
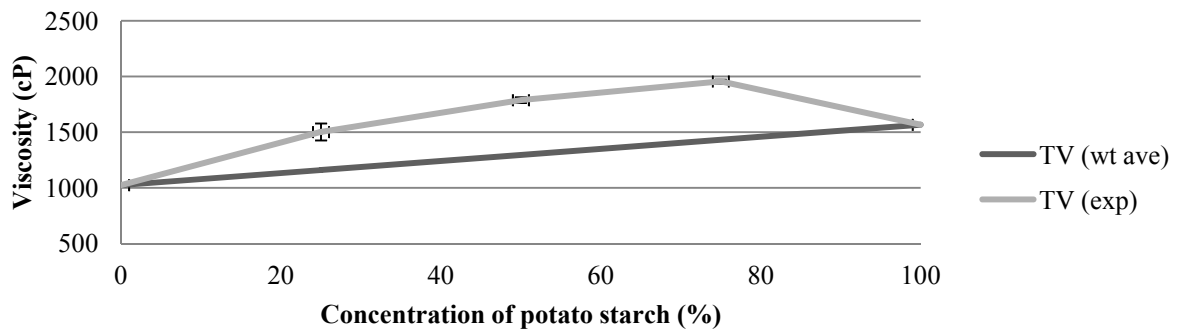
FV: pea starch and corn starch
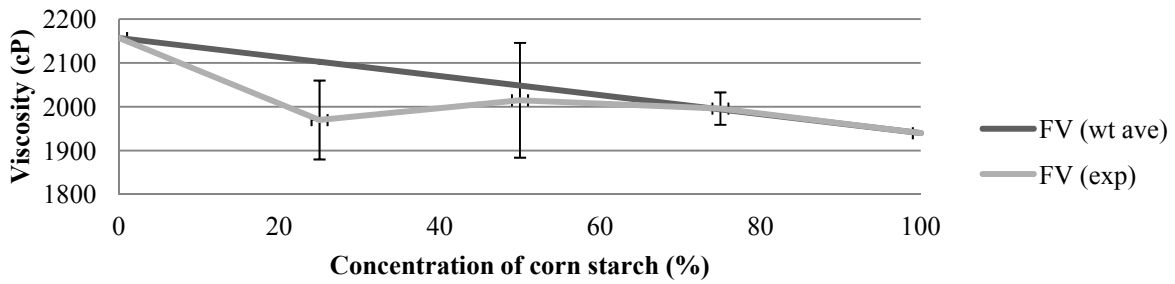
FV: pea starch and waxy corn starch
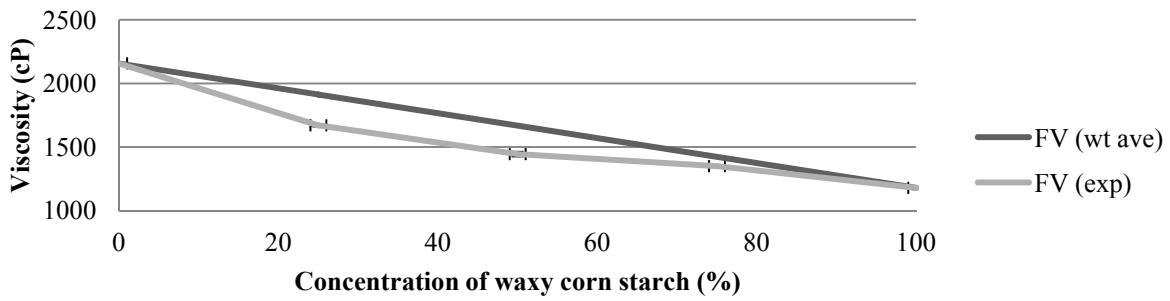
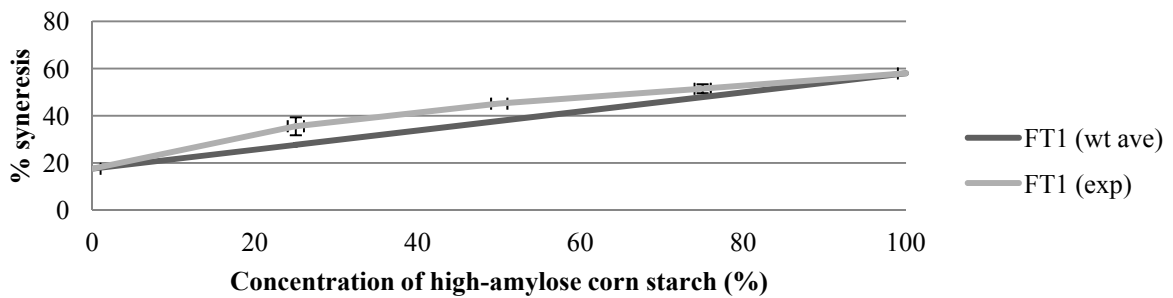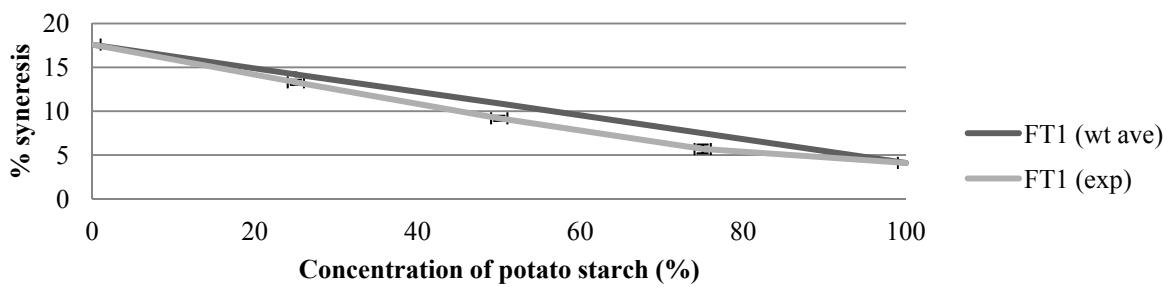**FV: pea starch and high-amylose corn starch**
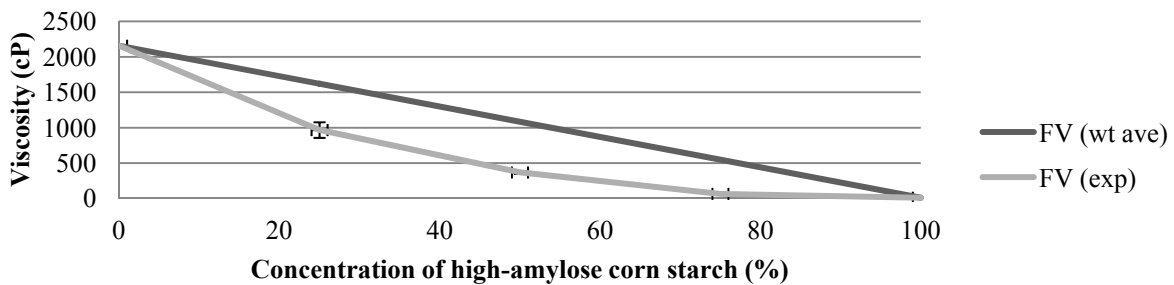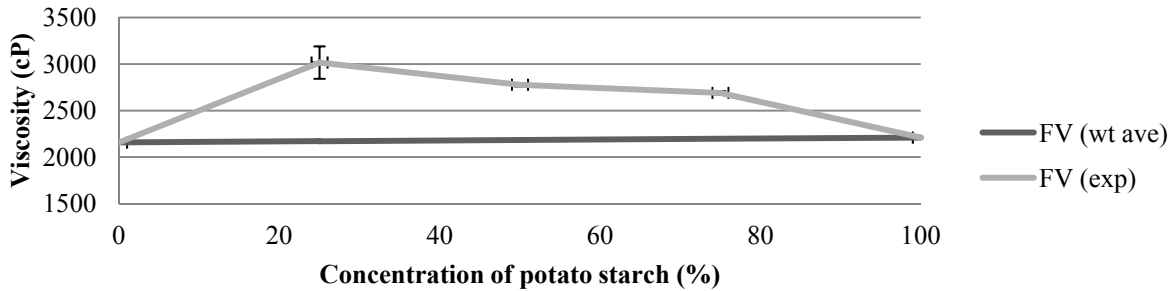
FV: pea starch and potato starch

SP 65°C: pea starch and corn starch
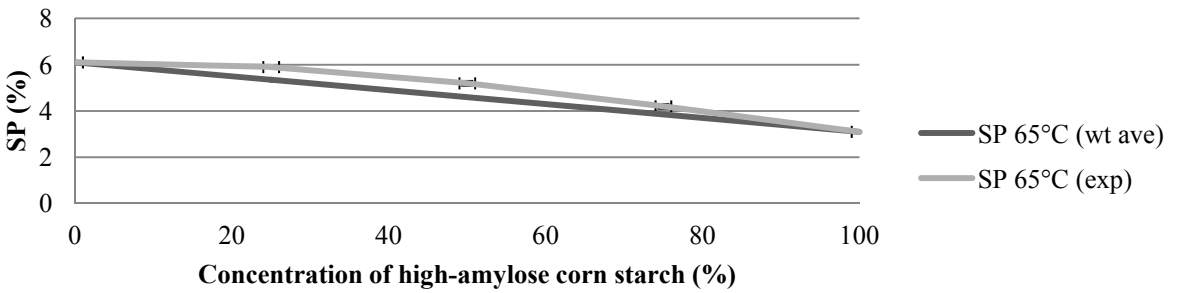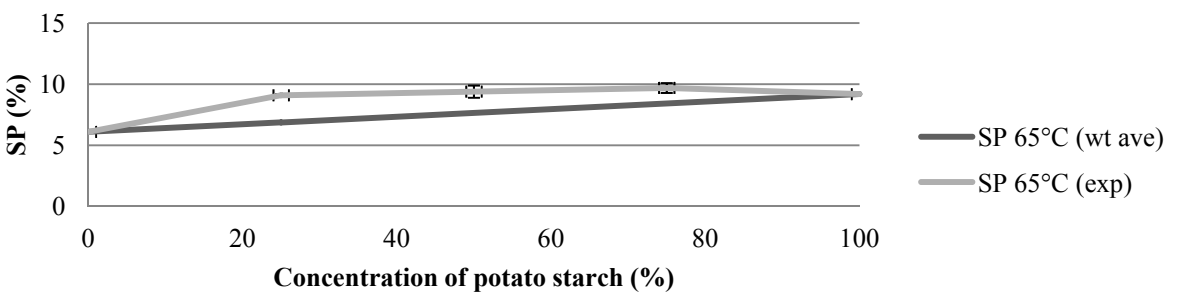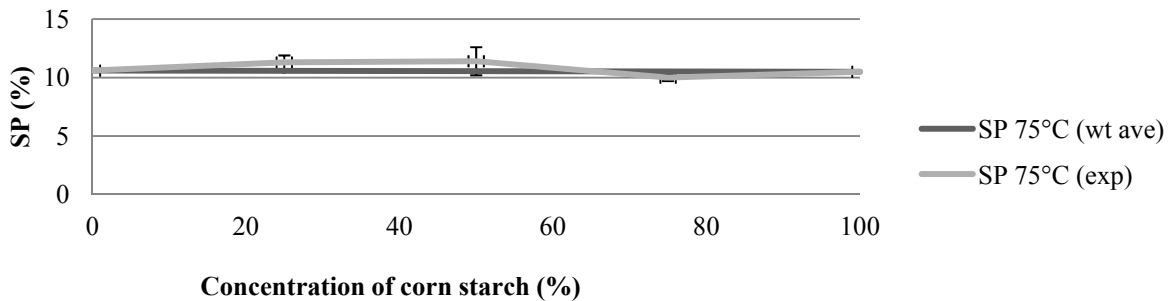
SP (%)

10
8
6
4
2
0

0   20   40   60   80   100

Concentration of corn starch (%)

SP 65°C (wt ave)
SP 65°C (exp)

SP 65°C: pea starch and waxy corn starch

SP (%)

7
6
5
4
3

0   20   40   60   80   100

Concentration of waxy corn starch (%)

SP 65°C (wt ave)
SP 65°C (exp)

SP 65°C: pea starch and high-amylose corn starch

SP (%)

8
6
4
2
0

0   20   40   60   80   100

Concentration of high-amylose corn starch (%)

SP 65°C (wt ave)
SP 65°C (exp)

SP 65°C: pea starch and potato starch

SP (%)

15
10
5
0

0   20   40   60   80   100

Concentration of potato starch (%)

SP 65°C (wt ave)
SP 65°C (exp)

SP 75°C: pea starch and corn starch

SP 75°C: pea starch and waxy corn starch
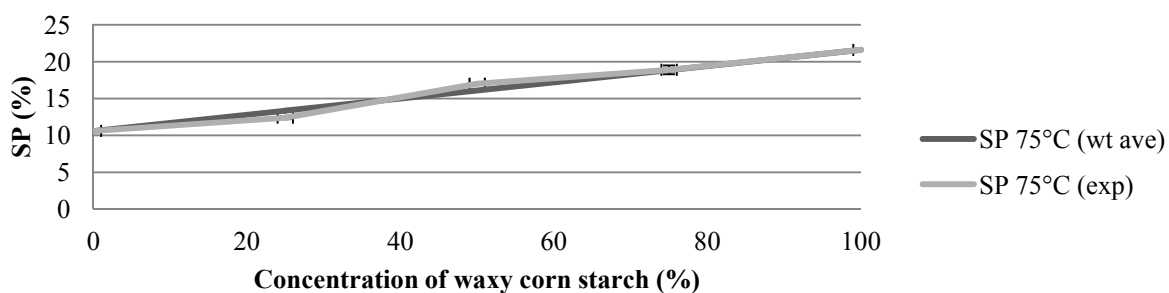
SP 75°C: pea starch and high-amylose corn starch
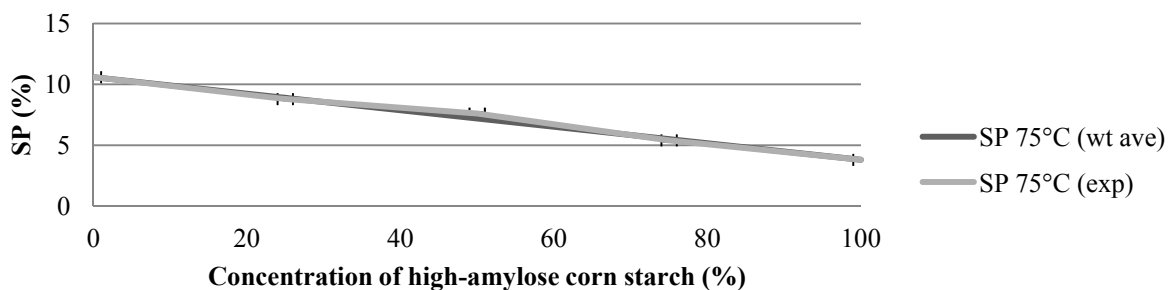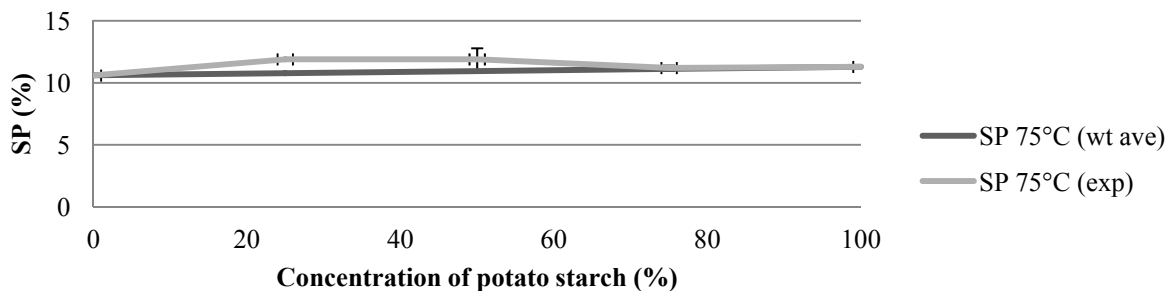
SP 75°C: pea starch and potato starch

SP 85°C: pea starch and corn starch
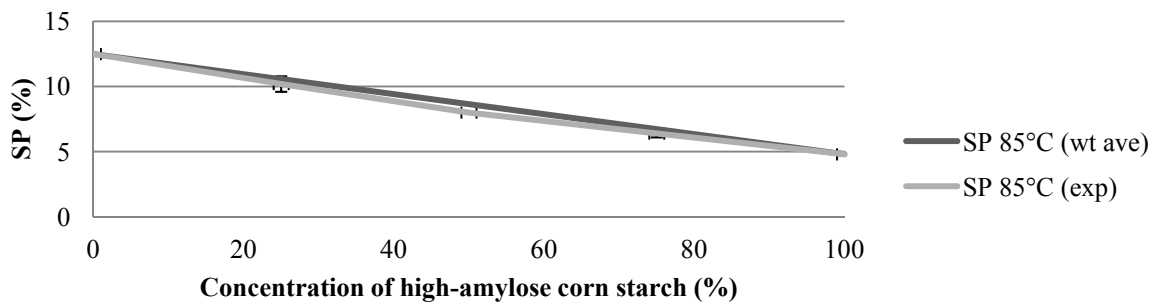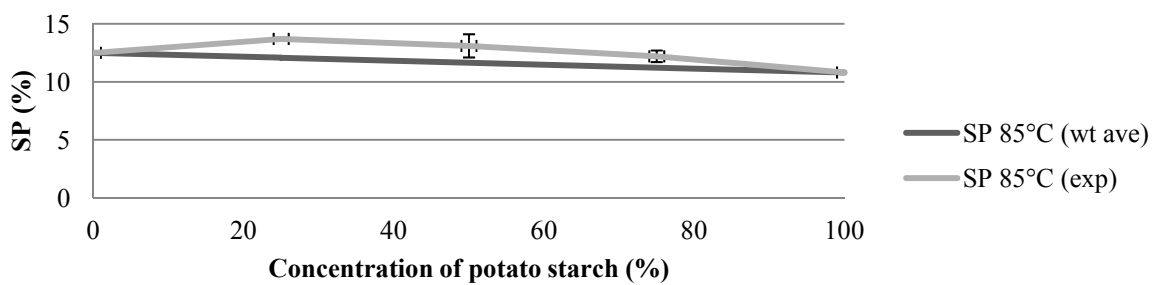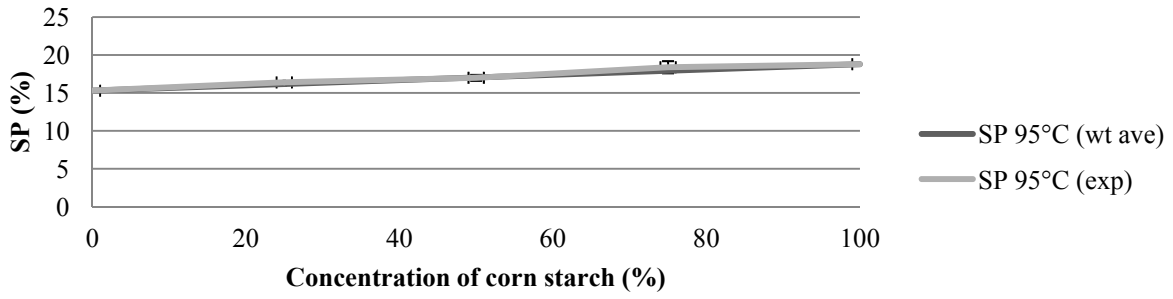
SP (%) — Concentration of corn starch (%)

— SP 85°C (wt ave)
— SP 85°C (exp)

SP 85°C: pea starch and waxy corn starch

SP (%) — Concentration of waxy corn starch (%)

— SP 85°C (wt ave)
— SP 85°C (exp)

SP 85°C: pea starch and high-amylose corn starch

SP (%) — Concentration of high-amylose corn starch (%)

— SP 85°C (wt ave)
— SP 85°C (exp)

SP 85°C: pea starch and potato starch

SP (%) — Concentration of potato starch (%)

— SP 85°C (wt ave)
— SP 85°C (exp)

SP 95°C: pea starch and corn starch

SP 95°C: pea starch and waxy corn starch
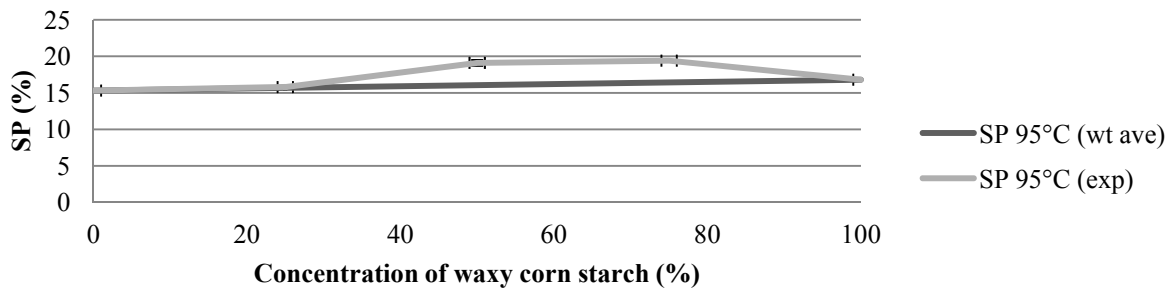
SP 95°C: pea starch and high-amylose corn starch
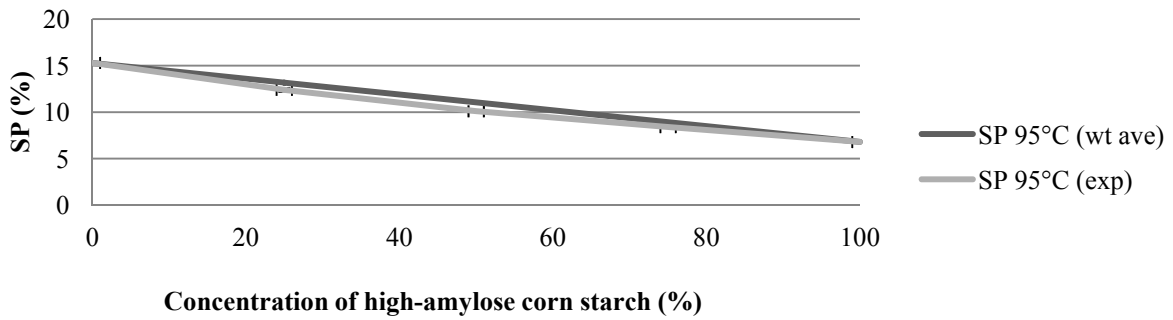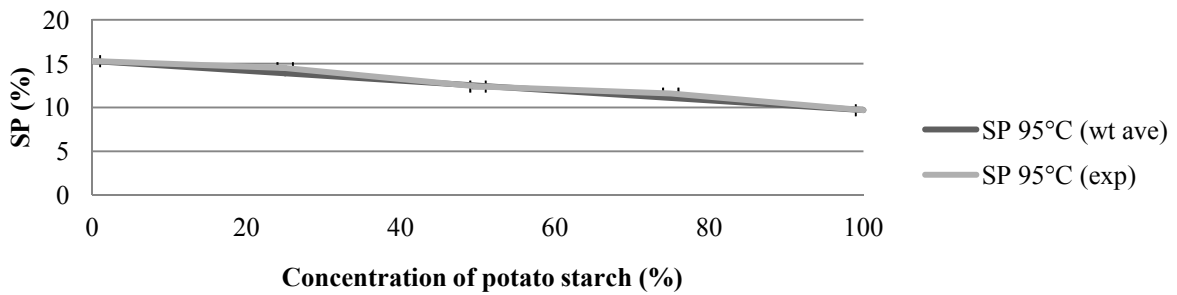
SP 95°C: pea starch and potato starch

WSI 65°C: pea starch and corn starch
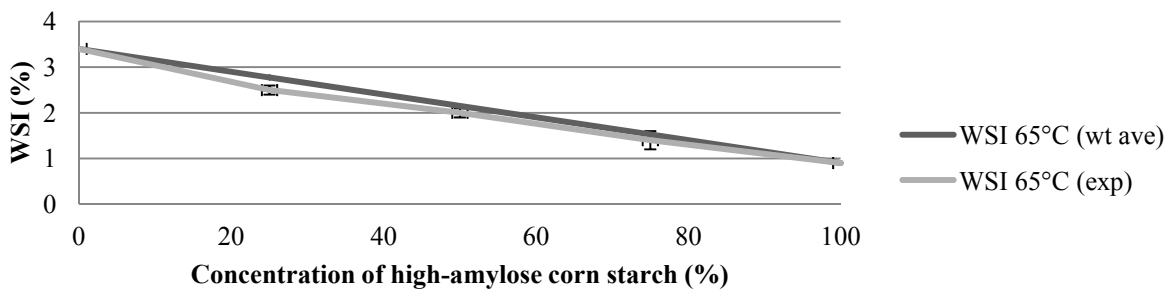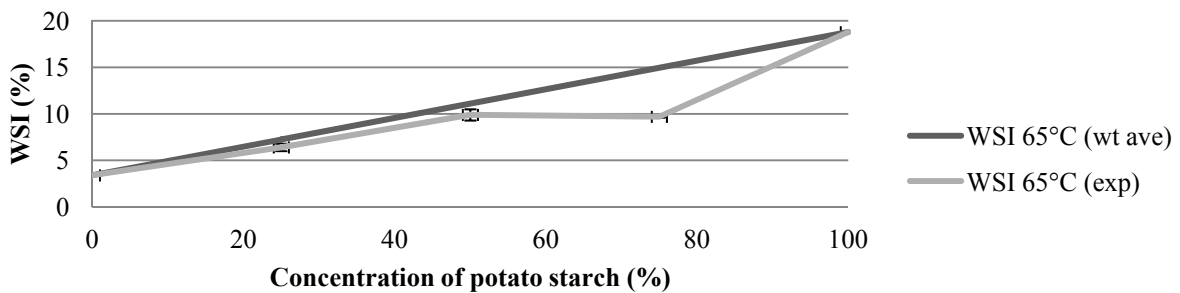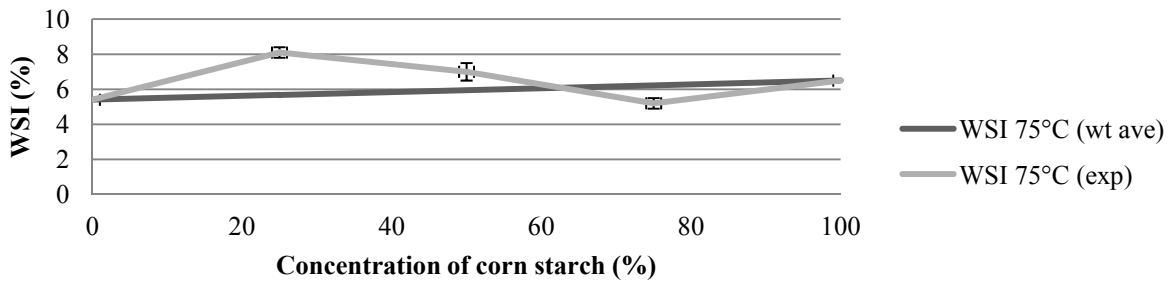
WSI (%) vs Concentration of corn starch (%)

— WSI 65°C (wt ave)
— WSI 65°C (exp)

WSI 65°C: pea starch and waxy corn starch

WSI (%) vs Concentration of waxy corn starch (%)

— WSI 65°C (wt ave)
— WSI 65°C (exp)

WSI 65°C: pea starch and high-amylose corn starch

WSI (%) vs Concentration of high-amylose corn starch (%)

— WSI 65°C (wt ave)
— WSI 65°C (exp)

WSI 65°C: pea starch and potato starch

WSI (%) vs Concentration of potato starch (%)

— WSI 65°C (wt ave)
— WSI 65°C (exp)

WSI 75°C: pea starch and corn starch

WSI 75°C: pea starch and waxy corn starch
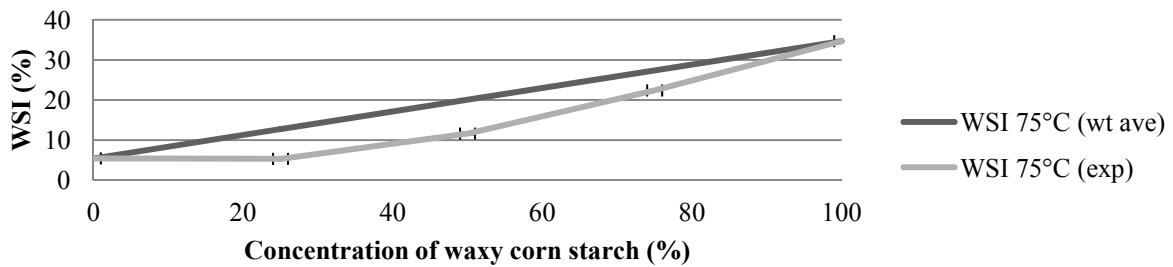
WSI 75°C: pea starch and high-amylose corn starch
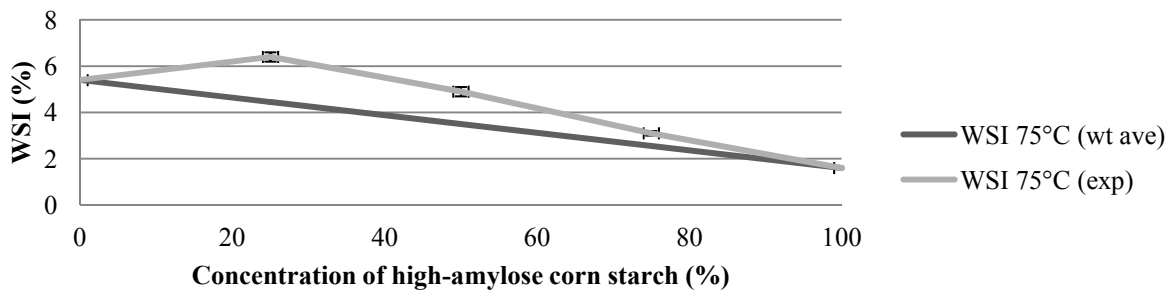
WSI 75°C: pea starch and potato starch
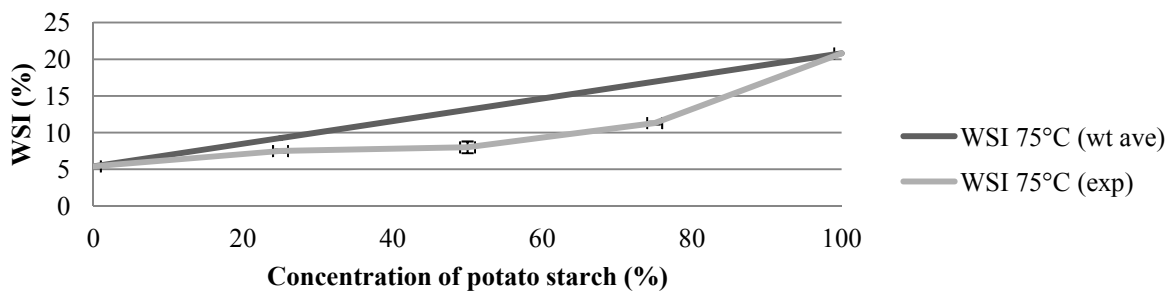
WSI 85°C: pea starch and corn starch
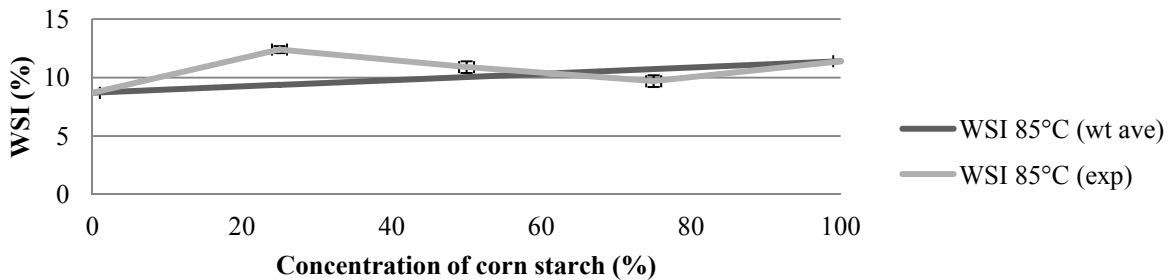
WSI 85°C: pea starch and waxy corn starch
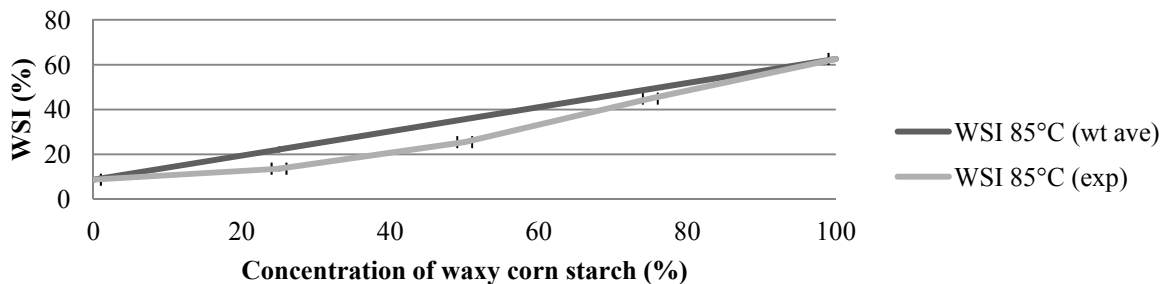
WSI 85°C: pea starch and high-amylose corn starch
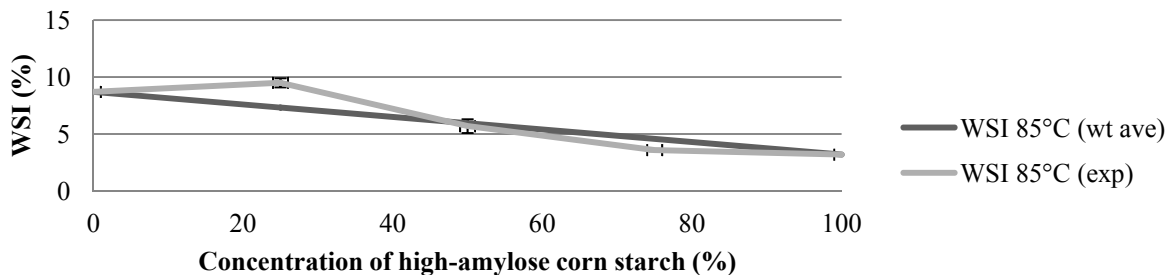
WSI 85°C: pea starch and potato starch

WSI 95°C: pea starch and corn starch
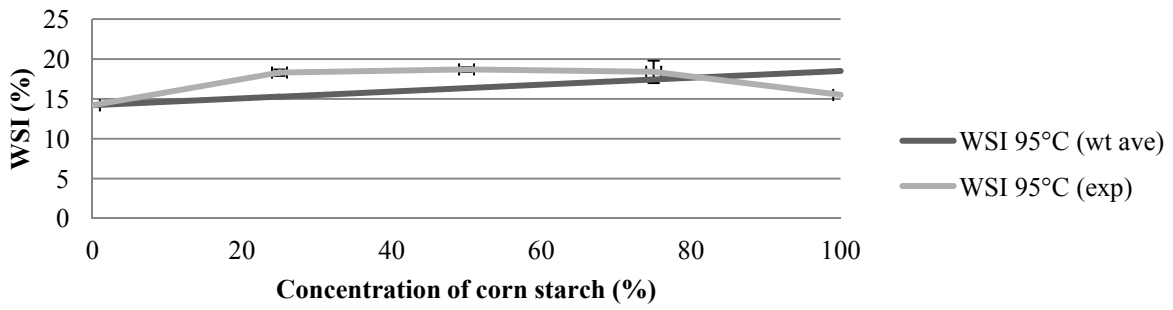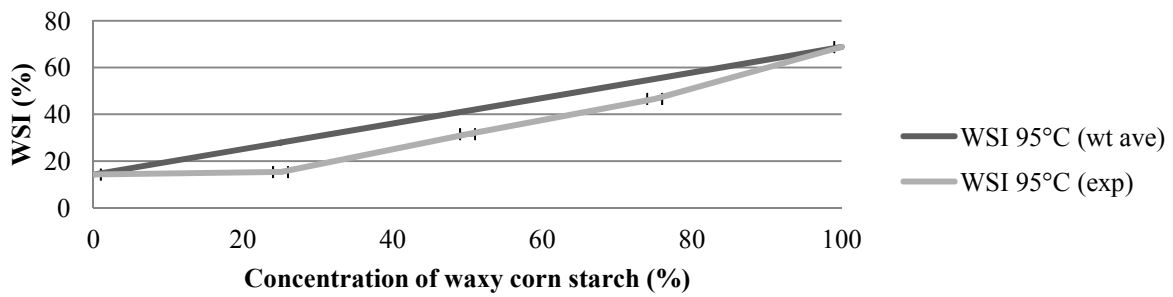
WSI 95°C: pea starch and waxy corn starch

WSI 95°C: pea starch and high-amylose corn starch

WSI 95°C: pea starch and potato starch

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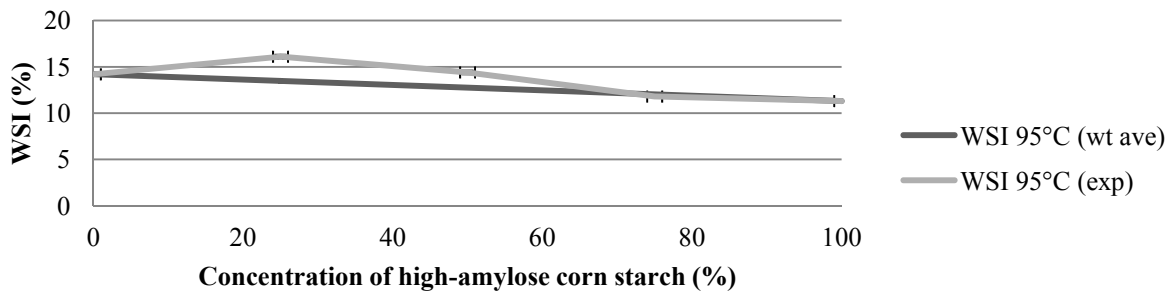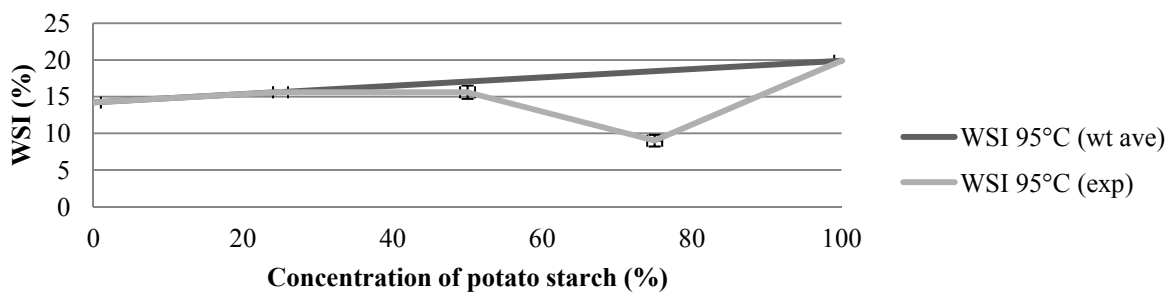
FT1: pea starch and corn starch
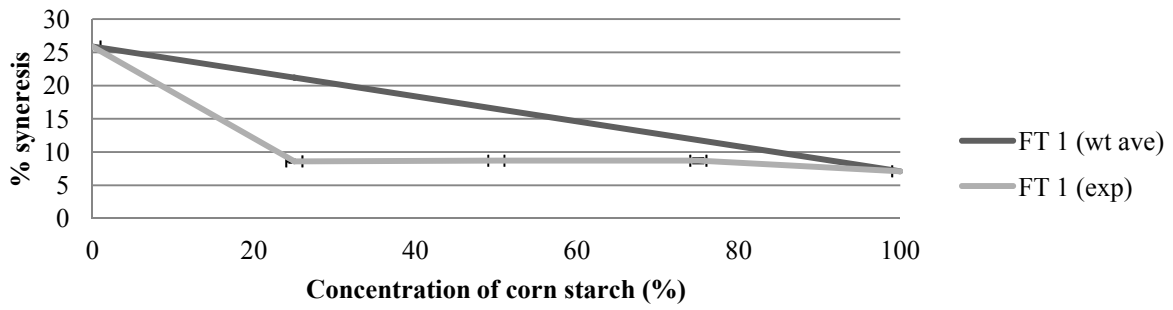
FT1: pea starch and waxy corn starch
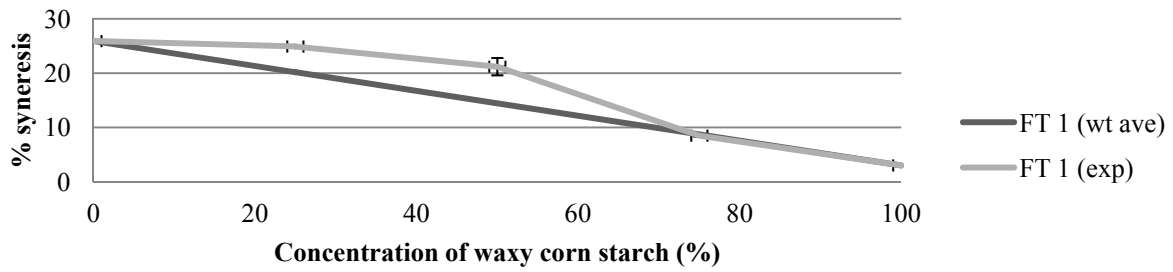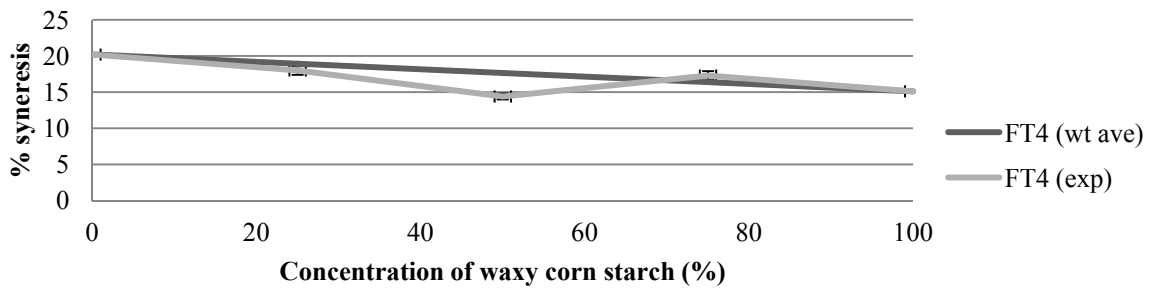

FT1: pea starch and high-amylose corn starch
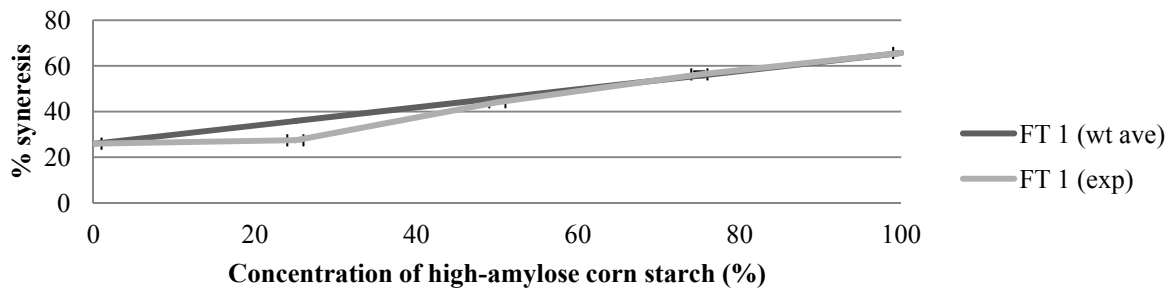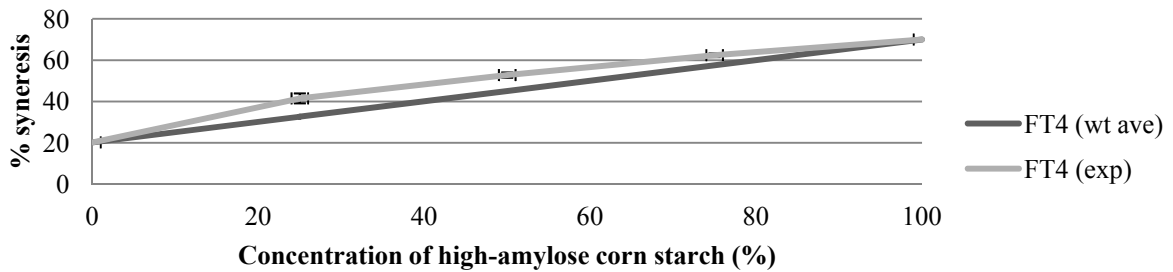

FT1: pea starch and potato starch
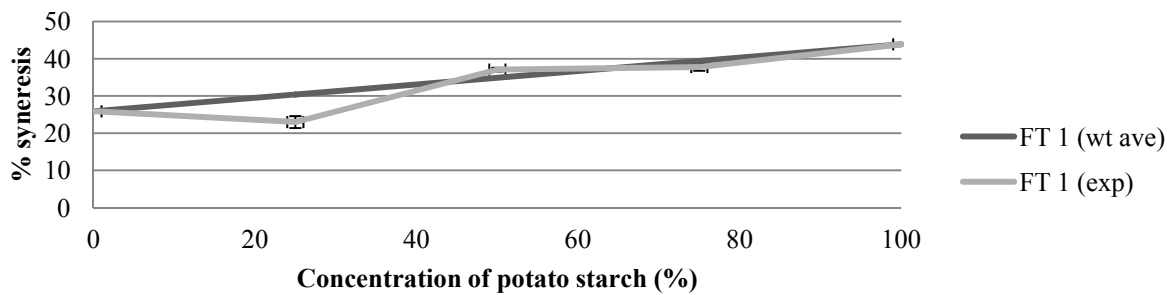
FT2: pea starch and corn starch
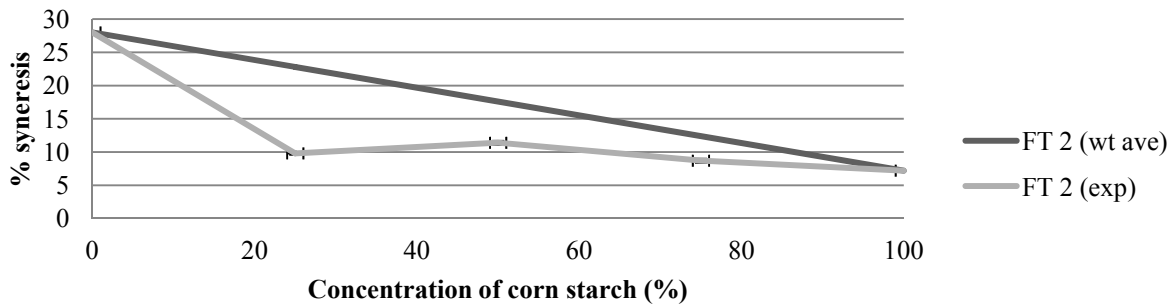
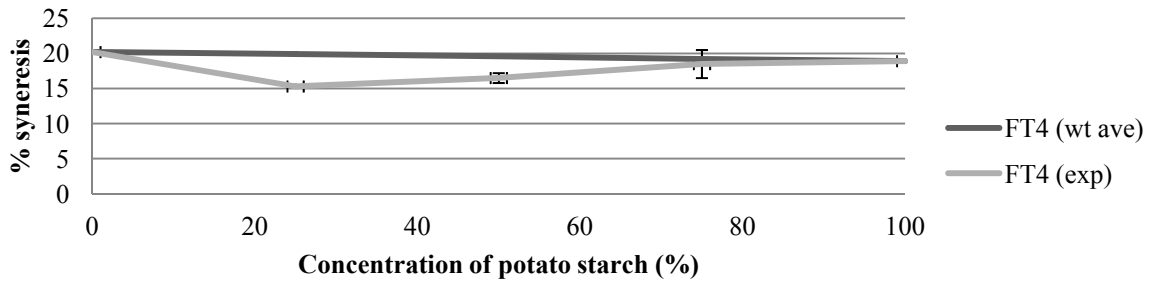**FT2: pea starch and waxy corn starch**
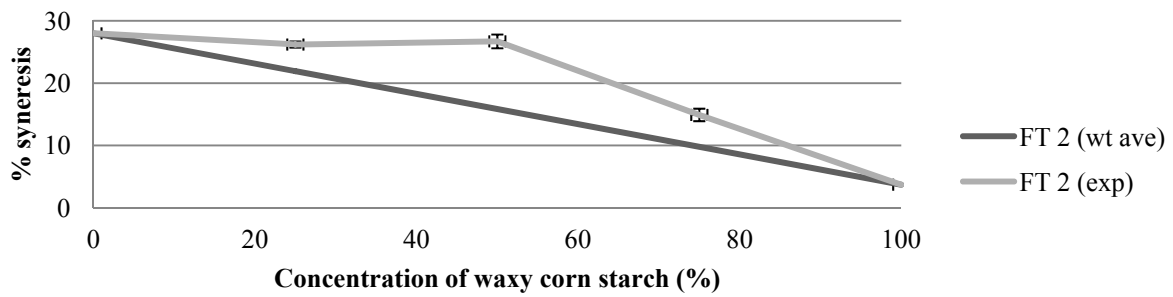
FT2: pea starch and high-amylose corn starch
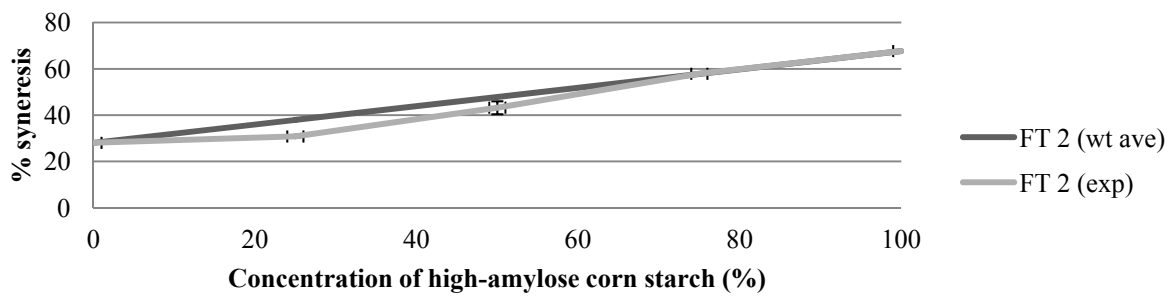
FT2: pea starch and potato starch
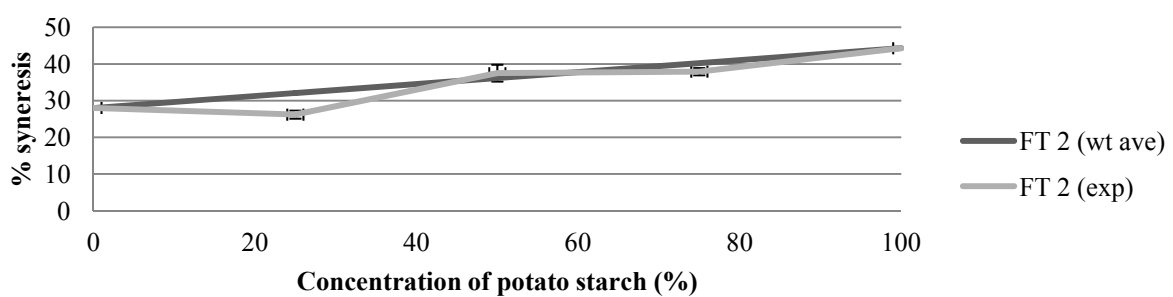
FT3: pea starch and corn starch
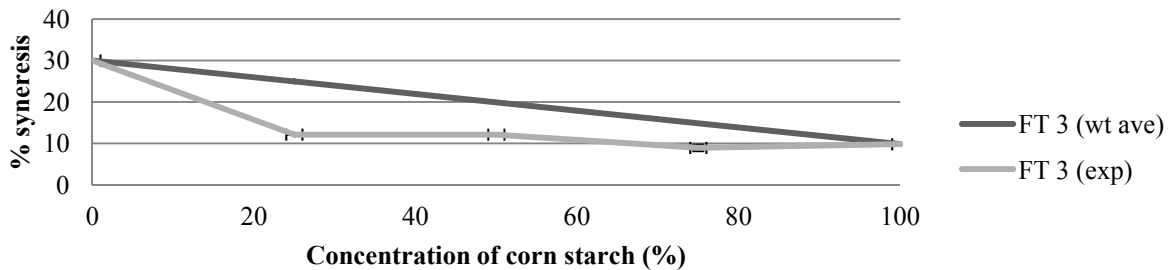
FT3: pea starch and waxy corn starch
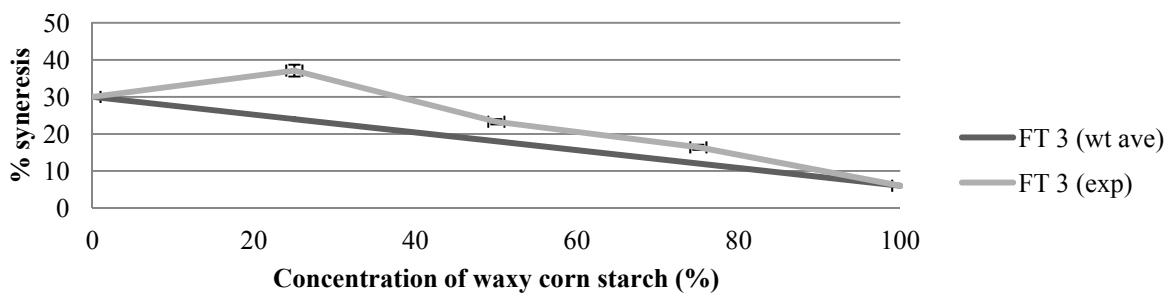
FT3: pea starch and high-amylose corn starch
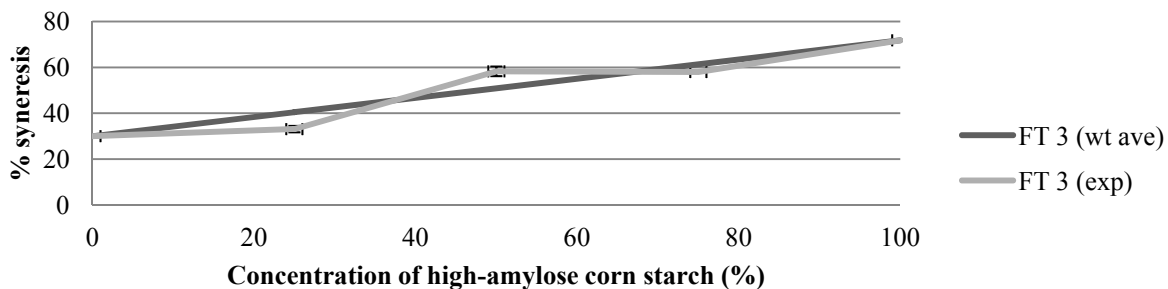
FT3: pea starch and potato starch
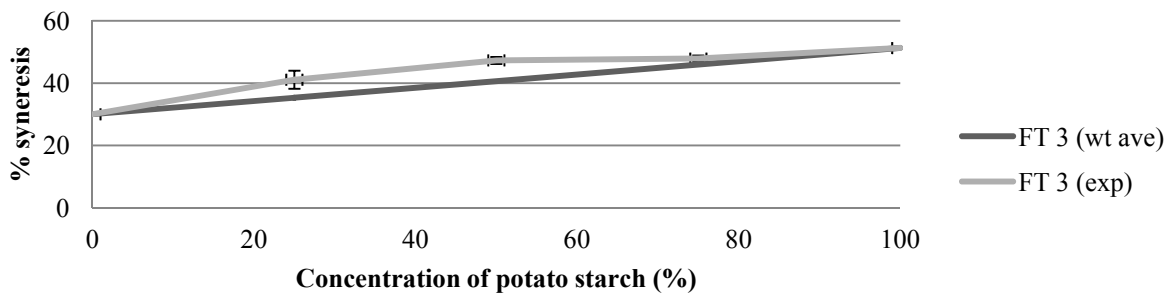
FT4: pea starch and corn starch
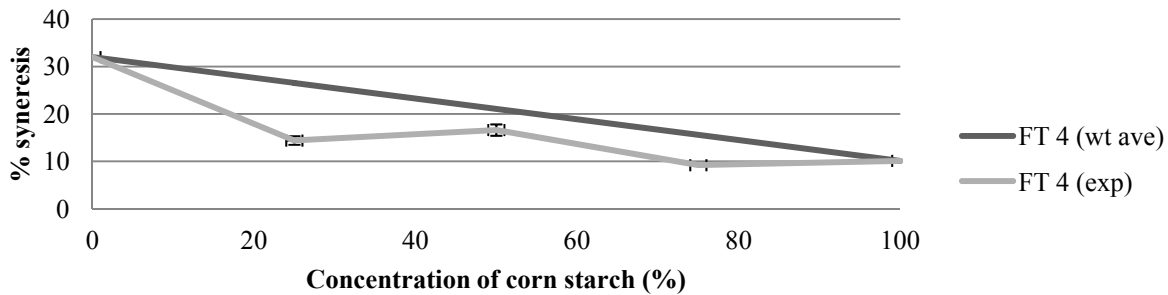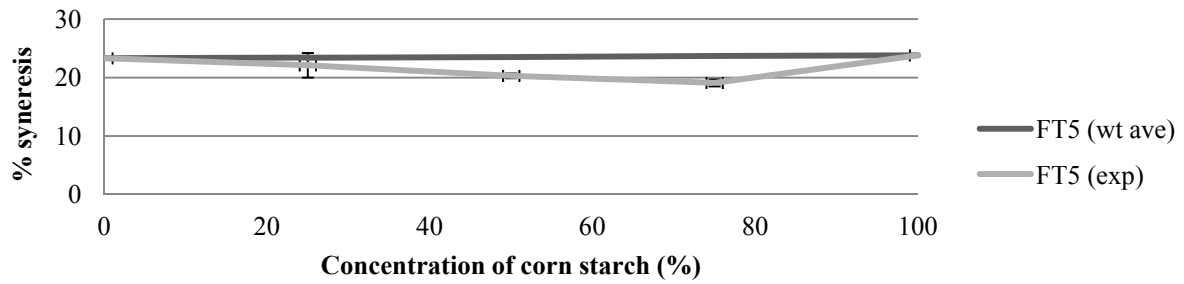

FT4: pea starch and waxy corn starch
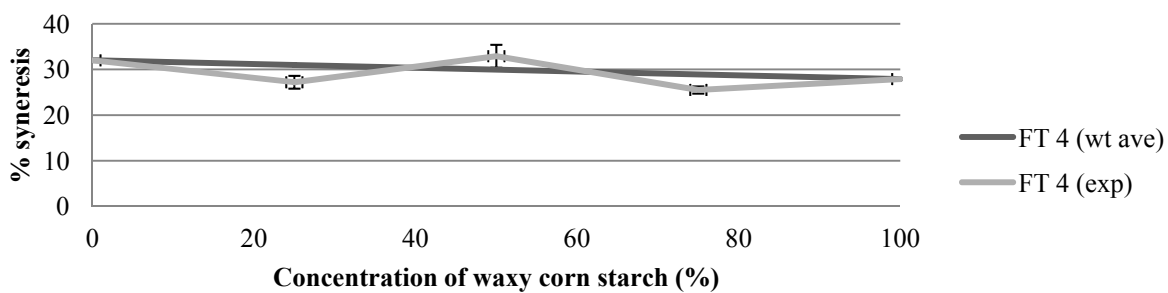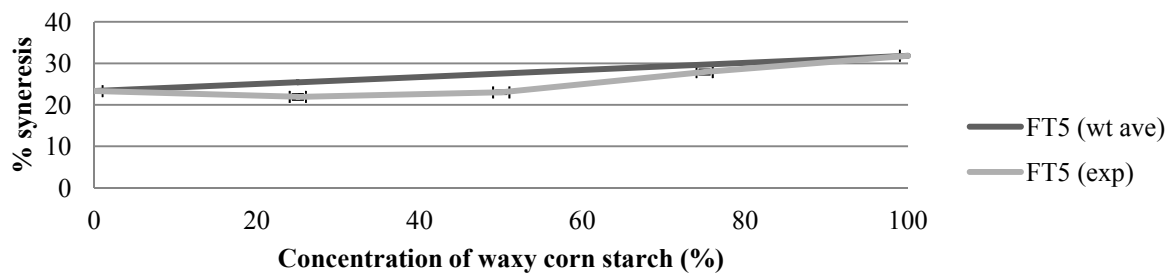

FT4: pea starch and high-amylose corn starch
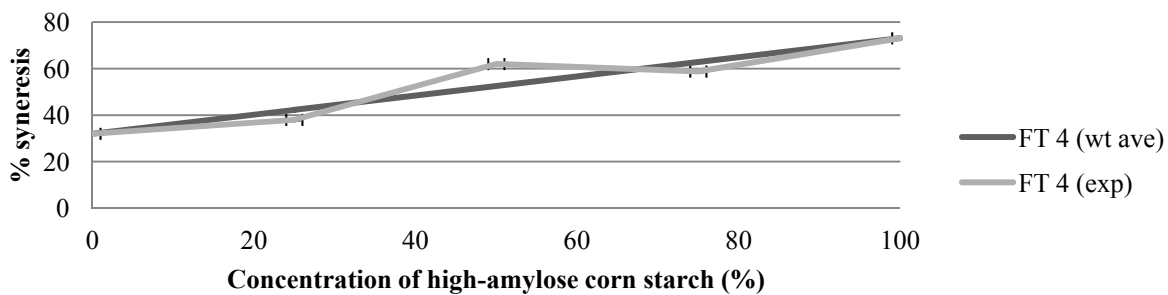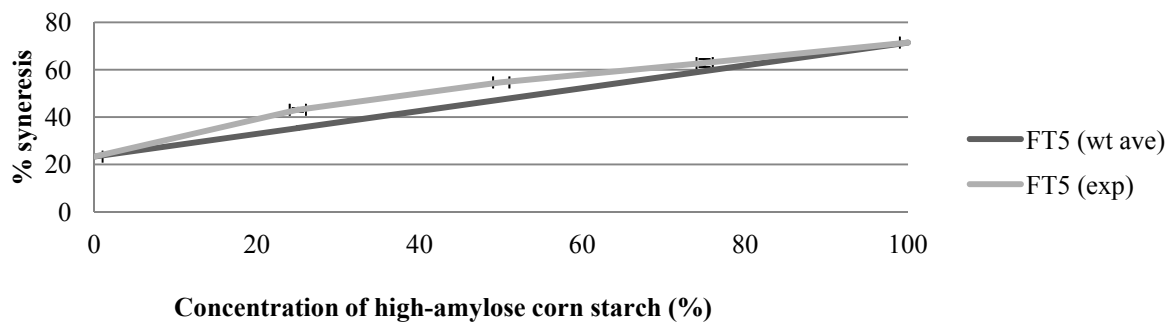

FT4: pea starch and potato starch
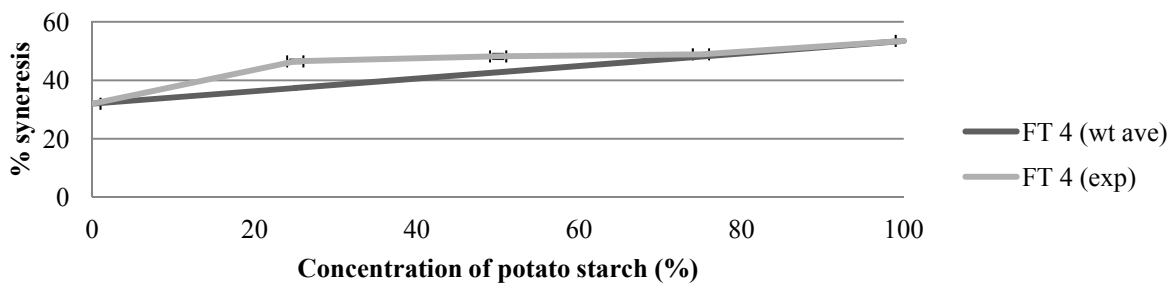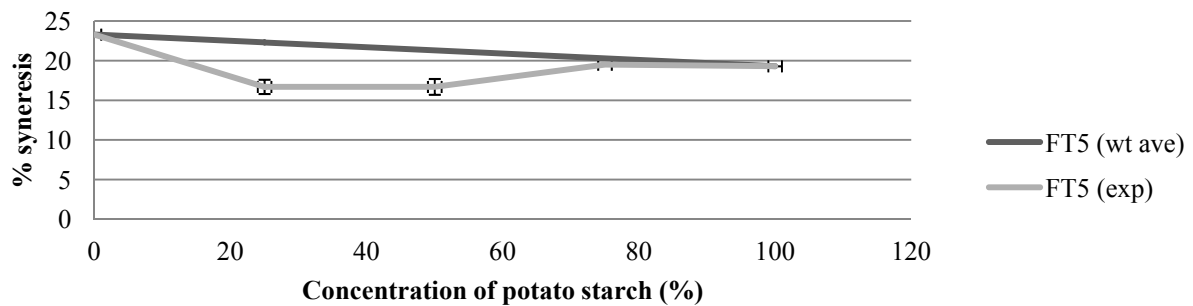
FT5: pea starch and corn starch
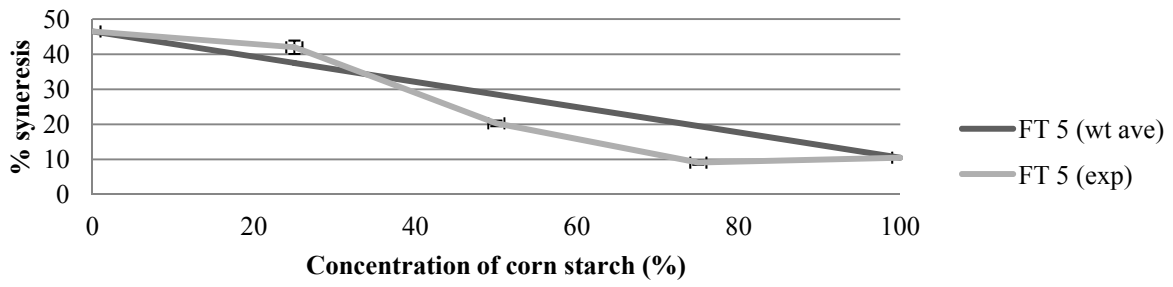
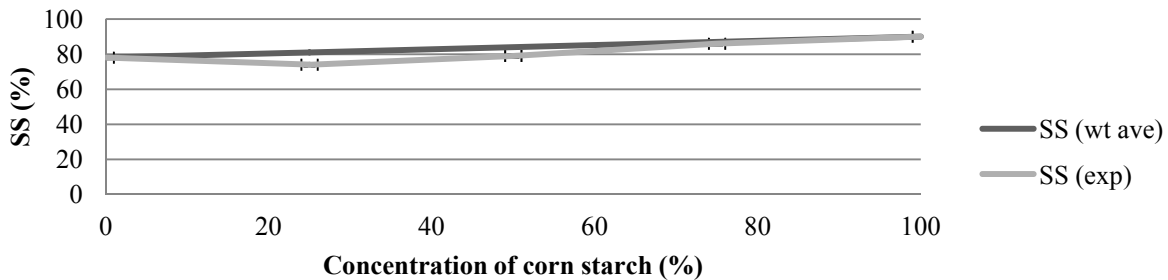**FT5: pea starch and waxy corn starch**
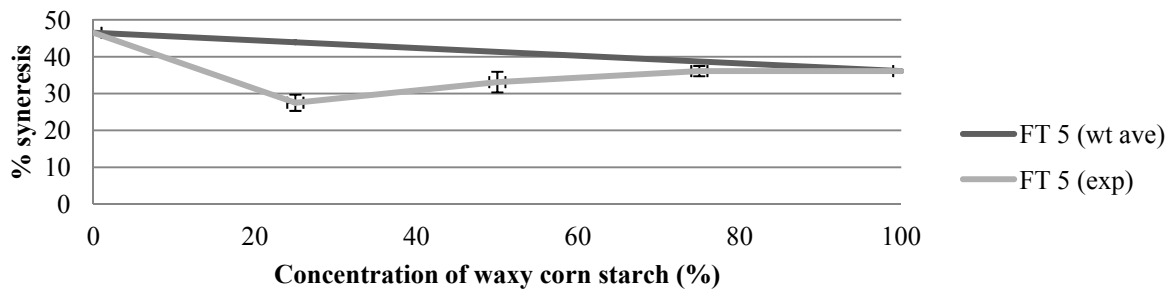
FT5: pea starch and high-amylose corn starch
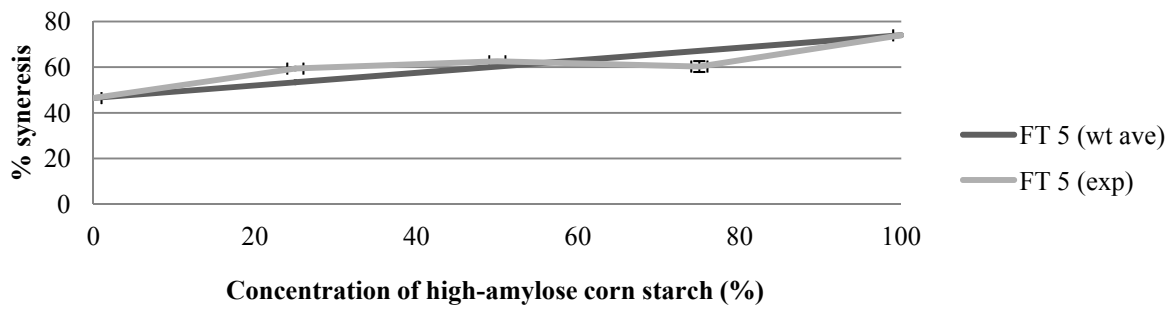
FT5: pea starch and potato starch
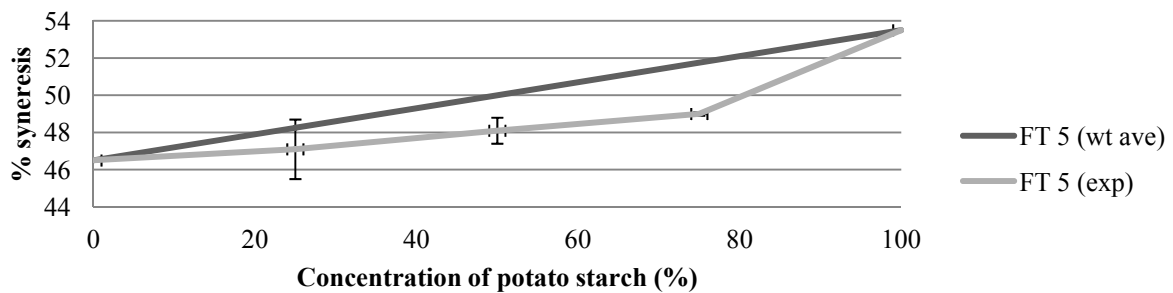
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SS: pea starch and corn starch
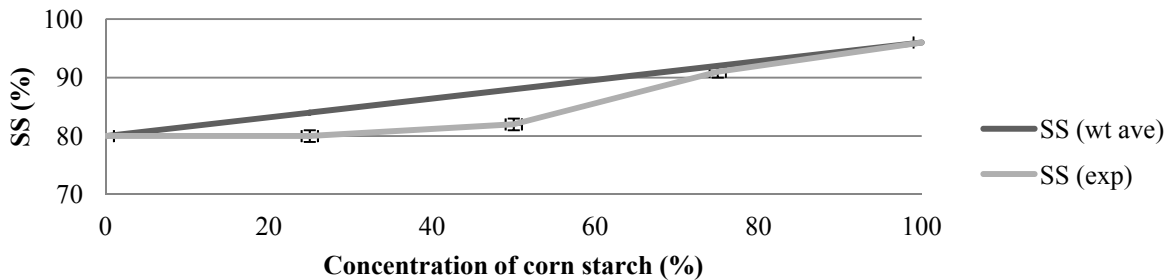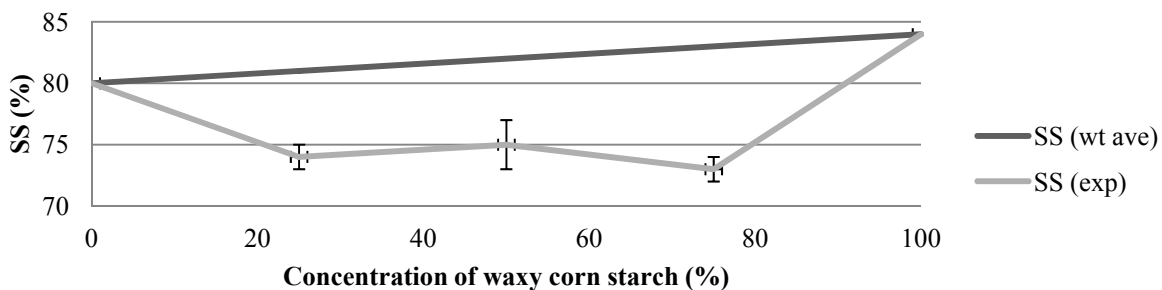
SS (%) vs. Concentration of corn starch (%)

SS (wt ave)
SS (exp)

SS: pea starch and waxy corn starch

SS (%) vs. Concentration of waxy corn starch (%)

SS (wt ave)
SS (exp)

SS: pea starch and high-amylose corn starch

SS (%) vs. Concentration of high-amylose corn starch (%)

SS (wt ave)
SS (exp)

SS: pea starch and potato starch

SS (%) vs. Concentration of potato starch (%)

SS (wt ave)
SS (exp)
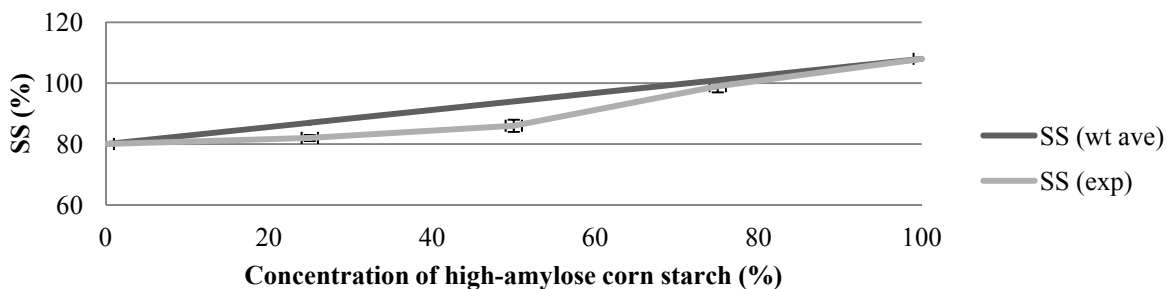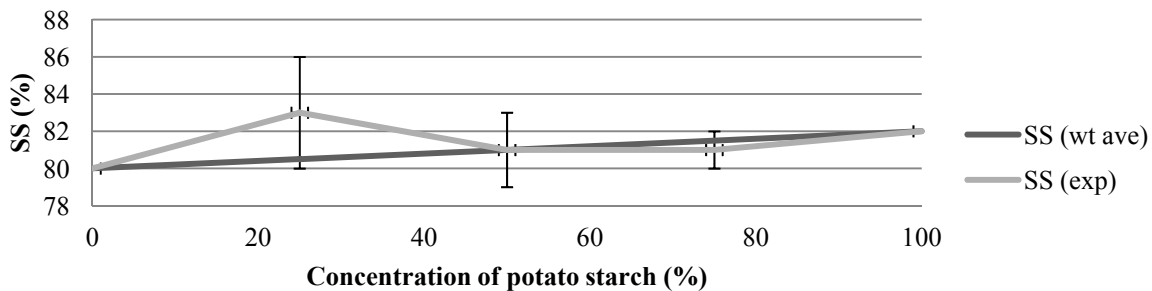
WBC: pea starch and corn starch
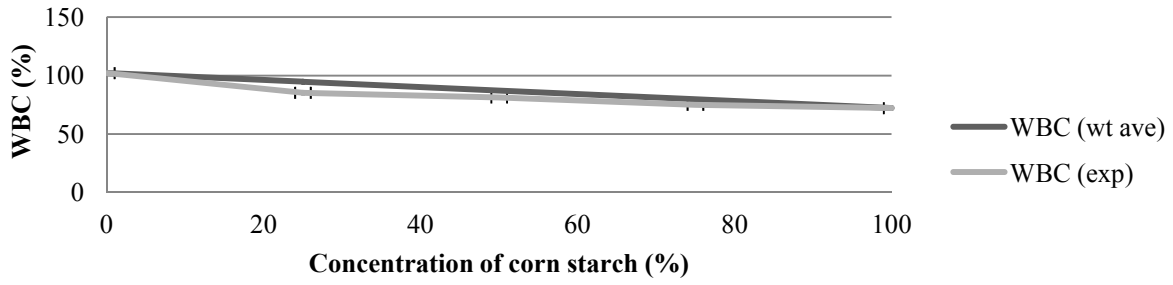
WBC: pea starch and waxy corn starch
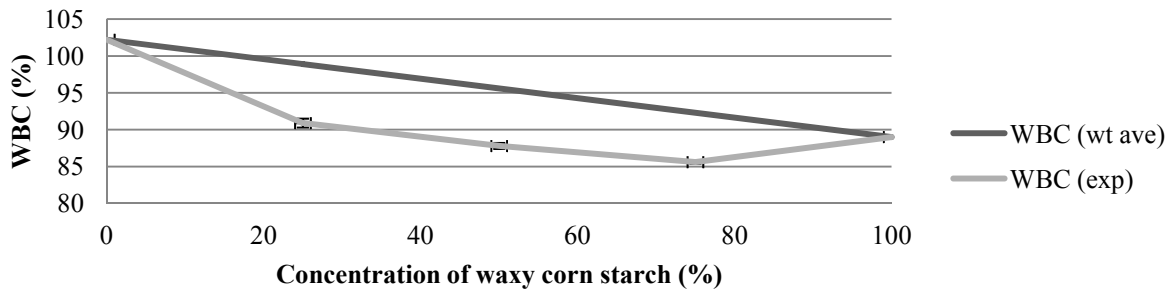
WBC: pea starch and high-amylose corn starch
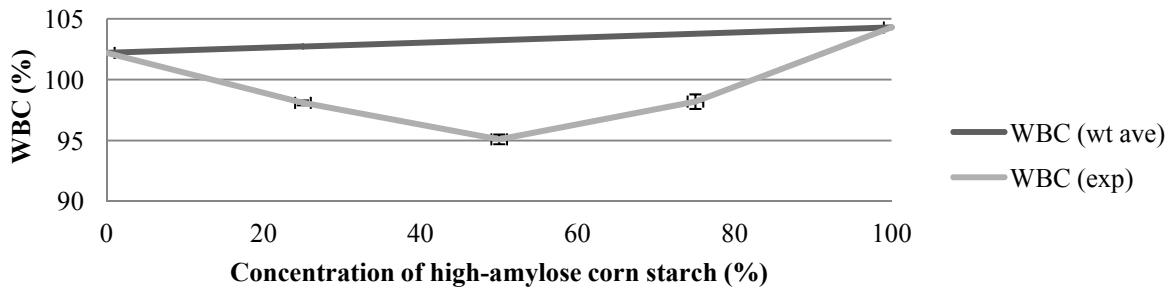
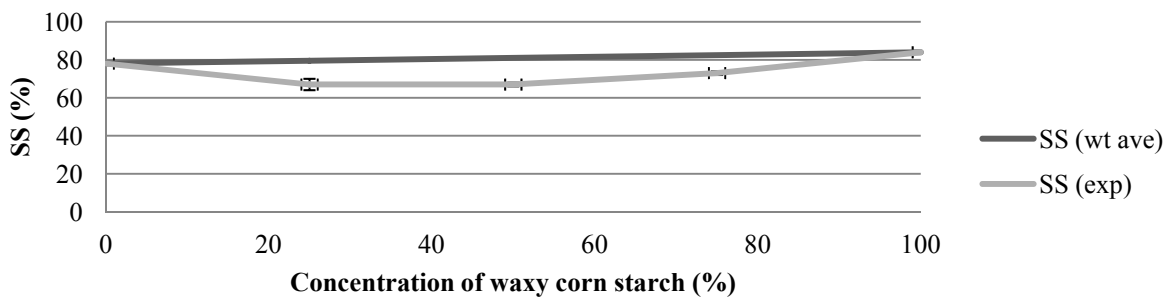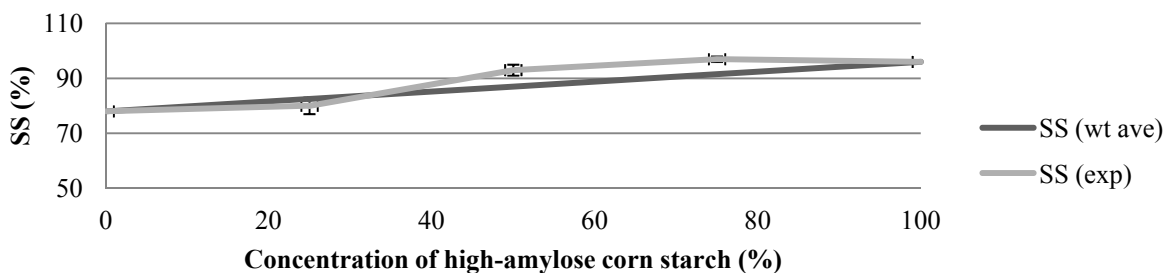**WBC: pea starch and potato starch**
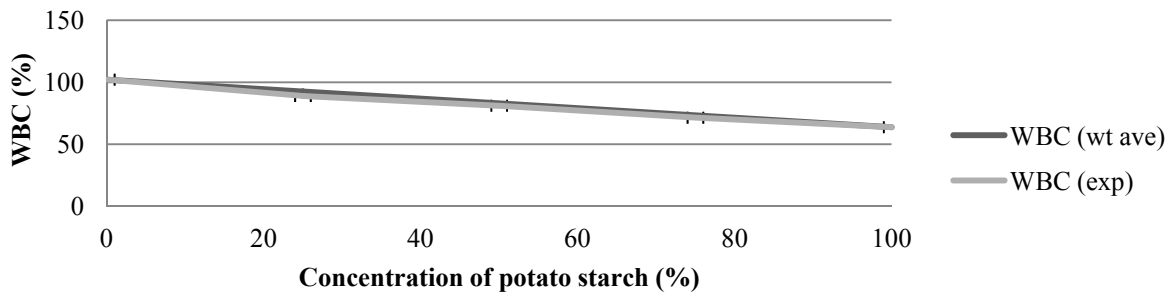
RS: pea starch and corn starch
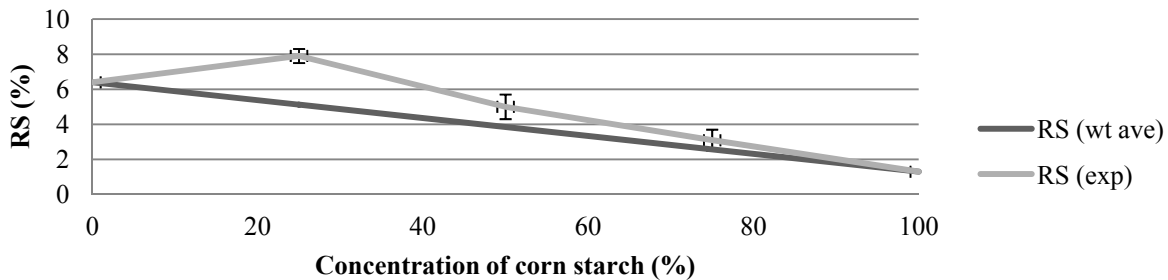
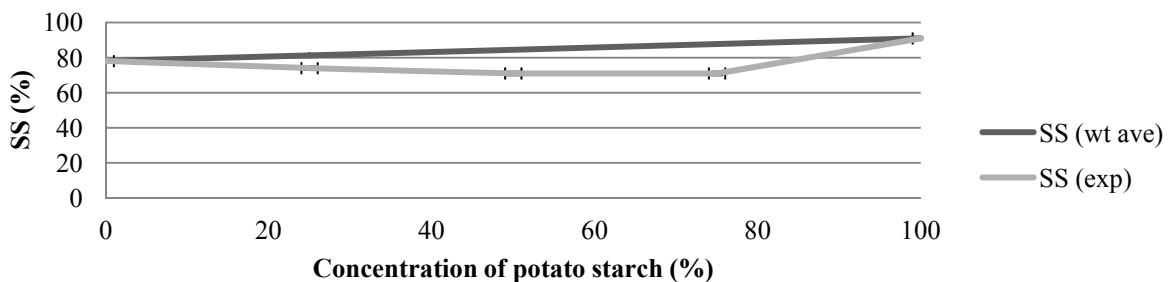**RS: pea starch and waxy corn starch**
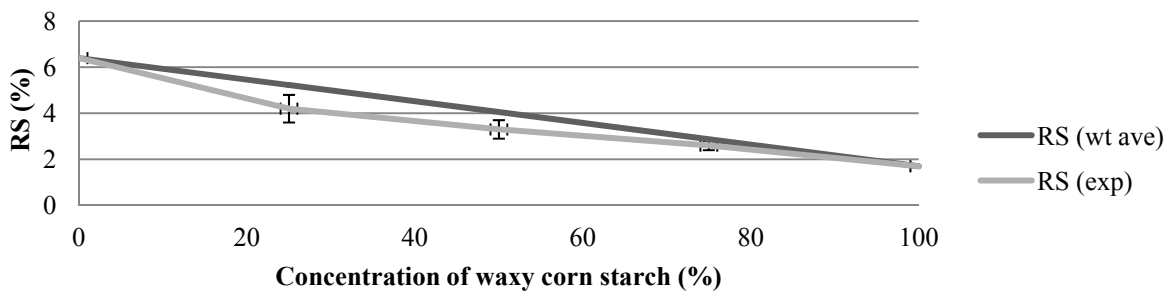
RS: pea starch and high-amylose corn starch
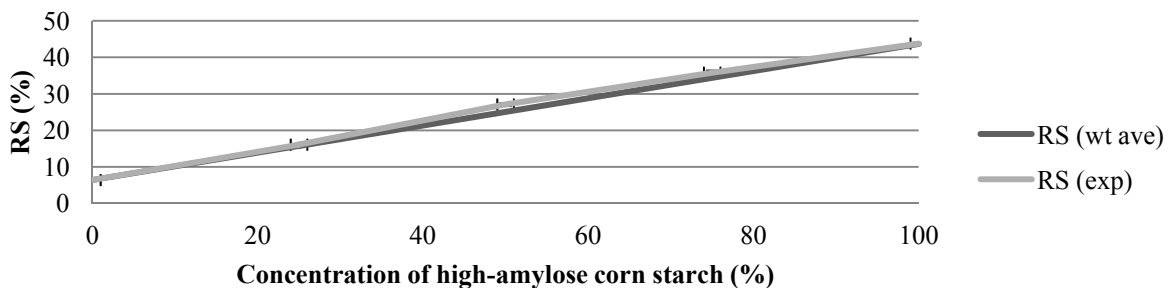
RS: pea starch and potato starch
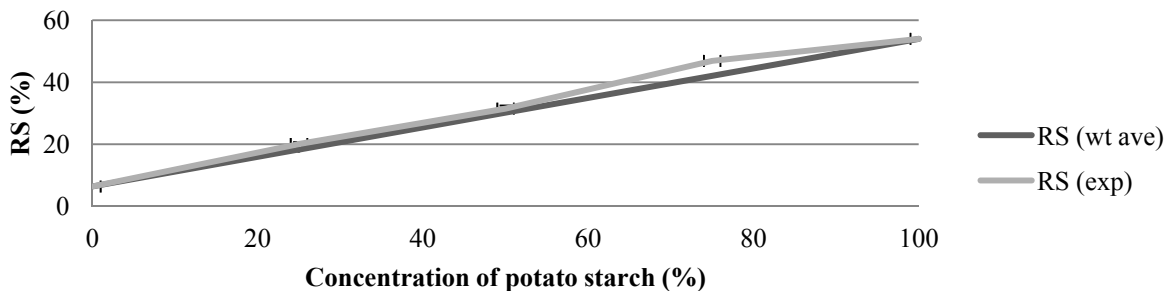
APPENDIX B

List of Abbreviations

ΔH   Endothermic enthalpy of gelatinization

exp   Experimental value

FT   Freeze-thaw cycle (FT1 = freeze-thaw cycle 1, etc.)

FV   Final viscosity

HMT Heat-moisture treated

PS   Pea starch

PT   Pasting temperature

PV   Pasting viscosity

RS   Resistant starch

SP   Swelling power

SS   Shear stability

T_c Completion temperature of gelatinization

T_o Onset temperature of gelatinization

T_p Peak temperature of gelatinization

TV   Trough viscosity

WBC Water binding capacity

WSI   Water solubility index

wt ave Weighted average value

T$_o$: HMT pea starch and corn starch

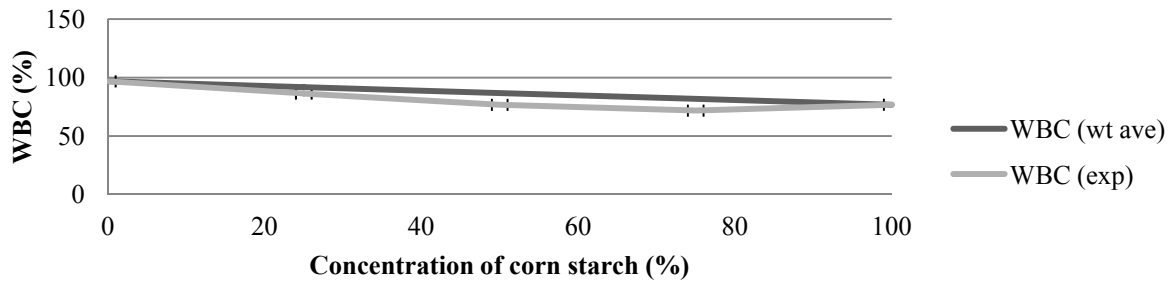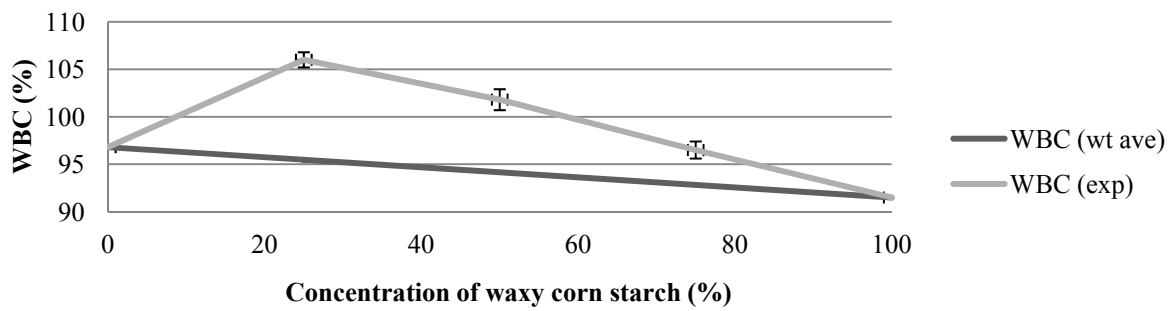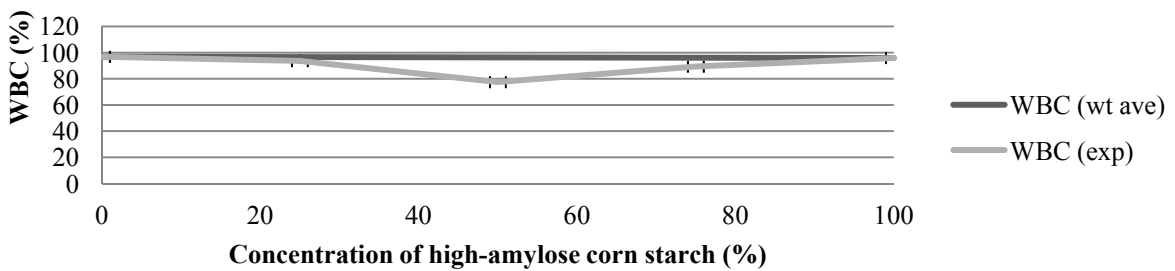**T$_o$: HMT pea starch and waxy corn starch**

T$_o$: HMT pea starch and high-amylose corn starch

T$_o$: HMT pea starch and potato starch

T_p: HMT pea starch and corn starch

Temp (°C) vs Concentration of corn starch (%)

Tp (wt ave)
Tp (exp)

T_p: HMT pea starch and waxy corn starch

Temp (°C) vs Concentration of waxy corn starch (%)

Tp (wt ave)
Tp (exp)

T_p: HMT pea starch and high-amylose corn starch

Temp (°C) vs Concentration of high-amylose corn starch (%)

Tp (exp)

T_p: HMT pea starch and potato starch

Temp (°C) vs Concentration of potato starch (%)

Tp (wt ave)
Tp (exp)
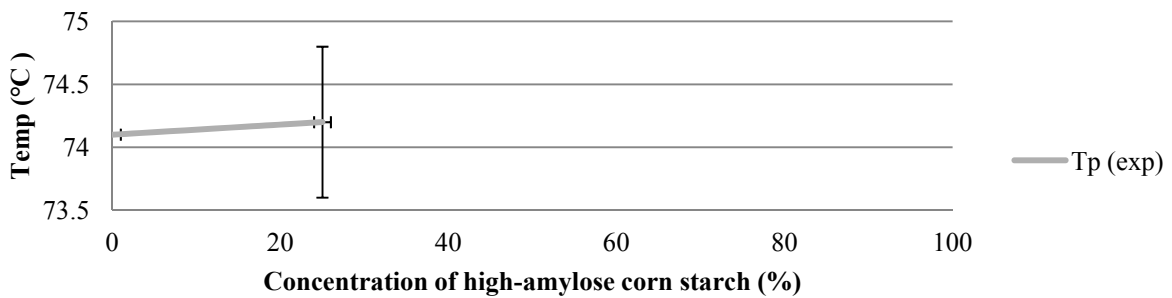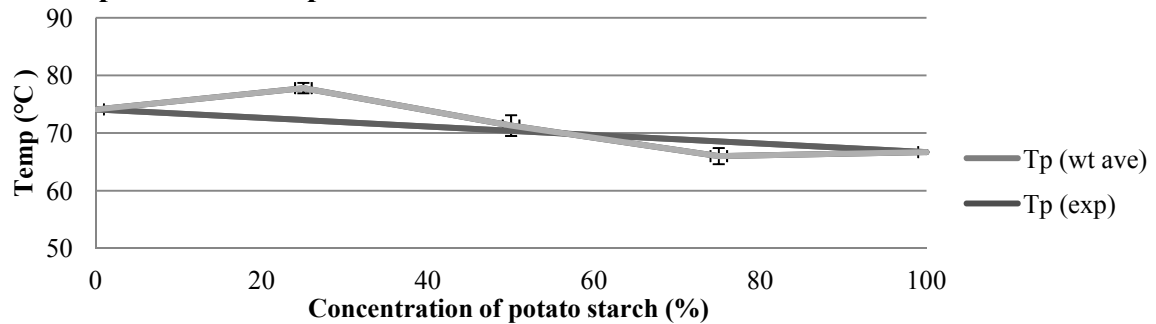
T$_c$: HMT pea starch and corn starch
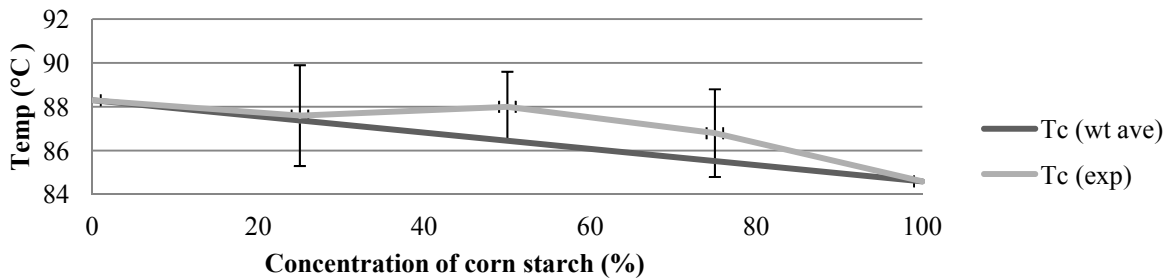
T$_c$: HMT pea starch and waxy corn starch
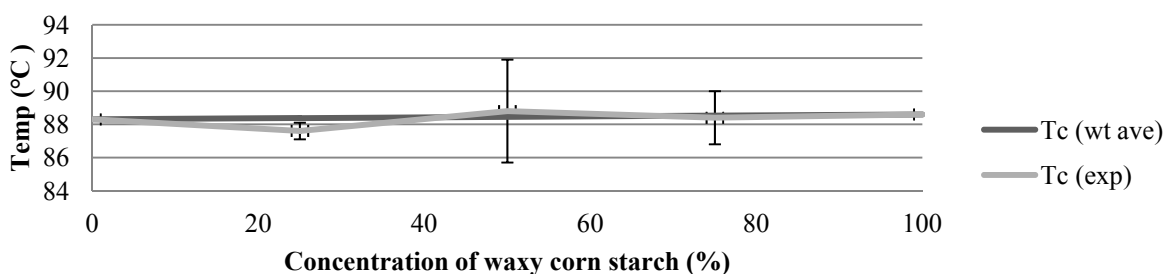
T$_c$: HMT pea starch and high-amylose corn starch
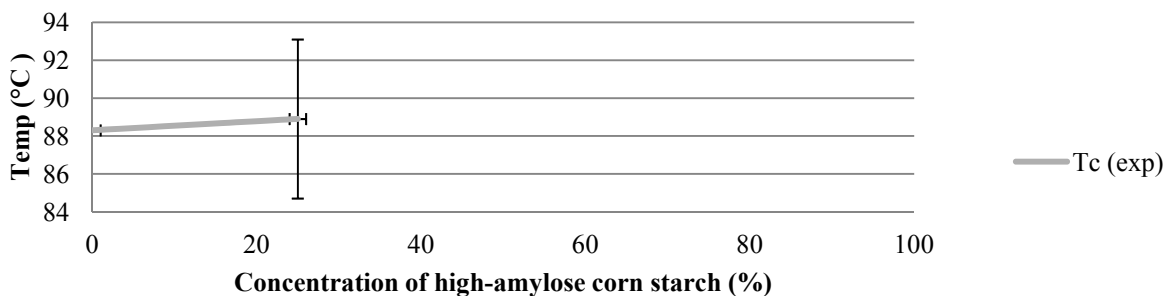
T$_c$: HMT pea starch and potato starch
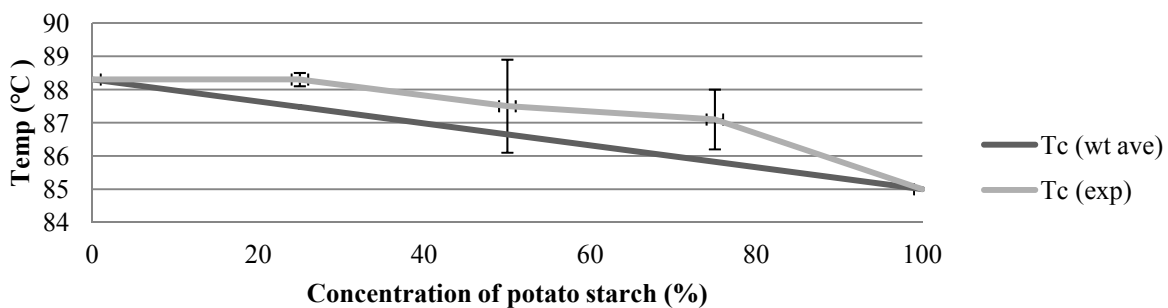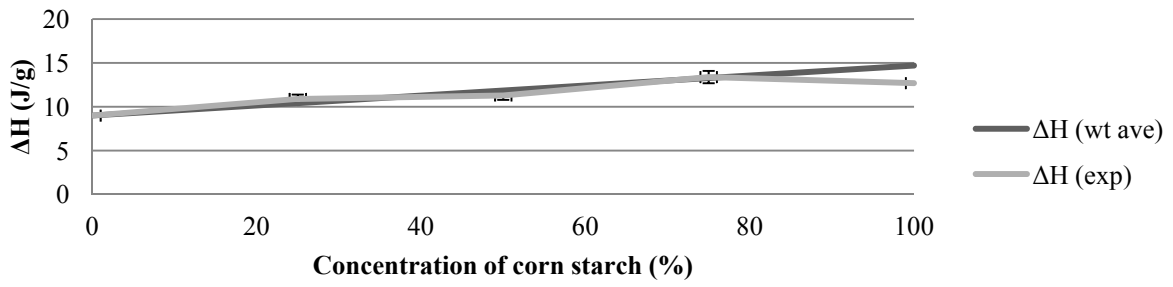
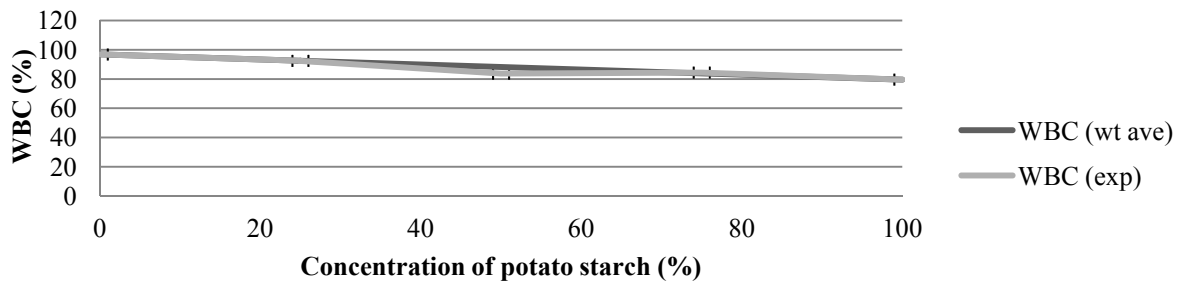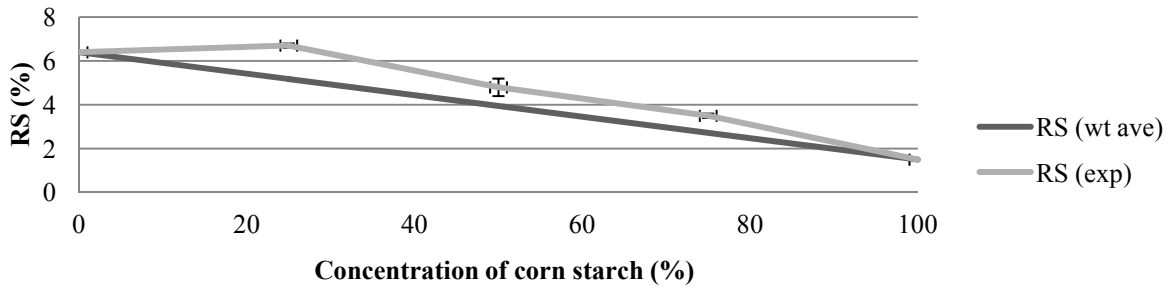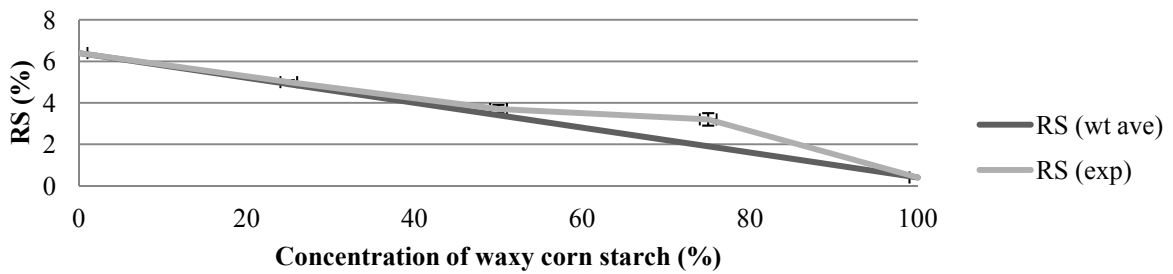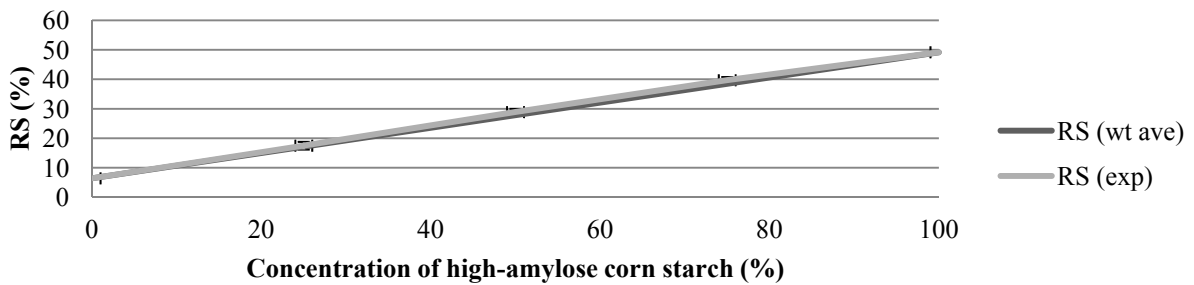**ΔH: HMT pea starch and corn starch**

ΔH: HMT pea starch and waxy corn starch

ΔH: HMT pea starch and high-amylose corn starch

ΔH: HMT pea starch and potato starch

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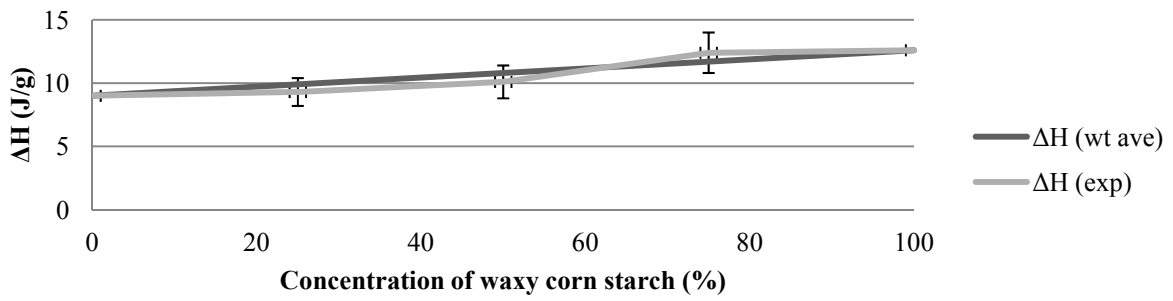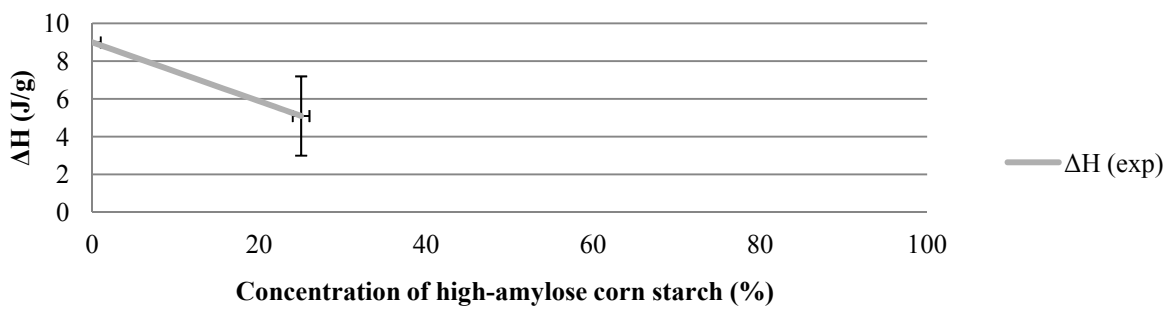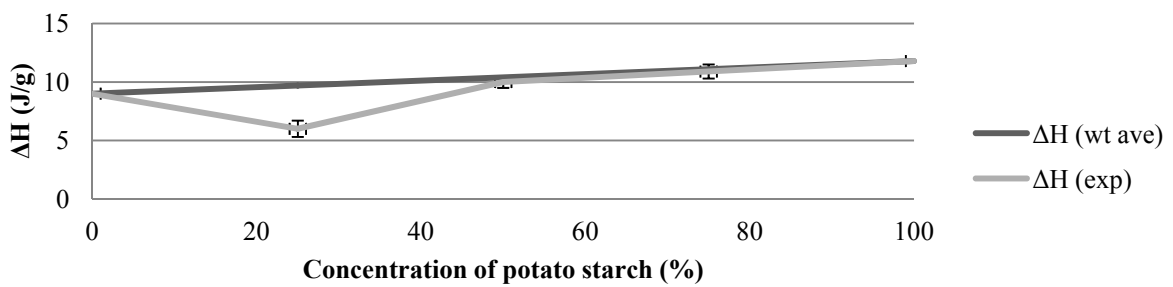
PT: HMT pea starch and corn starch
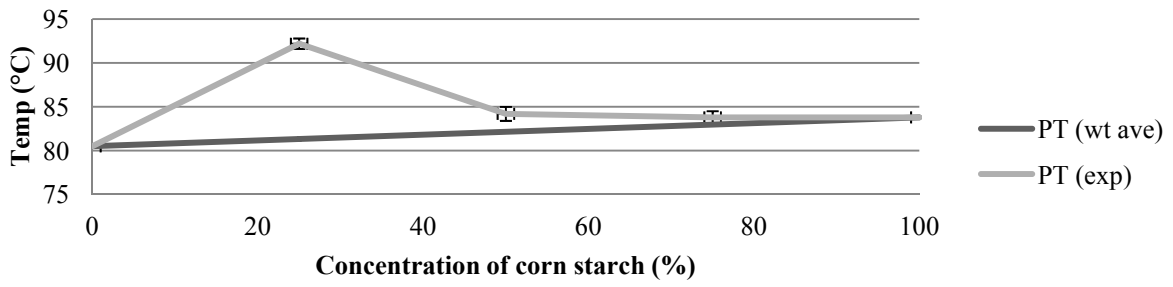
PT: pea starch and waxy corn starch
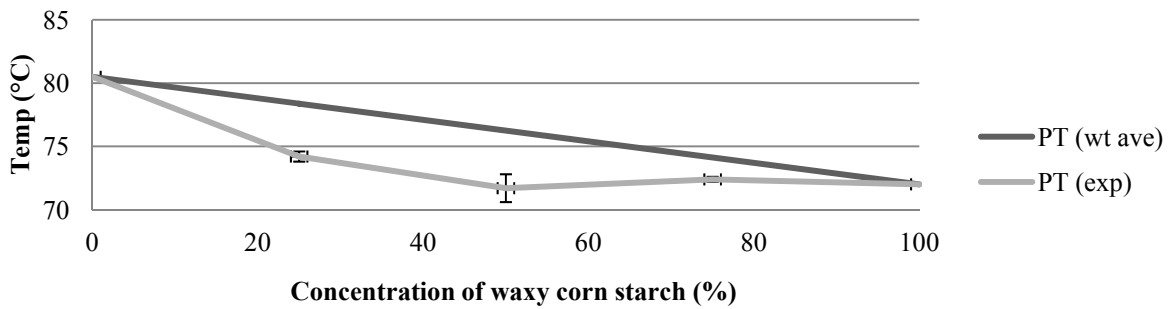
PT: HMT pea starch and high-amylose corn starch
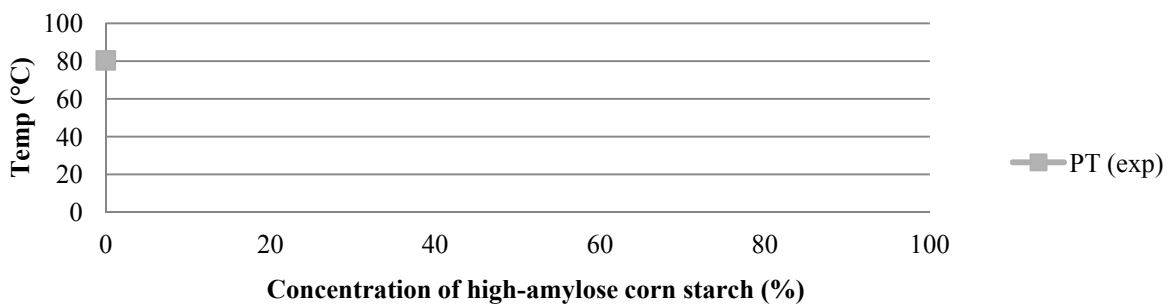
PT: HMT pea starch and potato starch
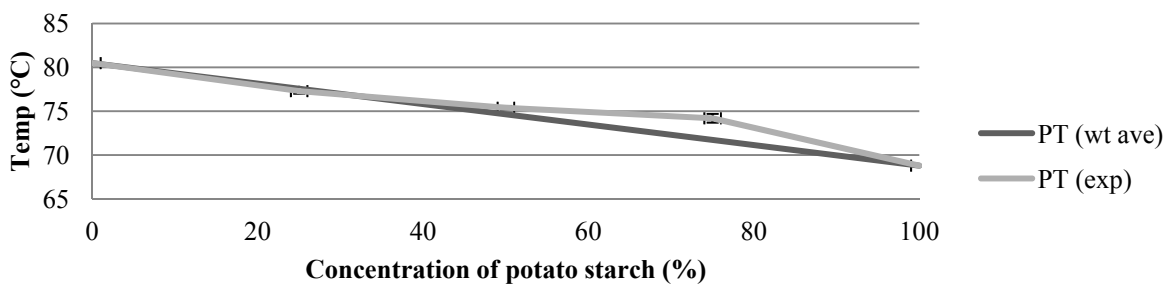
PV: HMT pea starch and corn starch
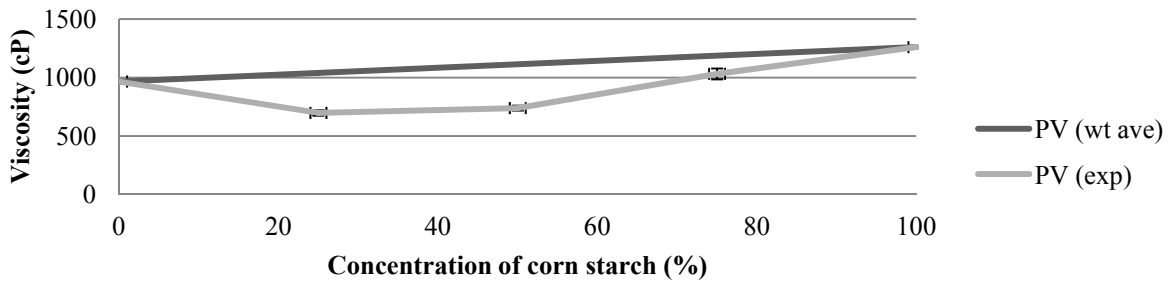
PV: HMT pea starch and waxy corn starch
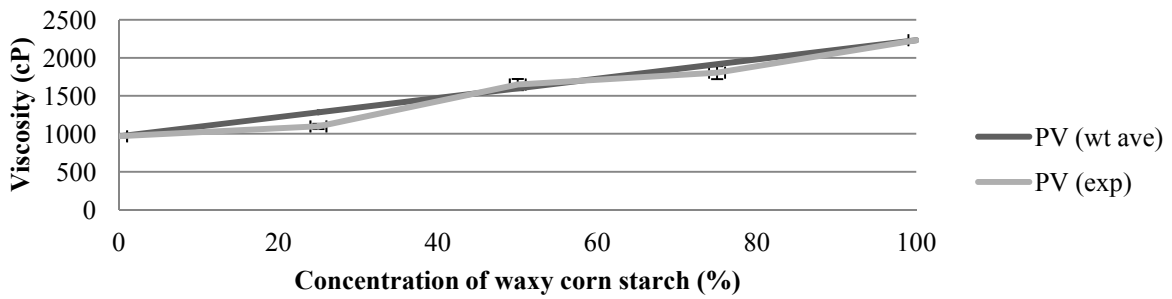
PV: HMT pea starch and high-amylose corn starch
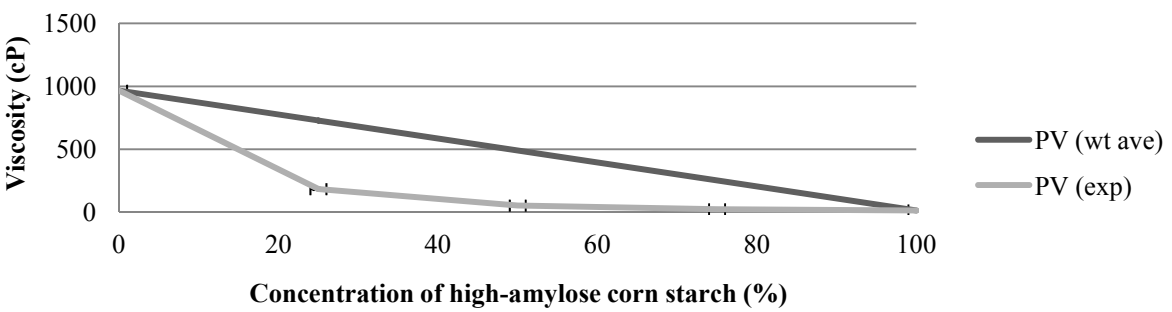
PV: HMT pea starch and potato starch
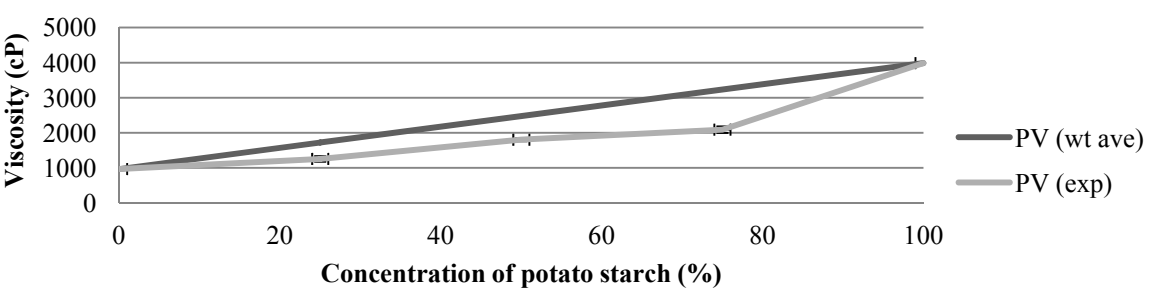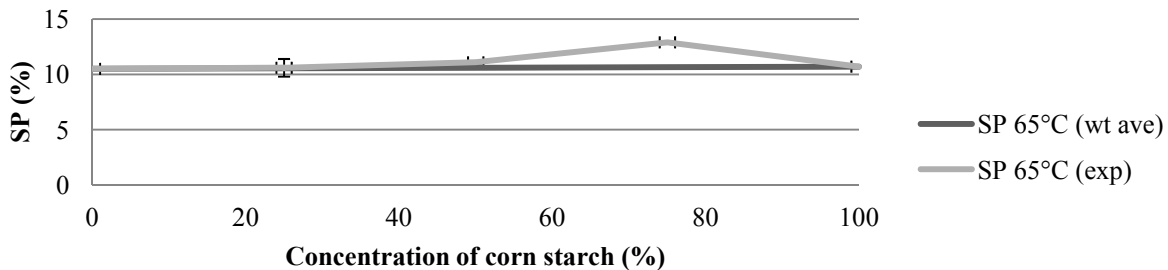
TV: HMT pea starch and corn starch
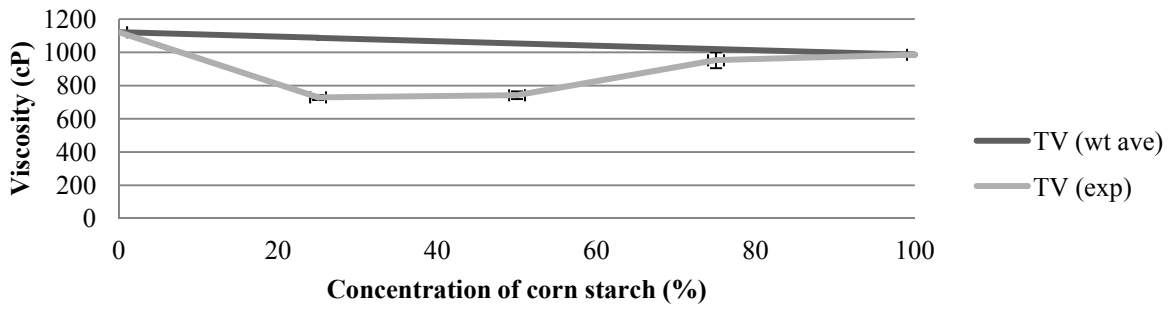
TV: HMT pea starch and waxy corn starch
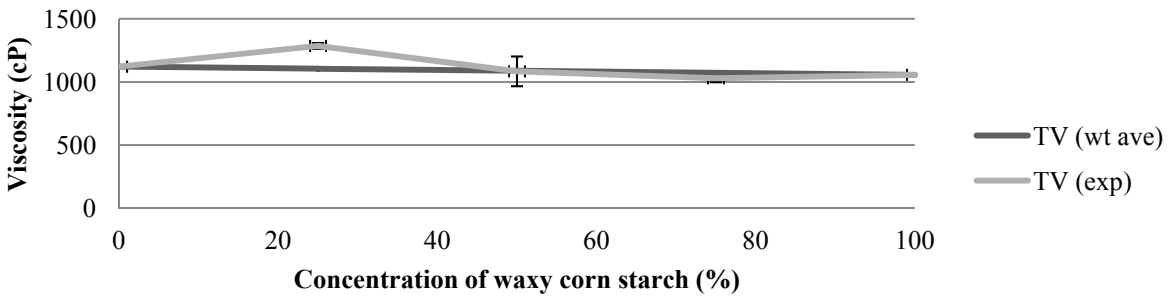
TV: HMT pea starch and high-amylose corn starch

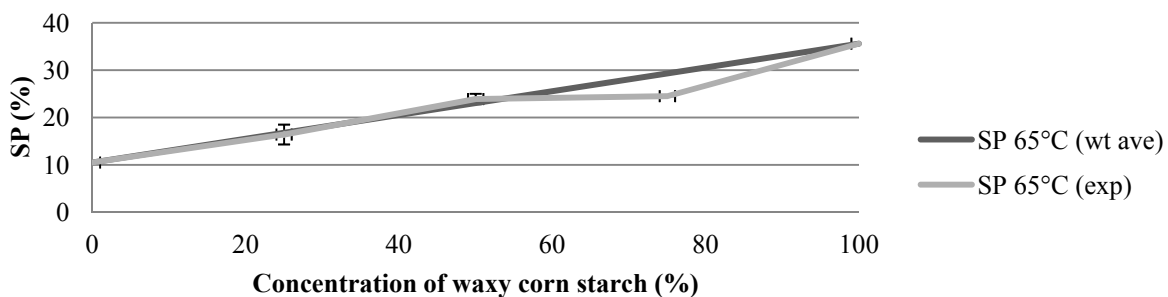**TV: HMT pea starch and potato starch**

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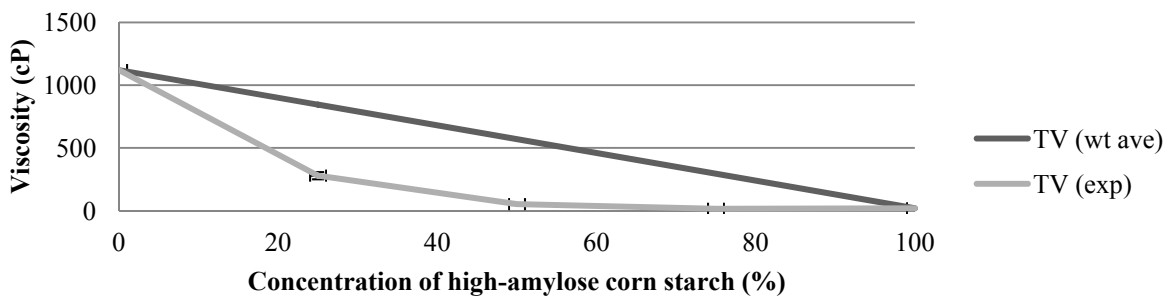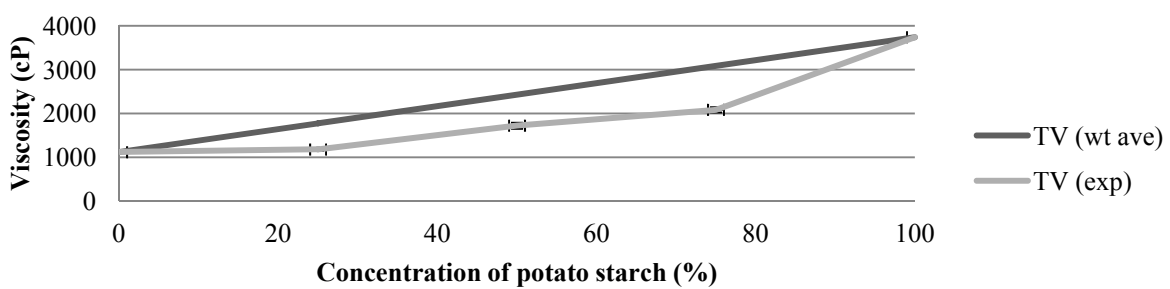
FV: HMT pea starch and corn starch
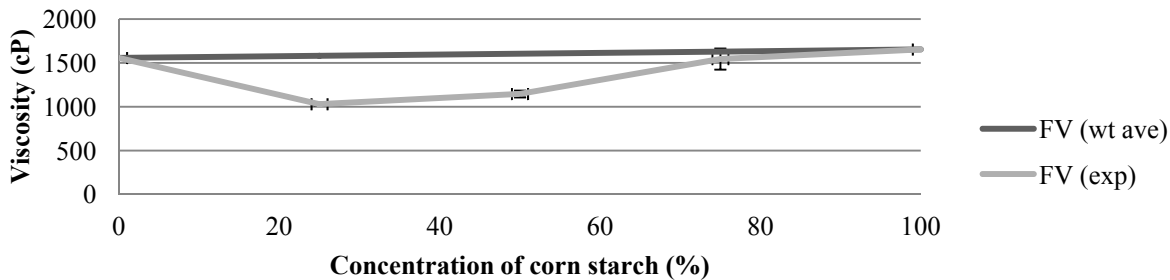
FV: HMT pea starch and waxy corn starch

FV: HMT pea starch and high-amylose corn starch
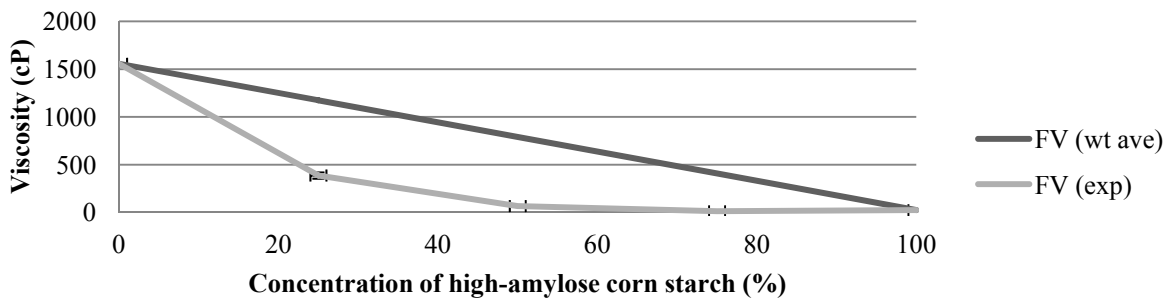
FV: HMT pea starch and potato starch
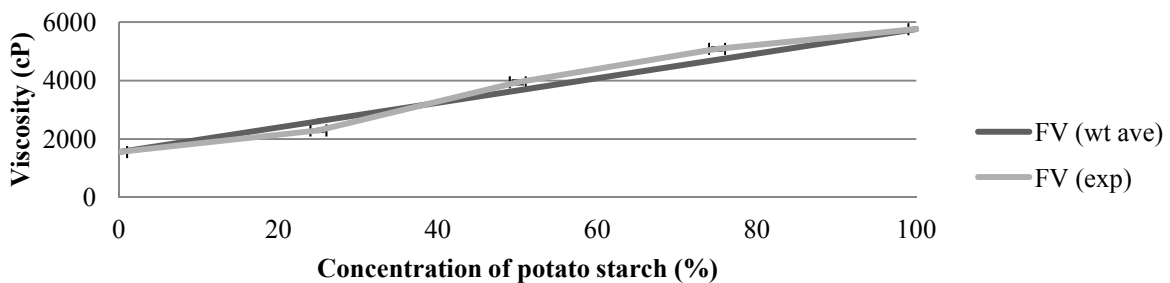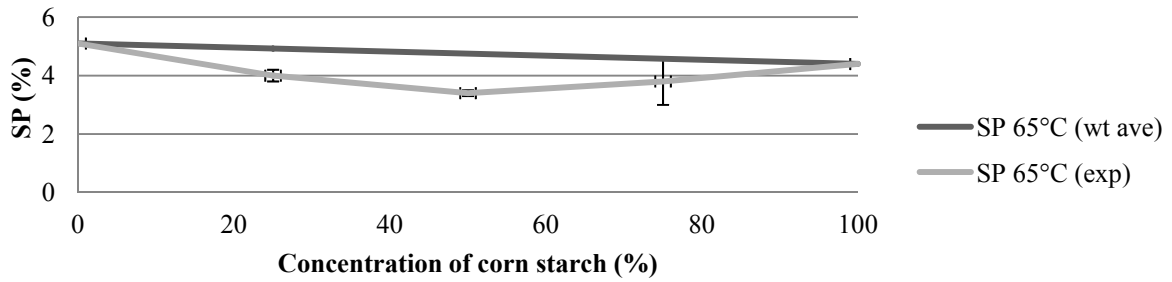
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SP 65°C: HMT pea starch and corn starch

SP (%) vs Concentration of corn starch (%)

SP 65°C (wt ave)
SP 65°C (exp)

SP 65°C: HMT pea starch and waxy corn starch

SP (%) vs Concentration of waxy corn starch (%)

SP 65°C (wt ave)
SP 65°C (exp)

SP 65°C: HMT pea starch and high-amylose corn starch

SP (%) vs Concentration of high-amylose corn starch (%)

SP 65°C (wt ave)
SP 65°C (exp)

SP 65°C: HMT pea starch and potato starch

SP (%) vs Concentration of potato starch (%)
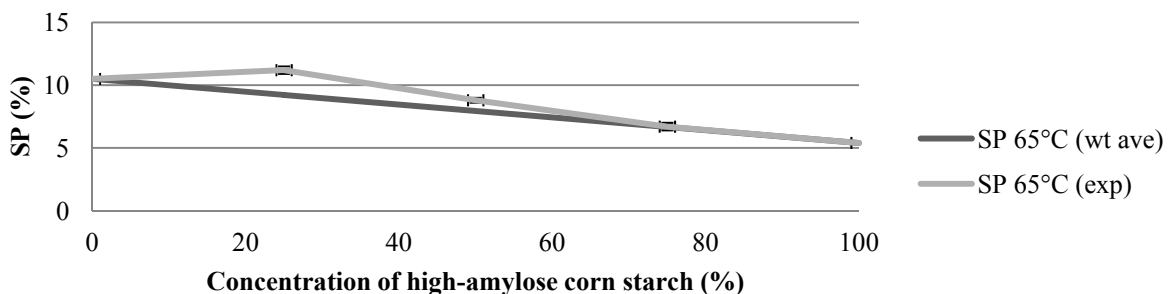
SP 65°C (wt ave)
SP 65°C (exp)

216
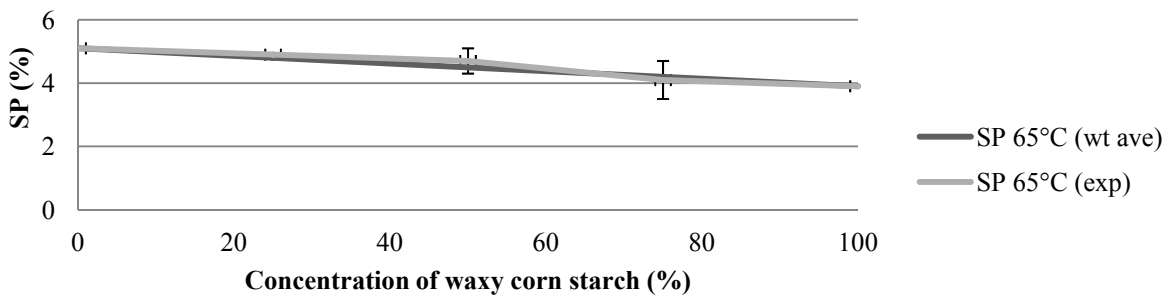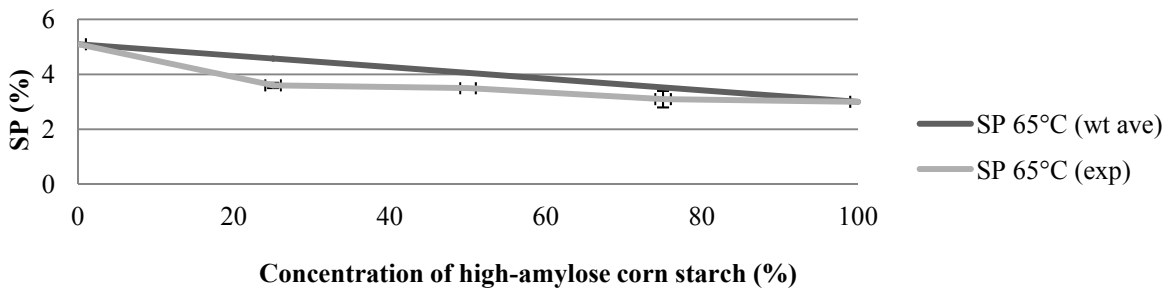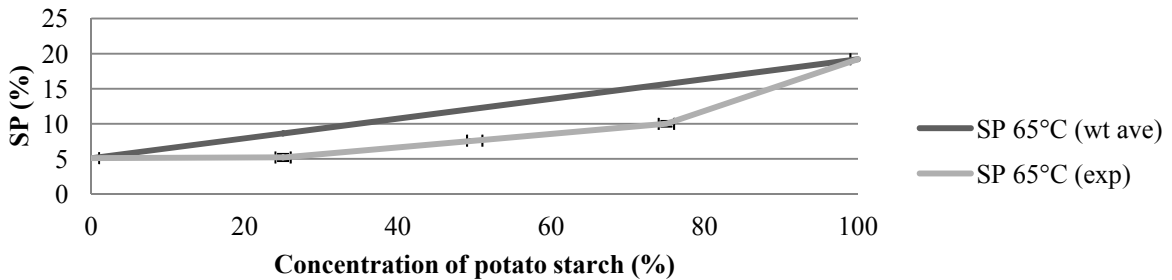
SP 75°C: HMT pea starch and corn starch
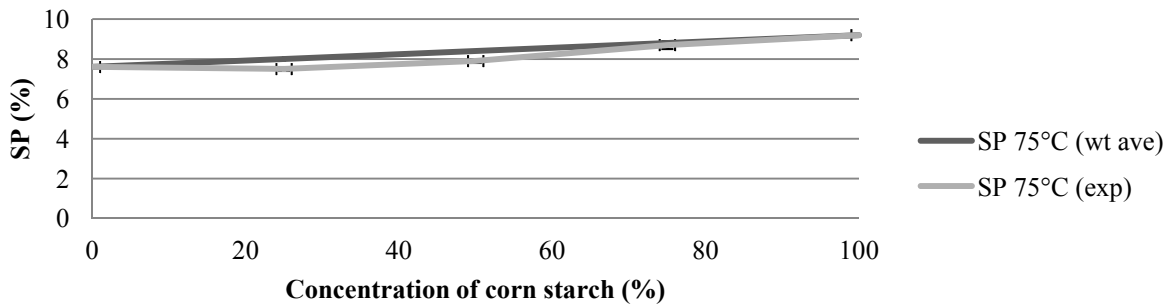
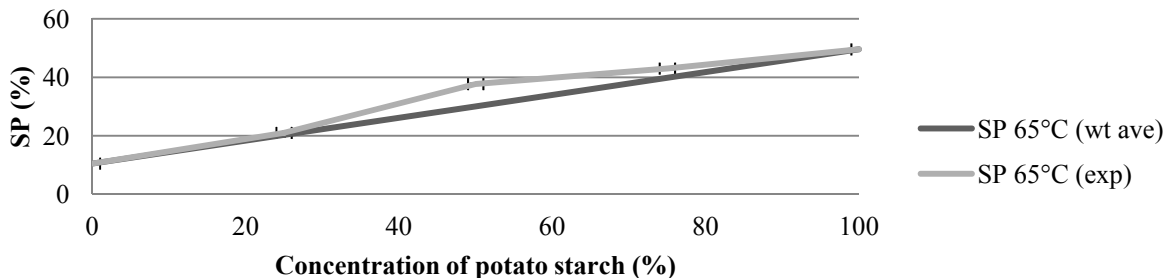## SP 75°C: HMT pea starch and waxy corn starch
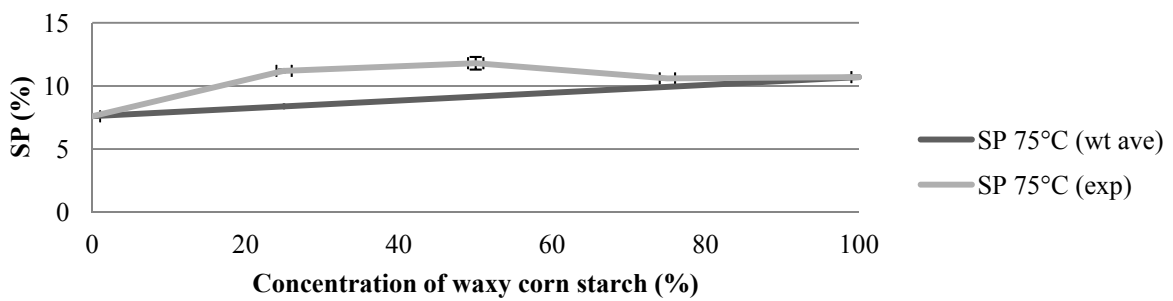
SP 75°C: HMT pea starch and high-amylose corn starch
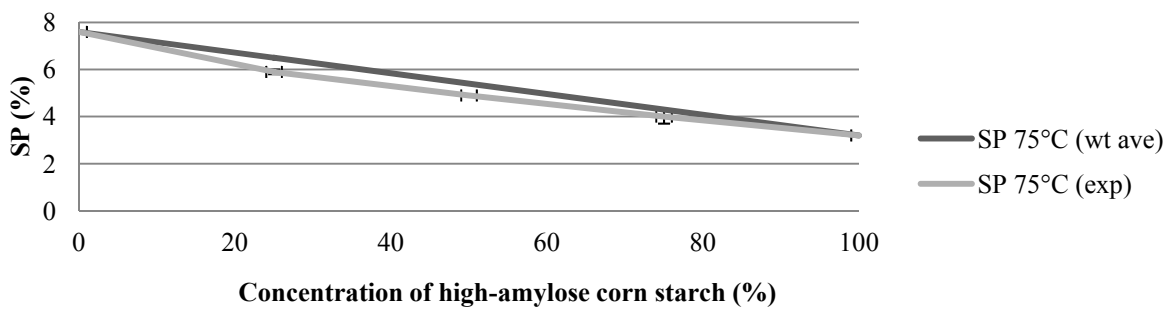
SP 75°C: HMT pea starch and potato starch
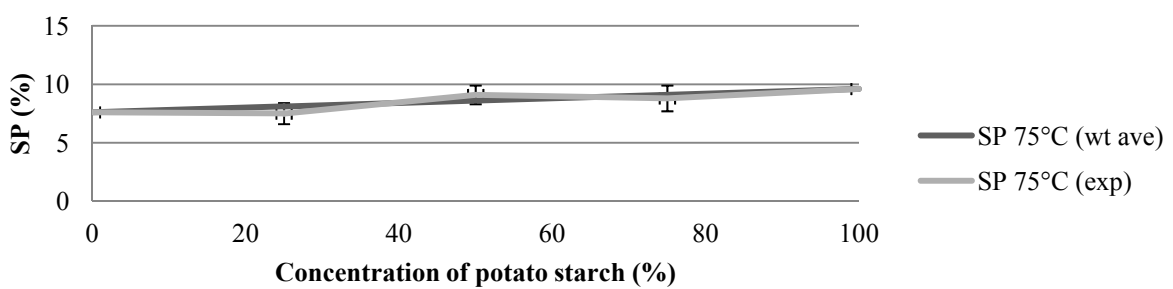
SP 85°C: HMT pea starch and corn starch

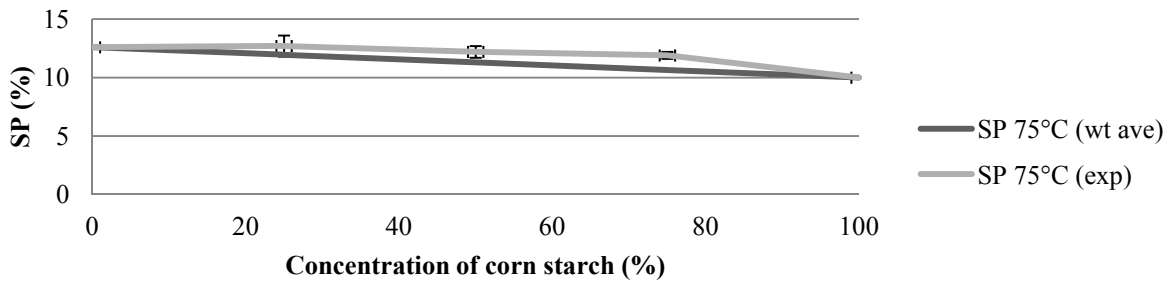**SP 85°C: HMT pea starch and waxy corn starch**
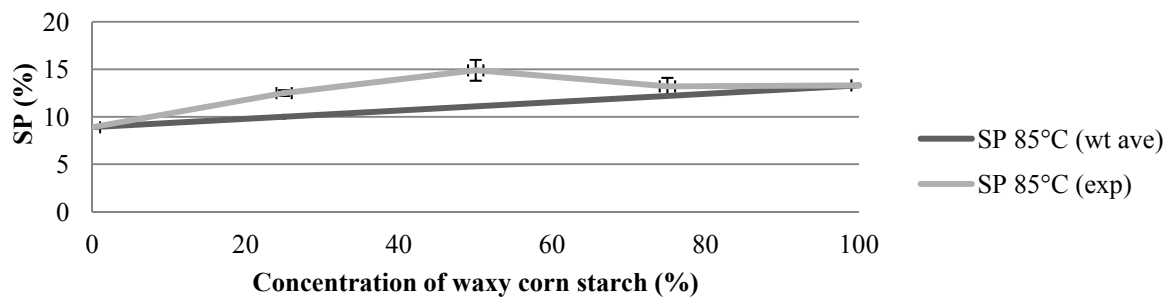
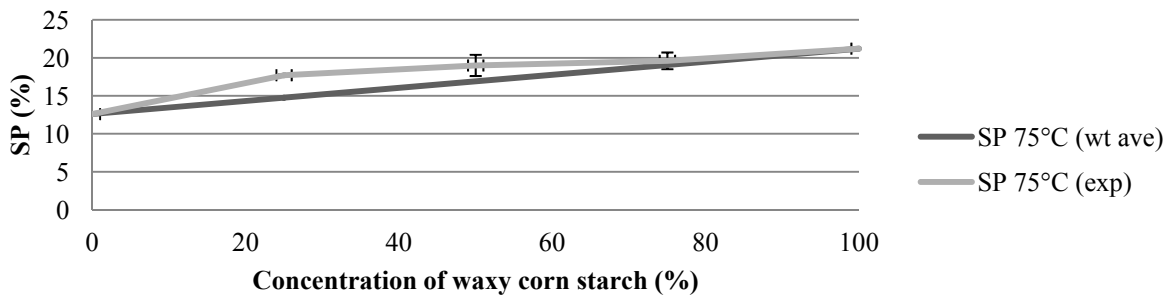**SP 85°C: HMT pea starch and high-amylose corn starch**
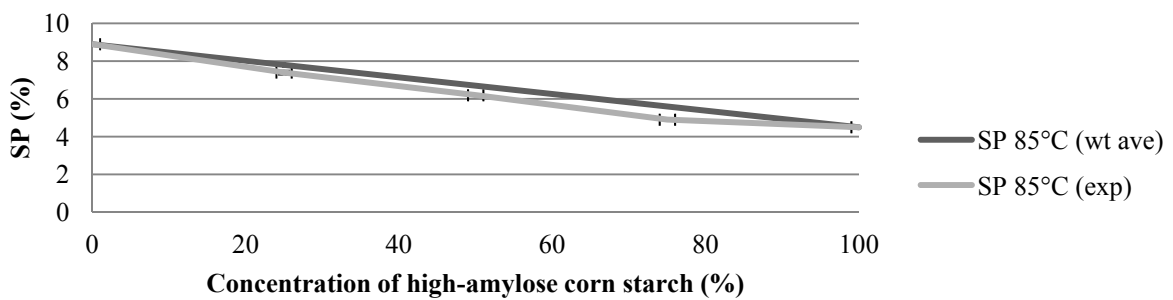
SP 85°C: HMT pea starch and potato starch

SP 95°C: HMT pea starch and corn starch
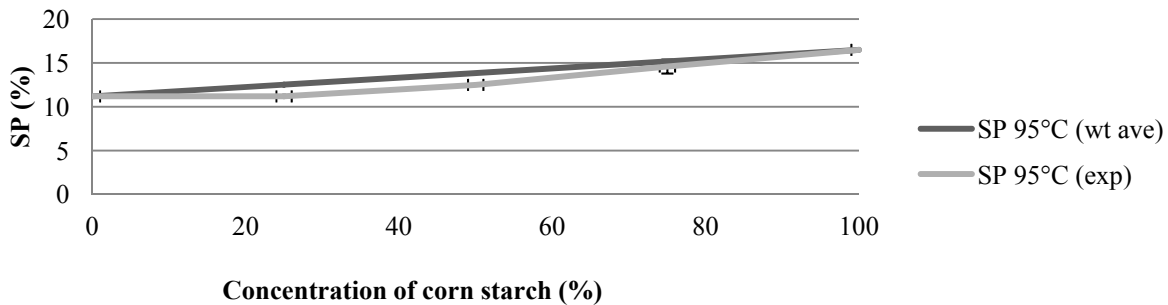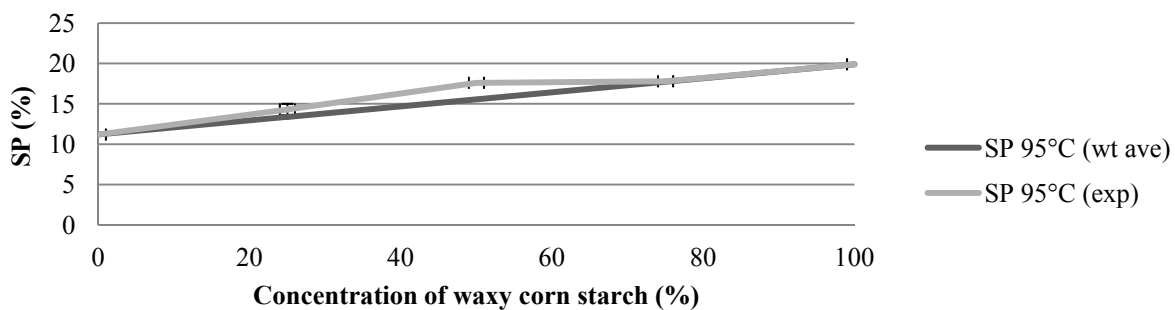
SP 95°C: HMT pea starch and waxy corn starch

SP 95°C: HMT pea starch and high-amylose corn starch
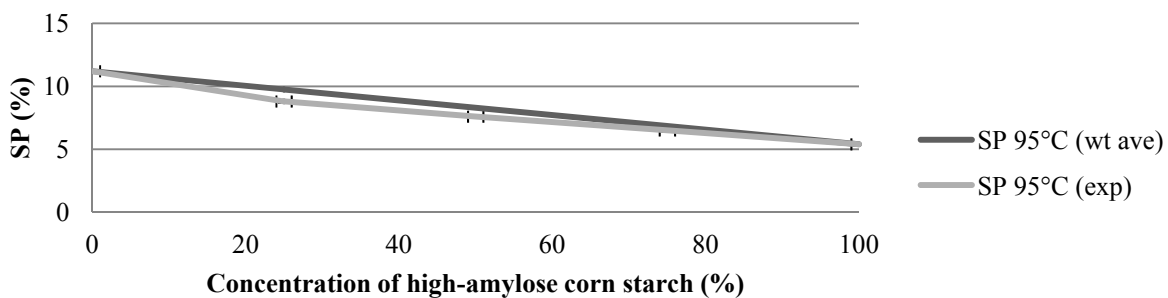
SP 95°C: HMT pea starch and potato starch
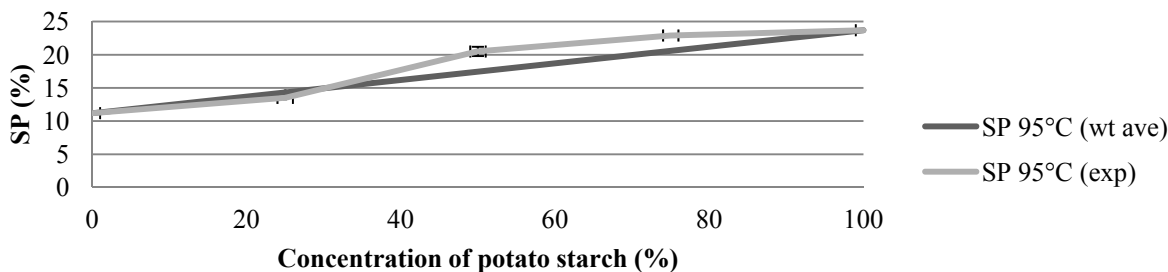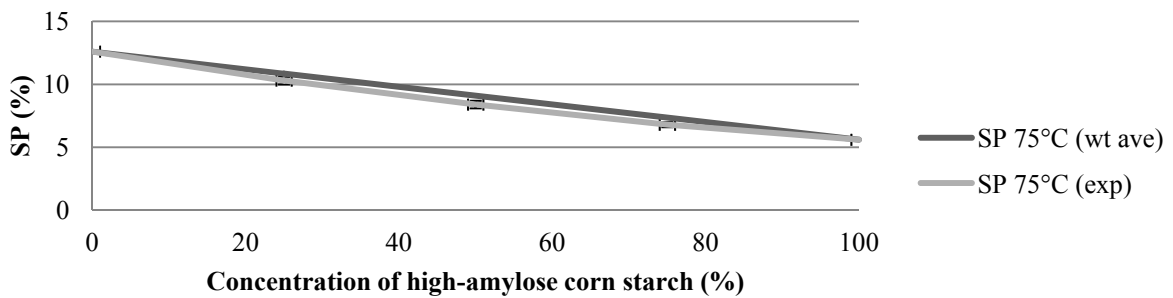
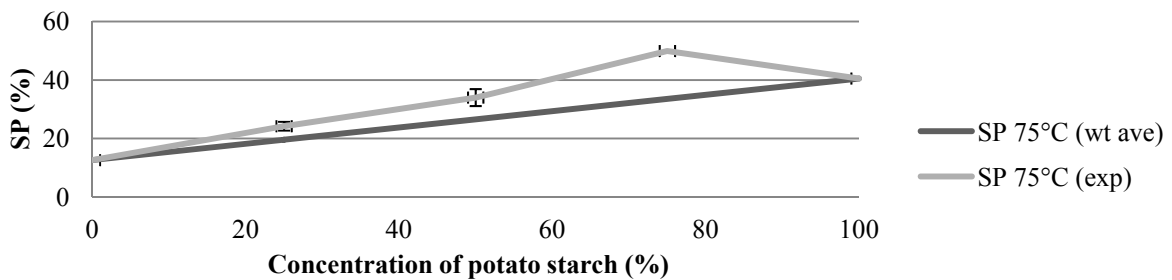**WSI 65°C: HMT pea starch and corn starch**
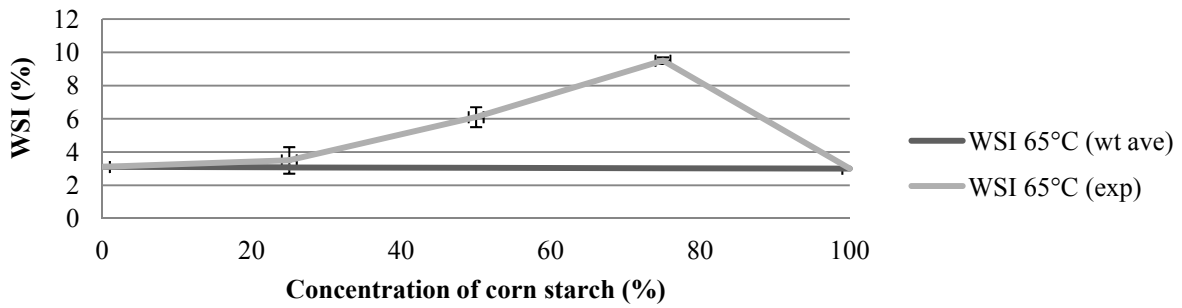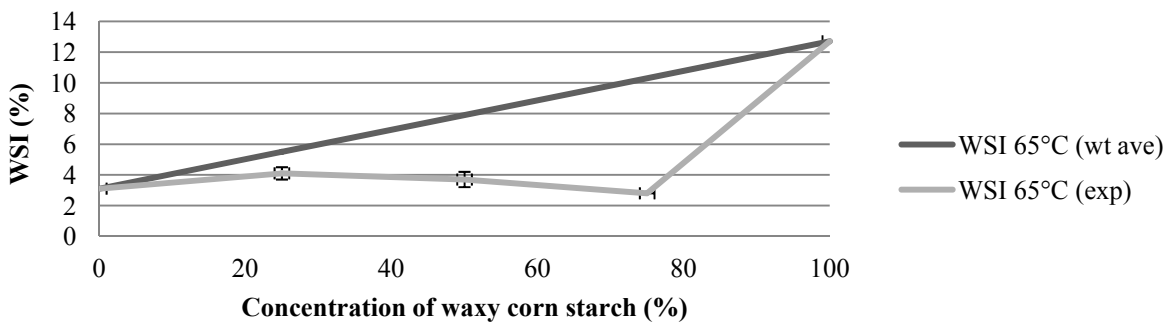
WSI 65°C: HMT pea starch and waxy corn starch

WSI 65°C: HMT pea starch and high-amylose corn starch
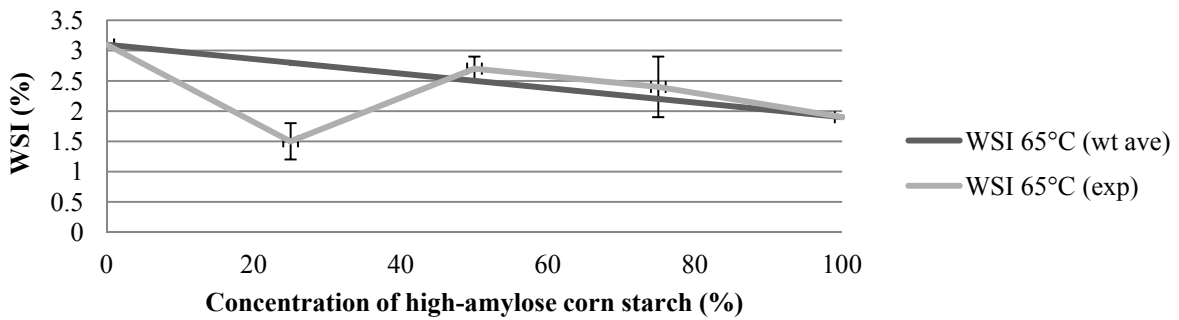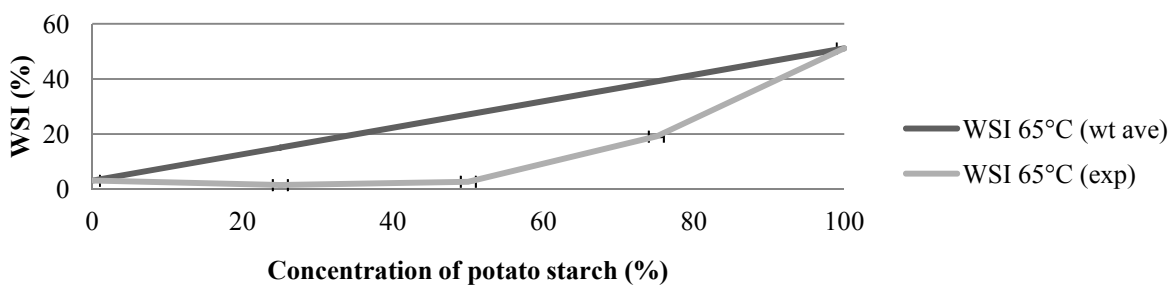
WSI 65°C: HMT pea starch and potato starch

WSI 75°C: HMT pea starch and corn starch
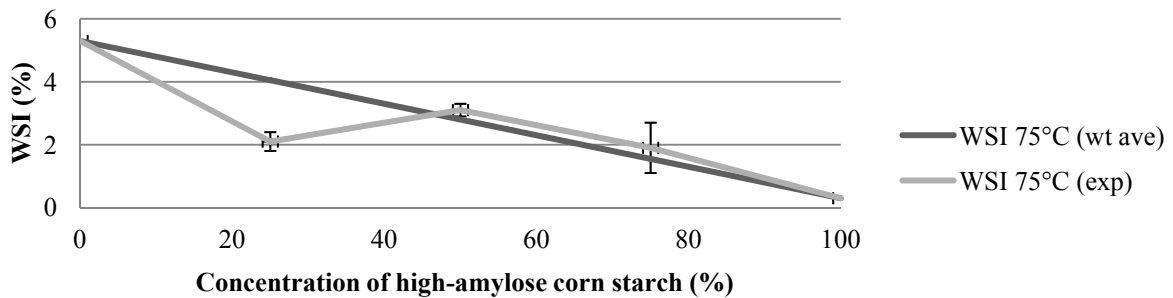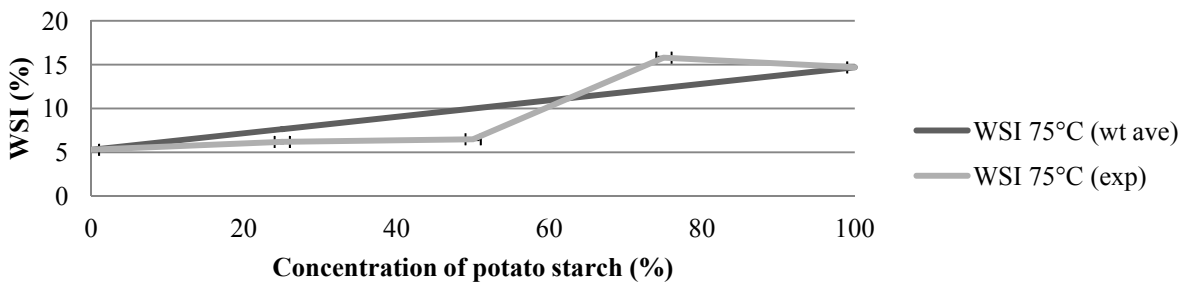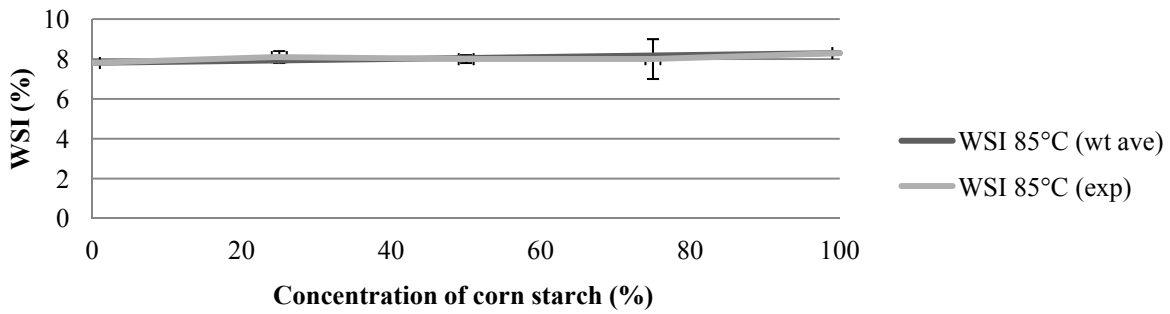
WSI 75°C (wt ave)
WSI 75°C (exp)

WSI 75°C: HMT pea starch and waxy corn starch

WSI 75°C (wt ave)
WSI 75°C (exp)

WSI 75°C: HMT pea starch and high-amylose corn starch

WSI 75°C (wt ave)
WSI 75°C (exp)

WSI 75°C: HMT pea starch and potato starch

WSI 75°C (wt ave)
WSI 75°C (exp)

WSI 85°C: HMT pea starch and corn starch

WSI 85°C (wt ave)
WSI 85°C (exp)

WSI 85°C: HMT pea starch and waxy corn starch

WSI 85°C (wt ave)
WSI 85°C (exp)

WSI 85°C: HMT pea starch and high-amylose corn starch

WSI 85°C (wt ave)
WSI 85°C (exp)

WSI 85°C: HMT pea starch and potato starch

WSI 85°C (wt ave)
WSI 85°C (exp)

WSI 95°C: HMT pea starch and corn starch

WSI (%) vs Concentration of corn starch (%)

WSI 95°C (wt ave)
WSI 95°C (exp)

WSI 95°C: HMT pea starch and waxy corn starch

WSI (%) vs Concentration of waxy corn starch (%)

WSI 95°C (wt ave)
WSI 95°C (exp)

WSI 95°C: HMT pea starch and high-amylose corn starch

WSI (%) vs Concentration of high-amylose corn starch (%)

WSI 95°C (wt ave)
WSI 95°C (exp)

WSI 95°C: HMT pea starch and potato starch

WSI (%) vs Concentration of potato starch (%)

WSI 95°C (wt ave)
WSI 95°C (exp)
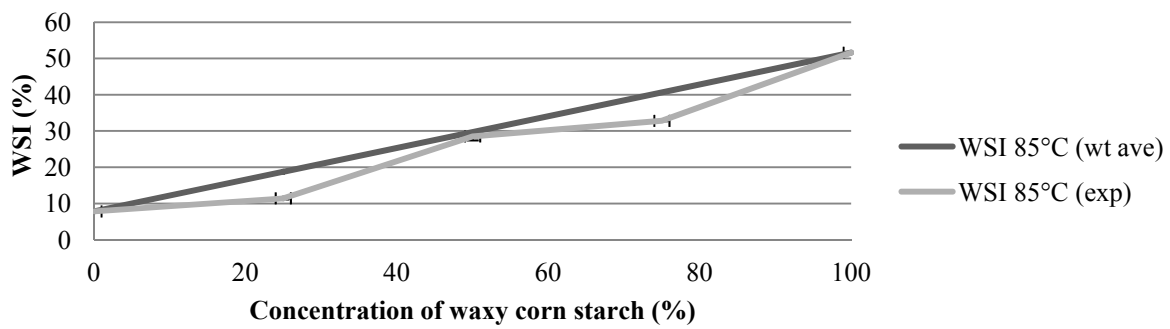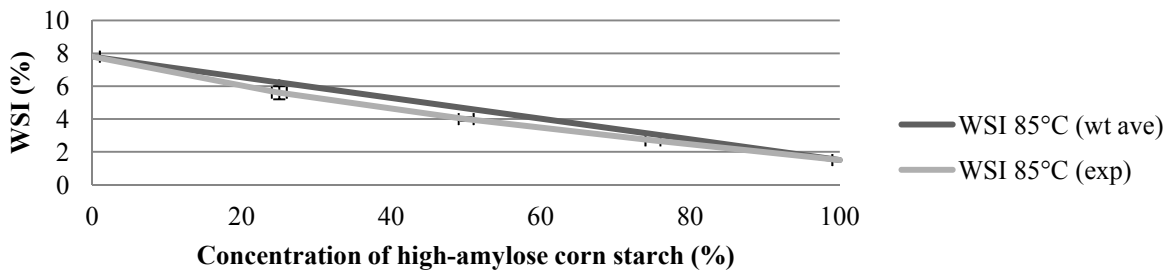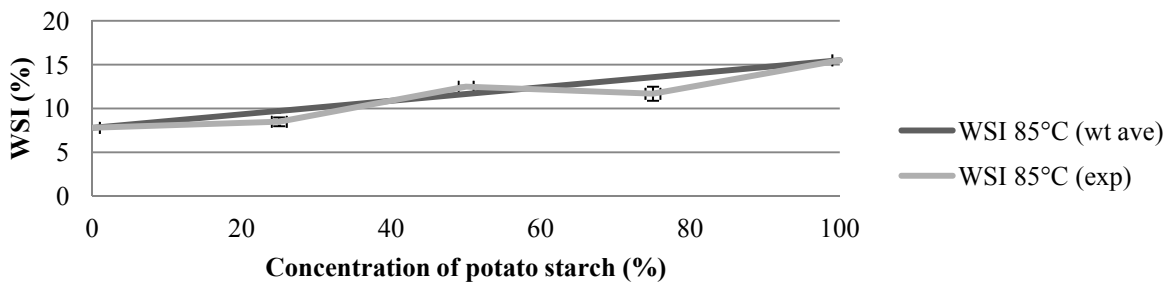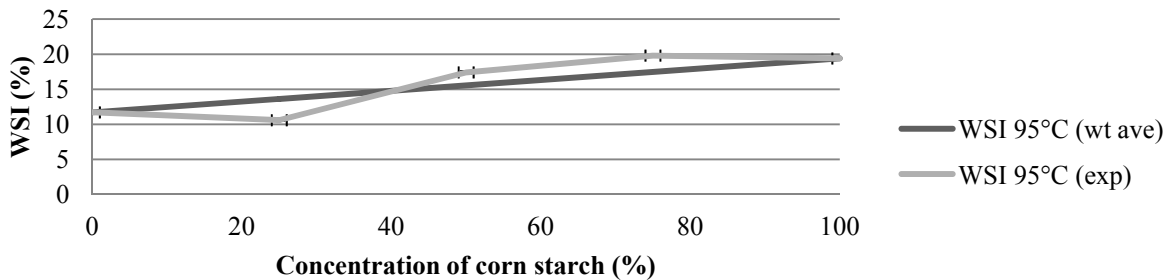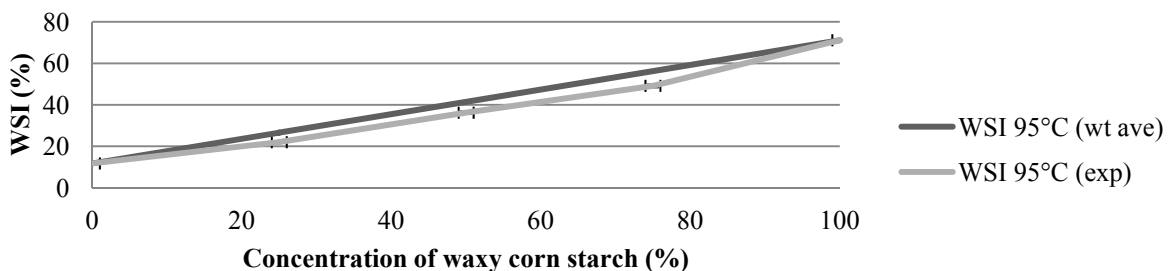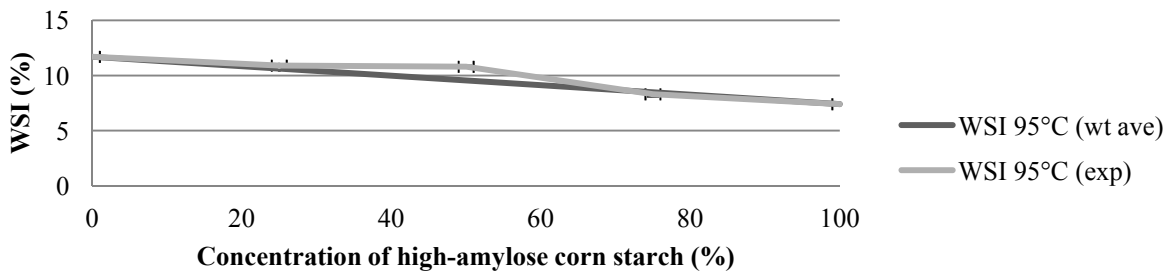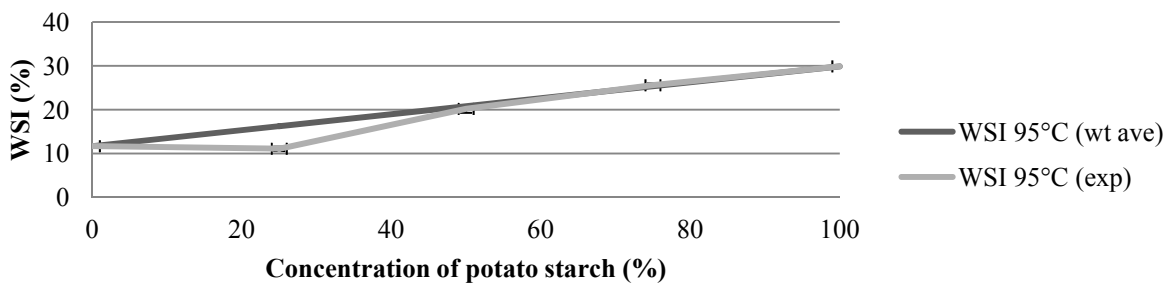
FT1: HMT pea starch and corn starch
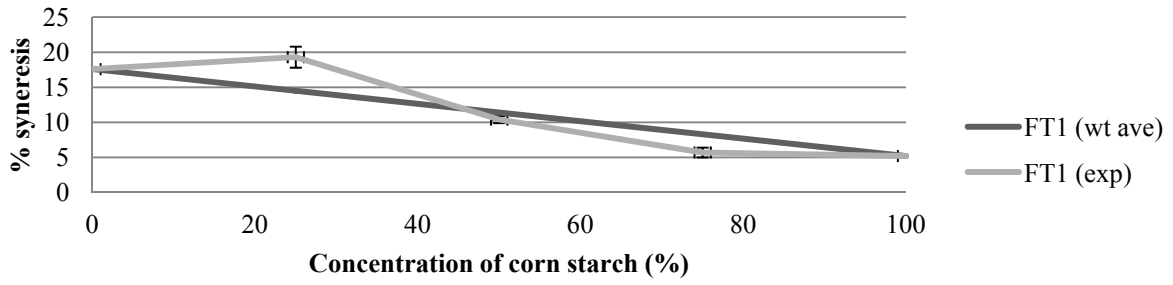
FT1: HMT pea starch and waxy corn starch
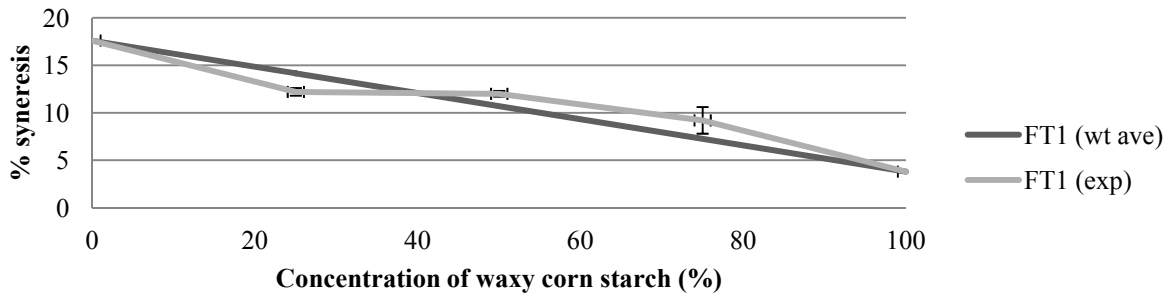
FT1: HMT pea starch and high-amylose corn starch

FT1: HMT pea starch and potato starch

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FT2: HMT pea starch and corn starch
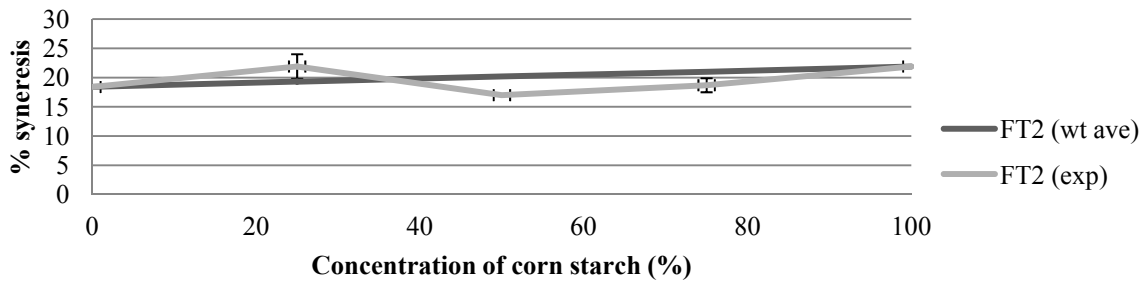
FT2: HMT pea starch and waxy corn starch
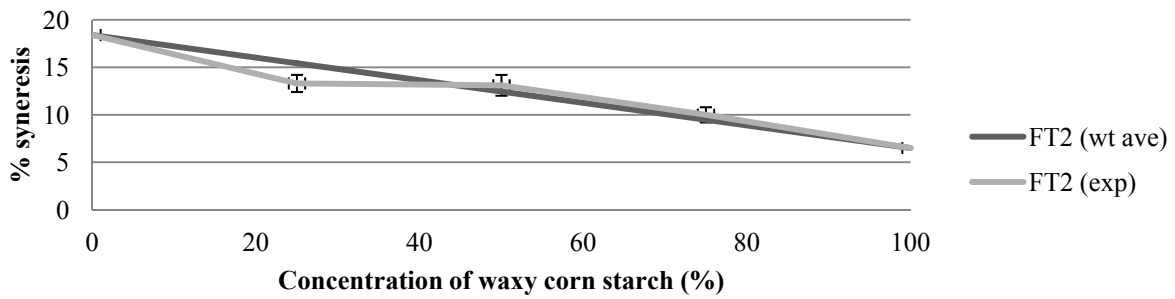
FT2: HMT pea starch and high-amylose corn starch
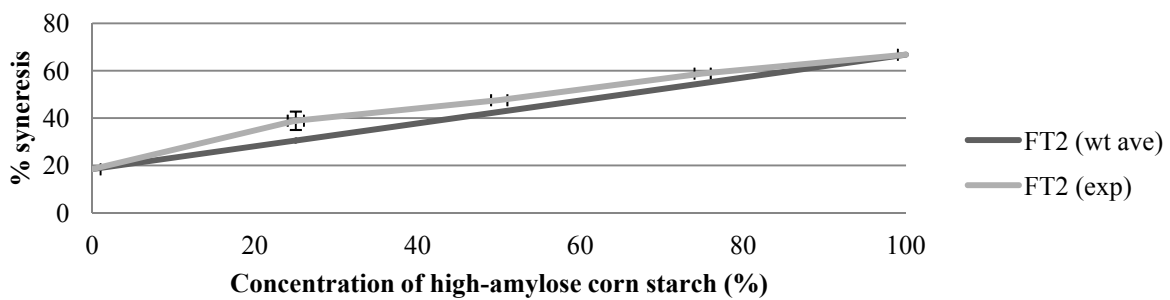
FT2: HMT pea starch and potato starch
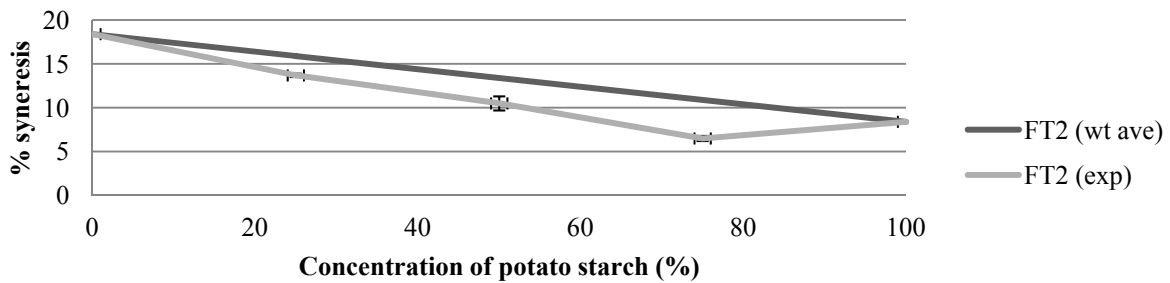
FT3: HMT pea starch and corn starch
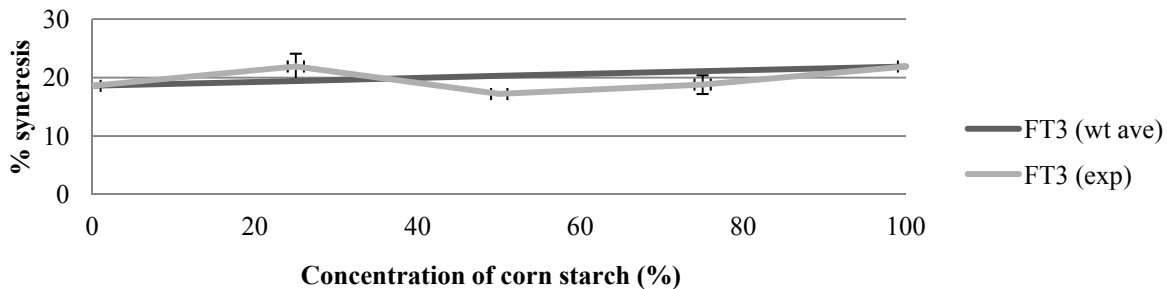
FT3: HMT pea starch and waxy corn starch
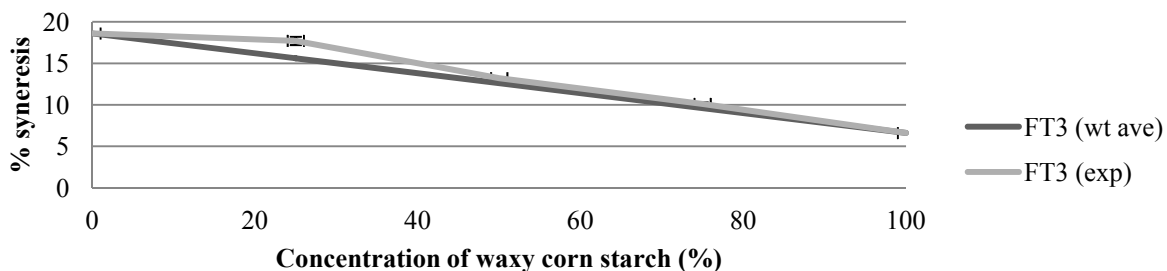
FT3: HMT pea starch and high-amylose corn starch
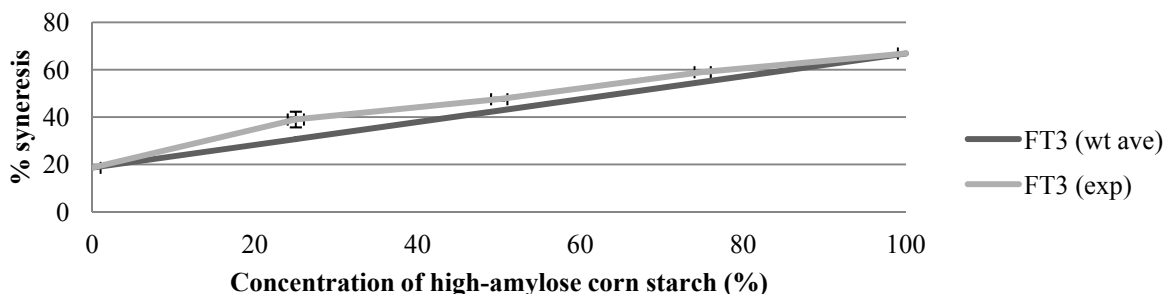
FT3: HMT pea starch and potato starch
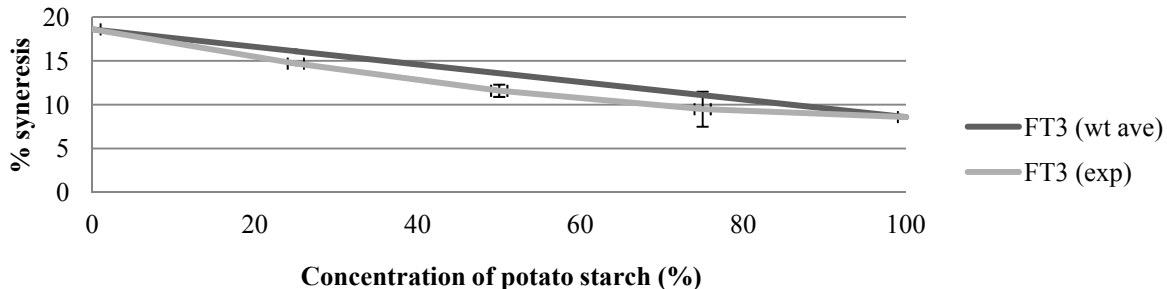
FT4: HMT pea starch and corn starch
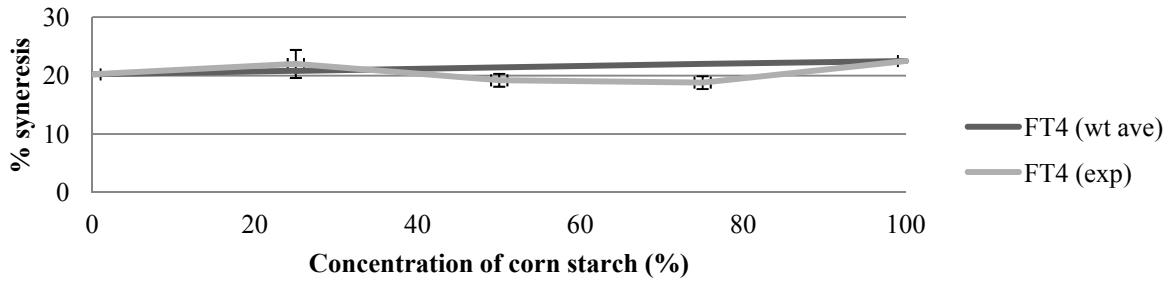
FT4: HMT pea starch and waxy corn starch

FT4: HMT pea starch and high-amylose corn starch

FT4: HMT pea starch and potato starch

FT5: HMT pea starch and corn starch

FT5: HMT pea starch and waxy corn starch

FT5: HMT pea starch and high-amylose corn starch

FT5: HMT pea starch and potato starch

SS: HMT pea starch and corn starch

SS (%) vs *Concentration of corn starch (%)*

— SS (wt ave)
— SS (exp)

SS: HMT pea starch and waxy corn starch

SS (%) vs *Concentration of waxy corn starch (%)*

— SS (wt ave)
— SS (exp)

SS: HMT pea starch and high-amylose corn starch

SS (%) vs *Concentration of high-amylose corn starch (%)*

— SS (wt ave)
— SS (exp)

SS: HMT pea starch and potato starch

SS (%) vs *Concentration of potato starch (%)*

— SS (wt ave)
— SS (exp)

WBC: HMT pea starch and corn starch

WBC: HMT pea starch and waxy corn starch

WBC: HMT pea starch and high-amylose corn starch

WBC: HMT pea starch and potato starch

RS: HMT pea starch and corn starch

RS: HMT pea starch and waxy corn starch

RS: HMT pea starch and high-amylose corn starch

RS: HMT pea starch and potato starch
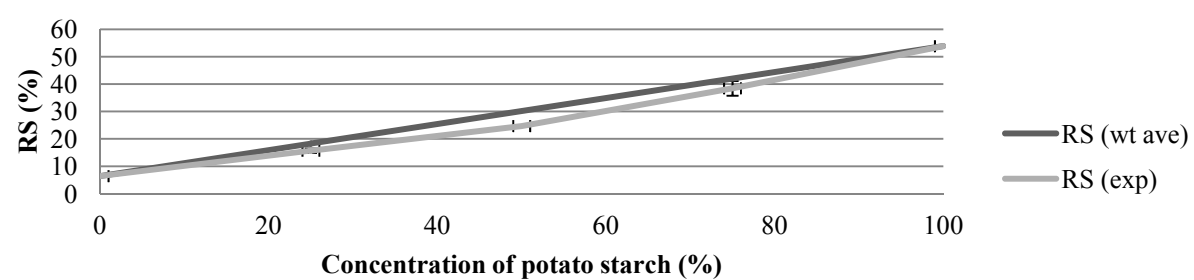
APPENDIX C

List of Abbreviations

ΔH Endothermic enthalpy of gelatinization

exp   Experimental value

FT   Freeze-thaw cycle (FT1 = freeze-thaw cycle 1, etc.)

FV   Final viscosity

PG   Pregelatinized

PS   Pea starch

PT   Pasting temperature

PV   Pasting viscosity

RS   Resistant starch

SP   Swelling power

SS   Shear stability

T_c Completion temperature of gelatinization

T_o Onset temperature of gelatinization

T_p Peak temperature of gelatinization

TV   Trough viscosity

WBC   Water binding capacity

WSI   Water solubility index

wt ave   Weighted average value

SP 65°C: PG pea starch and corn starch

SP 65°C: PG pea starch and waxy corn starch

SP 65°C: PG pea starch and high-amylose corn starch

SP 65°C: PG pea starch and potato starch
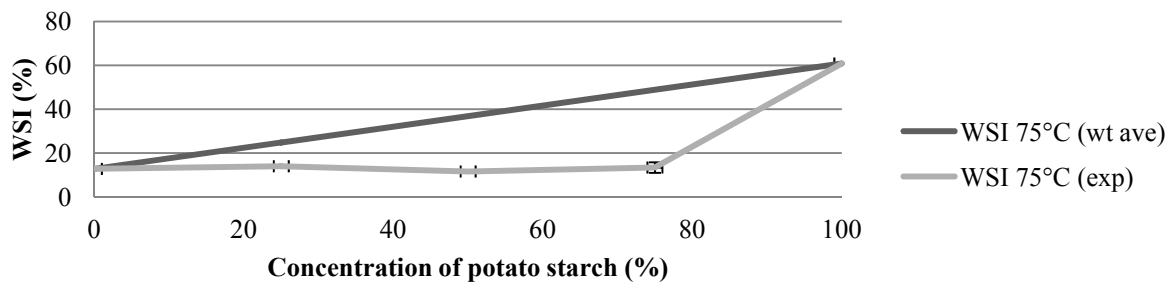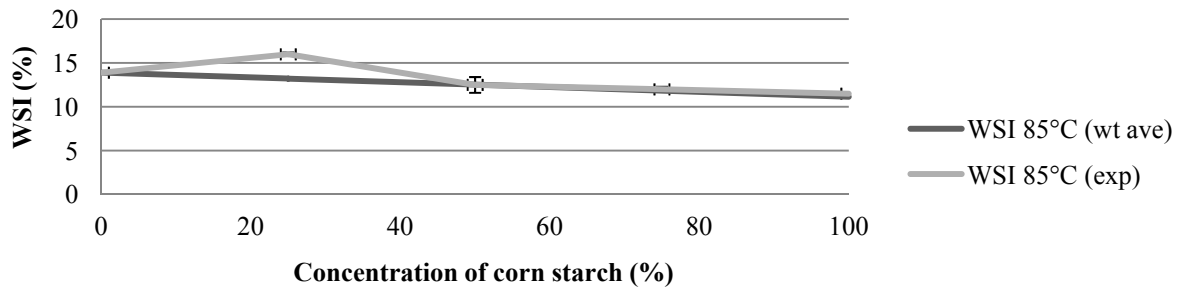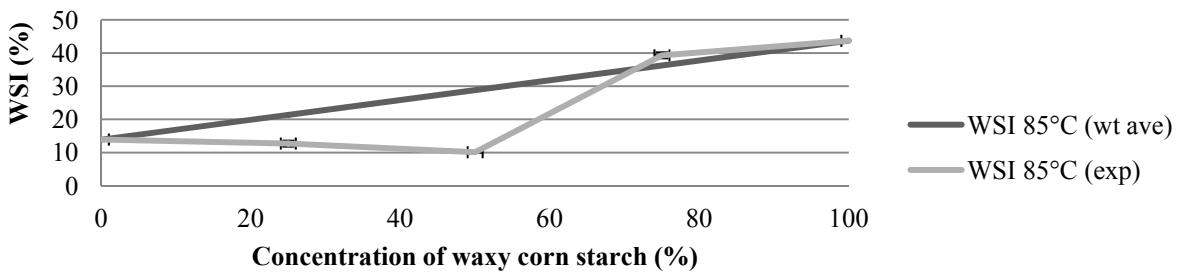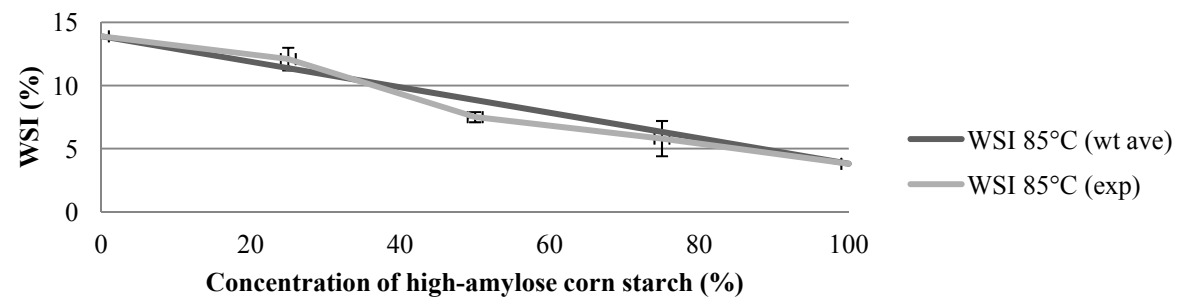
SP 75°C: PG pea starch and corn starch

SP 75°C: PG pea starch and waxy corn starch

SP 75°C: PG pea starch and high-amylose corn starch

SP 75°C: PG pea starch and potato starch

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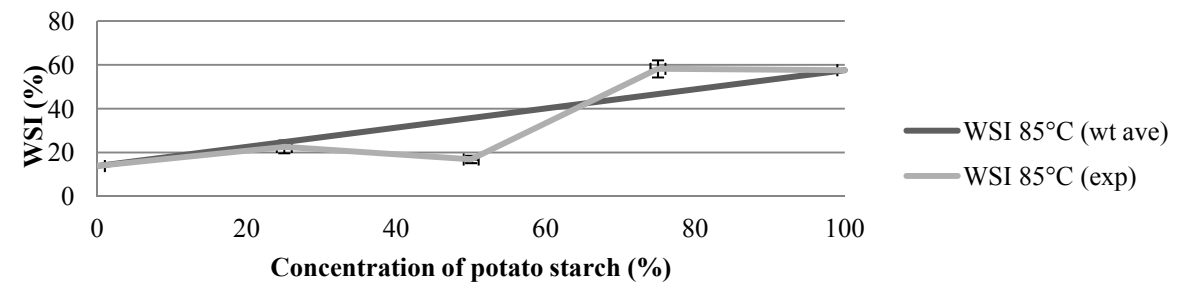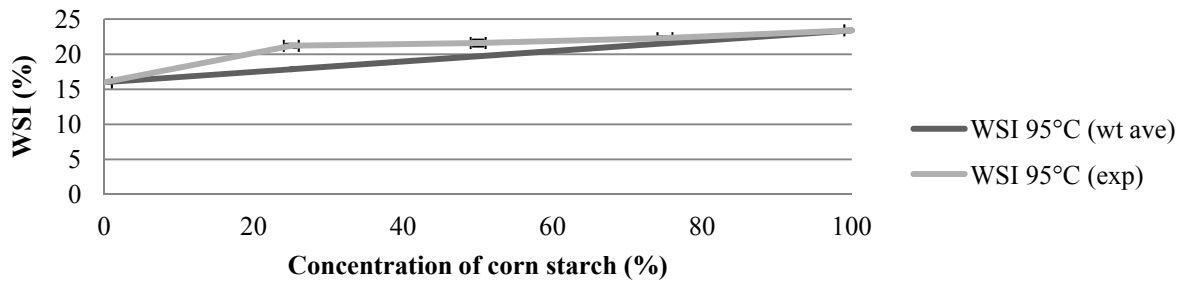**SP 85°C: PG pea starch and corn starch**

SP 85°C: PG pea starch and waxy corn starch

SP 85°C: PG pea starch and high-amylose corn starch

SP 85°C: PG pea starch and potato starch

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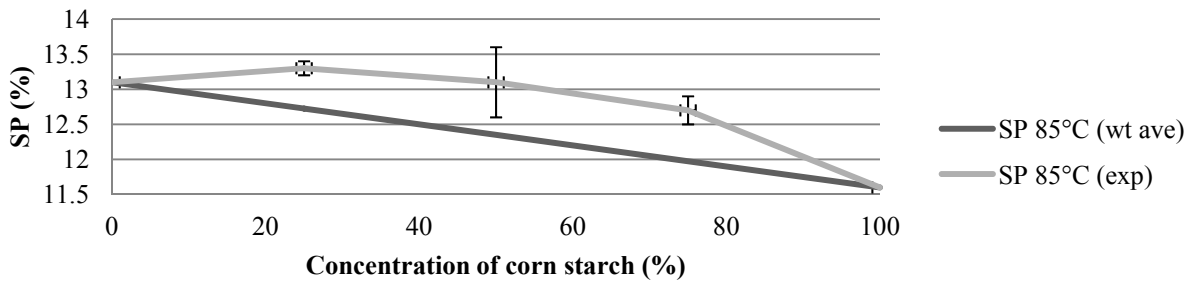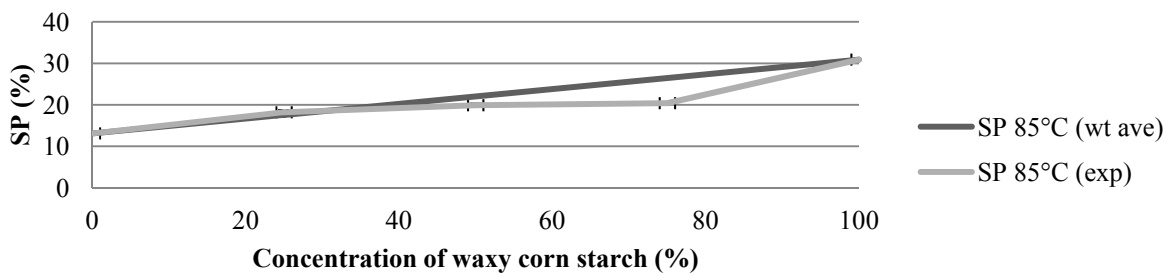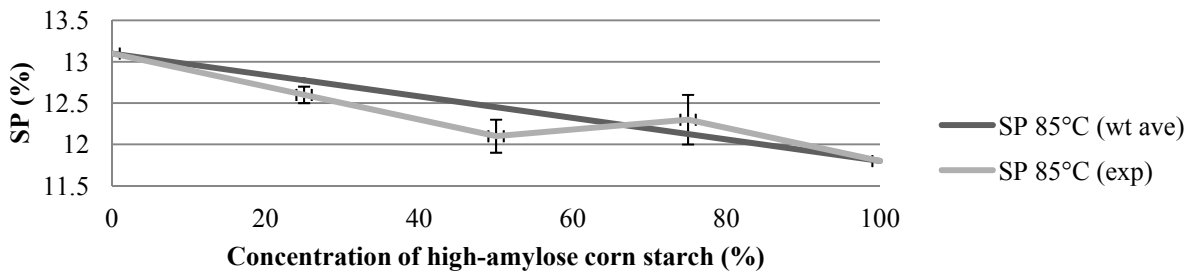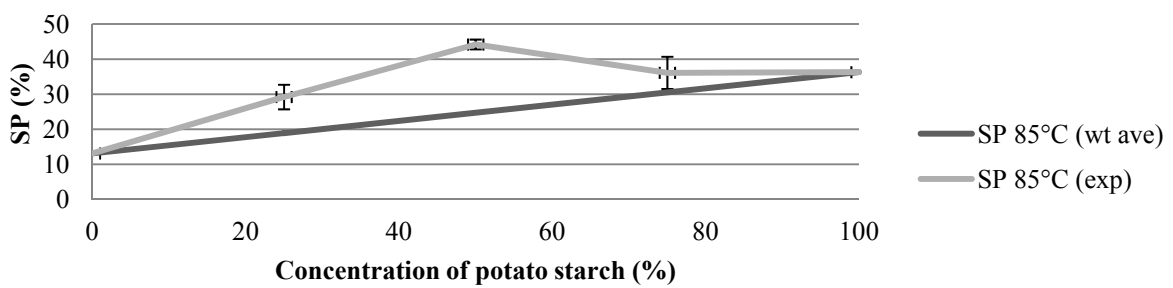
SP 95°C: PG pea starch and corn starch
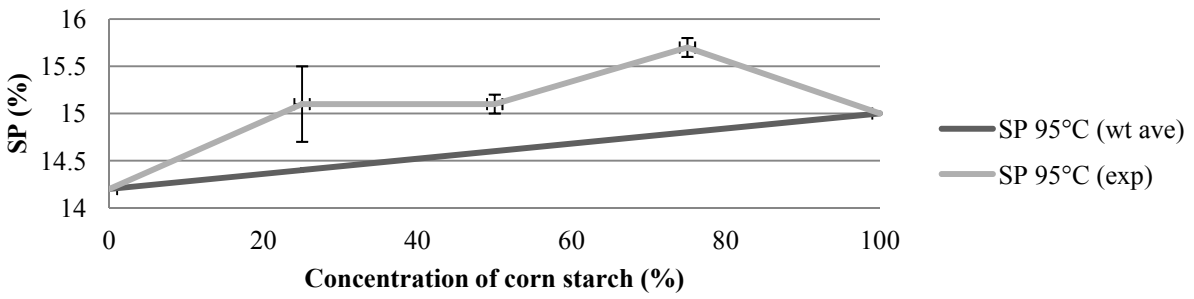
SP 95°C: PG pea starch and waxy corn starch

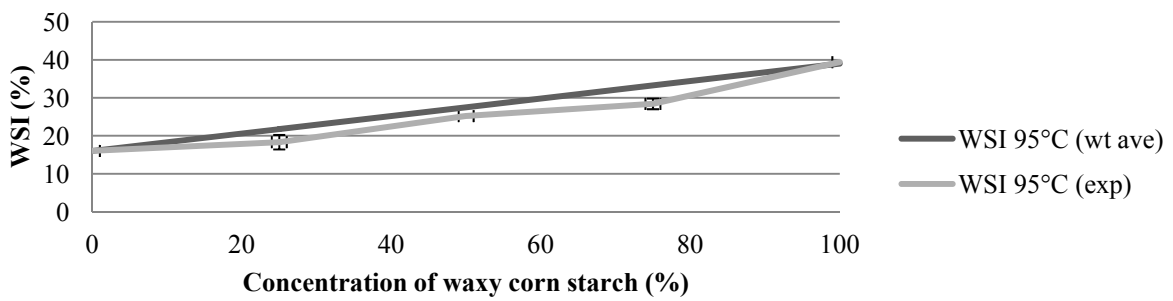**SP 95°C: PG pea starch and high-amylose corn starch**
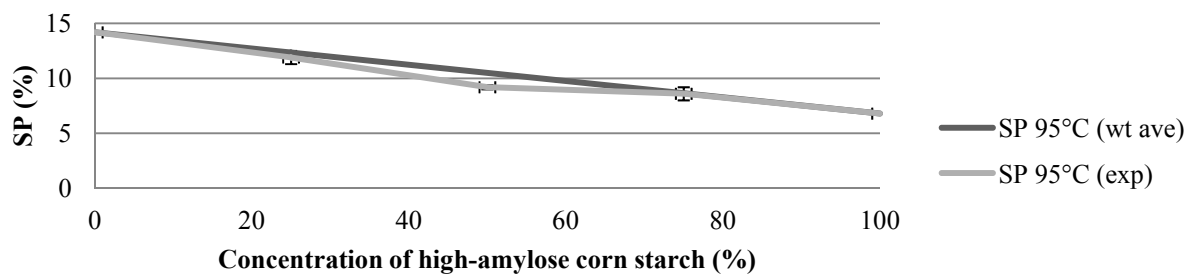
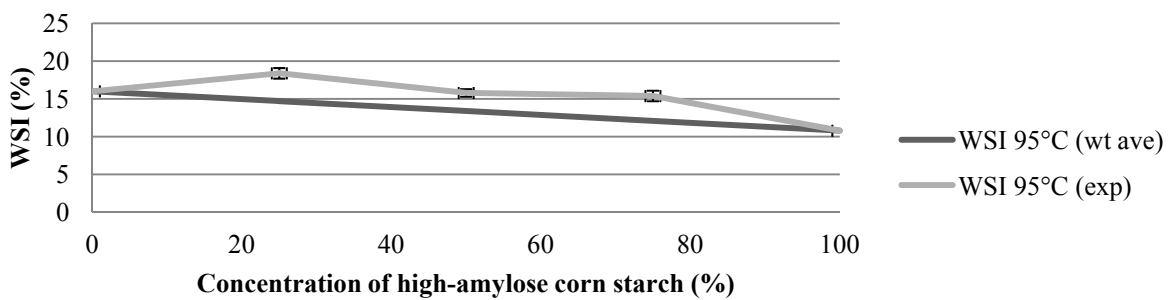**SP 95°C: PG pea starch and potato starch**

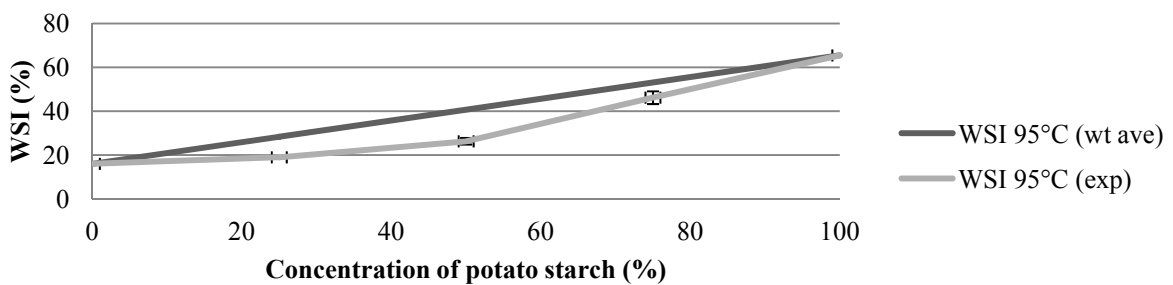**WSI 65°C: PG pea starch and corn starch**
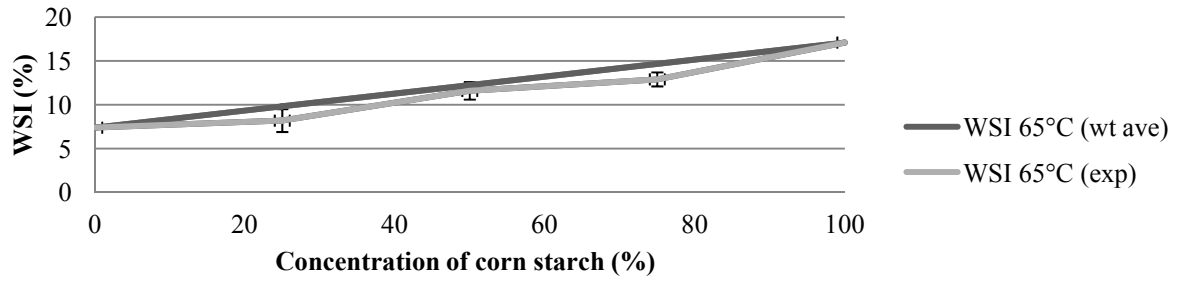
WSI 65°C: PG pea starch and waxy corn starch

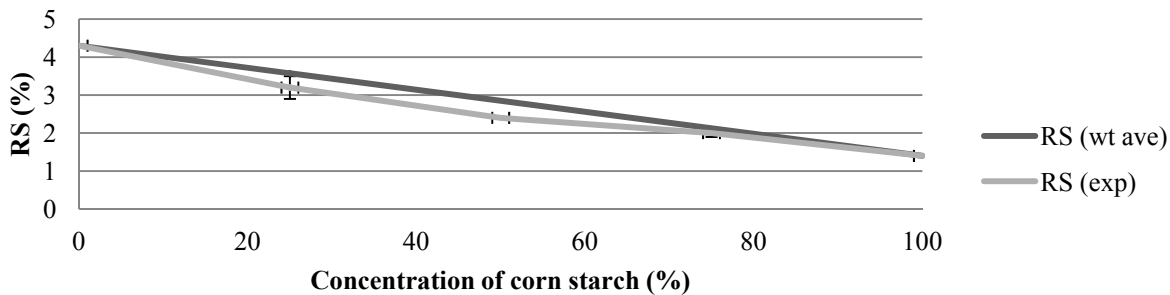**WSI 65°C: PG pea starch and high-amylose corn starch**

WSI 65°C: PG pea starch and potato starch

WSI 75°C: PG pea starch and corn starch
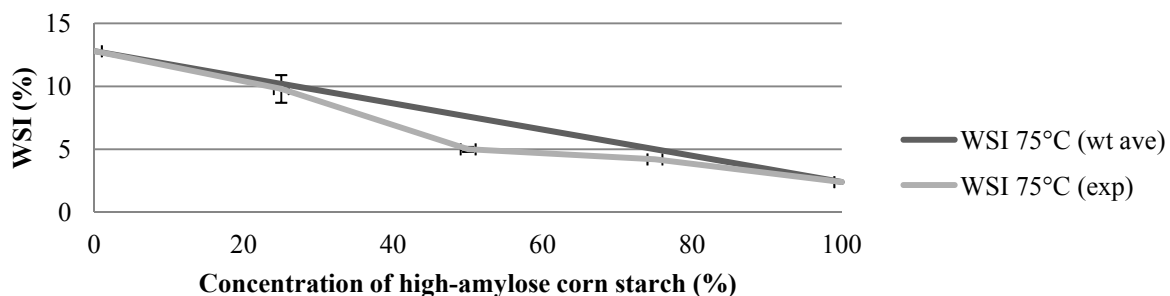
WSI 75°C (wt ave)
WSI 75°C (exp)

WSI 75°C: PG pea starch and waxy corn starch

WSI 75°C (wt ave)
WSI 75°C (exp)

WSI 75°C: PG pea starch and high-amylose corn starch

WSI 75°C (wt ave)
WSI 75°C (exp)

WSI 75°C: PG pea starch and potato starch

WSI 75°C (wt ave)
WSI 75°C (exp)

WSI 85°C: PG pea starch and corn starch

WSI 85°C (wt ave)
WSI 85°C (exp)

WSI 85°C: PG pea starch and waxy corn starch

WSI 85°C (wt ave)
WSI 85°C (exp)

WSI 85°C: PG pea starch and high-amylose corn starch

WSI 85°C (wt ave)
WSI 85°C (exp)

WSI 85°C: PG pea starch and potato starch

WSI 85°C (wt ave)
WSI 85°C (exp)

WSI 95°C: PG pea starch and corn starch

WSI 95°C: PG pea starch and waxy corn starch
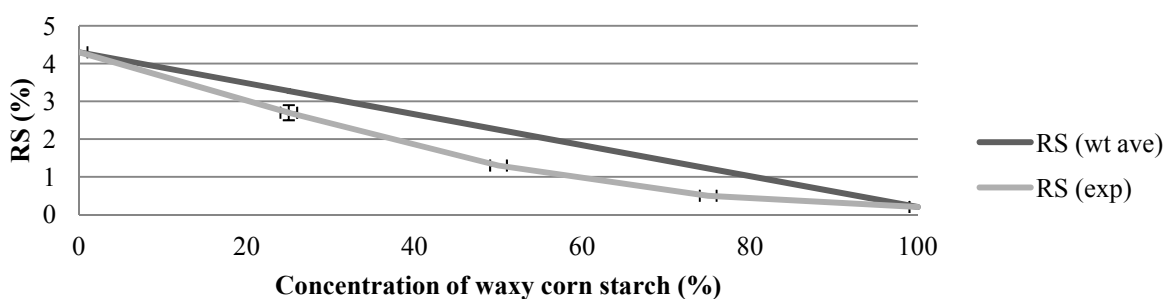

WSI 95°C: PG pea starch and high-amylose corn starch
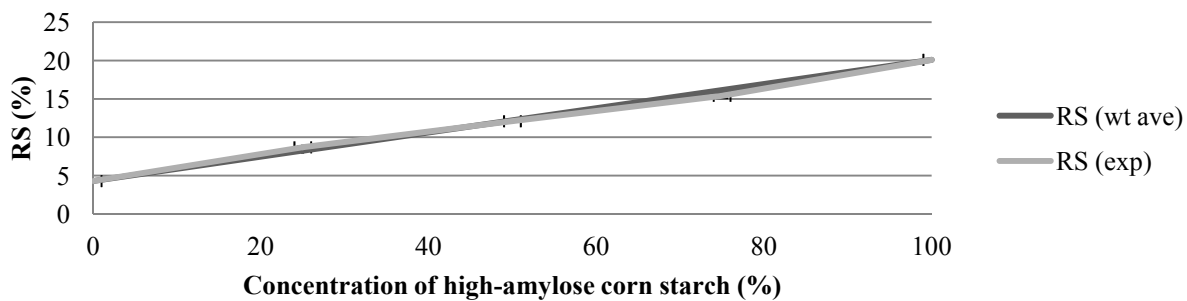

WSI 95°C: PG pea starch and potato starch

RS: PG pea starch and corn starch

RS: PG pea starch and waxy corn starch

RS: PG pea starch and high-amylose corn starch

RS: PG pea starch and potato starch