Effect of Different Modification Techniques on the Physicochemical and Thermoanalytical Properties of Wheat and Corn Starch

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The starches of wheat and corn treated with four different modification methods (pregelatinized, thinned with acid, cross-linked and dextrinized) were investigated in terms of changes in swelling, water-holding capacity, gelatinization and thermoanalytical properties. Modification processes caused significant changes in the physicochemical properties of the starches. Also, having effect on the thermoanalytical properties of starch, of modification process pregelatinization, cross-linking and dextrinization increased the temperatures of gelatinization initiation, peak, and final points. In addition, the modification process decreased the change in the value of entalphi. In general, peaks appeared in shorter time in corn starch amylograph than that in wheat starch for all the modified methods. The wheat starch had more swelling capacity than those of the corn starch at 30 and 40 ^oC. The modifications applied, in this study, decreased water-holding capacity of the starches of the wheat and corn at 70 ^oC.

Keywords: Modified starch, gelatinization, amylogram, water-holding capacity, swellabilty.

Farklı Modifikasyon Tekniklerinin Buğday ve Mısır Nişastasının Fizikokimyasal ve Termoanalitik Özellikleri Üzerine Etkisi

Bu araştırmada, farklı modifikasyon metotları (ön çirişlendirme, asit hidrolizi ile inceltme, çapraz bağlama, dekstrinizasyon) uygulanarak elde edilen buğday ve mısır nişastalarının su alıp şişme gücü, su tutma kapasitesi, jelatinizasyon ve termoanalitik özelliklerindeki değişimler incelenmiştir. Termoanalitik özellikler bakımından, ön çirişlendirme, çapraz bağlanma ve dekstrinizasyon işlemleri nişastaların jelatinizasyon başlangıç pik ve bitiş sıcaklıklarını artırırken, entalpi değişiminde ise azalmaya neden oldmuştur. Genelde, amilograf kurvesinde bütün modifiye metotları için mısır nişastası, buğday nişastasından daha kısa sürede pik oluşturmuştur. 30 ve 40 ºC'de buğday nişastası mısır nişastasından daha fazla su alıp şişme kapasitesine sahip olmuştur. Bu araştırmada uygulanan modifikasyon teknikleri hem buğday hem de mısır nişastasında 70 ºC'deki su tutma kapasitesinin düşmesine yol açmıştır.

Anahtar Kelimeler: Modifiye nişasta, jelatinizasyon, amylogram, su tutma kapasitesi, şişme gücü

Introduction

Starch is produced by using different methods in accordance with some properties of grain used as raw material. Progress in food industry has been rapid in varieties of product in markets, enhancing the usage area of starch and increasing demand for starch with specific properties (Karaoğlu, 1998). Scientific and technological developments in chemistry made it possible to obtain products with various properties via modification of starch. The basis of starch modification lies in the development of its functional properties by changing the physical and chemical properties of natural starch (Ortoefer, 1984).

Nonmodified starch cannot be gelatinized in cold water. Its high viscosity, amylose of nonmodified starch is prone to retrogradation. For this reason, much of in dustrial starch is modified to increase its dissolution in water, to decrease gel viscosity and minimize retrogradation tendency of amylose (Ertugay and Kotancılar, 1998; Keskin, 1987).

Chemical and physical modification of starch is widely used to produce novel products or to change physical properties of current products. Hofreiter et al. (1978) investigated effects of ∝-amylase obtained from *Bacillus subtilis* in hydrolysis of the corn starch. Those researchers determined that the short time hydrolysis (1-2 h) did not cause an important increase in compared to the control substrates in viscosity, but the long time hydrolysis (22 h) decrease in viscosity slightly.

Enzyme-resistant starch is produced through retrogradation of starch due to physical properties of crystallized amylose the main ingredient. Enzyme-resistant starch is resistant against ∝-amylase activity (Gruchala and Pomeranz, 1993). In a research, Differential Scanning Calorimetry (DSC) thermograms of resistant retrograted starch were obtained from bread, gelatinized pasta, and amylo corn starch gels by heating to 150 ^{o}C. Rather more enzyme resistant starch was found in cooked pasta than in bread, which probably was due to different degrees of starch gelatinization resulting from different process conditions. More water was available to gelatinize starch during pasta cooking than during bread baking (Sievert and Pomeranz, 1990).

In another study carried out by Donovan et al. (1983), raw potato and wheat starches were heat-treated at 100 ^{o}C for 16 h at moisture contents of 18, 21, 24, 27 and their certain properties were investigated with a DSC. It was reported that heat-treated samples showed a broadened gelatinization temperature range and shifting of the endothermal transition towards higher temperatures as compared to the untreated starches. The enthalpy values increased in with increasing moisture content of samples, and the changes were greater for potato starch than for wheat starch. In addition, they showed that, when samples were heated in the calorimeter with small amount of added water, the most extensively modified wheat starch showed three order-disorder transitions in addition to the gelatinization transition. These transitions were those for melting of amylopectin crystallites, the amylose-lipid complex and an unknown structure. Also, heat treated potato starch did not show the latter two transitions.

For cereal starch used in technical fields and in food industry, linear fraction is desired. Starch is modified with peroxide, hydroperoxide or genetically to decrease the effects of linear fraction such as gel, crust formation and extreme consistency. Thus, although both parts of starch are reacted, principial advantage is obtained by reducing the linear fraction. Starches modified in this way, not only produce clearer and stronger solutions, but also shows protective effects as emulsion constituting (Wurzburg, 1986, Çakmakcı and Çelik, 1995; Karaoğlu and Kotancılar, 2002).

Miller et al. (1991), in a study of the effects of heat process on swelling characteristics and dielectric properties of modified and nonmodified starches determined that dielectric properties and swelling characteristics of modified starch occurred at lower temperatures than they did in nonmodified starches.

Physicochemical and thermoanalytical properties of starch have a very important effect on product's quality characteristics, especially on texture and structure, made from them. The present study was conducted to determine the effects of different modified methods on the physicochemical and thermoanalytical properties of starch.

Materials and Methods

Wheat and corn starches were used as raw material in this study. The starches were purchased from a local market (Erzurum, Turkey).

Preparation of modified starch

Pregelatinization of modified starch: a 1:1 starch solution (750 g starch for 750 ml deionized water) was incubated at 63 ^{o}C for 5 min. Gelatinized starch was produced by drying and thinning at room temperature (20 ^{o}C) (Knight, 1969).

Modified starch diluted with acid: 375 ml of 0.1 M HCl solution was added to a mixture of 750 g starch and 375 ml deionized water and mixed for 30 min. Then, pH (2.26) was adjusted to 7.0 with 1 M NaOH (59.3 ml for wheat starch and 51.2 ml for corn starch). Neutralized starch was dried at room temperature following washing and then filtered through common filter paper (Çağlarırmak and Çakmaklı, 1993).

Cross-linked modified starch: The 750 g starch in 1850 ml deionize water was cooled to 5 °C and $POCl_3$ (0.25%) was slowly added for 15 min. During the addition of $POCl_3$, acidity was adjusted to pH 10 by adding 1 M NaOH (52 ml for wheat starch and 51 ml for corn starch) for 5 min. Then, the final pH of suspension was adjusted to 7.0. The suspension was filtered through common filter paper, and then washed and dried to 14-15 % moisture at room temperature (20 °C) (Karaoğlu et al. 1998). (The $POCl_3$ solution was prepared dissolving 1.7 ml $POCl_3$ in 25 ml deionized water).

Dextrinized modified starch: 750 g of starch mixed thoroughly with 600 ml of 0.1 M HCl. Then the mixture was dried at 50 °C for 32 hr until the moisture content dropped to 5 %. The dried starch was dissolved in 750 ml deionized water and then pH of which (for wheat starch 1.77 and corn starch 1.66) was adjusted to 7.0 by adding 1 M NaOH (80 ml for wheat and corn starch). The starch was dried at room temperature to moisture of 14-15 % (Çağlarırmak and Çakmaklı, 1993).

Differential Scanning Calorimetry (DSC)

Physicochemical properties of modified and nonmodified starch samples were determined with a DSC. Approximately 10 mg of starch was weighed into an aluminum pan and 20 µl of distilled water was added. The pan was sealed, allowed to equilibrate for approximately 2 h, and heated from 20 °C to 95 °C at a rate of 5°C/min (Anonymous, 1990). Initial (T_i), completion (T_c), and peak (T_p) temperature values were determined from recorded thermograms and transition enthalpy (ΔH) was calculated from the peak area.

Brabender Viscoamylograph Profiles

For viscoamylograph test, starches were scaled on a 14% moisture basis. A 45.5 g of wheat and corn starch were suspended into 360 ml of diluted amylograph buffer and transferred to the amylograph bowl by using 100 ml additional amylograph buffer. Gelatinization and pasting were determined in triplicate by heating from 30 to 95 °C at 1.5 °C/min, holding at 95 °C for 30 min. cooling from 95 to 50 °C at –1.5 °C/min and holding at 50 °C for 30 min. (Concentrated amylograph buffer was prepared by dissolving 14.8 g of sodium phosphate dibasic and 10.3 g of citric acid monohydrate in 1 L of deionized water. Diluted buffer was made by blending a 46 ml aliquot of the concentrated buffer with deionized water to 460 ml total volume) (Deffeenbaugh and Walker, 1989).

Water-Holding Capacity

Starch (1-5 g) was weighed into a tared 50-ml centrifuge tube, and 25 ml of distilled water was added, and the tube stoppered. The tube was shaken vigorously and allowed to stand for 20 min. at 25 and 75 °C, with shaking every 5 min. It was then centrifuged for 15 min at 1.000 x g; the supernatant was decanted, and the tube drained for 10 min at 45 °C. The tube was weighed, and the water-holding capacity was expressed as grams of water per gram of dry sample. Determinations were made at least in duplicate (Toykawa et al., 1989).

Swellability

Samples (1 g) were placed in a 10-ml graduated cylinders and dry volume was recorded. Ten milliliters of aqueous alcohol solution (10%, v/v) was added to each sample. The graduated cylinders were placed in a water baths set at 30 and 40 °C. The percentage increase in volume of swollen samples was calculated after 24 h (Chen and Jane, 1995). Values for investigated parameters were means of three replications.

Results and Discussion

Effect of Different Modification Techniques on Thermoanalytical Properties of Starch

Results of thermoanalytical analysis of starch samples with a DSC are shown in Table 1. As seen in the Table 1, the corn starch gelatinized at higher temperature than the wheat starch. Higher heat is required for gelatinization of the corn starch than that of the wheat starch. The botanical origin and genetic structure of starch is ones of the important factors that determine gelatinization temperature (Certel and Ertugay, 1992a)

Modification process had the same effect both on the corn starch and the wheat starch. In pregelatinized starch, initial (T_i), peak (T_p), and completion (T_c) temperatures increased while transition enthalpy (ΔH) decreased as compared to the nonmodified starch. Gelatinization temperature of starch was increased by the modification temperature and moisture content of starch (Certel and Ertugay, 1992b). The granule of starch was unfolded and degraded during pregelatinization process. Because of this, the temperature of gelatinization increased, while the amount of heat (ΔH) required for gelatinization decreased.

Since the peak (T_p) temperature of acid thinned wheat starch was about similar to that of nonmodified starch, initial (T_i) and completion (T_c) temperatures, and transition enthalpy (ΔH) were lower. Furthermore similar effects were seen for the corn starch samples. This result arised from the fact that acid-thinned modified starch was hydrated at low temperatures (Light, 1990; Çağlarırmak and Çakmaklı, 1993).

For the cross-linked modified starch, initial (T_i), peak (T_p), and completion (T_c) temperatures of the wheat or the corn starch samples were a little lower than those of nonmodified starch samples, at all. Endothermic breaking of the intra and intermolecular hydrogen bonds and their decrease during heating caused ultra molecular unfolding of starch (Certel and Ertgay, 1992a).

Increase in the number of intermolecular cross links resulted in an increase in the amount of the heat required for gelatinization.

For the all dextrinized starches, the initial (T_i), peak (T_p), and completion (T_c) temperatures were found to be higher than those of the nonmodified starch samples. While ΔH decreased in corn starch, it was increased in wheat starch samples. It has been reported that ΔH decrease with retrogratation of starch (Karim et al., 2000). Dextrinization process caused further increases in initial (T_i), peak (T_p), and completion (T_c) temperatures than both pregelatinization and cross-linking process. This increase was probably caused by sugars coming from degradation of starch. Sugar in media increased the gelatinization temperature of starch largely due to its amount (Bean et al., 1978). Fig. 1 shows typical DSC thermograms of modified and a non modified wheat and corn starch.

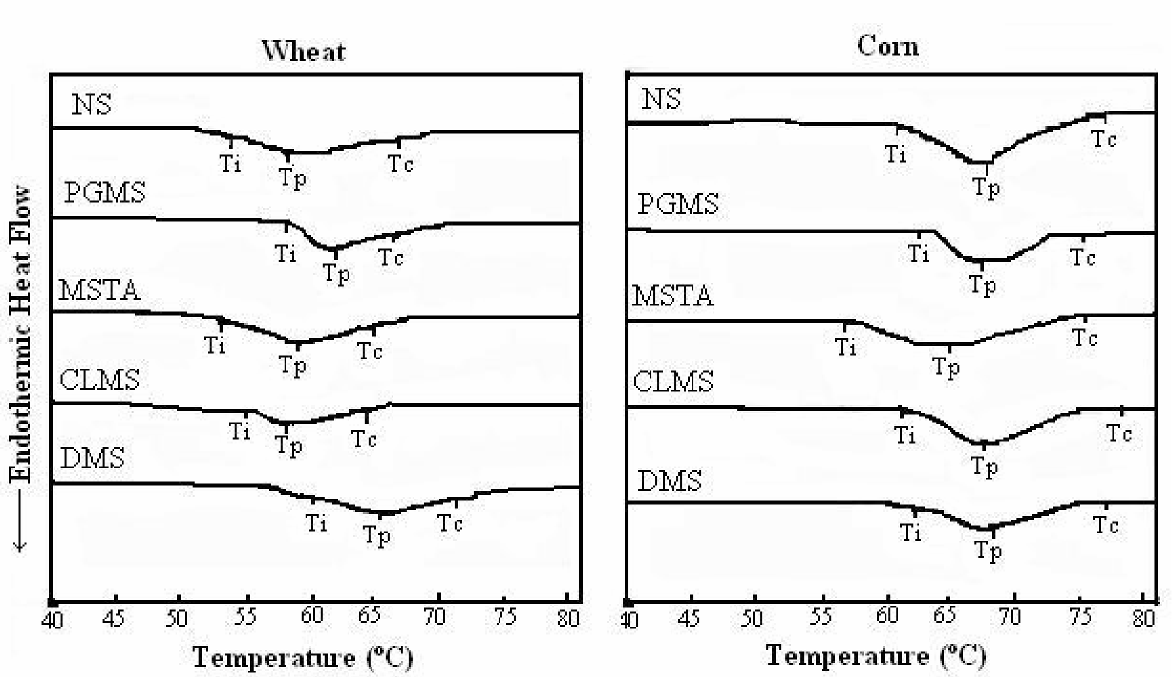
Effect of Different Modification Techniques on Pasting Properties of Starch

The amylograms of modified and nonmodified wheat and corn starches are shown in Fig. 2. The viscoamylograph is traditionally used to estimate gelatinization performance characteristics of starches. Parameters of starch cooking characteristics (peak viscosity, time to peak, viscosity at 95 °C, viscosity after 30 min at 95 °C, viscosity at 50 °C, viscosity after 30 min at 50 °C) from this viscoamylograph are reported in Table 2.

Table 1. Differential Scanning Calorimetry Characteristics of Modified Wheat and Corn Starches [a]

Starch Source	Modification	T_i	T_p	T_c	Enthalpy (j/g)
Wheat	Native	53.43	58.06	65.06	4.40
	Pregelatinized	*56.76*	*61.33*	*66.10*	*3.34*
	Thinned with acid	52.55	58.20	64.85	3.71
	Cross-linked	*53.76*	*58.01*	*65.10*	*2.07*
	Dextrinized	59.75	65.00	74.60	6.17
	X	55.25	60.12	67.14	3.93
Corn	Native	60.50	67.30	75.45	10.20
	Pregelatinized	62.00	69.15	75.30	9.10
	Thinned with acid	57.30	64.56	74.60	10.05
	Cross-linked	60.15	67.65	76.55	9.90
	Dextrinized	62.36	68.35	76.75	7.10
	X	60.46	67.40	75.73	9.27

[a] Gelatinization temperatures T_i (initial), T_p (peak), and T_c (completion)



NS = Native starch
PGMS = Pre-gelatinized modified starch
MSTA = Modified starch thinned with acid
CLMS = Cross-linked modified starch
Ti: Initial temperature
Tp: Peak temperature
Tc: Completion temperature
DMS = Dextrinized modified starch

Figure 1. Differential scanning calorimetry thermograms of native and modified wheat and corn starches

As seen in Fig. 2 and Table 2, the modification processes applied on wheat and corn starches significantly changed their cooking characteristics. Generally corn starch had shorter time than wheat starch to peak in all modified process. It is reported that wheat starch fails to show a measurable viscosity during the early stage of granule swelling (Christianson et al., 1981). The peak didn't form in the dextrinized wheat and corn starch and cross-linked corn starch. The reason of this might be that dextrinized modified starch had very low viscosity. These results were similar to the findings of Karaoğlu and Kotancılar (2001) and Luallen (1985) who reported that dextrin had a very low viscosity and very high dissociation value.

While the viscosity of pregelatinized wheat starch increasing at 95 °C, after 30 min at 95 °C, at 50 °C, after 30 min at 50 °C, it decreased for in the corn starch. When starch was cooked in water, the cohesive forces within the swollen granule weakened, and the viscosity of the paste decreased as the integrity of the granule was lost (Christianson et al., 1981). As seen in viscoamylograms (Fig. 2), as corn starch gelatinized in lover temperature than wheat starch, corn starch was affected more than wheat starch. Therefore, viscosity of pregelatinized corn starch decreased. However, when 63 °C-temperature applied in pregelatinization process affected the wheat starch less than the corn starch.

Thinned with acid process increased the viscosity at 95 °C, after 30 min at 95 °C, at 50 °C, and after 30 min at 50 °C in the both wheat and corn starches. On the contrary the dextrinization, thinned with acid process cut into pieces as partial starches. Arising of new region to do reaction with water in the molecule partially-broken starch may have on increased viscosity of the starches thinned with acid.

Cross-linked process decreased the viscosity at 95 °C, after 30 min at 95 °C, at 50 °C, after 30 min at 50 °C in wheat starch. This effect wasn't seen in corn starch. It was informed by Zheng et al. (1999) that cross-linking effectively inhibited breakdown of swollen granules, resulting in much higher viscosities in the modified starches than those in native starches.

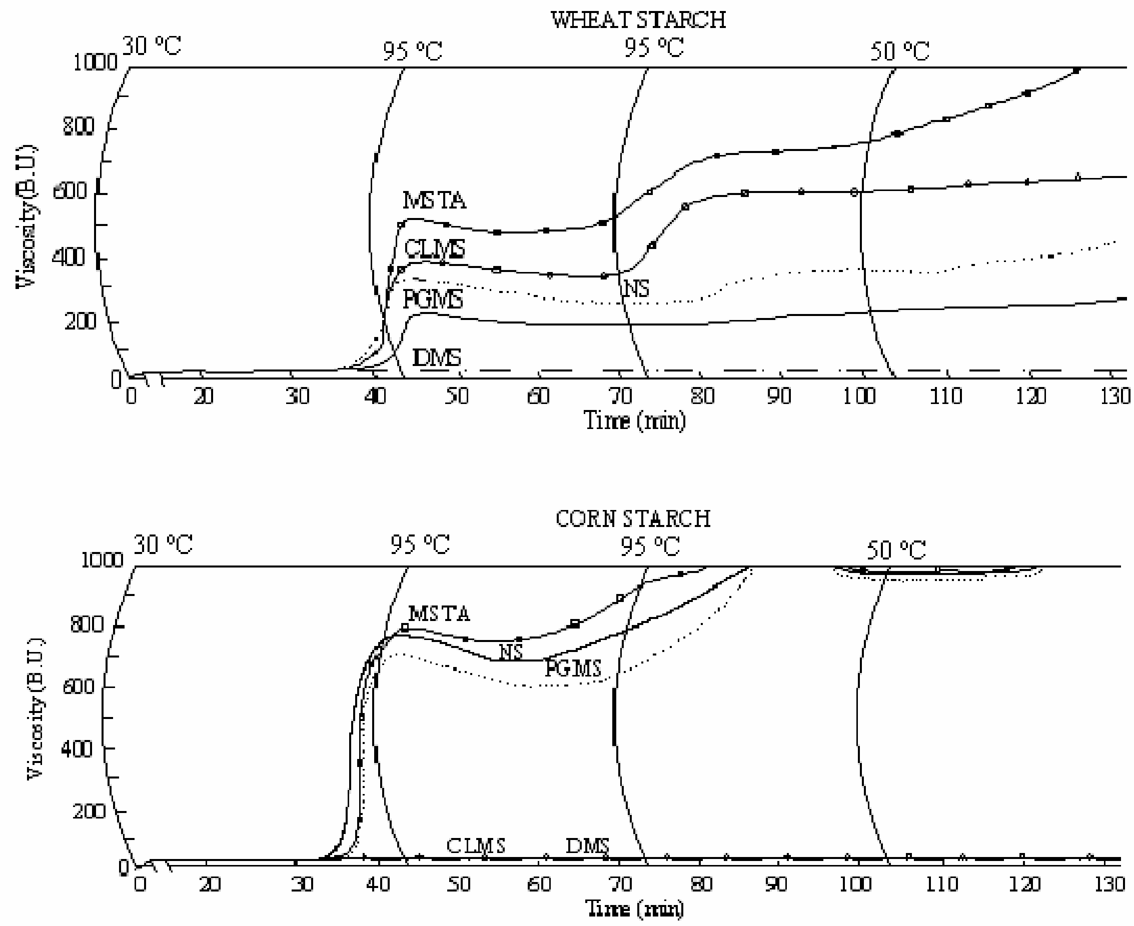


Figure 2. Brabender viscoamylograph of native and modified wheat and corn starches (NS: Native starch, PGMS: Pre-gelatinized modified starch, MSTA: Modified starch thinned with acid, CLMS: Cross-linked modified starch, DMS: Dextrinized modified starch)

Table 2. Parameters of starch cooking properties measured in viscoamylograph

Starch	Peak	Viscosity (BU)				
Source	Time (min)	Peak	at 95 °C	after 30 min at 95 °C	at 50 °C	after 30 min at 50 °C
Wheat						
Native	47	210	80	180	225	260
Pregelatinized	44	320	180	250	365	440
Thinned with acid	46	520	220	520	750	>1000
Cross-linked	51	370	200	340	600	640
Dextrinized	no peak	no peak	30	30	30	30
Corn						
Native	42	785	770	775	980	>1000
Pregelatinized	41	735	700	640	975	>1000
Thinned with acid	43	790	730	940	980	>1000
Cross-linked	no peak	no peak	30	30	30	30
Dextrinized	no peak	no peak	30	30	30	30

BU: Brabender unit

Effect of Different Modification Techniques on Swellability Properties of Starch

Swellability of native and the modified wheat and corn starches at 30 and 40 ^{o}C were shown in Fig. 3. Wheat starch had more capacity of swelling than corn starch. As wheat starch approximately contain 23% amylose, this proportion is % 27 in corn starch (Kent, 1970). Amylose content of starch significantly affects its swellability. It is informed that the former group (lower amylose content) swells more than the latter group (greater amylose content) (Toykawa et al., 1989). But, here the effective factor is the difference of the structure of the both starches than the amylose contents of them.

Effect of Different Modification Techniques on Water Holding Capacity of Starch

Water holding capacity of the native and modified wheat and corn starches were shown in Fig. 4. Native wheat starch had more water holding capacity than corn starch at 25 and 75 ^{o}C. As pregelatinization and dextrinization process increased the both water holding capacity of wheat and corn starches at 25 ^{o}C, thinned with acid and cross-linked processes decreased water holding capacity in wheat starch in the contrary to that of corn starch. Mechanical damage on starch granules increases the cold water absorption values (Comer and Fry, 1978). Because of granule of starch was bruised by pregelatinized process including heating and drying treatment, and starch was reduced into dextrin by dextrinization process. Water holding capacity of these starches were more than native starches in cold water. Because of structural differences between wheat and corn starches, thinned with acid and cross-linked processes had different effect on wheat and corn starches. On the contrary water holding capacity at 25 ^{o}C, the modification processes treated on native starches decreased water holding capacity at 75 ^{o}C. Because of modification treatments bruised granule of starch or caused to chemically and physical structural changes, modification processes decreased water holding capacity of starches at high temperature.

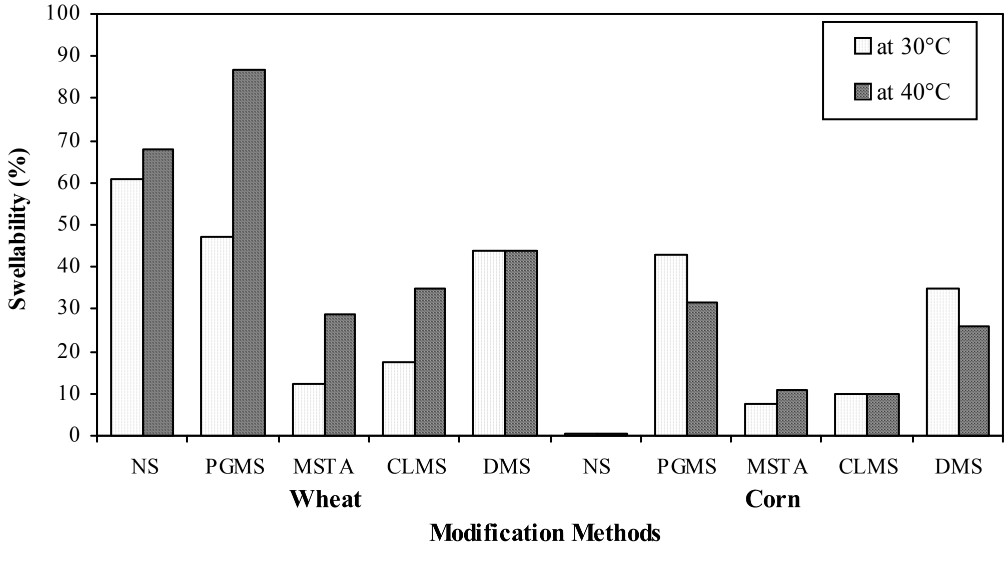


Figure 3. Swellability of granular cold-water-soluble-starch at 30 and 40 ^{o}C (NS: Native starch, PGMS: Pre-gelatinized modified starch, MSTA: Modified starch thinned with acid, CLMS: Cross-linked modified starch, DMS: Dextrinized modified starch)

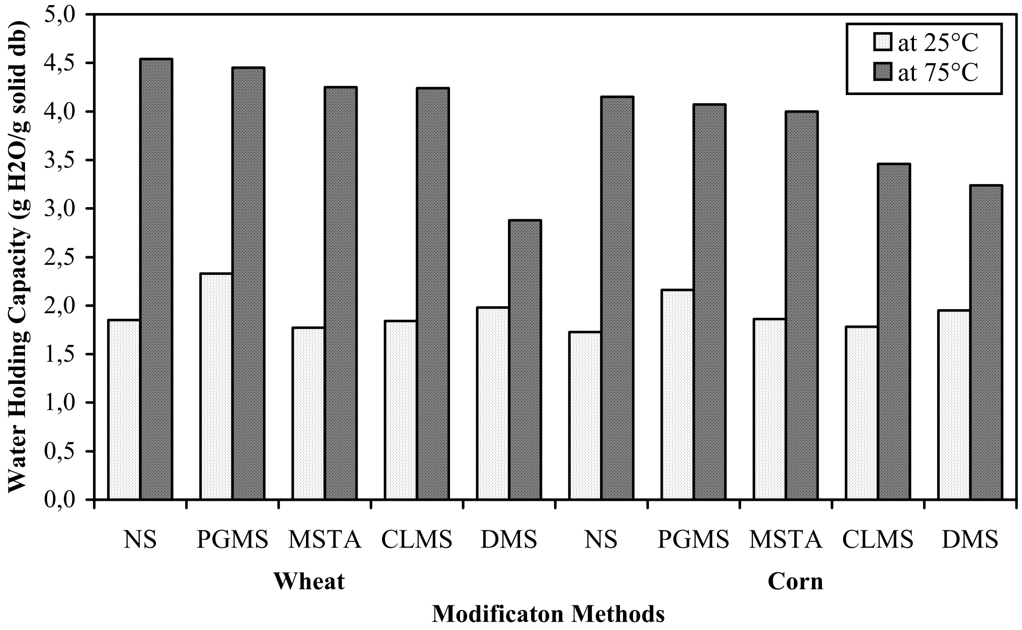


Figure 4. Water holding capacity native and modified wheat and corn starches at 25 and 75 °C (NS: Native starch, PGMS: Pre-gelatinized modified starch, MSTA: Modified starch thinned with acid, CLMS: Cross-linked modified starch, DMS: Dextrinized modified starch)

Conclusions

Each modification process caused to different structural changes in starches samples. The all properties of investigated starches were significantly affected by the modification processes applied in different manner. Consequently, by changing with proper modification method desirable properties of starches may be improved of quality of cereal products and especially product including considerably starch.

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