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Starch properties during processing are major determinants of starch employment for food development. The gelatinization, pasting, and retrogradation of starch can be modified by the addition of galactomannans, which can improve rheological, textural, and nutritional properties. Rheology is an important key to obtain information about thermal transitions of starch and controlling characteristics required in food applications and to enhance understanding of the effect of starch-galactomannans systems and starch properties. This chapter provides information on starch transitions under heating and after cooling, including a definition of the process, molecular mechanisms, and rheological methods and its modification using starch-galactomannans mixtures and explains interactions throughout several investigations. The chapter also discusses how the rheological properties can affect the rate of the enzyme digestibility of starch on in vitro measurements and presents the starch-galactomannan systems as an alternative that can be used in structured foods as functional ingredients.

Keywords: starch, galactomannans, rheology, structured food

1. Introduction

Starch is one of the most extensively used and studied biopolymers because of its low cost, accessibility, and ability to provide a wide range of functional properties to food systems. Time-effective structural changes (gel formation processes, retrogradation, and syneresis)
hamper the control of rheological behavior. The retrogradation of starch refers to the process in which disaggregated amylose and amylopectin chains in a gelatinized starch paste reassociate to form more ordered structures [1]. The aggregation and recrystallization of starch molecules are important processes to manage, because these factors contribute to the control of textural properties of starch-based products.

Since native starch pastes and gels often exhibit low resistance to processing conditions, the native starches are replaced by chemically modified starches in food products or mixed with other hydrocolloids. It is well known in the food industry that nonstarch hydrocolloids have many functions, such as improving texture and moisture retention, extending the shelf life of the product, and controlling rheological properties [2, 3]. The control of the rheological properties of starch is significant in order to regulate product processes and to optimize its applicability in food products. Researchers have studied the effect of hydrocolloids on the rheological properties of starches and found that viscosity, the retrogradation of starch dispersions, and syneresis of starch gels are influenced by the addition of hydrocolloids [4–6].

Galactomannans are widely used in the industry due to their functional properties such as thickening, binding, and stabilizing agents. Galactomannans are considered functional ingredients that can change the rate of degradation of carbohydrates such as starch during digestion, thus regulating insulin levels, which is key in the prevention of obesity and diabetes [7].

This chapter was aimed at reviewing detailed recent research on the rheological and functional properties of starches and their mixtures with some galactomannans to develop structured foods. Additionally, the understanding of the rheological characteristics of these products is important to acquire knowledge of these molecular interactions.

Rheological measurements can be important to control the physicochemical properties with the addition of specific carbohydrates such as starch and galactomannans. This research can result in the innovative development of products. Rotational and oscillatory experiments and viscosity behavior are presented as examples.

2. Rheological and viscosity measurement methods

Several techniques are usually employed to characterize the thermal transition of starch and to distinguish between the solid and liquid-like behavior of food. These can be useful in recognizing interactions and structural failures that starch alone can present, supporting the addition of hydrocolloids such as galactomannans, and finding the quantity and type required to enhance the properties of starch.

Pasting can be measured using a Rapid Visco Analyzer (RVA) in order to obtain the pasting profile and the parameters related to this phenomenon. The heating and cooling cycles are programmed to an inherent thermal program in the equipment.

In order to understand the pasting properties of starch after heating, we need to remember that steady shear measurements provide information on the effect of shear in the flow
behavior. It can be measured with controlled shear stress or controlled shear rate using a rotational rheometer. Thus, the rotational test is a helpful tool to characterize flow behavior. The flow behavior using the shear stress as a function of shear rate fits into different models, such as power law and Herschel-Bulkey and Bingham models [8]. The data obtained is usually fitted to the well-known power law as follows:

\[ \tau = K (\gamma)^n \]  

(1)

where \( \tau \) is the shear stress (Pa), \( K \) is the consistency coefficient (Pa s\(^n\)), \( \gamma \) is the shear rate (s\(^{-1}\)), and \( n \) is the flow behavior index (dimensionless).

The measurement is programmed to a ramp shear rate in two cycles (up curve and down curve) in order to characterize the flow of the paste and determine the hysteresis loop. This area is interpreted as a dimension of energy delivered to the system to break down its thixotropic structure [9]. All liquids with microstructure, like starch, can show thixotropic behavior. Thixotropy reflects the finite time necessary to move from any state of microstructure to another. The hysteresis loop can, to a certain extent, serve as a parameter for quality control. The hysteresis loop can be measured and related to shear rate and time simultaneously [10].

Dynamic rheological measurements reviewed in this chapter are amplitude sweep, frequency sweep, and temperature sweep, and these could be combined to obtain information about structures and interactions. Parameters like \( G' \) (storage modulus) and \( G'' \) (loss modulus) are important in these measurements. Loss tangent (\( \tan \delta \)) is another dynamic rheological parameter that can be used to describe the viscoelastic behavior. This parameter is directly associated with the energy lost per cycle divided by the energy stored per cycle (\( G'/G'' \)). Values of \( \tan \delta \) < 1 and \( \tan \delta \) > 1 indicate whether the behavior is elastic or viscous, respectively.

Amplitude sweep tests are done to obtain the strain and to ensure that all dynamic measurements were performed in the linear viscoelastic region (LVE). Amplitude sweep tests can be used to define material structural strength and to distinguish weak and strong gels. A strong gel remains at the LVE region longer compared to a weak gel [11].

The frequency sweep test is done once the LVE region is defined and a strain is fixed, subjecting the samples to oscillatory measurements at a certain frequency range. The information obtained is required to classify the dispersion within this classification: (i) dilute solution, (ii) entanglement network system (concentrated system), (iii) weak gel, and (iv) strong gel [11].

The frequency dependence is generally described by the following power law relationship [12]:

\[ \tau = K' \omega^{n'} \]  

(2)

\[ \tau = K'' \omega^{n''} \]  

(3)

where \( K' \) and \( K'' \) are constants and \( n' \) and \( n'' \) may be referred to as frequency exponents, and \( \omega \) is the angular frequency.
The temperature sweep measurements are performed to determine the viscoelastic properties of samples over a certain temperature range (50–95°C), with a strain and frequency defined and a heat rate and the parameters calculated that need to be similar to the RVA parameters [13].

3. Starch

3.1. Starch structure

Starch granules are found in seeds, roots, and tubers and are from different origins such as maize, wheat, potatoes, and rice. Native starch granules present a multilevel structure with at least five levels, ranging in scale from nanometer to micrometer. The size of intact starch granules could be between 1 and 100 μm, while semicrystalline and amorphous growth rings decrease in thickness from 450 to 550 nm near to the core and 80 to 160 nm near to the periphery that are originated most likely during various phases of biosynthesis of starch granules in which the deposition of crystalline layers alternate with amorphous layers. The next level is the blockets that vary from 20 to 500 nm. At a smaller size scale are the left-handed superhelices with their structural elements, crystalline, and amorphous lamellae with a periodicity of 9 nm. The smallest starch structure organization unit is the glucosyl unit (0.3–0.5 nm).

Native starch granules present a concentric three-dimensional structure with a total crystallinity between 15 and 45%, depending on the different sources [1].

Starch is mostly composed of two kinds of polysaccharides: amylose and amylopectin. Amylose is a linear α-(1→4) linked glucan, with a molecular weight of 105–106 and a degree of polymerization (DP) as high as 600. Amylose chains can form spiral-shaped single or double helices with a rotation of α-(1→4) link and six glucoses per rotation, and the hydroxyl groups are located toward the exterior of the helices. Otherwise, amylopectin is an α-(1→4) linked glucan with 4.2–5.9% α-(1→6) branch linkages, with constituting branching points every 22–70 glucose units and a high molecular weight of 107–109. This highly multiple structure has an important effect on physical and biological properties. Small amounts of lipids, proteins, and phosphorous, depending on its source, are also found in starch granules [14, 15].

Amylopectin forms double helices, which contribute to the crystalline structure of the granules. Therefore, depending on the branch-chain length (BCL) of amylopectin, native starches granules can present different X-ray diffraction patterns: A-, B-, or C-type. The A-type polymorphic starch consisting of more short branch chains (A and B1 chains) has the double helices packed in a monoclinic unit cell, while B-type starch consists of more long branch-chains (B2, B3, and B4 chains) packed in a hexagonal unit cell. The C-type is a mixture of A- and B-type polymorphs. A-type granules are disk-like or lenticular in shape. On the other hand, B-type starch granules are roughly spherical or polygonal in shape [8].

Potato starch granules (oval and lenticular shapes) are the largest in comparison with wheat (spherical and lenticular shapes), corn (angular shapes), and rice (pentagonal and angular shapes) starches.
3.2. Thermal transitions of starch

Starches are usually processed before eating; therefore, thermal transitions of starch represent a key point in the control of starch functions. The mechanisms involved in these thermal transitions are the same, no matter what the final use is. The associated properties developed on treated starches are related to phase transition, glass transition, physical aging, and to the plasticizing effect of water. Rheological measurements can be used to identify the optimal use of the concentration of carbohydrates, temperature, and heating rate for developing products.

3.2.1. Gelatinization

Gelatinization is presented when native starch granules are heated in the presence of water and is related to an irreversible disruption of their molecular order, semicrystalline structure, and three-dimensional architecture and describes the phase transition from the highly ordered structure of native starch granules to disordered structure in water. During gelatinization several events take place, diffusion of water inside the starch granule with a limited swelling, loss of birefringence, loss of crystallinity of the granule, endothermic phase transitions, granular swelling after loss of birefringence, and molecular solubilization [16].

Small amplitude oscillatory shear (SAOS) measurement is a particularly useful method to study the gelation/gelatinization phenomenon in monitoring the kinetics of network development, as long as the measurements are within the viscoelastic limit, and the strain is restricted to less than 5% [17].

Gelatinization exhibits a two-stage behavior: the first is a limited swelling and a low level of solubilization, which increases while passing through the gelatinization temperature (60–75°C), and the second is soluble polymer molecule leach from the swollen granules that allows these rheological properties as the storage modulus ($G'$) and loss modulus ($G''$) of starch to increase during change of temperature from 65 to 95°C.

At the beginning of heating, $G''$ had a higher value than $G'$, reflecting the liquid-like behavior. The crossover temperature in rice starch was in the range of 64.2–77.15°C and represented the gel point [18]. The increase of $G'$ could be attributed to the degree of granular swelling. At the end of the temperature sweep $G'$ was higher than the $G''$, representing the gel-like behavior that a frequency sweep can support, expressing the formation of a three-dimensional gel network by the intergranular contact of swollen granules [19]. A further increase in temperature led to a $G'$ decrement, indicating that the gel structure was destroyed during prolonged heating as presented in a temperature sweep performed to rice starch [20].

Many factors affect the gelatinization of starch. A positive correlation between the gelatinization temperature of starch and the branch-chain length of amylopectin is that long branch-chains of amylopectin form thermally stable crystallites [21]; therefore, granule botanical source can be important for the development of rheological properties.

The large and cuboidal or irregular-shaped granules in potato starch exhibited higher storage and loss modulus and lower tan δ than small oval granules [22], and the presence of a
high phosphate monoester content and the absence of lipids and phospholipids in the potato starch could be also responsible for high $G'$ and $G''$. The corn starch phospholipids and the more rigid granules could be important in the lower value of $G'$ in corn starch compared with potato starch $G'$, and also, the amylose lipid complex formation during gelatinization of corn starch lowers the $G'$ and $G''$ [23]. Amylose content enhanced the development of $G'$ and $G''$ in rice starch [24]. Also, the breakdown, that is, the difference between peak $G'$ (maximum $G'$) at $T_G'$ (onset temperature of $G'$ increasing) and minimum $G'$ was influenced by the granule rigidity and lipid content, and potato starch has a higher breakdown than corn, rice, and wheat starches, which are rich in lipids [23].

3.2.2. Pasting

The second step occurs above the gelatinization temperature. The granules lose their crystalline structure, absorb water, swell, and disrupt. Water controls the formation of starch pastes or gels by forming hydrogen bonds with available hydroxyl groups of starches.

The hot paste created have swollen granules, granule fragments, and a soluble portion (30–60%) [16]. These pasting and thickening properties of pastes are related to involve in applications. Starch paste and gel have rheological properties that depend on different factors, such as starch concentration, pasting conditions (temperature, shear rate, and heating rate), and storage. The viscosity profile of tapioca starch (6%) can be seen in Figure 1.

The pasting properties of starch are measured using an amylograph, such as Brabender amylograph and RVA, or using a dynamic rheometer in a flow temperature ramp mode. The dynamic rheology studied starch gelatinization and pasting from a different view from RVA and also requires small deformation on samples. These parameters of RVA measurements are the following:

• Pasting temperature: The point at which the temperature rises above the gelatinization temperature; this leads to starch granules swelling and results in increased viscosity;

• Peak viscosity: The maximum viscosity of material developed after the heating and is indicative of the water-holding capacity of starch;

• Trough viscosity: The lowest viscosity after the peak viscosity;

• Breakdown: The difference between peak viscosity and trough viscosity; represents the disintegration of starch granules under heating due to a rupture of granules and release of soluble amylose;

• Final viscosity: The viscosity value at the test ending;

• Setback: The difference between final viscosity and trough viscosity; is related to re-association between starch molecules, especially amylose; results in a viscosity increment and gel formation, and is related to retrogradation.

Meanwhile, the parameters obtained in a sweep temperature test using dynamic rheology are almost the same [13]:
• Ts: temperature at which complex viscosity ($\eta^*$) start increasing
• Tmax: temperature corresponding to maximum $\eta^*$
• $\eta_{\text{max}}$: maximum $\eta^*$ on test
• $\eta^*_f$: the end value of $\eta^*$ at 50°C
• $\eta_{\text{min}}$: minimum $\eta^*$ on test
• Setback: the difference between $\eta^*_f$ and $\eta_{\text{min}}$.

At this stage of heating, the $G'$ and $G''$ values of starch have reached their maximum values. Thereafter, a plateau (80–85°C) exists, and finally, $G'$ goes under heating and shear time, and the solubilization and swelling have an impact on the drop after the maximum peak. Amylopectin and its branch-chain length are the main components of starch responsible for the swelling power and viscosity development of starch, while amylose and lipids restrict the swelling of starch. Other components of starch are lipids and phosphate-monoester derivatives. Amylose-lipid complex formed in starch under heating develops entanglements with amylopectin molecules and restricts swelling and leads to higher pasting temperature and a lower peak viscosity.

Figure 1. Pasting properties of tapioca starch (TS) (6% w/w).
3.2.2.1. Rheological measurements after pasting: Steady shear measurements

After pasting, the starch molecules tend to re-associate and form a viscous paste; the viscosity of this starch paste can be measured using a viscometer, such as a capillary flow meter, falling ball viscometer, or rotational rheometer.

Generally, the viscosity of starch pastes presents a non-Newtonian feature: the shear stress does not increase linearly with the increase in shear rate. The viscosity of starch paste is also shear thinning (flow behavior index, \( n < 1 \)) because they become thinner and decrease viscosity with increasing shear rate and time [8].

At low shear rates, the Brownian motion kept all molecules at random despite the initial effects of shear orientation, and this makes pseudoplastic materials to behave like a Newtonian liquid [25]. At increasing shear rate, the viscosity decrease. This could be explained as follows: during the shear process, the molecules are more or less oriented in shear direction and the shear gradient direction also influences this orientation. The increased motion allows the molecules to disentangle to a certain extent, which reduces their flow resistance. Also, low concentrations of polysaccharides may involve completely disentangled chains with a high degree of orientation. The viscosity is affected by measurement temperature and increases with starch concentration and decreases with amylose content.

For instance, tapioca starch exhibited a wide hysteresis loop. The tapioca starch alone presented more remarkable thixotropy (higher shear stress of upward curve than that of downward curve). The clockwise loop (thixotropy) can be interpreted as a structure breakdown by the shear field to alter a structure or a form a new structure [25]. Waxy corn starch showed a combined hysteresis loop, a clockwise loop, and a counterclockwise loop (antithixotropic behavior), and the prevalence of one behavior against the other is due to the heating conditions. When starch suspensions from waxy maize are pasted completely with more heating time and agitation, the antithixotropic property becomes more significant [9].

3.2.3. Retrogradation

Starch paste usually ascribes to the hot freshly cooked system, and a gel is formed after cooling. The characterization of rheological properties of starch gel has been determined by different methods: using a texture analyzer to determine the starch gel strength as a single point measurement; using a dynamic rheometer that provides the continuous assessment of starch gel at various temperatures and shear rates. The hot pastes begin to cool, after becoming more elastic and start to develop solid properties. Transitions from viscous paste to an elastic gel can be evaluated by storage modulus \( (G') \), and loss modulus \( (G'') \), the loss tangent being \( \tan \delta = G''/G' \) [20]. The starch gel can behave more like a solid (a small \( \tan \delta \), \( G' \) is much larger than \( G'' \)); this reflects a recoverable deformation or more like a liquid (a large \( \tan \delta \), \( G' \) is smaller than \( G'' \)); it means that the energy employed to deform the gel is dissipated. During storage, \( G' \) and \( G'' \) increase, indicating the strength, and the starch gel becomes firmer [8].

Starch paste developed interactions between amylose and amylopectin molecules, and a formation of networks occurred to hold water in the swollen granules, and a starch gel was formed. The retrogradation is a two-step process; the short-term retrogradation involving...
primarily amylose gelation developed after cooking and lasts up to 48 h. Native starch with a greater amylose content tends to arrange a stronger gel at a faster rate. Amylose molecules are unstable, and retrogradation results in an increase of turbidity and eventual precipitation. The retrogradation occurs because amylose molecules shrink, which is caused by a decrease in kinetic energy and Brownian motion of the polymer and water molecules. The shrinkage results in the formation of new intra- and inter-molecular hydrogen bonding, and the intensity of these hydrogen bonds leads to precipitation of amylose [26].

The second stage of retrogradation involves the recrystallization of amylopectin, and the process takes a long time due to the presence of short and highly branched side chains (A and B1), which was caused by their high kinetic energy [26].

4. Galactomannans

Galactomannans are heterogeneous polysaccharides found in the endosperm of the seed of a certain variety of legumes formed by a β-(1-4)-D-mannan backbone with a single D-galactose branch linked α-(1-6). They differ from each other by the mannose/galactose (M/G) ratio. The major sources of seed galactomannans are locust bean gum (Ceratonia siliqua), with M:G ratio of ~3.5:1, guar gum (Cyamopsis tetragonoloba), with M:G ratio of ~2:1, tara (Caesalpinia spinosa), with M:G ratio of ~3:1, and fenugreek (Trigonella foenum-graecum L.), which has an M:G ratio of ~1:1 [27]. Galactomannans are widely used in the industry due to their functional properties as thickening, binding, and stabilizing agents, and because they are not significantly affected by pH levels, added ions, and/or heating processes [28].

The galactomannans in their basic structure consist of mannose, which contains cis-OH groups in the polymer. Therefore, the ability to form hydrogen bonds between each mannose chain is expected to be long as neighboring groups such as galactose do not develop steric hindrance that prevents each chain of galactomannans from getting too close and prevents the cis-OH groups of the mannose from forming hydrogen bonds. Thus, the galactomannans with additional cross-links via hydrogen bonds are less capable of hydration (locust bean gum, M:G ratio of ~4:1). On the other hand, a greater substitution (guar gum, M:G ratio of ~2:1) leads to improved solubility [27].

Challenges in the food industry bring an interest in starch-galactomannan systems, and researchers have done extensive work in this area. Changes in different stages of starch under heating-cooling processes are reviewed through the addition of different galactomannans.

4.1. Starch-galactomannans system in gelatinization and pasting

It is well known that the addition of hydrocolloids in specific galactomannans affects the rheological properties and influences the increase of viscosity of pastes or solutions. A significant increase of viscosity through the addition of galactomannans has been demonstrated using guar gum, locust bean gum, and fenugreek gum. A soluble complex was evidenced as a result of the molecular associations between the amylose and the polysaccharide, as the main cause for viscosity increases during gelatinization, lowering the pasting temperature.
A decrease in the pasting temperature in the presence of guar gum could be attributed to phase separation, an increasing gum concentration in the continuous phase, and an increased volume fraction of the starch granules (amylopectin) in the disperse phase as a result of the mutual exclusion between leached starch and hydrocolloid molecules based on thermodynamic incompatibility between the two polysaccharides. An increase in the effective concentration of leached starch molecules, primarily amylose and the hydrocolloid, in the continuous phase upon heating enhanced interactions between the swollen starch granules, allowing pasting at a lower temperature. However, interactions between leached starch molecules and hydrocolloid in the continuous phase should not be minimized as a factor that influences the lower pasting temperature [30, 31].

Funami [29] added 0.5% guar gum and fenugreek gum with various molecular weights to starch solutions (15%) and modified the gelatinization behavior of starch. Analyses were done on the RVA. The viscosity profiles and pasting temperature shifted to higher temperatures with increasing $M_w$ of each galactomannan and lower temperatures with starch concentration (5%). When $M_w$ was standardized by the molecular weight of mannose, the effect of each galactomannan on the pasting temperature overlapped each other better than when $M_w$ was standardized by the molecular weight of the galactose, and with a lower starch concentration (5%), pasting temperatures shifted oppositely to lower pasting temperatures with increasing $M_w$ of the polysaccharide.

An increase in the final viscosity and setback values suggested that the retrogradation of starch should be promoted at a very early stage of storage by the addition of galactomannans.

### 4.2. Starch-galactomannans system after pasting: Flow behavior

The addition of galactomannans also influences the flow behavior of starch pastes. Different authors correlate the effect of galactomannans to changes in flow behavior. Rheograms of rice starch-galactomannan (guar gum and locust bean gum) mixtures show more pseudoplastic behavior of guar gum mixtures ($n$ value of 0.17–0.18) than control (0.24) and rice starch-locust bean gum ($n$ value, 0.21–0.26) [32]. Other studies in wheat starch-galactomannan mixtures show a similar behavior [33]. These phenomena could be explained as follows: the gum structures of guar gum consist of a mannan backbone with alternate galactose branches present- ing much more steric hindrance and little ability to establish hydrogen bonds between links [27]. This keeps the molecule in its extended form, which can readily interact with amylose molecules through noncovalent hydrogen bonding, resulting in an extended conformation that increases the degree of pseudoplasticity. On the other hand, the locust bean gum has a $M$:G ratio of ~4:1; this lower and irregular degree of substitution of the galactose branches in the mannan backbone explains the galactomannan’s structure behavior, which tends to coil with the formation of intramolecular hydrogen bonds and thus interacts less with the linear amylose molecules due to the amount of hydroxyl groups available to form intermolecular hydrogen bonding with amylose are lower [32].

#### 4.2.1. Hysteresis

Figure 2 shows that the addition of guar gum (0.5%) to tapioca starch (6%) reduces the hysteresis loop. The addition of guar gum on different starches such as tapioca, potato, oat, and
corn resulted in highly negative hysteresis loops, which meant that in the presence of guar gum, shearing ordered structures generate more readily [34]. Pastes of waxy corn starch with guar gum and waxy corn starch alone exhibited similar combined hysteresis loops, which are anti-clockwise loops (antithixotropic behavior) at low shear rates and clockwise loops (thixotropic behavior) at higher shear rates ($\gamma > 50$ s$^{-1}$). These systems contained a large amount of amylopectin (waxy corn starch) that was responsible for shear-thickening properties and shear-induced structure formation and alteration, that is, antithixotropic behavior [9].

4.3. Starch-galactomannans system in retrogradation

Short-term retrogradation is accelerated by the addition of galactomannans in terms of rheology. An increase in the effective concentration of amylose in the continuous phase was suggested as the main cause, leading to the acceleration of retrogradation during storage for shorter periods while preventing molecular ordering or crystallization of starch, particularly the amylopectin fraction of relatively short-chain segments leading to the retardation of retrogradation during storage for longer periods [29]. Figure 3 shows the variation of $G'$, $G''$,
Figure 3. Variation of $G'$, $G''$ with angular frequency for 6% w/w TS/guar mixed pastes without guar gum (TS) and 0.5% w/w guar gum (TS/GG) measurements at 25°C and 1.5% strain.

and complex viscosity ($\eta^*$) for tapioca starch pastes (6% w/w) alone and with addition of 0.5% (w/w) at 25°C and a strain amplitude of 1.5%. Figure 4 depicts the variation of $\tan \delta$ of samples. $G'$, $G''$, and complex viscosity increased with the addition of guar gum. The $\tan \delta$ values of the starch-guar gum mixture was lower than the tapioca starch alone.

A starch-galactomannans mixture can be classified as a weak gel; in most cases $G'$ and $G''$ increases with an increase in frequency with a small dependency. Weak gels have intermediate rheological properties between solutions and real gels, under small deformation; weak gels mechanically behave like real gels, but with increasing deformation, the three-dimensional network undergoes a progressive failure into smaller clusters [20], while the $\tan \delta$ values directly state the $G'/G''$ ratio.

The $\tan \delta$ values of rice starch mixed with guar gum and locust bean gum were higher than those on control and increased with an increase in the gum concentration. This means a higher growth of $G''$ than $G'$ especially on starch-locust bean gum mixtures; the addition of the gums is not able to provide effective contribution to the elastic properties of starch dispersions [35]. On the other hand, a reduction in $\tan \delta$ by the addition of guar gum on cationic tapioca starch is also presented, similar to what is shown in Figure 4, and it is related to a more solid-like
behavior, that is, a stronger three-dimensional network constructed by amylose and an amylose-gum system [3]. This supports the hypothesis that the change in dynamic rheological properties is due to the thermodynamically incompatible network structure in which interactions between polymers of the same type are favored energetically in comparison with interactions with different polymers [35] and also the interactions of branched or linear molecules of, that is, guar gum that can interact with amylose via noncovalent hydrogen bonding [36].

The addition of these gums during aging (10 h at 4°C) increases the $G'$ value with the gum concentration (0.2–0.8%). The gum structure also had a main role in $G'$ development, while starch-guar gum mixtures exhibit a plateau. The starch-locust bean gum dispersion shows a continuous increase of $G'$. The unsubstituted smooth regions of mannan backbone in LBG tend to associate with each other, forming a three-dimensional network. The thickening effect of the gums restricts the mobility of amylose, resulting in interactions between neighboring amylose molecules more easily accelerating the short-term retrogradation [35].

Figure 4. Variation of tan $\delta$ with angular frequency for 6% w/w TS/guar mixed pastes without guar gum (TS) and 0.5% w/w guar gum (TS/GG) measurements at 25°C and 1.5% strain.
The molecular associations between gums and amylopectin fractions avoid the formation of crystalline structures during storage, affecting long-term retrogradation. Corn starch-fenugreek gum mixtures present another factor to inhibit long-term retrogradation: gums can stabilize water molecules; therefore, they can act as a water binder, depriving amylose, or amylopectin of usable water for crystallization [5]. In rice starch-galactomannans systems (guar gum and locust bean gum), it was found that the addition of galactomannans led to an increase in the viscous properties of starch resulting in retardation of retrogradation of starch [35].

5. Applications of starch-galactomannans systems in food development

Extensive research has been carried out on the application of starch-galactomannans systems in food development, formulation of sauces, soups, and caramel sauces, improving the texture, food quality, and stabilization, and in structured foods as functional ingredients that can change the rate of degradation of carbohydrates such as starch during digestion, thus regulating insulin levels, which is key in the prevention of obesity and diabetes.

Food structure has a significant impact on the food digestive behavior [37]. For instance, it has been demonstrated that adding dietary fiber such as galactomannans (guar gum, locust bean gum, and fenugreek gum), pectins, β-glucans, cellulose, and fibers into foods can notably delay the absorption of glucose into the bloodstream [38–40].

Dietary fibers are ingredients of food defined as a heterogeneous mixture of substances predominantly found in plant cell walls that the body cannot digest or absorb. Indigestibility implies that dietary fiber pass without much break-down to the enzymatic action in the upper part of the gastrointestinal tract because enzymes capable of cleaving β-1-4 bonds present in dietary fibers are not found in the human small intestines. Furthermore, dietary fibers or nonstarch polysaccharides (NSP) is used as a “fuel” for the gut microbiota which produces the short-chain fatty acids in the large bowel that are easily absorbed and contribute to energy metabolism [41].

Dietary fiber is classified into two categories: water-soluble/well-fermented fibers and water-insoluble/less-fermented fibers [42]. Soluble viscous fibers contribute to the formation of the unstirred layer in the intestinal lumen, which serves as a physical barrier to fats, including cholesterol and bile acid reabsorption. Water-insoluble fractions such as cellulose and lignin, and water-soluble components comprise the major part of hemicellulose compounds, gums, β-glucans, mucilages, and pectins [43].

The two major benefits associated with soluble and viscous dietary fibers are modulation of glycemic postprandial response and plasma cholesterol lowering [44]. The physiological value of soluble dietary fiber is based on its ability to thicken into swollen hydrated networks and ensue viscosity that shows its potential to exert biological effects through the stomach and small intestines [45]. Studies have shown that the addition of soluble fibers such as pectin, guar gum, and locust bean gum in food reduces gastric emptying, delays absorption of...
actives, reduces the plasma glucose response, and slows down the return of hunger. Soluble fibers have been combined in diets for treating pathological conditions such as obesity, hypercholesterolemia, and diabetes [46].

5.1. Galactomannans as dietary fibers

Guar gum contains soluble dietary fibers. The guar seed possesses 52–48% total dietary fiber on seed dry weight, and the water-soluble endosperm contributes 26–32% of soluble dietary fiber [47]. Previous studies in vivo have found that, when comparing guar gum with pectin and carboxymethylcellulose (CMC) on postprandial glucose and insulin levels, guar showed to be the most effective biopolymer on reducing plasma glucose levels [48]. This behavior was explained by the fact that guar showed the greatest stability and viscosity under acidic conditions in vitro, i.e., under gastric conditions. Jaime-Fonseca [41] stated that comparing the effect of guar gum and pectin by measuring the flow behavior and the overall mass transfer coefficient (OMTC) shows a crossover at 100 s\(^{-1}\) and values of OMTC very similar.

Locust bean gum has been studied as a galactomannan that falls under the category of viscous soluble fibers, and it was proposed flattening postprandial glycemia more consistently than wheat bran and other insoluble fibers. The addition of locust bean gum has a major impact on gastric emptying by delaying the emptying rate [49].

Fenugreek gum has beneficial physiological effects, including the antidiabetic and hypcholesterolemic effects, attributable to the intrinsic dietary fiber constituent that has promising nutraceutical values [34]. Dietary fiber on seeds is around 45.5% (32% insoluble and 13.3% soluble), which changes the texture of food and has a beneficial influence on digestion [50]. The galactomannan-rich soluble fiber fraction of fenugreek seeds may be responsible for the antidiabetic activity and can slow the rate of postprandial glucose absorption. This may be a secondary mechanism for its hypoglycemic effect [51].

5.2. Addition of galactomannans on starch-based products

5.2.1. Starch-galactomannan aqueous system

The carbohydrate content of food is important due to the postprandial glycemic effect on carbohydrate consumption. The increase in postprandial glycemia with the ingestion of carbohydrates and starch has been shown to be controlled by the addition of galactomannans.

Starch needs to be converted from its native form to the gelatinized state in order to be hydrolyzed and consequently release glucose. Direct cooking by heating to 100°C in excess water is the principal process facilitating starch availability for water penetration and consequent α-amylase action for several minutes [52]. It has been stated that guar gum, an industrial galactomannan, competes with starch for water in food systems and prevents starch gelatinization, thus depriving starch from accessing water [53]. Another hypothesis related to the role of dietary fibers is in the reduction of hydrolysis; therefore, the digestion rate is the capability to form a barrier around starch granules, with the result that starch can resist enzymatic degradation [54, 55].
In order to evaluate the effect of the dietary fibers, the conditions of the gastrointestinal tract (GIT) that comprises the secretion of fluids, enzyme hydrolysis, pH, and the presence of salts are simulated to obtain an in vitro digestion model and measure the glucose diffusion. The addition of galactomannans to different starch sources to evaluate whether the viscosity remains after passing through these conditions is reviewed on this section.

For this reason, rheological rotational (flow behavior) and oscillatory (frequency sweep and time sweep) measurements can give valuable information. The rotational tests can be used to mimic the shear rate found during digestion (100 s$^{-1}$) [11, 56]. It has been reported that shear rates of 10–100 s$^{-1}$ are found during the various processes of digestion. Oscillatory tests, such as time sweep and frequency sweep, can be useful to explain the structural changes during and after digestion, respectively, and demonstrate the rate of degradation of starch/galactomannans entanglements and the solid or liquid-like behavior during these processes. Additionally, viscosity measurements using RVA could be relevant to characterize the behavior of gelatinization-pasting of samples.

Brennan et al. [57] investigated the effect of guar gum, locust bean gum, and Arabic gum on wheat starch and flour viscosity and their effects on in vitro starch hydrolysis. Both guar gum and locust bean gum increased the peak and final viscosity on the resulting pastes, whereas Arabic gum significantly reduced the viscosities of pastes. Guar gum and locust bean gum reduced the amount of starch degradation; on the contrary, Arabic gum increased the amount of starch hydrolysis. The researcher thus concluded that the extent of starch hydrolysis was dependent on viscosity changes.

The reduction of starch hydrolysis with different polysaccharides (Arabic, carrageenan, guar, pectin, and xanthan) added to wheat, normal maize starch, and waxy maize starch was found by Tester and Sommerville [53]. The reduction on hydrolysis was related to a reduction in water accessibility and restricting water availability/mobility (due hydration) during the gelatinization event. Otherwise, the starch sources used in the study vary and may be another factor causing differences on glycemic results.

Dartois et al. [7] investigated the effect of guar gum on the digestibility of waxy maize starch in vitro under simulated gastric and intestinal conditions. No starch hydrolysis was observed under simulated gastric conditions, whereas more than 90% hydrolysis was observed at the end of digestion-simulated intestinal conditions. The addition of guar gum led to a significant decrease in both the rate and the extent of final starch hydrolysis and showed that starch digestion is not only delayed but also reduced in the presence of gum. Rheological measurements demonstrate that the viscosity of digesta decreased during intestinal digestion, but the extent of decrease was lower in the presence of guar gum. Frequency sweep tests showed that after 5 min of digestion, $G'$ and $G''$ were higher than samples with 30 s and 1 min of digestion and starch guar gum without enzymatic treatment due to the inhibition to starch components from leaching out of the granules into the continuous phase of starch pastes during gelatinization. Time sweep test demonstrated that $G'$ and $G''$ increased as digestion progresses and water is liberated, allowing the gum present in the system to take up water.

Fabek et al. [56] evaluated the ability of resist loss viscosity of locust bean gum, guar gum, fenugreek gum, and xanthan gum in a two-stage in vitro digestion (gastric and small intestinal)
phases and also studied starch (waxy corn starch) and protein (sodium caseinate) addition to simulate a food model for glucose release measurements. Flow behavior measurements showed that dilutions representing watery secretions during digestion were the most important factors to reduce viscosity, and changes in pH have an additive effect to that reduction. All gums demonstrated an ability to depress the glucose response. Xanthan gum had the ability to withstand reductions in viscosity and lowering glucose diffusion, and guar gum was the second; although it has the lowest glucose diffusion ratio among the other gums, it was not significantly different. However, the effect on attenuating glucose diffusion was not as pronounced, suggesting that viscosity alone may not be the only contributing factor in the reduction of postprandial glucose levels.

5.2.2. Starch-galactomannan system in extrusion cooking

Extrusion is a high-temperature, short-time, continuous processing method in which temperature, moisture, pressure, and shearing interact to develop products with functional properties [58]. When starch is processed by extrusion, many phenomena take place, including gelatinization, thermal melting, crystallite loss, and molecular degradation of amylose and amylopectin, which also makes this biopolymer available to digestive enzymes [59]. Low values of digestibility of starch-extruded products have been attributed to the formation of amylose lipid complex, starch protein interaction, and limited water availability that prolongs the starch digestibility during enzymatic hydrolysis. The fact that guar gum competes against starch for available water in gelatinization allows starch hydrolysis to investigate the addition of galactomannans to starch and evaluate its behavior.

Adamu [60] reported that when extruded samples of starch added to guar gum are cooled, re-association of the chains of the polysaccharide and the gum appears. The dissolution of an extruded sample previously added with guar gum in water generates swelling, followed by an interlocking of the chains in the polysaccharide. This provokes an increase in the viscosity of the solution [61].

Brennan et al. [62] evaluated the effects of the addition of dietary fiber (wheat bran, guar gum, inulin, hi-maize, and swede) at different concentrations (5–15%) and found that peak and final viscosities among the different extruded products increased with the addition of guar gum. Guar gum decreased readily digestible starch, being more effective than wheat bran.

Control of extrusion parameters as barrel temperature or moisture content of processing plays a main role in the thermal transitions of starch and its digestibility. Guar gum addition to different flours (maize, potato, rice, and wheat) and processed by extrusion presented low viscosity and has been associated with the gelatinization and disruption of the starch granules during the high shear and high temperature of extrusion. It is also probable that a more extensive starch dextrinization during extrusion of samples containing guar gum results in lesser viscosity of extrudates. These changes on extrudates resulted in starch being more rapidly digestible [63].

It has been proven that extrusion conditions can affect the depolymerization of guar gum; however, guar gum impair increasing viscosity values on corn starch extrudate samples.
with high moisture contents and low extrusion temperature during processing. Guar gum decreased gelatinization and promoted fusion and depolymerization of starch due to shear forces and temperature during extrusion by competing for the water available on this process and did not affect starch hydrolysis [64].

The effect of adding galactomannans such as guar gum on starch hydrolysis after direct cooking or extrusion cooking is inconclusive, and the mechanisms for the reduction of starch hydrolysis and reduced postprandial glycemia are not fully understood, but increased viscosity might be one of the most important factors. So rheological measurements are proven as an important tool, not only to provide information about texture and quality control, but also for the application of ingredients to elaborate functional foods.

6. Conclusion

In this chapter, rheological techniques were exposed to highlight the transitions of starch in aqueous systems during heating and after processing. The behavior of different starches with galactomannans is presented to understand the rheology of transitions of starch as a measure to control and understand the interactions inside the starch granules and the starch-galactomannan systems that can be used in food products and employed to develop structured foods.

Structural changes that occurred during the heating of starches can be determined using rheological measurements: rotational tests as steady shear measurements to determine the hysteresis loop; oscillatory tests (frequency sweeps, temperature sweeps, and time sweeps) combined with RVA measurements, DSC thermographs, texture analysis, and X-ray diffraction.

Starch modification through the addition of galactomannans is presented based on its interaction with starch molecules. Galactomannans affect the phase separation by occupying the continuous phase and therefore increasing the volume of starch granules in the disperse phase. They compete with starch for the available water, leading to further alterations in the structure and changing the pasting temperature, the gelatinization, and improving viscosities. Pseudoplastic behavior of starch-galactomannan mixtures presents less clockwise loops (thixotropic) and, in some stages, anti-clockwise loops. The less solid-like structure of pastes with galactomannans is shown. The short-term retrogradation is accelerated, and long-term retrogradation is diminished by interfering with amylopectin chains.

The role of rheological properties can be significant to reduce the starch hydrolysis by adding galactomannans to starch food products due to the increased viscosity of the system, which may have an affect not only on the mass transfer (diffusion coefficient) of the molecules but also on enzymatic reactions.

Novel applications and new galactomannans employments will fulfill the starch-based products field. Furthermore, the research and interests of finding new ways to improve food structure is always a never-ending discovery.
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