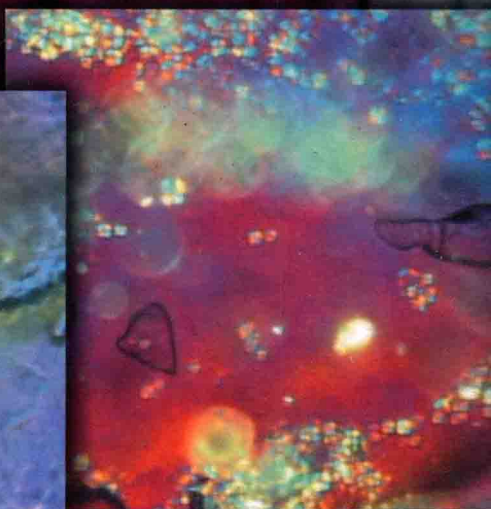


STARCHES

*Characterization, Properties,
and Applications*



Edited by
Andréa C. Bertolini

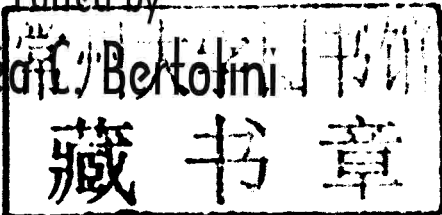


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Preface

Recent advances have been made in studies of the characterization, uses, and applications of starches. In past years, several modified starches and their derivatives have been used as new food ingredients. However, innovations have proposed the use of starch and new starch-based materials in products others than those manufactured by the food, pharmaceutical, and paper industries. As a consequence, changes in world starch production and diversification in sources of starch have been observed. Also, there has been a considerable impact on research about starch and the techniques proposed for starch characterization, both at the granular and macromolecular levels.

The aim of this book is to contribute a modern overview of trends and advances in the production and applications of starches, with emphasis on some recent techniques used in starch characterization as well as some aspects of production, properties, and biodegradation of starch-based products. This book discusses starch characterization, modified starches, starch-based plastics and nanocomposites, and biodegradation of starch blends. It is a comprehensive reference book for researchers, teachers, and other professionals who are interested in recent advances in starch and starch-based products. The book also may be suitable as a reference or textbook for graduate courses on starches and biopolymers.

An outstanding team of collaborators with complementary expertise from several research areas contributed to this book. This has resulted in an updated overview with an innovative and multidisciplinary approach to trends in production, characterization, properties, and applications of starch. There are ten chapters covering trends in starch production and applications, advances in starch characterization utilizing several techniques, the main new starch-based products, and starch biodegradability. A general discussion is provided about trends in starch production and the application of starch in the food, textile, pharmaceutical, chemical, agricultural, and plastic industries as substitutes for synthetic polymers (Chapter 1). This book also covers recent advances in starch characterization using several techniques such as atomic force microscopy (Chapter 2), high-performance size-exclusion chromatography and sedimentation

field flow fractionation (Chapter 3), nuclear magnetic resonance (Chapter 4), and starch thermal transitions (Chapter 5), providing an overview of starch characterization at the granular, macromolecular, and rheological levels. The main industrial concerns about starch applications, such as amylase production employed in starch hydrolysis (Chapter 7) and main modified starches (Chapter 8), are also discussed in this book. Properties and applications of new starch-based products, including starch-based plastics (Chapter 6) and starch-based nanocomposites (Chapter 9), are discussed with emphasis on starch properties, as well as the biodegradability of starch-based blends (Chapter 10).

I would like to acknowledge all of the collaborators for their important contributions and the expertise devoted to this book. Finally, I would also like to thank everyone who contributed, directly or indirectly, to this work.

Andréa C. Bertolini

About the Editor

Andréa Curiacos Bertolini is involved in scientific research on starch and biopolymers. She has a PhD in food science from the Université de Nantes in France, where she worked with a concentration on starch chemistry at the Institute Nationale de Recherche Agronomique (INRA) in partnership with the Centre de Coopération Internationale en Recherche Agronomique pour le Développement (CIRAD). As an invited researcher, she worked at the Fonterra Research Centre in New Zealand and at the University of Idaho in the United States on modified starches and starch rheology.

At present she is a food scientist at the Empresa Brasileira de Pesquisa Agropecuária (EMBRAPA–Brazilian Agricultural Research Corporation, Brazil). Her interests include biopolymers with an emphasis on starch characterization, modified starches, and starch as an ingredient in food and nonfood products.

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Trends in starch applications

Andréa C. Bertolini

EMBRAPA Agroindústria de Alimentos

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1.1 Introduction: The starch granule

1.1.1 Granular structure

Starch is organized in discrete particles, granules whose size, shape, morphology, composition, and supramolecular structure depend on the botanical source. The diameters of the granules generally range from less than 1 μm to more than 100 μm , and shapes can be regular (e.g., spherical, ovoid, or angular) or quite irregular. Starch granules are partially crystalline particles composed mainly of two homopolymers of glucopyranose with different structures: amylose, which is composed of units of D-glucose linked through α -D-(1-4) linkages and amylopectin,

the branching polymer of starch, composed of α -D-(1-4)-linked glucose segments containing glucose units in α -D (1-6) branches. Amylose is an essentially linear polymer, although evidence has suggested some branches in its structure. Consequently, 4–9% of the population called “intermediate material or amylose-like” has been considered part of normal and high amylose starches (Tang, Mitsunaga, and Kawamura, 2006). Amylose can also present as a hydrophobic helix, allowing the forming of a complex with free fatty acids, fatty acid components of glycerides, some alcohols, and iodine (Thomas and Atwell, 2005). Amylopectin is larger than amylose in most normal starches and their chains are classified as small chains, with an average degree of polymerization (DP) of about 15, and large chains, in which the DP is larger than 45. This unique configuration ordered in the packing arrangement contributes to the crystalline nature of the starch granule. This crystallinity reflects the organization of amylopectin molecules within the starch granules, whereas amylose makes up most of the amorphous materials that are randomly distributed among the amylopectin clusters (Blanshard, 1987). Under polarized light, the starch granule shows a characteristic Maltese cross (Figure 1.1), reflecting its birefringent structure, which was suggested as a correlation between the molecular and principal optic axes, underscoring that packing of the amylose and amylopectin is radial (Banks et al., 1972). This observation can be corroborated by results obtained by x-ray diffraction (Waigh et al., 1997).

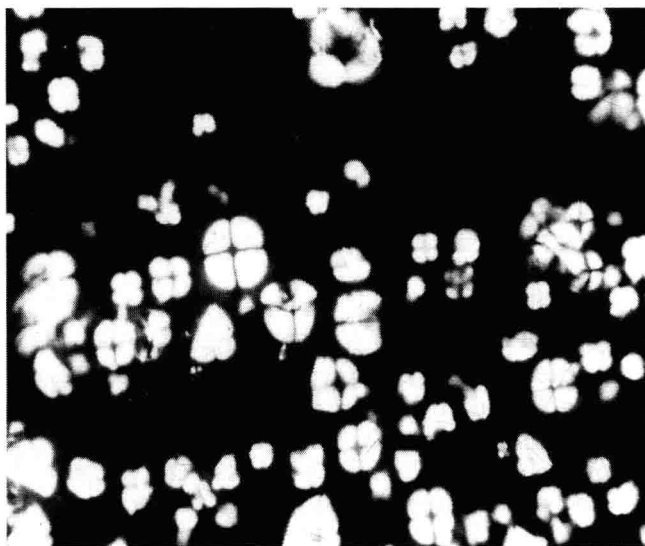


Figure 1.1 Maltese cross in starch granules observed under polarized light.

Consequently, the architecture or structure of a starch granule is influenced in part by the fine structures and ratios of amylose and amylopectin molecules. Finally, the granule architecture in turn determines the accessibility of the starch structure to water and chemical reagents, affecting molecular reaction patterns and properties of modified starches. The chemistry and technology of starch have been reviewed in detail several times (Whistler, BeMiller, and Paschall, 1984; Zobel, 1988; Eliasson, 2004; BeMiller, 2007). Some aspects of granule starch observations are considered in Chapter 2 and details of starch macromolecular structure are discussed in Chapters 3 and 4.

1.1.2 *Starch gelatinization*

Starch gelatinization involves granule melting in an aqueous medium under heating. In water, granule swelling increases with temperature and it leads to a transfer of water in the suspension to water associated with starch components: amylose and amylopectin. When starch temperature reaches 60–70°C, insoluble granules are disrupted by the energy supplied, resulting in a loss of molecular organization and, consequently, loss of its crystallinity. This process leads to increasing viscosity and starch solubilization, which is a result of irreversible changes such as the disruption of granular and semicrystalline structure, also seen as a loss of birefringence (Douzals et al., 1996). After heating followed by gelatinization, during the cooling phase, starch undergoes retrogradation in which the starch chains tend to reassociate in an ordered structure. It is followed by another rise in viscosity, usually referred to as setback. The pasting profile of previously gelatinized starch does not show a viscosity increase when exposed to changes in temperature, evidence that this starch sample was already gelatinized (Rosa, Guedes, and Pedroso, 2004).

Differences in swelling among native starches have been attributed to interplay of factors such as granule size, crystallinity, amylose–lipid complex content, and interaction among starch chains in the amorphous region. The physicochemical properties of amylose and amylopectin are quite diverse and they contribute in different ways to the pasting properties of starch. In Figure 1.2, the viscoamilographic graph shows the differences of pasting profiles of cassava and corn starches.

Understanding starch thermal transitions and starch rheological behavior is essential for studying starch structure, as well as for proposing new starch applications. The main aspects of rheological and thermal properties of starches are discussed in detail in Chapters 5 and 6.

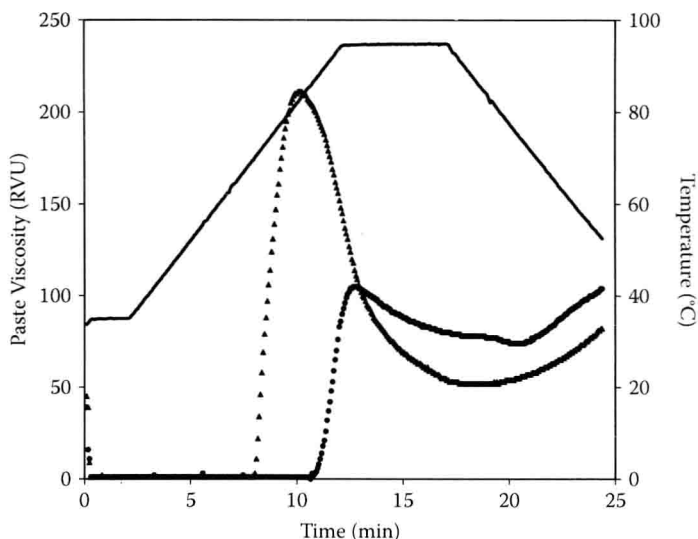


Figure 1.2 Pasting profiles of cassava (▲) and corn (●) starches, under temperature (–) changes.

1.2 Sources and producers of starch

Starches are the major storage polysaccharides in foods of plant origin. Worldwide dry starch production is actually estimated at more than 64 million tons and almost 75 million tons are expected by 2012 (Patil, 2009). Current annual production for primary starch sources is estimated to be 46.1 million tons of corn, 9.1 million tons of cassava, 5.15 million tons of wheat, and 2.45 million tons of potato (Röper and Elvers, 2008).

Starches from cereals come mainly from corn and wheat. European countries are responsible for around 60% and Asia produces 20% of the global production of wheat starch used in dextrin and modified starches. The United States is still the largest producer of corn starch in the world (LMC, 2008). In Western Europe, 46% of produced starch is from corn, 36% from wheat, and 19% from potato starches (Röper and Elvers, 2008), whereas North American production of starch is based almost entirely on corn (LMC, 2008). Actually, the Asian corn starch sector, particularly in China, is growing consistently at over 15% per year, competing with United States and European producers (LMC, 2008).

Because of their lower moisture content, cereals have longer storage times and their starch extraction is easier and faster than in roots and tubers. For example, in cassava, high water consumption is a critical factor in the starch extraction process. In this process, water is used during the grinding, decantation, and washing steps and these large quantities

of water are converted to wastewater, which must be treated before being released to the environment. Liquid waste has a high biochemical and chemical oxygen demand; its treatment comprises several steps and requires a long retention time. After extraction and separation, starch moisture content is from 35 to 40%, requiring a great deal of energy in the drying process (Sriroth et al., 2000).

Although cassava production is growing and starch from cassava competes with the corn processors (Patil, 2009), corn still remains the main starch source in the world, followed by cassava, potato, and wheat. More than 70% of starch produced in the world is from corn (Röper and Elvers, 2008) (Figure 1.3). However, starch from roots and tubers shows some particular rheological and physical properties, such as clear gel, high viscosity, and lower retrogradation, which are required in the formulation of specific products. Demand for cassava starch has grown in the past few years and it is actually the most widely traded form of native starch in the world, mainly in Thailand and East Asia. Asia contributes around 90% of cassava starch produced for use in industry (LMC, 2008), with Thailand being the major producing country, followed by China and Indonesia (FAO, 2008). In 2006, around 3.5×10^6 tons of cassava starch were produced in Thailand. Of this amount, 2.3×10^6 tons were exported, with 1.67×10^6 tons as native starch and 638×10^3 tons as modified starches (Röper and Elvers, 2008). In South America, which is responsible for the other 10% of cassava starch production, Brazil is the main producer (FAO, 2008).

Considering starches from roots and tubers, potato starch is the second largest starch source. In Europe, strong support of the grain sector has resulted in decreasing production of potato starch (LMC, 2008). However,

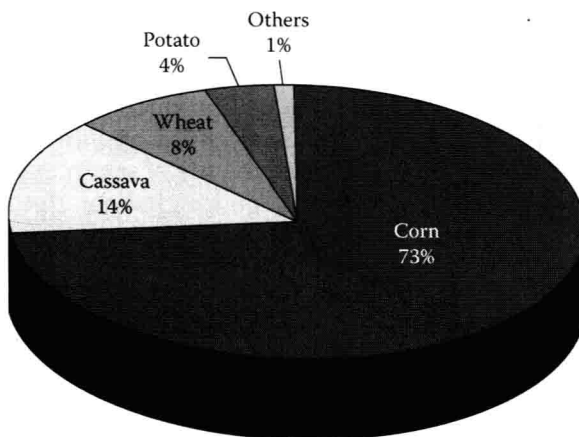


Figure 1.3 Starch production according to botanic sources. Source: Röper and Elvers (2008).

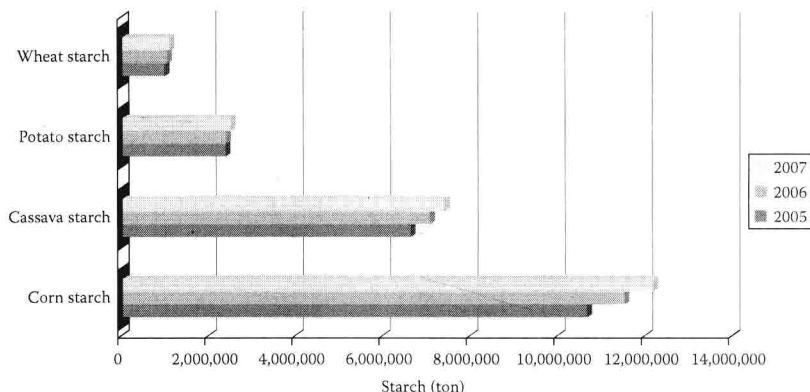


Figure 1.4 Amounts of starches used as food ingredients, dextrins, paper coatings, and adhesives between 2005 and 2007. Source: LCM (2008).

European countries are still responsible for 80% of potato starch production in the world (LMC, 2008), with the Netherlands, France, Belgium, Germany, and Switzerland as the main potato producers (FAO, 2008).

Figure 1.4 illustrates the amounts of starches from several sources used in syrup production or fermented products, used as food ingredients, dextrin, paper coatings, and adhesives for three consecutive years (LMC, 2008). A small amount of rice starch production originates from Europe and Asia (LMC, 2008), while arrowroot, amaranth, banana, mung bean, sweet potato, taro, and yam are considered as minor sources of starch produced in tropical countries.

1.3 Starch applications

Due to its low cost, availability, and ability to impart a broad range of functional properties to food and nonfood products (Jane, 1995; BeMiller, 2007), starch is utilized in several industrial applications (Whistler, BeMiller, and Paschall, 1984). Although the use of starch was always considered essential as a staple food and food ingredient, due to its attractive cost and performance, starch has been one of the most promising candidates for future materials (Rindlav-Westling et al., 1998). Starches are used mainly in the food and paper industries, with 57% of produced starch consumed in the food industries and 43% in the nonfood sector (LMC, 2008). Modified and native starches represent more than 85% of all hydrocolloids used in food systems (Wanous, 2004). In the food industry, the main trend in starch applications remains in syrup production and formulation of ready meals and various sauces.

From total worldwide starch production, excluding starch used to produce syrups and fermented products, more than 30 million tons of natural

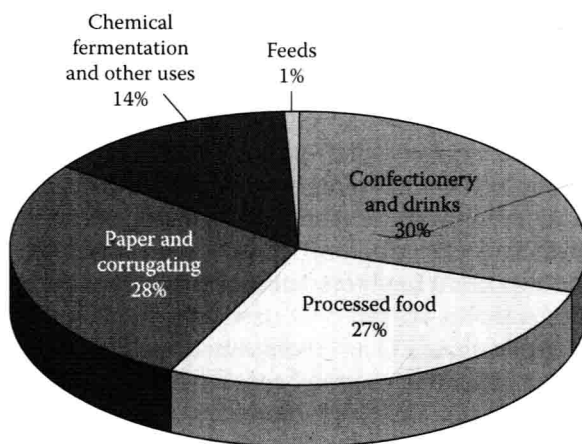


Figure 1.5 Use of starches and their derivatives by European industries. Source: Röper and Elvers (2008).

and modified starches are used in the production of dextrin, food ingredients, paper coatings, and adhesives (LMC, 2008). In Europe, 57% of produced starch is used in sweeteners and hydrolized, 23% as native starch, and 20% as modified starch. In European industries, the use of starch in sweet, drink, and fruit processing is equivalent to 30% of produced starch. Convenience foods, bakery, food ingredients, and dairy products account for 27%; the paper industry consumes 28%; and chemical, fermentation, and other industrial products utilize 14%. Starch usage in feeds is 1% (Röper and Elvers, 2008) (Figure 1.5). However, in the United States most production is not destined for native and modified starch products, but for sweeteners, particularly high fructose corn syrup (LMC, 2008). More than 73% of corn starch produced in North America is used in U.S. production of refinery products such as glyucose syrups, high fructose syrups, syrup solids, maltodextrins, and fructose (Röper and Elvers, 2008).

In addition to the demand for starch to produce syrups and dextrin, the demand for modified starches has grown in past years. Modified starches are produced mainly in North America and Europe. Europe is still one of the leading producers of modified starches and its paper and food industries tend to be at the forefront in their use of innovative new products (LMC, 2008). In Table 8.1 of Chapter 8, which provides details about modified starches, the main industrial applications of modified starches are summarized.

Asian markets, among others, demand large amounts of starches used in fermentation. The United States, following the world economy, has focused on starch to biofuel production. However, there is a trend for