

STARCHES, CURRENTLY A SOURCE POTENTIAL FOR THE DEVELOPMENT OF BIOCOATINGS

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Abstract

Food applications of biopolymers are currently one of the fields of greater interest in the developments of macromolecules, for use as a biocoating. The polymers were included officially in the pharmaceutical field in 1980 in the American Pharmacopoeia USP XX and since then have been used as containers and packaging materials. This paper presents a review of trends in the use of biopolymer to design biocoating with food applications, as well as the current trend of the use of starches in this field required that the engineer must know to obtain a material that can be used in the food field and aims to serve as a reference to the State of the art in this specific field of knowledge.

Keywords: *biopolymers, starch, bio-coatings.*

Introduction

Currently, packaging represents one of the areas of application of synthetic polymers, of greater consumption. In the current context relation between to the environment and the continuous accumulation of solid waste from industrialization and consumption of petroleum-derived polymers increases due to the average life time of these materials. One of the most persistent remnant materials is plastics, which remain in land extension practically indestructible for thousands of years [1-7].

According to the above, new technologies in the development of sustainable processes has focusses in creation of biodegradable polymers, which have a few properties comparable with synthetic plastics [4]. To counteract this situation, new alternatives have been developed with similary characteristics to traditional polymers but being environmentally friendly. Some of these biopolymers are mostly based in starch [8-12].

Edible films and coatings are made from biopolymers, such as proteins, lipids and polysaccharides derived from renewable natural sources that are completely biodegraded in a considerably short period of time, thus helping to reduce environmental pollution [3,13-18]. These new products are a subject of great interest because they have a great potential to prevent the deterioration of many food products besides their biodegradability [3].

The aim of this work is to present a review on starches as current material with a potential source for the development of new films and coatings.

Methods

A search for original and review articles in english and Spanish in the last ten years was carried out in the following databases: MedLine, Library Plus, ProQuest, NCBI and ScienceDirect.

Results

Starch is the main source of carbohydrates in the human diet because it is widely distributed in nature; It is the food reserve of vegetables and is stored in the form of granules in their different

structures, with the seeds containing the highest concentration of this polymer, which varies depending on the genus and species. It is found in cereal seeds (corn, wheat, rice, sorghum), in tubers (potatoes), in roots (yucca, sweet potato, arrowroot), in seeds of legumes (beans, lentils, peas), fruits (bananas, apples and green tomatoes), trunks (palm, sago) and leaves (tobacco) [19-23].

Physicochemical properties determine the use of starch according to proximal composition (content of crude protein, ether extract, crude fiber, ash and moisture), characteristics of the granule (size, color and shape, crystalline nature), molecular weight and amylose content [19-23].

Depending on the properties of starch can be used as a raw material to elaborate pharmaceutical products because presents absorbent and emollients properties for skin. Some formulas are prepared in form of powders, ointments and enemas. They form gels with water and polyalcohols that are used in the treatment of eczema, dermatosis, irritations, etc. In other cases, starch is used as a lubricant, diluent and disintegrant of capsules and tablets, as well as for the coating of the latter [19-23].

Starch generally contains about 20% amylose which is soluble in water and 80% amylopectin, insoluble in water [12]. Amylose (Figure 1), it is a linear polymer consisting of glucose molecules linked by glycosidic bonds α -D-(1 \rightarrow 4), the number of units varies between the different types of starches, but is generally between 1000 units of glucose per molecule of amylose and It has a spiral shape. At one end of the macromolecule, the glucose unit contains a hydroxyl group on the free anomeric carbon, which is why it is called the reducing end. At the opposite end, or non-reducing, the hydroxyl at the anomeric carbon forms part of the glycosidic bond. The abundance of hydroxyl groups gives hydrophilic properties to the polymer, imparting affinity for water. However, due to their linearity, the amylose polymers tend to cluster very closely in parallel through the formation of hydrogen bonds between the hydroxyl of the adjacent polymers thereby reducing their affinity for water. The presence of hydrogen atoms in the interior of the

propeller makes hydrophobic amylose and allows it to form complexes with free fatty acids, with glyceride components of fatty acids, iodine and some alcohols [12,23-26].

The amylopectin chain (Figure 2) consists of several units of D-glucose, branched in the form of a shrub in short chains of 20-25 glucose units. The units along the chain are α - (1,4) glycosidic and α - (1,6) glucosidic at the branching points. Its relative molecular mass of 200000 to 1000000 Dalton and even higher [12,27-30].

The amylopectin chains are radially arranged within the granule with their non-reducing terminal ends oriented towards the surface, with alternation of crystalline structure (like a double helix) and amorphous regions (with the regions of the points of Branching [12].

The functionality and properties of starch, such as mechanical strength and flexibility, related to the character of the crystalline region, depend on the relationship between amylose and amylopectin, the degree of branching and the molecular weight distribution [6,12, 26-30].

One of the main characteristics of the starch is its granular form, which through its size allows the identification of the type of plant that comes from it. The starch granule is formed by concentric crystalline structures assembled from the radially oriented amylopectin molecules. The percentage of crystalline area in the starches is around 15-40% and is connected to the amorphous zones in the granules [6,31] (Figure 3).

Biopolimers from starch

Biodegradable polymers are a new generation of materials that are still in development. Among the biodegradable polymers, starch is probably the most abundant and least expensive natural polymer available. In addition, its use reduces the demand for petrochemicals and the negative impact on the environment caused by non-biodegradable plastic waste [7].

The starch is a good film former, however, it must be solubilized in water. To increase the solubility in water, the starch can be esterified with propylene oxide and thus allow the gelatinization of the starch and its subsequent formation of the

film [5,32-37]. These films can be obtained from native starch, or from its components (amylose and amylopectin) separated, by two different techniques: solubilizing in hot water and subsequent drying or with a thermoplastic drying process [38].

The coatings formed with starch, specifically amylose and hydroxypropyl amylose, have a barrier capacity against oxygen and lipids, in addition to improving the appearance, texture and subsequent handling in the industry [39]. In combination with other compounds that can confer properties on the coating (antimicrobials, emulsifiers, antioxidants, etc.) is a good material to form edible coatings. Biocoating made from biopolymers have numerous advantages, including being biodegradable, recyclable, can transport additives, have good barrier and mechanical properties; They improve the appearance of food and protect its properties during storage and handling. They maintain or improve sensory characteristics and texture in foods [3].

Currently there are numerous studies and work done with starch as an edible coating applied to fruits, the results being successful.

Discussion

Recent investigations by Alvis et al., [32] evaluated physicochemical, morphological and viscoamylogram properties of the native starches of yam, cassava and potato, finding differences in the behavior of the properties between them, attributing their difference to the amylose / amylopectin ratio.

Other studies like Hernandez-Medina et al., [8] characterized the physicochemical properties of tubular starches: makal (*Xanthosoma yucatanensis*), sweet potato (*Ipomea batata*), cassava (*Manihot esculenta* Crantz) and sago (*Marantha arundinacea*) grown in Yucatan, Mexico, showed various properties physicochemical and functional that make them feasible for use in various food systems or other industrial applications. The size of the granules of makal, sweet potato and sago starches were 12,40, 12,41, and 10,64 μm , respectively. Except for the sago (0,64%), the starches had low protein

content (0,05+0,22%), which makes it feasible for use in the preparation of glucosed syrups. The makal and the sago, due to their high gelatinization temperatures, could be used in products that require high temperatures, such as canned products, baby food, etc. Cassava starch had the highest swelling power (58,83 g water.g⁻¹ starch), so it could be used in products that require water to be retained, such as meat products, such as sausages, jellies, etc. The starches of sweet potato and cassava presented greater clarity than those of makal and sago, so they could be applied in confectionery products. The firmness and elasticity, as well as the high stability to the refrigeration and freezing of sweet potato and yucca starches, indicate that they could be used as thickeners and stabilizers in food systems that need to be refrigerated and frozen.

Rodríguez et al., [14] performed the characterization of some physicochemical and pharmacotechnical properties of yellow arracacha starch (*Arracacia xanthorrhiza*), showing a particle size between 5 and 35µm, the shape, evaluated as irregular polyhedral, the temperature range of gelatinization, is between 49 and 55 ° C; the content of amylose, is close to 18%, the behavior against relative humidity classifies it as a moderately hygroscopic material and its pharmacotechnical properties demonstrate a low bulk, poor flow and a good performance under compression.

Chiumarelli and Hubinger [40] formulated a coating with cassava starch, carnauba wax, glycerol and stearic acid to apply on apple slices, with the results of a decrease in the respiratory rate of the fruit, good resistance to water vapor and better mechanical properties. and film makers.

In the same way, García et al., [41] formulated an edible coating based on cassava starch with or without the addition of potassium sorbate on strawberries. They observed a decrease in the respiratory ratio, as well as a decrease in firmness and texture. Potassium sorbate did not have the expected antimicrobial functions, and samples coated with cassava starch with potassium sorbate deteriorated faster (9 days) than those

without potassium sorbate (12 days) due to the attack of microorganisms.

The starch of yam (*Dioscorea* sp) is considered a good source for the production of films and edible coatings, for its amylose content, its stability at high temperatures and low pH [42]. Films made from yam starch and glycerol have permeability to water vapor of 4.58 g mm kPa⁻¹ d⁻¹ m⁻² which transforms it into a material with great potential for application in the food industry [43].

Torrenegra et al., [18] evaluated an edible biocoating based on modified yam starch on the melon by determining sensory and physicochemical properties. The results showed that all the variables are significantly influenced by the biomolecule used "modified starch", observing a favorable performance in edible biorecovering.

In this same context, Saavedra and Algecira [44] evaluated the edible cassava starch films and isolated soy protein for conservation of strawberries. Edible films were made by the casting method. In the formulations containing protein, a greater elasticity was observed, thermal events at lower temperature compared with those of the mixtures, a more homogeneous surface, allowing to improve some properties of the fruit during its storage as the loss of weight.

Meneses et al., [45] synthesized and characterized a biodegradable polymer from cassava starch, highlighting that it is feasible to produce a product that does not require a very high tensile strength and should not be exposed to water or high humidity conditions; therefore, the potential manufacture of plastic coatings (such as capsules) or the manufacture of plastic bags or plastic packaging are the uses that could be given to the polymer to try to replace a product whose generation of waste is massive, in order to try to solve the non-biodegradability of conventional plastics.

The properties conferred to starches allow their use in the food field and one of the most promising applications is in the improvement of the mechanisms of biocoating of food matrices.

The scientific and technological breakthrough that has led to the incursion of biopolymers in the area of food technology is evident.

Biorecoverings made from biopolymers have numerous advantages, including being biodegradable, recyclable, can transport additives, have good barrier and mechanical properties; They improve the appearance of food and protect its properties during storage and handling. They maintain or improve sensory characteristics and texture in foods [3].

This review is a valuable contribution to collect current information and show a global view of the new trends in the design and development of biorecoverings made from starches, as well as the characteristics of this material used for this purpose. However, its validity could be short, to the extent that every day there are constant advances in science and engineering of materials that are surprising.

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References

- [1]. Serna-Cock L, Rodriguez-de Stouvenel A. Producción biotecnológica de ácido láctico: Estado del arte. *Cienc. Tecnol. Aliment.* 2005; 5(1): 54-65.
- [2]. García CA, Arrázola GS, Durango AM. Producción de ácido láctico por vía biotecnológica. *Temas Agrarios.* 2010; 15(2): 9 – 26.
- [3]. Durango AM, Soares NF, Arteaga MR. Filmes y revestimientos comestibles como empaques activos biodegradables en la conservación de alimentos. *Biotecnología en el Sector Agropecuario y Agroindustrial.* 2011; 9(1):122 – 128.
- [4]. Arévalo-Niño K, Alemán-Huerta ME, Rojas-Verde MG, Morales-Rodríguez LA. Películas biodegradables a partir de residuos de cítricos:

propuesta de empaques activos. *Rev Latinoam Biotecnol Amb Algal.* 2010; 1(2):124-134.

[5]. Janjarasskul T, Krochta JM. Edible Packaging Materials. Annual review food science technology. 2010; 1: 415-448.

[6]. Campos-Rosillo S, Vargas-Colás M. Recubrimientos biodegradables de biopolímeros para su aplicación en frutas. [Tesis de pregrado]. Valencia; Universitat Politècnica de València; 2014. Disponible en:

https://riunet.upv.es/bitstream/handle/10251/46173/TFC%20Sergio%20Campos_SEPTIEMBRE%202014.pdf?sequence=1

[7]. Avendaño-Cetina GL, Guevara-Velandia O. Diseño y evaluación de las propiedades mecánicas y de barrera de un biopolímero obtenido a partir de almidón de papa para ser empleado en empaques para alimentos. [Tesis de pregrado]. Duitama; Universidad Nacional Abierta y a Distancia -UNAD-; 2009.

[8]. Hernández-Medina M, Torruco-Uco JG, Chel-Guerrero L, Betancur-Ancona D. Caracterización físicoquímica de almidones de tubérculos cultivados en Yucatán, México. *Cienc. Tecnol. Aliment., Campinas.* 2008;28(3):718-26.

[9]. Bello-Pérez LA, Contreras-Ramos SM, Romero-Manilla R, Solorza-Feria J, Jiménez-Aparicio A. Propiedades químicas y funcionales del almidón modificado de plátano *Musa paradisiaca* L. (var. Macho). *Agrociencia.* 2002;36(2):170.

[10]. Peñaranda O, Perilla J, Algecira N. Revisión de la modificación química del almidón con ácidos orgánicos. *Revista Ingeniería e Investigación.* 2008;28(3):47-8.

[11]. Velasco RJ, Luna WA, Mera JA, Villada HS. Producción de dextrinas a partir de almidón nativo de yuca por ruta seca en una agroindustria rural. *Información Tecnológica.* 2008;19(2):15-22.

[12]. Stasiak M, Molenda M, Horabik J, Mueller P, Opaliński I. Mechanical properties of potato starch modified by moisture content and addition of lubricant. *Int. Agrophys.* 2014;28:501-9.

- [13]. Zavareze ER, Pinto VZ, Klein B, Halal SLM, Elias MC, Prentice-Hernandez C, Dias ARG. Development of oxidized and heat-moisture treated potato starch film. *Food Chem.* 2012;132:344-50.
- [14]. Rodríguez D, Espitia M, Caicedo YE, Córdoba YE, Baena Y, Mora CE. Caracterización de algunas propiedades fisicoquímicas y farmacotécnicas del almidón de arracacha (*Arracacia xanthorrhiza*). *Rev. Col. Cienc. Quím. Farm.* 2005;34(2):140-6.
- [15]. Zambrano F, Camargo C. Otimização das condições de hidrólise ácida de amido de mandioca para obtenção de substituto de gordura, *Brazilian Journal of Food Technology.* 2001;4:147-54.
- [16]. Torrenegra ME, León-Méndez G, Matiz-Melo GE, Sastoque Gómez JD. Lipofilización del almidón de *Dioscorea rotundata* P. y su posible uso como agente emulsificante. *Rev Cubana Farma.* 2015;49(4):605-617.
- [17]. Matiz-Melo GE, Fuentes-López K, León-Méndez G. Microencapsulación de aceite esencial de tomillo (*Thymus vulgaris*) en matrices poliméricas de almidón de ñame (*Dioscorea rotundata*) modificado. *Rev. colomb. cienc. quim. farm.* 2015; 44(2): 189-207.
- [18]. Torrenegra M, León G, Matiz G, Pájaro N, Sastoque JD. Evaluación de un biorecubrimiento comestible a base de almidón de ñame modificado. *Revista Chilena de Nutrición.* 2016; 43(3): 284-289.
- [19]. Aristizábal J, Sánchez T, Mejía-Lorío D. "Guía técnica para producción y análisis de almidón de yuca", *Boletín de Servicios Agrícolas* 163, FAO Editor, Roma, 2007.
- [20]. Sweedmana MC, Tizzotti MJ, Schäferb C, Gilberta RG. Structure and physicochemical properties of octenyl succinic anhydride modified starches: A review. *Carbohydrate Polymers.* 2013;92:905-20.
- [21]. Chao L, Xiong F, Faxing L, Qiang H. Effects of maltose on stability and rheological properties of orange oil-in-water emulsion formed by OSA modified starch. *Food Hydrocolloids.* 2013;32:79-86.
- [22]. Jeon Y, Lowell A, Gross R. Studies of starch esterification: Reactions with alkenylsuccinates in aqueous slurry systems, *Starch - Stärke.* 1999;51(2-3):90-3.
- [23]. Chi H, Xu K, Xue D, Song C, Zhang W, Wang P. Synthesis of dodecanyl succinic anhydride (DDSA) corn starch, *Food Research International.* 2007;40:232-8.
- [24]. Rincón M, Rached L, Aragoza L, Padilla F. Efecto de la acetilación y oxidación sobre algunas propiedades del almidón de semillas de Fruto de pan (*Artocarpus saltilis*). *Archivos Latinoamericanos de Nutrición.* 2007;57(3):287-294.
- [25]. Betancur AD, Chel GL, Cañizares HE. Acetylation and characterization of *Canavalia ensiformis* starch. *Journal of Agricultural and Food Chemistry.* 1997;45(2):378-82.
- [26]. Wang S, Jinglin Y, Wenyuan G. Morphological and granular changes in native yam (*Dioscorea bulbifera*) starch during acid hydrolysis. *Carbohydrate Polymers.* 2007;69:286-292.
- [27]. Bernal C, Leal A, Garzón J. Obtención, a escala de laboratorio, de Octenilsuccinato Aluminico de almidón de Quinoa, con miras a su utilización en un producto cosmético. *ReCiTeIA.* 2011;11(1):47-56.
- [28]. Tetchi F, Rolland A, Amani G, Colonna, P. Molecular and physicochemical characterization of starches from yam, cocoyam, cassava, sweet potato and ginger produced in the Ivory Coast. *Journal of the Science of Food and Agriculture.* 2007;87:1906-1916.
- [29]. Yu B, Fuji S. Physicochemical property of Huaishan (*Rhizoma Dioscorea*) and Matai (*Eleocharis dulcis*) starches. *Starch/Stärke.* 1999;51:5-10.
- [30]. Peshin A. Characterization of starch isolated from potato tubers (*Solanum tuberosum* L.). *Journal of Food Science and Technology.* 2001;38(5):447-449.
- [31]. Rivero-Duarte IE, Bálamo V, Müller A. Desarrollo de mezclas de polietileno lineal de baja densidad y almidón de yuca. [Tesis de pregrado].

Sarteneja; Universidad Simón Bolívar; 2007.
Disponibile en:

<http://159.90.80.55/tesis/000145909.pdf>

[32]. Alvis A, Vélez CA, Villada HS, Rada-Mendoza M. Análisis físico-químico y morfológico de almidones de ñame, yuca y papa y determinación de la viscosidad de las pastas. *Información Tecnológica*. 2008; 19(1), 19-28.

[33]. Angellier H, Molina-Boisseau S, Belagcem MN, Dufresne A. Surface chemical modification of waxy maize starch nanocrystals. *Langmuir*. 2005; 21: 2425-2433.

[34]. Bao JS, Xing J, Phillips DL, Corke H. Physical properties of octenyl succinic anhydride modified Rice, wheat, and potato starches. *Journal of Agricultural and Food Chemistry*. 2003; 51: 2283-2287.

[35]. Betancur-Ancona D, Garcia-Cervera E, Canizares-Hernandez E, Chel-Guerrero L. Chemical modification of Jack Bean starch by succinylation. *Starch/Stärke*. 2002; 54: 540-546.

[36]. Sívoli L, Pérez E, Rodríguez P. Análisis estructural del almidón nativo de yuca (*Manihot esculenta* C.) empleando técnicas morfométricas, químicas, térmicas y reológicas. *Rev. Fac. Agron. (LUZ)*. 2012, 29: 293-313.

[37]. Velasco RJ, Luna WA, Mera JA, Villada HS. Producción de dextrinas a partir de almidón nativo de yuca por ruta seca en una agroindustria rural. *Información Tecnológica*. 2008; 19(2), 15-22.

[38]. Paes SS, Yakimets I, Mitchell JR. Influence of gelatinization process on functional properties of cassava starch films. *Food Hydrocolloids*. 2008; 22: 788-797.

[39]. Pagella C, Spigno G, De-Faveri DM. Characterization of starch based edible coatings. *Trans IChemE*. 2002; 80, Part C.

[40]. Chiumarelli M, Hubinger MD. Evaluation of edible films and coatings formulated with cassava starch, glycerol, carnauba wax and stearic acid. *Food Hydrocolloids*, 2014; 38: 20-27.

[41]. García LC, Pereira LM, De Luca Sarantópoulos CIG, Hubinger MD. Effect of antimicrobial starch edible coating on shelf-life of fresh strawberries. *Packaging Technology and Science*. 2012; 25 (7): 413-425.

[42]. Mali, S, Grossmann MVE, Garcia MA, Martino MN, Zaritzky NE. Microstructural characterization of yam starch films. *Carbohydrate Polymers*. 2002; 50: 379-386.

[43]. Durango A, Soares NE, Andrade N. Extração e caracterização do amido de inhame e desenvolvimento de filmes comestíveis antimicrobianos. *Temas Agrarios*. 14(2), 2009, 1-18.

[44]. Saavedra N, Algecira NA. Evaluación de películas comestibles de almidón de yuca y proteína aislada de soya en la conservación de fresas. *NOVA - Publicación Científica en ciencias biomédicas*. 2010; 8(14): 121 - 240.

[45]. Meneses J, Corrales CM, Valencia M. Síntesis y caracterización de un polímero biodegradable a partir del almidón de yuca. *Revista EIA*. 2007; 8: 57-67.

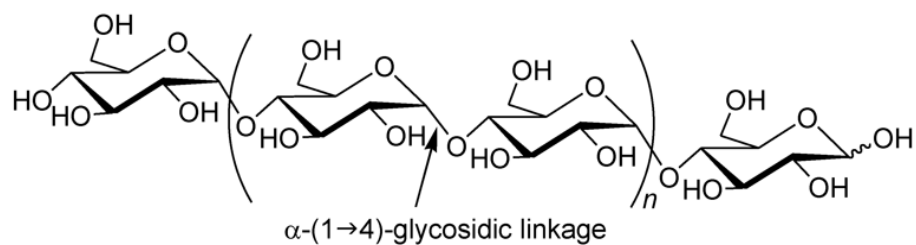


Figure 1. Chemical structure of the Amylose [19].

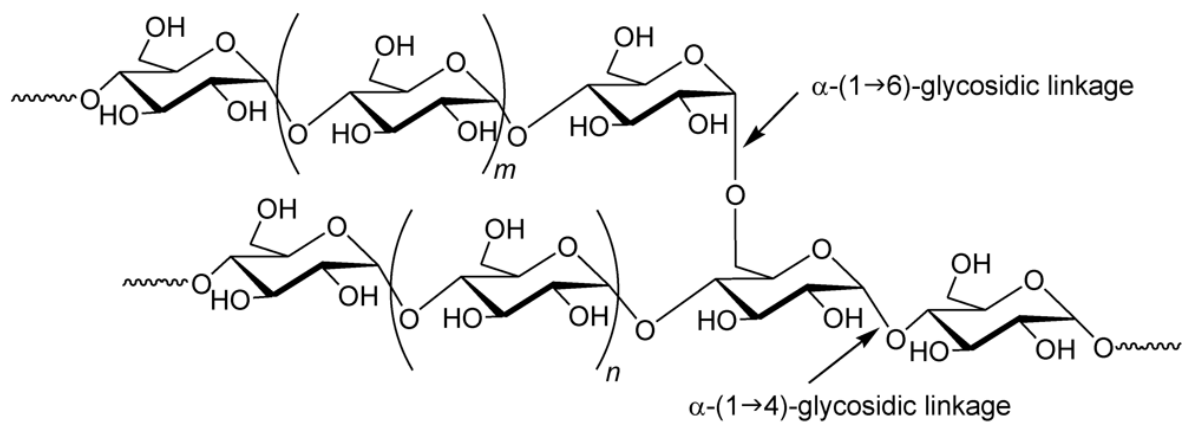


Figure 2. Amylopectin Chemical structure [19].

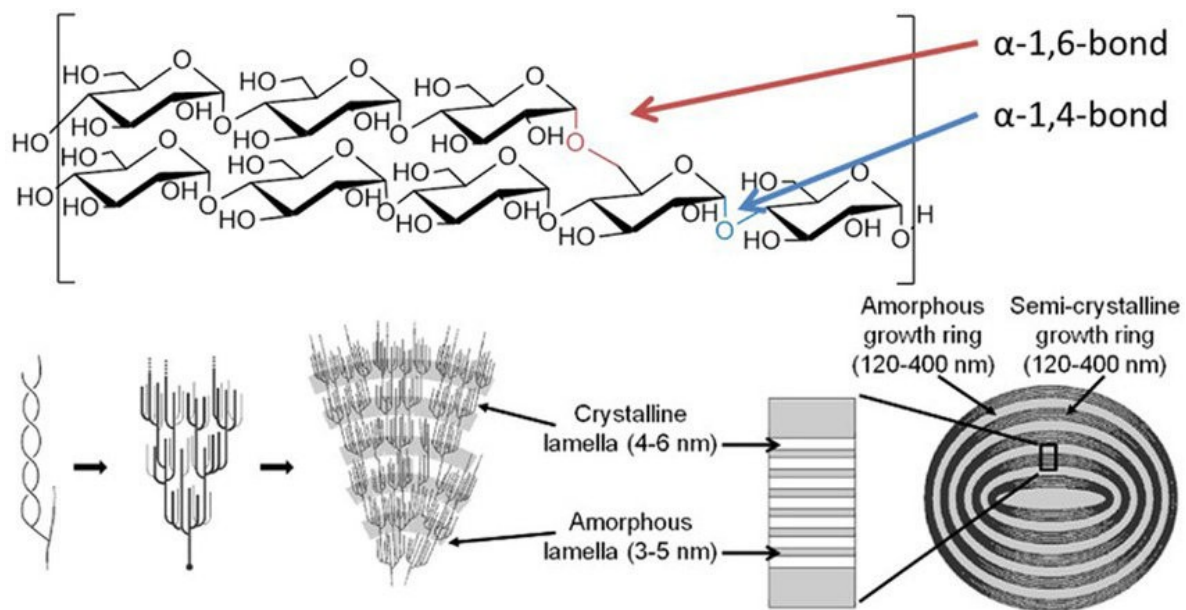


Figure 3. Crystalline and amorphous regions of the starch granules [31].