

Review

Versatile Polysaccharides for Application to Semi-Solid and Fluid Foods: The Pectin Case

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Abstract: Pectin is a versatile polysaccharide produced mainly from natural food sources and agro-industrial wastes, adding value to these by-products. For food applications, it is necessary that pectin first interacts with water for technical purposes. As a food additive, pectin acts as a solution thickener and gelling agent for food formulation, even in concentrations of less than 1 (g/100 mL or g/100 g), and it is sufficient to influence food products' stability, rheology, texture, and sensory properties. Therefore, this review paper attempts to discuss the versatility of pectin use, focusing on food application. It starts by showing the chemical structure, the sources' potential, thickening, and gelling mechanisms and concludes by showing the main applications to the food sector and its rheological properties.

Keywords: pectin; chemical structure; chemical properties; physical properties; semi-solid foods; fluid foods



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1. Introduction

Food processing is an important scientific area that not only maintains the security of foods through storage time but also improves the sensorial and nutritional quality of processed foods [1,2]. In addition, scientific research and the food industry have greatly improved the development of more stable foods, aiming to increase shelf-life by adding food additives [3]. Thus, to currently develop new food additives, their structures, properties, and processes must be considered, as is the case of pectin. It is essential to investigate the molecular structure, chemical and physical properties, functionality, and applications [4,5].

Food can be categorized in different ways, such as solids, gels, homogeneous liquids, suspensions of solids in liquids, and emulsions [6]. In this review, we focus on fluid and semi-solid foods, which can exhibit a wide variety of rheological behavior ranging from Newtonian (water) to non-Newtonian behavior of aqueous dispersion. For example, when packaged, fluid foods retain the shape of the container [6]. Newtonian behavior is likely expected when fluid foods contain dissolved low molecular weight compounds, such as sugars, and a minimum amount of a polymer or insoluble solids. However, adding a small amount of polymer can increase the viscosity and change the flow characteristics from Newtonian to non-Newtonian. Also, many non-Newtonian foods can show viscoelastic behavior, which is characterized by both viscous and elastic properties [6,7].

The food components are part of a complex structure not simply homogeneously dispersed or in an accessible form [5,8]. Among these components, additives such as polysaccharides (e.g., pectins) can be added to food products during the processes with a technological purpose [8]. The main beneficial effect of pectins as food additives for

technical purposes is the ability to interact with water, acting as solution thickeners and gelling agents, foam stabilizers, emulsions, and dispersions [9–12]. Pectins are added to food formulation in concentrations of less than 1 (g/100 mL or g/100 g) to be sufficient to influence food products' stability, rheology, texture, and sensory properties. For example, in acidified milk drinks, pectin addition provides a great stabilizing behavior, inhibiting the aggregation of proteins because of the formation of larger electrostatic repulsive and steric repulsive forces [9,10,13,14].

Pectin is commercialized in a dry powder form, and its use as a stabilizer can be applied to food products, such as fruit drinks and fruit and tomato pastes. Also, pectin's ability to form gels under specific parameters allows its use as a gelling agent in jams, jellies, and marmalades [15]. For food applications, pectin—marketed in a powder form—needs to be completely dissolved in water, and its interaction is essential for food applications [16]. The dissolution of pectin in water can be elucidated as a two-stage phenomenon, as documented in prior studies [16,17], as depicted in Figure 1. Initially, water molecules adhere to the surface and infiltrate the pectin particles, constituting the solvent penetration stage [17]. This process leads to swelling and forming a gel-like layer on the particle surface. Notably, this stage can give rise to the occurrence of the fish-eye effect, a phenomenon characterized by the creation of adhesive and partially undissolved powder aggregates [18,19]. Subsequently, in the second phase, termed chain disentanglement [19], the pectin polymers transit from the core of the powder to the liquid phase, facilitating the overall dissolution process.

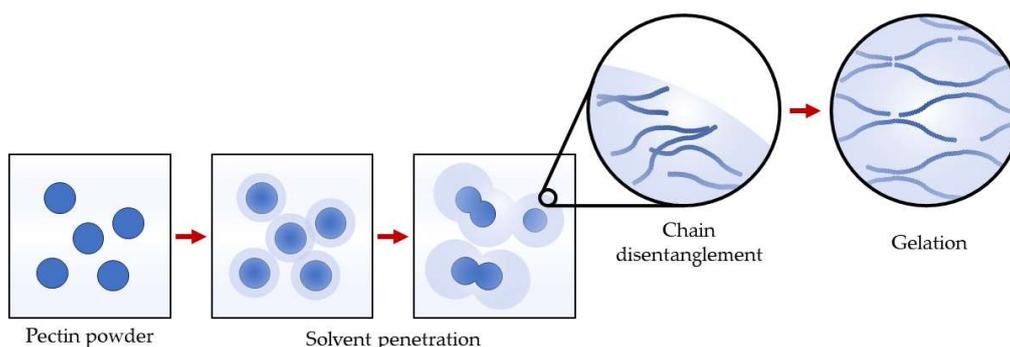


Figure 1. Pectin: from powder form to gelation—mechanism of pectin dissolution in water.

The dissolution process of pectin is influenced by intrinsic and extrinsic factors. Intrinsic factors comprise the number and distribution of hydrophilic groups and neutral sugars. Also, particle properties are part of the intrinsic factors essential for pectin dissolution. The particle properties include size, form, density, porosity, and crystallinity combined with their surface characteristics, such as chemical surface composition, which are mainly soluble component contents in the surface [20,21]. Particularly, the properties of the particles influence the wettability of the powder, which is the time required to complete the wetting and immersion of a powder on a liquid surface [22]. For example, in the first step of pectin dissolution, the formation of lumps can be avoided by modifying the particle properties using the agglomeration process for the pectin, and an instant pectin powder can be obtained with better wettability [23]. The extrinsic factors are mainly temperature and mechanical energy input. The water uptake velocity of powder defines the stirring strength of dry components in water [16], and vigorous stirring is important to prevent any undissolved powder lumps that may form [18]. Regarding temperature, depolymerization of the macromolecules can occur at temperatures above 30 °C with intensive mechanical energy input, influencing the properties of the final food product [16].

This review paper discusses the versatility of using pectin in food, focusing on its application in liquid and semi-solid foods and exploring pectin's rheological properties. The review starts by showing the pectin chemical structure, the sources' potential, thickening, and gelling mechanisms, and concludes by discussing the leading applications in the food sector.

2. Chemical Structure of Pectin—A Heterogeneous Polysaccharide

In plants, pectin is naturally located in the cell walls and is restricted to the primary cell walls and middle lamella, remaining almost absent in the secondary cell walls [24–26], as depicted in Figure 2. Pectin functionality, combined with cellulose and hemicellulose, provides mechanical strength, contributing to plant growth, morphology, development, and defense [27–29]. The primary cell wall composition consists of approximately 35% pectin, 30% cellulose, 25% hemicellulose, and 10% protein, depending on the plant species, ripening stage, and cell differentiation [30]. Note that pectin is the most abundant macromolecule in higher plants, creating valuable opportunities for using pectin to develop new food products. In addition, the circular economy can be increased by stimulating the use of pectin from the by-products of the agricultural, agribusiness, and food industries.

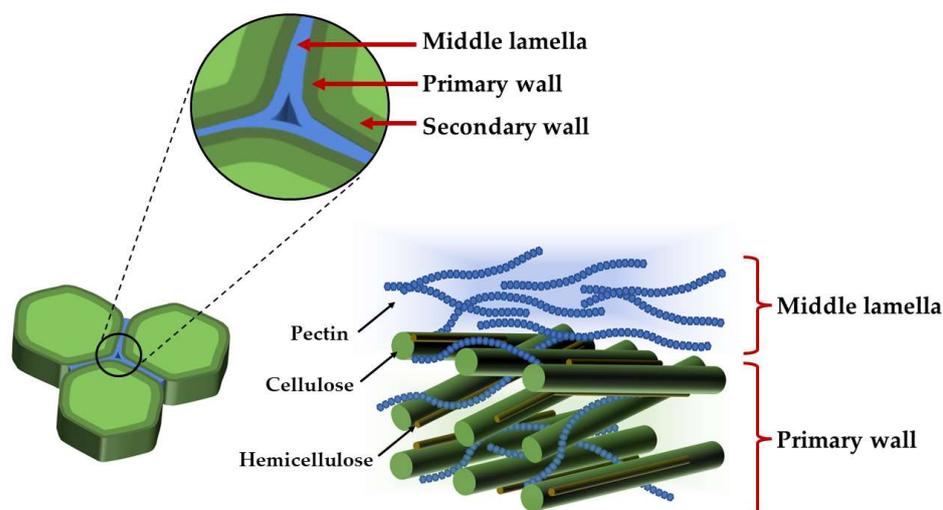


Figure 2. Schematic representation of the localization of pectin in the cell walls.

It is practical to start by defining the chemical structure of pectin, highlighting that it is a group of polysaccharides rich in galacturonic acid (GalA), which is present in two major structural features that form its backbone. There are three polysaccharide segments mainly found in all pectin species: homogalacturonan (HGA), rhamnogalacturonan-I (RG-I), and rhamnogalacturonan-II (RG-II) [26,29,31], as depicted in Figure 3. For food applications, it is important to understand the changes in the structural characteristics of these three polysaccharide segments. For instance, HGA is the most abundant and widespread segment of pectin, known as the “smooth” region. The degree and distribution of esterified D-galacturonic acid units in the HGA segment cause relevant modifications in pectin’s gelling and stabilizing properties [32,33]. The degree of methoxylation (DM) of pectin is the ratio of methoxylated D-galacturonic acid units to total D-galacturonic acid units [34,35], and is classified as high methoxylated pectin (HM, DM > 50) and low methoxylated pectin (LM, DM < 50). HM pectin is especially used to prepare jams, jellies, or marmalades due to its ability to form a gel under acidic conditions and high concentrations of sugar [34,36]. In contrast, LM pectin can form a gel by interacting with divalent cations, such as Ca^{2+} , following the egg box model. For this reason, LM pectin can produce a gel with less dissolved solids, creating great interest in preparing products with reduced caloric value [34,36,37].

RG-I is a more complex structure than HGA [31], constituting a backbone of repeat units of the disaccharide (1→2)- α -L-rhamnose-(1→4)- α -D-galacturonic acid and neutral sugar side chains attached to the C-4 of rhamnose units [38,39]. Generally, the RG-I structure is not associated with gel formation and is removed by hot acid in commercial pectin production. The low gelling capacity of RG-I is due to the rhamnose inserts on the backbone producing molecular twists, limiting cross-linking. However, studies have reported new perspectives for the branched gelation of RG-I, showing that the side chains of the RG-I re-

gion showed strong water binding capacities and stabilized the gel network structures [40]. Liu et al. [41] and Wang et al. [42] showed gel formation stemming from RG-I-rich pectic polysaccharide under divalent ions (Ca^{2+} and Mg^{2+}), and sucrose can strengthen the gel network [40]. In addition, the RG-I-rich pectic polysaccharide, mainly from fruits and vegetables, is suggested to have potential health benefits, such as modulating the gut microbe and promoting cell adhesion and migration [40,43].

RG-II presents the most complex structure compared to the other segments of pectin [44,45]. Additionally, RG-II is present in pectin in smaller amounts, and its structure is rather conservative [46], demonstrating its importance in biological functions in plant cell walls [45]. Thus, RG-II is not a common part of commercial pectins for gelling purposes. Commercial pectin is predominantly homogalacturonans and contains low amounts of short neutral side chains in the form of RG-I [47]. The impact for the final consumer regarding safety is negligible, and health benefits are related only to the HGA portion, the one presented in high amounts. The chemical structure of the three polysaccharide segments mainly found in pectin is described separately below.

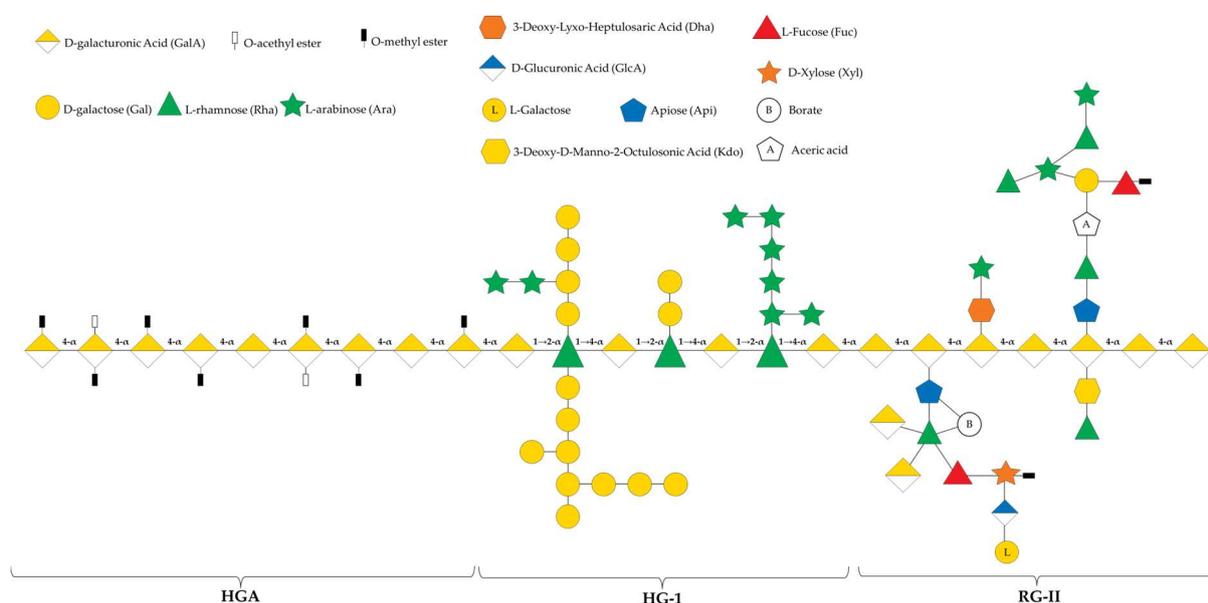


Figure 3. Representation of the three polysaccharide segments found mainly in all pectin species: homogalacturonan (HGA), rhamnogalacturonan-I (RG-I), and rhamnogalacturonan-II (RG-II). Figure 3 was drawn using the symbol nomenclature for glycans guidelines [29,48,49].

2.1. Homogalacturonan

Comprising approximately 65% pectin, HGA is a linear homopolymer of (1→4)- α -linked-D-galacturonic acid that contains some 100–200 GalA residues [29,31,50], and 70–80% of GalA residues are methylesterified at the C-6 carboxyl. In turn, the absence of methyl ester groups results in the ability of HGA to form gels by being cross-linked with calcium [51]. Also, GalA residues can be O-acetylated at C-3 or C-2. Especially, acetylated HGA appears to be abundant in sugar beet roots and potato tubers [31,52,53]. When the GalA of HGA is substituted at C-3 with residues of xylose, a domain called xylogalacturonan (XGA) is produced, which is more often found in apple pectin, watermelon fruit, and carrot cells [31,54–56]. Finally, the substitution of GalA at C-2 or C-3 with apiose results in the formation of apiogalacturonan, which is more usually found in duckweeds [57].

2.2. Rhamnogalacturonan-I

RG-I is considered a heterogeneous domain, constituting approximately 20–35% of pectin at 100 repeat units of the disaccharide (1→2)- α -L-rhamnose-(1→4)- α -D-galacturonic acid [38,39]. About 20–80% of rhamnose units in RG-I are substituted at C-4 by neutral

sugar side chains, where the size can vary from 1 to 50 (or more) glycosyl residues [31,38]. L-arabinosyl and D-galactosyl residues are widely found in the side chains [58]. A range of other linkages can also be present, including arabinogalactan type I and type II [59,60]. The large and highly variable branched nature of RG-I has become known as the “hairy” region of pectin [61].

2.3. Rhamnogalacturonan-II

The most complex structure, comprising only 10% pectin, is RG II. Although RG II is in minor amounts, it is crucial for normal plant growth and development [29]. Interestingly, the structure of RG-II is unrelated to RG-I, as it is a branched pectic domain containing an HGA backbone [31]. RG-II has a backbone of approximately nine GalA residues, which are (1→4)- α -linked and are substituted by four heteropolymeric side chains containing eleven different sugars in more than twenty different linkages, including the rare sugars apiose and aceric acid [31,62]. The RG-II domain appeared structurally conserved and widespread when isolated from cell walls by endopolygalacturonase cleavage, indicating covalent attachment to HGA [31]. For this reason, RG-II may indicate a specific structural function since it provides stable links at key regions of HGA chains within the pectin network [31].

3. Pectin and Its Potential Sources

Pectin is usually commercially produced from apple pomace or citrus peel (lemon, lime, grapefruit, orange) and is subsequently obtained from sugar beet pulp as a by-product of sugar production [63,64].

Depending on the application, a suitable pectin with specific characteristics is required. For example, pectin from the apple source is commonly used for fillings in baking and similar products, as this source produces a heavier and more viscous gel. In contrast, pectin from the citrus source results in a lighter color and is more acceptable in confectionery jellies [63]. The sugar beet pectin has poor gelling capacity compared to the apple and citrus sources due to the high content of acetyl groups and neutral sugars and the higher content of proteinaceous materials bonded covalently to the side chains [64,65]. Pectin from sugar beet is commercially used as a food emulsifier, and its capacity to stabilize oil emulsions was verified by Leroux et al. [66]. They found that the molecular weight, protein, and acetyl contents of the sugar beet pectin significantly influenced the emulsifying properties and were able to reduce the interfacial tension between the oil and water phases.

Pectin extraction methods have some variables depending on the technique, such as solid–liquid ratio, acid strength, temperature/power, extraction time, and precipitation method. Pectin yield is affected by these variables but rather affects pectin qualities in terms of the degree of esterification (DE), molecular weight, composition, purity, and color [53]. A study by Kaya et al. [54] demonstrated that pectin extraction methods from citrus peel influence its structure, recovering pectin with different molecular weights and varying RG-I content [53]. Wang et al. [55] studied pectin extracted from apple pomace and citrus peel by subcritical water and found different molecular weight values. The highest molecular weight for citrus peel was ~70 kDa at 120 °C. Additionally, the highest molecular weight for apple pomace was ~65 kDa obtained at 130 °C. Table 1 presents the pectin molecular weight (Mw) values of pectin associated with its source and extraction method. It contains data from apple, citrus, or beet sources, which are the most commonly used plant sources to produce pectin at the commercial level.

Table 1. Molecular weight values of pectin from apple, citrus, or beet sources associated with their extraction method.

Source of Pectin	Type of by-Products	Extraction Methods	Mw (KDa)	References
Navel orange (<i>Citrus sinensis</i>)	Orange peels	CE * (acid; HCl)	212.9	[67]
		CE (alkali; NaOH)	153.0	[67]
		Hydrothermal	109.2	[67]
Pomelo (<i>Citrus grandis</i>)	Pomelo peels	Hydrothermal	134.0	[68]
		CE (acid; citric acid)	188.5	[68]
		CE (EDTA-2Na)	220.4	[68]
		SWE * (hydrothermal)	56.3	[68]
		SWE (acid; citric acid)	88.4	[68]
		SWE (EDTA-2Na)	137.1	[68]
		Lukan Ponkan Shatangju Wogan Citrus Limetta	Citrus peels	CE (acid; acetic acid)
CE (acid; acetic acid)	173			[69]
CE (acid; acetic acid)	40			[69]
CE (acid; acetic acid)	163			[69]
Hydrothermal	330.9			[70]
Citrus Limetta	Citrus peels	CE (acid; HCl)	296.2	[70]
Malus domestica “Fälticeni” apples	Apple pomace	CE (acid; citric acid)	263	[71]
		MAE *	264	[71]
		UAE *	386	[71]
		EE * (cellulase or/ Celluclast®1.5 L)	(118/117)	[71]
		UAEH *	260	[71]
		EAU *	117	[71]
Fuji Jingshiji Ruixue	Apple pomace	CE (acid; citric acid)	1541	[72]
		CE (acid; citric acid)	1787	[72]
		CE (acid; citric acid)	1626	[72]
Blanca de Asturias	Apple pomace	CE (AP *:HCl; 1:15; 20 min)	865	[73]
		CE (AP:HCl; 1:20; 20 min)	850	[73]
		CE (AP:HCl; 1:25; 20 min)	836	[73]
Beet	Sugar beet pulp	MAE * (precipitate A)	488	[74]
		MAE (precipitate B1)	474	[74]
		MAE (precipitate B2)	523	[74]
Beet	Sugar beet pulp	CE (acid; nitric acid; 1 h)	913	[75]
		CE (acid; nitric acid; 2 h)	824	[75]
		CE (acid; nitric acid; 4 h)	695	[75]
		CE (acid; nitric acid; 16 h)	286	[75]

CE *: conventional extraction. SWE *: subcritical water extraction. MAE *: microwave-assisted extraction. UAE *: ultrasound-assisted extraction. EE *: enzymatic extraction. UAEH *: ultrasound-assisted extraction—heating treatment. EAU *: enzyme-assisted extraction—ultrasound treatment. AP *: dried apple pomace.

In addition to the molecular weight of pectin being affected depending on the extraction method, its purity can also be affected. For conventional pectin extraction, high temperatures (80–90 °C), acidic pH (2–3), long time (1–5 h), and a high solid-to-liquid ratio (1:30–1:50) [65] are commonly used, as described in Table 2. Conventional extraction is initiated using organic acids to break the cell wall fibers (Figure 1), releasing pectin chains. When combined with high temperature, it will accelerate molecular motion, facilitating the dissolution of pectin in an aqueous medium. When working with low methoxylated pectin (LM), citrates, oxalates, and polyphosphates (named chelators) are added to capture Ca²⁺, allowing the disaggregating of pectin chains [65,66]. Then, the aqueous medium is treated with alcohol to create the pectin precipitate, and filtration is performed to isolate the pectin [65]. Usually, these formed pectin isolates contain a considerable number of contaminants, such as free neutral components, which may include monomeric sugars, oligosaccharides, and high molecular weight polysaccharides [67,68], which can affect the gelling properties of pectin [68]. Studies have reported that the final purity of isolated pectin can be influenced by the purification method used [68], such as ultrafiltration [65], dialysis [68], and metal ion precipitation [68]. For instance, Yapo [68] found that the gel

prepared with pectin purified by the metal ion-precipitation procedure formed the gel more rapidly and with much higher strength than non-purified pectin. Muhidinov et al. [69] showed that the di-ultrafiltration (DUF) process was able to separate the pectin oligosaccharides (POS) extracted together with the pectin. Interestingly, oligosaccharides have been classified as a potential prebiotic; for this reason, the authors suggested that the DUF method was preferable to the hydrolysis-extraction method for pectin production. Pectin purification can effectively remove possible contaminants, improving pectin gelling properties [65,69] and creating the possibility of a new ingredient. However, it is essential to highlight that the DUF process can produce pectin at different costs [69].

The pectin from apple, citrus, or beet sources can be considered low-cost and highly available, as it comes from food and agro-industrial waste [76]. According to the Food and Agriculture Organization [77], 17% of global food production is estimated to be wasted, with about 14% of the food produced being lost between harvest and retail. For this reason, the significance of research that explores new alternative sources to produce pectin, mainly from food and agro-industrial wastes, adds value to these by-products. Some relevant factors should be considered to evaluate the feasibility of using new alternative sources for pectin extraction, such as the selection of raw materials and the pectin characteristics. For raw material selection, it is necessary to consider the pectin content, quality, ripeness, availability, seasonality, and logistics (it may be required to dry the raw material to avoid microbial growth and chemical deterioration). Furthermore, it is important to consider the chemical composition, structure, molecular features, and gel-forming capacity of pectin [63,76]. Table 2 presents an overview of the optimized parameters of extraction methods and yield (%) of different pectin sources considered by-products. The studies found covered the last four years and show potential pectin sources, including banana peels, berry fruits, cacao pod husks, eggplants, mangos, pineapple and jabuticaba peels, watermelon rinds, and papaya pulp [76,78].

Table 2. Overview of optimized parameters of extraction methods and yield (%) of different types of by-products.

Type of by-Products	Extraction Methods	Optimized Parameters	Yield (%) *	References
Artichoke by-products	UAE + EE (Celluclast)	20 KHz, 30% amplitude, pulse (2 s on/1 s off), pH: 5.0, 200 rpm, 6 h, 50 °C, S:L * 1:15	13.9	[79]
Banana peels	UAE	40 KHz, 185 W, pH: 3.68, 200 rpm, 17.12 min, 33.12 °C, S:L 1:12	2.62	[80]
Berry fruits (raspberry)	CE	58 °C, 60 min, orbital shaking, 250 rpm, pH: 3, citric acid, S:L 1:4	8.8	[81]
Berry fruits (raspberry)	EE (Celluclast)	40 °C, 90 min, orbital shaking, 200 rpm, pH: 5, S:L 1:20	9.9	[81]
Dragon fruit peels	UAE	37 KHz, 330 W, pH: 2, 25 min, 65 °C, S:L 1:20	6.27	[82]
Eggplant peels	UAE	50 W, pH: 2.25, 30 min	27.60	[83]
Jabuticaba peels	UAE + Heating 40 °C + Microwave reactor	20 KHz, 500 W, 15 min + 40 °C + 150 W, 3 min, pH: 1.8, S:L 1:29	17.79	[84]
Pistachio hulls	CE	90 °C, 30 min, magnetic stirrer, 200 rpm, pH: 0.5, S:L 1:50	32.3	[85]
Citrus <i>limetta</i> peels	UAE	20 KHz, 500 W, 37% amplitude, pulse (15 s on/15 s off) pH: 1.9, 24 min, 40 °C, S:L 1:30	28.73	[86]
Grapefruit and or/tangerine wastes	UAE	20 KHz, 130 W, 90% amplitude, pulse (5 min on/2 min off) pH: 2.5, 30 min (grapefruit), 15 min (tangerine), 80 °C, S:L 1:30	26.05 and or/13.46	[87]
Papaya pulp (fourth day after harvest)	CE	30 min, magnetic stirrer, 80% boiling ethanol, S:L 1:40	35.45	[78]

Table 2. Cont.

Type of by-Products	Extraction Methods	Optimized Parameters	Yield (%) *	References
Apple pomace	CE	90 °C, 120 min, pH: 1.5, citric acid, S:L 1:10	38.91	[88]
Apple pomace	MAE	420 W, pH: 1.5, 120 s, S:L 1:15	45.15	[88]
Orange peels	CE	500 rpm, 1 h, 65 °C, citric acid	19.65	[89]
Custard apple peels	UAE	20 KHz, 70% amplitude, pH: 2.3, 18.04 min, 63.22 °C, S:L 1:24	8.93	[90]
Cocoa pod husks	MAE	400 W, pH: 1.16, 15 min, S:L 1:25	9.64	[91]
Watermelon rinds	CE	95 °C, 90 min, pH: 1.36, magnetic stirring, S:L 1:20	13.4	[92]
Mango peels	MAE	606 W, pH: 1.83, 5.15 min, S:L 1:20	18.94	[93]
Pequi mesocarp	CE	80 °C, 160 min, magnetic stirring, 1500 rpm, citric acid, S:L 1:31	26.6	[94]
Pineapple peels	CE	95 °C, 60 min, water bath, pH: 2.2–2.4, citric acid, S:L 1:40	1.02	[95]
Pineapple peels	ME *	420 W, 85–90 °C, pH: 2.2–2.4, citric acid, 60 min, S:L 1:40	2.12	[95]
Persimmon peels	CE	90 °C, 120 min, water bath, 500 rpm, pH: 2, citric acid, S:L 1:20	NA	[96]
Durian rinds	CE	93.3 °C, 185 min, shaking water bath, 90 rpm, S:L 1:50	12.12	[97]
<i>Cinnamomum cassia</i> barks	MAE	600 W, pH: 2, 3 min, S:L 1:40	13.48	[98]

* Pectin extract yield: expressed as the weight of dried pectin extracted from the raw material used for extraction; NA: not available. ME *: microwave heating extraction. S:L *: solid-liquid ratio.

4. Pectin as a Thickening and Gelling Agent and Its Application to Semi-Solid and Fluid Foods

The two types of water immobilization by hydrocolloids are thickening and gelling attributes. Pectin has these attributes due to its ability to bind a large amount of water and form a gel. After many years of scientific discussion, a definition was that gel is a system comprising at least two components containing a substantial quantity of a liquid, resulting in soft, solid, or solid-like products [16,99]. Only after using rheological oscillation measurements was it possible to describe the difference among the gels formed in the products [16,100,101].

The thickening behavior of pectin due to the formation of a structure increases the viscosity of products and is the main characteristic of its use as an emulsifying, stabilizing, and bodying agent in foods for determined technological functions [102]. It is worth mentioning that thickening behavior occurs above a certain/critical concentration named overlap concentration (C^*) when the product behaves as a non-Newtonian fluid. Otherwise, below this concentration, the product behaves as a Newtonian fluid [10,102].

Regarding the gelling behavior, pectin can form a true gel and, as aforementioned, is applied to foods such as jams, jellies, or marmalades [16]. Pectin forms a three-dimensional network in which a solid matrix involves the liquid phase and immobilizes the liquid within it, forming a rigid structure resistant to flow. A gel is considered a colloidal dispersion; the continuous phase is a solid matrix and the discontinuous phase is a liquid [103]. In rheology, G' represents the storage modulus, which characterizes the solid-like elastic attributes of a system, while G'' denotes the loss modulus, quantifying the liquid-like or viscous characteristics of the system [16], and a gel is a viscoelastic system with $G' > G''$ [102].

Water Inclusion Ability of Pectin

There are two mechanisms for the water inclusion of pectin: (i) cold-set gelation and (ii) ionotropic gelation.

Cold-set gelation is formed in a two-step process during cooling [104]. Pectin in its powder form is treated with water at a high temperature or boiling point and is then cooled at room temperature [104]. First, at temperatures above 50 °C, hydrophobic interactions are formed between the hydrophobic pectin methoxyl groups. After that, during cooling,

these hydrophobic interactions are loosened and cleaved, following the replacement by hydrogen bonds formed between hydrophilic carboxyl, hydroxyl, or amidated pectin (amide groups) [16,105], leading to a three-dimensional network. This mechanism demands a low pH (2.0–2.3), which is achieved by adding organic acids below the pKa of pectin, which is 3.5. The low pH allows a high share of undissociated carboxyl groups (–COOH) for hydrogen bonds [16,106]. Finally, for pectin macromolecules to interact and form bonds, adding a high sugar concentration (~65%, at least 55%) is necessary. The sugar is hydrophilic and competes with pectin molecules for water solvation, reducing the chains' hydration and allowing them to interact with each other [16,107,108]. The cold-set gelation process usually immobilizes a large amount of water (up to 50%), even with a final pectin concentration in the gel of less than 1%, and these pectins are commonly known as high methoxylated (HM).

In turn, the ionotropic gelation mechanism [104] occurs in the presence of divalent cations, which provides a cross-bridge between cations and the charged carboxyl groups of pectin. This process is independent of temperature, starting instantly after adding a divalent cation to the system. For this application, a food-grade calcium ion (Ca^{2+}) is used. Ürüncüoğlu [103] studied the cooperativity of six different cations, using three pectins (sugar beet, high and low methyl esterified pectins) to investigate the formation and stability of oil-in-water emulsions. It was verified that the cations influenced the stability of the emulsion in the following order, from the most stable to the least stable: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Al}^{3+} > \text{Cr}^{3+} > \text{Zn}^{2+} > \text{Fe}^{3+}$. In addition, the effect of monovalent and divalent cation ions on the gelation of fish gelatin—by incorporating *Nicandra physalodes* pectin—was studied by Yan et al. [104]. The authors concluded that when Na^+ and Ca^{2+} were used alone, there was a decrease in the electrostatic association, forming a weak gel. However, when *Nicandra physalodes* pectin was associated with low Ca^{2+} concentrations, they could form tertiary complexes that provided additional crosslinks, thus increasing the system's gel strength.

The pH of the system should be above the pKa value of pectin (>3.5) because, for the calcium bridges to form, a certain share of dissociated carboxyl groups (–COO[−]) is necessary. Thus, the ionotropic gelation mechanism is the main process for low methoxylated pectin [16,106].

Regarding the water retention ability of pectin, it is known that after a certain time, the immobilized water will drain, and the gel shrinks and collapses. This process is known as syneresis [16,109].

Liu et al. [110] studied the rheological characterization of pectin from passion fruit (*Passiflora edulis f. flavicarpa*) peel extracted by high-speed shearing. Rheological measurements of pectin were performed using a Rheometer with parallel plate geometry. The flow behavior and viscoelastic properties of the pectin solution were analyzed at different pectin concentrations of (0.1 to 3.0) g/100 mL. Flow behavior analysis was performed in the shear rate range of (0.1 to 100) s^{-1} at 25 °C, and the power-law model was fitted to the flow curves data, according to Equation (1).

$$\tau = \kappa \times \dot{\gamma}^n \quad (1)$$

where τ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s^{-1}), κ is the consistency index (Pa · s^n), and n is the flow index [6].

The flow behavior showed that all pectin solutions exhibited shear-thinning behavior in a low shear rate range (<10 s^{-1}). However, at a high shear rate range (>10 s^{-1}), there was no change in the apparent viscosity behavior. It is known that apparent viscosity decreased with increasing shear rate, which is commonly a consequence of insufficient entanglement in the structural chain [111]. It was verified that with the increase in pectin concentration, the apparent viscosity of pectin solutions increased. At a pectin concentration of >1 (g/100 mL), the shear-thinning behavior of the solutions was enhanced, probably due to the increase in hydrogen bonds, in which pectin molecules became closely bound, restricting movement and allowing for an increase in viscosity. In turn, at a pectin concentration of

less than 1 (g/100 mL), the pectin solution was more similar to Newtonian fluid (η value was closer to 1), which is characterized as a diluted solution with low viscosity.

The viscoelastic properties of pectin solutions were analyzed by frequency and temperature sweeps. Vibration sweeps were conducted under a strain range of (0.1 to 100) % at 1 Hz (25 °C) to determine the linear viscoelastic region. After that, frequency sweeps at 25 °C in the frequency range of (0.1 to 20) Hz within the linear viscoelastic region (1.0% strain) were performed. Finally, temperature sweeps were carried out, using a frequency of 1 Hz and strain of 1.0% with heating (20 to 70) °C and subsequent cooling (70 to 20) °C at a rate of 5 °C/min. Different pectin solutions at different concentrations showed viscoelastic properties ($G'' > G'$), characterizing the typical behavior of fluid throughout the entire frequency range. A pectin solution at 3 g/100 mL showed a higher effect on viscoelasticity, corroborating the apparent viscosity and the formation of a rigid network structure with increased pectin concentration [104]. It was observed that while heating a gain of G' and a decrease in G'' during cooling, both G' and G'' increased, indifferent to the concentration. In pectin solutions at a concentration of 3%, G'' was dominant whether heating or cooling. The results indicated that G'' was dominant at high pectin concentrations, and the “reptation” model explained this. The side chains of molecules further tighten the network structure through entanglement and topological constraints [107,108]. In other words, viscoelasticity behavior is reflected by macromolecular motion, and as chain size increases, linear polymers become entangled and are forced to move (“reptate”) along their contours. Consequently, their stress relation function exhibits a plateau similar to elastic materials and starts to decay with time [109].

Thus, this study suggested that pectin from passion fruit peel extracted by high-speed shearing demonstrated enormous potential as an additive to rheology modifier in all dairy beverages. Therefore, Table 3 presents an overview of studies on pectin as a thickening and gelling agent and its application to semi-solid and fluid foods focusing on rheological properties.

Table 3. Studies on pectin as a thickening and gelling agent and its application to semi-solid and fluid foods.

Source/Family of Pectin	Food Application	Rheological Measurements (Rheometer or Viscometer)	Pectin Concentration (g/100 mL or g/100 g)	Mains Results of Rheological Properties
Apple peels/HM * [112]	Flavored probiotic Yogurt drinks	Geometry: cone and plate (4°, 40 mm in diameter). Oscillatory measurements: frequency range of (0.1 to 10) Hz. Linear viscoelastic behavior region found (10% strain)	0.1, 0.2, 0.3, 0.4, 0.5	Shear-thinning flow behavior, gel-like network at low frequencies. A total of 0.5 g/100 mL of pectin showed the highest G' and G'' and stability during storage
Apple pomace (AP) powder/NA [113]	Set type yogurt	Geometry: concentric cylinder (diameter of cup and bob: 28.92 and 26.66 mm, respectively). Oscillatory measurements: frequency of 1 Hz and 0.5% strain. Fermentation of skim milk fortified with AP was performed in situ in the rheometer	0.1, 0.5, 1.0	Yogurts containing 1.0 g/100 g of apple pomace and cooled to 4 °C showed a higher G' than that the control, causing a firmer and more consistent gel without disrupting gelation
Citrus peels/HM [114]	High-protein cultured milk beverages	Geometry: vane (ST24–4V-30). Oscillatory measurements: frequency range of 0.1 Hz and strain of 0.5%	0.15, 0.50, 0.85, 1.00	All samples formed gels. It was indicated that in aged samples a high concentration of pectin slowed the formation of elastic bonds Higher pectin concentration led to a strong gel with higher G' values. This result could be attributed to the formation of complexes, and the mechanical spectra prove the hypothesis that pectin forms strands with caseins micelles
Citrus peels/LMA * [115]	Acidified camel milk	Geometry: cone and plate (3.5 cm diameter; 2° angle). Oscillatory measurements: frequency range of (0.1 to 20) Hz. Linear viscoelastic behavior region found (0.1% strain)	0.5, 1.0, 1.5, 2.0	Low-fat yogurt revealed pseudoplastic shear-thinning behavior. When increasing the concentrations of LMP, both G' and G'' increased. The increasing elastic modulus evinced that the LMP addition might have enhanced the strength of bonds in protein structure
Citrus peels/LM * [116]	Low-fat set yogurt	Geometry: concentric cylinder (32.40 mm bob diameter, 12 mm length). Oscillatory measurements: frequency range of (0.1 to 16) Hz. Linear viscoelastic behavior region found (0.1% strain)	0.05, 0.10, 0.20, 0.40, 0.60, 0.80, 1.00	The increase in pectin led to a rise in apparent viscosity, firmness, and consistency
Citrus peels/HM [117]	Marmalade prepared from black plum peel	Geometry: bob and cup (bob length: 60 mm; bob diameter: 14 mm; gap width: 1 mm). Flow curves measurements: shear rate (20 to 300/s over a timelapse of 400 s). Apparent viscosity: shear rate of 40/s	0.3, 0.4, 0.5, and 0.6	All samples tested presented gel behavior as G' , G'' . Nonfilled gels presented a lower G' than emulsion-filled gels (EFG), indicating that the former had a weaker three-dimensional polymer network structure
Citrus peels/PLMA * [118]	Vegan gummy candies	Geometry: cone and plate geometry (2°, 60 mm diameter). Oscillatory measurements: frequency range of (0.01 to 10) Hz. Linear viscoelastic behavior region found (8 Pa)	4	

Table 3. Cont.

Source/Family of Pectin	Food Application	Rheological Measurements (Rheometer or Viscometer)	Pectin Concentration (g/100 mL or g/100 g)	Mains Results of Rheological Properties
NA—/HM [119]	Jelly candy (3D printing)	Geometry: parallel plate. Oscillatory measurements: frequency range of (0.01 to 0.16) Hz. Linear viscoelastic behavior region found (5% strain)	10, 12, 14 and 16	A total of 16 (g/100 g) of pectin had the height of G' and G'' , and all pectin jelly candy showed the characteristic of pseudoplastic shear-thinning
Pomegranate peels/HM [112]	Flavored probiotic yogurt	Geometry: cone and plate (4°, 40 mm in diameter). Oscillatory measurements: frequency range of (0.1 to 10) Hz. Linear viscoelastic behavior region found (10% strain)	0.1, 0.2, 0.3, 0.4, 0.5	All samples showed Newtonian flow behavior and liquid-like behavior over the frequency range
Potato pulp/LM [120]	Acidified milk drinks	Geometry: NA. Oscillatory measurements: frequency range of (0.1 to 10) Hz. Linear viscoelastic behavior region found (1% strain)	0.1, 0.2, 0.3, 0.4, 0.5	The storage modulus (G') was higher than the loss modulus (G'') for all the samples, indicating a gel-like structure
Sunflower by-products /LM [37]	Low-sucrose strawberry jams	Geometry: parallel plate. Oscillatory measurements: frequency range of (0.1 to 10) Hz. Controlled stress of 5 Pa	1.0	G' was higher than G'' over the whole frequency range for almost every formulation. A sample presented a sol–gel transition at higher frequencies. This fact could be related to the use of glucose and fructose syrup instead of sucrose

PLMA * Partially amidated low methoxylated (PLMA). LM * Low methoxylated pectins (LM). LMA * Low methoxyl amidated pectin (LMA). HM * High methoxylated pectins (HM). NA: not available.

5. Conclusions

From the perspective of regulatory expertise, such as ANVISA in Brazil, the European Food Safety Authority (EFSA) in Europe, and the Food Drug Administration (FDA) in the USA, pectin is permitted in food under their defined conditions. During food processing, texture is one of the most important attributes considered during food development to achieve quality. Food raw material is highly variable and is a challenge to the food industry, which aims to maintain the quality standard of products for good consumer perception. Therefore, most of the time, additives are used to standardize the quality of the finished product. Pectin is a polysaccharide found in many plant sources and agro-industrial wastes, and this natural origin causes a high acceptance among consumers.

Pectin, as a food additive, is well-known for its gelling and thickening properties. Its application to semi-solid and fluid foods such as jams, jellies, and marmalades provides firmness and spreadable texture. In beverages, pectin produces a stable drink without sedimentation, which improves the mouthfeel. In stirred yoghurt mixed with fruit, pectin acts as a thickener. In yogurts with fruit on the bottom of the container, pectin can be used as an excellent stabilizer between the two phases (fruit preparation and yogurt). From the studies, it was possible to notice that researchers are continuously innovating in their studies, showing the desired rheological proprieties in many innovative food products that are desirable for some consumers, such as low-fat and low-sugar products, enriched and fortified foods, vegan products, and candy 3D printing. Therefore, there are many opportunities for new and exciting studies using pectin as an additive for application in different food matrices relating to its rheological properties. In addition, pectin is a good source of soluble dietary fiber, which can provide an additional health benefit for developed food products.

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