Industrial Pectins: Sources, Production and Applications

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ABSTRACT

Industrial pectins are a specific group of carbohydrate polymers composed largely of galacturonic acid units, part of the wider class of plant pectic substances. The normal raw materials are apple pomace and citrus peels, from which pectin is obtained by acid extraction and precipitation using alcohols or aluminium salts. Other raw materials (beet, sunflower, etc.) have been considered and their potential is discussed. Pectin is the traditional gelling agent for jams and jellies, but its applications extend to fruit products for the food industry, dairy products, desserts, soft drinks and pharmaceuticals.

WHAT IS PECTIN?

The exact definition of commercial pectin as used in the food and pharmaceutical industries has varied over the years as its structure and relationship to other plant polysaccharides containing galacturonic acid units has become clearer. This broader class of pectic substances has been studied extensively (BeMiller, 1986; Northcote, 1986) both in regard to its biosynthesis and its involvement in the structure of plant tissues. Many of these materials contain very substantial amounts of a range of neutral sugars, especially arabinose and galactose, with smaller amounts of rhamnose, xylose and glucose, and they are frequently closely associated with other polymers containing entirely neutral sugars.

In contrast, the pectins of commerce are characterised by a high content of galacturonic acid, and this has become part of the legal definition for pectin used as food additives or for pharmaceutical purposes. Typical requirements are for a minimum of 65% of galacturonic acid on the ash and moisture-free substances. This requirement in itself limits the potential sources of food and pharmaceutical pectins. Such

pectins contain a linear backbone of galacturonic acid units interrupted by occasional neutral sugar residues (rhamnose). Current evidence (de Vries *et al.*, 1986*a*) suggests that the remaining neutral sugars are mainly present as side chains, largely arabinogalactans, which are attached to short blocks of neighbouring galacturonic residues to form 'hairy regions'. The intervening regions of the chain are claimed to be very largely composed of galacturonic acid with up to 4/5 of the acid groups esterified with methanol. Although these studies relate to apple pectin, there is evidence (de Vries *et al.*, 1984) that the structure of citrus pectin is similar. It has been suggested that the pectin chain consists of repeating units (de Vries, 1988) or even repeating units within repeating units, but up till now this evidence is not entirely conclusive and the nature of such units has not been clarified.

Part of the difficulty may lie in the fact that extracted pectins normally come from a range of botanically different tissues, which perhaps contain somewhat different pectin structures. Another possible variation in the structure of pectins lies in the distribution of methyl ester groups along the backbone chain. Citrus pectins can be extracted with up to 75% or more esterification, and apple pectins with at least 80%. Some of this difference may be due to the presence of pectin esterase in citrus peel. Under any commercial conditions of pectin extraction there is certainly going to be some opportunity for this enzyme to act on the pectin present between the mechanical disruption of the tissue which accompanies juice extraction and the application of sufficient heat in blanching to denature the enzymes. It has been suggested (de Vries *et al.*, 1986*b*) that in native pectin or protopectin before extraction there is a regular pattern of five esterified residues followed by one free acid, repeated along the chain. Certainly pectin which has been chemically esterified and hydrolysed back to its original degree of esterification is subtly different (e.g. in its rate of reaction with degrading enzymes and in the distribution of oligomers formed on degradation) from the native starting material. However, the differences are not sufficient to produce significant functional differences. A high content of galacturonic acid is not alone sufficient to define a commercially relevant pectin. The market in pectin has been very closely linked to the preserves industry from its beginnings, and thus one of the essential hallmarks of a useful pectin has been its gelling power. It has been the pectins capable of supplementing the pectin extracted from the fruit during jam making that have found most practical use. In fact, the origins of pectin production go back to the practice by preserves manufacturers of making a pectin-rich extract from fruit trimmings and waste materials, such as apple peels and cores, in order to supplement the gelling power of 'difficult' fruits.

Seeing this and the quantities of fruit residues produced as a waste material from the juice and cider industries, a number of enterprises were started in the 1920s and 1930s. Apple residues proved very suitable for the production of a concentrated pectin extract which could be preserved chemically for sale in barrels and eventually in road tankers. This practice continues today, although transport costs limit the economic radius of distribution. In contrast, manufacturers who started with lemon or orange peel as a raw material found that the simple extracts were unacceptable in flavour for most applications and soon produced solid pectins by metallic salt or alcohol precipitation. This initiative was eventually followed by the apple pectin producers, and the present structure of the industry has gradually evolved. In recent years other economic factors have become increasingly important, and environmental costs and restrictions have led to the abandonment of pectin manufacture by major producers, especially in the United States. From being a major force in pectin technology and production, the United States now imports most of its pectin requirements, a major part of it from Europe. In the future it is probable that Central and South America, with their extensive citrus industries, will play a more important role, with the commercial and technical support of existing pectin producers.

RAW MATERIALS FOR PECTIN PRODUCTION

It is possible to produce commercially acceptable pectins from either apple pomace or citrus peel. These two raw materials do however produce slightly different pectins which make one or the other more suitable for specific applications. Apple pectin will commonly produce a heavier more viscous gel, well suited to certain types of bakery fillings and the like. The lighter colour of citrus pectin is more acceptable in confectionery jellies, but in certain traditional orange marmalades the colour provided by liquid apple pectin is a positive attribute.

To support a viable pectin operation, it is not enough to have a raw material of the right quality; it is also necessary to have sufficient quantity to run a cost-effective production operation. In addition, apple pomace and citrus peel are, in the wet state, very perishable commodities. Both can be attacked by moulds, which produce a wide variety of pectic enzymes, both de-esterifying (pectin methylesterase, EC 3.1.1.11) and degrading (polygalacturonase, EC 3.2.1.15; pectin lyase, EC 4.2.2.10; pectate lyase, EC 4.2.2.2), and these easily render the pectin in the raw material unacceptable for most end uses. Citrus raw materials also

naturally contain significant amounts of native pectin methylesterase; orange peel is particularly rich in this enzyme. This fruit enzyme, in contrast to fungal pectin methylesterase, produces blocks of de-esterified material rendering the pectin more sensitive to calcium than indicated by its overall degree of esterification. This can be a disadvantage in many specific applications. It is therefore inadvisable to store wet pomace or peel, unless specially treated, for more than a few hours. Even the time taken to transport raw material from outlying juice plants to a central location can give rise to a loss in the quality of the final pectin produced. Pectin can therefore either be extracted from the fruit residue soon after the pressing of the juice, or the residue can be dried. It is then stable for many months. In the latter case, the dried material can be transported long distances to the pectin factory. Inevitably some quality is lost in the drying process, as pectin is a fairly heat-labile material, but 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 enzymes and moulds without destroying the pectin, very acceptable pectin can be produced from it. Wet raw material will ideally need blanching as soon after pressing as possible, and can only be stored for a few days at most. There are also only a few areas where suitable citrus peel is available all year round from processing factories, so in many places a plant will have to switch to dried peel, or to close down, outside the fresh fruit season.

A pectin plant using wet peel may be able to produce excellent pectin when the raw material is at its best, but it is entirely dependent on the quality of fruit being processed in its supplying juice plants on a day-to-day basis. If the juice market demands that very ripe fruit be processed, or a fruit variety with poor quality pectin such as some types of mandarin, the pectin producer must do the best he can with what is available. Against this, the cost of wet peel may be low, since to the juice manufacturer it is otherwise a waste material which will present a disposal problem, or at best a significant cost to dry it for sale as cattle feed. Having dried the residue, sales and prices will depend on the vagaries of the feed market. On the other hand, the pectin producer using dried peel can buy peel of a number of qualities from various countries, depending on availability, quality and price. He can then select from his stock the most appropriate for the manufacture of a particular grade of pectin. He is also more protected against the effects of adverse climate or a poor crop in one region. These considerations apply mainly to the citrus pectin producer. Apple pomace is usually only produced over a limited season and in insufficient quantity within an area to supply an economic pectin factory. Pomace is also difficult to process unless it is first dried and

stored for a while. Pomace is therefore usually bought from over a wide area from a number of drying plants.

The quality of raw material is a matter of considerable concern to the pectin producer, as it has a marked effect on processing costs and product characteristics. Amongst citrus peels, lime has the highest quantity of pectin of probably the highest molecular weight, but good lemon peel may show a higher degree of esterification. Orange is very variable, depending on variety and source, and needs prompt processing to avoid enzyme de-esterification and resulting calcium sensitivity. Amongst apples, the traditional cider varieties of the West of England and Northern France give some of the best apple pomace. Perhaps because of the high polyphenol content, the fruit is firm and easy to press, even after some storage. The juice of many other varieties of apple can only be extracted efficiently after enzyme treatment of the pulp, and this damages the pectin considerably. Soft over-ripe or cold-stored fruit in any case contains poorer pectin, of lower molecular weight.

Other sources have been considered for the extraction of commercial pectins. During the Second World War sugar beet residues were used to supplement apple pomace both in England and in Germany. The products were not of very high quality in terms of gelation. Beet suffers from several disadvantages as a competitor to apple and citrus pectins. Most seriously, it is difficult to obtain as high a molecular weight and hence a good quality of gel and the content of neutral sugars is distinctly higher, often reducing the galacturonic acid content below the legally permitted limit, even if the other disadvantages of lower degree of esterification and the presence of acetyl groups which block gelation can be overcome by chemical modification. Treatment in acidic methanol can remove the acetyl groups and increase the proportion of ester groups, but it could further reduce the already poor molecular weight. However, beet pectin is capable of being cross-linked through ferulic acid residues when treated with peroxidase and hydrogen peroxide, to form a thermally stable covalently cross-linked gel which may for example be dehydrated and rehydrated (Rombouts & Thibault, 1986). It may thus lend itself to applications quite different from those of current commercial pectins, including materials that can absorb and hold many times their weight of water.

Another pectin-containing material potentially available in quantity is the seed head of the sunflower. The white tissue that holds the seeds is rich in high molecular weight pectin which is very high in galacturonic acid. It too is acetylated and somewhat low in esterification, and it appears to contain a low level of amidation (Lim *et al.*, 1976). If it can be processed in perfect condition, the product could then be further

modified to yield a useful material. However, farming practice is to wait until the seed head has softened, making threshing of the seeds easier, and at this stage oil yield is also at a maximum. Unfortunately by this time the heads have often been infected with mould, with disastrous results for the pectin.

A recent paper has claimed that pectin of quite high quality can be produced from onion (Fatah, 1987), but whether it would be commercially attractive either from the availability of sufficient raw material or from the image of 'onion pectin' is not certain.

THE PRODUCTION OF PECTIN

Commercially, pectin is extracted (Fig. 1) by treating the raw material with hot dilute mineral acid at pH ~ 2. The precise length of time varies with raw material, the type of pectin desired, and from one manufacturer to another. The hot pectin extract is separated from the solid residue as efficiently as possible. This is not easy since the solids are by now soft and the liquid phase is viscous, the viscosity increasing with pectin concentration and molecular weight. There is a compromise between efficient extraction and solids separation (both favoured by a large amount of liquid) and operating cost (favoured by producing a more concentrated extract). The pectin extract may be further clarified by filtration through a filter aid such as kieselguhr. Apple pectin to be sold as liquid is then treated with carbon to remove colour and with α-amylase (EC 3.2.1.1) to degrade starch which would otherwise precipitate from the liquid product. The clarified extract is then concentrated under vacuum. This provides efficient concentration at low temperature and prevents degradation of the pectin. Throughout the process unnecessary holding times at high temperatures are avoided. Powdered pectin can be produced by mixing the concentrated liquid from either apple or citrus with an alcohol (usually isopropanol, although methanol and ethanol are also permitted). The pectin separates as a stringy gelatinous mass, which is pressed and washed to remove the mother liquor, dried and ground. An alternative precipitation process (Joseph & Havighorst, 1952) was often used in the past and is still in use in some plants processing fresh citrus peel. This utilises the fact that pectin can be coprecipitated in the presence of colloidal aluminium hydroxide. One of the advantages is that the pectin extract does not have to be concentrated and certain impurities are more readily eliminated. The extract is cooled and mixed with a solution of an aluminium salt and sufficient ammonia or sodium carbonate to give a pH of about 4. The pectin separates as a
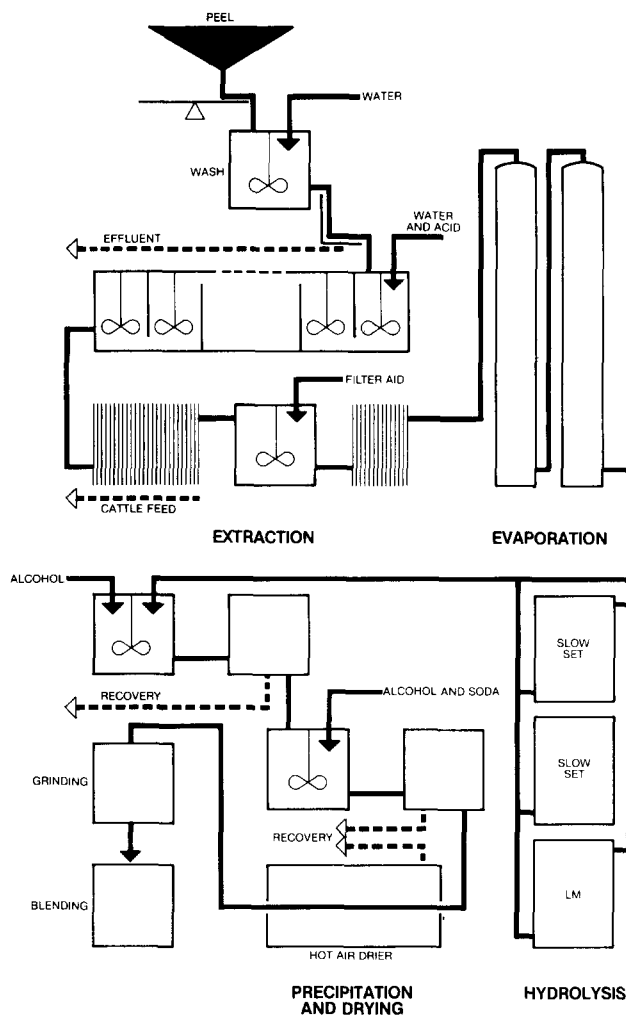
Fig. 1. Typical process for pectin production from dried citrus peel.

greenish-yellow floc which tends to float on the liquor. It is separated by a screen or by flotation and pressed to remove as much aqueous liquor as possible. To remove the aluminium, the yellow mass is suspended in alcohol and treated with acid in a series of stages, then partially neutralised before drying. Unfortunately highly esterified pectin (much above 70% ester) does not precipitate well with aluminium (Joslyn & de Luca, 1957) and the overall recovery is normally poorer than with the alcohol process. Because pectin is produced from variable raw materials it is in itself somewhat variable. To produce a product that is consistent over a range of properties, it is usual to blend together a number of production

batches and dilute them with sugar or dextrose to a standard perform-ance.

These processes yield a pectin of around 70% esterification (or methylation), called 'rapid set' pectin. To produce other types, some of the ester groups must be hydrolysed. This is commonly carried out by the action of acid, either before or during a (prolonged) extraction, in the concentrated liquid, or in an alcoholic slurry before separation and drying. This process can produce a range of slower setting high methoxyl and calcium reactive low methoxyl pectins further described below. Alkaline treatments can also be used but, because pectin readily degrades at neutral or alkaline pH by a β-elimination reaction, this must be carried out at low temperature. Hydrolysis using ammonia results in the conversion of some of the ester groups into amide groups, producing 'amidated pectins'. These are also usually of the low methoxyl type; their advantages in particular situations are discussed below.

Effluent has become a major consideration in the pectin industry; indeed, effluent problems have caused some plants to close. In produc-ing a powder pectin, at least an equal amount of non-pectin organic material is solubilised, from sugars and hemicelluloses in the raw material. This organic material ends up in the aqueous stream from alcohol recovery, or in a more dilute form in the aqueous mother-liquor from aluminium precipitation. It is increasingly a major cost and sometimes a serious technical problem to the pectin manufacturer, either to treat this effluent or to pay a local authority for its treatment.

PECTIN PROPERTIES

The best known property of pectin is that it forms gels with sugar and acid. This can be seen as a partial dehydration of the pectin molecule to a degree where it is intermediate between solution and precipitation. The particular structure of pectin imposes some specific constraints. High methoxyl pectin, unlike alginate, does not contain sufficient acid groups to gel or precipitate with calcium ions, although other non-food ions such as aluminium or copper cause precipitation under certain conditions. At a pH well above the pK value for the acid groups, the molecule possesses sufficient negative charge to prevent gelation under practical conditions in sugar–water systems. As the pH is gradually reduced, the pectin is capable of forming a gel at first at very high sugar contents (around 80% on the refractometric scale), and at gradually lower sugar contents as the pH is reduced. At pH values well below 3·0 a very rapid setting pectin with a degree of esterification of above 72% will

form a gel with 55% or somewhat less of sugar. There is some evidence that in the junction zones of such a gel hydrophobic bonds between methyl ester groups are involved as well as hydrogen bonds (Oakenfull & Scott, 1984). If the sugar content is held constant, as would be normal in preserves manufacture, the effect of a change in pH is seen as a loss in strength above a certain critical pH and a gradual lowering of the setting temperature as pH increases towards this value. Very high setting temperatures define the lower limit of the practical pH range for making a gel by concentrating the system by boiling off water. As the setting temperature approaches the boiling point, the gel structure is disrupted by boiling and subsequent shearing of the mass. Because the gelation mechanism is not fully reversible, a complete gel network can no longer form, and the system is prone to syneresis, or in more extreme cases a non-homogeneous 'broken' texture results. The simplest modification of a pectin is to decrease the degree of esterification by mild hydrolysis. The slow setting pectin so produced has a degree of esterification of 58–65%, and hence bears more charge at a given pH. In consequence, the gel strength and setting temperature curves are displaced to lower pH (Fig. 2). These pectins are used where a lower setting temperature is required, or where the rate of set would otherwise be too high because of the increased sugar solids of the product.

Once other sugars such as glucose and later high fructose syrups became available, it became clear that the nature of the sugar cosolute as well as its concentration were important (May & Stainsby, 1986). It has long been known in practice that jams cannot be made satisfactorily with very high proportions of corn or glucose syrups, and this is made clear if the gelation curves are examined (Fig. 3). Not only is the optimum pH increased but the rate of change of setting temperature with pH is very much steeper. It is just not possible in practice to control pH sufficiently accurately. On the other hand, high fructose syrups cause a substantial lowering of setting temperature and it would be difficult to control fruit separation in a jam. A judicious mixture of glucose syrup and high fructose syrup enables a workable system to be constructed once more, although its behaviour is not identical to that of sucrose and is subject to the exact ratio and type of the syrups used. The simple inference that the molecular weight, or the presence of starch oligomers, might be responsible for this effect cannot be sustained, as gels made with maltose show very similar behaviour to those made with 42DE glucose syrups.

Low methoxyl pectins are produced by further de-esterification to a point where less than 50% of the total carboxyl groups are esterified. If this process is carried out using acid or alkali, the balance exists as free
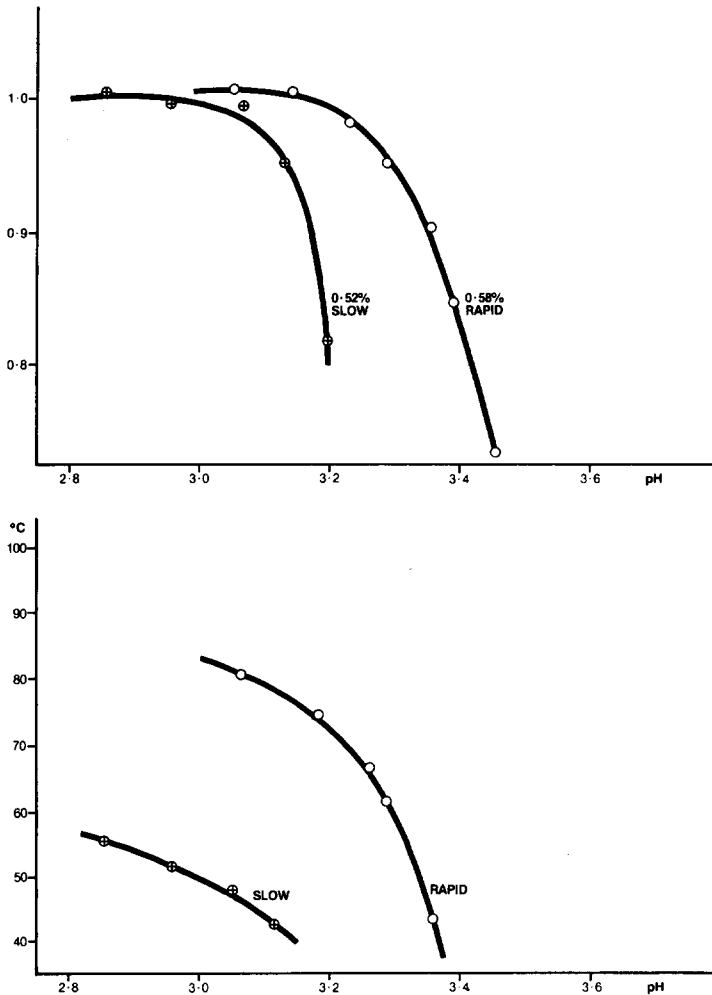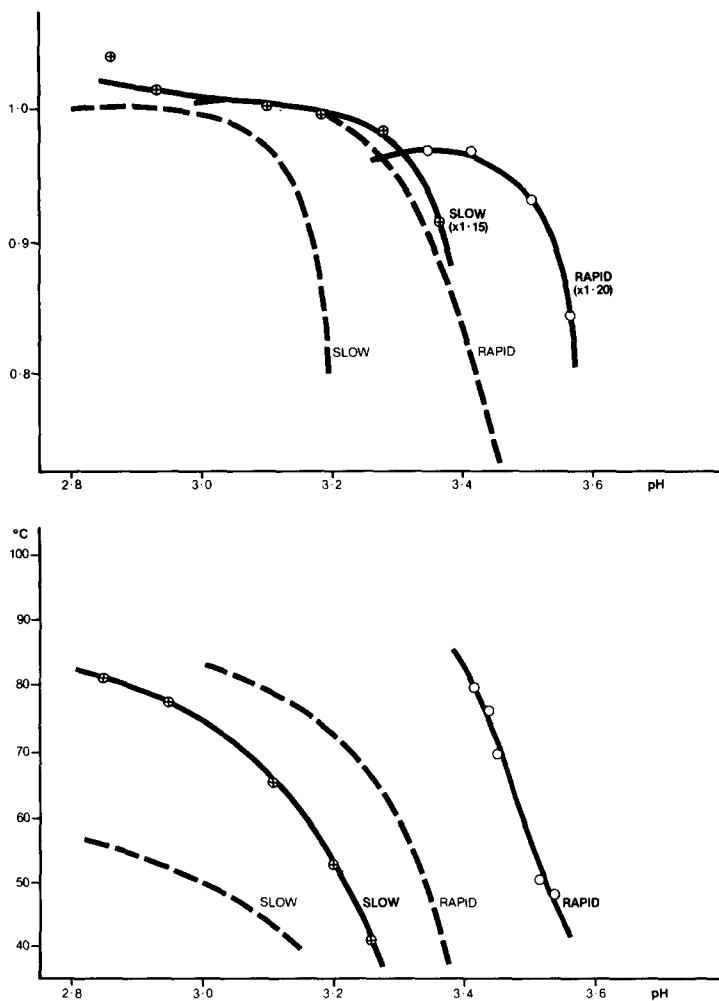
Fig. 2. Effect of pH on gel strength and setting temperature: sucrose at 65% by refractometer.

acid groups; these pectins are termed conventional or non-amidated low methoxyl pectins. Alternatively, pectin may be reacted with ammonia, usually by a heterogeneous reaction in an aqueous alcohol suspension. This reaction produces an amidated pectin, containing acid amide groups in addition to acid and ester groups. Both types of low methoxyl pectin form gels by reaction with calcium. Low methoxyl pectins are believed to gel by the 'egg box' mechanism (Grant *et al.*, 1973) first suggested for alginates. A section of two pectin chains, which must be free of ester groups, is held together by a number of calcium ions. In such a structure amide groups can be accommodated but do not add to the

Fig. 3. Effect of pH on gel strength and setting temperature: (———) 42DE glucose syrup (pectin increased as indicated); (– – –) sucrose.

strength of the junction zone. A range of different reactivities can be prepared by controlling the number of free acid groups. Amide groups increase the tolerance to different levels of calcium by broadening the gel strength versus calcium curve (Fig. 4). This means that they are significantly easier to control in the more critical applications, especially those at very low sugar contents. Under suitable conditions, gels with sugar contents below 20% can be made with acceptable texture.

As well as the concentration of calcium in the system, a number of other parameters affect the gelation of low methoxyl pectins. Sequestrants are present in most practical gelling systems, and their

nature and concentration can have a marked effect. Sequestrants may not only be citrate and other fruit anions, but also sugars such as fructose. The sugar alcohol sorbitol has an even more marked effect (Fig. 5). Gels can be prepared over a range of pH values, at least from pH 3 to 6, but the rate of set increases with lower pH. To some extent this effect can be offset by an increase in the amount of calcium at higher pH values. The texture of low methoxyl pectin gels can be controlled by adjusting the calcium to pectin ratio. A high content of pectin with relatively little calcium will give an elastic gel, while the use of more calcium with a minimum of pectin will produce a much more brittle product, possibly with some syneresis. The interplay of all these factors makes low methoxyl pectins very versatile thickeners and gelling agents.

In order to control the gelation properties of pectins a number of test methods have been used. Some of them depend on elastic deformation of the gel, and some on measuring a breaking point. The standard method used today is the IFT (1959) standard acid in glass (SAG) method agreed by a committee set up by the IFT in 1948. In this method a very low pH eliminates many of the differences between different pectins, and leads to reproducible results which are not too sensitive to slight variations in pH. However, a pectin solution at 65% solids and such a low pH would normally pregel. This is avoided by placing the acid in the jelly glass where the gel is to set, then pouring in the rest of the mixture which has been boiled to the correct concentration. By taping the rim of the glass, the gel can later be cut off flush to the rim of the glass
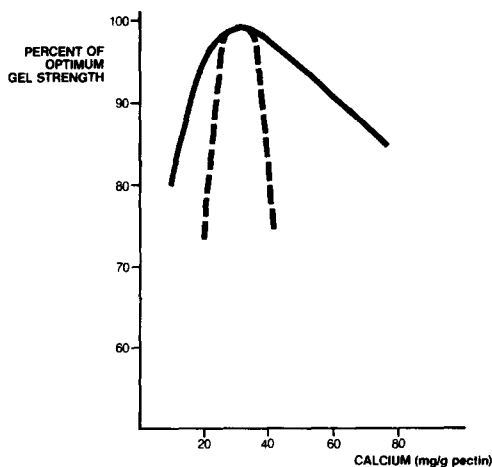
Fig. 4.   Gel strength curves for (———) amidated low methoxyl pectin, DM 27%, DA 18%, and (– – –) non-amidated low methoxyl pectin, DM 27%. Gel pH 3·0, 31% sugar by refractometer.
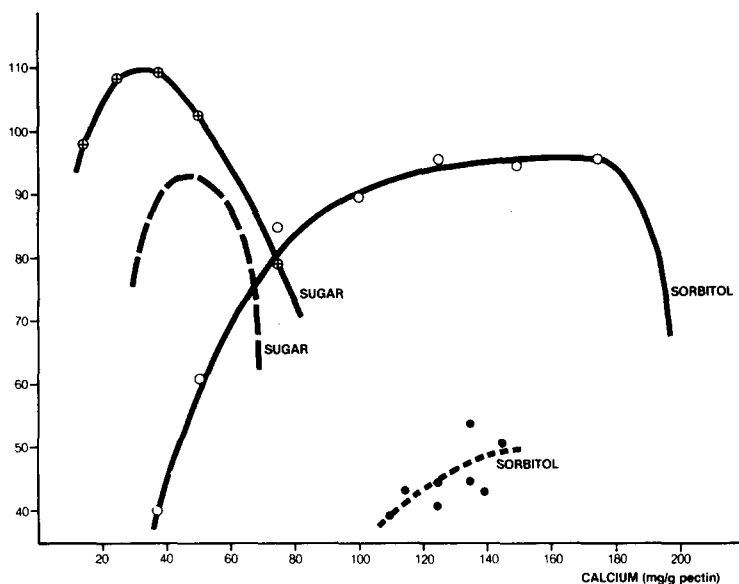
Fig. 5. Gel strength curves for (———) amidated low methoxyl pectin, DM 27%, DA 18%, and (– – –) non-amidated low methoxyl pectin, DM 34%, with sugar or sorbitol. Conditions as for Fig. 4.

after incubating for 20–24 h at 25°C. It is then turned out carefully onto a glass plate. Measurement of the height of the jelly after 2 min standing time gives a reproducible measure of gel strength, which can be converted to a 'jelly grade' of the pectin used. Other authors (Olliver *et al.*, 1957) have preferred to make test jellies closer in composition to typical jams and jellies. Such methods may have poorer reproducibility between different laboratories but are a better basis for studying the effects of changes in the composition of pectins, pH, sugar content and so on.

For some purposes, specifically in jelly preserves made from fruit juices, the gel breaking strength may be important. A number of methods have been described to measure this property, including the Tarr–Baker gelometer (Bender, 1949) and the Herbstreith Pektinometer (Zedler, 1983), a derivative of the Lüers & Lochmüller (1957) instrument. Break strength measurements are inherently more subject to error than elastic measurements, and are more affected by the molecular weight of the pectin (Christensen, 1954) (Fig. 6). Although breaking strength measurements can be made on slices of a jelly made by the IFT method, the rapid setting of these jellies tends to give them a less uniform texture, making the breaking strength more variable. Most breaking strength measurements are therefore made on jellies at a pH of around 3, so that
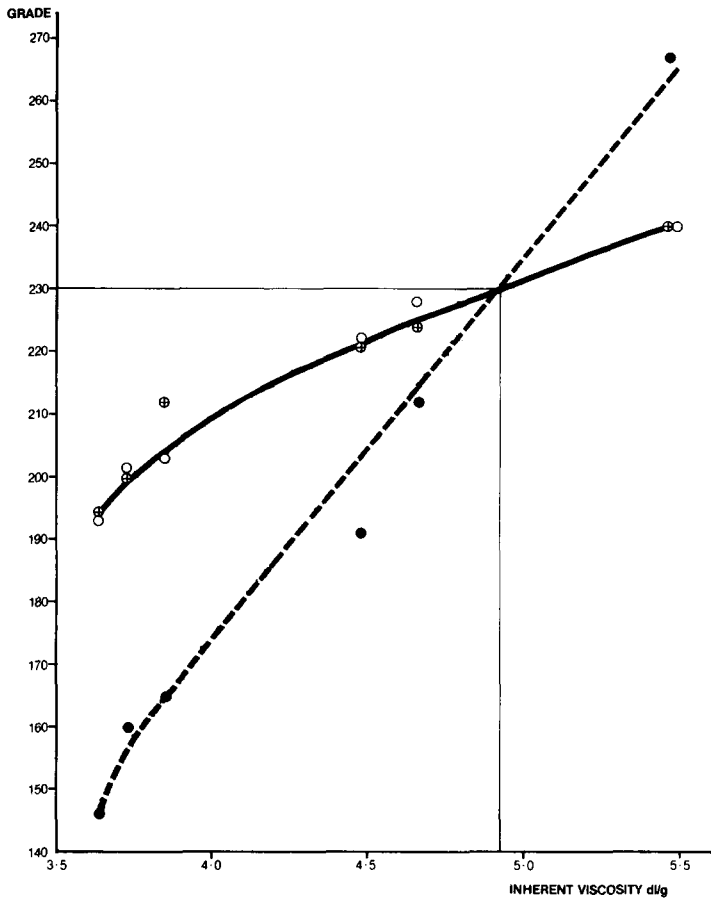
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Fig. 6. Pectin gelling grade by (———) sag type and (- - -) break strength (Tarr–Baker)
methods.

the jellies set slowly and uniformly. A new formulation based on
American practice is currently being developed by the International
Pectin Producers' Association. The jelly is formulated to match the pota-
ssium and calcium content, the pH and the refractometer solids content
of a typical grape jelly. The jelly mixture is poured into taped Petri dishes.
After incubation, the gels are tested on a freshly cut surface using a 12·3
mm cylindrical plunger descending at 0·5 mm/s. The maximum load is
determined using a chart recorder or a peak recording millivoltmeter.

Setting rate is another very important parameter for high methoxyl
pectins. There is a need for better generally accepted methods which are
realistic and not too labour-intensive, as most of the existing methods
suffer on one count or the other. One of the most widely quoted is the

setting time by the Joseph & Baier (1949) technique. This uses the IFT acid in glass formulation, at pH 2·3, and therefore does not relate directly to setting rates in actual products. A jelly tumbler is prepared with tartaric acid solution containing coarsely ground pepper. It is placed in a back-lit water bath at 30°C, and the jelly mix is poured in at time zero. At suitable intervals the glass is twisted slightly and as the jelly sets the pepper can be seen to swing back slightly before coming to rest. The setting time is reached when this set reaches 6 mm from the gel surface. The technique is rapid, but very operator-dependent, and inter-lab agreement is particularly difficult to obtain. Another technique is based on the Olliver *et al.* (1957) procedure. Portions of the jelly mixture at pH 3·1 and 70–71% solids are poured into 25 mm test tubes to a depth of about 50 mm. The tubes are already in a boiling water bath, which is then allowed to cool naturally but with stirring. The set is detected by inverting the stoppered tubes at intervals. This method can be very time-consuming but can be adapted to different pH values and sugar composi-tions in the gel. Another method which has been used is simply to pour portions of gel at different temperatures from a boiled jelly mix and measure the breaking strength of each jelly produced. A marked discontinuity in breaking strength occurs at the setting temperature.

There is no uniform method for the grading of low methoxyl pectins, but most are tested by a variant of the 'exchange' method developed by Sunkist Growers and reported in Food Chemicals Codex II (1972). However, for different pectin types, either the sugar or calcium content of the gels may be varied. In the original method there is no provision for adjusting the pH of the system to allow for variations in the solution pH of the pectin, and this has frequently been allowed for by using differing amounts of citric acid. This is not good practice, as the degree of complexing of the calcium is also altered. We prefer to add a constant quantity of total citrate and adjust pH with a mineral acid or alkali which has little or no complexing ability.

Some pectins for non-gelling end uses are graded by other more relevant techniques. They may be blended to constant solution viscosity for mouth feel and suspending power in soft drinks. Pectins for use in the stabilisation of acid milk systems such as yogurt drinks can be standardised to constant stabilising ability using a method based on the paper of Glahn (1982) where acidification with glucono-δ-lactone replaces culturing of the milk. Other specialised methods may be developed to meet the needs of specific users and processes.

Various techniques have been used to measure the molecular weight of pectin, and there is no universal agreement as to their validity, or to what extent such measurements may be affected by aggregation. The

GPC results and interpretation of Fishman (1986), for example, met with considerable disbelief at the symposium at which they were presented, most present finding the results unexpectedly low. Other workers have also used gel permeation techniques (Deckers *et al.*, 1986) and these seem to be able to distinguish pectins with different functional behaviour.

Another area which will be of interest in the practical applications of pectin is the determination of the distribution of ester groups, both within and between pectin molecules. It is known that many commercial pectins show different setting rates or different sensitivities to calcium at the same overall degree of esterification, and this may well relate to the mixing of molecules of different composition from the mixture of fruit used in production. It is to be hoped that convenient routine techniques will soon be available to evaluate the DM distribution of different samples of pectin.

One property that is specific to pectin is its degradation in neutral or slightly alkaline conditions, in contrast to its relative stability in acid conditions. This is associated with the structure and conformation of the molecule which facilitates an elimination reaction involving the glycosidic oxygen that is held *trans* to the activated proton adjacent to the ester group. High methoxyl pectins degrade rapidly, though not completely, in non-acid solutions at elevated temperatures, for example in an hour at 80°C at pH 6. Even at more acid pH values, for example between 3 and 4, pectin in solution at or above this temperature degrades sufficiently in a few hours to affect jelly texture. Low methoxyl and amidated low methoxyl pectins are rather more stable in this respect, and sodium pectate which has been totally de-esterified can be retorted at neutral pH with little loss of gelling ability.

APPLICATIONS OF PECTIN

The use of pectin in traditional high sugar jams is one of the best known applications and still one of the largest markets for pectin. Because pectin is present in the fruit and the added pectin is supplementing this, pectin has a unique place and is often the only permitted gelling agent, and is certainly the most obvious choice. Typically only 0·2–0·4% of pectin will need to be added, depending on the type and quantity of fruit. Within the EEC there are two standards, jam and extra jam, containing, with some exceptions, a minimum of 30% or 45% of fruit pulp respectively. The higher quality of jam tends also to be made with better quality fruit, so it requires significantly less pectin. Table 1 indicates which fruits require high, moderate or low additions of pectin. Jellies are often made

TABLE 1
Relative Pectin Additions to Jams and Preserves

High	Medium	Low
Cherry	Apricot	Apple
Peach	Blackberry	Blackcurrant
Pear	Loganberry	Damson
Pineapple		Gooseberry
Raspberry		Greengage
Strawberry		Guava
		Plum
		Redcurrant

High fruit: lower pectin addition.
Low fruit: higher pectin addition.

from depectinised fruit concentrates and will then require the full amount of added pectin irrespective of the fruit type. One of the more difficult products in recent years has been a citrus marmalade, especially lemon or grapefruit, where a higher than normal fruit content has been requested by the customer. The problem here is too much pectin from the fruit, leading to an over-strong gel or even to pregelation and syneresis. Attempts to regulate the texture and setting rate by raising the pH lead to a situation where control is extremely critical and a high rejection rate inevitable. One solution has been to work at a pH where the fruit pectin no longer forms a gel. Gelation can then be achieved by adding an amidated low methoxyl pectin which is capable of gelling at the high pH.

High methoxyl pectins are only useful in standard jams, above about 60% soluble solids. Many countries now permit reduced sugar jams of perhaps 30–55% soluble solids, or even lower. In certain countries, for example Scandinavia, these are now the major product. Here low methoxyl pectins, used at 0·75–1·0%, are cabable of giving excellent results. Selection of the correct pectin is important (the lower the soluble solids, the more calcium-sensitive the pectin that should be used) but fruit content is also important. Sometimes, especially at very low solids, it may be necessary to add a calcium salt to get the best result. Occasionally neutral gums are added to reduce syneresis, but every attempt should be made to optimise the type and level of pectin and the exact pH before such addition is considered, as gums can mask the delicate flavour of these products.

Jam manufacturers also make a very wide range of jams, fillings and toppings for the bakery and related industries. Many of these employ

pectin as a gelling or thickening agent but, because the requirements of the customer depend so much on their processing conditions, it is very difficult to generalise. Jams may be prepared with high methoxyl pectins in liquid or powder form, or special textures may be prepared using low methoxyl pectins. Suitable formulations using amidated low methoxyl pectins will be thermally reversible — they will melt and reset to a good gel on cooling. On the other hand, high sugar jams made with high methoxyl pectins can resist baking, for example in jam tarts. Biscuit jams are prepared to have a low water activity so they do not transfer water to the biscuit. Many other specialised requirements can be met by skilled formulation.

A range of glazes for pastries and flans can be prepared. By careful formulation with amidated low methoxyl pectin and calcium sequestrants such as diphosphates, products which are pasty but stable as supplied at 65% sugar solids can be diluted and melted, to reset as a clear shiny glaze. Pectin manufacturers offer ready-made blends of pectin and other ingredients for products of this type.

A growing area of the fruit products industry in recent years has been the production of fruit bases for addition to yogurts and similar products. Many of these have been made with modified starch as thickener to ensure an even distribution of fruit even after transport to the dairy, along with the pumpable texture. Unfortunately, although starches are relatively cheap, they can mask delicate fruit flavours and lead to a floury texture. These bases have sugar contents of between 30% and 60%, so high methoxyl pectins are only applicable at the top of this range. Low methoxyl pectins, selected according to the solids level, can be used very effectively. Amidated pectins are less critical of exact conditions of use, and give a greater degree of thixotropy, but conventional low methoxyl pectins give a 'cleaner' more acceptable label, in that declaration of 'amidated pectin' is avoided.

Pectin has other uses in the dairy field. High methoxyl pectin will prevent the aggregation of casein on heating at pH values below 4·3. It can therefore be used as a stabiliser for UHT-treated drinkable yogurts and for blends of milk and fruit juices. It will also stabilise acidified soya milk drinks and products based on whey, where precipitation of the whey proteins is prevented. Spoonable yogurt can be thickened by adding very low levels of amidated low methoxyl pectin before culturing. Although this is not permitted in many countries, a suitable pectin incorporated in a fruit base can, with careful formulation, have a comparable effect in a fruit yogurt.

Pectin has been used for many years to make high quality, tender, confectionery jellies with particularly good flavour release. Unlike some

other products, pectin jellies can be manufactured to the desired final solids content and do not require stoving to remove excess moisture. At these high sugar contents, it is essential to use a slow setting pectin with a blend of sugars, including glucose syrup to prevent sugar crystallisation. A suitably acid taste together with the close pH control necessary is achieved by adding a fruit acid buffer system. Unless the product is being cooked and deposited continuously it is essential to reserve the addition of part of the acid until shortly before depositing into suitable moulds. In this way cooking is carried out at a pH of around 4·5 at which the pectin is stable but will not gel, and the pH is only reduced to around 3·6 when a set is required. Once acid has been added, there is only a limited time available for depositing the product into moulds, as setting is both time and temperature dependent. If a non-acid product is required, such as Turkish Delight, a low methoxyl pectin can be used at around pH 4·5. Such a system would pregel at the high sugar content of confectionery, but addition of a blend of diphosphates controls the pH and sequesters a controlled addition of calcium so that setting rates can be precisely controlled. Such control is essential for modern continuous production processes.

Low calorie soft drinks are often thin and lack the characteristic mouth feel provided by sugar in conventional soft drinks. A low level of pectin (usually of controlled viscosity) can be used to improve the texture of such products, and also to replace some of the texture due to fruit pulp in low juice formulations.

In water ices, pectin can be used to control ice crystal size in both sorbets and ice pops. In ice pops and lollies this will also reduce the tendency for flavour and colour to be sucked out of the ice structure.

Chutneys and sauces are also sweetened acidic products and depend on the natural pectins from fruits and vegetables for their texture. In cases where, because of the type of fruit base which has been used, or the nature of the process, insufficient body can be developed, the addition of pectin, either high or low methoxyl depending on the solids level and other factors, will improve the texture and also the uniformity from batch to batch.

Gelatin has been the traditional base for dessert jellies, including trifles, fruit in jelly and similar products. Although the melt-in-the-mouth character helps to give good flavour release compared with some of the alternative gelling agents such as carrageenan, the low melting point can lead to melting of retail products during the journey home in hot weather or warm climates. The slow build-up of set is a marked disadvantage on a production line where it is desired to deposit another layer of cream, custard or other topping on top of a jelly. Low methoxyl pectin gels,

especially those made with amidated pectins, can be formulated to precisely controlled melting points and can be successfully deposited at their setting temperature. In fact, amidated pectin systems can be held in a stirred tank slightly below their setting point, the set being suppressed by gentle shearing; they will then set virtually immediately after depositing. Although full strength is only developed with time, cream can be deposited at an adjoining station without the need for an intervening chilling tunnel which would be essential with a gelatin system.

In addition to an increasing range of food uses, pectin has a number of applications in the pharmaceutical sphere. For these applications a pure pectin to the standard of the US Pharmacopoea is readily available. Special requirements such as controlled viscosity or a more tightly controlled particle size can often be met but, because these requirements vary greatly, they are commonly the result of discussions between buyer and seller, unlike the situation in the food industry where most needs can be met from a range of standard types. A traditional use of pectin has been in diarrhoea mixtures, often in conjunction with kaolin and sometimes bismuth compounds. Pectin is also used to maintain the viscosity of some syrups. Newer uses are as one of the hydrophobic fillers in self-adhesive colostomy flanges and in wound dusting powders and ulcer dressings where pectin appears to have some specific activity in promoting healing.

Pectin is therefore more than just 'the stuff that makes jam set'. It is a versatile and safe material which is derived from natural sources. There is even evidence that it has a beneficial effect by reducing the cholesterol level in the bloodstream when taken in sufficient quantity. It can certainly claim to be a food additive with a healthy image, a welcome contrast to the current concern about health risks from additives.

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