

## REVIEW ARTICLE

# Pectins And Their Role in Food and Pharmaceutical Industry: A Review

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### Abstract

Pectin is an important polysaccharide with applications in foods, pharmaceuticals and other industries. It has excellent biodegradable and biocompatible nature. Pectin is commercially extracted from different citrus products like apple, pomace, and oranges under mildly acidic conditions. Cell walls of most plants, apple, pomace and orange peel are the major sources of commercial pectin due to the poor gelling behavior of pectin from other sources. Pectins are broadly divided into high methoxyl and low methoxyl pectins. In low-methoxyl pectin, gelation results from ionic linkage via calcium bridges between two carboxyl groups belonging to two different chains in close contact with each other. In high-methoxyl pectin, the cross-linking of pectin molecules involves a combination of hydrogen bonds and hydrophobic interactions between the molecules. Pectins are both polydisperse and polymolecular and the composition varies with the source and the conditions applied during isolation. The importance of pectins in the food sector lies in their ability to form gel in the presence of  $\text{Ca}^{2+}$  ions or a solute at low pH. Depending on the pectin, coordinate bonding with  $\text{Ca}^{2+}$  ions or hydrogen bonding and hydrophobic interactions are involved in gel formation methoxyl pectin. In food industry, pectin is used in jams, jellies, frozen foods, and more recently in low-calorie foods as a fat and/or sugar replacer. In the pharmaceutical industry, it is used to reduce blood cholesterol levels and gastrointestinal disorders. This article briefly describes the general properties, structure, chemistry of gelation, extraction, sources, interactions, and applications of pectins.

## INTRODUCTION

Pectin is one of the major plant cell wall components and probably the most complex macromolecule in nature, as it can be composed out of as many as 17 different monosaccharides containing more than 20 different linkages. It is obtained by aqueous extraction of the appropriate edible plant materials, mainly from citrus peel and apple pomace, followed by a selective precipitation using alcohol or salts. The raw materials used contain a large amount of pectin with superior quality and are available in sufficient quantities to make the manufacturing process more cost effective. The main functional feature of pectin as a gelling agent is the ability to form gels in aqueous solutions in the presence of a certain amount of sugar and acid or calcium ions. In addition, pectin can absorb and rid the body of biogenic toxins, anabolic steroids, xenobiotics, metabolites, and biologically harmful substances capable of accumulating in the body. The degree of esterification of glucuronic acid residues of pectin is the most important parameter which affects the solubility of pectin and its gelling and film forming properties. The degree of esterification varies according to the origin of plant source, when and where the plant has been harvested and processing conditions such as storage, isolation, purification and extraction etc.<sup>1</sup> Pectins have the following advantages as additives in food and pharmaceutical products:

1. Pectins have the desirable stability under acidic conditions even at higher temperature which makes them ideal candidate to be used in drug delivery system (DDS).<sup>2</sup>
2. Pectins have unique gel forming ability in presence of divalent cations which makes them ideal carriers for delivering bioactive agents.<sup>2</sup>
3. Pectins have long standing reputation of being non-toxic, high availability and low production cost.<sup>3</sup>
4. Pectins can be used for delivering drugs orally, nasally, and vaginally and it has been well accepted by patients.<sup>3</sup>

## General Properties of Pectins

Pectins are soluble in pure water. Monovalent cation (alkali metal) salts of pectinic and pectic acids are usually soluble in water; di- and trivalent cations salts are weakly soluble or insoluble. Dry powdered pectin, when added to water, has a tendency to hydrate very rapidly, forming clumps. These clumps consist of semidry packets of pectin contained in an envelope of highly hydrated outer coating. Further solubilisation of such clumps is very slow. Clump formation can be prevented by dry mixing pectin powder with water-soluble carrier material or by the use of pectin having improved dispersibility through special treatment during manufacturing.<sup>1</sup> Dilute pectin solutions are Newtonian but at a moderate concentration, they exhibit the non-Newtonian, pseudoplastic behaviour. As with solubility, the viscosity of a pectin solution is related to the molecular weight, DE, concentration of the preparation, and the pH and presence of counterions in the solution. Viscosity, solubility, and gelation are generally related. For example, factors that increase gel strength will increase the tendency to gel, decrease solubility, and increase viscosity, and vice versa. These properties of pectins are a function of their structure, which is that of a linear polyanion (polycarboxylate). As such, monovalent cation salts of pectins are highly ionized in solution, and the distribution of ionic charges along the molecule tends to keep it in an extended form by reason of coulombic repulsion. Furthermore, this same coulombic repulsion between the carboxylate anions prevents aggregation of the polymer chains.<sup>4</sup> (The number of negative charges is, of course, determined by the DE). In addition, each polysaccharide chain, and especially each carboxylate group, will be highly hydrated. Solutions of monovalent salts of pectins exhibit stable viscosity because each polymer chain is hydrated, extended, and independent. As the pH is lowered, ionisation of the carboxylate groups is suppressed, and this results in a reduction in hydration of the carboxylic acid groups. As a result of reduced ionisation, the polysaccharide molecules no longer repel each other over their entire length, and as a result, they can associate and form a gel.<sup>5</sup> Apparent pK-values (pH at 50% dissociation) vary with the DE of the pectin a 65% DE pectin has an apparent pK of 3.55, while a 0% DE pectic acid has an apparent pK of 4.10. However, pectins with increasingly greater degrees of methylation will gel at somewhat higher pH, because they have fewer carboxylate anions at any given pH. Dissolved pectins are decomposed spontaneously by deesterification as well as by depolymerisation; the rate of this decomposition depends on pH, on water activity, and on the temperature. In general, maximum stability is found at pH 4. The presence of sugar in the pectin solution has a certain protective effect while elevated temperatures increase the rate of degradation. At low pH-values and elevated temperatures degradation due to hydrolysis of glycosidic linkages is observed.

Deesterification is also favored by low pH. By deesterification, a HM-pectin becomes slower setting or gradually adapts LM-pectin characteristics.<sup>6,7</sup> At near-to- neutral pH (5-6), HM-pectin is stable at room temperature only. As the temperature (or pH) increases, a so-called elimination starts which results in chain cleavage and very rapid loss of viscosity and gelling properties. LM-pectins show a somewhat better stability at these conditions.<sup>8</sup> At alkaline pH-values pectin is rapidly deesterified and degraded even at room temperature.<sup>1</sup> Powdered HM-pectins slowly lose their ability to form gels if stored under humid or warm conditions while LM-pectins are more stable and loss should not be significant after one year storage at room temperature (Hercules Incorporated, 1999).<sup>3-5</sup>

### Classification of Pectins

Pectins are classified according to the degree of methoxylation (DM). The degree of methoxylation is expressed as a percentage of esterified galacturonic acid units to total galacturonic acid units in the molecule of pectin.<sup>6</sup>

- a. Pectin produced by the normal extraction process contains more than 50% of methoxyl groups and is classified as high methoxyl (HM) pectin. HM pectins are capable of forming gels in aqueous systems with high contents of soluble solids and low pH values.<sup>7</sup>
- b. Modification of the extraction process, or continued acid treatment, will yield conventional low methoxyl (LMC) pectin with less than 50% methoxyl groups. These pectins are characterized by their ability to form gels in the presence of bivalent salts, normally  $\text{Ca}^{2+}$  ions, in system with low solids content and a wide pH range.<sup>7</sup>
- c. Some pectin can be treated during manufacture with ammonia to produce amidated low methoxyl (LMA) pectin with less than 50% methoxyl groups and from 5 to 25% of amidated groups.<sup>8</sup>

### Structure of Pectins

Pectin is an essentially linear polysaccharide. Like most other plant polysaccharides, it is both polydisperse and polymolecular and its composition varies with the source and the conditions applied during isolation. The composition and structure of pectin are still not completely understood although pectin was discovered over 200 years ago. The structure of pectin is very difficult to determine because pectin can change during isolation from plants, storage, and processing of plant material. At present, pectin is thought to consist mainly of D-galacturonic acid (GalA) units, joined in chains by means of  $\alpha$ -(1-4) glycosidic linkage. These uronic acids have carboxyl groups, some of which are naturally present as methyl esters and others which are commercially treated with ammonia to produce carboxamide groups. Like most other polysaccharides, pectins are both polymolecular and polydisperse, that is, they are heterogeneous with respect to both chemical structure and molecular weight. Their composition varies with the source and conditions of extraction, location, and other environmental factors. Pectic substances in the primary cell wall have a relatively higher proportion of oligosaccharide chains on their backbone, and the side chains are much longer than those of the pectins of the middle lamella. Pectins are block copolymers, that is, branched blocks containing a main galacturonan chain interrupted and bent by frequent rhamnose units (many of them carrying side chains) alternating with unbranched blocks where rhamnose units are rare. These branched and unbranched blocks may be extracted separately from cell walls degraded by purified pectic enzymes or separately after chemical or enzymatic depolymerization of pectins in solution. Polygalacturonic acid could be considered as a rod in solution, whereas pectins are segmented rods with flexibility at the rhamnose tees. The size, charge density, charge distribution, and degree of substitution of pectin molecules can be changed biologically or chemically.<sup>9-12</sup>

### Degree of Esterification

The polygalacturonic acid chain is partly esterified with methyl groups and the free acid groups may be partly or fully neutralized with sodium, potassium or ammonium ions. Pectin might be formed initially in a highly esterified form, undergoing some deesterification after they have been inserted into the cell wall or middle lamella. There can be a wide range of DEs dependent on species, tissue, and maturity. In general, tissue pectins range from 60 to 90% DE. It seems that the distribution of free carboxyl groups along the pectin chains is somewhat regular, and the free carboxyl groups are largely isolated from one another. The pectin classes based on the DE are high methoxyl (HM) pectins, and the low methoxyl (LM) pectins which are either the conventionally demethylated or the amidated molecule. DEs values for commercial HM-

pectins typically range from 60 to 75% and those for LM-pectins range from 20 to 40%. These two groups of pectin gel by different mechanisms. HM pectin requires a minimum amount of soluble solids and a pH within a narrow range, around 3.0, in order to form gels. HM-pectin gels are thermally reversible. In general, HM-pectins are hot water soluble and often contain a dispersion agent such as dextrose to prevent lumping. LM-pectins produce gels independent of sugar content. They also are not as sensitive to pH as the HM-pectins. LM pectins require the presence of a controlled amount of calcium or other divalent cations for gelation.<sup>13-15</sup>

### Gel Formation Properties of Pectins

The most important use of pectin is based on its ability to form gels. HM-pectin forms gels with sugar and acid. The particular structure of pectin imposes some specific constraints. HM-pectin, unlike LM-pectin, does not contain sufficient acid groups to gel or precipitate with calcium ions, although other ions such as aluminium or copper cause precipitation under certain conditions. It has been suggested by Oakenfull that hydrogen bonding and hydrophobic interactions are important forces in the aggregation of pectin molecules.<sup>17</sup> Gel formation is caused by hydrogen bonding between free carboxyl groups on the pectin molecules and also between the hydroxyl groups of neighboring molecules. In a neutral or only slightly acid dispersion of pectin molecules, most of the unesterified carboxyl groups are present as partially ionised salts. When acid is added, the carboxyl ions are converted to mostly unionised carboxylic acid groups. This decrease in the number of negative charges not only lowers the attraction between pectin and water molecules, but also lowers the repulsive forces between pectin molecules. Sugar further decreases hydration of the pectin by competing for water. These conditions decrease the ability of pectin to stay in a dispersed state. When cooled, the unstable dispersing of less hydrated pectin forms a gel, a continuous network of pectin holding the aqueous solution. The rate at which gel formation takes place is also affected by the degree of esterification. A higher DE causes more rapid setting. Rapid-set pectins (i.e., pectin with a DE of above 72%) also gel at lower soluble solids and higher levels than slow-set pectins (i.e. pectin with a DE of 58- 65%). LM-pectins require the presence of divalent cations for proper gel formation. The mechanism of LM-pectin gelation relies mainly on the well-known 'egg-box' model. The mechanism involves junction zones created by the ordered, side-by-side associations of galacturonans, whereby specific sequences of GalA monomer in parallel or adjacent chains are linked intermolecularly through electrostatic and ionic bonding of carboxyl groups. It is generally accepted that the junctions consist of dimers in 21 helical symmetry, similar to the 21 model proposed for alginates. The oxygen atoms of the hydroxyl groups, the ring oxygen atoms, and the bridging oxygen atoms of the component sugar units participate in the bonding process through their free-electron pairs. The life of the junction depends on the strength of the electrostatic bonds. The bonds are stable when there are at least seven consecutive carboxyl groups on the interior of each participating chain. Nevertheless, all LM-pectin gels seem to develop similar, if not identical, junction zones. Furthermore, amidation increases or improves the gelling ability of LM-pectin: amidated pectins need less calcium to gel and are less prone to precipitation at high calcium levels. The amount of LM-pectin required for the formation of such gel decreases with the DE. The strengths of such ionic bonded gels are strongly dependent on the DE. Monovalent ions such as sodium, which can also react with free carboxyl groups, can affect gel formation because they decrease the cross-linking reaction of calcium and improve the solubility of LM-pectin in the presence of calcium. Although sugar is not essential for gel formation with LM-pectins, the presence of small amounts (10-20%) of sugar tends to decrease syneresis and adds desirable firmness of these gels. When some sugar is present, the amount of calcium required to form gel is reduced. High concentrations of sugar (60% or higher) interfere with gel formation because the dehydration of the sugar favours hydrogen bonding and decreases cross-linking by divalent ion forces.<sup>16-19</sup>

### Nutritional Aspects of Pectins

#### Source of Dietary Fibre

Pectin is sourced from plant cell walls and is analysed as a soluble and insoluble fraction as galacturonic acid after hydrolysis. The fruits and vegetables which are especially rich in pectins have dietary fibre contents in the range of 1-2%. In order to increase societal intake in fibre it is therefore preferable to add products concentrated in fibres. Pectin fibres exhibit higher hydration properties than other fibres and this property is exploited in its use as a structural component in foods, for example in bakery products. Studies have shown that substitution of flour with citrus fibres, apple flakes and concentrates in bakery and confectionery

products had a positive sensory effect. Pectin's adsorbent and bulk-forming properties have promoted its use in some multi-ingredient anti constipation and anti diarrhoeal preparations.<sup>20</sup>

### **Mineral Binding**

Another functionality of dietary fibre is in mineral and ion absorption and exchange. Pectin has the ability to associate ions due to a high content of negative charges and calcium binding is an example of binding strength and specificity. Pectin rich fibres can behave as weak cation exchange resins and are reversible depending on pH conditions.<sup>21</sup>

### **Prebiotic Effect**

Following ingestion of pectin, very little of it gets digested in the small intestine. Some fermentation of pectin takes place in the large intestine via the action of bacteria. Pectin substituents (homogalacturonans) are fermented in the colon with the formation of short chain fatty acids. It has been shown that non-methyl-esterified pectins were more rapidly fermented than methyl-esterified pectins. The final products of fermentation of pectin are the short-chain fatty acids, acetate, propionate and butyrate, as well as hydrogen and carbon dioxide. The short-chain fatty acids that escape colonic metabolism are transported via the portal circulation to the liver where they undergo metabolism. The short-chain fatty acids that are not metabolised in the liver enter the systemic circulation and are distributed to the various tissues of the body. Acetate appears to be the principal short-chain fatty acid to reach the systemic circulation from the liver. Pectins are therefore beginning to gain interest as prebiotics. Studies on the metabolising of pectin chains has shown that many bacteria can degrade certain regions of the polymers, generally the HG regions. This use of a plentiful polysaccharide in maintaining and encouraging digestive flora is of advantage in assessing pectin uses in the future.<sup>22</sup>

### **Cholesterol Regulation**

The mechanism of the possible hypocholesterolemic activity of pectin is not well understood. It appears that the viscosity of pectin is related to its possible hypocholesterolemic activity. Pectin preparations with high viscosity appear to be more effective in lowering cholesterol than are pectin preparations with lower viscosity. High viscosity pectin is thought to lower cholesterol levels by raising the excretion of fecal bile acids and neutral sterols. High-viscosity pectin may interfere with the formation of micelles and/or lower the diffusion rate of bile acid and cholesterol-containing micelles through the bolus, consequently diminishing the uptake of cholesterol and bile acids. Numerous studies have demonstrated that pectin has favourable effects on lipids. In a small early study, administration of 15 g of pectin daily for three weeks resulted in a mean 13% reduction in plasma cholesterol levels. There was no effect on plasma triglyceride concentrations. Subsequently, giving 40 to 50 g of pectin daily significantly lowered cholesterol levels in both normolipidemic and hyperlipidemic subjects. In another study, a pectin-supplemented diet (without other dietary or lifestyle changes), significantly reduced plasma cholesterol in volunteers evaluated to be at medium to high risk for coronary heart disease due to hypercholesterolemia. This was a double-blind, placebo-controlled trial. Treatment continued for 16 weeks. The pectin was credited with decreasing plasma cholesterol 7.6% and LDL cholesterol 10.8%.<sup>22</sup>

### **Anti-cancer Properties**

Modified citrus pectin, when administered orally to rats, was found to inhibit spontaneous prostate carcinoma metastasis. It had no effect on the growth of the primary tumour. Injected modified citrus pectin was found to inhibit metastasis of melanoma cells in mice. The mechanism of these anticarcinogenic effects is not clear. Galectins comprise a family of galactoside-binding mammalian lectins. Lectins themselves comprise a group of hemagglutinating proteins found in plant seeds, which bind the branching carbohydrate molecules of glycoproteins and glycolipids on cell surfaces, resulting in agglutination or proliferation, among other things. Galectins are proteins that can bind to carbohydrates via carbohydrate recognition domains (CRDs). At present, the galectin family includes 10 members. Apparently, galectins are secreted from cells via nonclassical secretory pathways. Galectin-3, one of the members of the family, is thought to be involved in mitosis and proliferation. On the cell surface, galectin-3 mediates cell-cell adhesion and cell-matrix interaction via binding to its complementary glycoconjugates, such as laminin and fibronectin, and thereby is thought to play an important role in the pathogenesis of cancer metastasis. Some metastatic events may involve cellular interactions that are mediated by cell surface components, including galectins. The

galactose-containing carbohydrate side chains of modified citrus pectin may interfere with these cellular interactions by competing with the natural ligands of the galectins and by doing so, inhibit the metastatic process. It is thought that galectins may play a role in human prostate cancer, and in particular, human prostate cancer metastasis.<sup>23</sup>

## EXTRACTION OF PECTINS

The production of pectin is considered to be the most reasonable utilization approach from both economical and ecological points of view. Pectin consists of 10-15% of apple pomace, on a dry weight basis and is recovered by acid extraction and precipitation. Pectin currently produced from apple pomace has more superior gelling properties than citrus pectin but presents a brown hue that may limit its incorporation into light-color foods. The color of apple pomace and extracted pectin is formed by the oxidation of phenolic constituents that are co-extracted with pectin and partially precipitated. Apple pomace has been shown to be a good source of polyphenols which are predominantly localized in the peels and are extracted into the juice to a minor extent. Major compounds isolated and identified include catechins, hydroxycinnamates, phloretin glycosides, quercetin glycosides, and procyanidins. Apple pomace contains polyphenols like epicatechin, its dimer (procyanidin B2), trimer, tetramer and oligomer, quercetinglycosides, chlorogenic acid, phloridzin and 3-hydroxy phloridzin.<sup>24-26</sup>

## Sources of Pectin

Although pectin occurs commonly in most of the plant tissues as a cementing substance in the middle lamella and as a thickening on the cell wall, the number of sources that may be used for the commercial manufacture of pectins is very limited. Because the ability of pectins to form gel depends on the molecular size and DM, the pectin from different sources does not have the same gelling ability due to variations in these parameters. Therefore, detection of a large quantity of pectin in a fruit alone is not in itself enough to qualify that fruit as a source of commercial pectin. At present, apple pomace and citrus peels are the main sources of commercially acceptable pectins. They, however, produce slightly different pectins, which make one or the other more suitable for specific applications. Other sources of pectins that have been considered are sugar beet and residues from the seed heads of sunflowers. Pectin contents of other fruits are also reported in the literature. Some of the common fruits and their pectin content are given in Table 1. In order to have a viable pectin production facility, it is necessary to have a sufficient quantity of raw material of the right quality. In the wet state, the raw material can be prone to fungal growth that produces a wide variety of pectic enzymes, both deesterifying (pectin methylesterase and depolymerizing (polygalacturonase, pectin lyase, pectate lysase). Citrus peel contains significant amounts of native pectin methylesterase. This fruit enzyme, in contrast to fungal pectin methylesterase, produces blocks of deesterified material. This may not be desirable in some specific applications. It is therefore necessary to extract pectin from raw material immediately after juice extraction or dry the residual material. It can then be stored for many months. Inevitably, some quality is lost during the drying process, as pectin is a fairly heat labile material. However, if the fruit residue (especially if it is citrus peel containing much citric acid) is well washed before drying and dried under conditions sufficient to destroy the enzyme and molds without destroying the pectin, very acceptable pectin can be produced from it. Wet raw material needs blanching soon after pressing to inactivate the enzymes. Because suitable citrus peel is not available all year round from processing factories in many places, plants have to switch to dried peels or close down during the off season of fresh fruits. Apple pomace is difficult to process unless it is first dried and stored for a while. Pomace is therefore usually brought from over a wide area from a number of drying plants. In some varieties of apples, juice can only be extracted efficiently after enzyme treatment of the pulp, and this considerably damages the pectin. Pectin from sugar beet has several disadvantages as a commercial source of pectin. In spite of its high pectin content, availability, and relatively low cost, sugar beet is not used as a raw material due to the poor gelling ability of its pectin compared with those from apple and citrus pectin. This is ascribed mainly to the high content of acetyl groups and the relatively small molecular size of pectin. Even if the other disadvantages of a low degree of esterification and the presence of an acetyl group that blocks gelation could be overcome by chemical modification, beet pectins contain a high amount of neutral sugars, often reducing the galacturonic acid contents below legally permitted limits. Studies on the structure of sugar beet pectin show that in contrast to apple and citrus pectin, beet pectin contains ferulic acid residue (0.6% w/w) bound to the non-reducing residue of side chains, as found in spinach pectin. Of the feruloyl groups, 20 to 30% are

carried by the arabinans, and the remaining groups are attached to the galactose residue. Beet pectin can be cross-linked through ferulic acid residue by treating with peroxidase and hydrogen peroxide to form a thermostable gel that may be dehydrated and rehydrated. Sugar beet pectin may therefore be used in application quite different from those of current commercial pectins, including material that can absorb and hold many times their weight of water. Michel et al. reported the extraction and characterization of pectin from sugar beet. Sunflower head residue is another potential source of available pectin. Mature sunflower heads contain 3.3 to 5.0% water soluble highmethoxyl (HM) pectin and 11.8 to 14.3% insoluble low-methoxyl (LM) pectin, while stalks have about 5% insoluble pectin. Commercially available LM pectin is obtained by deesterification of HM pectin extracted from apple pomace or citrus peel. Sunflower head residue (the white tissue that holds the seeds) is naturally rich in LM pectins. It is very high in galacturonic acid and contains low levels of amidation. If it can be extracted in perfect condition, it could further be modified to yield a useful material. Unfortunately, by the time the crop is harvested, the heads have been infected with molds, yielding poor quality pectin. Myamoto and Chang reported the extraction and physicochemical properties of pectin from sunflower head residue.<sup>27-29</sup>

Table 1. Pectin content of some fruits

Fruits	Pectic substances (% Wet Weight)
Apple ( <i>Malus spp.</i> )	0.5-1.6
Apple pomace	1.5-2.5
Banana ( <i>Musa acuminata L.</i> )	0.7-1.2
Beet pulp ( <i>Beta vulgaris</i> )	1.0
Carambola ( <i>Averrhoa carambola</i> )	0.66
Carrot ( <i>Daucus carota</i> )	0.2-0.5
Giant granadilla ( <i>Passiflora quadrangularis L.</i> )	0.4
Guava ( <i>Psidium guajava L.</i> )	0.77-0.99
Lemon pulp ( <i>Citrus limon</i> )	2.5-4.0
Lychee ( <i>Litchi chinesis S.</i> )	0.42
Mango ( <i>Mangifera indica L.</i> )	0.26-0.42
Orange peel ( <i>C. sinensis</i> )	3.5-5.5
Papaya ( <i>Carcia papaya</i> )	0.66-1.0
Passion fruit ( <i>Passiflora edulis S.</i> )	0.5
Passion fruit rind	2.1-3.0
Peaches ( <i>Prunus persica</i> )	0.1-0.9
Pineapple ( <i>Ananas comosus L.</i> )	0.04-0.13
Strawberries ( <i>Fragaria ananassa</i> )	0.6-0.7
Tamarind ( <i>Tamarindus indica L.</i> )	1.71
Thimbleberry ( <i>Rubus rosalfolius</i> )	0.72
Tomato fruit ( <i>Lycopersicon esculentum</i> )	0.2-0.6

## INTERACTIONS OF PECTIN WITH OTHER HYDROCOLLOIDS

### Interactions between Pectins and Alginates

Mixtures of pectins with other polysaccharides such as alginate has found that good gels are formed from high methoxy pectin and guluronic rich alginates. A pH above 4 also hinders the gel formation. This finding, with the added evidence of low methoxy pectin gelation with alginate at very low pH, indicates that the

chains must be sufficiently charge neutralised before interaction can occur, and that esterification is required only to reduce electrostatic repulsion. These mixed systems work well with cold setting conditions.<sup>30,31</sup>

### Interactions between Pectins and Proteins

Understanding interactions between pectins and proteins is thought to be central to developing satisfactory food texture. Mixtures of proteins and polysaccharides are prone to incompatibility or undesirable complex formation. However, due to the number of interactions possible with pectins, there are many opportunities to explore different systems. One such system sees LM pectin interacting with poly-L-lysine. In pectins with a DE of 36%, strong gels crosslinked by physical bonds with the protein were obtained at pH's close to neutrality. These clear, elastic gels had controlled increase in gel strength with added cross-linker up to an optimum. Excess protein caused increased opacity and eventual network collapse. Poly-L-lysine also serves to control network swelling. As with some hydrocolloids, chain length of the protein was found to have an optimum value, which may correspond to the different regions of the pectin molecule.<sup>32</sup>

### Interactions of Pectins with Gelatin

Gelatin is used almost exclusively in confectionery products, in which long, tough, gum-like textures are desired. For these products a dosage of 7-10% gelatin is required to reach a sufficient firmness. In some gum products even up to 15% gelatin may be necessary to obtain the desired firmness. When using gelatin alone, the low-melting temperature of the products may prove to be a disadvantage. This may be compensated by combining it with pectin. Here a part of the gelatin is replaced by a substantially smaller amount of pectin. The products are more stable at higher temperatures, thus increasing the storage stability of the confectionery products. Texture and chewing behavior of the product can be regulated by the pectin/gelatin ratio. Depending on the ratio of the two gelling agents either the pectin or the gelatin has a greater influence on the texture of the gels. With increasing pectin share the texture of the gum articles becomes more elastic and brittle, with increasing gelatin share the products become more viscous. A further positive effect of adding pectin is the reduction of the setting time compared to a pure gelatin system. With that the residence time in the mogul plant is shorter, resulting in higher production capacity.<sup>32</sup>

### Interactions of Pectins with Starch

One example of a product produced using a combination of pectin and starch, are the so-called “jelly beans”. The consumer expects a very special texture of this product and this is regulated with the pectin/starch ratio. Compared with jelly products the texture is long and viscous. Alterations in consistency can be achieved by changing the pectin/starch ratio or by the choice of the pectin or starch used. When selecting the gelling agents, the manufacturers should be consulted.<sup>33</sup>

### Combination of Pectins with Agar-agar

Agar-agar is often used as the classic gelling agent in aerated confectionery products such as marshmallows. In these products a more viscous texture can be achieved by replacing the agar-agar partially or completely with pectin. This enhances the mouth-feel factor and hence provides a more distinctive flavor. The water binding is positively influenced by pectin thus leading to better preservation and longer storage stability.<sup>33</sup>

### Interactions with Other Polymers

Interactions with other hydrocolloids has been studied in depth recently. Gel formation of LM pectins with guar, locust bean gum, oxidised starch, potato maltodextrin and gum arabic have shown there to be specific interactions between polysaccharide complexes. Complex formation between gum arabic and LM pectin (DM 31) was found to be enhanced when there was specific spatial compatibility between the HG areas of the pectin and the gum arabic fibrils. These interactions were found to be non-ionic and were more likely a hydrophobic association and stabilisation which resulted in differing gel properties. Branched hydrocolloids caused faster destabilisation of calcium induced LM pectin than linear polymers. This takes into account the interactions of branched regions in pectins with other branched regions, interactions that are highly hydrophobic and non-ionic.<sup>34</sup>

## USES OF PECTIN IN FOOD INDUSTRY

Pectin is used in foods mainly as gelling, stabilizing, or thickening agent in products such as jam, yoghurt drinks, fruity milk drinks, and ice cream. Most of the pectin used by food industry originates from citrus or apple peel from which it is extracted at low pH and high temperature and is primarily a homogalacturonan. In products that naturally contain pectin, e.g., fruit and vegetables, important quality changes during storage and processing are related to changes in pectin structure. Native or added pectic enzymes can play an important role in these changes. Pectin has always been a natural constituent of human foods. Its use is allowed in all countries of the world. The joint FAO/WHO committee on food additives recommended pectin as a safe additive with no limit on acceptable daily intake except as dictated by good. Pectin is used in a number of foods as a gelling agent, thickener, texturizer, emulsifier, and stabilizer. In recent years, pectin has been used as a fat or sugar replacer in low-calorie foods. The multifunctionality of pectin originates from the nature of its molecules in which there are polar and nonpolar regions that enable it to be incorporated into different food systems. The functionality of the pectin molecule is determined by a number of factors, including degree of methoxylation and molecular size. Because these parameters are too complicated to be determined in the industrial usage of pectins, for commercial use, functionality is evaluated by pectin grades. Pectin grades are based on the number of parts of sugar that one part of pectin will gel to an acceptable firmness under standard conditions of pH 3.2 to 3.5, sugar 65 to 70%, and pectin at the limits of 1.5 to 2.0%. Pectins of 100 to 500 grades are available in the market. Their application as a food hydrocolloid is mainly based on their gelling properties. Selection of pectin for a particular food depends on many factors, including the texture required, pH, processing temperature, presence of ions, proteins, and the expected shelf life of the product. Different uses of pectin in food and other industries are discussed in the following sections.<sup>35</sup>

### Jams, Jellies, and Preserves

Jams and jellies are the major food type using large amounts of pectins. Jam making consists of brief cooking of the fruit to liberate juice and pectin through conversion to protopectin to soluble pectin. Depending upon the requirements, additional pectins may be added at any point during this process. Pectin may be added as a dry powder mixed with sugar as dispersing medium or as a solution. It is, however, desirable to use concentrated pectin solutions due to their convenience and complete dissolution of pectin and because pectin can be added late in the process, subjecting it to less heating. Pectin solutions of concentrations ranging from 4 to 8% can be prepared by adding pectin mixed with sugar to water in a high-speed mixer. When dry powder is used, it is important to dissolve it completely before adding sugar, as sugars in excess of 20% retards the hydration of pectin. The demand for jams and jellies with less or even without sugar is on the increase, partly due to calorie-conscious consumers and partly to fill the need for sugar-free products for diabetics. In such products, LM pectin is used that forms pectin-calcium gels in the products. Other natural gums such as agar and carrageenan are also used in low-sugar products. The advantages of LM pectins over these gums is its greater stability under acid conditions, although the difficulty of controlling the setting time of LM pectin gels may be a disadvantage.<sup>35</sup>

### Conserves

Conserves are products that do not contain a sweetener other than the fruit juice or fruit concentrate. As a result, their soluble solid contents are slightly lower than the products containing sweetener. They are rated high in quality by consumers, as they do not contain any added sweetener. The soluble solid content of conserves is 55 to 62%. At the upper soluble level, a rapid set HM pectin is used, while at the lower limit, a LM pectin is added to give the desired mouth feel and body to the products.<sup>36</sup>

### Bakers' Jellies

Pectin is used to make instant jellies that are applied to many bakery products. HM pectin, being thermally stable, is used to make jellies that are placed in the batter or dough and baked without it fluidized. If the fiber content of the formula is increased, fiber entanglements will further reinforce the gel structure, making it more stable. LM pectin can be used to produce bakery jams or jellies with a wider applicable soluble solids range and acidity. The use of LM pectin requires a higher amount of pectin in the formula, compared with HM pectin, to approximate the same firmness.<sup>36</sup>

### Confectionery Products

HM pectin is used to make flavored candies. Neutral flavor pectin (no fruit flavor) can be used to make confectionery products to which an extraneous flavor of choice may be added. Pectin is also used to make artificial cherries, where the completely synthetic medium makes it possible to control setting conditions. Pectin is used in edible coatings to inhibit lipid migration in confectionery products.<sup>37</sup>

### Frozen Barriers

Pectin is used in frozen foods to retard crystal growth, loss of syrup during thawing, and to improve their shape. The greatest firming effect on frozen-then-thawed fruits are due to  $\text{Ca}^{2+}$  and pectins. Sliced fruits are firmed more than whole fruit by  $\text{Ca}^{2+}$  and pectin treatment. Drained weight is also reduced by pectin,  $\text{Ca}^{2+}$ , sucrose, and vacuum in frozen-then-thawed fruits. Coatings containing LM pectins are used to improve the texture and quality of fruits for use in ice creams. Pectin improves the texture of frozen foods by controlling the ice crystal size in them. In ice pops and lollies, pectin also reduces the tendency for flavor and color to be sucked out of the structure. Pectin is used in the preparation of gelled pudding desserts, which involves the mixing of fruit syrup containing pectin with cold milk. This results in a dessert with the consistency of a pudding without refrigeration. Use of HM pectin has been suggested for the stabilization of certain sour milk products. LM pectin is used to prevent the floatation and uneven distribution of the fruit pieces in stirred or Swiss-style yogurt. A desired product viscosity can be obtained by post fermentation mixing of stirred yogurt with pectin and fruit concentrate. Compared to starch and gum, a pectin-stabilized yogurt-fruit preparation is believed to have superior flavor release properties. LM pectin in combination with gelatin has been suggested for use in the manufacture of a sour cream mix to prevent wheying off and provide body.<sup>37</sup>

### Beverages

Dietetic soft drinks enjoy a significant share of the beverage market. Reduction in the amount of sweetener (sucrose, high fructose corn syrup, or a combination of both) deprives the beverage of a certain mouthfeel or body present in conventional soft drinks. This loss of mouthfeel can be restored by the addition of 0.05 to 0.10 % HM pectin. The addition of pectin to a dietetic fruit juice beverage containing fruit pulp reduces "hardpacking" (deposition of fruit pulp into a hard mass that is difficult to disperse) in them. Pectin is also used as a beverage-clouding agent.<sup>37</sup>

### Barbecue Sauce

In some retail brands of barbecue sauce, LM pectin is added due to its flavor release attributes and the texture it provides. The LM pectin and calcium content in the formula determines the product's final consistency and texture.<sup>38</sup>

## USES OF PECTINS IN PHARMACEUTICAL INDUSTRY

Pectin has applications in the pharmaceutical industry. Pectin favorably influences cholesterol levels in blood and also acts as a natural prophylactic substance against poisoning with toxic cations. It has been shown to be effective in removing lead and mercury from the gastrointestinal tract and respiratory organs. When injected intravenously, pectin shortens the coagulation time of drawn blood, thus being useful in controlling hemorrhage or local bleeding. Pectin sulfate, on the other hand, prolongs clotting time and can be used in place of heparin. Pectin sulfate, however, is toxic, and this limits its long-term and high-dose uses. A complex of degraded pectin iron is reported to be useful for the treatment of iron deficiency anemia. A bismuth-D-galacturonan mixture is found to be an effective means of administering bismuth in medicinal preparations. Pectin has been reported to help reduce blood cholesterol in a wide variety of subjects and experimental conditions. Consumption of at least 6 g/d of pectin is necessary to have a significant effect on cholesterol reduction. Amounts less than 6 g/d are not effective. Mietinnen and Tarplia reported a 13% reduction in serum cholesterol within 2 weeks of treatment. Cedra et al. found that pectin supplementation in the diet of patients at risk of coronary heart diseases decreased their blood cholesterol by 7.6%. Prickly pear (*Opuntia spp.*) pectin intake decreased plasma low-density lipoprotein (LDL) concentration without affecting cholesterol absorption in guinea pigs by altering hepatic cholesterol homeostasis. DM has no effect on the cholesterol-lowering effect of pectin. In a few studies, pectin had no influence on blood cholesterol in tested subjects. Pectin and combinations of pectin with other colloids have been used

extensively to treat diarrheal diseases, especially in infants and children. Although a bactericidal action of pectin has been proposed to explain the effectiveness of pectin in treating diarrhea, most experimental results do not support this theory. However, some evidence suggests that under certain *in vitro* conditions, pectin may have a slight antimicrobial action toward *Escherichia coli*. Pectin reduces the rate of digestion by immobilizing food components in the intestine. This results in less absorption of food. The thickness of the pectin layer influences the absorption by prohibiting contact between the intestinal enzyme and the food, thus reducing the latter's availability. Due to its large water-binding capacity, pectin gives a feeling of satiety, thus reducing food consumption. Experiments showed a prolongation of the gastric emptying half-time from 23 to 50 min of a meal fortified with pectin. The gastric emptying half-time is doubled by the intake of 20 g of apple pomace per day for 4 weeks. These attributes of pectin are used in the treatment of disorders related to overeating. A mixture of LM pectin, aluminum hydroxide, and magnesium oxide has been reported to be useful in the treatment of gastric and duodenal ulcers. Pectin alone or in combination with gelatin is used as an encapsulating agent for the sustained release of medicine. HM pectin is claimed to promote sustained release of aspirin and act as a demulcent in minimizing the gastrointestinal irritation sometimes noted during its administration. Tests with human subjects and dogs indicate a lack of pectin-degrading enzymes in saliva and gastric juice. Likewise, trypsin, pepsin, and rennet have no effect on pectin *in vitro*; however, pectin incubated with feces is rapidly decomposed. Studies in human and animals with occurs chiefly in the colon, most likely by the action of bacterial enzymes. The main products formed during bacterial fermentation of pectin are carbon dioxide, formic acid, and acetic acid. Icostomies indicate that the breakdown of pectin occurs chiefly in the colon, most likely by the action of bacterial enzymes. The main products formed during bacterial fermentation of pectin are carbon dioxide, formic acid, and acetic acid.<sup>38,39</sup>

### OTHER USES OF PECTIN

Pectin has been found useful in other industrial applications. They function as an emulsion stabilizer for water and oil emulsions. Films made from natural products are of increasing interest because they are biodegradable and potentially recyclable and may even be used in some *in vivo* pharmaceutical applications. A number of studies have been done on pectin films. Because of its film forming properties, pectin is useful as a sizing agent for paper and textiles. It is useful for the preparation of membranes for ultracentrifugation and electro dialysis. Pectin is used in sulfuric sol for use in lead accumulators. Sol free of air bubbles are prepared by blending pectin at a level of approximately 1% into sulfuric acid. Blends of pectin and starch can be used to make strong, self-supporting films. Pectins have been used in making biodegradable drinking straws in which coloring and flavoring substances in a pectin layer are released when liquids pass through the straw. Other nonfood uses of pectin are reported by endress. The molecular basis of gelation in pectin has helped us to understand some aspects of this complex phenomenon. There are still some areas where our knowledge is limited. Rhamnose, as described earlier, interrupts junction zone formation in pectin by forming a kink in the molecule. There is no systemic study on the effect of rhamnose amount and arrangement in the polygalacturonic backbone on the gelation of pectins. Similarly, earlier studies have shown that calcium and other ions, in addition to LM pectin, also affect the gelation of HM pectin, but no further studies have been done in this direction. A systemic study of these observations will help understanding of the gelation process in pectin gels, resulting in better control of processes and product.<sup>40</sup>

### CONCLUSION

Pectin is one of extensively studied natural biodegradable polymer formulations for drug delivery, wound dressing and tissue engineering. Pectin has numerous benefits as formulation because it can be easily tailored in to hydrogels, films, scaffolds, microparticles, and nanoparticles. Pectin has been used from ancient times in food applications but its application in controlled delivery is still infancy. As the research and development continues in pectin based formulations, we expect to see many innovative and exciting applications in near future. At present great advances of fundamental importance have been made, especially in the elucidation of the main features of the chemical structure, physicochemical properties and biological activity of pectins.

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## DECLARATION OF INTEREST

It is hereby declared that this paper does not have any conflict of interest.

## REFERENCES

1. Rolin C, Vries J. Introduction of pectin. American Chemical Society, London: Elsevier. 1990; 14: 401–434.
2. Pilgrim GW, Walter RH, Oakenfull DG. The properties and advantages of pectin. Academic Press Inc. 1992; 13: 23–50.
3. Sakai T, Sakamoto T, Hallaert J, Vandamme E. Pectin, pectinase and protopectinase: production, properties and applications. *Adv Appl Microbiol.* 1993; 39: 213-294.
4. May CD. Industrial pectins, properties and applications. In: *Carbohydrate Polym.* 1990; 12: 91-107.
5. Crandall PG, Wicker L. Pectin internal gel strength: Theory, measurement, and methodology. ACS symposium series. 1986; 310: 88-102.
6. Axelos MAV, Thibault J.F. High methoxy and low methoxy pectin. Academic Press Inc. 1991; 10: 333-342.
7. Gross MO, Rao VNM, Smit CJB. Rheological characterization of low methoxyl pectin gel by normal creep and relaxation. *J Text Stud.* 1980; 11: 271-288.
8. Ridley B, Mohnen D. Pectins: classification, structure, biosynthesis and Oligo galacturonide-related signaling. *Phytochemistry.* 2001; 57: 929-967.
9. Vincken JP, Schols HA, Oomen RJFJ. If homogalacturonan were a side chain of rhamnogalacturonan I: implications for cell wall architecture. *Plant Physiol.* 2003; 132: 1781-1789.
10. Schols HA, Voragen AJ. Pectin structure. In *Pectin and Pectinase Elsevier Science: Amsterdam.* 1996; 12: 3–19.
11. Behall K, Reiser S. Structural Chemistry and Function of Pectins. *Am Chem Soc.* 1991; 32: 248–265.
12. Jarvis MC. Structure and properties of pectin gels in plant cell wall. *Plant Cell Environ.* 1984; 7: 153-163.
13. Tolkunova NN, Zhitnikova VS, Kozicheva MA. Analysis of the activity of soluble pectin from the degree of etherification and complexing ability. *Technology and Merchandizing of Innovation Food Products.* 2012; 2: 24-28.
14. Wolf S, Mouille G, Pelloux J. Homogalacturonanmethyl-esterification and plant development. *Mol. Plant.* 2009; 2: 851–860.
15. Oakenfull DG, Scott AG. Gelation of high methoxy pectins. *Food Technology in Australia.* 1985; 37: 156–158.
16. Willats WGT, Knox P, Mikkelsen JD. Pectin: new insights into an old polymer are starting to gel. *Trends Food Sci Technol.* 2006; 17: 97-104.
17. Oakenfull D Scott A. Hydrophobic interaction in the gelation of high methoxyl pectins. *J Food Sci.* 1984; 49: 1093-1100.
18. Hills HC, Mottern HH, Nutting GC, Rudolph S. Enzyme demethylated pectins and their gelation. *Food Technol.* 1949; 3: 90-112.
19. Morris ER, Gidley MJ, Murray EJ, Powell DA, Rees DA. Characterization of pectin gelation under conditions of low water activity by circular dichroism, comparative inhibition and mechanical properties. *Int J Biol Macromol.* 1980; 2: 327-333.
20. Rombout FM, Voragen AGJ, Pilnik W. Enzymic degradation of apple pectins, *Carbohydrate Polym.* 1982; 2: 82-90.
21. Shamkova NT. The binding ability of pectin-containing food systems. *Bulletin of Higher Educational Institutions, Food Technology.* 2006; 5: 20-22.
22. Gibson GR. Fibre and effects on probiotics (the prebiotic concept). *Clinical Nutrition Supplements.* 2004; 1: 25-31.
23. Hawang J, Kokini JL. Contribution of the side chains to rheological properties of pectins. *Carbohydrate Polym.* 1992; 41: 92-100.

24. Simpson BK, Egyankor KB, Martin M. Extraction, purification and determination of pectin in tropical fruits. *J. Food Process Preserv.* 1984; 2: 63-84.
25. Kratchanova M, Pavlova E, Panchev I. The effect of microwave heating of fresh orange peels on the fruit tissue and quality of extracted pectin. *Carbohydrate Polymers.* 2004; 56: 181–185.
26. Thibault JF, Ralet MC. Physico-chemical properties of pectins in the cell walls after extraction. *Advances in pectin and pectinase research.* 2003; 5: 91-105.
27. Srivastava P, Malviya R. Sources of pectin, extraction and its applications in pharmaceutical industry – An overview. *Indian J Nat Prod Resour.* 2011; 2: 10–18.
28. Barret AJ, Northcote DH. Apple fruit pectic substances. *Biochem J.* 1965; 94: 617-625.
29. Piriyaarasath S, Sriamornsak P. Flocculating and suspending properties of commercial citrus pectin and pectin extracted from pomelo (*Citrus maxima*) peel. In: *Carbohydrate Polym.* 2011; 83: 561-568.
30. Shalom N, Pinto R. Natural colloidal particles: the mechanism of the specific interaction between alginates and pectin. In: *Carbohydr. Polym.* 1997; 38: 179-182.
31. Powell DA. Conformation and interaction of pectins: II. Influences of residue sequence on chain association in calcium pectate gels. *Journal of Molecular Biology.* 1982; 155: 517-531.
32. Endress H. *The Interaction and Technology of Pectin.* Academic Press. 1991; 31: 251–268.
33. Marudova M, MacDougall A, Ring S. Physicochemical studies in pectin/poly-Llysine Gelation. *Carbohydrate Research.* 2004; 339: 209-216.
34. Nawawi SA, Heinkel YA. Factors affecting gelation of high ester citrus pectin. *Process Biochemistry.* 1997; 32: 381–385.
35. Pilgrim GW, Walter RH, Oakenfull DG. Jams, jellies, and preserves. *The Chemistry and Technology of Pectin.* Academic Press. 1991; 23: 211-216.
36. Hinton C L. The setting temperature of pectin jellies. *Journal of the Science of Food and Agriculture.* 1950; 1: 300-307.
37. Tikhomirova NA, Zaiko GM, Korneva OA. Functional beverage foods based on soy milk and pectin-containing wild-growing plant raw materials. *Bulletin of Higher Educational Institutions, Food Technology.* 2012; 2(3): 95-96.
38. Thakur BR. Chemistry and uses of pectin – A review. *Critical Reviews in Food Science and Nutrition.* 1997; 37: 47-73.
39. Yamada H, Kiyohara H, Matsumoto T. *Advances in pectin and pectinase research.* Kluwer Academic Publishers. 2003; 21: 481–490.
40. Demidova TI, Shevernitskaya ON. Priority directions of development of technologies for the manufacture of pectin-containing products. *Food Industry.* 2010; 9: 18-19.

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