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PHYSICOCHEMICAL PROPERTIES OF EXTRACTED AND ACID MODIFIED STARCH FROM SOME IMPORTED AND IRAQI CORN GENOTYPES

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Abstract
The starch of ten corn genotypes (Sara, Al-Maha, Fajar -1-, Bagdad -3-, ZP.434*A, ZP.434*B, MSI*B, Dhqan, Corpeto, Dracma) were isolated, and purified to study their physicochemical and rheological properties. The capability of these natural and gelatinized starches to produce resistant starch by their responses to citric acid modification and increasing of their content of amylose also was studied. The results showed that there were significant differences among the starch in their characteristics, amylose content ranged from 19.935 to 31.095%, peak viscosity 400.00 - 584.66 AU, gel consistency 67- 121 mm, water release and light transmittance (clarity), 5.46 - 13.83%., 24.122 – 52.855% during 120h of storage respectively. On the other hand, citric acid modification of natural and gelatinized starch caused increasing of amylose content, and water binding. Acid modifying of starch increased swelling properties but caused decreasing of this characteristic for acid modified gelatinized starch.
Key words: corn starch, Amylose, Gel consistency, citric acid modification, pasting properties and resistance starch.

Introduction
Corn (Zea mays L.) is the third most important cereal crop and a major source of energy and nutrients and it is make up more than 80% of the world market for starch (Jobling, 2004 ;Jompuk et al., 2011). Corn starch is popular amongst processors because it is a valuable ingredient to the food industry due to their desirable physicochemical and techno-functional properties and being widely used as a thickener, stabilizer, textural modifiers, gelling, bulking, and water retention agent in food formulations (Yousif, 2012, Lin et al., 2015). There is also a wide range of genetic variation available in maize, producing starches with different chemical and functional properties (Wang, et al 1998). It occupies an important place either as raw material or as a food additive in the preparation of puddings, pies, confections, and salad dressings (Arocas et al., 2009). Diversity of corn genotypes has impact on different properties of starches as reported by several researchers. (Ali, et al., 2016; Sandhu and Singh, 2007) Several factors, including variety, rainfall, temperature, soil type, and growing conditions, in addition to its composition, amylose/amylopectin ratio and

granular size affect starch properties and may sometimes exhibit considerable influence than genotypic difference. (Beckles and Thitisaksakul, 2014; Lu et al., 2015).

Starch is the most abundant storage polysaccharide in plants, the second-most abundant natural biomaterial, next to cellulose (Sablani, Kasapis, & Rahman, 2007). It is present in high amounts in roots, tubers, cereal grains and legumes and also occurs in fruit and vegetable tissues. In food industries, it performs various functions as thickener, binder, disrupting agent, stabilizer, texture modifier, gelling and bulking agent, useful in the preservation of canned and frozen foods, in the formulation of syrups, essences and beverages, in confectionery and bakery, snacks and marshmallows (Copeland et al., 2009; Burrell, 2003). Another benefit of starch is improved into sugars, for instance by malting, and the starch is fermented to form ethanol, which is used in the production of whiskey (by brewing) and biofuel. Inside the pharmaceutical business, starch was used as an excipient, pill crumble, and folio (Basiak et al., 2017).

Corn also produces high amylose starch; it has an elevated level of gelatinization temperature compared to other types of starch and maintains its resistant starch content during baking, mild extrusion, and in further food processing techniques. (Eckhoff and Watson, 2009). It was utilized as an insoluble dietary fiber in processed foods—for example, bread, pasta, cookies, crackers, pretzels, and other low moisture foods (Mishra and Rai, 2006). It has been suggested that starch gives the medical advantages of unblemished entire grains (Yousif et al., 2012). Most dietary starch is consumed in cooked foods where the starch is generally fully gelatinized and readily digestible. Typically, around 95% of starch consumed is digested and absorbed as glucose within the upper gastrointestinal tract (Cassidy et al., 1994). For the remaining 5% of starch many extrinsic and intrinsic factors influence the reduced digestibility of the starch in the upper gastrointestinal tract. Therefore, a number of studies have demonstrated that a part of the starch present in the foods, called resistant starch (RS), escapes enzymatic digestion in the small intestine and reaches the large bowel where it is fermented, to a variable extent, by the colonic microflora (Sievert and Pomeranz., 1989). Authors classify starches as Slowly digestible starch (SDS), Rapidly digestible starch (RDS) and non-digested (RS). Slowly digested and non-digested starches are linked to energy control intake, while rapidly digested – to overconsumption. Starches that are relatively high in amylose content tend to be more resistant to digestion than starches with higher amylopectin content (Aller et al, 2011). A starch rich diet is associated with lower body weight, and fat mass (Raben et al., 1997). Cissé et al. (2013) have characterized the pasting properties of starches from different corn genotypes and observed considerable variability in these properties. In order to orientate the use of corn in food processing, there is a need to have knowledge of their physicochemical properties and to assess the pasting properties of the starch. The present study aims to investigate the relationship between physicochemical characteristics and pasting properties of some local and improved corn genotypes cultivated in Iraq.

Material and Methods

-Materials

Ten corn genotypes used in this study were; (Sara, Al-Maha, Fajar -1-, Bagdad -3-, ZP.434*A, ZP.434*B, MSI*B, Dhqan, Corpeto, Dracma) and synthetic variety (Sara, Al-Maha, Fajar -1- and Bagdad -3-) were obtained from the General Commission for Agricultural Research - Field Crops Research Section - Iraqi Ministry of Agriculture, while genotypes; (ZP.434*A, ZP.434*B and MSI*B) were collected by Ministry of Agriculture in Kurdistan region-Iraq, (Dhqan genotype) were produced from College of Agriculture, the University of Kurdistan, Sianandaj, Iran. Corpeto genotype from Syngenta company and Dracma genotype from Syngenta Italia S.p.A company. Six of these genotypes which are (ZP.434*A, ZP.434*B, MSI*B, Dhqan, Corpeto and Dracma) has been cultivated in the year 2019 in Qlyasan research station location of College of Agriculture Engineering Science in Sulaimani University to produce seeds.

- Methods

-Starch isolation

Corn grains (about 1 kg) has been ground by a laboratory blender, then the corn flour was mixed with water to making a ball of dough manually and the dough was immersed in a pot with a few of water and let it rest for 1 hour. the mixture (dough with water) was pressed through clean cheese cloth. The solids retained by the cloth were mixed with 1 liter of distilled water and the resulting slurry pressed through clean cheese cloth. This process was repeated until there was little or no starch in the residue. The obtained slurry was then filtered through a 75 µm mesh sieve to separate the fiber. The slurry was centrifuged at 4000 rpm. for 20 min. The grey colored, top protein-rich layer was removed using a spatula. Excess water was added to re-suspend the sample, and centrifugation was done again for 15 min. Washing and centrifugation were repeated several times until the top starch layer was white. The crude starch was purified by using proteinase-k solution (activity) to remove as it is possible of protein. The purified starch was washed with distil water and centrifuged again to discard the soluble protein. The starch was dried for 24 h at 40°C (Grant, 1998; Sandhu, Singh, and Malhi. 2005).

- Chemical composition

Moisture, for each starch sample was determined according to (AACC44-15, 2000), while protein, lipid, and ash were determined according to (AOAC, 2012). Total carbohydrate was calculated by the differences also according to (Moraes et al., 2010).

-Amylose content

Amylose content of the isolated starch was determined by using the method of Williams, Kuzina and Hlynka (1970). A starch sample (20mg) was taken and 10ml of 0.5N KOH was added to it. The suspension was thoroughly mixed. Then the sample was transferred to 100ml volumetric flask and makes the final volume to the mark with distilled water. 10ml of test starch solution was pipette out into 50ml volumetric flask and 5ml of 0.1N HCl was added followed by 2 ml of iodine reagent. The volume was diluted to 50ml and the absorbance (A) was measured at 625 nm, and the amylose content was calculated by using the following equation;

$$\text{Amylose content (\%)} = (85.24 \times A) - 13.19$$

Amylopectin (%) = 100 - % Amylose

-Amylograph Barbender

Rheological properties of native isolated corn starch pastes were measured by using Barabender amylograph (OHG Duisburg kulturstra Be 51–55, D-4100 Duisburg, Germany) according to Merco and Juliano (1981) as follows: a slurry of 50 g of starch was mixed with 450 ml of distilled water in the bowel of the amylograph. The mixture was shaken and the temperature of the sample was increased from 30 to 95 ˚C at a rate of 1.5 ˚C per min. The sample was left at 95 ˚C for 20 min, while stirring and recording the viscosity continuously. The starch paste was then cooled at 50 ˚C at a rate of 1.5 ˚C per min, while stirring and recording viscosity continuously, the viscosity in Amylograph Barabender Units (A.U.) was calculated from the obtained amylograph.

-Swelling power and solubility

Swelling power and solubility of the samples were determined according to the method of (Wang et al., 2010) with slight modification. Starch samples (500 mg) were heated with 50 mL of distilled water at a temperature of 90°C for 30 min. The samples were then cooled to the room temperature and centrifuged at 2500 × g for 15 min. The supernatant was decanted, and the residue was weighed for the estimation of swelling power. The supernatant was poured into a Petri dish and dried at 105°C and weighed. The swelling power and solubility were calculated as follows:

$$\text{Swelling power (g/g)} = \frac{\text{weight of wet sediment}}{\text{Weight of sample} - \text{weight of dried supernatant}}$$

$$\text{Solubility (\%)} = \frac{\text{weight of dried supernatant}}{\text{weight of wet sediment}} \times 100$$

-Water Binding Capacity (WBC)

Water banding capacity (WBC) of the starches from different corn cultivars was determined using the method described by Yamazaki (1953) as modified by Medcalf and Gilles (1965). A suspension of 5 g starch (dry weight) in 75 ml distilled water was agitated for 1 h and centrifuged (4000 g) for 20 min. The free water was removed from wet starch, drained for 10 minutes and wet starch was weighed.

$$\text{Water banding capacity \%} = \frac{\text{Weight of residue} - \text{Weight of sample}}{\text{Weight of sample (dwb)}} \times 100$$

-Clarity (Light transmittance %)

Turbidity of starch samples from different corn cultivars were measured by the method of (Wang et al., 2010) with slight modification. Aqueous suspension (2%) of starch each cultivar was heated in a boiling water bath at 90C˚ for 1 h with constant stirring. The suspension was cooled to room temperature, and then stored for 7 days at 4°C in a refrigerator. Transmittance was determined every 24 h by measuring absorbance at 640 nm against a water blank with an ultraviolet-visible (UV-Vis) Spectrophotometer (Refrigerated UV-M6100, Grmany).

-Syneresis

The syneresis of each starch was determined according to the method described by (Singh et al., 2006). Dispersions of 2% starch (dry base) were prepared with distilled water and heated at 90 °C for 30 min in a water bath with stirring (GFL, 1083, Germany); then cooled rapidly to 25 °C (in 6 min) using a bath with crushed ice. Samples were stored for 24, 48, 72, 96 and 120 h at 4 °C. Syneresis was determined at every 24 h and the amount of water released (expressed as a percentage of the sample mass) after the sample centrifugation (Refrigerated UV-M6100, Grmany) at 4000 rpm for 15 min.

-Determination of starch granule size

The size of starch granules was obtained from extracted corn varieties starch samples as described by (Amoo et al., 2014). A small amount of starch powder was scooped with a spatula onto a clean micro-slide (75 x 25 mm). A drop of distilled water was added and distributed thinly on the slide and covered with a glass cover slip. Starch granules were observed under a light microscope (LEICA CME, Leica Microsystems) and sizes were determined by measuring the granule diameter with an ocular micrometer fixed to the lens of the microscope. The actual sizes of the granules were calculated by multiplying their mean diameters by a factor of 2.5 µm (i. e. the factor for objective magnification that was used) which was calculated earlier using the parallax obtained between a stage micrometer (Graticules Ltd, Tonbridge, England) and the calibrations of the eye piece. A minimum of 20 granules were selected randomly and measured for each variety. Observation was done under 400x magnification. A digital camera was used in obtaining images of the starch granules under the microscope.

-Acid modification of natural and gelatinized starch

The method was done according to (Kasikitwiwatet al., 2012) with some modification. Corn starch, (15 gm) was dispersed in 40 ml of 0.1 M citric acid. The starch slurry was autoclaved at temperature 120 C˚ for 45 minutes. After heated, the mixture was cooled at room temperature in water for 30 minutes. Then the sample was incubated at 24 hours. After that, adding 30 ml of distil water and mixed well, and neutralizing with 1 M NaOH. The suspension was centrifuged at 4000 rpm for 15 minutes. The water was decanted and the pellets was washed, washing and centrifuge repeated several times. The precipitated was dried at 40 C˚ until moisture content was below 12%. Finally, the modified starch was grounded and sieved through 100 mesh screens. The same procedure was repeated with gelatinized starch (prepared by drying the starch paste that was obtained from amylograph after the test finished).

Statistical Analysis

For the analytical data, mean values and standard deviation are reported. The obtained data were subjected to one-way analysis of variance (ANOVA) at $P < 0.05$. It was performed and the results were separated using the Multiple Range Duncan's test using XLSTAT 2016 software statistical software.

-Results and Discussion

-Chemical composition

The chemical composition of the starches for ten corn genotypes are analyzed in this study is shown in (table.1) Moisture content ranged from (9.253 to 12.245%). According to statistical analysis of the results, moisture content is high and it is near to permissible value, this may be due to storage reasons. Therefore, the low moisture content reduces the risk of microbial growth during so, this will be correct (Alcázar-Alay & Meireles, 2015). The protein content of starches ranged from (0.770 to 1.540 %). Statistical analysis of the results showed significant differences among five samples of starch in their protein content The oil content of these ten starches ranged from (0.309 to 0.664 %), which is not uncommon in starches. Likewise, it has been reported that low fat and protein contents indicate high purity of isolated starches (Tirado-Gallegos et al., 2016). Ash content ranged from (0.122 to 0.214 %), These results were in a good agreement with the values reported by (Abdalla et al., 2009; Ali HEA., 2008). So, these starches obtained from hybrid corn could be classified and used as normal corn starches (Aparicio-Saguilán et al., 2004; Hardacre & Clark, 2006). The higher values of the chemical components may attribute to their responses to extraction treatments due to their differences in their structure or the physical state surrounding or the inner of starch granules.

Table.1: Proximate analysis of cornstarch extracted from studied corn genotypes

Genotypes	Ash content %	Moisture content %	Oil content %	Protein content %	Carbohydrate content %
Sara	0.126 ± 0.001^{h}	9.812 ± 0.001^{h}	0.453 ± 0.001^{h}	1.433 ± 0.058^{b}	88.176 ± 0.055^{c}
Al Maha	0.194 ± 0.001^{b}	9.253 ± 0.001^{j}	0.491 ± 0.001^{f}	1.210 ± 0.010^{d}	88.852 ± 0.009^{a}
Fajr-1	0.146 ± 0.001^{e}	10.212 ± 0.001^{d}	0.461 ± 0.001^{g}	1.433 ± 0.015^{b}	87.748 ± 0.013^{f}
Bagdad-3	0.141 ± 0.001^{f}	10.283 ± 0.001^{c}	0.592 ± 0.002^{c}	1.250 ± 0.010^{c}	87.734 ± 0.006^{f}
ZP.434*A	0.122 ± 0.001^{i}	12.245 ± 0.001^{a}	0.432 ± 0.001^{i}	1.150 ± 0.010^{e}	86.051 ± 0.010^{h}
ZP.434*B	0.214 ± 0.001^{a}	10.152 ± 0.001^{e}	0.612 ± 0.002^{b}	1.540 ± 0.010^{a}	87.482 ± 0.009^{g}
MSI*B	0.136 ± 0.001^{g}	9.644 ± 0.001^{i}	0.664 ± 0.001^{a}	1.433 ± 0.015^{b}	88.123 ± 0.014^{d}
Dhqan	0.172 ± 0.001^{d}	9.953 ± 0.001^{g}	0.584 ± 0.002^{d}	1.150 ± 0.010^{e}	88.141 ± 0.006^{d}
Corpeto	0.176 ± 0.001^{c}	10.563 ± 0.001^{b}	0.309 ± 0.002^{j}	1.143 ± 0.015^{e}	87.809 ± 0.015^{e}
Dracma	0.136 ± 0.001^{g}	10.143 ± 0.001^{f}	0.507 ± 0.002^{e}	0.770 ± 0.010^{f}	88.444 ± 0.011^{b}

Results are expressed as mean values ± standard deviation of three determinations.
Different letters in the same column indicate significant difference ($p < 0.05$). by Duncan's Test.

-Amylose and Amylopectin content

The results showed that there was a significant difference between corn varieties starches in their content of amylose and amylopectin (table 2). The amylose content varied among all of the variety's starches. The maximum value of amylose was recorded for ZP.434*B which was (31.095%) and minimum value was recorded by Sara which was (19.935%). These values of amylose percentages are in agreement with Wu, et al., (2006) who found that the range of amylose was between 18-35% for studied normal starch.

Table 2. Some physiochemical properties of cornstarch extracted from studied corn genotypes

Genotypes	Amylose %	Amylopectin %	Granule size µm
Sara	19.935 ± 0.010^{j}	80.078 ± 0.004^{a}	13.126 ± 0.001^{h}
Al Maha	24.113 ± 0.012^{g}	75.897 ± 0.001^{d}	13.863 ± 0.001^{c}
Fajr-1	20.140 ± 0.002^{i}	79.864 ± 0.002^{b}	13.730 ± 0.036^{d}
Bagdad-3	20.271 ± 0.005^{h}	79.735 ± 0.001^{c}	12.795 ± 0.001^{i}
ZP.434*A	26.669 ± 0.005^{e}	73.344 ± 0.004^{g}	13.360 ± 0.010^{f}
ZP.434*B	31.095 ± 0.003^{a}	68.910 ± 0.002^{j}	13.317 ± 0.001^{g}
MSI*B	29.531 ± 0.025^{d}	70.486 ± 0.001^{h}	15.915 ± 0.001^{a}
Dhqan	30.192 ± 0.002^{b}	73.811 ± 0.002^{e}	13.520 ± 0.010^{e}
Corpeto	29.944 ± 0.003^{c}	70.061 ± 0.002^{i}	14.415 ± 0.001^{b}
Dracma	26.319 ± 0.002^{f}	31.647 ± 0.001^{g}	13.370 ± 0.010^{f}

Results are expressed as mean values ± standard deviation of three determinations.
Different letters in the same column indicate significant difference ($p < 0.05$). by Duncan's Test.

The percentage of amylose to amylopectin plays the most important role in effect of all physical and biochemical properties which the resistant starch formation completely depends on this ratio.

-Physical properties of extracted starch

-Granule size

Starch granules consisted of different shapes. For corn starch, Generally, most of the varieties exhibited spherical shaped granules. There are differences among starch granule size that shown in (table.2). Mean granule size varied from (15.915 µm) for MSI*B to (12.795 µm) for Bagdad-3. The difference in granular size of starch is related to the variation in genetic makeup and geographical conditions, and it is an important factor that affects the starch quality (Li et al. 2008; Singh et al. 2010). Leonel et al. (2003) reported that granule shape and size are also important characteristics for the starch extraction industry since they define mesh size for application and purification sieves. Starch granule size influences water absorption, solubility, and swelling power (Hedayati et al., 2016). As well, Agnes et al. (2017) reported small starch granule sizes exhibited higher solubility and increased water absorption capacity.

Syneresis %

Significant difference is observed in syneresis % of starch gels among the corn cultivars for 5 days' storage period that shown in (table.3). The syneresis % of gels prepared from starches was measured as

Table 3. Effect of storage duration on the syneresis of starches separated from different corn genotypes.

Varieties	0 h	24 h	42 h	72 h	96 h	120 h	*%Water release increment
Sara	80.173 ±0.001^{b}	81.757 ±0.001^{b}	83.382 ±0.002^{c}	85.656 ±0.002^{b}	86.574 ±0.002^{a}	86.625 ±0.002^{a}	8.047
Al Maha	78.133 ±0.002^{f}	79.852 ±0.001^{f}	80.229 ±0.002^{i}	81.867 ±0.002^{h}	81.986 ±0.001^{j}	82.403 ±0.002^{j}	5.465
Fajr-1	78.267 ±0.001^{e}	80.658 ±0.001d	80.846 ±0.001^{f}	81.419 ±0.002^{i}	83.077 ±0.002^{h}	83.633 ±0.002^{i}	6.856
Bagdad-3	80.411 ±0.002^{a}	82.346 ±0.001^{a}	84.568 ±0.001^{b}	84.854 ±0.004^{c}	85.310 ±0.002^{c}	85.804 ±0.002^{d}	6.706
ZP.434*A	75.467 ±0.001^{j}	78.575 ±0.002^{h}	82.628 ±0.002^{d}	82.911 ±0.001^{e}	83.634 ±0.003^{g}	85.907 ±0.002^{c}	13.833
ZP.434*B	79.268 ±0.001^{c}	81.723 ±0.002^{c}	84.912 ±0.001^{a}	86.348 ±0.001^{a}	86.479 ±0.002^{b}	86.614 ±0.002^{b}	9.267
MSI*B	75.851 ±0.001^{i}	77.013 ±0.001^{i}	79.774 ±0.002^{j}	81.375 ±0.001^{j}	82.438 ±0.10^{i}	84.858 ±0.001^{g}	11.874
Dhqan	78.616 ±0.001^{d}	80.115 ±0.007^{e}	80.567 ±0.001^{h}	82.392 ±0.002^{f}	85.244 ±0.002^{d}	85.368 ±0.002^{e}	8.588
Corpeto	76.512 ±0.001^{h}	79.576 ±0.002^{g}	80.609 ±0.002^{g}	82.335 ±0.002^{g}	84.284 ±0.002^{f}	84.506 ±0.001^{h}	10.448
Dracma	77.443 ±0.001^{g}	79.853 ±0.002^{f}	81.742 ±0.001^{e}	83.983 ±0.002^{d}	84.563 ±0.002^{e}	85.326 ±0.001^{f}	10.179

Results are expressed as mean values ± standard deviation of three determinations.
Different letters in the same column indicate significant difference ($p < 0.05$). by Duncan's Test.

$$\text{*Water release incremer} \quad \frac{\text{Water release at 5 days-water release at zero time}}{\text{Water release at zero time}} \times 100$$

(Alfauomy et al., 2017)

amount of water release from the gels during storage, is an undesirable property in both food and non-food applications (Ali et al., 2016). Bagdad-3 starch paste shown the highest value (80.411%) of syneresis while ZP.434*A starch paste showed the lowest value which was (75.467%) on the zero day of storage (table.3). Al Maha starch paste showed a slower increase (78.133- 82.403) of syneresis whilst ZP.434*A showed a sharper increase (75.467-85.907%) as reported by (Ali et al., 2016). The syneresis percentage of different corn starches increased in the order of ZP.434*A > MSI*B > Corpeto > Dracma > ZP.434*B > Dhqan > Sara > Fajr-1 > Bagdad-3 > Al Maha. The syneresis percentage of starches gradually increased with the increase in storage duration. The increase in syneresis percentage during storage has been attributed to the interaction between leached amylose and amylopectin chains which leads to development of functional zones and released of water (Perera & Hoover, 1999). Amylose aggregation and crystallization have been reported to be complete within the first few hours of storage while amylopectin aggregation and crystallization occur during later stages (Miles et al., 1985). The syneresis of starch gels are indirectly affected by the structural arrangement of starch chains within the amorphous and crystalline regions of un-gelatinized granule, which in turn affects the extent of granule breakdown during gelatinization and the interaction that occurs between starch chains during gel storage (Sandhu et al., 2004). Literature also showed the differences in syneresis due to the variation in amylose, starch granule morphology, and the presence of other components in the starch (Abegunde et al., 2013).

Clarity (light transmittance %)

Clarity is a key parameter to determine the application of starches in food products because they can give brilliance or opacity to final product (Torruco-Uco and Betancur-Ancona, 2007).

Table 4. Effect of storage duration on the light transmittance percentage of starches separated from different corn genotypes.

Varieties	0 h	24 h	42 h	72 h	96 h	120 h
Sara	50.712 ±0.039^{i}	50.156 ±0.057^{h}	48.360 ±0.008^{h}	39.275 ±0.010^{i}	38.033 ±0.010^{g}	36.654 ±0.010^{f}
Al Maha	60.266 ±0.013^{d}	40.746 ±0.009^{i}	39.407 ±0.047^{i}	38.924 ±0.019^{j}	37.856 ±0.010^{h}	28.202 ±0.020^{i}
Fajr-1	59.31± 0.034^{f}	58.751 ±0.004^{b}	49.541 ±0.028^{g}	47.326 ±0.011^{f}	46.246 ±0.008^{e}	44.171 ±0.012^{d}
Bagdad-3	45.416 ±0.033^{j}	42.860 ±0.006^{i}	42.462 ±0.008^{i}	41.126 ±0.011^{h}	46.246 ±0.011^{e}	34.923 ±0.009^{g}
ZP.434*A	59.574 ±0.007^{e}	58.222 ±0.011^{d}	54.576 ±0.004^{d}	54.341 ±0.015^{c}	45.635 ±0.011^{f}	37.511 ±0.013^{e}
ZP.434*B	58.790 ±0.056^{h}	55.853 ±0.006^{f}	55.343 ±0.009^{c}	44.472 ±0.005^{g}	30.145 ±0.009^{j}	24.122 ±0.023^{j}
MSI*B	64.576 ±0.030^{b}	57.553 ±0.010^{e}	52.769 ±0.138^{f}	51.291 ±0.005^{e}	47.873 ±0.008^{d}	29.800 ±0.019^{h}

Dhqan	67.295 ±0.006[a]	63.981 ±0.007[a]	63.690 ±0.007[a]	59.313 ±0.018[a]	54.340 ±0.014[c]	51.898 ±0.017[b]
Corpeto	59.179 ±0.023[g]	54.522 ±0.0036[g]	53.623 ±0.030[e]	53.669 ±0.504[d]	50.026 ±0.013[c]	48.535 ±0.007[c]
Dracma	61.385 ±0.010[c]	58.285 ±0.0056[c]	56.911 ±0.015[b]	56.901 ±0.021[b]	56.635 ±0.009[a]	52.855 ±0.009[a]
Results are expressed as mean values ± standard deviation of three determinations. Different letters in the same column indicate significant difference ($p < 0.05$). by Duncan's Test.						

In (table.4) shown the transmittance value of all corn varieties starch suspension after 24 hours of storage at 4C° significantly varied, which are ranged from (40.746 – 63.981 %). The light transmittance of the (MSI*B and ZP.434*B) varieties gel decreased sharply from (64.576 and 58.790 %) to (29.800 and24.122 %) respectively after 5 days which storage at 4C° which represented a third of light transmittance reduction. While Dracma variety gel recorded maximum value of light transmittance (52.855 %) after 5 days with storage at 4C°, and the decrease of light transmittance was slightly after the same duration of storage, the same results was reported in previous studies by (Ashwar et al., 2014; Simi and Abraham, 2008). Sandhu and Singh (2007) also reported an increase in turbidity of corn starch gels with storage. The light transmittance of starch paste is a function of the amount of swollen starch granules in the paste, which refracts light (Mahto and Das 2014). The increase in turbidity value during storage duration perhaps due to granule swelling, granule remnants, the leached amylose and amylopectin chains, the aggregation and crystallization of amylose that leads to the development of turbidity and decreased light transmittance in starch pastes during refrigerated storage (Sandhu et al., 2008; Kaur et al., 2007; Perera & Hoover, 1999). In some products like soups, sauces and puddings low transmittance is not an obstacle while in jellies and fruit fillings types of products starch pastes with high clarity are desired (Sindhu and Khatkar 2018). Phosphorus is present in starches in the shape of phosphate monoesters and phospholipids. The phosphate monoesters bound covalently to the amylopectin fraction of the starch and improve starch paste clarity and viscosity while phospholipids bound to the amylose fractions of the starch results in opaque and reduce viscosity pastes of starch with reduced light transmittance percentage (Craing 1989). Gradual storage at refrigeration temperature (4C°) transmittance was found to decrease significantly in all starch samples as shown in table 3. Shorthand in paste clarity during storage was also observed by (Ali et al., 2016) in rice and corn starches. Retrogradation of gelatinized starch during storage develops the turbidity in paste. Existence of amylose and amylopectin with long chain are liable to retrograde rapidly consequently, influences the light transmittance of starch paste during storage, that will be suggested by (Bhupender et al., 2013).

Pasting Properties

The pasting properties of starches is a one of most important rheological parameter which are determined by amylograph. Pasting properties may affect by the starch granules composition and structure such as amylose/amylopectin ratio and branched chain length and numbers, in addition to other factors, lipid, protein contents, and swelling power (Uarrota et al., 2013; Li et al., 2008). The differences in pasting properties of corn varieties are also reported in literature (Amaya-Llano et al., 2011; Ketthaisong et al., 2013).

1-Pasting temperature

As can be observed (table.5), the past temperature (temperature at the onset of rise in viscosity) significantly varied among all corn genotypes and ranged from (85 to 73˚C). the highest pasting temperature was recorded by (Dracma and Dhqan) varieties which were (85 and 84° C) respectively, while the lowest value was (73˚ C) which recorded by (Corpeto) genotype. The high pasting temperature for corn starches indicated their higher resistance towards swelling. All the starch samples showed gradual increase in viscosity with the increase in temperature (Singh et al., 2004). The pasting temperature provides an indicator of the minimal temperature required for sample cooking, energy cost involved and another components stability (Ikegwu et al., 2009). It also provides an indicator for the gelatinization time during processing (Odedeji nnd Adeleke, 2010).

2-Peak viscosity

The peak viscosity values of corn varieties starches were in the range of (584.667 – 400 B.U) and varied ($p < 0.05$) (table.5) among the corn genotypes. Dracma had the highest peak viscosity of (584.667 BU) followed by Corpeto which record (561 B.U), whiles MSI*B had the lowest peak viscosity of (400 B.U). The high peak viscosity observed in Dracma means that it may be suitable for products requiring high gel strength and thick paste (Amoo et al., 2014). high peak viscosity in carbohydrate food is an indication of high starch content (Adebowale et al., 2005; Shimelis et al., 2006). Peak viscosity is a measure of the water-holding capacity of the starch in terms of the resistance of swollen granules to shear and the swelling performance of granules (Newport Scientific,1995). Schoch & Elder (1955) had reported that higher peak viscosity indicates higher swelling power. The swelling behaviors of the starches may be affected by the structural arrangements of their constituent amylose and amylopectin.

4- Peak (Cooking) time

This parameter is used to determine the spent time to reach to peak viscosity during increasing the temperature 1.5°C /min. from 30°C to 95°C. As shown in (table.5) Peak time was significantly varied among corn starch varieties and ranged from (52.5 to 43 min). Among the varieties, the highest peak time was observed by Dhqan which was (52.5 min) while the lowest peak time was recorded by ZP.434*B which was (43 min). peak time and pasting temperature were similar in Dhqan and MSI*B which both required a longer time to reach maximum viscosity Unlike the rest, which they required moderate peak time and pasting temperature for reaching maximum viscosity. The similar results were reported by (Jiménez-Hernández et al., 2007).

5- Trough viscosity or Hot Paste Viscosity (HPV)

The Trough Viscosity or Hot Paste Viscosity (HPV) After a 20 min hold at 95°C, ranged from (521 to 425 BU) in (table.5) which are recorded for the first four of corn starch genotypes Sara, Al Maha, Fajr-1 and Bagdad-3 (425, 441, 515 and 521 BU) respectively. HPV is influenced by the rate of amylose exudation, amylose-lipid complex formation, friction between swollen granules and granule swelling, and competition between exudate amylose and residual granules for free water (Zhang and Zhai., 2020; Olkku and Rha, 1978). Starches whose amylose portion leaches out into the aqueous phase more fast, have been shown to readily undergo re-association leading to higher hot paste viscosities (Singh et al., 2006).

6- Breakdown viscosity

According to results which shown in (table.5), the breakdown viscosity was recorded only for Sara, Al Mhah, Fajr-1 and Bagdad-3 which were (43, 40, 25 and 45 BU) respectively. The maximum value was by Bagdd-3 (45 BU) and the minimum value was recorded by Fajr-1 (25 BU), and the other corn genotypes didn't record any values. breakdown (BD, the difference between peak viscosity and the hot paste viscosity). Breakdown viscosity is caused by the disintegration of gelatinized starch granule structure during continued stirring and heating (Huber and BeMiller, 1997). The differences in moisture content of corn starch have excessively influenced the breakdown viscosities, this intention perhaps applied for corn varieties starch. furthermore, the decrease in breakdown viscosities of starches might be due to incomplete pasting and swelling of starch granules, crosslinking, and greater resistance to snip and heat of starch paste, and a minimum degree of expansion of starch granules (Gao et al., 2020)

7- Peak viscosity at cooling or Cool Paste Viscosity (CPV)

According to results which shown in (table.5), peak viscosity at cooling or means cool paste viscosity (CPV) was significantly difference among corn starch genotypes and ranged from (1220 to 840 BU), the highest value recorded by Dhqan which was (1220 BU) and the lowest value was recorded by MSI*B which was (840 BU). Cool paste viscosity for all the starches were higher than their corresponding peak viscosity (PV) and hot paste viscosity (HPV). The increase in CPV of all the starch varieties could be attributed to aggregation of the amylose molecules on cooling (Kaur et al., 2007). There was a general increase in viscosity when paste was cooled to 50°C. Final viscosity formed at the end of cooling at 50°C is called cold paste viscosity (CPV). The differences amongst varieties in CPV may be associated with differences in amylose contents. High amylose starches have been found to re-associate more easily than high amylopectin starches. This is because the linear chains can orient parallel to each other, moving close enough together to bond (Shimelis et al., 2006). This type of viscosity is used to define a particular quality of starch, and it also indicates the stability of cooked starch paste in actual use. In addition to, it indicates the ability of a starch to form a paste or gel after cooling (Shimelis et al., 2006). This viscosity is an important property if extruded starch is to be used as an ingredient in foods that require cold thickening capacity like instant creams, sauces or (Alves et al., 1999). Collado et al., (2001) also reported that, the starches that have high cold positive viscosities are better for production of noodles. A side from the sensory properties, stronger gels are preferred for noodles making, because they are more stable to boiling and will maintain its structure (Hou, 2010). It has also been suggested, that the starch used for preparing noodles must restrict swelling and maintain or increase its viscosity during continued heating and shearing (Collado et al., 2001).

8-Setback viscosity

Setback viscosity it means the difference between cold paste viscosity (CPV) and hot paste viscosity value (HPV) (Chinnasamy et al., 2022). According the results that shown in (table.5), the setback viscosity of corn starches was in the range of (735 to 375 BU) and varied ($p < 0.05$) among genotypes. Which the highest value recorded to Bagdad-3 and the lowest value recorded to Dracma. The differences in setback viscosity among genotypes could be attributed to variations in amylose contents and its gelation capacities. There was a negative correlation between setback viscosity and amylose content (Chisenga et al., 2019). This suggests that starches with high amylose content had low setback viscosity values. This is in agreement with (Morante et al., 2016), who reported, the setback viscosity values in cassava waxy starches higher than normal starches. This observation could be related to the failure of short chains to form double helices and therefore responsible for less organized granular structure (Morante et al., 2016). Low setback viscosity values are useful for products like weaning foods, which require low viscosity and paste stability at low temperatures (Oduro et al., 2001).

Table 5. Pasting properties of starch from ten corn genotypes.

Varieties	Past Temp.	Peak Viscosity	Peak Temp	Peak Time	Heat stability (trough viscosity)	Break down viscosity	Peak viscosity at cooling	Peak set
Sara	78.000 ±1.000[c]	483.000 ±1.000[f]	97.000 ±1.000[e]	44.500 ±0.100[d]	441.000 ±1.000[c]	43.000 ±1.000[b]	1130.000 ±1.000[e]	700.000 ±1.000[c]
Al Maha	77.500 ±0.100[cd]	555.000 ±1.000[c]	97.000 ±1.000[e]	45.500 ±0.100[cd]	521.000 ±1.000[a]	40.000 ±1.000[c]	1130.000 ±1.000[e]	605.000 ±1.000[e]
Fajr-1	77.000 ±1.000[cd]	541.000 ±1.000[d]	99.000 ±1.000[d]	46.000 ±1.000[c]	515.000 ±1.000[b]	25.000 ±1.000[d]	1010.000 ±1.000[f]	500.000 ±1.000[h]

Bagdad-3	80.000 ±1.000^{b}	468.000 ±1.000^{g}	97.000 ±1.000^{e}	45.500 ±0.100^{cd}	425.000 ±1.000^{d}	45.000 ±1.000^{a}	1145.000 ±1.000^{d}	735.000 ±1.000^{a}
ZP.434*A	77.500 ±0.100^{cd}	463.000 ±1.000^{h}	102.000 ±1.000^{c}	48.000 ±1.000^{b}	0.000	0.000	1180.000 ±1.000^{b}	705.000 ±1.000^{b}
ZP.434*B	76.533 ±0.058^{d}	468.000 ±1.000^{g}	95.000 ±1.000^{f}	43.000 ±1.000^{e}	0.000	0.000	1175.000 ±1.000^{c}	635.000 ±1.000^{d}
MSI*B	79.500 ±0.100^{b}	400.000 ±1.000^{i}	136.000 ±1.000^{a}	47.500 ±0.100^{b}	0.000	0.000	840.000 ±1.000^{i}	560.000 ±1.000^{g}
Dhqan	84.000 ±1.000^{a}	535.000 ±1.000^{e}	109.000 ±1.000^{b}	52.500 ±0.100^{a}	0.000	0.000	1220.000 ±1.000^{a}	600.000 ±1.000^{f}
Corpeto	73.000 ±1.000^{e}	561.000 ±1.000^{b}	101.000 ±1.000^{c}	48.500 ±0.100^{b}	0.000	0.000	990.000 ±1.000^{g}	405.000 ±1.000^{i}
Dracma	85.000 ±1.000^{a}	584.667 ±0.577^{a}	99.000 ±1.000^{d}	46.000 ±1.000^{c}	0.000	0.000	985.000 ±1.000^{h}	375.000 ±1.000^{j}

Results are expressed as mean values ± standard deviation of three determinations.
Different letters in the same column indicate significant difference ($p < 0.05$). by Duncan's Test.
*BU: Barbender unit; Temp; Tempreture

-Physicochemical properties of modified starch

-Amylose content

The main goal of modify starch by citric acid is to increase amylose content which it can increases resistant starch formation (ref). The results in (table.6) showed that citric treatment of both natural and gelatinized starch caused significantly increasing of their amylose content of all corn varieties starches. Corpeto exhibited a slight increase in amylose content. On the other hand, Sara showed a highly response toward citric acid treatment since its content of amylose increased from 19.935 to 31.22 and 30.069 of acid modification for both starch and gelatinized starch respectively. This behavior of this type of starch may due to its structure more than amylose formation. It was noticed (unpublished data) that the natural starch of this variety of corn had a highly resistance to amylases activity but after acid treatment it lost its resistance which may attribute this behavior somewhat to its structure.

The increment of amylose content may be attributed to the formation of intra- and inter-molecular bonds between amylose chains, resulting in an increase in the length of these chains which derived from the acid hydrolysis of amylopectin side chains and produce amylose that bind can with iodine (Shin et al., 2004; Bao et al., 2022). Another possible reason may be attributed to the de-polymerization of amylopectin fractions on continuous acid hydrolysis. High degree of acid hydrolysis led increased apparent amylose content of starch (Betancur and Chel., 1997).

Table 6. Effect of citric acid modified on amylose content of studied cornstarch genotypes

Genotypes	Amylose %		
	Normal Starch	Acid modified starch	Acid modified gelatinized starch
Sara	19.935 ±0.010^{j}	31.220 ±0.001^{h}	30.069±0.001^{f}
Al Maha	24.113 ±0.012^{g}	29.730 ±0.002^{j}	28.066±0.001^{h}
Fajr-1	20.140 ±0.002^{i}	33.863 ±0.001^{c}	35.396±0.001^{b}
Bagdad-3	20.271 ±0.005^{h}	33.138 ±0.001^{d}	34.676±0.001^{d}
ZP.434*A	26.669 ±0.005^{e}	32.498 ±0.001^{f}	30.197±0.001^{e}
ZP.434*B	31.095 ±0.003^{a}	35.612 ±0.001^{b}	35.269±0.001^{c}
MSI*B	29.531 ±0.025^{d}	35.722 ±0.001^{a}	35.152±0.001^{a}
Dhqan	30.192 ±0.002^{b}	32.584 ±0.001^{e}	27.298±0.001^{i}
Corpeto	29.944 ±0.003^{c}	29.942 ±0.001^{i}	29.473±0.001^{g}
Dracma	26.319 ±0.002^{f}	31.647 ±0.001^{g}	30.070±0.001^{f}

Results are expressed as mean values ± standard deviation of three determinations. Different letters in the same column indicate significant difference ($p < 0.05$). by Duncan's Test.

-Swelling power g/g

The swelling power g/g values as shown in (table. 7) was significantly varied among corn starch varieties.

Swelling power is determined after heating the starch in surplus water and is expressed as the ratio of the wet weight of the (sediment) gel formed to its dry weight. It depends on the processing conditions such as (temperature, time, stirring, and centrifugation) and is thought of as its water binding capacity (Raungrusmee and Anal., 2019). The swelling power of acid modified starches was lower in all cases as compared to native starches except two varieties. The recorded values for native starches ranged from (15.232 to 11.906 g/g). The maximum values recorded by V10 which was (15.232 g/g), while the minimum value recorded by V4 which was (11.906 g/g). Kaur et al. (2007) studied the effect of aqueous HCl on properties of wheat starch and found that swelling power decreased from 15.4 to 5.0 g/g with increase in modification time. The reduction in swelling power of acid modified starches was reported due to increase in high proportion of soluble dextrin of both small and medium chain lengths in starch granules (John et al., 2002). Swelling power of starch is greatly affected by the amylopectin content and the amylose/amylopectin distribution. The devastation of the starch granular structure during acid hydrolysis may be responsible for the lower swelling power of lintnerized-autoclaved starch. The acid hydrolysis results in leaching of the amylose and in increasing short chain amylopectin results in a branched structure with less ability to swelling (Winarti et al., 2014).

Table 7. Effect of citric acid modification on swelling power of studied cornstarch genotypes

Genotypes	Swelling power g/g		
	Normal starch	Acid modified starch	Acid modified gelatinized starch
Sara	14.705 ±0.001^{b}	11.315 ±0.015^{f}	8.924 ±0.009^{h}
Al Maha	14.416 ±0.001^{d}	10.611 ±0.014^{g}	9.059 ±0.005^{g}
Fajr-1	14.267 ±0.002^{e}	7.839 ±0.019^{j}	8.424 ±0.008^{i}
Bagdad-3	11.906 ±0.001^{j}	9.307 ±0.014^{i}	8.921 ±0.007^{h}
ZP.434*A	13.852 ±0.001^{g}	13.042 ±0.007^{c}	10.277 ±0.005^{d}
ZP.434*B	13.360 ±0.031^{i}	10.193 ±0.006^{h}	9.134 ±0.005^{f}
MSI*B	14.026 ±0.001^{f}	11.871 ±0.009^{e}	9.492 ±0.005^{e}
Dhqan	13.546 ±0.005^{h}	12.336 ±0.010^{d}	10.811 ±0.014^{b}
Corpeto	14.527 ±0.010^{c}	13.566 ±0.009^{a}	10.585 ±0.007^{c}
Dracma	15.232 ±0.003^{a}	13.196 ±0.010^{b}	12.391 ±0.006^{a}

Results are expressed as mean values ± standard deviation of three determinations.
Different letters in the same column indicate significant difference ($p < 0.05$). by Duncan's Test

-Solubility %

The solubility % values as shown in (table.8) was significantly varied among corn starch genotypes. Solubility index of native starches was lower compared to acid modified starches. The values which recorded by modified starches ranged from (14.497 to 6.274 %), the maximum value recorded by Bagdad-3 which was (14.497%)while the minimum value recorded by Al Maha which was (6.274%), although Al Maha value is low but it is more than its counterpart in native starch. It has been reported that starches treated with citric or lactic acid had a higher solubility than untreated starch (Hung et al., 2016). Fannon et al. (1992) reported that channels existent in starch granules may also be responsible for

Table 8. Effect of citric acid modification on solubility of studied cornstarch genotypes

Genotypes	Solubility %

	Normal starch	Acid modified starch	Acid modified gelatinized starch
Sara	9.142±0.001^{b}	10.254±0.009^{d}	5.020±0.001^{c}
Al Maha	7.721±0.001^{d}	6.274±0.009^{j}	3.052±0.001^{j}
Fajr-1	5.522±0.001^{i}	14.215±0.009^{b}	6.558±0.001^{a}
Bagdad-3	5.783±0.002^{h}	14.497±0.013^{a}	3.583±0.001^{h}
ZP.434*A	7.122±0.010^{f}	9.573±0.006^{f}	4.175±0.002^{f}
ZP.434*B	8.608±0.007^{c}	10.168±0.007^{e}	4.573±0.002^{d}
MSI*B	7.526±0.005^{e}	9.160±0.006^{g}	3.813±0.007^{g}
Dhqan	7.066±0.003^{g}	8.364±0.008^{h}	4.478±0.002^{e}
Corpeto	5.019±0.007^{j}	6.320±0.014^{i}	3.355±0.004^{i}
Dracma	9.363±0.003^{a}	12.281±0.004^{c}	5.537±0.003^{b}
Results are expressed as mean values ± standard deviation of three determinations. Different letters in the same column indicate significant difference ($p < 0.05$). by Duncan's Test			

assisting permeation and increase the potential surface area available for reaction and penetration of reagents in granules. This increase in solubility capacity of lintnerized-autoclaved starch is attributed to change in granule structure, decrease in molecular weight and increase in amylose content (Raungrusmee and Anal., 2019). Previous research which studies by KoKsel et al., (2007) and Ozturk et al., (2009) have been reported a significant increase in water solubility capacity and water banding capacity as a result of heating and autoclaving treatments. This increase in solubility capacity of treated starch refers that the lintnerization-autoclaving treatment method for the preparation of resistant starch is convenient for the development of food products requiring high water binding properties (Dundar and Gocmen., 2013).

-Water Binding Capacity % (WBC)

A significant difference was observed in the Water Binding Capacity WBC among the corn genotypes starches which shown in (table.9). For normal corn genotypes starches the highest value was recorded by Bagdad-3 (165.341 g/g) while the lowest value was recorded by Dracma (109.896 g/g), also Sara, Fajr-1 recorded maximum value which was (157.520 and 157.506) g/g respectively. While the treated starches by acid modification were dominated normal starches in recoding values, the maximum value was recorded by Dracma which was (243.400 g/g) and the minimum value recorded by MSI*B which was (141.114 g/g) and WBC for each of Al Maha and Fajr-1 in treat starches were (227.065 and 217.980) g/g respectively. While for the third type of starches which was amylograaph starch result and treat by

Table 9. Effect of citric acid modification on water binding capacity of for cornstarch genotypes	
Genotypes	water binding capacity %

	Normal starch	Acid modified starch	Acid modified gelatinized starch
Sara	157.520 ±0.010[b]	243.400 ±2.052[a]	212.200 ±1.542[a]
Al Maha	123.880 ±0.010[h]	227.065 ±1.001[b]	211.973 ±1.529[a]
Fajr-1	157.506 ±0.001[c]	217.980 ±5.863[c]	187.128 ±1.022[c]
Bagdad-3	165.341 ±0.001[a]	203.640 ±0.995[d]	176.255 ±1.010[d]
ZP.434*A	131.235 ±0.001[f]	153.583 ±1.046[f]	192.640 ±1.028[b]
ZP.434*B	134.746 ±0.001[d]	156.081 ±1.061[f]	127.735 ±1.020[h]
MSI*B	123.126 ±0.001[i]	141.114 ±1.005[h]	135.342 ±0.587[f]
Dhqan	131.414 ±0.005[e]	145.213 ±0.985[g]	130.593 ±1.024[g]
Corpeto	125.692 ±0.001[g]	167.409 ±1.004[e]	157.655 ±0.995[e]
Dracma	109.896 ±0.001[j]	154.566 ±1.001[f]	176.971 ±1.007[d]
Results are expressed as mean values ± standard deviation of three determinations. Different letters in the same column indicate significant difference ($p < 0.05$). by Duncan's Test			

acid, the maximum value recorded by Sara and Al Maha which were (212.200 and 211.973) g/g respectively, and the minimum value was recorded by ZP.434*B which was (127.735 g/g). These results agree with Babu et al., (2015a) and Wani., (2015) whom reported that acid modify may probably increase the low molecular weight starch fraction with hydroxyl groups which may hold water molecules forming hydrogen bonds consequently increasing the WHC. therefore, this high water holding capacity of citric acid treated starches may find a significant role as a fat replacer Babu et al., (2015b).

Conclusion

This research found that although, there is an effective effect of cornstarch content of amylose and amylopectin on its functions and properties but the packing of amylose and amylopectin in the inner of starch granules had important role in determine the starch response to physiochemical treatments. This phenomenon is closely attributed to the difference in corn types that were used in this research. To produce resistance starch, using of citric acid to increase amylose content in natural cornstarch and gelatinized starch emphasized that in general natural cornstarch more response to this treatment than gelatinized starch may due to the formation of different crystal which somewhat resists citric acid treatment. Citric acid treatment had different effects on main starch properties such as swelling power, solubility and water binding.

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