Nirmal Mazumder ·
Md. Hafizur Rahman *Editors*

Advanced Research in Starch

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Preface

In the dynamic landscape of modern scientific research, our understanding of fundamental elements often unfolds in unexpected and enlightening ways. The exploration of starch, a ubiquitous and complex carbohydrate, has been no exception. *Advanced Research in Starch* is a testament to the relentless pursuit of knowledge in this field, capturing the essence of breakthroughs and innovations that propel starch science into new frontiers. This book brings together a collection of chapters penned by esteemed researchers and scholars who have dedicated themselves to advancing our comprehension of starch, from its molecular intricacies to its wide-ranging applications. The multidisciplinary approach adopted in these chapters reflects the diverse facets of starch research, encompassing chemistry, biology, physics, engineering, and applied sciences. As we delve into the pages of this book, readers will embark on a journey through the latest discoveries, methodologies, and technologies that define the forefront of starch-related studies. From the elucidation of starch biosynthesis pathways to the exploration of novel applications in various industries, each chapter contributes a valuable piece to the intricate puzzle of starch science.

Starch, a crucial carbohydrate for plants and animals, is a primary energy source. Its diverse functional properties make it valuable in the food industry. However, native starches may not always meet specific functional requirements for certain foods. Thus, starch is modified to enhance its functional attributes for application in different food formulations. The first chapter by Navaf and Sunooj titled 'Physical Modifications of Starch' discusses the different physical modifications of starch and their techniques. The second chapter authored by Ali et al. elucidates the preparation, applications, and safety assessment of cross-linked, esterified, etherified, oxidized/bleached, and acid-thinned starches along with the impact of these modifications on the structural, functional, and digestibility characteristics of starches. After the physical and chemical modification of starches, the third chapter authored by Saeid et al. dives into the topic of enzymatic modification of starches. The main focus here is the starch modifying enzymes, which are discussed in detail, including their properties, mechanisms of action, and industrial applications. Chapter 4 by Hadi and Rahman discusses the modification of starches by solvent methods. The chapter also elucidates the application of supercritical carbon dioxide ($ScCO_2$) and ionic liquids (ILs) in the modification of starches, with a focus on sustainable starch modifications. The next few chapters discuss the characterization of starch through

various methods. Chromatographic techniques such as gel permeation chromatography, high-performance size exclusion chromatography coupled with different detectors (multi-angle laser-light scattering, refractive index, intrinsic viscosity), and high-performance anion-exchange chromatography used for the characterization of starch are discussed in Chap. 5 by Luis et al. The chapter also discusses the existing gaps in the study of starch structures using chromatographic methods. The surface morphology of starch granules are observed with greater resolution through electron microscopes such as scanning electron microscopes than optical microscopes. Chapter 6 authored by Anusha and Mazumder elucidates the characterization of starch granules derived from various sources. The chapter also discusses the application of electron microscopes to study the effect of enzymatic degradation patterns on starch. Vibrational spectroscopy plays a very vital role in the characterization of materials. It is one of the first pillars of spectroscopic tools that enable researchers to investigate the primary configuration of the object under investigation. Rajib Biswas in Chap. 7 outlines the role of vibrational spectroscopy in the analysis and characterization of starch. In Chap. 8, Deka et al. elucidate the various tools used for microscopic assessment, thermal characterization, rheology measurement, and the digestibility analysis of starch. This chapter is most useful for those with basic knowledge on the principles, working, and applications of analytical tools. After studying the characterization of starches, the book delves into the applications of modified starches in various fields such as biomedical, industrial, and food technologies. Chapter 9 by Mateti et al. elucidates starch modification methods for its use in the food industry and as a biomaterial for biomedical applications such as wound healing and its prospects. Chapter 10 authored by Lobo et al. explores the Andean grains used in traditional cooking. The writers elucidate the characteristics, modifications performed for industrial and nutraceutical applications. Eventually, the book takes us through genetic modifications of starch and the advantages of resistant starch. The last Chap. 11 by Sarmah et al. sheds light onto resistant starch and its various applications in the biomedical and nutraceutical fields. The chapter also discusses the exciting possibilities of genetically modified resistant starches, and their great potential to improve human health.

As we delve into the pages of this book, readers will embark on a journey through the latest discoveries, methodologies, and technologies that define the forefront of starch-related studies. From the elucidation of starch biosynthesis pathways to the exploration of novel applications in various industries, each chapter contributes a valuable piece to the intricate puzzle of starch science. We express our deepest appreciation to the contributors, whose intellectual prowess has shaped this compilation into a comprehensive reference for scientists, academics, and industry professionals. We are grateful to the reviewers for devoting their time to providing insightful recommendations and comments on the chapters. We also acknowledge our colleagues who helped us with this volume's suggestions. It is our hope that *Advanced Research in Starch* will not only serve as a reservoir of knowledge but also inspire future research endeavours, fostering a community committed to unravelling the complexities of starch in all its forms. Machi Sugimoto and Swati Sharma

(Springer Nature Publishing) deserve special thanks for their contributions to the book. May this book be a source of inspiration, a catalyst for scientific inquiry, and a cornerstone for the ongoing advancement of starch research. More importantly, we wish our readers a pleasant and productive browsing experience.

Manipal, Karnataka, India — Nirmal Mazumder
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Md. Hafizur Rahman is currently working as a Lecturer at the Department of Quality Control and Safety Management, Faculty of Food Sciences and Safety, Khulna Agricultural University (KAU), Bangladesh. He acquired his Ph.D. from the Laboratory of Food Chemistry and Nutrition Science, Institute of Food Science and Technology, Chinese Academy of Agricultural Sciences (CAAS), China, in August 2020. Then, he worked as a Postdoctoral Fellow in the Department of Agro-Product Processing Technology, Jashore University of Science and Technology, Bangladesh, from June 2021 to June 2022. He has extensively worked for a long time on the comparative study of different starch properties after physical modification and its effects on the different gluten-free model dough. He has also investigated the effects of different sugars and different level of salt concentrations on the rheological, fermentation, water mobility, and microstructural properties of starch-based

gluten-free model dough prepared from corn, potato, and sweet potato starches and he developed some novel starch-based gluten-free model dough. He has published several research articles in different peer-reviewed international journals.

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Physical Modifications of Starch

1

Muhammed Navaf
and Kappat Valiyapeediyekkal Sunooj

Abstract

Starch is a carbohydrate that serves as a primary source of energy for plants and animals. Various functional properties of starch make it an ideal ingredient for the food industry. It is generally considered that native starches do not always meet the necessary functionalities required for specific foods. Starch is typically modified to enhance its functional attributes for application in different food formulations. Different techniques are employed to synthesize starch with various functional attributes and applications. Food processors prefer to use physically modified starches rather than chemically modified starches, so it is becoming increasingly important to use functional starches that have not been chemically modified. The physical modification of starches via physical treatment is investigated as a method to modify starch properties without chemically modifying them. Since they are free of chemicals or biological agents, physically modified starches are a less expensive option than chemically and enzymatically modified starches.

Keywords

Physical modifications · Heat moisture treatment · Annealing · Irradiation · Ultrasonication · High pressure treatment · Cold plasma treatment

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1.1 Introduction

Starch is a natural polymer originating from various plant sources, i.e., fruits, vegetables, cereals, etc., and it has great utility in different industries, e.g., paper, textile, pharmaceuticals, etc. Starch granules mainly consist of two polymeric chains, amylose and amylopectins. Starch in its native form cannot always meet the demand for the wide utility of starch in industrial sectors. The properties like low gelatinization temperature, higher swelling, etc. may affect the industrial demand for starches in their native form. It is important to consider the composition and structure of starches when determining their functional properties. For example, starch with high amylopectin facilitates film formation, while starches with high amylose form soft gels. Therefore, starches are modified in such a way that they provide specific functionalities.

Figure 1.1 illustrates four general methods of modifying starches: physical, chemical, enzymatic, and genetic engineering. Physical modification is widely accepted and has been practiced for decades. Physical modifications of starch have the advantages of being non-toxic, cost-effective, and green methods. It offers the advantage of the absence of any reagents in the process and is free from byproducts released into the environment.

There are different types of physical methods adopted to modify the starches. Hydrothermal treatment, i.e., heat moisture treatment, annealing, etc., is one of the early techniques in starch modification. During hydrothermal modification, water and heat break down starch intermolecular bonds (Adewale et al. 2022). Recent past, new nonthermal methods have been adopted to modify starches, e.g., pulsed electric field treatment, high-pressure treatment, plasma treatment, etc. (Wu et al. 2022). Physical modifications affect the structural and packing arrangement of starch granules, thus leading to significant changes in its various functionalities. In

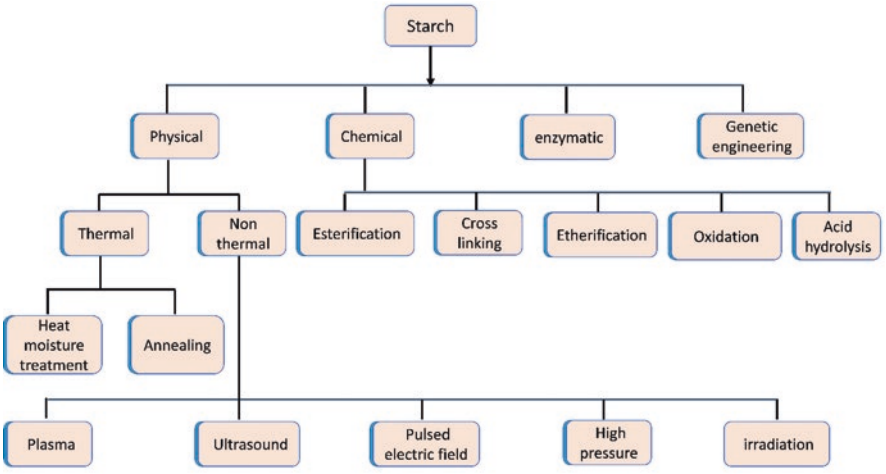

Fig. 1.1 An overview of starch modifications

addition, the type of starch and modification has a potential contribution to desired changes of physically modified starches.

1.2 Heat Moisture Treatment (HMT)

During HMT, starch with 10–30% moisture is exposed to a temperature of 90–120 °C for up to 16 h, viz., above the glass transition temperature (Tg) and below gelatinization. HMT alters starch properties and structure, varying with the starch source and composition. The mechanism of HMT includes facilitating the interactions of starch chains. In the beginning, HMT damages crystalline structures, dissociates double helix structures, and then reassembles them. HMT also alters the ordered arrangement of the starch crystallites (Hoover and Manuel 1997; Pratiwi et al. 2018). The changes in physicochemical and functional attributes of HMT-treated starches are discussed below.

1.2.1 Impact of HMT on Gelatinization Characteristics

Gelatinization and pasting are two terms used to explain the changes in starch when it is cooked in water. Gelatinization is the process of disordering the molecular structure of starch, resulting in permanent alteration in their functionalities. In its native form, starch can absorb roughly 30% (w/w) of moisture after being suspended in a high amount of water at certain conditions. The amorphous region of starch is easily accessible to water molecules. Granules of starch become amorphous and lose their crystalline structure when heated to a specific temperature with excess moisture content. This temperature-dependent transformation of starch structure is termed as gelatinization, and the temperature is termed gelatinization temperature (Mason 2009). Gelatinization results in changes in properties like swelling power (SP), starch solubilization, crystalline melting, etc. Differential scanning calorimetry is used to study the gelatinization characteristics of starch.

The impact of HMT on starch gelatinization characteristics varies with the starch source, treatment conditions, moisture content (mc) of starch, etc. HMT generally shifts the gelatinization temperature to a higher value and widens the temperature range. When mc and treatment temperature are increased, the gelatinization temperatures increase as well. An increase in gelatinization temperature has been noted in starches of wheat (Xie et al. 2018a), rice (Arns et al. 2015), pearl millet (Sharma et al. 2015a), kithul (Sudheesh et al. 2020a), grass pea (Piecyk et al. 2018), Indian water chestnut (Yadav et al. 2013a), etc. The changes in gelatinization characteristics of HMT starch are summarized in Table 1.1. A higher gelatinization attribute of HMT starch could be ascribed to its structural changes during HMT, and it induces interactions of starch chains within the granules. Additionally, it promotes starch diffusion and intermolecular links between amylose and amylopectin through inter- and intramolecular linkage (Schafranski et al. 2021). As the gelatinization process proceeds, crystallites and double helices melt, and starch granules become hydrated

Table 1.1 The gelatinization characteristics of starches

Starch	HMT conditions		T_O (°C)	T_P (°C)	T_C (°C)	ΔT (°C)	ΔH (J/g)	References
	Moisture (%)	Temperature						
Sorghum	20	110 °C, 8 h	66.46	70.29	76.41	9.95	10.11	Singh et al. (2011b)
	30		67.43	71.47	81.55	14.12	9.47	
	40		67.62	72.45	84.85	17.23	10.96	
Chinese yam	20	100 °C, 10 h	86.8	89.2	91.5	4.7	6.21	Yu et al. (2021)
Field bean	15	100 °C, 2 h	60.7	66.4	74.4	13.7	10.6	Piecyk and Domian (2021)
	30		65.6	77.7	83.0	17.4	10.3	
	15	120 °C, 2 h	61.1	68.2	77.8	16.7	12.0	
	30		65.2	83.8	89.5	24.3	13.7	
Corn	30	100 °C, 2 h	71.9	82.1	90.6	18.7	7.5	Chung et al. (2009a)
Pea			69.4	83.4	94.2	24.8	7.9	
Lentil			72.5	84.7	94.5	22	9.6	
Corn	30	120 °C, 2 h	67.8	82.2	88.8	21.0	6.1	
Pea			64.3	88.6	97.5	33.2	7.1	
Lentil			65.9	86.4	96.3	30.4	8.0	
Potato	20	120 °C, 4 h	63.65	69.52	76.15	12.5	6.96	Yang et al. (2022)
Water chestnut	20	110 °C, 16 h	75.53	78.85	89.01	13.48	19.18	Yadav et al. (2013b)
	25		81.09	85.48	90.25	9.16	12.65	
	30		82.98	87.35	91.87	8.89	12.84	

and swell. In HMT-treated starch, the interactions result in increased swelling temperature, which destabilizes the starch crystalline domain, triggering a higher transition temperature (Zavareze and Dias 2011). On the contrary, Zhang et al. (Zhang et al. 2020) noticed a reduction in the gelatinization temperature of proso millet starch after HMT. Upon heating, the glycosidic linkages are broken resulting in molecular degradation, and the unwinding or breakdown of the double helix leads to disruption of starch chains.

The enthalpy of gelatinization (ΔH) implies the amount of double helix and crystalline order. In general, HMT decreases the ΔH value. A decrease in ΔH values by HMT has been reported in potato, brown rice starches (Chakraborty et al. 2021), peas, lentils, navy bean starches (Chung et al. 2010), etc. Contrary to these, the ΔH value increased in field bean starches treated at 15% and 30% mc at 120 °C (Piecyk and Domian 2021). The disordering of the double helix structure could account for the reduction in ΔH values after HMT. In addition, the researchers also added that the partial gelatinization of starch during HMT also ends in a decreased ΔH value, indicating reduced stability (Zavareze and Dias 2011).

1.2.2 Effect of HMT on Pasting and Rheological Attributes

In pasting, the viscosity of the sample is measured during and after gelatinization. When the starch is continuously heated, starch granules will swell, disrupt, and exudate molecular components, i.e., leaching of amylose, which gives viscosity to the aqueous medium. The process of development of viscosity in the above process is termed the pasting. Rapid Visco Analyzer (RVA) is used to analyze the pasting behavior of starch gels.

HMT significantly affects starch's pasting profile. It was reported that irrespective of HMT conditions, HMT-treated starch had lower peak viscosity (PV), final viscosity (FV), breakdown viscosity (BV), and setback viscosity (SV). However, it had a high pasting temperature (PT) and thermal shear stability. HMT promotes intermolecular interaction, and thus high energy is needed for the disruption of HMT starches. The restricted swelling and solubility in HMT starches may decrease the pasting profile (Hoover 2010). The PT of HMT-treated starch increased with the mc and heating temperature.

The HMT of waxy and normal potato starches decreased the PV and BV. However, the normal starch has reduced SV, whereas waxy starch exhibited higher SV (Varatharajan et al. 2010). The authors also added that the increased SV of waxy starch could be due to its higher SP. The PV, trough viscosity (TV), SV, and FV of the HMT potato starches were decreased with a prolonged processing time from 2 to 12 h. at 120 °C (Zhang et al. 2020). Similarly, the pasting profile of pearl millet starch was reduced at an exposure of 110 °C for 4 h. (Sharma et al. 2015a). Brahma and Sit (2020) studied the effect of HMT at different conditions (30 and 35% moisture and 100 and 120 °C) on potato starch. They observed that the starch treated at 100 °C had a higher PT than starch treated at 120 °C. However, the PT increased with a change in mc from 30% to 35%. In addition, the PV, TV, BV, and FV were

lower for HMT treated at 100 °C as compared to the potato starch sample treated at 120 °C.

HMT significantly changes the rheological attributes, i.e., storage modulus (G') and loss modulus (G") of starches. The impact of HMT on starches varies with starch and treatment conditions (Sharma et al. 2015b). The molecular rearrangement caused by HMT hinders the swelling and amylose leaching, which results in increased G' and G" values. Starches, such as sohphlang starch (Marboh and Mahanta 2021), potato starch (Yang et al. 2022), etc., exhibited a higher G' and G" values. Contrary to the above, HMT of black rice starch decreased the G' and G" values (Dhull et al. 2021), as a result of molecular disintegration and degradation of starch structure (Ji et al. 2022) during HMT.

1.2.3 Impact of HMT on Structural Properties

HMT potentially impacts the starch structure, and the extent of structural alteration varies with the starch type and HMT parameters. It alters the polymorphic structure or the crystallinity of starch. A transformation of the B to a combination of A and B-type patterns was observed in HMT normal and waxy potato starches (Varatharajan et al. 2010). Studies revealed that crystalline structure transformation could result from water molecules' dehydration in the central cavity of B-type starches and the motion of double-helix molecules. Similarly, a change from A-type to a blend of A and V-type crystalline patterns was observed in maize starch (Wang et al. 2021). This kind of transformation to V type was prominent at HMT at high moisture levels. The HMT of lycoris starch at 120 °C for 6 h changed the crystalline pattern from type A to type B (Zhang et al. 2018).

HMT enhanced the relative crystallinity (RC) of Chinese yam starch treated at 100 °C for 10 h (Yu et al. 2021), amaranth starch treated at 85 °C (Sindhu et al. 2019), and sweet potato starch treated at 100 °C for 6 h. The improved crystallinity of HMT starches implies that the higher chain mobility during HMT promoted further interaction between starch chains.

The HMT of starches, like corn starch (Chung et al. 2009b), mungbean starch (Zhao et al. 2020), amaranth starch, etc., decreased the RC (Sindhu et al. 2019). The disruption of the amylopectin chain and the conversion of the semicrystalline fraction to an amorphous fraction during HMT treatment resulted in decreased RC. In addition, the partial gelatinization of starch during HMT may also contribute to a decreased RC (Brahma and Sit 2020).

1.2.4 Impact of HMT on Starch Digestibility

Starch is categorized into three categories: rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS), depending on how much glucose is produced during enzymatic hydrolysis. After consuming RDS, blood glucose levels rise rapidly. However, RS is the fraction resistant to digestion. The SDS is the portion of starch that converts to glucose after 20–120 min of hydrolysis.

The HMT process is widely reported to increase SDS and RS content in starch-based products, improving their nutritional value. The digestibility of HMT starch varies with the source, crystallinity, granule size, amylose, and amylopectin ratio, and the HMT conditions, which are connected to the alteration in crystallinity and morphology of treated starches (Zavareze and Dias 2011). In general, HMT improves the crystalline perfection of starches and thus decreases their digestibility. The HMT of rice starch reduced the digestibility (Wang et al. 2018), whereas SDS content increased in waxy rice starch (Zeng et al. 2015). Similarly, the HMT of maize starch increased the SDS and RS content (Park et al. 2018). At the same time, waxy maize starch increased the RDS and SDS content (Park et al. 2018).

1.2.5 Impact of HMT on Granule Morphology

The surface attributes of starch have a potential role in its various applications. It is mainly studied using a scanning electron microscope, polarized microscope, confocal microscope, etc. In HMT starches, the extent of morphological changes may vary, and it depends on treatment conditions like moisture, time and temperature, and source of starch. A higher mc promotes their expansion and provides morphological changes during heating (Schafranski et al. 2021). The HMT of starches like potato, sweet potato, yam, etc., at lower mc and temperature, did not cause any visible changes in granule morphology (Hoover 2010).

Piecyk and Domian (Piecyk and Domian 2021) reported that the HMT of field pea starch with 15% mc at 120 °C did not cause any noticeable effect on the granule morphology. However, indents in the center of particular granules are evidenced in 30% mc. Similarly, the HMT of rice starch with 10% mc. At 20 and 30% mc, the surface became rough and showed evidence of agglomeration (Wang et al. 2018). Similarly, the HMT-treated potato starch also exhibited agglomeration (Brahma and Sit 2020). The morphology of pearl millet starch was evidenced by dents or holes (Sharma et al. 2015b). A decrease in particle size was noticed in HMT-treated sorghum starch treated at 40% mc (Singh et al. 2011b) (Fig. 1.2).

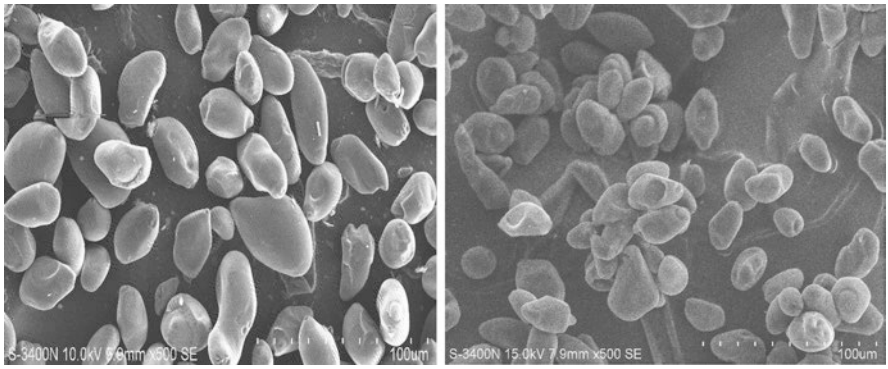

Fig. 1.2 Micrograph of native and heat moisture-treated talipot starches

1.2.6 Impact of HMT on Starch Functional Attributes

The HMT-induced alteration in the structural characteristics of starches leads to modification in their functional properties. The improved crystalline perfection by HMT may diminish the SP of starches. A decrease in SP after HMT was noticed in many starches, such as maize (Liu et al. 2016a; Xie et al. 2018b), pearl millet (Sharma et al. 2015a), grass pea (Piecyk et al. 2018), rice bean (Thakur et al. 2021), normal and waxy potato (Varatharajan et al. 2010), etc. It was observed that the impact of HMT on SP depends on its mc, and it could be due to the rearrangement of starch chains, thus limiting the granules' hydration capacity.

The solubility of starch is primarily due to the leaching of amylose molecules during heating and swelling. Solubility indicates the change in molecular structure from a stable to a destabilized structure during gelatinization. The restricted swelling and increased rigidity of HMT starches reduce the amount of leached amylose and its solubility. The solubility of potato starch was decreased when it was treated at different mc and temperatures (Brahma and Sit 2020). Similarly, a decrease in solubility was reported in starches, such as oat (Kaur and Singh 2019), sorghum (Singh et al. 2011b), proso millet starch (Zhu et al. 2020), etc.

The HMT significantly alters the gel textural properties of starch. The HMT of talipot starch (Navaf et al. 2021), potato starch (Yang et al. 2022), water chestnut starch (Yadav et al. 2013b), sorghum starch (Singh et al. 2011b), potato starch (Brahma and Sit 2020), etc. significantly increased the gel hardness. The higher chain interaction, restricted swelling, and the development of more junction zones in starch suspension, etc. are responsible for HMT starches' improved gel hardness. It also depends on mc and temperature. The HMT with high moisture and temperature shows higher gel hardness (Brahma and Sit 2020). On the contrary, hardness was reduced in HMT amaranth starch, possibly due to its decreased solubility and increased SP (Sindhu et al. 2019).

The ability of starch to transmit light is an important function that has practical applications in various industries. The gel's light transmittance (LT) measures its paste clarity, mainly influenced by the remnants of swollen granules, leached amylose, etc. (Jyothi et al. 2010). HMT significantly decreases starch's LT and paste clarity. Researchers observed a reduction in LT of mango kernel starch (Bharti et al. 2018), cassava, potato, arrowroot (Jyothi et al. 2010), oat (Kaur and Singh 2019), water chestnut (Yadav et al. 2013b) starch, etc., after HMT treatment. The decrease in LT of HMT starch could be due to the enhanced flexibility of its chains in the amorphous area, amylose leaching, and granule remnants in the starch gel.

The percentage syneresis value was increased in HMT potato (Brahma and Sit 2020) and amaranth (Sindhu et al. 2019) starches. However, it was decreased in water chestnut starch (Yadav et al. 2013b). The higher reassociation between starch chains and exudation of water molecules increases the syneresis in HMT-treated starch. HMT of amaranth starch increases its syneresis value and depends on the treatment intensity (Sindhu et al. 2019).

1.3 Annealing

Annealing (ANN) involves the holding of starch in excess (>60% [w/w]) or at intermediate (40% [w/w]) mc at a temperature above the Tg and below the To of gelatinization for a defined period of time (Jayakody and Hoover 2008). The annealing of starch alters the physicochemical properties, such as crystallinity, by enhancing interactions between its chains. Amylopectin and starch molecules are reorganized by ANN so that their structures acquire a more organized state. The pictorial representation of annealing on starch granules is given in Fig. 1.3. Depending on the origin and kind of starch, the degree of starch chain interaction and the realignment of double helices may differ. The annealing of starch brings the following changes: (1) reorganization of the granular structure, (2) improved granular stability, (3) enhanced crystallinity, (4) enhanced interaction of starch chains, and (5) development of double helices. The effect of annealing on the physicochemical and functional attributes of starch is discussed below.

1.3.1 Impact of Annealing on Gelatinization Properties

Annealing potentially impacts the gelatinization characteristics of starch. Annealing has been extensively studied for its impact on starch gelatinization properties. Annealing increases the gelatinization temperature. However, it decreases the range of gelatinization temperature (ΔT). Annealing treatment will also alter the ΔH, and it varies among the different sources of starches. The gelatinization characteristics of some annealed starches are summarized in Table. 1.2. The gelatinization temperature increases with an increase in annealing time and is more visible in the onset gelatinization temperature, least at the conclusion temperature. The rise

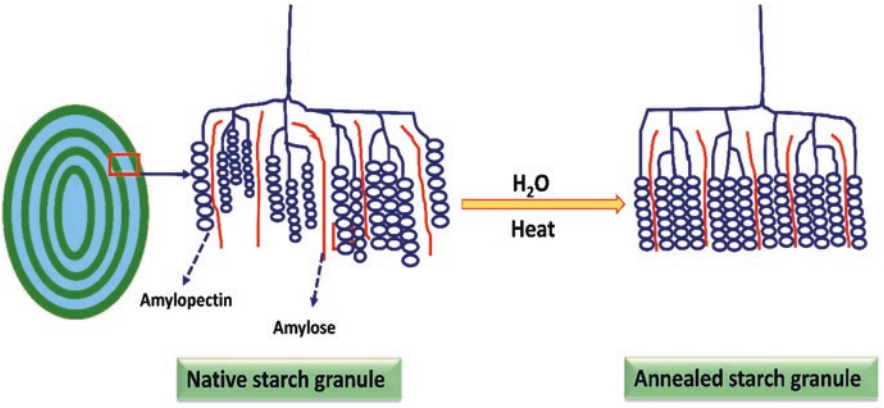

Fig. 1.3 The pictorial representation of annealing on starch granule

Table 1.2 The gelatinization characteristics of annealed starches

Starch	Annealing conditions	T_O (°C)	T_P (°C)	T_C (°C)	ΔT (°C)	ΔH (J/g)	References
Corn	55 °C, 24 h	70.9	75.4	82.4	11.5	8.2	Ariyantoro et al. (2018b)
Pea	70% moisture, 24 h	67.5	71.5	84.2	14.7	14	Chung et al. (2009a)
Lentil		71.8	75.0	86.8	15	13	
Kithul	1:4 (starch/water), 60 °C, 24 h	77.75	82.13	90.11	12.36	5.65	Sudheesh et al. (2020b)
Chestnut	1:2 (starch/water) 65 °C, 24 h	81.58	84.96	88.12	6.54	12.59	Yadav et al. (2013a)
Sorghum	1:4 (starch/water), 50 °C, 24 h	67.83	70.42	74.59	6.76	12.71	Singh et al. (2011a)
Sweet potato	90% water, 55 °C, 72 h	72.1	76.4	81.0	8.9	8.9	Song et al. (2014)

in gelatinization temperature of annealed starch could be due to the perfection of pre-existing crystallites (Ariyantoro et al. 2018a), and it can also be associated with decreased swelling of annealed starches (Zavareze and Dias 2011). The development of more homogeneity and cooperative melting of crystallites results in narrowing the gelatinization range of annealed starches (Jayakody and Hoover 2008). A higher gelatinization temperature was reported in normal and waxy corn starches after ANN (Rocha et al. 2012). However, the ΔH was increased only in waxy starch. Similarly, the ΔH value was increased in maize starch annealed with 80% moisture at 50 °C for 24 h. (Chen et al. 2021). Contrary, the annealing (1:4 starch/water) of maize and potato starch at 50 °C for 24 h. significantly decreased the ΔH values (Chi et al. 2019).

1.3.2 Impact of Annealing on Pasting and Rheological Properties

Several factors, like amylose leaching, chain length distribution, amylopectin, RC, etc., influence annealed starches' pasting properties. The annealing-induced variations in the pasting profile of starch are complex and vary among starch sources (Zavareze and Dias 2011). According to Yu et al. (Yu et al. 2021), annealing of Chinese yam starch at 50 °C for 24 h. (70% moisture) significantly decreased the PV, TV, BV, and SV. Similarly, the PV, BV, and FV values decreased in talipot starch (Navaf et al. 2021). Contrary to these observations, a higher pasting profile was observed in annealed kithul starch (Sudheesh et al. 2020a) and wheat starch (30 and 40 °C) (Wang et al. 2017a). At the same time, annealing of wheat starch at 50 °C decreased the pasting viscosities and increased the PT. The annealing of waxy maize starch for 24 h. at 45 °C did not alter its pasting attributes. However, the extended period decreased the PV, TV, and FV (Wang et al. 2014). The annealing of sweet potato starch at 45 °C for 24 h. did not show any significant changes in PT, whereas it decreased the pasting viscosities (Trung et al. 2017).

The higher PT of annealed starches can be ascribed to their higher crystalline perfection and decreased swelling (Sudheesh et al. 2020a). The reorganization within modified starch is believed to reduce the pasting profile. Consequently, SP was limited, and a minimal amount of amylose could leach into the water to increase viscosity (Yadav et al. 2013a). Contrary to this, the lower degree of deformation and increased rigidity of the granules could cause the increased pasting profile of annealed starch (Sudheesh et al. 2020a).

The dynamic rheological characteristics, i.e., G' and G" of annealed starches, were found to be increased. Since annealing results in a more ordered structure, the annealed starches show improved rheological characteristics. Yan et al. (Yan et al. 2022) reported the annealing of potato and pea starch with normal and plasma-activated water considerably increased the G' and G" values. Similarly, a rise in rheological attributes by annealing is reported in starches like Andean oca (Puelles-Román et al. 2021), talipot (Navaf et al. 2021), kithul (Sudheesh et al. 2020a), etc. It implies that the annealing of starch enhances the stiffness of macromolecular chains, and it forms a strong gel.

1.3.3 Impact of Annealing on Structural Attributes

Annealing potentially impacts the structural characteristics of starch, and it varies with the type of starches and annealing conditions. It was noted that annealing has a more dominant effect on type B starches than on type A starches (Jayakody and Hoover 2008). In a few starches, the annealing changes the weak polymorphic structure to a more stable one. Genkina et al. (Genkina et al. 2004) reported that annealing of sweet potato starches for up to 8–10 h resulted in a gradual change in crystalline pattern from B to A type. Similarly, changes from B-to A-type crystalline patterns were observed in cassava starch annealed at 50 °C up to 192 h (Gomes et al. 2004). Likewise, upon annealing, a shift to A-type polymorphic structure was also observed in barley starches (Waduge et al. 2006).

On the other hand, the annealing did not impact the crystalline pattern for many starches but altered the RC. The annealing of yam starch with 70% moisture at 50 °C didn't affect its crystalline pattern. However, it increased the crystallinity (Yu et al. 2021). Similar observations were made in talipot (Navaf et al. 2021) and kithul (Sudheesh et al. 2020a) starches. Yeum et al. (Yeum et al. 2021) stated that the mc has a potential role in the crystalline-type formation of annealed starches, and higher mc favors the reordering of the crystalline area.

The increase in RC of annealed starches is due to alteration in the orientation of starch crystallites, crystalline perfection, amylopectin content, etc. (Yu et al. 2021). In ANN, starch chains are realigned both amorphous and crystalline areas, enhancing the granule's stability and increase the crystallinity (Zavareze and Dias 2011). Additionally, the association of smaller crystallites during annealing also facilitates increased crystallinity (Liu et al. 2016a).

Chung, Hoover, and Liu (Chung et al. 2009b) noticed that annealing of corn starch at 50 °C for 24 h did not affect the polymorphic structure and relative

crystallinity. However, prolonged annealing reduced the RC. Similarly, 48 h of annealing reduced the RC of maize and pea starches (Zheng et al. 2023). Rice starch with different amylose content also exhibited a reduction in RC after annealing treatment (Dias et al. 2010).

1.3.4 Impact of Annealing on Starch Digestibility

Annealing is a hydrothermal treatment used to alter the digestibility of the starches, and its digestibility varies with the starch origin and annealing parameters. Annealing may enhance the starch chain interactions. It increases crystalline perfection and reduces the granules' enzyme accessibility, resulting in decreased digestibility. Contrary, an increased digestibility was also observed in annealed starches. The development of pores on granules during annealing may facilitate more accessibility of the enzymes and thus increase the RDS content in annealed starches.

The annealing of maize starch with different amylose content for 24 h and 74 h did not impact their digestibility (Wang et al. 2014). In contrast, it increased the digestibility of sweet potato starch (Song et al. 2014). Likewise, the annealed waxy rice starch exhibited enhanced digestibility (Zeng et al. 2015). Contrary to the above, annealed yam (Yu et al. 2021) and potato starches (Chi et al. 2019) exhibited a decreased digestibility.

1.3.5 Impact of Annealing on Granule Morphology

Many researchers observed that annealing did not have a profound effect on granule morphology. The starches like banana (Cahyana et al. 2017), maize, barley, sorghum wheat (Ariyantoro et al. 2018a), etc. did not cause any visible change in granule morphology. However, there are some contrasting observations. The annealed kithul exhibited large holes and fissures in the granule surface (Sudheesh et al. 2020a). Likewise, dents and cracks were formed in annealed pea and potato starches (Yan et al. 2022) and pores in high-amylose rice starches (Dias et al. 2010) (Fig. 1.4).

1.3.6 Impact of Annealing on Functional Properties

Annealing promotes the interplay between starch chains, such as it promotes the interaction between starch chains, increased crystalline perfection, etc. Annealing restricts the hydration ability of starch, thereby reducing its SP (Zavareze and Dias 2011). The ANN has decreased the SP of Bambara ground nut starch (Oyeyinka et al. 2018), rice starch (Wang et al. 2017b), kithul starch (Aaliya et al. 2022), yam starch (Yu et al. 2021), potato starches (Xu et al. 2018), etc. It was noticed that as the annealing duration increased, the SP reduction intensity

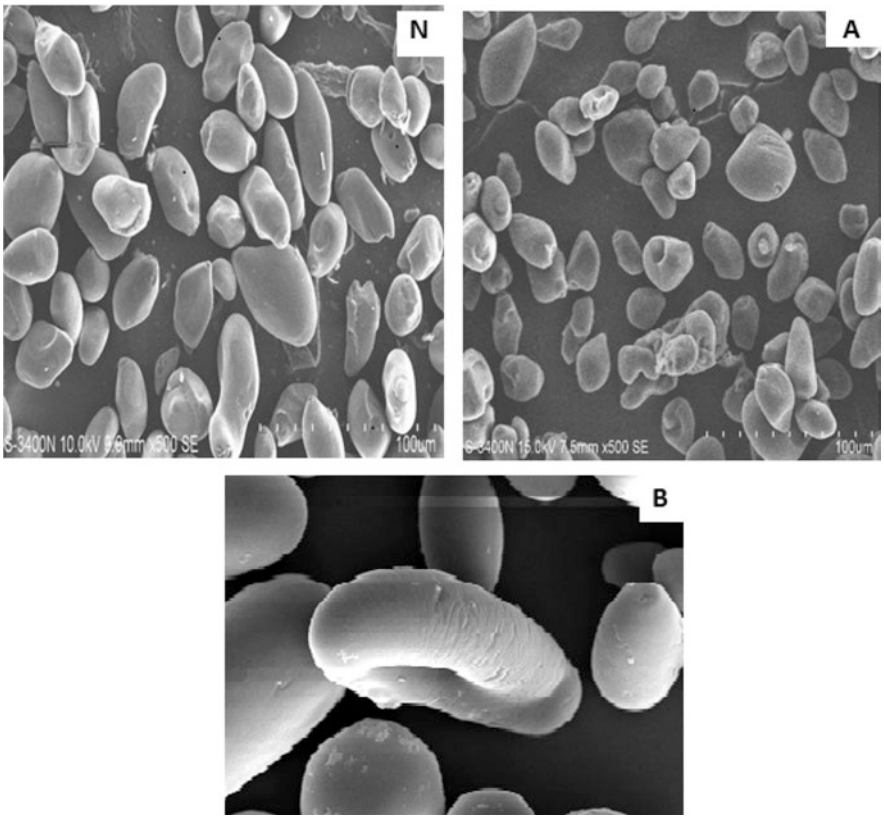

Fig. 1.4 SEM images of native (N) and annealed talipot starch (**a**), kithul starch (**b**)

increased, since it enhances the interaction between the starch chain and the crystallinity of starches.

Similarly, the ANN of starches significantly decreases the solubility. A decrease in solubility was reported in ANN kithul starch (Sudheesh et al. 2020a), water chestnut starch (Yadav et al. 2013b), sorghum starch (Ogundiran and Adeniyi Afolabi 2018), etc. The enhanced starch chain interaction by ANN improves the crystalline perfection, restraining the amylose leaching and resulting in a predominant reduction in solubility.

The impact of ANN on gel hardness may vary with the origin of starch and treatment parameters. The annealing of sorghum starch increases the gel hardness (Singh et al. 2011a), whereas it was decreased in maize starch (Liu et al. 2016a). The enhanced molecular arrangement and decreased swelling of annealed starches contributed to its higher gel hardness. ANN of starch significantly increases its LT. The ANN of corn starch (Ariyantoro et al. 2018b), banana starch (de Almeida et al. 2020), etc. pronouncedly increased the LT. The researchers stated that the increased

interaction of starch chains restricts the leaching of amylose. The reduction in amylose leaching minimizes the interaction between amylose and other components of starch granules, resulting in increased LT (de Almeida et al. 2020). Nevertheless, a decrease in LT was reported in ANN kithul starch (Sudheesh et al. 2020b). It was speculated that a higher rate of retrogradation of annealed kithul starch decreases the LT and paste clarity.

The ANN treatment had a potential impact on the syneresis values of starches. The annealing of Bambara groundnut starch significantly decreased the syneresis (Nwaogazie et al. 2022). The syneresis value of maize, potato, and pea starches increased with an increase in annealing time (Zheng et al. 2023). The leached water molecules can be easily expelled from the granules of annealed starches, contributing to increased syneresis (Zheng et al. 2023).

1.4 Irradiation

Gamma (γ) rays are electromagnetic radiation. Food processing uses γ-rays that can penetrate up to several feet into the food product and kill microorganisms or insects or break bonds. γ-rays are created by decaying radioactive isotopes (cobalt-60 or cesium-137). The irradiation of starch with γ-rays results in the breakdown of H_2O into free radicals (OH* and H*) and electrons. They induce molecular changes in the starch by fragmentation or crosslinking, thus modifying it. The irradiation of starch and starch-containing foods undergoes significant changes in their physiochemical and functional properties, which are discussed in the following sections. The pictorial representation of gamma irradiation on starch granules is given in Fig. 1.5.

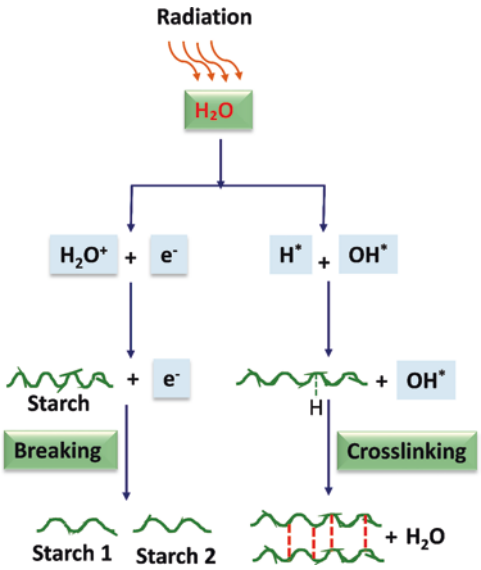

Fig. 1.5 The pictorial representation of γ-irradiation on starch granule

1.4.1 Impact of Irradiation on Gelatinization Properties

The impact of irradiation on the gelatinization attributes of starch is influenced by the starch type, its mc, and the irradiation parameters, i.e., radiation dose and dose rate (Zhu 2016). The gelatinization characteristics of some irradiated starches are summarized in Table 1.3. A 2–10 KGy irradiation of amaranth starch did not affect the gelatinization temperatures. Besides, the ΔH shows a slight fluctuation, but it is not obvious (Kong et al. 2009). The irradiation of potato starch with a low dose (0. 01, 0.05, 0.1, and 0.5) of radiation significantly increased the gelatinization temperature and ΔH values (Singh et al. 2011c). The increased gelatinization properties can be explained by the degradation of a weak crystalline structure, leaving crystallite with high stability. It can also be explained due to the increase in the metastable phases (Zhu 2016). Othman et al. (Othman et al. 2015) stated that the degradation

Table 1.3 The gelatinization characteristics of irradiated starches

Starch	Radiation dose (kGy)	T_O (°C)	T_P (°C)	T_C (°C)	ΔT (°C)	ΔH (J/g)	Reference
Talipot	20	78.79	82.24	85.52	6.73	8.40	Navaf et al. (2022a)
	50	77.47	82.43	86.63	9.16	8.13	
	80	72.53	76.97	81.57	9.04	7.48	
	100	72.04	76.72	81.45	9.41	7.41	
Amaranth	2	69.51	73.40	80.06	10.55	16.10	Kong et al. (2009)
	4	69.83	73.69	79.85	10.02	15.77	
	6	69.78	73.51	79.62	9.84	15.49	
	8	69.39	73.35	80.03	10.64	15.34	
	10	69.47	73.21	79.38	9.91	5.38	
Brown rice	5	63.05	65.89	70.11	7.06	7.11	Kumar et al. (2017)
	10	62.21	65.14	68.65	6.44	6.05	
	15	59.14	61.55	65.48	6.34	4.19	
	20	58.58	60.10	65.11	6.53	3.01	
Chickpea	0.5	63.63	69.17	76.00	12.37	8.17	Bashir and Aggarwal (2017)
	2.5	63.15	68.04	75.22	12.07	6.78	
	10	62.29	66.66	74.08	11.79	6.26	
Arrowroot	5	66.55	74.0	84.7	18.15	22.0	Barroso and del Mastro (2019)
	10	66.7	74.0	83.9	17.2	23.4	
	15	67.9	74.1	83.9	16	22.3	
Wheat	1	56.3	63.0	71.4	15.1	12.7	Kong et al. (2016)
	5	56.4	62.8	71.2	14.8	12.5	
	9	56.5	62.8	71.3	14.8	12.5	
Quinoa	1	44.3	55.8	72.3	28	9.5	
	2	44.7	55.9	72.0	27.3	9.2	
	4	44.7	55.5	72.0	27.3	9.0	
	8	45.0	55.0	71.7	26.7	9.1	
Rice (PR121)	2	60.1	64.2	71	10.9	10.2	Gul et al. (2016)
	5	60.0	63.7	71.4	11.4	10.9	
	10	58.6	63.0	70.7	12.1	11.3	

of molecules by irradiation leads to the formation of monosaccharides, thus increasing the gelatinization temperature.

The irradiation (3–50 KGy) of wheat starch did not cause any changes in gelatinization temperatures. At the same time, the ΔH value increased at a lower dose (3 and 5KGy) and did not show a significant difference at the higher doses (Atrous et al. 2015). The work concluded that the depolymerization of the starch chain into fragments did not influence the melting of starch crystallites; hence ΔH value did not change significantly. Similarly, the irradiation of kithul starch at up to 2.5 KGy significantly decreased the gelatinization properties. However, 5 and 10 KGy doses significantly increased the gelatinization properties (Sudheesh et al. 2019a). Contrary to the above observations, a decrease in gelatinization temperatures and ΔH values was reported in rice starch (1, 5, and 10 kGy) (Gul et al. 2016) and talipot starch (20, 50, 80, and 100 KGy) (Navaf et al. 2022a). The structural degradation and depolymerization of granules during irradiation lead to the loss of ordered structure, and it negatively impacts its gelatinization characteristics.

1.4.2 Impact of Irradiation on Pasting and Rheological Attributes

Irradiation of starch significantly changes their pasting profile. The impact of irradiation pasting properties varies with the irradiation dose, types of starch, mc, etc. An irradiation above 20 kGy significantly decreased the PT, and a dose of 500 kGy did not show any PT (Dikkala and Shirisha 2018). Irradiation of potato starch at 0.1 and 0.5 KGy radiation significantly increased the PT, PV, TV, FV, and SV (Ezekiel et al. 2007). Contrary to this observation, a progressive reduction in the PV of potato starch was noted at a dose of 0.1–0.5 kGy (Singh et al. 2011c). A considerable reduction in pasting profile was noted in maize starch with irradiation of 1–500 kGy (Liu et al. 2012). Similarly, irradiation of bean starch with 10 and 50 kGy decreased the PV, FV, and SV (Chung and Liu 2010). When starch is γ-irradiated, it destroys amylopectin and amylose, leading to a decline in water retention ability. As a result, PV is significantly reduced since starch granules are less prone to swelling. The PV of corn starch was decreased by 49, 83, and 95%, respectively, when irradiated at a dose of 3, 5, and 10 kGy, and a dose of 20 kGy did not show any pasting profile (Polesi et al. 2016). The limited SP and disintegration of intra-and intermolecular glycosidic linkage that damages the starch granules structure may cause the reduced pasting profile of irradiated starches.

γ-irradiation of starch causes molecular depolymerization, forming a gel with weak consistency. The rheological studies of irradiated starch show that irradiation reduces both G' and G". The irradiation of kithul starch by 10 kGy (Sudheesh et al. 2019a), potato starch by 0.01–0.5 kGy (Singh et al. 2011c), and amaranth starch by 2–10 kGy reduced the G' and G" values (Kong et al. 2009). Amaranth starch exhibited a crossover of G' and G" at a higher dose of 6, 8, and 10 kGy. It indicates the liquid-like characteristics of irradiated amaranth starch. Likewise, higher-dose irradiation (20–100 kGy) of talipot starch considerably decreased its rheological attributes (Navaf et al. 2022a). Irradiation of starch causes the depolymerization and