Journal of Food Science and Technology (Iran)

Homepage:www.fsct.modares.ir

Scientific Research

Physicochemical and functional properties of modified quinoa starch with adipic acid and acetic anhydride mixture

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ABSTRACT

In this research, quinoa starch samples were evaluated in 9 treatments with different proportions of adipic acid and acetic anhydride mixture (ratio 1 to 30), along with a control sample in terms of physicochemical and functional characteristics and determining the optimal conditions for chemical modification. The mentioned treatments were designed by 3 independent variables affecting chemical modification, including chemical modifier concentration (2%, 4% and 6%), suspension pH (8, 8.5 and 9) and reaction time (60, 90, 120 minutes) by Taguchi method. became The swelling power and water absorption capacity of sample T2 (modifier concentration 2%, suspension pH 9 and reaction time 120 minutes) significantly increased compared to the control sample, which is a sign of the formation of crosslinks along with the formation of stable three-dimensional gel networks. Spectroscopy results showed that except for T2 sample, the rest of the samples had a slight tendency to retrogradation, which was a sign of the high stability of the said sample during the retention period to syneresis ($p<0.05$). Acetylation significantly improved the solubility characteristics compared to the control sample due to the better dispersion of starch in the aqueous medium. With the increase in the modifier concentration, the stability of the samples against the freeze-thaw cycle decreased significantly ($p<0.05$). The investigated parameters in measuring the thermal characteristics of modified quinoa starch were evaluated with a significant difference more than the control sample. The apparent viscosity of the T2 sample at the shear speed of 20, 50 and 100 rpm increased significantly compared to the control sample, but the other samples showed a lower viscosity. Also, using Taguchi analysis, the optimal treatment of modified quinoa starch with 2% modifier concentration, suspension pH 9 and reaction time 120 minutes was determined.

ARTICLE INFO

Article History:

Received 2022/ 01/ 05
Accepted 2023/ 02/ 02

Keywords:

Acetylation,
Adipic acid,
Chemical modification,
Cross-linking,
Functional properties,
Quinoa starch,
Taguchi Method.

DOI: 10.22034/FSCT.19.135.113
DOR: 20.1001.1.20088787.1402.20.135.10.6

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[DOR: 20.1001.1.20088787.1402.20.136.10.8]

[DOI: 10.22034/FSCT.20.136.117]

1. Introduction

Quinoa is a plant with a scientific name (*Chenopodium quinoa Willd*) which recently attracted a lot of attention and today its cultivation has spread in several countries such as Australia, Canada, Peru, China and England [1]. Quinoa is a semi-cereal and due to its high genetic diversity, it has high resistance to biological stresses, which leads to its adaptation and growth in adverse environmental conditions [2]. Quinoa is naturally gluten-free and provides a valuable source of digestible protein for gluten-sensitive individuals (coeliac patients).[1]) provides [3]. In addition, quinoa seeds contain bioactive compounds such as carotenoid, phenolic compounds, which in many studies are protective against diseases such as cancer, allergies, inflammatory diseases and the possibility of reducing the risk of cardiovascular diseases [4]. One of the main components of quinoa seed is starch, which makes up more than 50% of its dry weight [5]. Quinoa starch has polymorph[2] Type A and small granules approximately between 1-3 µm with a high potential for food applications distinguish it from other starches [6]. Starch is mainly composed of amylose and amylopectin. Amylose is a linear glycosyl chain connected by (4 and 1)-α linkages. While amylopectin has many side branches that are connected with (6 and 1)-α connections [7]. The amount of amylose on the functional and physicochemical characteristics of starch, including the characteristics of pasting, gelatinization, and retrogradation.[3] And inflation has an effect. The distribution of branches along the amylopectin chain and its internal structure has a significant effect on the physicochemical properties of starch such as swelling ability, adhesion, retrogradation, thermal properties and its solubility ratio in water [8, 9]. The use of starch in a normal or unmodified form[4] It is very little, but its hydrolyzed and modified product is widely used [10]. Problems such as insufficient solubility of starch in water, retrogradation, syneresis[5] and separation of serum, reduction of viscosity due to decomposition of glycosidic bands during treatment, high temperature of starch gelatinization, reduction of resistance and decomposition in long heat treatments, shear force or acid conditions, and the absence of some important functional groups create limitations, which result in rubber paste , weak and undesirable gel is produced, and in order to overcome these shortcomings and strengthen the functional properties of starch in food, it is necessary to modify[6] Starch is formed [11-13]. Common solutions to improve and modify the functional characteristics of starch include: modification of starch by physical, chemical, enzymatic methods or a combination of them. In this research, chemical modification of starch by creating crosslinks[7] with adipic acid[8] and esterification[9] with the acetyl group of acetic anhydride[10] And replacing the hydroxyl groups of glucose monomers by groups such as carboxyl or acetyl (alkyl or aryl derivatives) is done in the presence of an alkaline catalyst such as sodium hydroxide. Starch chains are connected through crosslinks with bifunctional or multifunctional compounds such as adipic acid, which leads to an increase in the molecular weight of the polymer [14-16]. Famous crosslinkers are: adipic acid and acetic anhydride, octenyl succinic anhydride.[11]Sodium tripolyphosphate[12] which lead to the creation of amorphous starch with transverse connections [17].

Physical properties of acetylated starch, especially its behavior in water, with degree of substitution[13] (DS) is determined. The relationship between the amount of morphological changes and the degree of substitution with acetyl group shows that starch with high DS practically does not dissolve in water and has more morphological changes than starch with lower DS and does not form a colloidal solution, on the other hand, starch with low DS has very high solubility in water. It shows higher water and swelling power compared to unmodified starch [18-21]. Change in the size of the granules during the acetylation process[14] It causes the acetylated starch to be granular be different compared to unmodified starch [22]. During the acetylation

1. Coeliac disease
2. Poly morph
3. Retrogradation
4. Native starch
5. Syneresis
6. Modification
7. Cross-Linking
8. Adipic acid
9. Esterification
10. Acetic anhydride
11. Octenylsuccinic anhydride
12. Sodium tripolyphsphate
13. Degree of substitution
14. Acetylation

process, depolymerization is possible[15] starch occurs, which causes a significant decrease in the molecular weight of acetylated starch compared to its unmodified type [23, 24]. The change in molecular weight is dependent on the change in amylose and amylopectin content of starch [25, 26]. During the modification process, the physicochemical and functional characteristics of quinoa starch in terms of resistance to heat treatment, acidic conditions and shear stress[16] and preventing the reduction of viscosity caused by the breakdown of glycosidic bonds, stability and emulsifying properties[17], freeze-thaw cycle[18] and syneresis, increasing viscosity, preventing retrogradation of starch, increasing swelling power[19] And lowering the gelatinization temperature improves. Kapelko et al. Effect of cross-linking rate on functional properties of retrograde adipate starch[20] Potatoes were examined. The results indicated a decrease in the swelling power, solubility, as well as the pasting temperature and viscosity of modified starch pastes with an increase in the degree of substitution with adipic acid [27]. Aghili Dehnavi et al.'s research on the combined effect of acetylation and cross-linking process on the physicochemical and functional properties of chickpea starch showed that acetylation and cross-linking increase and decrease amylose content, respectively. Syneresis decreased with increasing acetylation. Investigating the thermal properties of starches showed that by applying the process of acetylation and cross-linking, the enthalpy of gelatinization decreased and increased, respectively [28]. Amaranth starch modified with a mixture of adipic acid and acetic anhydride by Mohammadi et al improved the characteristics of swelling power, dissolution and transparency of starch paste compared to the unmodified type, while gelatinization enthalpy and stability against freezing-thawing decreased. The apparent viscosity characteristic of modified amaranth starch was also increased [29]. Zieba et al evaluated the selective properties of normal and retrograde potato starch modified with a mixture of adipic acid and acetic anhydride, and the results showed that the resistance of the modified starch to amylolysis increased compared to the unmodified type. The chemical modification operation increased the viscosity of starch paste, which was effective in increasing the flow index and consistency coefficient of potato starch samples [30]. In this research, the possibility of using modified quinoa starch as a rich and new resource and modifying its physicochemical and functional characteristics by creating crosslinks with adipic acid and esterification with acetic anhydride is evaluated.

2- Materials and methods

Quinoa seeds were purchased from Kian Perto Tehzih Company (Tehran). Acetic anhydride and adipic acid and other chemicals used in this research were manufactured by Merck, Germany, with high purity and specific for chemical analysis.

2-1- Quinoa starch extraction

Quinoa seeds were weighed in 100 grams using a scale (Mettler Toledo-ME 1002 Switzerland). In order to improve the grinding process, it was immersed in liquid nitrogen to a temperature of -196°C for two minutes and then ground by a coffee bean grinder for one minute. 100 grams of quinoa flour in 1 liter of sodium borate buffer (0.5% sodium didecyl sulfate[21] (SDS) and 5/0% $Na_2S_2O_5$ by weight/volume at pH 10 and with a concentration of 12.5 mM) was mixed and stirred until protein and lipid were completely removed from quinoa flour. The residue was separated by a centrifuge (Sigma 3-30K - Germany) at 3000 rpm for 10 minutes. The recovery step and protein and lipid removal was repeated and then the residue was washed by 1 liter of deionized water. The residue was subsequently suspended in distilled water and placed on a heater stirrer (Heidolph MR Hei-End - Germany) by a magnetic stirrer, and stirring was continued overnight to separate the protein from the starch granules. After that, the starch slurry was passed through Whatman filter paper with a hole size of 140 µm. The resulting slurry was centrifuged and the brown layer formed on top of the starch layer was scraped off with a spatula and discarded. This step was repeated 6 times to remove brown particles and SDS. The remaining amount of starch was dried in an oven (Memmert – Germany) at 35°C for 48 hours, turned into powder, and packed and stored in airtight plastic bags [31].

15. Depolymerization
16. Shear stress
17. Emulsifying properties
18. Freeze-Thaw stability
19. Swelling power
20. Retrograded starch adipate
21. Sodium dodecyl sulfate

[DOR: 20.1001.1.20088787.1402.20.136.10.8]
[DOI: 10.22034/FSCT.20.136.117]

[DOR: 20.1001.1.20088787.1402.20.136.10.8]

[DOI: 10.22034/FSCT.20.136.117]

2-2- Experiment design and chemical modification of quinoa starch

The chemical modification of quinoa starch using a mixture of adipic acid and acetic anhydride was done by considering three factors: the concentration of the chemical mixture of the modifier, the reaction time and the pH of the suspension (independent research variables) each at three levels. Based on this, 9 treatments (modified quinoa starch) along with a control sample (unmodified quinoa starch) were designed using the Taguchi method in order to find the optimal treatment (Table 1). The process of acetylation was done with acetic anhydride and creating cross-links with adipic acid. Starch slurry was prepared by adding 500 g of dried starch to 930 g of deionized water at room temperature in a 2 L reaction tank equipped with a jacket. The pH was kept in the range between 9-8 (8, 8.5 and 9) by normal sodium 1 aqueous solution. The temperature was increased by a temperature controller to 35 °C and in order to carry out the chemical modification process, 2%, 4% and 6% ADA mixture (the mixture of adipic acid and acetic anhydride was prepared by mixing the two substances with a ratio of 1 to 30) It was added drop by drop to the slurry. The slurry was kept at 35°C for 60, 90 and 120 minutes, and during this period the pH was kept close to the desired pH by 1 normal sodium hydroxide solution. Then the pH was adjusted by diluted hydrochloric acid in the range of 6.5. The obtained starch suspension solution was filtered under vacuum and passed through Whatman filter paper with a hole size of 110 microns and was washed again with distilled water at the rate of 1.25 liters and once again with alcohol. After that, the obtained (recycled) starch was dried in an oven (Memmert - Germany) under air flow at 40°C for 24 hours. The dried starch is slowly placed in a mortar to pass through a 100 mesh fine sieve [32].

Table 1 Sample of modified quinoa starch with different composition percentages designed by Taguchi method (ADA – pH – Time)

Treatment (Runs)	**Percentage** (%)	**pH**	**Time** (min)
T1	2	8.5	90
T2	2	9	120
T3	2	8	60
T4	4	9	90
T5	4	8	120
T6	4	8.5	60
T7	6	9	60
T8	6	9	90
T9	6	8.5	120
T10	Native starch (Control)		

2-3- The swelling power of starch

The swelling power was determined using the Leach Mc Co-*wen & Schoch method [33]. Starch samples (0.25 g, db) were accurately weighed and transferred to a dry and clean test tube and weighed with the test tube. (W1) 50 mL of distilled water was added to the test tube and thoroughly mixed with a Wari wh/irl mixer (Model: A901, Salver Chem. Chicago, IL, USA) for 30 seconds. Due to the difference in swelling characteristics of native quinoa starch and ADA starch (Acetylated distarch adipate), slurry is obtained and then heated in a water bath at a specific temperature from 62 to 74 degrees Celsius with a 2 degree interval for native quinoa starch and from 64 to 92 degrees Centigrade was heated from 4 degrees apart for ADA starch. Then the suspension was quickly cooled at room temperature and then centrifuged at 5000 rpm for 15 minutes (Sigma 3-30K – Germany) and the residue was precipitated. The resulting weight (after emptying the overflow solution) (W2) was determined.

= swelling power of starch

Starch weight (based on dry matter) W2 - W1 /

2- 4- Solubility and water holding capacity

Solubility and water holding capacity at 60, 70, 80, 90 °C were performed according to the method of SATH et al. with a slight change in the working method [34]. Briefly, 40 mL of a 1% (w/v) starch suspension was prepared in a previously weighed 50 mL centrifuge tube. A magnet was placed inside the tube and placed in a boiling water bath at constant temperatures of 60, 70, 80 and 90 for 30 minutes. The

resulting suspension was centrifuged at 2120 rpm for 15 minutes. We poured the clear layer into a container and weighed the swollen granules. 10 ml of this transparent layer floating on the surface was dried in an oven (Memmert - Germany) at a temperature of 120 for 4 hours until it reached a constant weight. The percentage of solubility and SP was calculated with the following formula.

= percentage of solubility

$$\frac{100 \times \text{dry weight at 120 degrees Celsius}}{\text{Sample weight}}$$

= water storage capacity

$$\frac{100x \text{ the weight of swelling granules}}{\text{Sample weight} \times (100\% \text{ solubility})}$$

5-2- Stability in the cycle of freezing - thawing

This test is performed by putting 5% weight/volume of starch paste in repeated cycles of freezing and thawing and then measuring the amount of separated water resulting from centrifuging the melted pastes. The paste used for this test was prepared by Rapid Visco-Analyzer (RAV) according to the method (AACC, 2000). The dough was stored at -18°C for 18 hours and then defrosted at room temperature for 6 hours, and in the next step, separation was performed in a centrifuge at 4300 rpm for 10 minutes. Stability against freeze-thaw cycles was expressed as the amount of water separated from the starch paste after each centrifugation [5].

6-2- transparency of starch paste

The transparency of starch pastes was determined at room temperature and also at 4°C. The transparency of starch paste was determined by placing a 3% w/v starch suspension in distilled water. The samples were placed in a plastic tube and placed in a boiling water bath for 30 minutes. The tubes were thoroughly shaken every 5 minutes, and after cooling to room temperature (14 minutes), the transmittance was measured at a wavelength of 650 nm using a spectrophotometer (Cary 300 Conc Spectrophotometer, USA). For each sample at 4°C for 8 days and once every 24 hours, the percent passage was read by an observer [35, 36].

2-7- Apparent viscosity

The viscosity of starch samples was measured using Brookfield viscometer model (model DV-II + Pro, Netherland). In this work, spindle number 3 was chosen to measure viscosity. The viscosity of the samples was read at a temperature of 25°C, rotation speeds of 20, 50 and 100 rpm after 5 seconds of spindle rotation [36 and 37].

8-2- Thermal properties of starch

Thermal properties of starches were measured using DSC 131 differential calorimeter (Setaram 131 - France). Samples (15 mg starch) were weighed directly into 100 mL aluminum containers and water (45 mg) was added with a Hamilton microsyringe. Before the heating process, the containers were sealed and kept at 25°C for 24 hours. The samples were heated from 25 to 120 °C at a rate of 10 °C/min. DSC calibration was performed with indium and an empty container was used as a reference. After analysis, all containers were kept at 4°C for 14 days to allow retrogradation of starch and were analyzed again (25-120°C at a rate of 10°C/min) to study retrogradation. Onset temperature (TO), peak temperature (TP) and gelatinization (DH) were calculated. Samples were evaluated at least in duplicate [38].

9-2- Statistical analysis

In order to investigate the relationship between independent variables (reaction pH, percentage of acetic adipic anhydride (ADA) composition and reaction time) and responses (characteristics of modified quinoa starch), the experimental results were analyzed through MINITAB version 18 software, where the error probability value P was <0.05. Simultaneous comparison of multiple sets of observations was followed by parametric analysis of variance (ANOVA) on normal data series distribution to examine the identified differences at the 0.05% probability level. Tukey's two-way comparison test was also used to check the significance of the mean of the sample results [39].

3. Results and Discussion

3-1- Swelling power, water holding capacity and dissolution

The swelling power, water holding capacity and solubility of the modified quinoa starch samples and the control sample are shown in Table 2. T1 and T2 starches compared to other samples and the control sample (T10) showed an increase in swelling power ($P<0.05$). In fact, starch chains with strong cross-links make it relatively resistant to swelling and water absorption [40]. The results showed that increasing the concentration of ADA from 2 to 4 and 6% due to the increase in creating cross-links with adipic acid reduces the swelling power of starch. However, with less effect, the introduction of acetyl groups (C=O) of acetic

[DOR: 20.1001.1.20088787.1402.20.136.10.8]
[DOI: 10.22034/FSCT.20.136.117]

[DOR: 20.1001.1.20088787.1402.20.136.10.8]

[DOI: 10.22034/FSCT.20.136.117]

anhydride among the quinoa starch chains leads to structural rearrangement due to steric repulsion and leads to repulsion between starch molecules and finally facilitates the increase of water penetration into the amorphous areas of the granule. and the power of inflation increases [41]. This increase in the swelling values of the acetylated samples can be explained by the establishment of hydrophilic segments that allow the retention of water molecules due to their ability to form hydrogen bonds. These results have been confirmed by Choi et al., Kaur et al. [42, 43]. The results related to the water holding capacity (g/g) of the samples showed that in all treatments, the percentage of acetylated adipic starch (ADA) of quinoa decreased from 6 to 4 and 2%, leading to a significant increase in the water holding capacity of the samples (P<0.05). In fact, the cross-linking process leads to stronger and more stable covalent bonds between quinoa starch chains and reduces the starch granule's ability to swell and retain water. In fact, transverse connections strengthen the structure of starch granules against acid, heat and shear stress treatments, but by limiting the mobility of starch chains in amorphous regions, it prevents water absorption [44]. However, the presence of acetyl groups can produce a network of chain branches in the starch structure, and the WRC values[22] increase Similar results in this regard were reported by Mirmoghtadaie et al. on oat starch [45]. During the reduction of the amount of ADA compound to the quinoa starch suspension, the hydrogen bonds between the crystalline structures of the starch granules are weakened and the granules gradually swell with the formation of hydrogen bonds with water, which facilitates the entry of water into the granules. Meanwhile, sample T2 (with 2% acetic adipic anhydride composition) had a significant difference in water holding capacity with the control sample (P<0.05).

In this regard, the water holding capacity stated in Table 2 was also positively correlated with the swelling power of quinoa starch. Also, the different behavior among the samples may be attributed to the difference in the amylose/amylopectin ratio as reported in other starches [46, 47]. At a temperature of 90°C, the difference was significant for samples T1, T2 and T3 compared to other samples, and sample T2 significantly showed the highest value (P<0.05). Among the samples, T2 showed the highest solubility value, which had a statistically significant difference with the control sample T10 (P<0.05). The acetylation process significantly increased the solubility. This increase in solubility indicates a better dispersion of starch in aqueous systems because the acetyl groups prevent chain linkage. Bello-perez et al. conducted a similar study on banana starch, which had similar results to this study [36]. In addition, in sample T2, due to the lower concentration of ADA and as a result, less cross-links, the possibility of more hydrogen bonds with water and increased mobility between starch chains in amorphous regions causes more water molecules to be accepted.

Table 2 Swelling power and water retention capacity and Solubility properties of modified quinoa starch samples

Sample	Swelling power (SP)	Water retention capacity (WRC)	Solubility (S)
T1	6.399 ± 0.12 ^{b}	6.165 ± 0.04 ^{b}	4.4 ± 0.00 ^{a}
T2	7.911 ± 0.01 ^{a}	7.601 ± 0.06 ^{a}	4.45 ± 0.07 ^{a}
T3	5.514 ± 0.11 ^{d}	5.390 ± 0.02 ^{d}	4 ± 0.00 ^{ab}
T4	5.210 ± 0.03 $^{It\ is}$	4.936 ± 0.08 $^{It\ is}$	3.6 ± 0.00 ^{bc}
T5	5.882 ± 0.08 ^{c}	5.671 ± 0.05 ^{c}	4.35 ± 0.07 ^{a}
T6	5.185 ± 0.05 ^{if}	4.929 ± 0.07 $^{It\ is}$	3.2 ± 0.00 ^{c}
T7	5.027 ± 0.009 ^{fg}	4.936 ± 0.08 ^{if}	4 ± 0.00 ^{ab}
T8	5.100 ± 0.001 ^{if}	4.838 ± 0.02 ^{if}	4.3 ± 0.42 ^{a}
T9	4.902 ± 0.002 ^{g}	4.655 ± 0.04 ^{f}	4.3 ± 0.14 ^{a}
T10	6.333 ± 0.05 ^{b}	6.199 ± 0.07 ^{b}	3.6 ± 0.00 ^{bc}

Values followed by different letters in the same column are significantly different (P<0.05).

[22].Water retention capacity

T1: Concentration=2%, Time= 90 min and pH=8.5, T2: Concentration=2%, Time= 120 min and pH=9, T3: Concentration=2%, Time= 60 min and pH=8, T4: Concentration=4%, Time= 90 min and pH=9, T5: Concentration=4%, Time= 120 min and pH=8, T6: Concentration=4%, Time= 60 min and pH=8.5, T7: Concentration=6%, Time= 60 min and pH=9, T8: Concentration=6%, Time= 90 min and pH=9, T9: Concentration=6%, Time= 120 min and pH=8.5, T10: Native starch (Control).

2-3- Stability in freezing-defreezing cycle

The stability of modified and raw quinoa starch samples in the freeze-thaw cycle is shown in Table 3. The use of modified quinoa starch significantly increased the stability of the sample against freezing-thawing ($P<0.05$). On the first day, sample T2 showed the highest and sample T7 showed the lowest level of instability against the freeze-thaw cycle. Syneresis in starch gels is due to the increase of molecular connections between starch chains at low temperature and the exit of water from the gel structure. Indirectly, the characteristics of retrogradation of starches (synersis) are influenced by the structural arrangement of starch chains in the crystalline and amorphous regions of granules [48]. Adipicated acetylated starches T7, T8 and T9, which had more number of cross-links, showed a much higher syneresis rate than the control sample T10, but the adipicated acetylated sample with less number of cross-links (T2) had significantly less syneresis than all samples. had ($P<0.05$). In fact, gel setting is due to rearrangement and cross-linking between amylose and amylopectin chains; But since the acetyl groups attached to amylose and amylopectin have steric hindrance during the acetylation process, this steric repulsion during the storage period of starch gel prevents the chains from getting too close to each other and reducing syneresis [41 and 49]. The reduction of syneresis in acetylated starches can be caused by the presence of acetyl groups, which increases the water retention capacity of starch molecules. Mirmoghtadaie et al and Sodhi and Singh presented similar results on rice starch and oat starch [45, 50]. Kaur et al conducted a similar study on potato starch, which showed an increase in syneresis in cross-linked potato starch gels compared to the conventional type [43]. Since the process of cross-linking in starch granules takes place mostly in its amorphous regions and makes the granule structure more regular, therefore, the creation of a regular granule structure can lead to an increase in syneresis in starch and lack of granule control in water absorption [28]. Modified treatments with 4% and 6% ADA concentration were observed completely.

Table 3 Synersis rate of modified quinoa starch samples during 8 days

Sample	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8
T1	0.508 ± 0.00 [f]	0.112 ± 0.00[i]	0.074 ± 0.00 0.074 ± 0.05[b]	0.013 ± 0.00 [d]	0.007 ± 0.00[f]	0.008 ± 0.00[b]	0.001 ± 0.00[f]	0.000 ± 0.00[d]
T2	0.289 ± 0.00[j]	0.263 ± 0.00[c]	0.028 ± 0.00[f]	0.040 ± 0.00[a]	0.037 ± 0.00[a]	0.055 ± 0.00[a]	0.018 ± 0.00[d]	0.008 ± 0.00[a]
T3	0.442 ± 0.00[h]	0.219 ± 0.00[f]	0.047 ± 0.00[It is]	0.005 ± 0.00[fc]	0.012 ± 0.00[d]	0.007 ± 0.00[c]	0.000 ± 0.00[g]	0.001 ± 0.00[cd]
T4	0.566 ± 0.00[d]	0.231 ± 0.00[It is]	0.064 ± 0.00[cd]	0.014 ± 0.00[d]	0.008 ± 0.00[if]	0.003 ± 0.00[g]	0.000 ± 0.00[g]	0.001 ± 0.00[cd]
T5	0.487 ± 0.00[g]	0.268 ± 0.00[b]	0.058 ± 0.00[d]	0.002 ± 0.00[g]	0.033 ± 0.00[b]	0.009 ± 0.00[b]	0.034 ± 0.00[c]	0.004 ± 0.00[b]
T6	0.512 ± 0.00[It is]	0.263 ± 0.00[c]	0.072 ± 0.00[b]	0.029 ± 0.00[b]	0.006 ± 0.00[g]	0.009 ± 0.00[b]	0.051 ± 0.00[b]	0.008 ± 0.00[a]
T7	0.795 ± 0.00[a]	0.200 ± 0.00[g]	0.065 ± 0.00 0.065 ± 0.00[cd]	0.009 ± 0.00 ± 0.00[It is]	0.007 ± 0.00[f]	0.004 ± 0.00[fg]	0.000 ± 0.00[g]	0.002 ± 0.00[c]
T8	0.715 ± 0.00[b]	0.197 ± 0.00[h]	0.071 ± 0.00[bc]	0.013 ± 0.00[d]	0.004 ± 0.00[h]	0.005 ± 0.00[if]	0.004 ± 0.00[It is]	0.002 ± 0.00[c]
T9	0.615 ± 0.00[c]	0.379 ± 0.00[a]	0.050 ± 0.00 0.050 ± 0.00[It is]	0.020 ± 0.00[c]	0.009 ± 0.00[It is]	0.006 ± 0.00 ± 0.00[of]	0.000 ± 0.00 ± 0.00[g]	0.001 ± 0.00 ± 0.00[cd]
T10	0.376 ± 0.00 ± 0.00[i]	0.241 ± 0.00 ± 0.00[d]	0.085 ± 0.00 ± 0.00[a]	0.039 ± 0.00 ± 0.00[a]	0.014 ± 0.00 ± 0.00[c]	0.006 ± 0.00 ± 0.00[cd]	0.061 ± 0.00 ± 0.00[a]	0.002 ± 0.00 ± 0.00[c]

[DOR: 20.1001.1.20088787.1402.20.136.10.8]
[DOI: 10.22034/FSCT.20.136.117]

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T1: Concentration=2%, Time= 90 min and pH=8.5, T2: Concentration=2%, Time= 120 min and pH=9, T3: Concentration=2%, Time= 60 min and pH=8, T4: Concentration=4%, Time= 90 min and pH=9, T5: Concentration=4%, Time= 120 min and pH=8, T6: Concentration=4%, Time= 60 min and pH=8.5, T7: Concentration=6%, Time= 60 min and pH=9, T8: Concentration=6%, Time= 90 min and pH=9, T9: Concentration=6%, Time= 120 min and pH=8.5, T10: Native starch (Control).

In general, the T2 starch sample provided the best result during the 8-day freeze-thaw cycle, which was a sign of the high stability of this sample in this cycle. The samples modified with 6% ADA concentration (T7, T8, T9) lost a significant percentage of their water in the first 3 days of the cycle, indicating the existence of more crosslinks in the amorphous regions. The control sample had the highest syneresis on the third and seventh days. These results show that sample T2 is more suitable for use in frozen products (ice cream and frozen desserts) and products that undergo pasteurization heat treatment (ketchup), but starches treated with ADA concentration of 4% and 6% as expected. They did not recover.

3- 3- The transparency of the dough

Pass percentage[23] (% T)[1] Among the quinoa starch samples at room temperature (first day) and at 4 degrees Celsius (second to eighth day) are shown in Table 4. On the first and second day, the T1 sample had the highest passing rate, but from the third to the eighth day, the T2 sample showed the highest passing percentage, but this difference was not significant ($P<0.05$). Low temperature (4 degrees Celsius) increased the phenomenon of starch retrogression. Miles et al showed that retrogression involves two separable processes: gelation of amylose molecules released from granules during gelatinization and recrystallization of amylopectin [51, 52]. Gidley et al stated that amylose gelation through the formation of helical chain segments[24] The left-fold doublet followed by the helix-helix assembly of the B-type structure takes place [53]. In this research, keeping samples of modified and raw quinoa starches at refrigerator temperature may lead to the formation of incomplete crystals compared to samples kept at room temperature (first day) and according to the amylose content of the researched starches, the accumulation of amylose chains may be High speed should be done, so with the increase of storage days, the percentage of passage in the samples decreased significantly, except for the T2 sample, but this difference was not significant ($P>0.05$). Also, the storage time is responsible for these low pass percentage values, which is most likely due to the retrogradation of the samples. The T2 sample significantly had the highest passing value over the course of 8 days compared to the control sample T10, which is a sign of less retrogradation of this sample ($P<0.05$). Regardless of the type of chemical modification, the control sample T10 had a lower pass value than all the samples except the first day (room temperature) and the fifth day (refrigerator temperature). It is important to mention that the control sample at zero time had a higher pass percentage value than the T7 and T9 samples, which decreased with the passage of time and storage in the refrigerator, which indicates the role of starch acetylation in reducing the retrogradation process.

Table 4 Transition values of quinoa starch samples during 8 days

Sample	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8
T1	$0.220^{\pm 0.00}$ ± 0.00^{a}	0.211 $^{\pm 0.00}$ ± 0.00^{a}	0.205 ± 0.00 $^{\pm 0.00}$ ± 0.00^{a}	$0.190^{\pm 0.00}$ ± 0.00^{b}	0.200 $^{\pm 0.00}$ ± 0.00^{ab}	0.218 $^{\pm 0.00}$ ± 0.00^{b}	0.200 $^{\pm 0.00}$ ± 0.00^{b}	0.202 $^{\pm 0.00}$ ± 0.00^{a}
T2	$0.211^{\pm 0.00}$ ± 0.00^{d}	$0.210^{\pm}$ ± 0.00^{ab}	$0.207^{\pm 0.00}$ ± 0.00^{a}	$0.195^{\pm 0.00}$ ± 0.00^{a}	0.201 $^{\pm 0.00}$ ± 0.00^{a}	0.225 $^{\pm 0.00}$ ± 0.00^{a}	0.205 $^{\pm 0.00}$ ± 0.00^{a}	0.205 $^{\pm 0.00}$ ± 0.00^{a}
T3	$0.217^{\pm 0.00}$ ± 0.00^{b}	0.208 $^{\pm 0.00}$ ± 0.00^{b}	$0.189^{\pm 0.00}$ ± 0.00^{c}	$0.194^{\pm 0.00}$ ± 0.00^{a}	0.197 $^{\pm 0.00}$ ± 0.00^{bc}	0.217 $^{\pm 0.00}$ ± 0.00^{b}	0.200 $^{\pm 0.00}$ ± 0.00^{b}	0.196 $^{\pm 0.00}$ ± 0.00^{b}

[23]. Transmitance

[24]. Helix

[DOR: 20.1001.1.20088787.1402.20.136.10.8]
[DOI: 10.22034/FSCT.20.136.117]

T4	0.216±0.00 ± 0.00b	0.206 ±0.00 ± 0.00c	0.197±0.00 ± 0.00b	0.182±0.00 ± 0.00d	0.194 ±0.00 ± 0.00c	0.206 ±0.00 ± 0.00c	0.200 ±0.00 ± 0.00b	0.198 ±0.00 ± 0.00b
T5	0.206±0.00 ± 0.00It is	0.194±0.00 ±0.00 ± 0.00It is	0.191±0.00 ±0.00 ± 0.00c	0.181±0.00 ±0.00 ± 0.00d	0.185 ±0.00 ±0.00 ± 0.00of	0.201 ±0.00 ±0.00 ± 0.00cd	0.184 ±0.00 ±0.00 ± 0.00c	0.186±0.00 ±0.00 ± 0.00c
T6	0.213±0.00 ±0.00 ± 0.00c	0.200±0.00 ±0.00 ± 0.00d	0.189±0.00 ±0.00 ± 0.00c	0.178±0.00 ±0.00 ± 0.00It is	0.177 ±0.00 ±0.00 ± 0.00f	0.194 ±0.00 ±0.00 ± 0.00if	0.185 ±0.00 ±0.00 ± 0.00c	0.196 ±0.00 ±0.00 ± 0.00b
T7	0.190±0.00 ±0.00 ± 0.00g	0.185 ±0.00 ± 0.00h	0.180 ± 0.00 0.180±0.00 ± 0.00d	0.171±0.00 ± 0.00f	0.175 ±0.00 ± 0.00f	0.188 ±0.00 ± 0.00fg	0.177 ±0.00 ± 0.00It is	0.176±0.00 ±0.00 ± 0.00of
T8	0.207±0.00 ± 0.00It is	0.191±0.00 ±0.00 ± 0.00f	0.190±0.00 ±0.00 ± 0.00c	0.187±0.00 ±0.00 ± 0.00c	0.181 ±0.00 ±0.00 ± 0.00It is	0.196 ±0.00 ±0.00 ± 0.00of	0.180 ±0.00 ±0.00 ± 0.00d	0.185 ±0.00 ±0.00 ± 0.00c
T9	0.188±0.00 ± 0.00h	0.187±0.00 ±0.00 ± 0.00g	0.191 ± 0.00 0.191±0.00 ± 0.00c	0.179±0.00 ± 0.00It is	0.183 ±0.00 ±0.00 ± 0.00of	0.195 ±0.00 ±0.00 ± 0.00of	0.183 ±0.00 ±0.00 ± 0.00cd	0.178±0.00 ±0.00 ± 0.00d
T10	0.193±± 0.00f	0.184 ±0.00 ± 0.00h	0.172±0.00 ±0.00 ± 0.00It is	0.170±0.00 ±0.00 ± 0.00f	0.185 ±0.00 ±0.00 ± 0.00d	0.186 ±0.00 ±0.00 ± 0.00g	0.168 ±0.00 ±0.00 ± 0.00f	0.174±0.00 ±0.00 ± 0.00It is

Values followed by different letters in the same column are significantly different (p<0.05).
T1: Concentration=2%, Time= 90 min and pH=8.5, T2: Concentration=2%, Time= 120 min and pH=9, T3: Concentration=2%, Time= 60 min and pH=8, T4: Concentration=4%, Time= 90 min and pH=9, T5: Concentration=4%, Time= 120 min and pH=8, T6: Concentration=4%, Time= 60 min and pH=8.5, T7: Concentration=6%, Time= 60 min and pH=9, T8: Concentration=6%, Time= 90 min and pH=9, T9: Concentration=6%, Time= 120 min and pH=8.5, T10: Native starch (Control).

3- 4- Apparent viscosity

The results of measuring the apparent viscosity of raw and modified quinoa starch samples with rotation speeds of 20, 50 and 100 rpm are shown in Table 5. The effect of the concentration of ADA mixture, as well as the reaction time and the pH of the suspension used to modify the quinoa starch samples on the viscosity was significant (P<0.05.

The process of modifying starch by acetylation and creating cross-links with adipic acid caused a significant increase in the apparent viscosity of the T2 sample compared to the control sample T10 at different shear speeds, but the apparent viscosity of the rest of the samples did not improve (P<0.05. In fact, in the T2 sample due to A lower concentration of ADA and as a result of reducing crosslinks and having more amorphous and crystalline regions, has more water absorption capacity than the modified samples with 4% and 6% ADA concentration, and these amorphous regions are able to create more hydrogen bonds due to the reduction of intramolecular connections. with water molecules and as a result have a higher viscosity. Thaiudom and Khantarat in a similar research used sodium starch octenyl succinate at three levels of 25%, 50% and 75% as a fat substitute in mayonnaise, and the viscosity results showed that the samples containing 25% and had 50% more viscosity than the control sample, while increasing the amount of starch reduced the viscosity to 75% [54]. The apparent viscosity of all starches decreased significantly with increasing shear rate (P<0.05.

Table 5 Apparent Viscosity values of modified quinoa starch samples

Sample	IN_{cp} (20rpm)	IN_{cp} (50rpm)	IN_{cp} (100rpm)
T1	112±0.00±0.00 ± 1.41c	98.5 ± 1.41c	72 ± 1.41c
T2	244 ± 1.41a	192 ± 0.00a	180 ± 2.83a

[DOR: 20.1001.1.20088787.1402.20.136.10.8]
[DOI: 10.22034/FSCT.20.136.117]

T3	$93 \pm 1.41^{\pm 1.41}{}_{d}$	$79 \pm 0.00^{\pm 0.00}{}_{d}$	67 ± 2.83^{c}
T4	$62 \pm 0.00^{It\ is}$	$51 \pm 1.41^{It\ is}$	48 ± 2.83^{d}
T5	49.5 ± 1.41^{f}	36.4 ± 1.41^{f}	34.55 ± 2.90^{if}
T6	58 ± 2.83 $58 \pm 2.83^{It\ is}$	$51.4 \pm 0.14^{It\ is}$	39.60 ± 1.27^{def}
T7	32 ± 1.41^{g}	34.45 ± 0.49^{f}	43 ± 0.00^{of}
T8	$21.5^{\pm 1.41} \pm 1.41^{h}$	27.55 ± 1.48^{g}	37.15 ± 1.91^{if}
T9	13.5 ± 0.009^{i}	23 ± 0.00^{h}	31.70 ± 1.84^{f}
T10	208.5 ± 0.70^{b}	178 ± 0.00^{b}	163 ± 2.83^{b}

Values followed by different letters in the same column are significantly different ($p<0.05$)

T1: Concentration=2%, Time= 90 min and pH=8.5, T2: Concentration=2%, Time= 120 min and pH=9, T3: Concentration=2%, Time= 60 min and pH=8, T4: Concentration=4%, Time= 90 min and pH=9, T5: Concentration=4%, Time= 120 min and pH=8, T6: Concentration=4%, Time= 60 min and pH=8.5, T7: Concentration=6%, Time= 60 min and pH=9, T8: Concentration=6%, Time= 90 min and pH=9, T9: Concentration=6%, Time= 120 min and pH=8.5, T10: Native starch (Control).

In fact, when shear force is applied, the swollen granules of quinoa starch are placed in a direction parallel to the direction of the applied force, and as a result of this force, larger particles are broken and turned into smaller particles. As a result, the tension and resistance caused by the interaction between the granules are reduced and they flow, which ultimately leads to a decrease in the apparent viscosity of the quinoa starch suspension [55]. This decrease in apparent viscosity with increasing shear rate indicates pseudoplastic (shear thinning) behavior of quinoa starch samples. A study by Bello-perez et al. on banana starch showed similar results [36]. In general, the apparent viscosity of all starch samples did not change much during the test period, and this indicated the stability of the starch paste under the test conditions.

5-3- Thermal properties of starch

DSC test results[25] The modified and raw quinoa starch samples are shown in Table 6. The energy required to transform the crystal structures of quinoa starch into amorphous parts can be determined by differential calorimetry. Gelatinization and swelling power of starch depends on the structure of amylopectin molecule, as well as the ratio of amylose to amylopectin, fat and protein content, and granule structure (crystal to amorphous ratio) [56]. Usually swelling of starch granules in T_{onset} DSC endothermic transition starts [57]. Probably, the higher amylose, protein and fat contents hindered the swelling properties of starch and thus T_{onset} increases ($P<0.05$). Meanwhile, sample T7 significantly has the highest T $value_{onset}$ showed ($P<0.05$). In addition, the length of amylopectin chains plays an important role in starch gelatinization behavior, so that longer chains require more energy than shorter chains for complete separation [58]. It has been reported that high-amylose starch with longer chains presents a higher transition temperature [59]. Low gelatinization enthalpy indicates a granular structure with less molecular order and shorter amylopectin double helix [60]. In addition, the above sample has a lower crystallization percentage and a higher amylose content. Among the samples, T3 significantly ($P<0.05$) showed the lowest enthalpy and also the lowest crystallization. Sample T2 significantly has the highest enthalpy, which indicates the highest water absorption ability and the swelling and crystallization power of starch ($P<0.05$).

Table 6 Gelatinization characteristics of modified quinoa starch samples

Sample	Enthalpy (E)	Onset temperature (To)	Peak temperature (Tp)
T1	3.414 ± 0.001^{b}	38.345 ± 0.27^{d}	67.45 ± 0.19^{f}
T2	5.770 ± 0.009^{a}	42.520 ± 0.84^{cd}	73.785 ± 0.21^{cd}
T3	1.088 ± 0.006^{h}	39.135 ± 0.40^{d}	77.230 ± 0.55^{b}
T4	1.882 ± 0.014^{f}	47.58 ± 0.11^{ab}	70.105 ± 0.12^{if}
T5	2.425 ± 0.003^{d}	47.38 ± 3.32^{ab}	73.940 ± 1.03^{cd}

[25]. Differential Scanning Calorimetry

[DOR: 20.1001.1.20088787.1402.20.136.10.8]
[DOI: 10.22034/FSCT.20.136.117]

T6	1.816 ± 0.002[c]	45.44 ± 0.18[bc]	71.085 ± 0.21[of]
T7	2.863 ± 0.006[c]	50.085 ± 0.09[a]	83.08 ± 0.11[a]
T8	2.119 ± 0.005[It is]	47.405 ± 0.31[ab]	75.17 ± 1.87[bc]
T9	2.404 ± 0.009[d]	46.140 ± 0.26[abc]	72.205 ± 0.79[cde]
T10	1.631 ± 0.04[g]	46.565 ± 0.3[abc]	67.875 ± 0.44[f]

Values followed by different letters in the same column are significantly different ($p<0.05$).
T1: Concentration=2%, Time= 90 min and pH=8.5, T2: Concentration=2%, Time= 120 min and pH=9, T3: Concentration=2%, Time= 60 min and pH=8, T4: Concentration=4%, Time= 90 min and pH=9, T5: Concentration=4%, Time= 120 min and pH=8, T6: Concentration=4%, Time= 60 min and pH=8.5, T7: Concentration=6%, Time= 60 min and pH=9, T8: Concentration=6%, Time= 90 min and pH=9, T9: Concentration=6%, Time= 120 min and pH=8.5, T10: Native starch (Control).

During the heating of starch granule in the presence of excess water in the environment, the crystal structures which are mainly composed of branched structures of amylopectin turn into amorphous parts during an endothermic process. Applying the thermal process caused a significant increase in the gelatinization temperature of the granules, while the gelatinization enthalpy of quinoa starch decreased from 5.770 in sample T2 to 1.631 J/g in sample T10. The decrease in enthalpy in sample T10 (120.8, 5.6%) indicates that some crystal structures that have little thermal resistance have been removed during the intense thermal process. In fact, with the increase in the percentage of acetylation, the thermal parameters decrease due to the weakening of the starch structure, but the enthalpy of the modified quinoa samples increases with the decrease in the amount of cross-links with adipic acid. Jayakody et al.'s studies on modified chickpea starch confirm the results obtained from the test of this research [61].

6-3- Optimizing starch modification conditions

In order to determine the optimal conditions for the chemical modification of quinoa starch with a mixture of adipic acid and acetic anhydride, Taguchi's signal-to-noise analysis was used in the Mini Tab software with two patterns, "larger value is better" and "smaller value is better" [62]. For the tests of swelling power, solubility, water holding capacity, paste clarity and apparent viscosity of the "bigger is better" pattern (Relation 4) and for the results of thermal properties tests (according to the final product) and freeze-thaw cycle of the "smaller is better" pattern (Relation 5) was considered. After analysis, weights of 1 to 5 (1 being the most important and 5 being the least important) were given to each of the starch characteristics based on their importance [63]. Descale results with RPD method[26] took place (Relation 6). Finally, all the results with the same weight are included in the final answer and the unweighted results were analyzed by Taguchi method. The determined optimal conditions were: 2% concentration of the modifier mixture, 120 minutes of reaction time, and 9 pH of the suspension.

$$S/N = -10 \times \log 10\left[Sum(1/Y^2)/n \right] \quad (4)$$

$$S/N = -10 \times \log 10\left[Sum(Y^2)/n \right] \quad (5)$$

In which, Y = answers for the factor level combination and n = the number of answers in the factor level combination.

$$RPD = \frac{(Sol - BestSol)}{BestSol} \times 100 \quad (6)$$

where ins*un* The amount of data in an experiment and*best sol* The best data is among all the data in an experiment.

[26]. Related Percentage Deviation

[DOR: 20.1001.1.20088787.1402.20.136.10.8]
[DOI: 10.22034/FSCT.20.136.117]

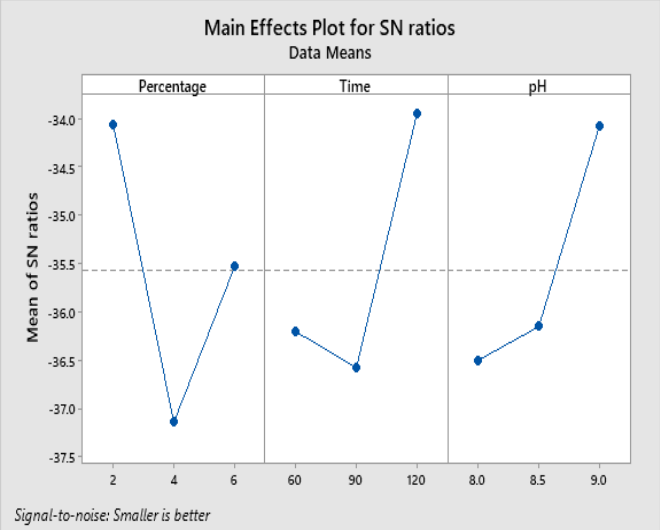

Fig 1 Main effect of each factor using S/N ratio.

5- General conclusion

Chemical modification of quinoa starch by ADA led to improvement of physicochemical and functional characteristics of quinoa starch significantly compared to raw starch. Higher gelatinization enthalpy, lower pasting temperature, higher water holding capacity and lower syneresis were observed in T2 sample (2% ADA mixture concentration, 9 pH suspension and 120 minutes reaction time) compared to the control sample. Meanwhile, sample T2 significantly showed the highest viscosity ($P<0.05$). The swelling power of quinoa starch showed a significant decrease ($P<0.05$) with the increase of crosslinks, and acetylation increased the solubility of modified quinoa starch compared to the control, but with the increase of acetylation and crosslinks, the parameters of swelling power, solubility, and water holding capacity decreased. and this decrease was not significant in terms of solubility ($P>0.05$). With the increase of storage time, the transparency of the paste in the samples decreased significantly, except for the T2 sample, but this difference was not significant ($P>0.05$). The T2 sample significantly had the highest amount of paste transparency with the passage of time in 8 days compared to the control sample, which was a sign of its less retrogradation than all the samples. In general, sample T2 showed the best and most optimal physicochemical and functional characteristics of modified quinoa starch with adipic acid and acetic anhydride mixture compared to other samples of this research.

5- Thanks and appreciation

Thanks to the technical and financial support of the Research and Development Unit of Behrouznik Food Industry Company (Karaj, Iran).

6- Resources

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[DOR: 20.1001.1.20088787.1402.20.136.10.8]

[DOI: 10.22034/FSCT.20.136.117]

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سایت مجله: www.fsct.modares.ac.ir

مقاله علمی_پژوهشی

ویژگی‌های فیزیکوشیمیایی و عملکردی نشاسته کینوا اصلاح‌شده با مخلوط آدیپیک اسید و استیک انهیدرید

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اطلاعات مقاله

تاریخ های مقاله :

تاریخ دریافت: ۱۴۰۱/۱۰/۱۵

تاریخ پذیرش: ۱۴۰۱/۱۱/۱۳

کلمات کلیدی:

اتصالات عرضی،

استیلاسیون،

اصلاح شیمیایی،

آدیپیک اسید،

روش تاگوچی،

نشاسته کینوا،

ویژگی‌های عملکردی.

DOI: 10.22034/FSCT.19.135.113

DOR: 20.1001.1.20088787.1402.20.135.10.6

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چکیده

در این پژوهش، نمونه‌های نشاسته کینوا در ۹ تیمار با نسبت‌های متفاوت از مخلوط آدیپیک اسید و استیک انهیدرید (نسبت ۱ به ۳۰)، به همراه یک نمونه شاهد از نظر ویژگی‌های فیزیکوشیمیایی و عملکردی و تعیین شرایط بهینه اصلاح شیمیایی مورد ارزیابی قرار گرفتند. تیمارهای مذکور توسط ۳ متغیر مستقل مؤثر بر اصلاح شیمیایی شامل غلظت اصلاح‌کننده شیمیایی (۲٪، ٤٪ و ٦٪)، pH سوسپانسیون (۸، ۸/۵ و ۹) و زمان واکنش (٦۰، ۹۰، ۱۲۰ دقیقه) به روش تاگوچی طراحی گردیدند. قدرت تورم و قابلیت جذب آب نمونه T2 (غلظت اصلاح‌کننده ۲٪، pH سوسپانسیون ۹ و زمان واکنش ۱۲۰ دقیقه) به‌طور معنی‌داری نسبت به نمونه شاهد افزایش یافت که نشانه تشکیل اتصالات عرضی همراه با تشکیل شبکه‌های سه‌بعدی ژل پایدار است. نتایج طیف‌سنجی نشان داد که به‌جز نمونه T2، بقیه نمونه‌ها تمایل جزئی به رتروگراداسیون داشتند که نشانه پایداری بالای نمونه مذکور در طول مدت زمان ماندگاری به سینرسیس بود (P<0.05). استیلاسیون به دلیل پراکندگی بهتر نشاسته در محیط آبی ویژگی حلالیت را به‌طور قابل‌توجهی نسبت به نمونه شاهد بهبود بخشید. با افزایش غلظت اصلاح‌کننده، پایداری نمونه‌ها در برابر چرخه انجماد-انجمادزدایی به‌طور معنی‌داری کاهش یافت (P<0.05). پارامترهای بررسی شده در اندازه‌گیری ویژگی‌های حرارتی نشاسته اصلاح‌شده کینوا با اختلاف معنی‌داری بیشتر از نمونه شاهد ارزیابی شدند. ویسکوزیته ظاهری نمونه T2 در سرعت برشی ۲۰، ۵۰ و ۱۰۰ دور در دقیقه نسبت به نمونه شاهد به‌طور معنی‌داری افزایش یافت ولی بقیه نمونه‌ها ویسکوزیته کمتری را نشان دادند. همچنین، با بهره‌گیری از آنالیز تاگوچی تیمار بهینه نشاسته اصلاح‌شده کینوا با غلظت اصلاح‌کننده ۲٪، pH سوسپانسیون ۹ و زمان واکنش ۱۲۰ دقیقه تعیین گردید.