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The significant effect of cold plasma on the modification of the characteristics of cereal starches

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ABSTRACT

Native starches have limited use in the food industry owing to their insolubility in cold water and lack of reactivity. Native starches are susceptible to chemical, physical, and enzymatic modification. This article examines cold plasma as one of the physical mechanisms of starch modification. The structure of each system is analyzed, and the effects of cold plasma at atmospheric pressure on the functional, thermal, molecular, morphological, and physicochemical aspects of various starches researched by different researchers are described. Changes in the characteristics of DBD plasma-modified starch are primarily caused by the depolymerization and cross-linking of amylose and amylopectin side chains. The molecular weight, viscosity, and gelatinization temperature decrease after DBD plasma treatment. The plasma etching of starch granules improves their surface energy and hydrophilicity. Cold plasma is an alternate approach for changing starch characteristics; it may be inferred.

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1- Introduction

Starch is a renewable, biodegradable polymer and a source of energy storage in plants, which contains two main components, amylose and amylopectin. Amylose is a linear polysaccharide consisting of alpha units-D-Glucose is made and through glycosidic bondsa(1→4) are connected to each other. This polysaccharide is approximately 20-30٪ It consists of starch [1]. Amylopectin is a highly branched polymer with linear chains of units a-(1→4)-D-Glucosyl is linked witha(1→6) Linked together, this polysaccharide is approximately 70-80٪ It forms the total starch [2].

Starch is synthesized in granular form and can be obtained from granules, roots, tubers, leaves, pollen and even algae. Starch granules appear under the microscope in different shapes such as spheres and ovals. The diameter of starch granules can vary from 0.1 µm to more than 100 µm depending on their plant origin [3]. Important sources of starch for commercial applications are: corn, potato, cassava and wheat [4]. The starch market is expected to grow at an average growth rate of 4.7% during 2020-2030. Market growth is primarily driven by consumer demand, research and development activities, and increased awareness of starch applications. In a recent study, Trade Market Profile(TMR)[1] It indicates that the value of the global starch market in 2020 is estimated to be more than 1.7 billion dollars. According to this report, it is expected that the global market value will exceed 2.7 billion dollars by 2030, with a growth of 4.7%, because starch has many applications in food and non-food industries.

Starch can be used as a gelling, thickening, stabilizing, and flavor-encapsulating agent in baking, brewing, and confectionery processes, as well as as a coating and film in the food industry [5]. Non-food applications of starch include adhesives for making boards. It is an antifreeze and retarding agent for concrete, as well as fermentation raw materials for pharmaceutical products [6]. However, due to intermolecular and intramolecular hydrogen bonds and semi-crystalline structure, it is impermeable to water at ambient temperature, and insoluble in cold water [7]. On the other hand, starch is easily retrograde. Therefore, starches should be modified to increase solubility, improve textural properties and increase heat tolerance for various industrial applications [8]..

The rheological properties of starch refer to the pasting properties of starch during gelatinization and the dynamic rheology of gel formation [9]. These properties are an important goal for starch modification, which affects its final use. Rheological properties are the deformation and flow behaviors of a material in response to stress, which can be determined by measuring viscosity, and viscosity is defined as the resistance of a fluid (or semi-fluid) to flow when shear stress is applied [10].

2- Methods of starch modification

Usually, starch can be chemically, enzymatically, and physically modified [11, 12]. Chemical modification includes oxidation, succinylation, esterification, esterification and phosphorylation[13]. In this starch modification method, the combination of different functional groups with the starch molecule improves the functional properties and changes in the starch gelatinization temperature.pH and the rheological properties and pasting properties of starch [12].

1-Trade Marketing Representative

Nabshama[2] et al. (2001), reported that cassava starch phosphate has greater resistance to high temperature,pH It has low and creates a higher viscosity, also this modified starch creates textural properties [14]. Also Beamiller[3] et al. (2007), found that modified starch using succinate leads to favorable properties such as high thickening power, low gelatinization temperature and low tendency to retrogradation [15]. On the other hand, Ziauddin et al. (2015), reported that acetylated starch has many uses in the food industry, such as baked products, sauces, frozen foods, baby foods, and snack foods [16]. Chemical modification techniques are the most used and most effective, but there are many concerns about environmental pollution, wastewater treatment, food safety, and high costs related to existing chemical modification methods [17].

An alternative approach is enzymatic modification, which is considered more environmentally safe compared to chemical modification. Amylases are enzymes that are commonly used to hydrolyze starch molecules to low dextrose equivalents by breaking the bond.a(1→4) Between two glucose molecules, they improve the sweetening capacity of starch, increase the browning capacity and improve the texture of the gel.[12] But the use of dual enzyme modification may involve more measures and costs [18]. what[4] et al. (2009), reported that starch treated with a combination ofa-Amylases andb-Amylases oraAmylases and amylglucosidases improve sweetening capacity and browning capacity [19]. Also Hansen[5] et al. (2008), reported that potato, corn and pea starch treated with amylomaltases improves gel texture (formation of gel network, increase in compression force and little or partial gel breakage).[20] On the other hand, Ao[6] et al. (2007), found that the enzymatic hydrolysis of starch using amylases leads to a decrease in the digestion rate due to the increase in starch branch density and crystalline nature. Also, enzymatic hydrolysis leads to starch with a low glycemic index, which makes foods suitable for diabetics from this type of starch [21].

Physical modification can be thermal (wet heat treatment, spray drying, pre-gelatinization, etc.) or non-thermal (pulsed electric field, ultrasound, high hydrostatic pressure, cold plasma technology)[7] (CP) and...) be Physical modification methods of starch are fast and environmentally compatible replacement without producing chemical residues and toxic substances [22]. Physical methods can destroy or influence branching of amylose and amylopectin side chains of starch and influence the shape and size distribution of starch granules [12, 23].

Han[8] et al. (2009), reported that pulsed electric field treatment causes rearrangement and destruction of starch granules, leading to a decrease in relative crystallinity, gelatinization, and viscosity characteristics [24]. Gail[9] et al. (2019), reported that sonication can change the morphological characteristics of granules, crystal pattern, pasting properties (e.g., gelatinization), rheological behaviors, and other characteristic properties of starch granules. Also, ultrasonic treatment can cause visible cracks and pores on the granule surface, decrease relative crystallinity, depolymerization of molecular chains, and increase the swelling power and solubility of starch granules from different sources, such

2 -Nabeshima
3 -Bemiller
4-Chiu
5-Hansen
6 -To the
7 -Cold Plasma
8 -He
9 .Gill

as corn, rice, wheat, cassava, and potato starch [25, 26]. . However, results regarding other properties, such as pasting properties (e.g.,RVA) and thermal behaviors (e.g.,DSC) are sometimes opposite. For example, sonication reduced the pasting viscosity of corn, rice, and wheat starch, but increased the viscosity of potato starch, the reason for this difference being that the amorphous and crystalline structures of starch granules were affected differently after sonication [27, 28]. Physical modification methods have been proven as successful starch modification methods [29]. Cold plasma affects the granule and crystalline structure of starch and changes the physicochemical properties of starch without forming unwanted or unusable products [30].

3-Plasma

Plasma term by Irving Langmuir[10] In the 1920s, it was introduced as the fourth state of matter in addition to solids, liquids, and gases. Before that, in 1816, Michael Faraday[11] He stated the existence of the fourth state of matter, which he called radiant matter. William Crooks[12] He already proved the existence of plasma as a (radiative substance) in the tube in 1879 [31].

Plasma is an ionized gas whose main components include charged particles, free radicals, molecules, atoms, molecules in ground or excited states and carries a net neutral charge. According to thermodynamic equilibrium, plasma can be divided into complete thermodynamic equilibrium plasma, local thermodynamic equilibrium plasma, and non-thermodynamic equilibrium plasma. Complete thermodynamic equilibrium plasma (thermal plasma) in which the following relationship is established in this type of plasma: electron density[13] (The) = ion temperature(Of) = Gas temperature[14] (Tg), local thermodynamic equilibrium plasma (The,[15]Ti, Tglocally reach thermodynamic equilibrium), non-thermodynamic equilibrium plasma (cold plasma) in this type of plasma, unlike thermal plasma, the electron density is higher than the ion temperature and the gas temperatureThe≫ Ti ≈ Tg)) [32].

Cold plasma (non-thermal plasma) is a semi-ionized gas that is produced by applying sufficient energy (thermal, electromagnetic or electric fields, microwaves and radio frequencies) to neutral gas at low pressure or atmosphere [33]. When energy is applied, the free electrons naturally present in the gas receive the energy faster than the ions. The accelerated electrons then transfer energy to heavier gas molecules through elastic and inelastic collisions. As a result of these collisions, the gas undergoes several phase reactions, ionization, excitation and undergoes dissociation to produce several reactive species (reactive oxygen species and reactive nitrogen species), electrons, ions, and new free radicals. Mila[16]and Palumbo[17] In 2014, they found that the electron temperature in cold plasma is relatively high (eV 1-10), while the transition energy of heavy particles (molecules, ions) is close to room temperature. Because electrons have a lighter mass than heavy particles [34].

10-Irving Langmuir
11-Michael Faraday
12-William Crookes

13- Electron Density
14-Gas Temperature
15 -Ion Temperature
16-Milella
17-Palumbo

Therefore, electrons reach higher kinetic energy (temperature) faster than heavy particles. Therefore, cold plasma is unbalanced in thermodynamic equilibrium due to this difference in temperature between electrons and heavy particles [35].

Cold plasma requires much less input power compared to thermal plasma. Thermal plasmas are produced at high temperatures of 20,000-4,000 K and pressures above 105 pas [33]. Thermal plasmas are fully ionized gases because all species (electrons, ions, heavy particles) have the same temperature. Thermal plasma applications are diverse, some of which include extractive metallurgy, fine powder synthesis, and coating technology [35]. Thermal plasma is not suitable for heat-sensitive starches due to high pressure and temperature, that is why cold plasma is a more suitable method for starch modification and other food applications [36].

The purpose of this study is to divide and investigate the structure of cold plasma producing systems and investigate the effect of cold plasma on different types of starches.

4- Classification of cold plasma producing systems

Cold plasma can be produced in low pressure and atmospheric pressure systems.

4-1- Systems producing cold plasma at low pressure

Initial setup of a low-pressure cold plasma system requires a vacuum chamber, a pumping unit (to remove unwanted gases in the system), gas feed tanks, gas controllers, and pressure gauges. In addition to the mentioned components, there is a need for electrodes, which can be generated by electromagnetic generators using direct current.DC, alternating current(AC), radio frequencies or microwave frequencies are fed. This low pressure system can be controlled by a microcontroller and computer. The main advantage of these cold plasma producing systems at low pressure is the easier control of the amount and composition of the critical gas atmosphere from which the plasma is produced; Because this system is placed in a closed wallet under vacuum. On the other hand, due to the fact that these systems are in a closed chamber, uniform plasma distribution takes place [37]. However, low-pressure plasma generator systems are not suitable for continuous on-line processing and can only operate discontinuously. On the other hand, the vacuum equipment required for plasma regulation is expensive [38].

4-1-2- Classification of low pressure cold plasma producing systems for starch modification and use in the food industry

4-1-2-1-radiation discharge cold plasma

In this system, a cold plasma is produced by applying an electric current (100 V or higher) to the gas in a pair or series of electrodes. This electric current can be alternating current(AC), direct current(DC), low frequency (50 Hz) or radio frequency[18] (RF) (40 kHz, 13.56 MHz). Electrons produced in this type of plasma gain enough energy through excited collisions and photons produce visible radiation [39, 40]..

4-1-2-2-Cold plasma radio frequency discharge(RF)

This type of plasma usually works in the radio frequency range of 1-100 MHz. The power supplied from the electric field can be coupled to the plasma in two ways: capacitive [41] or inductive [42]. Capacitively coupled radio frequency plasma consists of two parallel electrodes. One electrode is connected to the radio frequency power source and the other electrode is connected to the ground [42]. The creation of an electric field between two electrodes causes the acceleration of electrons and

18 -Radio Frequency

through the inelastic collision with neutral gas species causes the production of secondary electrons and positive ions [42]. Inductively coupled radio frequency plasma induces a magnetic field in the radio frequency plasma by introducing an electric current into a coil. On the other hand, the magnetic field creates an induction field and accelerates the electrons that lead to the production and stability of the plasma. Inductively coupled RF plasma offers higher efficiency compared to capacitively coupled RF plasma [43].

4-1-2-3-Cold microwave discharge plasma

This plasma production system is an electrodeless method that usually works with an electromagnetic frequency of 2.45 GHz [40]. In the microwave discharge plasma, a magnetron emits electromagnetic waves and causes an electrical discharge [44]. A waveguide directs electromagnetic waves through a treatment chamber filled with gaseous electrons. As a result, electrons absorb microwave energy and undergo ionization reactions through inelastic collisions and produce plasma. Compared to the cold plasma system of radio frequency discharge(RF), the microwave discharge cold plasma system produces more active species and has a higher electron density, because the electron collision frequency is close to the microwave frequency [44]. Another advantage of this system is its efficiency at low pressure and atmospheric pressure [45]. However, its operation is expensive and not very useful in starch modification [46].

4-2-Cold plasma producing systems at atmospheric pressure

Types of plasma generating systems that operate at atmospheric pressure include plasma jet, dielectric barrier discharge, and corona discharge. These systems are widely operated at higher voltages (in kilovolts). The advantage of atmospheric systems is that the sample can be treated continuously, and on the other hand, they do not need expensive vacuum equipment [38].

4-2-1-plasma jet[19] (APPJ)

These plasma generating systems operate at atmospheric pressure and do not require vacuum chambers, which is why they are easy to manufacture compared to low pressure plasma systems. This system can be divided into dual electrode systems and end field jet (single electrode) based on the type of settings and stimulation mode on food systems.

The dual electrode system includes the plasma generator and the air flow and gas inlet control system. The plasma generator usually consists of an outer casing that serves as the ground electrode and an inner electrode that is connected to the power source and the material of this electrode is stainless steel, Pyrex tube, or glass. By establishing a high electric current (2.5 kV to 60 kV), the gas placed between these two electrodes is ionized. These electrodes can be rectangular, conical or cylindrical [47]. Gases used for plasma production that have better storage properties are compressed air or a combination of argon/nitrogen and oxygen/compressed air [48]. The choice of gas flow rate to achieve the required length of the plasma jet varies greatly based on the design parameters of the plasma jet system. The end-field jet system (single electrode) consists of a Teflon body in which a copper wire is placed inside the capillary tube, and this copper wire supplies high voltage [49]. Compared to the double electrode system, this system requires less gas input per minute to produce plasma [50].

19 -Atmospheric Pressure Plasma Jets

4-2-2- Evacuation of the dielectric barrier[20] (DBD)

Dielectric barrier discharge system(DBD) It consists of electrodes covered with dielectric material such as plastic, quartz or ceramic. To prevent plasma particles from coming out, the electrodes are usually placed in a closed container, in this system the sample is placed between the electrodes for direct treatment. To prevent sparks, the electrodes are covered with dielectric materials, and on the other hand, the air used in these systems acts as a flow barrier. This system requires high voltage ignition (10 kV)[51] which can be supplied by the sourceAC OrDC be produced Design parameters in the construction of the device using round-edge electrodes [52], selection of dielectric materials [53] and higher voltage applications are considered. Applying high voltage prevents arcing during plasma production. The gases that are usually used in this system include atmospheric air, nitrogen, argon, and helium.

4-2-3-Corona discharge plasma systems

This system is a pulse discharge plasma system that operates at atmospheric or near atmospheric pressure. When the non-uniform electric field exceeds the breakdown threshold, corona discharge takes place. Setting up a corona discharge system requires a high voltage power supply, electrodes (which are often asymmetric; such as a point and a plate [54]) and a sample treatment chamber. Corona discharge appears as a bright radiation around the tip of the electrode [55]. Depending on the type of high voltage applied to the electrodes, corona discharge can be positive (high voltage at the anode) or negative (high voltage at the cathode). The gases used to produce corona discharges usually include air, nitrogen, argon, a mixture of helium and oxygen, or argon and oxygen [56]. The placement of samples in this system is under the electrode or through hoses to the treatment chamber.

Plasma, as a non-thermal processing technique, has been investigated for a wide range of applications in the food industry, such as food microbial decontamination, food preservation, enzyme inactivation, and modification of the functional characteristics of some food components. Cold plasma has been investigated in the modification of food components such as starch, protein, food enrichment[57], modification of films[58], printability in packaging, etc.[59, 60]. Due to the ease of access with continuous processing systems, plasma jet is used in the processing of food such as nuts, fruit juices, spices and vegetables [50, 61, 62].

5- Investigating the effect of atmospheric cold plasma on the properties of starch from different sources

5-1-Molecular properties

Short-range molecular arrangement, molecular weight and amylose content are investigated under the title of molecular properties of starch, and to analyze the molecular properties of different starches after modification with cold plasma, techniques such as high-performance anion exchange chromatography can be used. (HPAEC)[21], high-performance chromatography with multi-angle laser light scattering (HPSEC-MALLS-RI)[22،23]FTIR،NMR[24] and X-ray photoelectron spectroscopy[25] (XPS) used [30].

20- Dielectric Barrier Discharge

21 -High-Performance Anion-Exchange Chromatography
22 -High-Performance Size-Exclusion Chromatography coupled with Multi-Angle Laser Light Scattering
23 -Fourier-transform infrared spectroscopy
24 -Nuclear Magnetic Resonance
25 -X-ray Photoelectron Spectroscopy

5-1-1-Examination of short-range molecular arrangement

Structural changes at the molecular level of starch (short-range molecular arrangement) can be detected using the spectrumFTIR It did a little [63] because the tapesFTIR At 1000, 1022 and 1047 cm, they are sensitive to changes in the starch structure [64]. The bands at 1000 and 1047 cm are more prominent in the crystalline structure of starch, while the band at 1022 cm is more dominant in the amorphous structure.[65]. Therefore, the band ratios at 1000/1022 cm and 1047/1022 cm are generally considered as a measure of short-range molecular order in starch [65, 66].

Goo[26] et al. in 2022, reducing the intensity of the bandFTIR at 2871 cm in potato treated with plasmaDBDThey observed that this decrease is due to the removal of some water molecules from starch by plasma treatment. Also Yan[27] et al. in 2019 by examining tapesFTIR, reported changes in the short-range molecular arrangement of potato starch after plasma jet treatment. On the other hand, Yan et al. in 2021 observed the loss of molecular order in the short-range order of rice starch after cold plasma treatment, which is because the cold plasma treatment destroys amylopectin side chains and starch fragments. produces a smaller On the other hand, cold plasma treatment can break down amylose in the amorphous region and produce and release a large amount of smaller amylose, which as a result reduces the molecular order in the short-range order. Also B[28] And Colleagues in 2016 and Zhu[29] et al. in 2019 observed a decrease in the ratio of 1047/1022 band in corn starch after treatment with cold plasma. Similarly, Carvalho[30] et al. in 2021, by examining the spectrumFTIR Arya starch after treatment with cold plasma found a decrease in the ratio of 1022/1047 band. On the other hand, Yan et al. (2020) by examining the spectrumFTIR After banana starch treatment with cold plasma, they reported an increase in the absorption intensity ratio at 1022/1047 cm. Sun[31] et al. in (2022), observed an increase in the absorption intensity ratio at 1022/1047 cm. The decrease in the short-range order of starch after plasma treatment is due to the polymerization of glycosidic bonds in starch [67]. Also sand[32] et al. 2022 by examining the spectrumFTIR After treating wheat starch with cold plasma, they reported a decrease in the absorption intensity ratio at 1022/1047 cm, which degree of decrease was proportional to the time of plasma treatment, because plasma treatment caused the depolymerization of starch molecules [68].

On the other hand, the increase in the ratio of 1022/1047 cm is due to the decomposition and release of amylose from the amorphous regions, which reduces the amorphous structure [69]. Cold plasma treatment can cause the formation of short-range double helical bonds, which increase the short-range order of starch [70]. In addition to investigating the short-range molecular order, the spectraFTIR It can be a method to detect cross-linking in starch. 1160 cm, 1084 cm, 1018 cm, 921 cm peaks in the spectrumFTIR Indicates link expansion and contractionC-O-C In the six-membered ring are carbon-oxygen. Cold plasma causes a significant reduction of the peak at 921 cm; Because depolymerization mainly by breaking glycosidic bondsC-O-C Starch molecules occur. Cold plasma treatment stimulates the production of different active

[26] -Guo
[27] -Yan
[28] - It falls
[29] -Zhou
[30] -Oak
[31] -Sun
[32] - Shen

particles, which react with starch and destroy the polymer structure. Also, the formed free radicals destroy the glycosidic bond at the carbon number 1 position of the glucose molecule in the starch macromolecule and lead to the depolymerization of the starch chain [71]. On the other side of the spectrumFTIR The 2930 cm peak expresses the tensionC-H Is. Also, the peak of 3430 cm indicates the peak of absorption of tensile vibrationO-H Is.

In 2021, Carvalho et al. reported an increase in the area of graftsC-O-C They observed dielectric discharge (10-14 kV) in Arya starch after plasma treatment. Also Wongsagunsap[33] et al. in 2014 and Diaei et al. in 2013 showed an increase in the relative areas of the grafts.C-O-C observed in starch after plasma treatment.

In addition, Vengsagunsap et al. in 2014, decreasing the relative intensity of protonsOH^- They observed granular and non-granular tapioca starch after plasma treatment at 50 and 100 W. This is due to crosslinking in these starches and elimination of groupsOH Was.

5-1-2- Molecular weight

analyzeXPS Increase in linksO--C-OH in corn starch and the subsequent reduction in bondsC (C-H)، C-O AndO-C-O due to oxidation of these bonds by plasma reactive species against carboxyl groups(O--C-OH) showed [72]. In 2022, Shen et al. reported that increasing plasma treatment time significantly decreased the molecular weight of amylopectin of wheat starch molecules, while increasing the molecular weight of intermediates and amylose compared to the original substance. Because plasma treatment can gradually depolymerize starch molecules with increasing treatment time[68].

Also, Bei et al. in 2016 found that applying plasma treatment on corn starch increased the averageThis increase in molecular weight is due to the polymerization of starch by plasma. On the other hand, Sun et al. in 2022 observed that the application of dielectric discharge plasma treatment on rice starch increased the molecular weight of amylose. Researchers attributed this increase to the polymerization of amylose chains, caused by plasma treatment. On the other hand, Kalayondan[34] et al. in 2022, observed that the application of 170 V plasma treatment on mango starch increasedViscosity molecular weight[35](MWv)became. Although increasing the plasma treatment to 230 volts causes a decreaseM_{Wv} became The reason for this increase and decrease was stated as the lower treatment voltage causes the intermolecular connection of non-polymerized starch molecules in the adjacent chains and as a resultM_{Wv} increases. Whereas, at higher treatment voltage, depolymerization occurs completely inside the starch molecule and thereforeM_{Wv} reduces. Also Shayzen[36]et al. in 2022, found that the molecular weight of amylose and amylopectin gradually decreases with the increase of cold plasma treatment time, this decrease in molecular weight indicates that the plasma successfully destroys starch molecules. This is with the observations of J[37] et al. in 2021. On the other hand, Shaijn et al. in 2021 observed that the application of dielectric discharge plasma treatment on azuki beans caused a decrease in molecular weight, which was attributed to the breaking or depolymerization of the side chain of the amylopectin polymer. attributed Also Saranjekt[38] et al. found in 2022 that increasing the voltage and time of plasma

[33] -Wongsagonsup

[34]- Kalaivendan

[35]-Molecular Weight Viscosity

[36] -Xiangzhen

[37] -Ge

[38] - Srangsomjit

treatment decreased the molecular weight of tapioca starch and attributed this decrease to the depolymerization of plasma treatment [73].

The reduction of molecular weight by cold plasma treatment can be due to the following two reasons: 1- The reaction between high-energy ions created by cold plasma treatment with the side chains of amylose and amylopectin of the starch molecule causes depolymerization and the formation of smaller pieces. 2- The high oxidation ability of reactive species produced by cold plasma with the reducing end of the starch molecule causes the decomposition of the starch molecule. [12] On the other hand, Shaizhen Sun[39] et al. in 2022, observed that the application of cold plasma treatment on rice starch increased the molecular weight of amylose from 0.75 x 105 g/mol to 3.82 x 105 g/mol. However, the molecular weight of amylopectin first increased and then decreased, as the cold plasma treatment time was prolonged. Weight Gain Molecular amylopectin is mainly attributed to the polymerization of starch molecules caused by active radicals [30].

The different effects on molecular weight between amylopectin and amylose after cold plasma treatment may be attributed to the structure of amylopectin, which is more sensitive to the combination of treatments. This can be linked to spatial hindranceA'1 → 6) that of the linka (1 → 4) Smaller is explained, so the linka (1 → 6) It breaks more easily [74].

5-1-3-Amylose content

In 2021, Carvalho et al. observed that the application of dielectric barrier discharge plasma treatment up to 14 kV on Aria starch caused a decrease in amylose content, which they attributed to the depolymerization of Aria starch to simple sugars. While increasing the plasma production voltage up to 20 kV led to an increase in amylose content, therefore, plasma production with a higher voltage causes the polymerization of Aria starch chains. Also, cold plasma treatment of amylose content of quinoa starch [71] and rice starch [41] reduced In addition, the mechanism of cold plasma depolymerization causes a significant reduction of amylose content [72]. Also, Shen et al reported in 2022 that the amylose content of wheat starch decreases with the increase in plasma treatment time, which they attributed to the partial depolymerization of amylose chains that are attacked by active plasma species[68].

On the other hand, Shaijen Sun et al. in 2022 found that cold plasma treatment increased the amylose content of rice starch. However, you will see[40] et al. in 2018, observed that cold plasma treatment can reduce the amylose content of corn starch. Also, in 2022, Saranjenjekt et al. found that increasing the voltage and time of plasma treatment increased the amylose content of tapioca [73].

These results show that cold plasma treatment has different effects on the amylose content of starch from different sources. The increase in amylose content can be attributed to the fact that cold plasma treatment can cause the polymerization of amylose chains, change the helix structure of amylose and improve the amount of amylose. Also, depolymerization of amylose chains can reduce the amylose content of starches.

In addition, the molecular weight of amylose can affect the amylose content. As a result, atmospheric pressure plasma systems can depolymerize starch molecules or cause cross-linking. It depends on various factors

[39] -Xiangxiang Sun

[40] -Banura

such as treatment time, applied power, pressure, type of gas and plant source of starch [12].

5-2- Granule morphology

Okira[41] et al. in 2019, after applying radio frequency plasma treatment(RF) 120 W for 60 min did not observe any effect on the shape of corn, rice and potato starch granules.

On the other hand, Zhang[42] et al. in 2015, by examining conventional and polarized light microscope images, the morphology of potato starch after treatment with nitrogen plasma for 30, 45 and 60 minutes did not report any changes. In addition to conducting studies on the morphology of starch granules after treatment with cold plasma, studies have also been reported on the presence of deposits in starch after treatment with cold plasma. In 2018, Binira et al. showed the existence of uneven deposits on the surfaces of corn starch granules after treatment in plasma.RF Capacitive coupled reported 60 watts for 20 minutes. The results of this study are in agreement with the previous reports of Lee[43] et al. in 2002, is consistent. After potato and corn starch were exposed to radiation plasma for 30 minutes, researchers observed deposits on the surface of these two starches. Pankaj on the other hand[44] et al. in 2017, from[45]AFM To study the surface topography of modified films with atmospheric cold plasma at high voltage(HVAC) they used They observed an increase in the surface roughness of these modified films due to plasma etchability. The researchers reported that the rice starch film was more sensitive to surface etching. On the other hand, Sheikhi et al. in 2020 also reported an increase in wheat starch film roughness after treatment with radiant discharge plasma. Cracks, voids, deposits and roughness are caused by the etching mechanism of reactive species created during the modification of starches with cold plasma [12, 64, 75]. The effects of plasma on starch morphology depend on the treatment conditions, the type of plasma and the plant source of starch.

Also, Shen et al reported in 2022 that wheat starch treated with plasma maintained its original granule shape, while it caused some indentations and corrosion on the granule surface due to the plasma etching phenomenon [68].

The results of studies have shown that radiation discharge plasma treatment can effectively cause cracks in starch. On the other hand, Shaijn et al. reported in 2022 that after applying 40V dielectric discharge cold plasma treatment for 9, 6, 3, 1 minutes on rice starch, no changes were observed in the morphology of starch granules. Also, in 2022, Shaijen Sun et al., by examining the morphology of rice starch granules after cold plasma treatment of dielectric discharge of 40 volts for 10,6,2, concluded that cold plasma treatment can cause a slight change in the morphology of starch granules. However, the integrity of the starch granules is maintained, indicating that this modification occurs mainly within the starch granules. From Gate[46] et al. in 2021, after treating redazuki bean starch with cold plasma of 40V dielectric discharge for 10,5,1 minutes, observed that the integrity of redazuki bean starch granules did not change after cold plasma treatment. Dielectric discharge plasma treatmentDBD Due to the production of highly energetic species during plasma production, it bombards the surface of the starch granule, which causes the evaporation of the starch surface (plasma etching). Also

[41] - Big
[42] -Zhang
[43] -Lee
[44]- Pankaj
[45] -Atomic Force Microscopy
[46] - Going

dielectric discharge plasma treatmentDBD It causes cracks on the surface of banana starch [69], red azuki bean starch [76] and potato starch [77]. became. On the other hand, Carvalho et al. in 2021 showed the formation of cracks and particle aggregation in Aria starch granules after plasma treatment.DBD (20 kV) observed.

5-3- Crystallinity

In 2019, Zuo et al. observed that the relative crystn[47] (RC) Waxy corn starch (7/46٪ - 0/42٪) and normal (1/40٪ - 7/35٪) decreased after plasma jet treatment [67]. Similarly, Yan et al. in 2019 observed that after plasma jet treatment of potato starch the relative crystallinity decreased without change in crystal structure [78]. On the other hand, Yan et al.'s study in 2020 showed that with the increase in dielectric discharge plasma treatment time, the crystal structure of banana starch of the typeC to typeA changed[69].Also, Guo et al. in 2022 showed a decrease in the relative crystallinity of potato starch after dielectric discharge plasma treatment without any change in the crystal structure of the typeB They saw. Similarly, Sun et al. (2022) reported a decrease in the relative crystallinity of rice starch after dielectric discharge plasma treatment without any change in the type crystal structure.A On the other hand, Shaijn et al. in 2022 observed that cold plasma treatment reduced the crystallization of rice starch [41]. The decrease in crystallization is due to the depolymerization of starch molecules [79]. The voltage and time of plasma treatment decreased the relative crystallization of tapioca [73].

Cold plasma treatment causes the partial decomposition of starch molecular chains, especially amylopectin in the surface layer of starch granules, followed by the loose rearrangement of damaged starch chains. As a result, the overall crystalline structure of the surface layer of rice starch is destroyed, and with the increase of amorphous regions, the molecular structure of starch tends to It becomes disordered. Also, Shaijen Sun et al. in 2022 observed that cold plasma treatment on rice starch does not change the crystalline structure of rice starch, because physical treatments mainly affect the amorphous region instead of the crystalline region of starch granules [25]. Researchers attribute this decrease in relative crystallinity to disruption in the reorganization of starch molecules. On the other hand, the depolymerization of starch chains caused by plasma treatment also reduces the relative crystallinity and changes the crystal structure of starch[80].

Although it was[48] et al. in 2018 observed an increase in the relative crystallization of banana starch after corona discharge plasma treatment. Also, Gao et al. reported in 2022 that increasing the duration and voltage of plasma treatment increased the relative crystallization of tartaric buckwheat starch [81].

This increase in relative crystallinity is due to the reaction of active species in the plasma with the starch molecule, which can cause the hydroxylation of the amorphous regions and through the formation of the ether bond, causes the starch molecules to turn into a more complete crystalline structure. The researchers concluded that atmospheric plasma can cause changes in starch crystallization typeB AndC More than type starchesA create

5-4- Gelatinization

In 2014, Vengsagunsap et al., increase inΔH observed granular tapioca starch modified with 50 and 100 W plasma. But the

[47]- Relative Crystallinity

[48]- Wu

gelatinization temperature was not significantly different from untreated samples. Also, Gao et al., in 2019, observed that cold plasma treatment on tartaric buckwheat starch caused an increase inΔH and increasing the gelatinization temperature of tartaric buckwheat starch. being highΔH and gelatinization temperature indicate the presence of longer double helices formed by the twisted ends of external chains in amylopectin [82]. High cross-linking starches are more resistant to heat and shear damage during heat treatment [83]. Also, Shen et al observed in 2022 that cold plasma treatment increases the gelatinization temperature and gelatinization enthalpy of wheat starch[68].

But, Wu et al., 2018, decreaseΔH Banana starch and the increase in gelatinization temperature after corona discharge plasma modification were observed. On the other hand, Carvalho et al. in 2021, reduced the gelatinization temperature in Aria starch after treatmentDBD (14 kV) observed. Also, Zhou et al. in 2019, decreaseΔH Waxy and normal corn starches were observed after treatment with plasma jet with power of 750 watts for 1-7 minutes. Similarly, Guo et al. in 2022, reductionΔH in potato starch after plasma treatmentDBD They saw.

The reason for the decrease in gelatinization temperature and enthalpy is attributed to the cold plasma treatment, which causes depolymerization of starch chains. The observed differences in enthalpies and gelatinization temperatures are all based on the type of plasma settings used, time, gas/gas, power and pressure used to modify the starch.

5-5-Massing properties

Yan et al. in 2020, observed that with increasing intensity of plasma treatmentDBD The maximum viscosity of banana starch decreases from 5242 to 153 centipoise. Also increasing the intensity of plasma treatmentDBD It caused a decrease in the values of final viscosity, breakdown viscosity, breakdown viscosity and rebound [69]. Because the intensity of plasma treatment increasesDBDIt reduced cross-links, van der Waals forces, and hydrogen bonds between damaged and sticky starch chains.

In 2019, Wu et al. observed that the application of plasma jet treatment to corn starch caused a decrease in final viscosity, fracture viscosity, and maximum viscosity, and at an intensity higher than 800 W, the viscosity decreased significantly to 410 cpoise, but there was no change in The temperature of starch paste is not created. Kalayundan et al., 2022, observed a decrease in peak viscosity, breakdown, flashback and final viscosity in mango starch after plasma treatment. The researchers attributed the decrease in the maximum viscosity to the depolymerization of the starch chains, and the reason for the decrease in the breaking, backward and final viscosity of mango starch was the stabilizing effect of the plasma treatment. Also, Shaijen Sun et al., 2022, observed that short-term cold plasma treatment did not cause any change in the maximum viscosity of rice starch. On the other hand, Shen et al. in 2021 did not observe any significant change in the maximum viscosity of rice starch after cold plasma treatment for a short time. However, cold plasma treatment for a longer time significantly decreased the maximum viscosity of rice starch. The decrease in maximum viscosity may be attributed to the association between starch chains and increased intramolecular bonding forces [71]. Similarly, Gait studies[49] et al. in 2019, and the study by Ji et al. in 2021, and the study by Shen et al.

[49]- Gaoet

2022 showed that cold plasma treatment reduces the maximum viscosity of starches. However, Tirumadas[50] et al. in 2017, found that the maximum viscosity of corn and tapioca starch increased after cold plasma treatment. Also, Carvalho et al. reported in 2021 that with increasing plasma production voltage, the maximum apparent viscosity values[51]FIGincreased significantly. The reason for this increase may be related to the cross-linking of amylose/amylopectin molecules [30], because the cross-linking of the chains reduces the breakdown of starch granules and may increase the dough viscosity [84]. Starches with low maximum apparent viscosity values may be damaged and disintegrate at low temperatures and have high dextrin levels or resistance grades. Viscosity breakdown[52](BD) An important parameter of dough properties is starch and it is related to the stiffness of swollen granules [85]. An increase in plasma production voltage leads to an increase in fracture viscosity[53](TAV) compared to natural (untreated) starch. In contrast, valuesBD Plasma production decreased with increasing voltage. Although other reports on the application of cold plasma in banana starch [86] and wheat flour [87] have shown that increasing the plasma voltage valuesTAV reduces.

Rebound viscosity (SB)[54] It is related to gelatinization and retrogradation of starch [71]. Increasing the cold plasma voltage increases the valuesSB It became natural in starch. However, different plasma voltage levels produce a change in breakdownSBdid not create Amylose and amylopectin content are important parameters for starch pasting properties, which depend on swelling index, solubility, crystalline properties and inter-rotational friction.

As a result, the pasting properties of starch modified with cold plasma depend on starch types, plasma types, plasma treatment conditions and reaction time.

5-6- Rheology

Modification of starches using atmospheric pressure plasma systems may produce stronger or weaker gels depending on the treatment conditions. In 2022, Guo et al. observed that the application of dielectric discharge plasma treatmentDBD It reduced the tendency to retrogradation of potato starch gels. On the other hand, researchers reported that dielectric discharge plasma treatmentDBD causing a significant increase in storage modulus and loss modulusG′ and G″ They attributed this increase to the formation of cross-links in starch molecules caused by plasma treatment.

Also, in 2014, Vongsagunsap et al. used plasma jet with argon feed gas as an alternative to chemical modification of starch. The researchers reported that subjecting tapioca starch granules to 50 W plasma treatment resulted in the formation of stronger gels. The reason for this increase can be attributed to the cross-linking of starch chains. However, 100 W plasma treatment weakened the gel structure due to depolymerization. On the other hand, Bei et al. in 2016 observed a decrease in the viscosity of corn starch after dielectric discharge plasma treatment. Zuo et al., 2004, found that active species in plasma cause cross-linking of side chains, which prevents starch granules from being washed into solution.[83] On the other hand, Gao et al. found in 2022 that both modulesG′ and G″Buckwheat tartar decreased with increasing duration and voltage of plasma treatment.G′ and G″ The bottom shows the weak structure of the starch gel formed

[50] - Thirumdas
[51] -Peak Apparent Viscosity
[52]- Breakdown
[53] -Trough Apparent Viscosity
[54]- Setback

during modification by plasma treatment. Because increasing the treatment voltage and the duration of the treatment leads to an increase in the average speed and the number of collisions, which increases the amount of molecular depolymerization and the formation of a weak gel structure. All these results showed that the effects of plasma treatment in bothG′ and G″ It depends on the treatment conditions such as plasma voltage and duration. Different treatment conditions play a key role in determining which of the two competing reactions (cross-linking and depolymerization) is dominant, leading to the formation of rival-modified starch [81].

5-7- Solubility and swelling power

Solubility is an essential indicator for the use value of starch soluble in cold water, which indicates the degree of dissolution and precipitation of molecular chains. Shaijn G[55] et al. in 2022, observed that cold plasma treatment reduced rice starch dissolution from 32.65 to 51.57٪ This increase shows that the cold plasma increases the ability of water to penetrate the starch granules. Because the strong semi-crystalline structure of natural starch prevents cold water from completely penetrating the starch granules [88]. In 2022, Shaizhan J et al observed that applying cold plasma treatment on rice starch causes easy formation of hydrogen bonds of starch chains in water, and these chains are easily dispersed in water. In addition, cold plasma treatment causes partial decomposition. Starch molecules create smaller pieces with higher swelling power and consequently higher solubility.[71] On the other hand, the studies of Shaijen Saab et al. in 2022 showed that cold plasma treatment causes damage to the surface of starch granules and may increase the leaching of amylose from the amorphous region and improve the solubility of starch.

Swelling strength reflects the interaction between starch chains in amorphous and crystalline domains. Amylose and long-chain amylopectin have a very good effect in preventing the swelling of starch granules [89]. But amylose and long-chain amylopectin decreased or completely disappeared in samples treated with cold plasma. These changes lead to an increase in the expansion force of the sample, and as a result, the cold plasma treatment increased the swelling capacity of starch. Similar results were reported by Thirumdas et al. in 2017, and Binira et al. in 2018.

Swelling power is related to hydration, interaction between amylose and amylopectin molecules, intramolecular bonds and the connection of starch crystal regions. In 2022, the studies of Shizhen Sun et al. showed that the swelling power of starch samples treated with cold plasma is higher than that of natural starch at a lower temperature (50-60°C), while the swelling power of natural starch was higher than starch samples treated with cold plasma at temperatures of (C° 70-90). In addition, Singh, Isuno and Noda in 2010 found that starch with higher crystallinity percentage showed lower swelling power [90].

[55]- Xiangzhen Ge

6-Conclusion

Starch modification using cold plasma technology has been proven to be a new alternative to chemical modifications. By using atmospheric cold plasma system compared to low pressure cold plasma systems,The sample can be treated continuously, on the other hand, this system requires equipmentExpensive doesn't make sense. It can also be concluded that cold plasma is a high-precipitation, easy-to-use, and environmentally friendly physical modification technology that can produce starch with high water absorption capacity and stability during the thermal process. Changes in starch properties depend on the type of gas used to produce the plasma, the operating conditions of the plasma (including power, time and pressure) and the source from which the starch is obtained. It is suggested that focusing on dual modification methods (eg, ozone and ultrasound) is necessary for further research.

7- Resources

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تأثیر پلاسمای سرد بر اصلاح ویژگی‌های نشاسته‌های غلات

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چکیده

نشاسته‌های طبیعی به دلیل ماهیت غیر واکنشی و نامحلول بودن در آب سرد، کاربرد محدودی در صنایع غذایی دارند. نشاسته‌های طبیعی را می‌توان با روش‌های شیمیایی، فیزیکی و آنزیمی اصلاح کرد. پلاسمای سرد یکی از روش‌های فیزیکی اصلاح نشاسته است که در این مقاله موردبررسی قرار می‌گیرد. سیستم‌های تولید پلاسمای سرد به دودسته فشار پایین و فشار اتمسفری تقسیم‌بندی می‌گردند، ساختار هر سیستم موردبررسی قرارگرفته و اثرات پلاسمای سرد در فشار اتمسفر بر خواص عملکردی، حرارتی، مولکولی، مورفولوژیکی و فیزیکوشیمیایی نشاسته‌های مختلف که موردمطالعه محققان مختلف قرارگرفته به بحث گذاشته می‌شوند. تغییر در خواص نشاسته اصلاح‌شده با پلاسما دی الکتریک عمدتاً به دلیل دپلیمریزاسیون و اتصال متقاطع زنجیره‌های جانبی آمیلوز و آمیلوپکتین است. پس از تیمار پلاسما دی الکتریک، وزن مولکولی، ویسکوزیته و دمای ژلاتینه شدن کاهش می‌یابد. حکاکی پلاسما انرژی سطحی و آب‌دوستی گرانول‌های نشاسته را افزایش می‌دهد؛ بنابراین می‌توان نتیجه گرفت که پلاسمای سرد به‌عنوان فناوری جایگزین برای اصلاح خواص نشاسته است.