A Review on Synthetic Approaches and Applications of Starch Nanomaterials, and Hydrolyzed, Esterified and Phosphorylated Starch Materials

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Abstract

Starch undergoes chemical modification through functionalization, and it naturally exists in numerous nano-sized semi crystalline block lets. From starch, low toxicity and eco-friendly compounds with high modification can be prepared for commercial applications. So, it is an interesting and advantageous bioactive polymer in the field of nanotechnology. The quality change in functionality of starch can be seen by the substitution of a new functional group in the starch molecule. Chemical modifications through the processes of hydrolysis, esterification, and phosphorylation have been reported to result in the starch functionalized derivatives of specific applications mainly in agricultural, food and non-food industries, water treatment, drug delivery and paper and textile industries. Varieties of nanomaterials can be extracted from starch for many purposes like fat mimic, delivery system, emulsion stabilizing and food packaging, DNA precipitation and cancer therapy.

Keywords: *Biopolymer; Chemical modification; Starch; Functionalized starch material; Starch nanomaterials*

1. Introduction

When carbon dioxide and water mix during photosynthesis in plants, an organic substance known as starch is formed (Teramoto et al., 2003). It is the most common type of carbohydrate that various plants store for energy (Buléon et al., 1998; Whistler & Paschall, 1965). It is without a doubt the most important biomass material due to its renewability and biodegradability (Velasco et al., 1996; Goni et al., 2002; Jenkins & Hudson, 2001; Zohuriaan-Mehr & Pourjavad, 2003). The use of polymers generated from petroleum chemicals has led to a major increase in environmental contamination in recent years. As a result, more biodegradable products based on starch are being produced and developed. In agricultural nations, starch is an intriguing renewable resource because it is simple to modify and easily accessible (Gupta & Sahoo, 2001; Mostafa, 1995). Despite having numerous beneficial qualities, starch restricts its usage in some applications with synthetic polymers. It has been discovered that derivatization, in which the hydroxyl groups (-OH) are replaced by different functionalities, improves the characteristics of starch (Mochamad et al., 2014; Whistler et al., 2009). By adhering to cellulose fibers, highly functionalized 2-hydroxy-3-triethylammoniumpropyl chloride starch (HPMA starch) with a degree of substitution (DS) between 0.25 and 1.54 can undergo chemical alteration (Whistler et al., 2009). Although it has certain drawbacks and restrictions, the use of cationic starches to improve filler retention and paper strength is standard practice in the papermaking industry (Whistler et al., 2009; Holmes, 2005). Quaternary ammonium structures play a crucial role in day-to-day activities and are widely employed as phase transfer catalysts (Codling et al., 2003; Gu et al., 2014). Due to their mass production, they are utilized as bactericides, insecticides, detergents, medications, and intermediates in numerous synthetic processes (Li et al., 2014; Mousavi et al., 2014; Lara-Martin et al., 2011; Martín-Carballo et al., 2007). The drawbacks of these quaternary products include their high cost, toxicity, lack of biodegradability, and environmental persistence because they are generated from petrochemicals (Lara-Martin et al., 2011; Tandukar et al., 2013). Therefore, the preparation of biogenic quaternary ammonium compounds (QAC) is required. Polysaccharides are readily available and environmentally benign biomaterials that can be functionalized into a wide variety of biogenic materials using straightforward techniques. Low-toxicity and environmentally friendly QAC can be made from starch with significant modification for use in commercial settings (Chauhan et al., 2015). It is possible to create cationic biopolymers such as 2,3-epoxypropyltrimethylammonium chloride (EPTMAC) and 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) by substituting positively charged groups for the hydroxyl groups in starch (Chauhan et al., 2015). Two glucan polymers that make up starch's chemical composition are amylose and amylopectin (Singh et al., 2010).

While amylopectin is composed of more than 1000 glucose units in a highly branched form, amylose is composed of 500–2000 glucose units in a linear form. The amylose and amylopectin together make up the majority of dry starch (98–99.9%) (Santana & Meireles, 2014). Due to their distinct physicochemical characteristics, the two components directly control starch properties (Santana & Meireles, 2014). The physicochemical and functional characteristics of starch – closely linked to the structural and molecular makeup of amylose and amylopectin, their percentage composition, granule size and shape, and starch source – dictate its possible applications in the food industry (Cornejo-Ramírez et al., 2018).

The physical and chemical characteristics of starch granules dictate their functions. Therefore, choosing the right starch with the required properties for a certain application is crucial. Selecting the starch source and appropriate modification methods is beneficial for obtaining the functional qualities needed for a given product (Emeje, 2020). Reactant concentration, reaction duration, modifying reagent, catalyst type, temperature, pH, substituent types, degree of substitution, and substituent distribution within the starch molecule all influence the functional characteristics of starch (Emeje, 2020). To improve its functionality for intended uses, natural starch is typically processed and modified using chemical techniques (Emeje & Asha, 2014).

When additional functional groups are added to starch molecules, the result is chemically modified starch that exhibits quality changes in pasting, gelatinization, retrogradation, and solubility (Tester et al., 2004). The two types of alpha-glucan that comprise starch granules are amylose and amylopectin. The great majority of amylose units (99%) are long and linear, and their size and structure vary depending on the plant they are generated from (Tester et al., 2004). Starch contains many hydroxyl groups, including one primary hydroxyl group at C-6 when unlinked and two secondary hydroxyls at C-2 and C-3. The presence of a hydroxyl group gives starch its particular reactivity (Copeland et al., 2009). Amylose and amylopectin are the two homopolymers that make up the majority of starch granules. While amylopectin is a highly branched polymer composed of (1,4)-linked glucan with (1,6) branching points and is the main granule component (72–82%) with molecular weight in the 50–500 ×10^6 range, amylose is linear (1,4)-linked glucan with degree of polymerization up to ~600, comprising 18–28% of natural granules (Perez et al., 2009; Kim et al., 2015; Kaur et al., 2007).

2. Starch nanomaterials and their applications

The promising potential of nanotechnology can be further enhanced by extracting nanomaterials from sustainable, natural resources. A range of natural biopolymers have been developed as building blocks for different nanomaterials used in food packaging, emulsion stabilization, delivery systems, and fat mimicking (Ali Razavi & Amini, 2016). Because it is non-toxic, biodegradable, biocompatible, inexpensive, and readily available, starch finds extensive usage in food, medicine, pharmaceuticals, and many other fields (Le Corre *et al.*, 2010; Morris, 2010; Lin *et al.*, 2011). Natural starch can be added in different forms or altered by physical, chemical, and enzymatic methods. A biopolymer that is easily accessible, biodegradable, affordable, edible, and modifiable, starch occurs in nature in various nanoscale, semi-crystalline block shapes. Thus, it has garnered a lot of attention from nanotechnology experts (Ali Razavi & Amini, 2016). Starch biopolymers have yielded a variety of nanomaterials with distinct chemical compositions and botanical sources (Ali Razavi & Amini, 2016). Starch nanomaterials (SNMs) are often categorized as nanoparticles and nanofibers based on their shape, physical characteristics, and other attributes (Ali Razavi & Amini, 2016).

2.1 Starch nanoparticles

The broadest class of starch nanomaterials (SNMs) are starch nanoparticles (SNPs), which have a wide range of functions and production techniques. Depending on preparation techniques, certain nanoparticles can be made from previously gelatinized starch, while others may have a low degree of crystallinity or be entirely amorphous. Starch nanoparticles can be created using various physical and chemical processes to form nanospheres, nanogels, nanosponges, and nanoparticles. For example, SNPs can be created by precipitating gelatinized normal corn starch with ethanol and then crosslinking it with citric acid (Ma *et al.*, 2008). Reports show that modified SNPs with particle sizes between 50 and 100 nm can tolerate gelatinization at temperatures up to 95 °C (Ali Razavi & Amini, 2016). SNPs have been proven useful for improving the controlled release of encapsulated bioactive substances in various industries, including food, cosmetics, and medical sectors (Morán *et al.*, 2021). One of the main medical applications of SNPs is cancer therapy. In a recent study, Alp *et al.* (2019) demonstrated the advantages of encapsulating anticancer medications in polymeric nanoparticles, which increase drug solubility, prolong systemic exposure, and reduce toxicity. El-Naggar *et al.* (2015) found that drug-loaded SNPs had no adverse effects on rat skin, suggesting potential use in therapy for rheumatoid arthritis and other chronic inflammatory conditions. SNPs are also used in DNA precipitation methods, where they interact with DNA to induce precipitation in ambient-temperature ethanol solutions (Ip *et al.*, 2014). An emerging application is sensor creation using starch nanoparticles (Sukyte *et al.*, 2010).

2.2 Starch nanofibers

Numerous studies have employed electrospinning to create fibers from various polymers, especially synthetic ones (Lin *et al.*, 2011). However, applying electrospinning to starch can be limited by certain issues. For most biopolymers, determining electrospinnability is essential to selecting an appropriate solvent that will promote chain expansion. Water, as a solvent, may fail during starch production due to a lack of long-range chain enlargement in aqueous solution (Ma *et al.*, 2008; Morán *et al.*, 2021). Sukyte *et al.* (2010) explored how potato starch affected the electrospinning of polyvinyl alcohol into nanofibers. They used a 3% starch content to create nanofibers, which increased to 5% with added ethanol solvent. By raising starch concentration in the spinning fluid while lowering nanofiber density, they found that non-woven textiles without spots could be produced (Ma *et al.*, 2008). Electrospun nanofibers have drawn much attention due to their potential in wound dressing, drug delivery, and tissue engineering. Their extremely high surface area, superior mechanical performance, high porosity, and ease of fabrication provide ideal vehicles for drugs, bioactive compounds, growth factors, even cells, DNA, RNA, viruses, antibacterial agents, and antioxidants, as well as scaffolds for cell adhesion and proliferation (Sill & von Recum, 2008). Numerous functional molecules (e.g., antibiotics, anticancer drugs, enzymes) can be delivered by electrospun nanofibers (Sill & von Recum, 2008; Kai *et al.*, 2016). Advanced delivery systems based on starch nanofibers include combinations of nanofibers and nanocontainers, coaxial electrospinning, emulsion electrospinning, and surface-functionalized electrospun nanofibers (Lancuski *et al.*, 2017). Drug release from electrospun fibers is typically faster than from a similar film due to the fibers' larger surface area (Kenawy *et al.*, 2002). The morphology of electrospun starch nanofibers – high surface area, high porosity, permeability, and a well-connected pore structure – is comparable to the natural extracellular matrix (ECM) (Tuzlakoglu *et al.*, 2005). Tissue engineering has utilized electrospun scaffolds for bone, cartilage, skin, nerves, tendons, and ligaments (Lu *et al.*, 2016). Non-woven starch nanofibers are promising for wound dressing because of their desirable properties (Lai *et al.*, 2014). Growth factors can be encapsulated and transported via starch nanofibers for dermal and epidermal regeneration and angiogenesis. Starch nanofibers can act as three-dimensional scaffolding for growth factors to aid in wound healing (Lai *et al.*, 2014).

3. Chemically modified starch materials and their applications

Adding functional groups to the starch molecule without changing its shape or granule size distribution is known as chemical modification of starch. By changing its physicochemical characteristics and structural features, modification can significantly enhance native starch qualities while raising its technical value (Alcázar-Alay & Meireles, 2015). Because starch has been functionalized through various chemical processes, its applications have greatly expanded (Yifei & Francesco, 2020). Substituting a new functional group for a hydroxyl group chemically alters starch, changing its physical characteristics (Emeje, 2020). The functional characteristics of modified starch are greatly impacted by variables such as starch source, pH, reaction time, reagent concentration, substituent type, degree of substitution, catalyst use, and substituent distribution (Emeje, 2020).

Starch can be functionalized using either monofunctional or bifunctional reagents, depending on their chemical characteristics (Wolf *et al.*, 1999). Monofunctional reagents give reactive groups that are cationic, non-ionic, covalent, or hydrophobic (Sui & BeMiller, 2013). Changing the pasting and gelatinization characteristics of starch produces a more stable derivative (Jeon *et al.*, 1999). Monofunctional reagents are employed in hydroxypropylation modification techniques (Pal *et al.*, 2002). Bifunctional reagents enable crosslinking of polymers by reacting with multiple OH groups, strengthening starch granules (Tharanathan, 2005; Wang & Wang, 2003). Common crosslinking agents like phosphoryl chloride and trimetaphosphate stabilize starch by altering its solubility, swelling, and mobility (Xiao, 2012).

3.1. Hydrolyzed starch materials

A hydrolysis process occurs when water molecules are introduced across a bond, breaking it and yielding compounds with an alcohol (-OH) functionality. There are two methods for hydrolyzing starch: enzymatic and chemical. In acidic or alkaline solutions, hydrolysis can extract fatty materials from natural starch. In an alkaline medium (heated aqueous KOH or NaOH), alkali-modified starch with enhanced reducing ability is created, whereas acid-modified starch is created in an acidic medium (water or dilute HCl) (Taylor & Salzman, 1933; Maher, 1983). The hydrolytic technique is extensively used in the food industry to produce starch derivatives with enhanced functionality and better processing properties (Santana & Meireles, 2014). Various starch modifications involving acidic and alkaline media are common in food processing. Acid and alkali-mediated isolation techniques impact the product’s amylose/amylopectin composition, lipid and protein content, granule size, and shape (Maher, 1983; Santana & Meireles, 2014).

3.2 Esterified starch materials

Alcohol and carboxylic acid condense to produce an ester in an esterification reaction, typically in acidic media (Carey, 2003). The reaction is usually reversible, with the forward reaction favored at low pH and high alcohol content (Carey, 2003). A reaction occurs between the alcohol group (-OH) of starch glucose units and the -COCl or -COOH of fatty acid chlorides. When multifunctional reagents are present, esterification is frequently employed to add lipophilic groups to starch, producing a more cross-linked starch polymer (Ackar *et al.*, 2015). Intermolecular bonding is weakened by esterification, which holds granules together and thus greatly affects granule shape, size, and functionalities (Ackar *et al.*, 2015). Esterified starch finds applications as adhesives and binding agents in textile, petrochemical, food, paper-making, and pharmaceutical industries (Shuangqi *et al.*, 2018).

3.2.1 Acetylated starch materials

Acetylation is the process of adding acetyl groups (–COCH_3) to polymeric starch, reacting with free hydroxyls to form an ester (Sweedman *et al.*, 2013). Acetylated starch is created when starch is treated with acetic anhydride. Acetylation results in starch molecules with acetyl functionality in glucose units, improving freeze-thaw stability and paste clarity (Sui *et al.*, 2013). The degree of substitution (DS) of hydroxyls with acetate groups is influenced by reaction conditions (Ackar *et al.*, 2015). Low-DS acetylated starch (DS 0.01–0.2) is used in food sectors as encapsulating agents, thickeners, stabilizers, texturizers, and film formers (Elomaa *et al.*, 2004). The FDA states that a maximum DS of 0.1 for acetylated starch can be used in food (Mason, 2009). Acetylated starch with high DS is soluble in acetone and chloroform and highly thermoplastic and hydrophobic, so it is mainly used in non-food applications (Ackar *et al.*, 2015). Mono-substituted acetylated distarch adipate is produced when adipic and acetic anhydrides are added to starch. It increases product stability in freezing and, due to strong temperature resistance, is used as a bulking, thickening, and stabilizing agent in foods like soups and sauces (Mason, 2009). Acetylated cross-linked waxy maize starch is used in frozen sauces, pastries, and vegetables for enhanced freeze-thaw resilience (Mason, 2009). Hydroxypropylation of cross-linked starch significantly improves stability of frozen sauces and puddings (Mason, 2009).

3.2.2. Succinylated starch materials

Starch granules react with succinic anhydride in an esterification to produce succinylated starch (Sui *et al.*, 2013). Combining starch with a succinic anhydride solution in acetone at 40 °C for four hours yields succinic esterified starch via green methods (Wang & Wang, 2003). At lower temperatures, succinyl groups facilitate solubilization, gelatinization, and swelling by weakening starch polymer chains. Starch succinate's ionic compounds serve as polyelectrolytes. At low DS, starch succinate in solution becomes more hydrophilic and viscous (Neelam *et al.*, 2012). Due to their higher viscosity, succinate starch biomaterials can improve the flavor of meat and fried foods and act as stabilizing/thickening agents in soups, snacks, and frozen items. Starch succinate offers clear paste, resistance to retrogradation, lower gelatinization temperature, high thickening, strong film-forming qualities, and freeze-thaw stability (Emeje, 2020). In alkali, starch reacts with octenylsuccinic acid or anhydride to produce starch octenylsuccinate, or with dodecylsuccinic acid to produce starch dodecyl succinate. These derivatives have dual lipophilic functionality, suitable for emulsification and encapsulation. Starch octenylsuccinate derivatives help stabilize oil-in-water emulsions in flavored beverage concentrates (Mason, 2009). Esterifying starch with acetyl malic acid involves acidifying malic acid with acetic anhydride, reacting it with thionyl chloride (SOCl_2) to form acetyl malic acid chloroanhydride, and then modifying starch with that compound in DMSO (Neelam *et al.*, 2012).

3.2.3. Starch-cinnamate materials

Thakore *et al.* (2000) prepared starch cinnamate by refluxing starch with cinnamoyl chloride, formamide, and potassium acetate at 110 °C for 3 h. Starch cinnamate can also be obtained by reacting cinnamic acid with starch in dichloromethane in the presence of 2,4,6-trimethylpyridine at 25 °C for 72 h (Eltaboni & Alabidi, 2017). Starch cinnamate is compatible with polar synthetic polymers (e.g., polyvinyl chloride, PMMA, styrene acrylonitrile) but incompatible with non-polar polymers like polystyrene. The resulting starch cinnamate/synthetic polymer blends can be used to develop partially biodegradable polymers (Thakore *et al.*, 2000; Thakore *et al.*, 2003).

3.2.4. Bromoisobutyryl esterified starch material

To synthesize a starch macroinitiator, hydrophobic 2-bromoisobutyryl substituents can be introduced via starch esterification. When acid-converted starch (ACS) is treated with 2-bromoisobutyryl bromide (BIBB) in tetrahydrofuran (THF), bromoisobutyryl esterified starch (BBES) is obtained. These substituents improve Van der Waals forces at the interface of starch adhesive layers with polyester or PLA fibers, yielding chemistry similar to the esters in polyester or PLA chains (Li *et al.*, 2019).

3.2.5. Phosphorylated starch materials

Phosphoric acid and phosphorous acid are inorganic esters; starch reacts with agents like phosphoric acid to form starch phosphate. Starch phosphorylated in this way is more stable at low and high temperatures, more resistant to acidic environments, and suitable as a thickener. Ortho-phosphate and pyrophosphate have been used at high temperature in mildly acidic conditions to phosphorylate starch (Huang *et al.*, 2013). Sodium trimetaphosphate, sodium tripolyphosphate, and phosphoryl trichloride have been used at higher pH to prepare mono- and di-starch phosphates (Korma *et al.*, 2016; Sechi & Marques, 2017). Depending on conditions, phosphorylation yields cross-linked mono- or di-starch phosphate derivatives. At higher DS, monoesters form instead of diesters (Neelam *et al.*, 2012). The degree of phosphorylation is determined by amylopectin chain length distribution (C-3 and C-6 positions) (Blennow *et al.*, 1998). Phosphate starch cross-linking strengthens the starch granule's mechanical structure, improving texture, firmness, and thermal stability. Distarch phosphate is stable against gelling, retrogradation, and syneresis, and can be used as a thickening and stabilizing agent (Neelam *et al.*, 2012).

4. Conclusion

Starch is a significant food product and a flexible biomaterial utilized in many industrial sectors, including the food, health, textile, chemical, and engineering industries. The functionality and physicochemical characteristics of starch are essentially what determine its adaptability for industrial applications. In its natural state, starch has limited uses and functions. However, advances in chemistry and biotechnology have allowed for extensive starch modification for a variety of uses. Therefore, different approaches or strategies are needed to develop starch based biodegradable polymers industry for enhancing their biocompatibility, bio-degradability and physical properties for their diverse applications. This article has summarized the production of modified starch with a variety of features and applications with a focus on the recent development to note the possibility of exploring the highly valuable functional perspectives with respect to their future applications.

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