Starch Modification

Subjects: Food Science & Technology

Contributor: Antoni Golachowski , Wioletta Drożdż , Magdalena Golachowska , Małgorzata Kapelko-Żeberska , Bartosz Raszewski

Currently, new methods for producing starch citrates with improved functional and rheological properties while maintaining the highest possible content of resistant starch are being sought. The entry presents an overview of recent studies on the production, properties. And applicability of starch citrates with special attention paid to their role as preparations of resistant starch (RS). The use of citric acid for modification of starch is better for the technology process, while using cross-linking is better than simply using esterification.It may be concluded that the work on starch citrate esters represent a topical and meaningful direction of investigations on modified starch preparations. The possibility of modifying starch preparations by esterification/cross-linking with citric acid allows for the production of modified starch, which can be used in the pharmaceutical, packaging, or food industries. Especially significant may be investigations of resistant starch produced via esterification with citric acid because this method produces preparations exhibiting significant resistance and, simultaneously, good functional properties, which are potentially applicable as health-promoting additives that increase the dietary fiber content of food products.

starch resistant citrate starch methods of starch citrification the properties of starch citrate

1. Introduction

Starch is one of the most ubiquitous storage substances in nature. In its native form, starch has limited applications due to properties that are not always desirable for certain types of processing. Examples of these shortcomings include its inability to withstand the high temperature, pressure, and some strong chemical reagents use in most industrial food and pharmaceutical processes. Starch modification, which implies the alteration of the physical and chemical characteristics of native starch, is used to improve its properties. The chemical modification of starch is directly related to the reactions of the hydroxyl groups of the starch polymer. Almost all glucose residues in starch chains possess three free-hydroxyl groups capable of oxidation, etherification, and esterification. Starch modification through esterification involves starch chain reactions with inorganic and organic acids, salts of inorganic acids, and anhydrides or chlorides of organic acids. A commonly used modified starch in the food industry is acetylated distarch adipate, obtained by the esterification of starch with adipic acid and acetic anhydride [1]. This preparation is characterized by a higher thermal stability, shear resistance, and acid resistance compared to native starch and forms strong and stable gels that are resistant to retrogradation [2]. For this reason, these starch modifications are widely used in food products as a thickener, stabilizer, and binder [3]. However, the acetylated distarch adipate has applications that are regulated by the degree of substitution (DS) or the percentage of acetyl groups (% Ac). These characteristics determine the use of starch acetate, for example, for food application; the United States Food and Drug Administration (FDA) recommends a percentage of acetyl groups of less than 2.5 g/100 g [4].

Recently, scientists have focused a lot of attention on the preparation and testing of the properties of starch modified with citric acid. Citric acid (2-hydroxypropane-1,2,3 tricarboxylic acid, $C_6H_8O_7$) itself is recognized as a safe food additive (GRAS) and is used widely in the food, cosmetic, and pharmaceutical industries [5]. The use of citric acid is considered safe for both the natural environment and human health [6]. The JECFA (Joint FAO/WHO Expert Committee on Food Additives) monograph on modified starches does not set any particular limitations on the use of starch citrate [7]. Citric acid has been used for starch modifications since the mid-20th century. A method for the production of its starch esters was patented in 1949 [8], whereas a preparation of starch crosslinked with this acid was patented in 1960 [9]. Citric acid is relatively often used in current investigations addressing starch modifications [6][10][11][12][13][14][15][16][17]. Mainly it serves as an acidity regulator. Citric acid is widely used as a reagent in reactions of esterification and crosslinking of starch conducted under various conditions and types of starch. It is also used for starch treatment at temperatures lower than its pasting temperatures [18][19][20][21][22][23]and in the heat moisture treatment of starch [24][25]. In the polymeric materials produced based on starch, it is used as a compatibilizer [26], a plasticizer [9], and a crosslinking agent [11][12][13][14][27][28]. In addition, it serves the role of a catalyst in carbonspheres production from starch that are used, i.e., lithium batteries [15]. In the production of starch citrate, citric acid is converted to its anhydride, which forms ester bonds with the hydroxyl groups in starch [29]. However, the superiority of citrates over other modifications can be explained by the cross-linking process itself. Crosslinking is a type of chemical modification that offers greater stabilization of the starch structure. It can be performed with polycarboxyl organic acids, which form bridges by reacting with hydroxyl groups of anhydroglucoses from the neighboring chains, thereby stabilizing the polymeric backbone. Citric acid was chosen for this overview because its heating with starch ensures high crosslinking of the latter. Its additional advantage to starch modification is the possibility of modelling starch resistance to amylolysis in a whole variability range (0–100%) because it is correlated with the process temperature and acid dose [30].

2. The Methods of Starch Citrate Preparation

In recent studies, processes of esterification/crosslinking with citric acid have been conducted with various starch types, including both these produced on the large industrial scale, i.e., “normal” and waxy maize starch [27][31][32][33][34][35][36], wheat starch and its A and B fractions [22][37], potato starch [38][39][40][41][42][43], rice starch [44][45], and cassava starch [14][43][46][47], as well as with starch extracted from local plants, i.e., from banana [43][48], taro [49], yam [50][51], sweet potato [43][52], acha and iburu [53], kidney bean [54], lentil [43], and barley [16]. Investigations have been carried out with native starch (non-modified) and with starch modified using physical and chemical methods—porous starch [11], retrograded starch [41][42], starch nanocrystals [11], carboxymethyl starch [55], starch coated with nanoparticles [56], and alkaline starch suspension [57].

The process of starch esterification has been performed with various methods, which affected the degree of substitution and properties of the modified preparations (Table 1). The most frequent has been the “dry” esterification/crosslinking described by Klaushofer et al. [7], in which starch is first mixed with an aqueous solution of citric acid and then dried and roasted. The preparation obtained is then rinsed with water or/and an ethanol solution, dried again, and disintegrated.

Table 1. Methods of citric starch samples preparation.

Method	Type	Degree of Substitution	References
Dry	Oven	0.01–0.42	[11][35][37][38][39][41][42][43][46][47][52][58]
	Extrusion	0.01–0.03	[31][45]
	Microwave with plasma	0.012–0.015	[36]
Wet	Water suspension	0.002–0.023	[50][51][53][54][57][59]
	Electrochemical	0.02–0.12	[55][56]

This method has been modified by many researchers and these modifications concerned the use of various citric acid to starch ratios (from 1 g to 60 g of citric acid per 100 g of starch) and performing this reaction at various pH values (3.5–5.5), roasting temperatures (110–140 °C), and roasting times (1–5 h).

Different conditions producrf modified preparations with a substitution degree ranging from 0.01 to 0.42, which was found to depend on the type of starch material and its earlier modifications [37][41][42][43], citric-acid-to-starch ratio [11][37][38][39][41][42][43][46][47][52][58], pH value of the reaction [35][58], and the time and the temperature of roasting [35][42][47].

“Dried” esterification was carried out not only in roasters but also in extruders. A study conducted by indicates that the molar substitution degree of the starch citrates obtained in the process of reactive extrusion ranges from 0.01 to 0.03 depending on the amount of citric acid, the temperature of extrusion, and the number of passages. The effect of the amount of citric acid added to extruded starch on the substitution degree of the modified preparation was also observed in the work by Ye et al. [45]. The degree of substitution and the properties of starch citrates produced with the extrusion method were also affected by the addition of galactomannans (guar gum, tara gum, and locust bean gum) [31].

Another procedure of “dry” esterification was described by Kim and Min [36]. The reaction was induced by microwave-discharged cold plasma. The molecular degree of substitution of the modified preparation reached 0.012–0.015 and was similar to that of starch modified with the “classic” method, i.e., through roasting at a temperature of 135 °C for 1 h.

Starch esterification and crosslinking may also be induced by exposing the reaction mixture to ultraviolet irradiation and applying sodium benzoate as a photosensitizer. This method was used for film production from thermoplastic starch [10].

The method of “dry” esterification of the starch through its roasting with citric acid was also used to produce many modified preparations of starch intended not for the food industry but for pharmaceutical or technical purposes. Preparations of this type included crosslinked starch nanocrystals potentially used as drug delivery vehicles and reinforcements for nanocomposites with a hydrophobic polymer matrix [28], crosslinked porous starch used for the absorption of heavy metal ions [11], starch films with good barrier and mechanical properties[13][28], novel starch foams that may replace petroleum-based foams [12], or hydrogels ensuring appropriate release of active substances of a drug [57].

Apart from the above-discussed “dry” esterification method described in a few works [49][50][52][53], recent investigations on starch citrates have also addressed “wet” esterification performed according to Agboola et al. [59]. This method consists in the localization of an aqueous starch suspension, the addition of a solution of citric acid and a solution of sulfuric acid as a catalyst, and keeping this suspension at room temperature. The next steps include rinsing with water to remove residues of reagents, drying, and disintegration. Depending on the amount of citric acid, the degree of substitution of the modified preparations ranged from 0.002 to 0.023 [59]. The “wet” esterification conducted under slightly different conditions was also employed to produce hydrogels capable of encapsulating nutraceuticals [57].

Hernandez-Jaimes et al. demonstrated the feasibility of producing starch citrates in the aqueous medium with the electrochemical method using a triangular-shaped potential cycle, with substitution degree of the obtained preparations ranging from 0.02 to 0.12 depending on the number of cycles [33]. The esterification/crosslinking of starch in an aqueous suspension was also used to produce “non-food” preparations, e.g., during production of curcumin-loaded starch coated with iron oxide nanoparticles [56], to be used in pharmacy (drug delivery systems) and during production of novel carboxymethyl starch-based biodegradable films with calcium montmorillonite that can be used for the production of seed tapes [55].

Heating a water suspension of starch, glycerol, and citric acid to the temperature of 75 °C and 85 °C was used to produce biodegradable and not-retrogradable eco films [14]. Authors of this work emphasized that, under these conditions, the reaction of esterification proceeds in two stages. In the first stage, citrate esters of glycerol are produced, and in the second stage, these esters react with starch, forming crosslinking bonds.

3. Summary

It may be concluded that the work on starch citrate esters represent a topical and meaningful direction of investigations on modified starch preparations. The possibility of modifying starch preparations by esterification/cross-linking with citric acid allows for the production of modified starch, which can be used in the pharmaceutical, packaging, or food industries. Especially significant may be investigations of resistant starch produced via esterification with citric acid because this method produces preparations exhibiting significant resistance and, simultaneously, good functional properties, which are potentially applicable as health-promoting additives that increase the dietary fiber content of food products.

References

1. Tian, S.; Chen, Y.; Chen, Z.; Yang, Y.; Wang, Y. Preparation and characteristics of starch esters and its effects on dough physicochemical properties. J. Food Qual. 2018, 7.
2. Zhang, D.; Lin, Z.; Lei, W.; Zhong, G. Synergistic effects of acetylated distarch adipate and sesbania gum on gelatinization and retrogradation of wheat starch. Int. J. Biol. Macromol. 2020, 156, 171–179.
3. Golachowski, A.; Zięba, T.; Kapelko-Żeberska, M.; Drożdż, W.; Gryszkin, A.; Grzechac, M. Current research addressing starch acetylation. Food Chem. 2015, 176, 350–356.
4. Colussi, R.; El Halal, S.L.M.; Pinto, V.Z.; Bartz, J.; Gutkoski, L.C.; Zavareze, E.R.; Dias, A.R.G. Acetylation of rice starch in an aqueous medium for use in food. LWT Food Sci. Technol. 2015, 62, 1076–1082.
5. Xie, X.S.; Liu, Q. Development and physicochemical characterization of new resistant citrate starch from different corn starches. Starch Stärke 2004, 56, 364–370.
6. Ciriminna, R.; Meneguzzo, F.; Delisi, R.; Pagliaro, M. Citric acid: Emerging applications of key biotechnology industrial product. Chem. Cent. J. 2017, 11–22.
7. Zehra, N.; Ali, T.M.; Hasnain, A. Comparative study on citric acid modified instant starches (alcoholic alkaline treated) isolated from white sorghum and corn grains. Int. J. Biol. Macromol. 2020, 155, 1331–1341.
8. National Starch Products Inc. US-Patent 2.461.139, 1949. Available online: https://patentimages.storage.googleapis.com/b4/db/56/50b269ac7ba9ab/US2461139.pdf (accessed on 20 March 2020).
9. National Starch and Chemical. Corp. US-Patent 2.935.510, 1960. Available online: https://patentimages.storage.googleapis.com/44/a7/cd/08cbecc4d8040f/US2935510.pdf (accessed on 20 March 2020).
10. Niazi, B.K.M.; Broekhuis, A.A. Surface photo-crosslinking of plasticized thermoplastic starch films. Eur. Polym. J. 2015, 64, 229–243.
11. Ma, X.; Liu, X.; Anderson, D.P.; Chang, P.R. Modification of porous starch for the adsorption of heavy metal ions from aqueous solution. Food Chem. 2015, 181, 133–139.

12. Pornsuksomboon, K.; Holló, B.B.; Szécsényi, K.M.; Kaewtatip, K. Properties of baked foams from citric acid modified cassava starch and native cassava starch blends. Carbohydr. Polym. 2016, 136, 107–112.
13. Saliu, O.D.; Olatunji, G.A.; Olosho, A.I.; Adeniyi, A.G.; Azeh, Y.; Samo, F.T.; Adebayo, D.O.; Ajetomobi, O.O. Barrier property enhancement of starch citrate bioplastic film by an ammonium-thiourea complex modification. J. Saudi Chem. Soc. 2018, 23, 141–149.
14. Seligra, P.G.; Jaramillo, C.M.; Famá, L.; Goyanes, S. Biodegradable and non-retrogradable eco-films based on starch-glycerol with citric acid as crosslinking agent. Carbohydr. Polym. 2016, 138, 66–74.
15. Supriya, B.S.; Nagraja, P.; Byrappa, K. Hydrothermal synthesis and characterization of carbon spherees using citric-acid-catalyzed carbonization of starch. e-Polymers 2015, 15, 179–183.
16. Punia, S.; Siroha, A.K.; Sandhu, K.S.; Kaur, M. Rheological behavior of wheat starch and barley resistant starch (type IV) blends and their starch noodles making potential. Int. J. Biol. Macromol. 2019, 130, 595–604.
17. Keenan, M.J.; Zhou, J.; Hegsted, M.; Pelkman, C.; Durham, H.A.; Coulon, D.B.; Martin, R.J. Role of resistant starch in improving gut health, adiposity, and insulin resistance. Adv. Nutr. 2015, 13, 198–205.
18. AACC. Approved Methods of the AACC, 10th ed.; Methods 46-13, 08-01, and 44-15; Cereals & Grace Association: St. Paul, MN, USA, 2000.
19. AOAC. Official Methods of Analysis of Association of Official Analytical Chemists International, 17th ed.; Method 991.43 Total Dietary Fiber. Enzymatic Gravimetric Method; Cereals & Grace Association: Gaithersburg, MD, USA, 2000.
20. Babu, A.S.; Parimalavalli, R.; Gaur, R.S. Effect of citric acid concentration and hydrolysis time on physicochemical properties of sweet potato starches. Int. J. Biol. Macromol. 2015, 80, 557–565.
21. Babu, A.S.; Parimalavalli, R.; Jagannadham, K.; Sudhakara Rao, J. Chemical and structural properties of sweet potato starch treated with organic and inorganic acid. J. Food Sci. Technol. 2015, 52, 5745–5753.
22. Huo, Y.; Zhang, B.; Niu, M.; Jia, C.; Zhao, S.; Huang, Q.; Du, H. An insight into the multi-scale structures and pasting behaviors of starch following citric acid treatment. Int. Biol. Macromol. 2018, 116, 793–800.
23. Martins, P.C.; Gutkoski, L.C.; Martins, V.G. Impact of acid hydrolysis and esterification process in rice and potato starch properties. Int. J. Biol. Macromol. 2018, 120, 959–965.
24. Hung, P.; Huong, N.T.M.; Phi, N.T.L.; Tien, N.N.T. Physicochemical characteristics and in vitro digestibility of potato and cassava starches under organic acid and heat-moisture treatments. Int.

J. Biol. Macromol. 2017, 95, 299–305.

25. Hung, P.; Vien, N.L.; Phi, N.T.L. Resistant starch improvement of rice starches under a combination of acid and heat-moisture treatments. Food Chem. 2016, 191, 67–73.
26. Fourati, Y.; Tarrés, Q.; Mutjé, P.; Boufi, S. PBAT/thermoplastic starch blends: Effect of compatiblizers on the rheological, mechanical and morphological properties. Carbohydr. Polym. 2018, 199, 51–57.
27. Shen, L.; Xu, H.; Kong, L.; Yang, Y. Non-toxic crosslinking of starch using polycarboxylic acids: Kinetic study and quantitative correlation of mechanical properties and crosslinking degrees. J. Polym. Environ. 2015, 23, 588–594.
28. Zhou, J.; Tong, J.; Su, X.; Ren, L. Hydrophobic starch nanocrystals preparations through crosslinking modification using citric acid. Int. J. Biol. Macromol. 2016, 91, 1186–1193.
29. Hong, J.S.; Chung, H.-J.; Lee, B.-H.; Kim, H.-S. Impact of static and dynamic modes of semi-dry heat reaction on thecharacteristics of starch citrates. Carbohyd. Polym. 2020, 233, 115853.
30. Kapelko-Żeberska, M.; Zięba, T.; Spychaj, R.; Gryszkin, A. Acetylated adipate of retrograded starch as RS3/4 type resistant strach. Food Chem. 2015, 188, 365–369.
31. Borries-Medrano, E.; Jaime-Fonseca, M.R.; Aguilar-Méndez, M.A.; García-Cruz, H.I. Addition of galactomannans and citric acid in corn starch processed by extrusion: Retrgradation and resistant starch studies. Food Hydrocoll. 2018, 83, 485–496.
32. Hedayati, S.; Niakousari, M. Microstructure, pasting and textural properties of wheat starch-corn starch citrate composites. Food Hydrocoll. 2018, 81, 1–5.
33. Hernandez-Jaimes, C.; Vernon-Carter, E.J.; Labato-Calleros, C.; Bello-Perez, L.A.; Alvarez-Ramirez, J. An electrochemical approach for citric acid treatment of corn starch granules. Starch Stärke 2016, 68, 558–567.
34. Kim, S.H.; Kim, H.S. Impact of reactive extrusion parameters on the resistant contents and pasting properties of starch citrates. Food Eng. Prog. 2015, 3, 193–200.
35. Kim, S.H.; Kim, H.S. Influence of semi-dry heating reaction conditions on resistant starch citrates. Food Eng. Prog. 2015, 4, 313–319.
36. Kim, S.H.; Min, S.C. Effects of microwave-discharged cold plasma on synthesis and characteristics of citrate derivatives of corn starch granules. Food Sci. Biotechnol. 2017, 26, 697–706.
37. Li, M.N.; Xie, Y.; Chen, H.Q.; Zhang, B. Effects of heat-moisture treatment after citric acid esterification on structural properties and digestibility of wheat starch, A- and B- type starch granules. Food Chem. 2019, 272, 523–529.

38. Butt, N.A.; Ali, T.M.; Hasnain, A. Rheological characterization of cold water soluble rice (Oryza sativa) starch lactates and citrates prepared via alcoholic-alkaline method. Int. J. Biol. Macromol. 2019, 123, 558–568.
39. Butt, N.A.; Ali, T.M.; Hasnain, A. Rice starch citrates and lactates: A comperative study on hot water and cold water swelling starches. Int. J. Biol. Macromol. 2019, 127, 107–117.
40. Harder, H.; Khol-Parisini, A.; Zebeli, Q. Treatments with organic acids and pullulanase differently affect resistant starch and fiber composition in flour of various barley genotypes (Hordeum vulgare L.). Starch Stärke 2015, 67, 512–520.
41. Kapelko-Żeberska, M.; Buksa, K.; Szumny, A.; Zięba, T.; Gryszkin, A. Analysis of molecular structure of starch citrate obtained by a well-stablished method. LWT Food Sci. Technol. 2016, 69, 334–341.
42. Kapelko-Żeberska, M.; Zięba, T.; Pietrzak, W.; Gryszkin, A. Effect of citric acid esterification conditions on the properties of the obtained resistant starch. Int. J. Food Sci. Technol. 2016, 51, 1647–1654.
43. Remya, R.; Jyothi, A.N.; Sreekumar, J. Effect of chemical modification with citric acid on the physicochemical properties and resistant starch formation in different starches. Carbohydr. Polym. 2018, 202, 29–38.
44. Kim, J.Y.; Lee, Y.K.; Chang, Y.H. Structure and digestibility properties of resistant rice starch cross-linked with citric acid. Int. J. Food Proper. 2017, 52, 52166–52177.
45. Ye, J.; Luo, S.; Huang, A.; Chen, J.; Liu, C.; McClements, J. Synthesis and characterization of citric acid esterified rice starch by reactive extrusion: A new method of producing resistant starch. Food Hydrocoll. 2019, 92, 135–142.
46. Mei, J.Q.; Zhou, D.N.; Jin, Z.; Xu, X.; Chen, H. Effects of citric acid esterification on digestibility, structural and physicochemical properties of cassava starch. Food Chem. 2015, 187, 378–384.
47. Srikaeo, K.; Hao, P.T.; Lerdluksamee, C. Effects of heating temperatures and acid concentrations on physicochemical properties and starch digestibility of citric acid esterified tapioca starches. Starch Stärke 2019, 71.
48. Sánchez-Rivera, M.; Nūnez-Santiago, M.D.C.; Bello-Pérez, L.A. Citric acid esterification of unripe plantaion flour: Physicochemical properties and starch digestibility. Starch Stärke 2017, 69, 1700019.
49. Pachuau, L.; Dutta, R.S.; Devi, T.B.; Deka, D.; Hauzel, L. Taro starch (Colocasia esculenta) and citric acid modified taro starch ass tablet disintegrating agents. Int. J. Biol. Macromol. 2018, 118, 397–405.

50. Falade, K.O.; Ayetigbo, E.O. Effects of annealing, acid hydrolysis and citric acid modifications on physical and functional properties of starches from four yam (Dioscorea spp.) cultivars. Food Hydrocoll. 2015, 43, 529–539.
51. Falade, K.O.; Ayetigbo, E.O. Effects of tempering (annealing), acid hydrolysis, low-citric acid substitution on chemical and physicochemical properites of starches of four yam (Dioscorea spp.) cultivars. J. Food Sci. Technol. 2017, 54, 1455–1466.
52. Xia, H.; Li, Y.; Gao, Q. Preparation and properties of RS4 citrate sweet potato starch by heat-moisture treatment. Food Hydrocoll. 2016, 53, 172–178.
53. Alimi, B.A.; Workneh, T.S. Structural and physicochemical properties of heat moisture treated and citric acid modified acha and iburu starches. Food Hydrocoll. 2018, 81, 449–455.
54. Gani, A.; Amreen, J.; Shah, A.; Masoodi, F.A.; Mudasir, A.; Ashwar, B.A.; Akhter, R.; Wani, I.A. Physico-chemical, functional and structural properties of RS3/RS4 from kidney bean (Phaseolus vulgaris) cultivars. Int. J. Biol. Macromol. 2016, 87, 514–521.
55. Wilpiszewska, K.; Antosik, A.K.; Spychaj, T. Novel hydrophilic carboxymethyl starch/montmorillonite nanocomposite films. Carbohydr. Polym. 2015, 128, 82–89.
56. Saikia, C.; Das, M.K.; Ramteke, A.; Maji, T.K. Effect of cross linker on drug delivery properties of curcumin loaded starch coated iron oxide nanoparticles. Int. J. Biol. Macromol. 2016, 93, 1121–1132.
57. Abhari, N.; Madadlou, A.; Dini, A.; Naveh, O.H. Textural and cargo release attributes of trisodium citrate cross-linked starch hydrogel. Food Chem. 2017, 214, 16–24.
58. Lee, S.Y.; Lee, K.Y.; Lee, H.G. Effect of different pH conditions on the in vitro digestibility and physicochemical properties of citric acid-treated potato starch. Int. J. Biol. Macromol. 2018, 107, 1235–1241.
59. Agboola, S.O.; Akingbala, J.O.; Oguntimein, G.B. Production of low substituted cassava starch acetates and citrates. Starch Stärke 1991, 43, 13–15.

Retrieved from https://encyclopedia.pub/entry/history/show/7254