

Germán Ayala Valencia *Editor*

Starch Nanomaterials and Food Applications

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Germán Ayala Valencia
Department of Chemical and Food
Engineering
Federal University of Santa Catarina
Florianópolis, SC, Brazil

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This book is dedicated especially to my daughter and wife Liz and Talita, respectively.

*Mi pequeña Liz, tu llegada ilumino mi vida.
Tu haz hecho los días más felices, divertidos y cálidos.*

*A tu lado siendo que todo lo he encontrado.
Talita, las palabras se quedan cortas para expresar el amor que siento por ti.
Tu eres tinta indeleble y parte de mí.
Simplemente, eres mi alma gemela*

I love you so much!

*Germán Ayala Valencia, Ph.D.
Editor*

Preface

Starch nanomaterials are a promising alternative for obtaining advanced structures with improved physicochemical properties. These nanomaterials can be used to stabilize hydrophilic and hydrophobic biomolecules, and to modify food texture and the physicochemical properties of packaging materials. Starch nanomaterials can be obtained by “top-down” and “bottom-up” approaches and are classified as starch nanocrystals, nanoparticles, nanofibers, nanomicelles, and nanovesicles. This book reviews concepts related to starch nanomaterials and their food and packaging applications. Thus, Chap. 1 introduces and classifies different starch nanoarchitectures. The methods used to produce starch nanocrystals, nanoparticles, nanofibers, nanomicelles, and nanovesicles have been reviewed in Chaps. 2, 3, 4, and 5. The potential applications of starch nanomaterials as adsorptive and encapsulating materials are reviewed in Chap. 6. Chapters 7, 8, and 9 analyze the use of starch nanomaterials as food emulsifiers and ingredients for the manufacture of functional foods and packaging, respectively. The digestibility of starch nanomaterials has been revised in Chap. 10. Finally, Chap. 11 reviews the degradation and environmental impacts of starch nanomaterials.

I would like to sincerely thank the contributors for their insights into *Starch Nanomaterials and Food Applications*.

Florianópolis, SC, Brazil

Germán Ayala Valencia

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About the Editor



Germán Ayala Valencia received his Ph.D. in food engineering in 2017 from the University of São Paulo, Brazil. Dr. Valencia is a professor at the Department of Chemical and Food Engineering in the Federal University of Santa Catarina, Florianópolis, Brazil. Prof. Valencia was the guest editor of a special issue published by *Starch—Stärke* (11–12/2021). Nowadays, Prof. Valencia is a Board Member of the *Journal of Packaging Technology and Science* and editor of the book *Natural Additives in Foods* published by Springer Nature. Prof. Valencia mainly works in the food science and technology area with an emphasis on packaging, pigments, nanotechnology, agro-industrial waste, and encapsulation of bioactive compounds.

Contributors

Edith Agama-Acevedo Instituto Politécnico Nacional, CEPROBI, Yautepec, Mexico

Carla Ivonne La Fuente Arias Research Institute of Food Engineering for Development (IIAD), Universitat Politècnica de València (UPV), Valencia, Spain

Germán Ayala Valencia Department of Chemical and Food Engineering, Federal University of Santa Catarina, Florianópolis, SC, Brazil

Luis A. Bello-Perez Instituto Politécnico Nacional, CEPROBI, Yautepec, Mexico

Valeria Cedeño-Fierro Faculty of Engineering and Administration, Universidad Nacional de Colombia, Palmira, Valle del Cauca, Colombia

Wilson Daniel Caicedo Chanon Department of Chemical and Food Engineering, Federal University of Santa Catarina, Florianópolis, SC, Brazil

Raul Remor Dalsasso Department of Chemical and Food Engineering, Federal University of Santa Catarina, Florianópolis, SC, Brazil

Samile Bezerra de Aguiar São Carlos Institute of Chemistry, University of São Paulo – USP, São Carlos, SP, Brazil

Shirley Duarte Faculty of Chemistry, National University of Asunción, San Lorenzo, Paraguay

Omayra Ferreiro Faculty of Chemistry, National University of Asunción, San Lorenzo, Paraguay

Juan F. Grisales-Mejia Faculty of Engineering and Administration, Universidad Nacional de Colombia, Palmira, Valle del Cauca, Colombia

Maria A. Hernandez-Aguirre Instituto Politécnico Nacional, CEPROBI, Yautepec, Mexico

Marco A. Maldonado-Campos Instituto Politécnico Nacional, CEPROBI, Yautepec, Mexico

Bianca Chierogato Maniglia São Carlos Institute of Chemistry, University of São Paulo – USP, São Carlos, SP, Brazil

Alcilene Rodrigues Monteiro Department of Chemical and Food Engineering, Federal University of Santa Catarina, Florianópolis, SC, Brazil

Sarah L. Paz-Arteaga Faculty of Sciences, Universidad Nacional de Colombia, Medellín, Antioquia, Colombia

Milena Dutra Pierezan Department of Food Science and Technology, Agricultural Sciences Center, Federal University of Santa Catarina, Florianópolis, SC, Brazil

Vania Zanella Pinto Food Engineering, Graduate Program of Food Science and Technology, Universidade Federal da Fronteira Sul, UFFS, Laranjeiras do Sul, PR, Brazil

Anna María Polanía Faculty of Engineering, School of Food Engineering, Universidad del Valle, Tuluá, Valle del Cauca, Colombia

Nathiely Ramírez-Gúzman Cuerpo Académico Agro-biotecnología, Facultad de Ciencias Biológicas, Universidad Autónoma de Coahuila, Unidad Torreón, Torreón, Coahuila, Mexico

Lina Maria Rayo-Mendez Food, Bioprocessing and Nutrition Department, North Carolina State University, Raleigh, NC, USA

Jaiber Humberto Rodriguez-Llanos Engineering Department, Anhanguera University, São Paulo, Brazil

Pedro Augusto Invernizzi Sponchiado Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto – FFCLRP, Universidade de São Paulo – USP, Ribeirão Preto, SP, Brazil

Cristian Torres-León Cuerpo Académico Agro-biotecnología, Centro de Investigación y Jardín Etnobiológico (CIJE), Universidad Autónoma de Coahuila, Unidad Torreón, Viesca, Coahuila, Mexico

Natalia S. Vargas-Marín Agroindustrial Engineering. Faculty of Engineering, Corporación Universitaria Minuto de Dios - UNIMINUTO, Valle del Cauca, Colombia

José Vega-Baudrit Centro Nacional de Alta Tecnología “Dr. Franklin Chang Díaz”, Laboratorio Nacional de Nanotecnología (LANOTEC), San José, Costa Rica POLIUNA, Escuela de Química, Universidad Nacional, Heredia, Costa Rica

Silvani Verruck Department of Food Science and Technology, Agricultural Sciences Center, Federal University of Santa Catarina, Florianópolis, SC, Brazil

Abbreviations

AgNPs	Silver nanoparticles
AH	Acid hydrolysis
ALNs	Amylolipid nano-vesicles
AM	Amylose
ANN	Annealing
AP	Amylopectin
AS	Acetylated starch
ASSR	Anti-solvent/solvent ratio
ASP	Anti-solvent precipitation
ASTM	American Society for Testing and Materials
BSN	Banana starch nanoparticle
BIO	Biodegradation
BOD	Biological oxygen demand
C	Control
CABSN	Citric-acid banana starch nanoparticles
CI	Complexity index
CM	Chlorpheniramine maleate
CMC	Critical micelle concentration
CNC	Cellulose nanocrystal
CNFs	Cellulose nanofibers
DDSA	Dodecenylsuccinic acid
DIC	Disseminated intravascular coagulation
DIS	Disintegration
DMSO	Dimethyl sulfoxide
DNA	Deoxyribonucleic acid
DPG	Dipalmitoylglycerol
DS	Degree of substitution
DSC	Differential scanning calorimetry
EAI	Emulsifying activity index

EE	Encapsulation efficiency
EH	Enzymatic hydrolysis
EN	European Standards
ESI	Emulsifying stability index
FAO	Food and agriculture organization
FDA	Food and drug administration
FTIR	Fourier-transform infrared spectroscopy
GHG	Greenhouse gas
GI	Gamma irradiation
GP	Gastric phase
GRAS	Generally recognized as safe
GRS	Glutinous rice starch
HMT	Heat-moisture-treatment
HDPE	High-density polyethylene
HPH	High-pressure homogenization
HS	Hydroxypropylated starch
ICM	Isolated crystalline material
IP	Intestinal phase
ISO	International organisation for standardisation
ISNPs	Insoluble starch nanoparticles
L	Large
LA	Lauric acid
LC	Loading capacity
LCA	Life cycle assessments
LDPE	Low-density polyethylene
M	Medium
MntMD	Montmorillonite modified with dimethyl dihydrogenated tallow ammonium
MPG	Monopalmitoylglycerol
MVBs	Multivesicular bodies
Ni	Not informed
NMnt	Natural montmorillonite
mRNAs	Messenger RNA
NREU	Non-renewable energy use
OP	Oral phase
OS	Octenyl-succinate starch
OSA	Octenyl succinic anhydride
O/W	Oil-in-water
PA	Palmitic acid
PBAT	Poly(butylene adipate-co-terephthalate)
PBS	Buffered solution
PCL	Polycaprolactone
PDI	Polydispersity index
PEG	Polyethylene glycol

PEGME	Poly(ethylene glycol) methyl ether
PHU	Polyhydroxyurethane
PLA	Poly (lactic acid)
PPC	Poly(propylene carbonate)
PU	Polyurethane
PVA	Polyvinyl alcohol
RC	Relative crystallinity
RDS	Rapidly digestible starch
RNA	Ribonucleic acid
RS	Resistant starch
RS1	Resistant starch (type 1)
RS2	Resistant starch (type 2)
RS3	Resistant starch (type 3)
RS4	Resistant starch (type 4)
RS5	Resistant starch (type 5)
RVA	Rapid visco analyser
S	Small
SDS	Slowly digestible starch
SEM	Scanning electron microscopy
SGC	Short glucan chains
SGF	gastrointestinal fluid
SIF	simulated intestinal fluid
SLR	Solid-liquid ratio
SMPs	Starch microparticles
SNCs	Starch nanocrystals
SNFs	Starch nanofibers
SNPs	Starch nanoparticles
SSNPs	Soluble starch nanoparticles
SNMs	Starch nanomicelles
SNMts	Starch nanomaterials
SNVs	Starch nanovesicles
SPI	Soy protein isolate
SSPS	Soluble soybean polysaccharide
TEM	Transmission electron microscopy
TG	Thermogravimetry
TPS	Thermoplastic starch
TPU	Thermoplastic polyurethane
WHO	World health organization
WPI	Whey protein isolate
W/O	Water-in-oil
XRD	X-ray diffraction
β LG	β -lactoglobulin
Δ H	Enthalpy change

Chapter 1

A Brief Introduction to Starch-Based Nanomaterials



Wilson Daniel Caicedo Chacon, Raul Remor Dalsasso, Vania Zanella Pinto,
and Germán Ayala Valencia

1.1 Introduction

Starch is a natural semicrystalline polymer composed of amylose, a linear biopolymer of α -D-glucose units linked by α -1,4-glycosidic bonds, and amylopectin, a highly branched biopolymer in which the α -D-glucose units are linked via α -1,4- and α -1,6-glycosidic bonds [1]. Starch is considered the second most common biomass on earth. This macromolecule is produced by green plants as an energy reserve and stored in tubers/roots, fruits, and grains/seeds in the form of granules with different shapes and particle sizes varying between 2 and 100 μm [2, 3].

Starch is used as a thickener, binding agent, emulsifier, clouding agent, or gelling agent in the food sector. However, this macromolecule has many disadvantages associated with poor water solubility and shear and thermal stability, resulting in insufficient physical and functional properties [4, 5]. Physical and chemical treatments have been used to improve the physicochemical properties of starch [6].

Modifying the starch architecture from the micro to the nanoscale is a recent alternative to alter the physicochemical properties of the resulting starch nanomaterials. Furthermore, these starch nanoarchitectures can be functionalized with bioactive compounds to acquire antimicrobial and antioxidant properties [2]. Starch nanostructures are defined as materials having at least one dimension

Authors W. D. C. Chacon and R. R. Dalsasso have equally contributed to this chapter.

W. D. C. Chacon · R. R. Dalsasso · G. Ayala Valencia (✉)

Department of Chemical and Food Engineering, Federal University of Santa Catarina,
Florianópolis, SC, Brazil

e-mail: g.ayala.valencia@ufsc.br

V. Z. Pinto

Engenharia de Alimentos, Programa de Pós-Graduação em Ciência e Tecnologia de Alimentos,
Universidade Federal da Fronteira Sul, Laranjeiras do Sul, Paraná, Brazil

e-mail: vania.pinto@uffs.edu.br

between 1 and 500 nm [7]. Dimensions lower than 1000 nm have also been used to classify this type of nanomaterial [2]. Several starch architectures can be produced at the nanoscale, and the most common starch nanomaterials (SNMts) are nanocrystals (SNCs), nanoparticles (SNPs), nanofibers (SNFs), nanomicelles (SNMs), and nanovesicles (SNVs) [2, 3, 8].

SNMts can be obtained using “top-down” approaches such as acid and enzymatic hydrolysis (EH), anti-solvent precipitation (ASP), high-pressure homogenization (HPH), and ultrasonication, as well as by means of “bottom-up” approaches using electrospinning and electrospraying, self-assembly, and emulsification [2, 3, 8, 9].

The present chapter aims to define and classify the different starch nanoarchitectures, as well as to discuss briefly the methodologies used to produce these nanomaterials. More information about the production of SNMts is discussed in Chaps. 2, 3, 4 and 5.

1.2 Preparation of Starch Nanomaterials

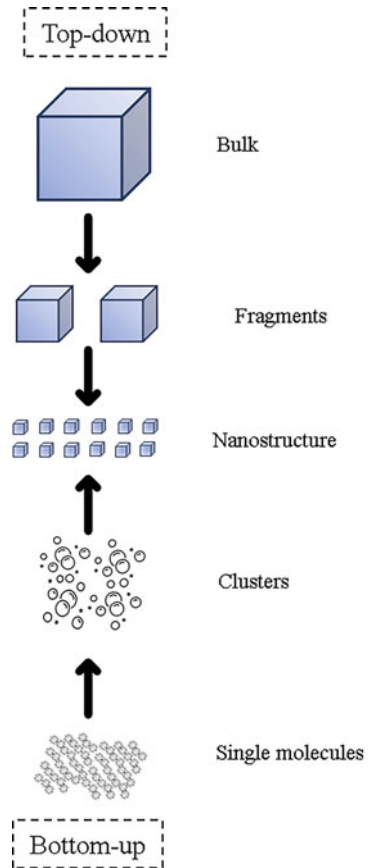
The building of nanostructures is based on the “top-down” and “bottom-up” approaches (Fig. 1.1). The “bottom-up” approach is based on building nanoparticles from smaller units or precursor molecules, whereas the “top-down” method involves reducing larger materials, such as starch blocks, to the nanoscale through decomposition or milling processes, resembling acidic, alkaline, and enzymatic hydrolysis [10].

Acid and enzymatic hydrolysis, ball milling, anti-solvent precipitation, high-pressure homogenization, microfluidization, sonication, electrospun fibers or electrospray, self-assembly, and emulsification can result in SNMts. Starch granule fragmentation can result in SNCs or SNPs, described as top-down processing, whereas starch solutions electrospun or precipitation or emulsification, described as bottom-up processing can result in SNFs, SNPs, SNMs, or SNVs.

The fragmentation of starch granules into a nano-sized structure is the main challenge for “top-down” materials building up. There are a few strategies that result in the formation of starch nanocrystals [11, 12]. However, most starch processing results in nanoparticles from starch granules. This is due to the structure crystallinity lost during the nanosizing.

The starch granules are insoluble in water and some other solvents at room temperature. To allow their use to build up SNPs or SNFs, the starch granules must be gelatinized by heating or chemically [13–15]. In addition, to obtain nanomicelles and nanovesicles, the starch granules must be in solution or gelatinized [16].

Fig. 1.1 Schematic representation of the top-down and bottom-up building up of nanostructures



1.3 Classification of Starch Nanomaterials

It is essential to specify the types of SNMTs (Fig. 1.2) because this significantly influences the stabilization capacity of the compounds and/or their use as a reinforcing material. In general, SNMTs can be classified as nanocrystals (SNCs), nanoparticles (SNPs), nanofibers (SNFs), nanomicelles (SNMs), and nanovesicles (SNVs).

1.3.1 Starch Nanocrystals

Starch granules have a highly organized structure, with amorphous and crystalline regions. The amorphous regions are the most susceptible to acid or enzymatic hydrolysis, as the crystallinity of starch is preserved under conditions below the

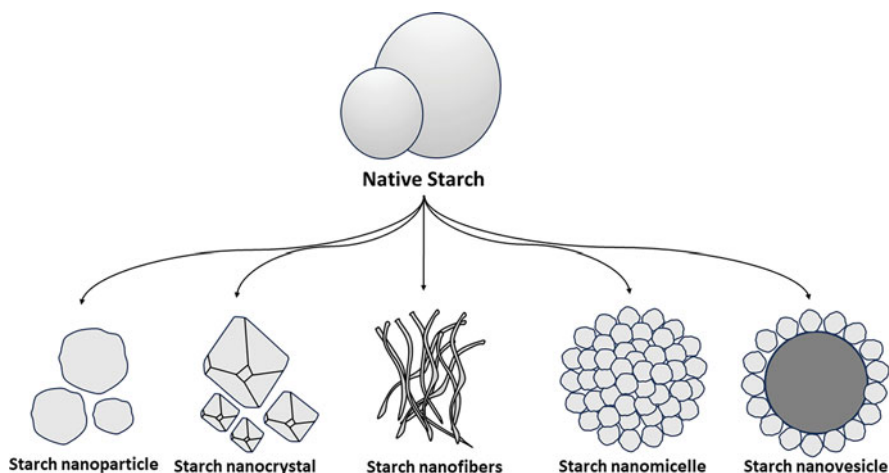


Fig. 1.2 Nanostructures derived from starch

gelatinization temperature [17, 18]. Therefore, by removing all or part of this amorphous region from the granule, platelets with high crystallinity are released, which occur between 30 and 80 nm, and are known as nanocrystals (SNCs) [8, 19–21]. Acid hydrolysis processes can also result in fragment starch [22], or even other crystalline structures [23], or amorphous starch nanoparticles (SNPs) [24]. This hydrolysis is a top-down approach using concentrated acids to isolate the SNC.

SNCs have often been prepared using waxy starch via sulfuric acid hydrolysis [25]. However, some other starches and hydrolysis processes have also been studied to produce SNCs. Corn or maize starch is the main source used to produce SNCs, with several reports about rice, potato, wheat, and bean starches, as well as cassava, quinoa, amaranth, and some fewer common sources such as starchy seeds from fruits and pines [2, 8, 11, 12, 26, 27]. Enzymatic hydrolysis, mixed acids, ball milling, and sonication-assisted isolation are also efficient for producing this crystalline nano-scale material [28–31].

The low SNCs yield after the acid hydrolysis isolation encouraged the alternative development to improve it. Therefore, starch pretreatments, such as physical, chemical, or enzymatic modifications, can affect not only the recovery yield of SNCs, but also their properties. Therefore, the new challenge is to understand how different starch sources and pretreatments, and the isolation processing reflect in the properties and applications of SNCs.

1.3.2 Starch Nanoparticles

SNPs are produced through controlled fragmentation of starch using the “top-down” and “bottom-up” techniques [10, 32–35]. The antisolvent or nanoprecipitation method is frequently used to produce SNPs [32]. This process involves dissolving starch in a miscible solvent such as water, typically hot water, and then adding it to another non-miscible solvent or antisolvent in water, such as ethanol (Fig. 1.3). The insolubility in the solvent triggers the precipitation of starch into nanoparticles. Solvents such as ethanol act as precipitation agents and help control the size and morphology of SNPs. This method is widely employed in starch nanotechnology because of its versatility and capability to generate nanoscale particles.

The synthesis of SNPs represents a significant advancement with substantial improvements in conventional starch properties. These SNMs, when reduced to the nanoscale, undergo a significant increase in their specific surface area. This not only enhances their capacity for compound absorption and release, as documented in previous studies [36–38], but also provides a versatile platform for multiple innovative applications. In addition to their impact on compound absorption and release, the synthesis of SNPs has proven particularly valuable in emulsion stabilization within the food industry [39]. These nanoparticles have also excelled in increasing the water adsorption capacity [40]. Furthermore, their versatility is evident in their ability to function as cross-linking agents and fillers with thermo-sensitive properties

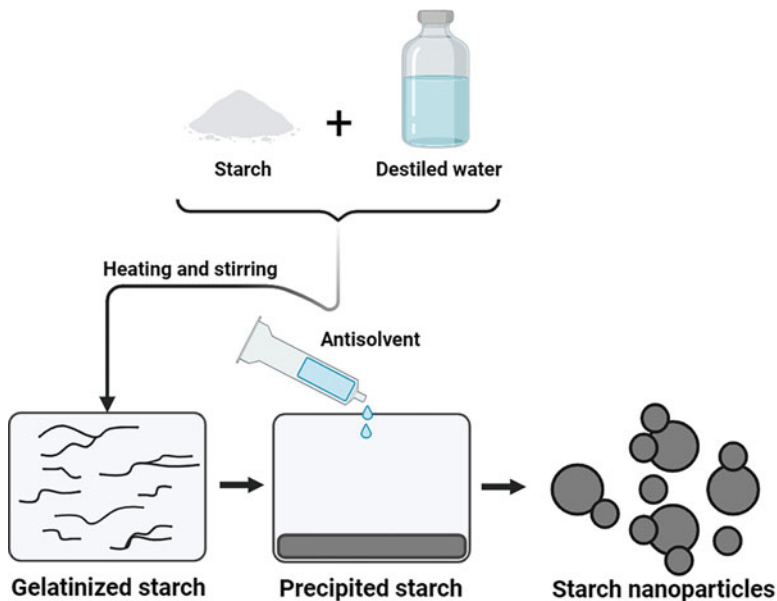


Fig. 1.3 General process for the production of starch nanoparticles by nanoprecipitation or antisolvent precipitation

[41]. However, their versatility is not limited solely to these applications. SNPs have served as precursors for the synthesis of carbon nanodots, expanding their utility in fields such as nanotechnology and electronics [42]. Beyond their physical properties and practical applications, it is essential to highlight that these SNPs can be functionalized with bioactive compounds, as documented in previous research [43–45]. This functionalization allows SNPs to acquire antimicrobial and antioxidant properties, further enhancing their utility in sectors that require food preservation and the improvement of pharmaceutical and cosmetic products. Collectively, these advancements illustrate the potential and versatility of SNPs in enhancing various areas of science and industry [46–48].

1.3.3 Starch Nanofibers

SNFs formation is based on a bottom-up approach by electrospinning. It involves an electrodynamic process that was first patented in 1934 by the invention “method and apparatus for preparing artificial threads”, describing the production system of polymer-based fibers using high-voltage static electricity [49]. Electrospun fibers are synthesized by applying a high-voltage electric field on the surface of polymer solution droplets, causing a liquid jet to be ejected through a spinneret [50]. By controlling the polymer concentration, molecular weight and viscosity, appropriate solvent, low surface tension, the solution electrical conductivity and feeding rate, and applied voltage, it is possible to produce fibers with different sizes and morphologies [51, 52]. Starch granules are not easily solubilized to produce an appropriate electrospun solution. Therefore, recently electrospinning setups and different solvents were investigated to produce this type of fibers from the starch polymers [13, 14, 53–55].

The two main approaches are using an electro-wet-spinning setup, which involves the formation of the fibers on a grounded metal mesh immersed in a pure ethanol bath [14, 55]. The starch granules were dissolved in an aqueous dimethyl sulfoxide solution of 95% (v/v). The other approach uses a traditional electrospinning setup and a starch dispersion in aqueous formic acid of 90% (v/v) [56]. Starch undergoes rapid esterification, generating esters in the starch glucose units. This process is also known as chemical gelatinization at room temperature [13]. In addition, starch modification and/or blending with other polymers were used to produce an appropriate dispersion for spin [57]. Each fiber processing is driven under particular conditions and reflects various properties, sizes, and morphologies [14, 55, 56].

1.3.4 *Starch Nanomicelles*

SNMs can be used to increase the solubility of compounds lower polarity compounds and have been studied as delivery systems for medical [58–60] and food applications, such as the delivery of curcumin [16, 61, 62] and β -carotene [63]. They are conventionally obtained using a down-top approach, as modified amphiphilic starch molecules emulsify an active hydrophobic compound. Starch is modified by hydrolysis esterification to form smaller chains with a hydrophilic and hydrophobic regions [60–62]. In this form, starch-based micelles act as the emulsifiers of hydrophobic compounds or solutions.

Therefore, the methods to form nanomicelles are based on using amphiphilic modified starch as the emulsifier of a hydrophobic phase, which is located in the core of the micelles. Usually, pre-emulsions are formed by self-assembly by mixing the hydrophobic solution, the amphiphilic starch, in an aqueous phase under high-shear homogenization [63]. If better homogenization or droplet size reduction is required, a high-energy nanoemulsification method can be further used on the pre-emulsion, such as ultrasonic treatment [16, 58–60]. Other methods, such as microfluidization, high pressure, and membrane homogenization, could also be effective for this purpose, but no studies using these techniques for obtaining starch nanomicelles have been informed. A solid-separation step such as filtration or centrifugation can be performed to use undissolved particles [59, 62].

Some specific procedures to obtain SNMs systems use organic solvents such as ethanol [64], chloroform [61], and acetone [58] to compose the hydrophobic solution. However, organic solvents are frequently dangerous and environmentally harmful; therefore, it is interesting to avoid their use when possible. If necessary, the use of solvents generally recognized as safe or with GRAS status, such as ethanol, should be preferable, especially for food and health applications.

Focusing on food applications of SNMs and micelles, it is noticeable that starch is a versatile, accessible, and environmentally friendly raw material for the formation of nanostructured systems aimed at the protection and delivery of bioactive compounds. The consequent protection and prolongation of the activity of sensible natural active compounds make the substitution of synthetic and unsustainable food additives more feasible in the future. This exchange can fulfill the expectations of health-worried consumers. It also contributes to the establishment of a greener chemistry and industry. However, there is a broad field to be explored, which includes the development systems for different encapsulated bioactive compounds, such as other vegetal and animal-derived extracts, such as essential oils and propolis, respectively. Studying how the nanostructures interact with different types of food media, such as muscle-based foods, water-based juices, milk-fat-based foods, vegetable cells, and bakery products, is also highly relevant.

1.3.5 *Starch Nanovesicles*

SNVs are nano-dimensional structures that encapsulate hydrophobic materials. Nanovesicles do not have a specified structure; however, they are usually charged with lipophilic bioactive substances aimed at their protection, controlled release, and increased stability in aqueous media [43, 65, 66]. Starches have gained attention for their applications because they are highly available, non-toxic, safe, biocompatible, and biodegradable, and their properties can be easily changed by chain modification and hydrolysis [65, 67, 68]. This characteristic is interesting for tailoring nanoparticle properties, such as size, active release rate, etc. The most studied applications of SNVs are in the medical field, for the delivery of drugs in medical applications [65, 66]. However, agriculture can also benefit from nanocarriers of pesticides [68, 69], nutrients, and biocontrol agents [70]. Food products have great potential to be improved as well, with the development of nanocarriers of natural compounds, including preservatives and bioactives that benefit the consumer's health, such as curcumin [43], but, this is a field of application that is yet to be explored.

The conventional way to obtain nanovesicles is by the dilution of an oil-in-water nanoemulsion of the desired hydrophobic molecule into a gelatinized starch solution, followed by its drying, forming oil-charged microcapsules [43, 65]. The conventional emulsification method uses high-shear mixing, but alternative methods can be used. An alternative method was reported by Li et al. [68], the premix glass membrane emulsification method. For this, an oil-in-water or water-oil-water pre-emulsion was obtained by mechanical stirring or sonication (top-down approach), followed by a membrane homogenization stage to reduce the particle's sizes by shear forces. This method has the advantage of easily controlling the particles size, being reproducible, and having a high production rate. To obtain nanovesicles, some systems may require organic solvents such as ethanol. When this is the case, the nanoemulsion loading stage must enable sufficient time and temperature to allow the evaporation of the organic solvent [43].

Native starches are sensitive to enzymatic degradation and water and tend to release the encapsulated material quickly because of the reduction of intermolecular forces and swelling when applied in water-based systems [71]. Like other polysaccharides, starch is hydrophilic and relatively chemically stable, and its easy modification or functionalization can be applied to solve these issues [72]. Several studies have applied modified starches with amphiphilic properties to form nanomicelles, which are starch-based polymers modified to have hydrophobic and hydrophilic regions [60–62]. SNVs have shown great stability and controlled release of active compounds, besides the advantages of using starch, such as non-toxicity, safety, biocompatibility, and biodegradability [62, 73].

1.4 Conclusions

Research on the production of starch nanomaterials (SNMts) is recent and could have promising applications. In general, starch nanocrystals (SNCs), nanofibers (SNFs), nanoparticles (SNPs), nanomicelles (SNMs), and nanovesicles (SNVs) can be obtained by using starch chains and the “top-down” and “bottom-up” approaches such as acid/enzymatic hydrolysis, antisolvent precipitation, electrospinning, self-assembly, among others. Particularly, SNCs and SNFs have been used as fillers in packaging materials, whereas, SNPs have been used to stabilize bioactive compounds to develop antioxidant and antimicrobial nanomaterials. SNMs and SNVs have been explored in medical applications to encapsulate hydrophobic materials and increase the solubility of compounds lower-polarity compounds. Further studies are required to optimize the production of SNMts and standardize their particle size and shape, and to explore food and food packaging applications.

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Conflicts of Interest The authors declare no conflicts of interest.

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