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Hydration level significantly impacts the freezable - and unfreezable -water contents of native and modified starches

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Abstract

The freezable- and unfreezable-water contents of corn and waxy corn starches (native, pregelatinized and retrograded) were analyzed at various hydration levels (25, 35, 45, 55, 65, 75, 85%) using Differential Scanning Calorimetry (DSC). The unfreezable water contents and also the temperature of onset (To), peak (Tp) and endset (Te) of the peaks' in all samples were increased with increasing hydration level. Water absorption index (WAI) and water solubility index (WSI) values of the pregelatinized and retrograded starch samples were significantly higher ($p<0.05$) than their native counterparts. RVA profiles revealed that modified starches had higher viscosity values than natural starches.

Keywords: corn-waxy corn starch; DSC; physical modifications; RVA; unfreezable water.

Practical Application: Starch is one of the most important vegetable polysaccharides and is used in many areas of the industry. Various modification techniques have been developed to improve the technological properties of native starches. Physical modification techniques are more preferred because there is no chemical application.

1 Introduction

Starch is not only being widely used in the production of many food substances (soups, salad dressings, bakery products, milk puddings, snacks, coatings, meat products) but it is also sought by the pharmaceutical industry, textile, paper industry, alcohol-based fuels and adhesives (Kaur et al., 2012; Fu et al., 2014). The chemical and physical features of starches affect the texture, viscosity, gel structure, stickiness, binding ability, water holding capacity and homogeneity of the products where they are used. These functional properties of the starch vary with the amylose-amylopectin content.

Amylose-amylopectin content in starches varies depending on the botanic source. In general, amylose and amylopectin content of native starches varies between 20-30% and 70-80%, respectively, while in waxy starches, which are mutant genotypes, the amylose amount is less than 1% (Kamal et al., 2007; Klaochanpong et al., 2015). Amylose/amylopectin ratio as well as branching density of starch impact its functional properties. High levels of chain branching improve of the solubility of starch while delay gel formation (Kohyama et al., 2004; Sasaki, 2005; Sajilata et al., 2006; Kaur et al., 2012). The granule type of starch also significantly impacts its functional properties such as water solubility, hydration temperature and swelling indexes.

Native starch granules do not dissolve in cold water but they absorb water and swell slowly. Also, native starch is a good texture stabilizator and regulator of food systems. However, due to low tensile strength, thermal strength, thermal decomposition and high retrogradation tendencies, the use of native starch is limited in some industrial food applications (Singh et al., 2007). Therefore, there is a need to perform certain modifications to increase the functional properties of starch (BeMiller, 1997). Through these modifications, the structure of starch molecule is changed. The cooking characteristics, paste's freezing-thawing stability, gel clarity and brightness, gel texture, film formation, adhesion, emulsion stabilization increase, while retrogradation, paste's gelling tendency and syneresis reduce (BeMiller, 1997). Starch modifications may be achieved in three different types, namely chemical (derivatization, acid thinning, dextrinization, oxidation, hydrolysis), physical (pregelatinized and granular cold-water swelling starches) and genetic (waxy, starch with high amylose) (BeMiller, 1997; Kaur & Singh, 2016). Physical modification techniques do not require chemical agents. Therefore, they are safer for human consumption and preferred more (Kaur et al., 2012; Majzoobi et al., 2015).

Physicochemical properties of the starch can be affected with the interactions between water and starch molecules. Starch-water interactions can be determined by the changes in the physical state of water. The physical state of the water in starch may be described as freezable (free) and unfreezable (bound) water. Water bonded tightly to the starch molecule is defined as unfreezable water, and it does not assume the role of a solvent, unlike free water. This water cannot be frozen even at very low temperatures subzero, and it can significantly affect the stability of starch-based products. Determining the unfreezable water content in starch-rich foods provides important information to establishing appropriate processing and storage conditions (Suzuki & Kitamura, 2008; Fu et al., 2014). Even though several studies have been performed on starch gelatinization (Fredriksson et al., 1998; Liu et al., 2006; Ratnayake & Jackson, 2006; Wang et al., 2014; Li et al., 2015) the number of studies on modified starch-water interactions is limited. Thus, the objectives of this study were:

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(1) to determine the freezable and unfreezable water contents of corn and waxy corn starches both native and physically modified (pregelatinized and retrograded) at different hydration levels by using DSC, (2) to determine water absorption – water solubility indexes and (3) to reveal the RVA properties.

2 Materials and methods

2.1 Materials

Corn and waxy corn starches used as material were obtained from Sunar Mısır Company (Adana, Turkey). Amylose/amylopectin ratios of corn and waxy corn starches were determined by spectrophotometric method (Garg & Jana, 2011) and found 27.6±0.3/72.4±0.3 and 0.8±0.2/99.2±0.2, respectively. Pregelatinized and retrograded starches were obtained from these starch samples by using the physical modification techniques described in the method section.

2.2 Methods

Preparation of physically modified starches and determination of pasting properties

The 12.28% suspension (w/w) of corn and waxy corn starch samples (3.5 g, dry basis) were prepared in RVA vessels with 25 ml distilled water, and the samples were loaded into RVA (RVA 4500, Perten, Sweden). Following RVA procedure was applied to obtain the RVA viscogram. The suspension was stirred in RVA at 400 rpm for 10 seconds and then held for 10 min at 30°C. At the end of this period, the temperature was risen to 95 °C at 10.83°C/min and held for at this temperature for 5 min. The samples were cooled from 95 °C to 50 °C in 4 min and kept at this temperature for 10 min. Pregelatinized starch samples were obtained at viscosity peak from the RVA viscogram, while retrograde starch samples were obtained after being stored for 120h at 4 °C of the completed RVA samples. After the mentioned periods, the samples were frozen by adding liquid nitrogen, and then freeze drying were carried out (Operon FDU-8612, Korea) was performed. The dried samples were powdered for the analysis by using a 1 mm mesh screened cyclone mill (Retsch ZM 200, Germany). The moisture content of the starch samples was determined by the oven drying method in an oven at 105 °C for 24 h. Starch concentration of the slurry used in pasting analyses was adjusted to 12.28%, and the pasting properties of starch samples (native, pregelatinized and retrograded) were determined by applying the above-mentioned RVA procedure. The RVA parameters were obtained from the RVA viscogram data according to Ragaee & Abdel-Aal (2006).

Water absorption and water solubility index

Water absorption index (WAI) in corn, pregelatinized corn, retrograded corn, waxy corn, pregelatinized waxy corn and retrograded waxy corn samples were determined based on the method described by Anderson (1969). For this purpose, 2.5 g sample was weighed into 50 ml tared centrifuge tubes and 30 ml distilled water was added to form suspension. The prepared samples were centrifuged (Hanil Combi 514R, Korea) at 3000 x g for 10 min. After the centrifuging process, the supernatant was carefully transferred into tared drying vessels and dried at 105 °C for 12 h in a drying cabinet. Water Solubility Index (WSI) was calculated in dried samples accordance with Equation 1. The pellet in centrifuge tubes was weighed and WAI was calculated accordance with Equation 2.

$$\text{WSI} = \frac{\text{weight after drying}(g)}{\text{dry weight of original starch}(g)} \quad (1)$$

$$\text{WAI} = \frac{\text{pellet weight}(g)}{\text{dry weight of original starch}(g)} \quad (2)$$

Freezable and unfreezable water contents by using Differential Scanning Calorimetry

DSC studies were conducted on samples at various hydration levels (25, 35, 45, 55, 65, 75, 85%). For this purpose, accurately 10 mg samples were weighed into the hermetic DSC pans (product number 03190029, Perkin Elmer, USA), and distilled water was added with a micro syringe to obtain the desired hydration-level samples. Pans were sealed and weighed (BEL M214Ai, Italy). The sealed pans were kept for 24 h at room temperature to ensure homogenous distribution of water. The freezable and unfreezable water contents of the samples were determined by using DSC (DSC 6000, Perkin Elmer, USA) with an intercooler system. The temperature and heat flow calibration of the DSC were performed by using indium (melting point: 156.6 °C, ΔH=28.47 J/g) and water (melting point: 0 °C, ΔH=333.20 J/g). An empty pan was used as reference. The following temperature program was used to determine freezable and unfreezable water contents of samples: (1) cooling from 20 °C to -80 °C at 5 °C/min; (2) holding at -80 °C for 5 min; (3) heating from -80 °C to 50 °C at 5 °C/min. To determine the freezable and unfreezable water contents of the samples at the end of the DSC analyses, the method used described by Fu et al. (2014). The method contains the ratio of the area corresponding to the melting enthalpy of the ice in the material to the pure water melting enthalpy (333.20 J/g). The exact moisture content of each sample was confirmed after collecting the calorimetric data. The sealed DSC pans were punctured and dried in an oven at 105 °C for 24 h and the reweighed to determine the exact water content in the sample. Unfreezable water content was defined by using Equation 3.

$$\text{Unfreezable water content} = \frac{m_w}{m_s} - \frac{\Delta H_s}{\Delta H_w} \quad (3)$$

Unfreezable water content: (g water/ g dry starch); m_w: water content in samples (g); m_s: dry starch in samples (g); ΔH_s: the ice melting enthalpies of moisture in starch samples (J/g); ΔH_w: the ice melting enthalpy pure water (J/g).

2.3 Statistical analysis

All the tests in the study were carried out in triplicate and the results were reported with mean values and standard deviation values. The acquired data were subjected to analysis of variance by using SPSS 22.0 (IBM Corp., Armonk, NY, USA) package program, and the average values of meaningful main variance sources were compared with Duncan's multiple comparison test (p<0.05).

Table 1. The viscosity values of starch samples.

Starch	Viscosity (RVU)					
	Initial	Peak	Trough	Breakdown	Final	Setback
Corn	2.00 ± 0.00^{e}	610.50 ± 1.40^{d}	269.80 ± 4.60^{c}	340.80 ± 3.20^{f}	752.00 ± 0.70^{c}	482.30 ± 5.30^{c}
Pregelatinized corn	58.00 ± 1.40^{c}	860.00 ± 0.00^{b}	485.50 ± 0.70^{b}	374.50 ± 0.70^{d}	1246.80 ± 0.30^{b}	761.30 ± 1.00^{a}
Retrograded corn	9.00 ± 0.00^{d}	2238.80 ± 0.40^{a}	723.50 ± 0.70^{a}	1515.30 ± 0.40^{a}	1393.90 ± 0.20^{a}	670.40 ± 0.50^{b}
Waxy corn	2.00 ± 0.00^{e}	538.50 ± 0.70^{e}	176.00 ± 1.40^{d}	362.50 ± 2.10^{e}	256.50 ± 0.00^{d}	80.50 ± 1.40^{d}
Pregelatinized waxy corn	97.50 ± 2.10^{b}	529.50 ± 0.70^{f}	99.50 ± 0.70^{e}	430.00 ± 0.00^{c}	141.00 ± 0.00^{f}	41.00 ± 1.40^{f}
Retrograded waxy corn	460.50 ± 0.70^{a}	712.00 ± 1.40^{c}	74.50 ± 0.70^{f}	637.50 ± 0.70^{b}	144.00 ± 0.00^{e}	69.50 ± 0.70^{e}

$^{a, f}$: Values in a column with the same superscript are not significantly different ($p<0.05$); ±: Standard deviation of three replicates.

3 Results and discussion

3.1 Rapid Visco Analyser

RVA results of corn, waxy corn and their physically modified forms were given in Table 1. The physically modified types of corn and waxy corn had higher initial viscosity values (the viscosity value at the starting point of gelation) when compared to their native forms. The highest initial viscosity value was observed in the retrograded waxy corn, followed by pregelatinized waxy corn. Obtaining higher initial viscosity values in physically modified waxy corn starches is due to the fact that amylopectin in the starch molecule is the main component responsible for swelling of starch and the physical modifications promote this swelling. The waxy corn starch granules exclusively consist of amylopectin, and thus swelled more readily than normal corn starch resulting in higher initial viscosity. It was also found that each form of the corn starch (native, pregelatinized, retrograded) had higher ($p<0.05$) peak, trough, breakdown, final and setback viscosity values than the waxy corn starches. This situation indicates that amylose plays an important role in providing the effects of physical modification on pasting viscosity. The heat treatment allowed water to diffuse inside granules causing granule swelling and amylose leaching (BeMiller & Huber, 2015). The released amylose has a strong tendency to aggregation. Zhang et al. (2018) reported that the starch matrix formed by amylose aggregation on the granule surface eventually increased the rigidity of starch granules.

Peak viscosity is an important characteristic to distinguish properties of starches, an indication of water holding capacity (Thakur et al., 2015). Similar to our results, Sun et al. (2014) reported that normal corn starch had higher peak viscosity value than waxy corn starch. High crystallinity in waxy corn may have been responsible for its lower peak viscosity than normal corn forms as observed earlier (Thakur et al., 2015). As the starch granules swell, the viscosity of the system increases, and when the amount of swollen granules reaches the highest level, the viscosity reaches the peak (BeMiller, 2019). As shown in Table 1, modified forms of starch samples have higher peak viscosity values than native forms. This indicates that physical modification significantly increases the swelling ability of the starch granules.

Significant differences were determined in the setback viscosity values of corn and waxy corn starch ($p<0.05$). Waxy corn starch forms showed much less setback viscosity values than does normal corn starch forms. This finding is attributable to an absence of amylose, because amylose interacts with amylopectin in the swelling (Kurakake et al., 2009). The increase in viscosity during cooling is called setback. Setback viscosity occurs as a result of rearranged amylose molecules in solution during cooling and it is considered to be the measure of starch gelation ability or retrogradation tendency of the starch (Alamri et al., 2013). It is being emphasized that the amylose content in starch is responsible for the higher setback values (Blazek & Copeland, 2009). This is probably due to cooling and the fact that it is linked to amylose, which leads to the lowering of the energy system.

Table 2. The water absorption and water solubility index of starch samples.

Starch	WAI	WSI
Corn	$0.72 \pm 0{,}00^{e}$	0.64 ± 0.03^{c}
Pregelatinized corn	4.74 ± 0.07^{c}	0.96 ± 0.01^{c}
Retrograded corn	4.20 ± 0.19^{d}	0.78 ± 0.01^{c}
Waxy corn	0.91 ± 0.00^{e}	0.20 ± 0.00^{d}
Pregelatinized waxy corn	8.16 ± 0.20^{a}	7.08 ± 0.49^{a}
Retrograded waxy corn	7.78 ± 0.02^{b}	2.18 ± 0.04^{b}

$^{a, e}$: Values in a column with the same superscript are not significantly different ($p<0.05$); ±: Standard deviation of three replicates.

3.2 Water absorption and water solubility indexes

The water absorption and solubility indexes of the starch samples were given in Table 2. Physically modified starches had higher water absorption and solubility indexes, compared to native starches. Both water absorption and water solubility indexes were determined to be at the highest level in pregelatinized starches. This is an indicator of higher water holding and better levels by swollen granules. Obtaining the highest water solubility index in pregelatinized starch samples may be associated with destruction of the regular structure, while obtaining lower values in retrograded samples may be attributed to retrogradation. The crystal structure re-appears with retrogradation and this lowers the solubility of starch. In addition, when waxy corn and its modifications are compared to corn starch and its modifications, it can be seen that waxy corn varieties have much higher absorption indexes (Table 2). The higher absorption index of waxy corn starch may be attributed to the high amylopectin content. This is due to the fact that much more water is absorbed in the three-dimensional branched structure of amylopectin (Wang et al., 2011; Wang et al., 2014).

3.3 Unfreezable water contents by DSC

A single endotherm was obtained in all studied starch samples, and increasing hydration level resulted in an increase in the sizes of the obtained endotherms. Similarly, T_o, T_p and T_e values of the endotherms were shifted towards higher temperatures with increase in hydration level (Table 3). T_o, T_p and T_e values of the endotherms were significantly different from each other ($p<0.05$, Table 3). These shifts are reflected to the increase in the size of the ice melting peak. In higher hydration level conditions, adequate amounts of water are present in the medium to form ice crystals, while in limited water conditions most of the water is bound to starch with a small freezable fraction. A similar situation was reported by Suzuki & Kitamura (2008), Tananuwong & Reid (2004), Tran et al. (2008) and Grunina et al. (2015).

The unfreezable water contents of the physically modified and unmodified starch samples in different hydration levels were given in Table 4. The obtained values were statistically significantly different from each other ($p<0.05$). This may be attributed to the different water binding sites present in the starch samples. These binding sites are hydroxyl groups and inter-glucose oxygen atoms in the starches. The interaction of these sites with water varies depending on the structural and compositional properties of the starches (Fu et al., 2014). The unfreezable water contents of corn starches were higher than those of the pregelatinized corn starches in all hydration levels. Retrograded corn starches had higher unfreezable water content than corn starches up to 45% hydration level. In general, pregelatinized and retrograded waxy corn starches were higher unfreezable water contents than that

Table 3. T_o, T_p and T_e values of the endotherms of starch samples with various hydration levels.

Starch	Hydration levels (%)						
	25	35	45	55	65	75	85
T_o (°C)							
Corn	0.78 ± 0.04^{aF}	0.91 ± 0.03^{aE}	1.10 ± 0.04^{aCD}	1.06 ± 0.00^{aD}	1.18 ± 0.01^{aBC}	1.23 ± 0.01^{aB}	1.48 ± 0.11^{aA}
Pregelatinized corn	-7.56 ± 0.19^{bF}	-3.52 ± 0.07^{eE}	-1.23 ± 0.02^{eD}	-0.13 ± 0.07^{cC}	0.27 ± 0.10^{cB}	0.38 ± 0.03^{cB}	1.07 ± 0.02^{bcA}
Retrograded corn	-11.99 ± 0.77^{eE}	-3.85 ± 0.02^{fD}	-0.88 ± 0.24^{dC}	-0.25 ± 0.13^{cB}	0.09 ± 0.01^{dB}	0.71 ± 0.07^{bA}	1.05 ± 0.05^{bcA}
Waxy corn	-13.86 ± 0.60^{fE}	-0.33 ± 0.08^{bD}	0.68 ± 0.06^{bC}	1.01 ± 0.04^{aBC}	1.15 ± 0.02^{aABC}	1.30 ± 0.06^{aAB}	1.57 ± 0.31^{aA}
Pregelatinized waxy corn	-9.98 ± 0.23^{dE}	-1.63 ± 0.21^{cD}	0.72 ± 0.05^{bB}	0.31 ± 0.06^{bC}	0.61 ± 0.16^{bBC}	0.76 ± 0.06^{bB}	1.32 ± 0.34^{abA}
Retrograded waxy corn	-8.40 ± 0.47^{cF}	-2.16 ± 0.02^{dE}	-0.57 ± 0.11^{cD}	-0.14 ± 0.10^{cC}	0.28 ± 0.10^{cB}	0.67 ± 0.08^{bA}	0.93 ± 0.01^{cA}
T_p (°C)							
Corn	1.41 ± 0.03^{aG}	2.76 ± 0.31^{aF}	3.97 ± 0.24^{aE}	4.71 ± 0.62^{bD}	7.31 ± 0.10^{aC}	8.15 ± 0.17^{cdB}	10.58 ± 0.31^{dA}
Pregelatinized corn	-1.21 ± 0.02^{bG}	1.80 ± 0.09^{dF}	2.99 ± 0.17^{cE}	3.98 ± 0.31^{cD}	6.00 ± 0.24^{bcC}	8.24 ± 0.34^{cB}	11.17 ± 0.25^{cdA}
Retrograded corn	-3.90 ± 0.06^{eG}	1.24 ± 0.22^{eF}	2.52 ± 0.31^{dE}	3.83 ± 0.02^{cD}	6.08 ± 0.02^{bcC}	7.67 ± 0.11^{dB}	11.49 ± 0.04^{bcA}
Waxy corn	-3.21 ± 0.64^{dG}	2.30 ± 0.05^{bcF}	3.60 ± 0.13^{bE}	4.85 ± 0.04^{bD}	5.77 ± 0.22^{cC}	9.09 ± 0.15^{bB}	12.23 ± 0.56^{aA}
Pregelatinized waxy corn	-2.18 ± 0.01^{cF}	2.66 ± 0.33^{abE}	4.10 ± 0.00^{aD}	5.96 ± 0.10^{aC}	6.31 ± 0.26^{bC}	9.85 ± 0.29^{aB}	11.82 ± 0.41^{abA}
Retrograded waxy corn	-1.57 ± 0.12^{bG}	2.23 ± 0.20^{cF}	3.39 ± 0.15^{bE}	5.96 ± 0.46^{aD}	6.94 ± 0.50^{aC}	10.30 ± 0.49^{aB}	12.38 ± 0.22^{aA}
T_e (°C)							
Corn	3.96 ± 0.54^{aG}	4.87 ± 0.63^{bcF}	7.32 ± 0.47^{bE}	8.66 ± 0.16^{bD}	10.83 ± 0.06^{deC}	12.16 ± 0.07^{eB}	18.23 ± 0.50^{cA}
Pregelatinized corn	2.81 ± 0.23^{bcG}	4.60 ± 0.30^{cF}	6.82 ± 0.20^{bcE}	8.35 ± 0.13^{bcD}	10.53 ± 0.33^{eC}	13.80 ± 0.48^{cB}	18.46 ± 0.71^{cA}
Retrograded corn	0.73 ± 0.02^{eG}	4.42 ± 0.27^{cF}	5.78 ± 0.02^{dE}	7.48 ± 0.33^{dD}	11.15 ± 0.20^{cdC}	12.91 ± 0.27^{dB}	19.53 ± 0.51^{bA}
Waxy corn	2.92 ± 0.29^{bG}	5.09 ± 0.02^{bcF}	6.28 ± 0.51^{cdE}	8.11 ± 0.38^{cD}	11.53 ± 0.46^{cC}	13.39 ± 0.43^{cdB}	18.57 ± 0.43^{cA}
Pregelatinized waxy corn	1.80 ± 0.09^{dG}	6.22 ± 0.42^{aF}	8.62 ± 0.40^{aE}	9.91 ± 0.21^{aD}	14.77 ± 0.39^{aC}	15.52 ± 0.10^{bB}	19.84 ± 0.22^{bA}
Retrograded waxy corn	2.38 ± 0.06^{cG}	5.52 ± 0.12^{bF}	8.06 ± 0.55^{aE}	9.45 ± 0.39^{aD}	13.01 ± 0.17^{bC}	16.94 ± 0.23^{aB}	21.45 ± 0.29^{aA}

$^{a,\,f}$: Values in a column with the same superscript are not significantly different ($p<0.05$); $^{A,\,G}$: Values in a row with the same uppercase letters are not significantly different ($p<0.05$); ±:Standard deviation of three replicates.

Table 4. The unfreezable water contents of the starch samples with various hydration levels (g water/ g dry starch x100).

Starch	Hydration levels						
	25	35	45	55	65	75	85
Corn	31.30 ± 0.28^{cG}	35.99 ± 0.05^{cF}	37.46 ± 1.42^{cE}	46.34 ± 0.54^{bD}	52.43 ± 0.52^{dC}	66.05 ± 0.36^{dB}	105.53 ± 1.04^{cA}
Pregelatinized corn	31.65 ± 0.55^{cG}	35.44 ± 0.55^{dF}	36.86 ± 0.22^{cE}	40.53 ± 0.36^{dD}	42.61 ± 0.35^{fC}	48.92 ± 0.14^{fB}	57.76 ± 0.57^{eA}
Retrograded corn	32.94 ± 0.62^{bG}	40.84 ± 0.02^{bF}	43.01 ± 0.07^{bE}	45.63 ± 0.34^{cD}	49.44 ± 0.38^{eC}	57.16 ± 0.83^{eB}	103.76 ± 1.06^{cA}
Waxy corn	30.02 ± 0.02^{dG}	33.01 ± 0.20^{eF}	35.62 ± 0.18^{dE}	38.22 ± 0.33^{eD}	55.46 ± 0.26^{cC}	80.36 ± 0.61^{aB}	116.21 ± 0.69^{bA}
Pregelatinized waxy corn	33.53 ± 0.21^{bG}	35.46 ± 0.17^{dF}	43.15 ± 0.06^{bE}	48.57 ± 0.06^{aD}	58.21 ± 0.11^{bC}	78.91 ± 0.91^{bB}	124.65 ± 0.08^{aA}
Retrograded waxy corn	35.21 ± 0.24^{aF}	44.98 ± 0.07^{aE}	45.58 ± 0.22^{aE}	48.32 ± 0.31^{aD}	59.69 ± 0.20^{aC}	69.29 ± 0.56^{cB}	93.98 ± 3.61^{dA}

$^{a,\,f}$: Values in a column with the same superscript are not significantly different ($p<0.05$); $^{A,\,G}$: Values in a row with the same uppercase letters are not significantly different ($p<0.05$); ±: Standard deviation of three replicates.

waxy corn starches up to 65% hydration level (Table 4). These results indicate that physical modifications may be effective in improving starch-water interaction. Fu et al. (2014) and Wootton & Bamunuarachchi (1978) reported that gelatinization process breaks the weaker bonds in the amorph zone of the granule, hence increasing the hydration capacity of the starch molecule. Similarly, Tananuwong and Reid (2004) emphasized that heating of native starch increases the unfreezable water content, and they have observed that the completely gelatinized starch samples contain more unfreezable water than that of partially gelatinized samples. The researchers emphasized that higher temperatures induce more damage to the structure of starch granule, leading to the emergence of more hydroxyl groups to interaction with water. Fu et al. (2014), on the other hand, determined lower unfreezable water content in fully gelatinized starch samples. The unfreezable water contents of all physically modified waxy corn starch samples were higher than all physically modified corn starch samples (Table 4). This indicates that amylopectin plays an important role in starch-water interaction. A similar situation was also emphasized by Tananuwong & Reid (2004). Furthermore, as a result of this study, much higher unfreezable water content was obtained in waxy corn starch above 55% hydration levels. When hydration level is increased from 55% to 85% in native corn starch, the increase in the unfreezable water content for corn starch was 227.73%, while for corn starch was 304.06%.

4 Conclusion

The highest WAI and WSI were obtained in the pregelatinized waxy corn starch samples. The T_o, T_p and T_e values of the DSC endotherms obtained from the starch samples were increased with increase in hydration level. Unfreezable water contents of starch samples were depended on hydration level. The highest unfreezable water content was determined in retrograded waxy corn starch samples (up to 65% hydration level), whereas the lowest unfreezable water content was determined in native waxy corn starch samples (up to 55% hydration level). Therefore, it is possible to state that much more stable products may be obtained if retrograded waxy corn starch is present in starch-rich foods.

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