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Chemistry and Uses of Pectin — A Review

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ABSTRACT: Pectin is an important polysaccharide with applications in foods, pharmaceuticals, and a number of other industries. Its importance in the food sector lies in its ability to form gel in the presence of Ca²⁺ ions or a solute at low pH. Although the exact mechanism of gel formation is not clear, significant progress has been made in this direction. Depending on the pectin, coordinate bonding with Ca²⁺ ions or hydrogen bonding and hydrophobic interactions are involved in gel formation. 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. A number of factors—pH, presence of other solutes, molecular size, degree of methoxylation, number and arrangement of side chains, and charge density on the molecule—influence the gelation of pectin. In the 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. Other applications of pectin include use in edible films, paper substitute, foams and plasticizers, etc. In addition to pectolytic degradation, pectins are susceptible to heat degradation during processing, and the degradation is influenced by the nature of the ions and salts present in the system. Although present in the cell walls of most plants, apple pomace and orange peel are the two major sources of commercial pectin due to the poor gelling behavior of pectin from other sources. This paper briefly describes the structure, chemistry of gelation, interactions, and industrial applications of pectin.

KEY WORDS: pectin, polysaccharide, hydrogen bonding, hydrophobic interactions.

I. PECTIN IN PLANT CELL WALLS

Pectins are a class of complex polysaccharides found in the cell walls of higher plants, where they function as a hydrating agent and cementing material for the cellulosic network.¹ They are commonly produced during the initial stages of primary cell wall growth and make about one third of the cell wall of dry substances of dicotyledonous and some monocotyledonous plants.²⁻⁴ The main exceptions are the cell walls of the Graminae family, which may contain pectin of normal structure but in very small amounts.^{5,6} There is limited information available on other monocotyledonous families, but at least some are known to have conventional or unconventional pectin in normal quantities.⁷⁻¹¹ Most plants con-

tain pectin in the intercellular layer between the primary cell wall of adjoining cells. The highest concentration of pectins in the cell wall is seen in the middle lamella, with a gradual decrease from the primary cell wall toward the plasma membrane. Pectins are found in relatively large amounts in soft plant tissues under conditions of rapid growth and higher moisture contents. They seem to play a role in control of the movement of water and plant fluids through the rapidly growing parts.¹² For many years it has been disputed whether calcium-stabilized ionic bonding is sufficient to retain pectins in the cell wall or whether other types of bonding, particularly the covalent bonds, are more important.^{13,14} Opposing views are reported in this regard.^{15,16} Covalent bonds between pectin and hemicellulose have been

reported in the plant cell wall,^{15,17} but it does not show that all the pectin fractions are held in this way. Some amounts of pectins are often removed from the cell wall during their preparation and extraction with cold water, indicating the presence of unbound pectin in them.¹⁸⁻²⁰

Pectins contribute to the firmness and structure of plant tissue both as a part of the primary cell wall and as the main middle lamella component involved in intercellular adhesion, similar to the intercellular substance of animal origin (e.g., collagen)^{12,21} (Figure 1). The strength of the plant cell wall depends on the orientation, mechanical properties, and links between pectic substances and cellulose fiber.²² Some pectin molecules are glycosidically linked to xyloglucan chains that can bind covalently to cellulose.^{15,17,23} The firming effect of pectin in tissues involves two separate phenomena: in fresh tissue, the formation of free carboxyl groups increases the possibilities and the strength of calcium binding between pectin polymers, and in heated tissue there is a combination of increased calcium binding and a decrease in the susceptibility of the pectin to

depolymerization by β -elimination.²⁴ In many tissues such as apple and tomatoes, the normal decrease in the degree of methoxylation (DM) (increase in carboxyl groups) is not accompanied by firming during ripening.^{25,26} Softening during the ripening of fleshy fruits is attributed to enzymatic degradation and solubilization of the protopectin.²⁷⁻³⁶ The general concept is that textural changes occur as cell wall pectins are hydrolyzed by polygalacturonases. This concept is based on the correlation observed between polygalacturonase activity and fruit softening in some fruits such as tomato.³⁷⁻³⁹ Robertson and Swinburne³⁵ reported a significant inverse relationship between the firmness of unpeeled kiwifruit and its water-soluble high methoxyl pectin content. Ben-Shalom et al.⁴⁰ found that after blanching and degradation, the molecular weight of the water-soluble pectin from carrot increased 2.5 fold and that of EDTA-soluble pectin increased 2.3 fold, compared with untreated tissues. Dehydration without blanching drastically decreased the molecular weight of pectin in both the fractions. The observed increase in molecular weight in blanched tissues can be attributed to

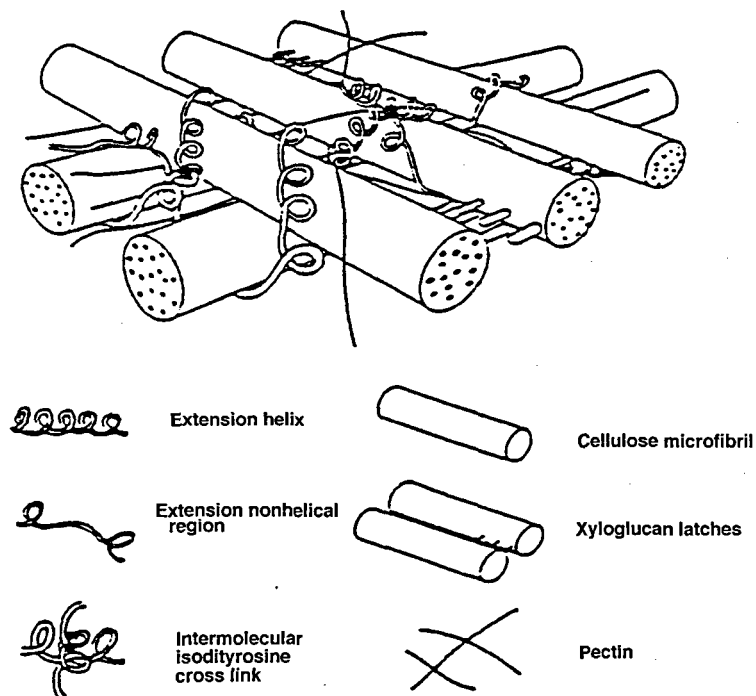


FIGURE 1. Three-dimensional view of polymer arrangement in the plant cell wall. (From Wilson, L. G. and Fry, S. C., *Plant Cell Environ.*, 9, 239, 1986. With permission.)

inactivation of pectolytic enzymes. A survey of 15 species of plants showed seven species having a preferential loss of galactose and seven having a preferential loss of arabinose during ripening.⁴¹ A good part of these neutral sugar residues can come from pectin side chains. This could increase the susceptibility of pectin to polygalacturonase (PG) and pectin methylesterase (PME) by making it more accessible to these enzymes. Loss of side chains would also reduce the entanglement of the pectin molecule increasing the slippage factor. A variety of glycosidases are implicated in the removal of neutral sugars from pectin side chains.⁴² Nonetheless, several other studies suggested that additional mechanisms are involved in tissue softening.⁴³⁻⁴⁸ Fishman et al.⁴⁸ suggested the possible loss of cell wall integrity and pectin degradation by mechanisms other than hydrolytic cleavage, that is, nonenzymatic mechanisms of pectin degradation such as by changes in the ionic strength of fluids that solvate the cell wall. In a recent study, Batisse et al.⁴⁹ reported that softening during ripening in cherry fruits does not depend upon pectin depolymerization. Pectins are among the cell wall components whose collective ability to contain the turgor pressure of the cell wall determines whether extension growth will take place.⁵⁰ As structural components of plant cell walls, native pectins play an important role in many quality aspects of fruits and vegetable products.⁵¹

Pectin synthesis beginning from UDP-D-galacturonic acid and taking place in the golgi system is performed during the early stages of growth in young enlarging cell walls.^{52,53} It has been suggested that the carboxyl groups of pectins are highly methylesterified when they are synthesized, but esters are later cleaved by PME present in the cell wall.^{54,55} Reduction in PME and PG activity in tomato fruits results in the pectin of higher DM and higher molecular weight.^{56,57} Tieman and Handa⁵⁸ reported that reduced PME activity in tomato causes an almost complete loss of tissue integrity during fruit senescence but shows little effect on fruit firmness during ripening. It also modifies both accumulation and partitioning of cations between soluble and bound forms of pectin and selectively impairs the accumulation of Mg^{2+} ions over other cations.

Pectins are present in various stages of molecular development and transformation that are

dependent on the specific morphology and taxonomy of the plants as well as the stage of growth and maturity.¹² For example, Li et al.⁵⁹ reported that the esterified pectin that prevents Ca^{2+} -induced gelation of pectates is located predominantly at the apex of the pollen tube of flowering plants. This is required for the tip wall loosening that is necessary for cell wall expansion during the growth of the pollen tube. The occurrence of unesterified pectins in other areas of the pollen tube wall suggests that deesterification of pectins following tip expansion leads to a more rigid form of pectin that contributes to the construction of the pollen tube wall. Pectin in *Populus x-auramericana* represents about 9% of the cell wall dry material in spring and 7% in summer and winters. Histochemical observation of the material treated with hot water and EDTA shows relatively low pectin content during the rest period.⁶⁰ In cell walls of elongating tobacco cells unadapted to a high concentration of sodium chloride, pectin molecules are oriented within the wall in a manner similar to cellulose, whereas in an adapted cell wall there is no clear orientation.⁶¹ Evidence from high-resolution images of the primary cell wall suggests that the tomato cell wall is constructed from at least two independent networks, one based on cellulose/hemicellulose and the other on pectin. Reduction in the cellulose/hemicellulose network does not affect the thickness of the cell wall formed or the spacing of pectin molecules.⁶² Esteban et al.⁶³ reported the role of pectic substances in the texture maintenance of eggplant fruit. Pectin esterification is also reported to play a role in plant resistance to certain diseases.⁶⁴

II. 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.⁶⁵ 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.⁶⁶ Other sources of pectins that have been considered are sugar beet and residues from the seed heads of sunflowers.^{67,68} Pectin contents of other fruits are also reported in the literature^{3,66-71} (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 methyl-esterase, EC 3.1.1.11) and depolymerizing (polygalacturonase, EC 3.2.1.15; pectin lyase, EC 4.2.2.10; pectate lysase, EC 4.2.2.2). Citrus peel contains significant amounts of native pectin

methylesterase. This fruit enzyme, in contrast to fungal pectin methylesterase, produces blocks of deesterified material.⁶⁶ 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.⁶⁶

Apple pomace is difficult to process unless it is first dried and stored for a while.⁶⁷ 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.⁷¹

Pectin from sugar beet has several disadvantages as a commercial source of pectin.⁶⁷ 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.^{67,69-71} 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.⁶⁶ 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 nonreducing residue of side chains, as found in spinach pectin.^{67,72} Of the feruloyl groups, 20 to 30% are carried by the arabinans, and the remaining groups are attached to the galactose residue.⁷³ Beet pectin can be cross-linked through ferulic

TABLE 1
Pectin Content of Some Fruits

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

^a Data taken from Reference 53.

^b Data taken from Reference 71.

^c Data taken from Reference 229.

acid residue by treating with peroxidase and hydrogen peroxide to form a thermostable gel that may be dehydrated and rehydrated.⁶⁷ 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.⁶⁶ Michel et al.⁶⁹ reported the extraction and characterization of pectin from sugar beet.

Sunflower head residue is another potential source of available pectin.⁷⁴ Mature sunflower heads contain 3.3 to 5.0% water soluble high-methoxyl (HM) pectin and 11.8 to 14.3% insoluble low-methoxyl (LM) pectin, while stalks have about 5% insoluble pectin.⁷⁵ 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.⁶⁸ Unfortunately, by the time the crop is harvested, the heads have been infected with molds, yielding poor-quality pectin.⁶⁶ Myamoto and Chang⁶⁸ reported the extraction and physicochemical properties of pectin from sunflower head residue.

III. STRUCTURE OF PECTIN

The chemical structure of pectin has been the subject of many scientific investigations for decades. Elucidation of pectin structure is important to understand its role in plant growth and development, during ripening of fruits, in food processing, and as a nutritional fiber. 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.⁷⁶ 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.⁵² Pectin extracted from the apple or sugar beet cell wall at different pHs and temperatures has different

amounts of neutral and acidic sugars, and its gelling properties decrease, while the ash content increases with increasing temperature of extraction.^{72,77} Pectins are primarily a polymer of D-galacturonic acid (homopolymer of [1 → 4]α-D-galactopyranosyluronic acid units with varying degrees of carboxyl groups methylesterified) and rhamnogalacturonan (heteropolymer of repeating [1 → 2]α-L-rhamnosyl-[1-L]α-D-galactosyluronic acid disaccharide units), making it an α-D-galacturonan.⁷⁸ The molecule is formed by L-1,4-glycosidic linkages between the pyranose rings of D-galacturonic acid units. As both hydroxyl groups of D-galacturonic acid at carbon atom 1 and 4 are on the axial position, the polymer formed is a 1,4-polysaccharide^{52,79} (Figure 2). 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.⁵⁰ These branched and unbranched blocks may be extracted separately from cell walls degraded by purified pectic enzymes^{10,80-83} or separately after chemical or enzymatic depolymerization of pectins in solution.^{19,84,85} Rhamnogalacturonan is primarily responsible for the chemical and structural complexity of the pectic substances. These rhamnosyl insertions are incompatible with the regular conformation of poly-D-galacturonates and therefore acts as a junction delimiting kinks during gelation of the pectin gels^{86,87} (as discussed later) (Figure 3). The frequency of rhamnose occurrence remains to be established, although it has been suggested that α-rhamnosyl units may be concentrated in rhamnose-rich areas interposing relatively long galacturonan segments.

In the unbranched blocks, rhamnose may be absent or may be spaced about 25 units apart.^{88,89} In the branched block of the molecule, both arabinan and galactan chains are attached to rhamnose, with further arabinan segments on the galactan chains.^{78,81,90} There may be different types of branched blocks in pectins from one cell wall or even within a single pectin molecule. Often, arabinan, galactan, or arabinogalactan side chains are linked [1 → 4] to the rhamnose. In the side chains, the arabinose units have [1 → 5] linkages, while galactose units are mutually joined by [1 → 4] linkages; [1 → 3] and [1 → 6] linkages also

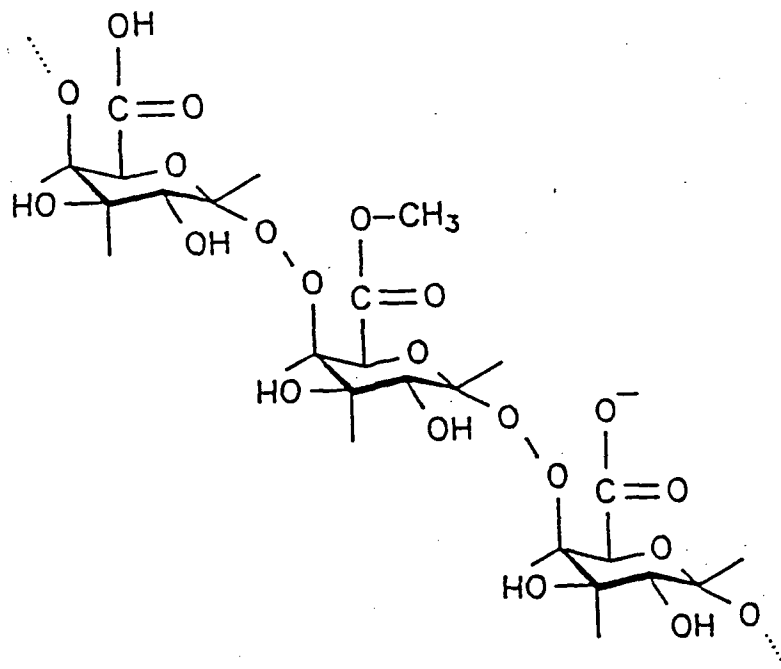


FIGURE 2. A repeating segment of the pectin molecule. (From Okenfull, D. G., in *The Chemistry and Technology of Pectin*, Walter, R. H., Ed., Academic Press, New York, 1991, 87. With permission.)

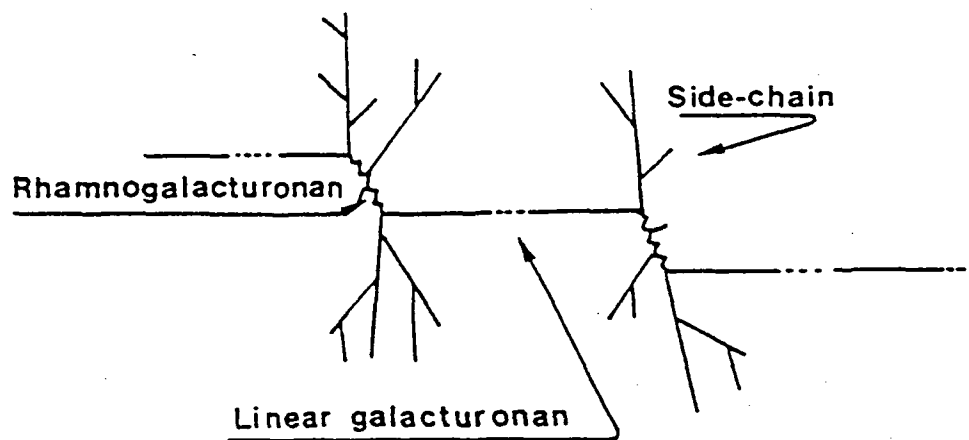


FIGURE 3. Schematic representation of pectin backbone showing the "hairy" regions (rhamnogalacturonan and side chains) and the "smooth" regions (linear galacturonan). (From Axelos, M. A. V. and Thibault, J. F., in *The Chemistry and Technology of Pectin*, Walter, R. H., Ed., Academic Press, New York, 1991, 109. With permission.)

occur. Neutral sugars other than L-rhamnose occur exclusively in the side chains of pectins. D-galactopyranose, and L-arabinofuranose occur most frequently; D-xylopyranose, D-glucopyranose, and L-fucopyranose are less common units, while rarely found sugars such as D-apiose, 2-O-

methyl-D-xylose, and 2-O-methyl-fucose are usually very minor but widespread constituents of pectin molecules.^{85,91,92} These neutral sugars amount to 10 to 15% of the pectic weight.^{93,94} The size of neutral sugar side chains differ between the sparsely rhamnosylated and the densely

rhamnosylated regions. The neutral sugar chain length in a sparse region may be nine to ten residues, while a dense region may have a chain length of 8 to 20 residues.^{85,95} The dense and sparse regions are also called hairy and smooth regions, respectively.⁸⁵ As stated earlier, pectin from sources such as beet have acylation on the uronide residue. Acylation occurs at the 3-O position of the uronide in the rhamnose-rich portion of the pectin molecule. Ferulate and coumarate are attached to the neutral sugar.^{96,97}

Polygalacturonic acid could be considered as a rod in solution, whereas pectins are segmented rods with flexibility at the rhamnose tees.⁹⁸ The size, charge density, charge distribution, and degree of substitution of pectin molecules can be changed biologically or chemically.⁹⁹

IV. INTERACTIONS OF PECTINS

A. Solubility and Dispersibility

Based on solubility, two different types of pectins exist: water-soluble or free pectin and the water-insoluble pectin. Solubility in water is related to their degree of polymerization and the number and distribution of methoxyl groups. Generally, solubility increases with decreasing molecular weight and increases in the esterified carboxyl groups, although solution pH, temperature, and the nature and concentration of the solute present have a marked effect on solubility.^{65,100} The solubility can be increased by preventing molecular association by sterical (presence of substituent group) or chemical (charge) factors.⁵³

The ease of solubilization of commercial pectin is usually more important than absolute solubility, and this in turn is determined largely by its dispersibility. 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 solubilization 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. Fine-powdered sugar or D-glucose are the com-

mon dispersing agents and are mixed with pectin in amounts of five to ten parts by weight to increase pectin dispersibility.¹⁰⁰

B. Gelation

The most unique and outstanding property of pectins is their ability to form gels in the presence of Ca^{2+} ions or sugar and acid. It is this property of pectins that makes them an important ingredient of many food products. The physical characterizations of gel are the consequence of the formation of a continuous three-dimensional network of cross-linked polymer molecules.¹⁰¹ On a molecular level, an aqueous gel consists of three elements:⁵⁰

1. Junction zones where polymer molecules are joined together
2. Interjunction segments of polymers that are relatively mobile
3. Water entrapped in the polymer network

A junction zone may involve a single covalent bond between two chains or a combination of hydrogen bonds and hydrophobic interactions between two polymer chains running side by side. Although the formation of a stable intermolecular junction is a critical requirement for gelation, some limitations on the interchain association is also necessary to give a hydrated network rather than an insoluble precipitate.⁸⁶ A polymer that forms no junction zones could simply remain in solution, and the one forming junction zones throughout its length would be insoluble unless entropic factors kept the chains apart.⁹⁶ It is possible to estimate the proportion of the chain involved in junction zones and interjunction zones by broadline H nuclear magnetic resonance (NMR) spectra.¹⁰² At the molecular level, pectin gels may be considered to be homogeneous and an "association network" as opposed to the particulate nature of many denatured protein gels.¹⁰³ In fruit products, pectins contribute to the consistency and texture of the products primarily through their ability to form gels that consist of a network of polymer molecules cross-linked to each other in a liquid medium. In pure pectin gels and fruit products, this liquid phase is water. The gel strength

and sometimes the overall characteristics of the gel can be altered by varying the degree of polymerization and the chemical functionality of the pectin chain. Such variations also cause changes in gel texture, which is one of the most important factors affecting consumer acceptability of gelled products. Degree of esterification, attached chains of neutral sugars, acetylation, and cross-linking of pectin molecules also affect the texture of pectin gels.⁶⁰ Pectin chains carry a negative charge, and the charge density is higher at a higher pH and lower DM.¹⁰⁴ Depending upon the charge density, pectin molecules repel each other, which interferes with the interchain association of pectin chains in solution. Conformation of the pectin molecule is not affected by the branching, but side branching in pectin can result in significant entanglement in concentrated solutions.¹⁰⁵

Depending on the degree of methoxylation, pectins are classified into (1) LM (25 to 50%) and (2) HM (50 to 80%) pectins and form gels of two types with occasional intermediates. They are called acid and calcium gels and are formed from HM and LM pectins, respectively. The mechanism of gel formation is different in both HM and LM pectins. HM pectins form gels if the pH is below 3.6 and a cosolute is present, typically sucrose at a concentration greater than 55% by weight. The function of sugar in the formation of gels of HM pectins is to stabilize junction zones by promoting hydrophobic interactions between ester methyl groups. The effect of sugars thus depends specifically upon the molecular geometry of the sugar and the interactions with neighboring water molecules.¹⁰⁶ Noncovalent forces (i.e., hydrogen bonding and hydrophobic interactions) are believed to be responsible for gel formation in HM pectins.¹⁰⁷⁻¹⁰⁹ In LM pectins, gel is formed in the presence of Ca^{2+} , which acts as a bridge between pairs of carboxyl groups of pectin molecules. LM pectins are chemically more stable to moisture and heat than are HM pectins because of the latter's tendency to deesterify in a humid atmosphere. The two kinds of pectins are relatively stable at the low pH levels existing in jams and jellies.¹¹⁰ Gelation in pectins is greatly affected by both intrinsic and extrinsic parameters, including the DM, charge distribution along the backbone, average molecular weight of the sample,

ionic strength, pH, temperature, and presence of cosolute. Pectins can be further divided into rapid-set, medium-set, and slow-set pectins, depending upon the time the gel takes to set.¹¹¹

1. Gelation of Low Methoxyl Pectins

Gelation in LM pectin results from ionic linkages via calcium bridges between two carboxyl groups belonging to two different chains in close contact.⁸⁶ The interactions between Ca^{2+} ions and carboxyl groups of the pectin are described by the egg box model involving a two stage process of initial dimerization and subsequent aggregation of preformed egg boxes^{14,89} (Figure 4). The mechanism involves the formation of junction zones consisting of dimers in 2_1 helical symmetry similar to the 2_1 model proposed for alginates.¹¹² The egg box structure has been suggested to provide stability to the middle lamella in the plant cell wall.^{14,113} The size of the egg box junction zones is limited by the presence of sequences containing mannuronate residues, which interrupt the polyguluronate blocks.¹⁰⁹ The pH should be higher in the gelation of LM pectin because only dissociated carboxylic groups take part in the salt-like cross-linkages.¹² The junctions are formed between unbranched nonesterified galacturonan blocks bound together noncovalently by coordinated calcium ions¹⁰⁹ (Figure 5). The strong interaction between calcium and other oxygen atoms on the pectin has been described by Rees et al.¹¹⁴ The complex involves coordination bonds utilizing the unfilled orbitals of the calcium ion. The oxygen atoms of the hydroxyl groups, the ring oxygen atom, and the bridging oxygen atoms of the component sugar units participate in the bonding process through their free electrons.¹¹² The calcium is particularly effective in complexing with carbohydrates, in large part because the ionic radius, 0.1 nm, is large enough to coordinate with oxygen atoms spaced as they are in many sugars and because of a flexibility with regard to the directions of its coordinate bonds.¹¹⁵ The presence of methyl groups prevents the formation of junction zones in the interjunction segments of molecules, making them more flexible. Side chains on the molecule prevent their aggregation.¹¹⁶ The

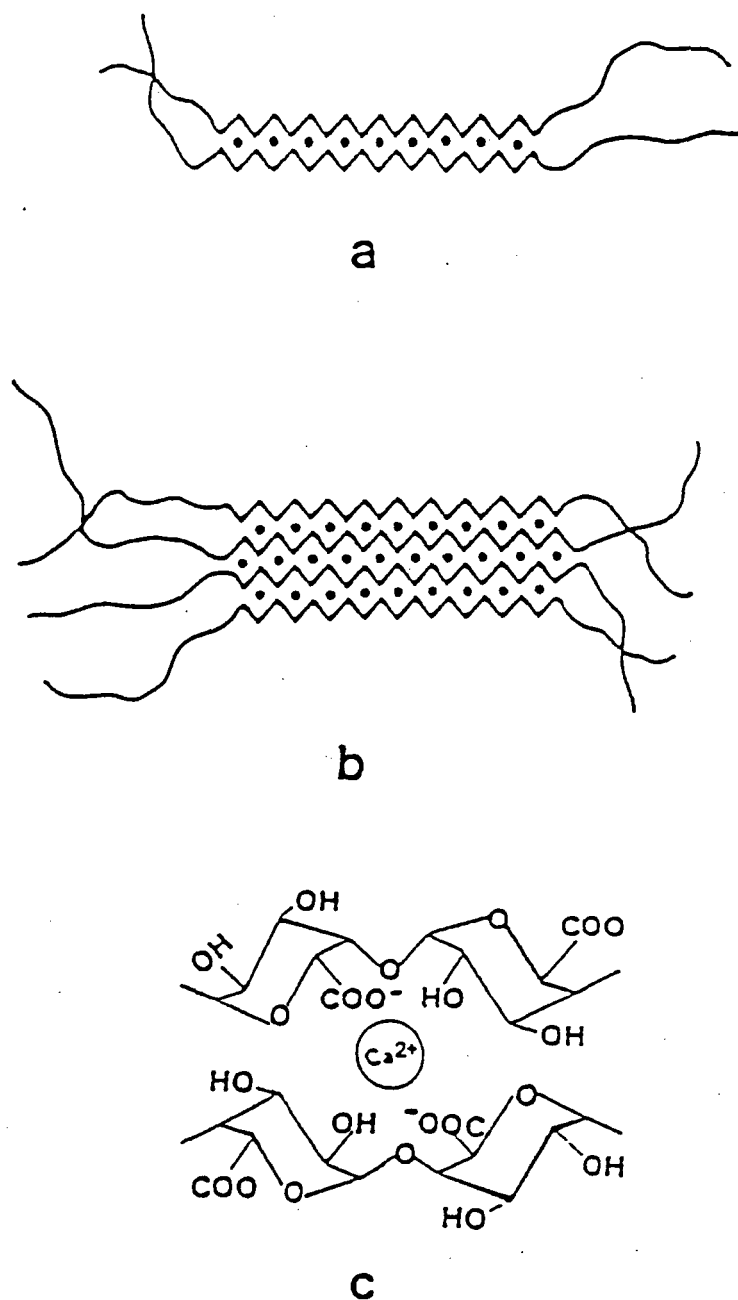


FIGURE 4. Schematic representation of calcium binding to polygalacturonate sequences. (a) "Egg-box" dimer; (b) aggregation of dimers; (c) an "egg-box" cavity. (From Axelos, M. A. V. and Thibault, J. F., in *The Chemistry and Technology of Pectin*, Walter, R. H., Ed., Academic Press, New York, 1991, 109. With permission.)

greater the number of reactive carboxyl groups that can form salt linkages, the more likely it is that the bridge will be formed.¹² In addition, the molecules with an increased number of charged groups and lower degree of methoxylation are straighter than esterified ones, and hence more

likely to form a Ca²⁺ bridge.^{12,117} The size of the aggregate that forms the junction zone depends on how much calcium is available. Depending on the calcium concentration, pectins have been suggested to form different types of aggregates.^{112,118} Under low calcium levels, polygalacturonate forms

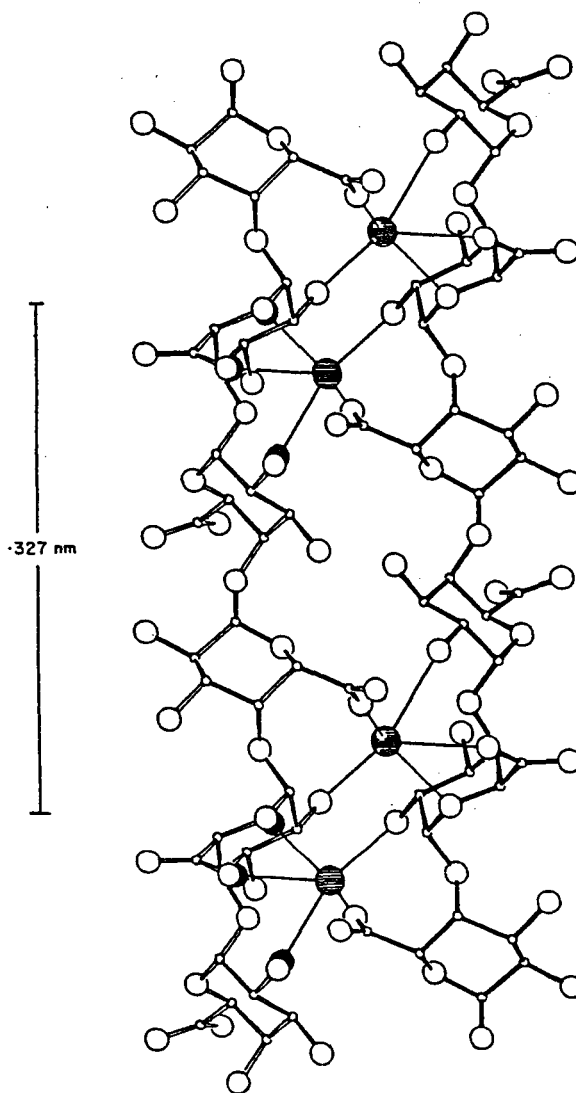


FIGURE 5. Calcium pectate unit cell viewed along the (100) direction. Coordination of calcium ions (striped circles) to polymer oxygen functions is denoted by thin, unbroken lines. (From Walkinshaw, M. D. and Arnott, S., *J. Mol. Biol.*, 53, 1075, 1981. With permission.)

primary units of two chains in antiparallel configuration with about 50% of the carboxyl groups neutralized with calcium. The combined effect of pH and sugar promotes gelation at a lower calcium level despite the decrease of the number of sequences of carboxyl groups for calcium binding. This is due to the specific effect of sugar on the water activity and hydrophobic effects. These effects are very complex, and a dependence of gel strength on the type of sugar has been reported.¹¹⁹ In the presence of excess calcium, several primary units form sheet-like aggregates, with excess calcium being weakly bound. These second-

ary aggregates have been suggested to add only little strength to polygalacturonase gels.⁸⁶ Higher Ca^{2+} concentrations at pH 3 to 5 can destroy the gel by increasing the cross-linking to such an extent that pectin is precipitated.¹² The lifetime of a junction zone in LM pectin gel depends on the strength of the electrostatic bonds, which in turn depends on the length of the uninterrupted pectin segments that can interact. The bonds are stable when there are at least seven consecutive carboxyl groups on the interior of each participating chain.⁸⁹ The strength of calcium-bonded gels depends on (1) molecular weight, (2) degree of po-

lymerization, and (3) calcium binding power.¹² Full binding strength is reached at about 14 units, although if sufficient calcium ions are present, a few methylester groups can be tolerated within this length.^{86,120} Acetyl substituents reduce the binding strength, and the kink that results from the insertion of an α -L-rhamnose unit terminates a binding segment.^{96,121,122} An increase in ionic strength as well as neutral pH and a decrease in setting temperature in the DM lowers the amount of calcium chloride required to obtain the sol-gel transition.¹²³ Calcium cooperative binding is negligible when the DM is higher than 45%.¹²⁴

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.¹²⁵ Ionization also prevents aggregation between the polymer chains, resulting in solutions of stable viscosity, as each polymer chain is hydrated, extended, and independent.¹²⁶ However, Thibault and Rinaudo¹²⁷ found that monovalent cations caused a decrease in viscosity, the degree of which was greater with decreasing DM. Addition of di- and trivalent cations had the opposite effect. The gel strength is reported to increase with decreasing DM in LM pectin.¹²⁸ Amidation of LM pectin increases its gel-forming ability.¹²⁹ Black and Smith¹³⁰ compared the gel characteristics of acid-deesterified and ammonia-alcohol-deesterified pectin having the same molecular weight and amount of free carboxyl groups. They found increased strength values for those gels made from amidated pectins. This increased strength of amidated pectin gels was reported to be due to hydrogen bonding between amide groups. Gels made from amidated pectins also showed improved texture and less tendency to syneresis, compared with commercially used pectins.¹⁰⁴ DM, attached chains of neutral sugars, acetylation, amidation, and cross-linking of pectin affects the textural properties of pectin gels.⁶⁶ The ash content of pectin can affect its ability to gel.⁶⁸ In general, enzyme-deesterified pectins make weaker gels than do acid-deesterified pectins.¹³¹

2. Gelation of High Methoxyl-Pectins

In HM pectins, the junction zones are quite different in structure, as shown by spectroscopic

studies.^{132–135} The cross-linking of polymer chains involves extensive segments from two or more pectin molecules to form junction zones. The junction zones are stabilized by a combination of hydrogen bonds and hydrophobic interactions between pectin molecules^{79,109} (Figure 6). The structure in Figure 6 would be stabilized by hydrogen bonds (indicated by dotted lines) and also by hydrophobic interactions of the ester methyl groups (indicated by filled circles). The hydrophobic effects arise from the unfavorable interactions between water molecules and the nonpolar methoxyl groups of pectin molecules. The methoxyl groups induce changes in water structure, decreasing its entropy. To minimize this change, the methoxyl groups are forced to coalesce, reducing their surface area of contact with water. This removal of nonpolar groups from contact with water makes major contribution to the free energy of conformational stabilization.¹³⁶ The driving force for this interaction is provided by the unique three-dimensional hydrogen-bonded structure of water. The length of the segment needed to give sufficient stability to these junction zones increases with increasing DM.¹³⁷ At a higher DM, almost the entire chain appears to be required; at the lowest DM studied (64.9%), the number of monomer units involved was 34 (17 from each chain). The analysis does not account for any possible difference in the number and distribution of rhamnose residues that would be expected to disrupt the regular helical structure.¹⁰⁶ The size and thermodynamic stability of junction zones depends upon the proximity of the two ester groups. Junction zones in acidic gels are more heat resistant than those in neutral gels.¹³⁸ Plaschina et al.¹³² has shown that attractive forces exist between pectin molecules due to their methoxyl groups. Walkinshaw and Arnott¹⁰⁹ also suggested the role of hydrogen bonding and hydrophobic interactions in the stability of HM pectin gels. Because the magnitude of hydrophobic interaction is affected by the solute (e.g., sugar) used and the temperature, gel strength and the rate of structure development is also affected by them.^{106,138} This is supported by the ability of urea to decrease the firmness of plant tissue, as urea is known to interfere with noncovalent interactions between polymer chains.^{139–141} This weakening effect of urea on hydrophobic interactions is due

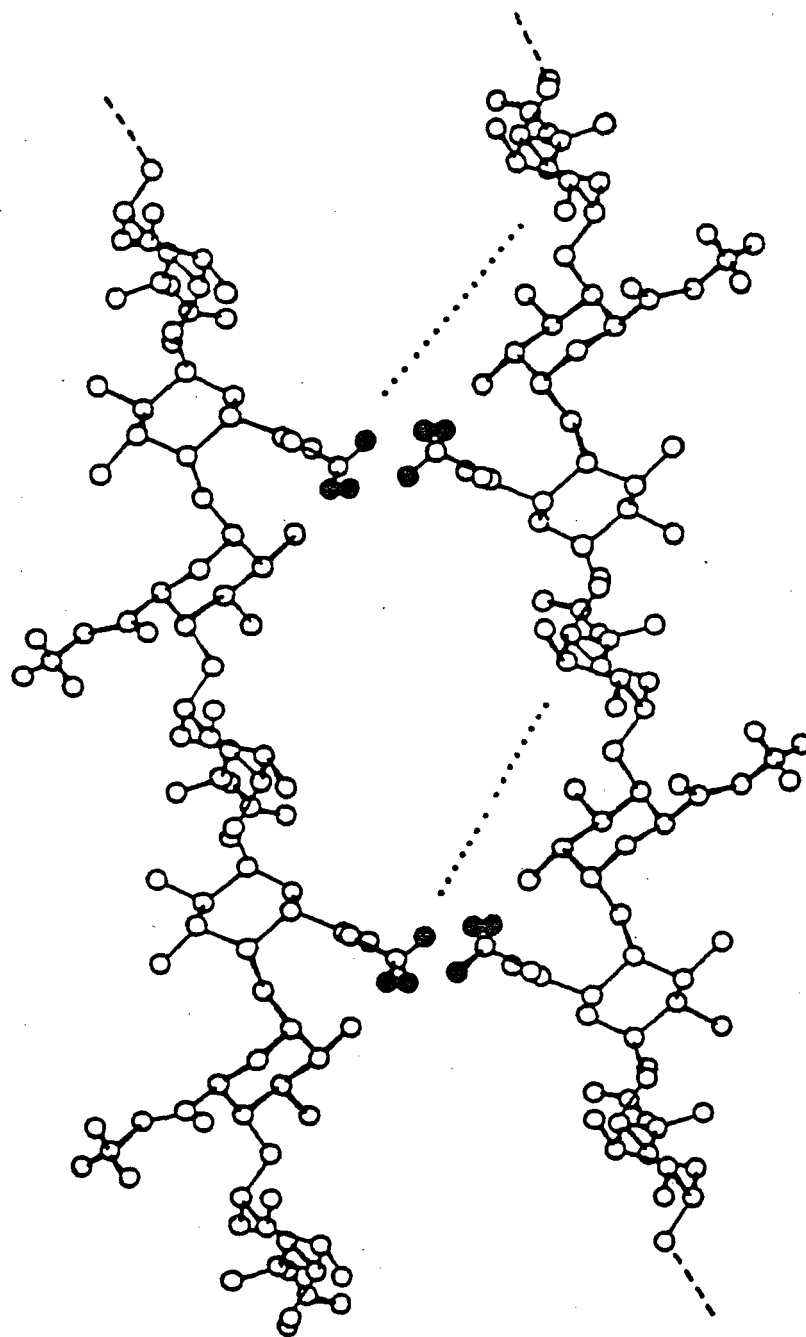


FIGURE 6. Structure of junction zones in gels of high methoxyl pectins inferred from X-ray diffraction studies. (From Okenfull, D. G., in *The Chemistry and Technology of Pectin*, Walter, R. H., Ed., Academic Press, New York, 1991, 87. With permission.)

to its ability (1) to alter the structure of water in a way that facilitates the solvation of nonpolar groups with water and (2) to solvate the nonpolar groups along with water. The stability of hydrophobic interactions can be modified by adding different sugars or polyols, ethanol, or dioxane, or

by changing the temperature.^{142,143} Watase and Nishinari¹⁴⁴ reported the effect of dimethyl sulfoxide (DMSO) on the gelation of HM pectin. A small amount of DMSO (less than 0.3 mf) promotes gel formation, while an excessive amount lowers the gelling ability. The mean end-to-end

distance (r_m) of chains that connect junction zones decreases, and the bonding energy (ϵ) increases with increasing DMSO content, up to 0.277 mf; the r_m increases and ϵ decreases beyond this DMSO content. The electrostatic repulsion between carbohydrate ions is lowered at lower pHs because of the suppression of the dissociation of the carboxylic group.

Hydrogen bonding in HM pectins occurs between functional oxygen atoms. Hydrogen bonds between pectin molecules are favored by the conformation of adjacent uronide residues.¹¹³ Individual hydrogen bonds are weak and easily broken, but a large number of them confer significant thermodynamic stability to the gel.¹⁴⁵ The firmness of the gel and its structure development is affected by the temperature of storage, pH, pectin concentration, and the sugar used. HM pectin/glucose gels were firmer than fructose gels.¹³⁷ This difference in gel strength may be due to the different effects sugars have on hydrophobic interaction in the gel. The contribution from hydrophobic interactions to the free energy of formation of junction zones is half that of hydrogen bonding, but is an essential requirement because hydrogen bonding alone is insufficient to overcome the entropic barrier to gelation.¹⁰⁶ The neutral side chains in the pectin molecule hinder gel formation. They themselves may be capable of weak noncovalent interactions. Computer models suggest that linear β -(1,4)-D-galactan chains can dimerize to form double helices.¹⁴⁶ Partly crystalline aggregates of linear α -(1,5)-L-arabinans have been described by Churms et al.¹⁴⁷

C. Pectin-Alginate Gels

With increasing demand for low-calorie foods, the need for products with low fat and sugar content is increasing. A pectin-alginate mixture forms thermoreversible gels that could be used in low-sugar, low-calorie jams and jellies. Toft¹⁴⁸ reported that a mixture of HMP and alginates with a high content of L-guluronic acid residue formed gels under conditions where neither alginate nor pectin gelled alone. It is possible to form pectin-alginate gels without adding sugar by using D-gluconobetalactone in a cold-set procedure as slow acidifier. The mechanical properties

(rigidity and break point) of the mixed gels depend on the pectin-to-alginate ratio, the mannuronic acid (MA) and guluronic acid (GA) ratio of the alginate, and the DM of the pectin.^{148,149} Alginate, with higher guluronic acid content, formed gels with higher stability. For example, gels formed by a cold-set procedure using HM pectin (~70% DM) and "high G" alginate (~70% guluronate) are about two to three times stronger, in terms of rigidity and break point, than those formed at equal pH by a typical "high M" sample (~60% mannurate).^{150,151} The nature of the interactions between pectin and alginates in mixed gels is not well known, but appears to be a heterogeneous association between specific chain sequences of two polymers: alginate poly-L-guluronate "blocks" and pectin poly-D-galacturonate sequences of low charge density (i.e., sequences with high DM).¹⁵⁰ The interaction between pectin and alginate is enhanced as the proportion of these sequences is increased. Although the conformation of individual chains is the same as in homotypic, calcium-mediated junctions, the geometry of the interaction is quite different, and instead of leaving cavities capable of accommodating metal ions, the near-mirror-image chains form a close-packed, nested structure.^{148,151,152} This results in favorable noncovalent interactions between methylester groups of pectin and the H-1 and H-2 of the polyguluronate.¹⁴⁹ For LM pectin, a much lower pH (to suppress dissociation of -COOH) is required to form a gel with high-G alginates. The melting point of these mixed gels increases with decreasing pH, and under sufficient acidic conditions, the gel structure could be retained at 100°C.¹⁵⁰ Potential applications of pectin-alginate gels in the food industry include the preparation of cold-setting fruit gels, stabilization of acidic emulsions such as salad cream or mayonnaise, and preparations of novel multitextured products.¹⁵²

It is important to know the conditions for the onset of gelation in technological processes involving gelling food products. Several methods are used to characterize this change in consistency.¹⁵³⁻¹⁵⁷ Technical tests are based on inverting a series of half-filled tubes to see if a coherent mass had been formed.^{153,154} Physically, the critical state of gelation may be monitored from the loss of fluidity or from the rise of the elastic property of the growing network.¹⁵⁸

D. Pectin-Protein Interactions

Fruit juices and concentrates are a complex mixture of carbohydrates, proteins, pigments, organic acids, and minerals. Interactions between these molecules, especially pectin and proteins, influence the consistency and texture of fruit products. The effect of pectin on the colloidal binding and coagulation of soluble proteins in model systems and in tissue extracts has been reported.¹⁵⁷⁻¹⁶² Enzymatic pectin degradation enables heat coagulation of proteins in the peel extracts, whereas without enzyme pectin degradation, the

heat coagulation is obstructed.¹⁵⁸ Shomer¹⁵⁹ concluded that the high molecular size of the pectic polymers is the factor that suppresses protein coagulation. Shomer et al.¹⁶⁰ further reported that the addition of high-molecular-weight pectin to a protein solution reduces heat coagulation and results in the delicate ultrastructure of the coagulate. Takada and Nelson¹⁶² studied the influence of pectin-protein interactions on the viscosity of tomato juice. They reported the formation of a reversible electrostatic complex between pectin and the proteins of tomato juice. The complex formation is pH dependent¹⁶² (Figure 7). Tomato

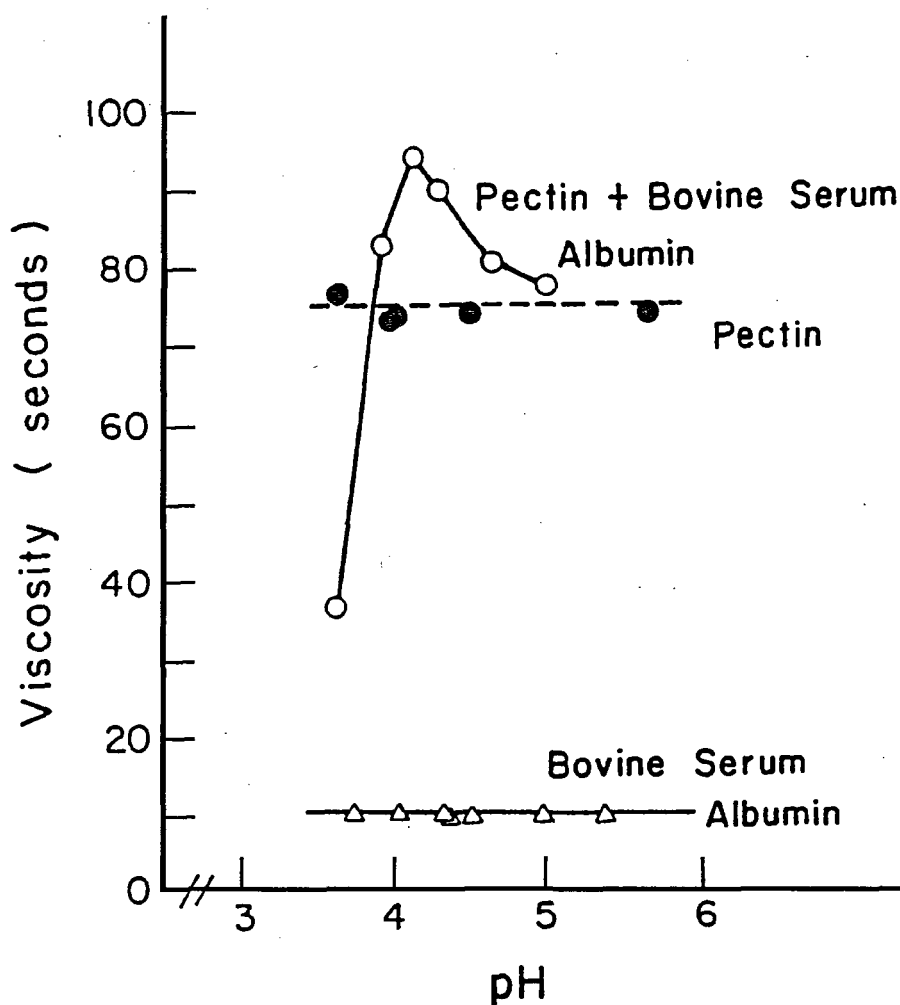


FIGURE 7. Interaction of pectin with protein at various pHs, as indicated by changes in viscosity in a model system containing pectin (0.6%) and protein (bovine serum albumin, 1.6%) at the same concentration as those found in tomato products at 10°C. pH of the system was adjusted using 6 N HCl or 6 N NaOH. (From Takada, N. and Nelson, P. E., *J. Food Sci.*, 48, 1408, 1983. With permission.)

puree diluted from higher solids such as 20° Brix, however, does not show a change in consistency with changing pH, as prolonged heating during the concentration of tomato juice may denature the protein and stabilize its complex with pectin, resulting in an irreversible complex. Figure 8 shows the suspected schematic models of pectin-protein interactions in tomato juice products as reported by Takada and Nelson.¹⁶² Pectins may also form cross-links with cell wall structural proteins from the matrix that envelops the cell.^{96,162,163} Many factors, including processing conditions, pH, and degree of esterification of pectin, may influence the nature of these interactions.

1. Effect of Temperature

The processing and preservation of pectin-containing food frequently involves heating.¹⁶⁴ It is therefore necessary to understand the effects of

high temperature on the structure and functional properties of pectin. As stated earlier, temperature affects the mechanical properties of pectin gels. Cooling the pectin/fructose gels from 50 to 10°C increased the storage (G') and loss moduli (G'') of the gel. An increased rate of cooling decreased the elasticity (G') of the gel; G'' , however, was not affected much by the rate of cooling.¹⁶⁵ The structure development rate (poise/min) of pectin gels increases at lower temperature, higher pectin concentration, and when pectin is prehydrated.¹⁶⁶

In heated tissues, firmness and intercellular adhesion are the result of the strength of the interaction of pectin chains with themselves and with other middle-lamella materials.¹³⁹ The increase in the relative amount of rhamnose compared with other sugars in heated tissue indicates possible degradation in the hairy region of the pectin molecule. In acidic solutions, at low temperature, deesterification of the pectin molecule is a domi-

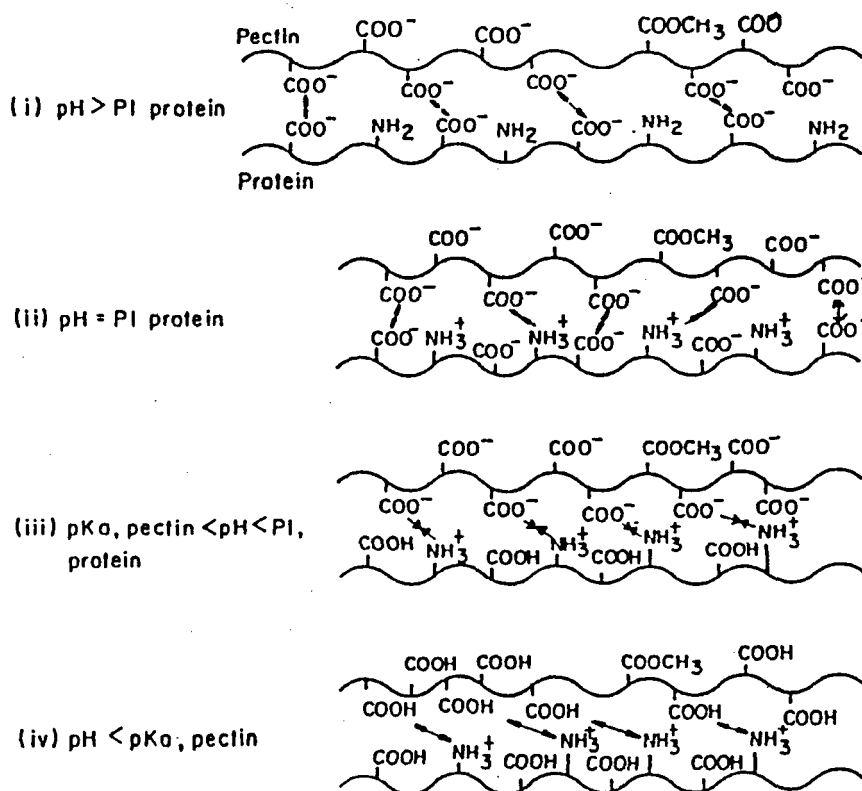


FIGURE 8. Suspected schematic model of pectin-protein interaction in tomato product. (From Takada, N. and Nelson, P. E., *J. Food Sci.*, 48, 1408, 1983. With permission.)

nant change, while at high temperature, depolymerization occurs more rapidly. In alkaline solution, at low temperature, saponification of the methyl ester groups occurs more rapidly, whereas at high temperature, depolymerization is predominant^{24,53} (Figure 9). Significantly, the degradation of the pectin molecule in alkaline solution is not due to hydrolysis of glycosidic bonds in the normal manner but rather the result of a β -elimination cleavage of the glycosidic linkage. This reaction only occurs at glycosidic bonds adjacent to an esterified carboxyl group.^{167,168} The degree of esterification affects the rate of degradation of pectin at pH 6.1, with a higher DM resulting in a greater rate of degradation²⁴ (Figure 10). Pectates are more stable at high temperature toward alkaline or neutral degradation than pectinates. The reason for this behavior is that pectic acids lack a methoxyl substitution at C6, have much less acidic proton at C5, and cannot be resonance stabilized in the transition state. They are therefore more resistant to base-catalyzed depolymerization. Further, the charge on the carboxyl groups repels the approaching hydroxy anion.¹⁶⁹

The nature and quantity of ions and salts in plant tissues affect the heat degradation of native pectin and the firmness of tissue. Sajjantakul et al.²⁴ reported that monovalent and divalent salts increase the heat degradation of chelator-soluble pectin from carrot, and at a similar level of methoxylation, divalent cations caused more depolymerization during the heating of pectin than did the monovalent cations. Potassium and calcium ions increase the solubilization of pectin from the potato cell wall; the promoting effect, however, is very small.⁹⁹ The softening effect of ions on plant tissue during heating has been reported by many workers.¹⁷⁰⁻¹⁷⁵ The complexity of plant tissue and the cell wall structure, however, make it difficult to identify unambiguously the degradation mechanism of pectic substances in cell walls.

V. USES OF PECTINS

Pectins have always been a natural constituent of human foods. Its use is allowed in all

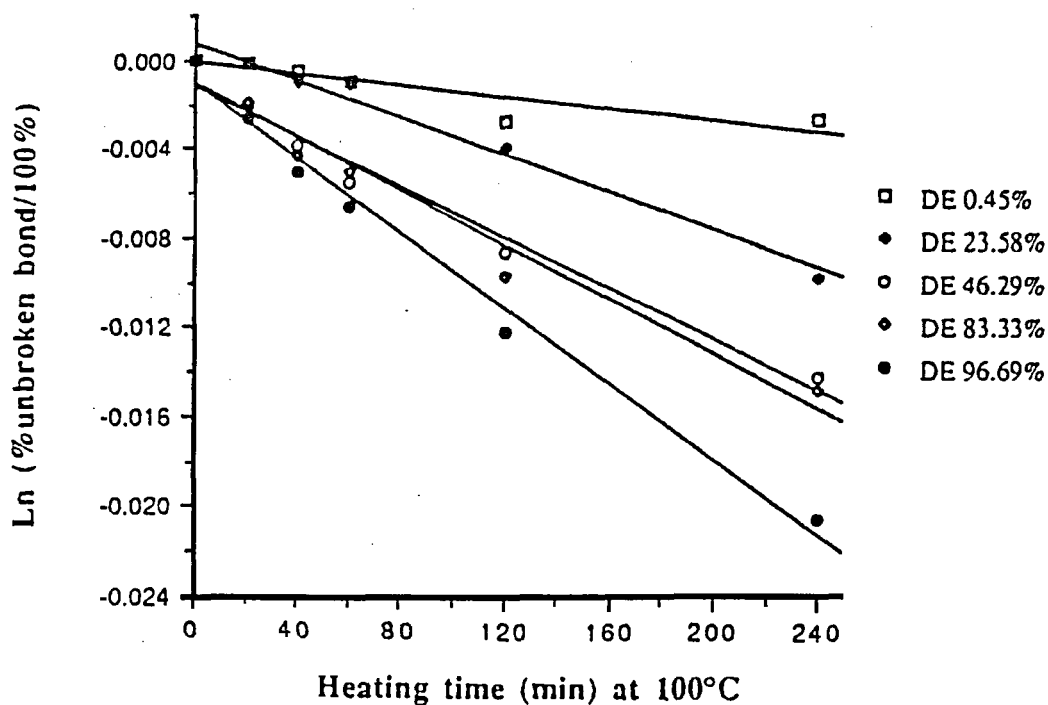


FIGURE 9. Effect of heating time at 100°C on glycosidic bond cleavage of different degree of esterification (DE) of chelator-soluble pectin (initial pH, 6.1). (From Sajjantakul, T., Buren, J. P. V., and Downing, D. L., *Carbohydr. Polym.*, 20, 207, 1993. With permission.)

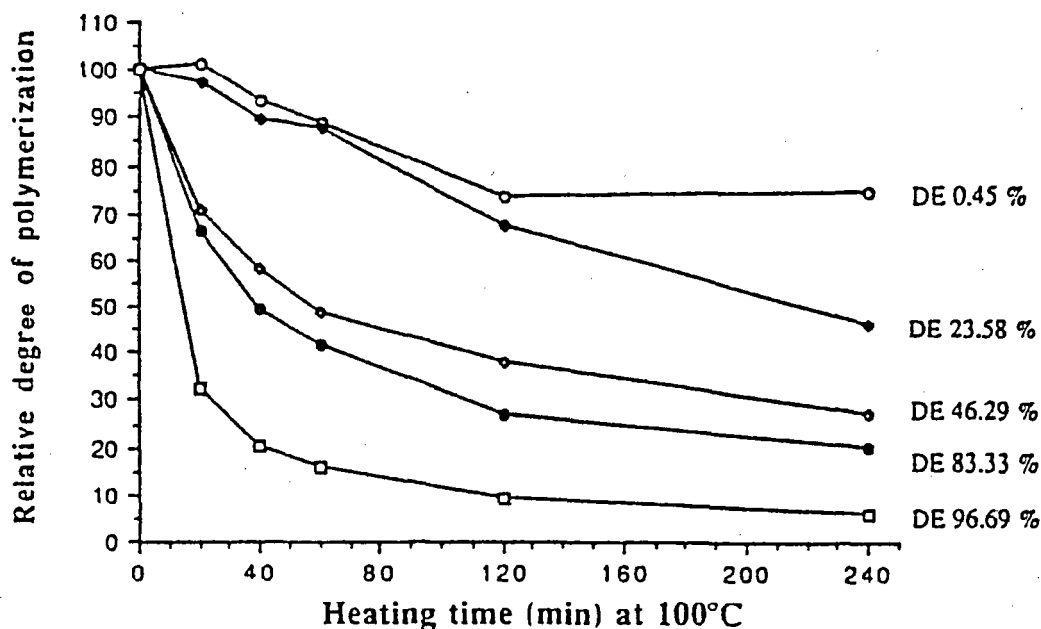


FIGURE 10. Effect of heating time at 100°C on the relative degree of polymerization of different degree of esterification (DE) of chelator-soluble pectin (initial pH, 6.1). (From Sajjanantakul, T., Buren, J. P. V., and Downing, D. L., *Carbohydr. Polym.*, 20, 207, 1993. With permission.)

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 manufacturing practice.¹⁷⁶ 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.¹⁷⁷ The functionality of the pectin molecule is determined by a number of factors, including degree of methoxylation and molecular size.¹⁷⁸ 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.⁵¹ 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.¹⁷⁷ Different uses of pectin in food and other industries are discussed in the following sections.

A. Jams, Jellies, and Preserves

Jams and jellies are the major food types 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.¹⁰⁰ 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.¹⁰⁰

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.¹⁷⁹

B. 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 is 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 mouthfeel and body to the products.¹⁰⁰

C. 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 having 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.¹⁷⁷

D. 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.¹⁷⁹ Pectin is used in edible coatings to inhibit lipid migration in confectionery products.¹⁸⁰

E. 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 Ca^{2+} and pectins. Sliced fruits are firmed more than whole fruit by Ca^{2+} and pectin treatment. Drained weight is also reduced by pectin, Ca^{2+} , sucrose, and vacuum in frozen-then-thawed fruits.^{172,181} Coatings containing LM pectins are used to improve the texture and quality of fruits for use in ice creams.¹⁸³ 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.¹⁷⁷ 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 postfermentation mixing of stirred yogurt with pectin and fruit concentrate.^{184,185} Compared to starch and gum, a pectin-stabilized yogurt-fruit preparation is believed to have superior flavor-release properties.¹⁷⁷ 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.¹⁸⁶

F. 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.¹⁷⁷ Pectin is also used as a beverage-clouding agent.¹⁸⁷

G. 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.¹⁷⁷

H. Pharmaceutical Uses

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.¹⁸⁸ When injected intravenously, pectin shortens the coagulation time of drawn blood, thus being useful in controlling hemorrhage or local bleeding.¹⁸⁹ Pectin sulfate, on the other hand, prolongs clotting time and can be used in place of heparin.^{180,191} 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.¹⁹² A bismuth-D-galacturonan mixture is found to be an effective means of administering bismuth in medicinal preparations.¹⁹³ Pectin has been reported to help reduce blood cholesterol in a wide variety of subjects and experimental conditions.¹⁹⁴⁻²⁰⁴ 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.^{201,202} Mietinnen and Tarplia²⁰³ reported a 13% reduction in serum cholesterol within 2 weeks of treatment. Cedra et al.²⁰⁴ 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.²⁰⁰ DM has no effect on the cholesterol-lowering effect of pectin.¹⁹⁹ In a few studies, pectin had no influence on blood cholesterol in tested subjects.²⁰⁵⁻²⁰⁷ 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.²⁰⁸⁻²¹⁰ 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.²¹¹ The gastric emptying half-time is doubled by the intake of 20 g of apple pomace per day for 4 weeks.^{212,213} These attributes of pectin are used in the treatment of disorders related to overeating.²¹⁴

A mixture of LM pectin, aluminum hydroxide, and magnesium oxide has been reported to be useful in the treatment of gastric and duodenal ulcers.²¹⁵ Pectin alone or in combination with gelatin is used as an encapsulating agent for the sustained release of medicine.^{216,217} 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.²¹⁸

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 ileostomies 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.

I. Other Uses

Pectins has been found useful in other industrial applications. They function as an emulsion stabilizer for water and oil emulsions.^{219,220} 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.²²¹ A number of studies have been done on pectin films.²²²⁻²²⁵ 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.²²⁴ 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.²²⁶ 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.²²⁷ Other nonfood uses of pectin are reported by Endress.²²⁸

VI. CONCLUSIONS

Pectin is widely used as a texturizer, stabilizer, and emulsifier in a variety of foods and other industries. Its use as a fat and sugar replacer in low-calorie foods is expected to increase in the future with increasing demand for these foods. In spite of its availability in a large number of plant species, commercial sources of pectin are very limited. There is, therefore, a need to explore other sources of pectin or modify the existing sources to obtain pectin of desired quality attributes. Modern tools of science such as genetic engineering can be used to modify pectins *in vivo*. Gelation is the most important property of pectin that makes it an important component of food and pharmaceutical products. Current knowledge of

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 products.

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