Introduction to GRINDSTED® Pectin

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THE BENEFITS
GRINDSTED® Pectin is the trade name for the pectin products manufactured by Danisco. The company's pectin production facilities are situated in Mexico, the Czech Republic and Denmark.

The pectin plants are equipped with the most up-to-date technology and are operated in accordance with stringent ISO and HACCP procedures. By focusing on applications and building up an in-depth knowledge of the molecular chemistry of pectin, Danisco has developed a wide pectin range for adding texture to or stabilising food and pharmaceutical products. Danisco manufactures exclusive pectin products with the following outstanding qualities:
- High degree of purity
- White pectin powder for high clarity solutions
- High level of process flexibility
- Broad formulation tolerance
- Controlled gelling
- High and uniform gel-breaking strength
- Excellent protein stabilisation

The Danisco pectin range includes a wide variety of high ester and low ester pectins. It is categorised in families designed for specific applications, as outlined later.

INTRODUCTION
The word pectin comes from the Greek word pektos, which means firm and hard, reflecting the ability of pectin to form gels.

Pectin is the name of a natural polymer used to stabilise or give texture to food and pharmaceutical products. The gelling properties of pectin have been known for centuries, but the isolation of commercial pectin only started at the beginning of the 20th century.

The development of pectin production technology has made it possible to manufacture a number of pectin types with a variety of functional properties. Commercial pectins are defined as high ester (HE) and low ester (LE) pectins, the latter being sub-divided into conventional pectin (LC) and amidated pectin (LA).

THE ORIGIN OF PECTIN
Pectin is a carbohydrate with a high molecular weight which is present in all plants, primarily in the form of protopectin. Together with cellulose, protopectin forms part of plant cell walls and is, therefore, essential for plants and their structure.

The term pectin relates to a number of polymers which vary according to their molecular weight, chemical configuration, degree of esterification, content of neutral sugars, etc. Different plant types produce pectin with different functional properties (especially gelling properties).

The pectin content of fruit used for commercial pectin production varies between 10% and 50% of the dry raw material used. Lime and lemon peel contain a particularly large amount of high quality pectin (see figure 1).

The pectin in citrus fruit is located primarily in the albedo and lamellae. The white layer of a citrus fruit, the albedo, is the inner layer of the peel and surrounds the juice segments. When juice and oils have been extracted from the fruit, the pectin remains.
Peel is used for pectin production (see figure 2).

Pectin today is commercially produced mainly from apple pomace and citrus peel by an extraction process followed by separation, purification, isolation and then drying, milling and standardisation (see figure 3).

PECTIN CHEMISTRY

Pectin basically consists of a chain of galacturonic acid units which are linked by \( \alpha-1,4 \) glucosidic bonds. The galacturonic acid chain is partly esterified as methyl esters. Pectin molecules can have a molecular weight of more than 150,000, corresponding to a degree of polymerisation of up to 1,000 units (figure 4).

Commercial pectins are divided in two major groups: HE and LE pectins. The division is related to the number of ester groups in the pectin molecule and, thus, the functional properties. If the number of galacturonic acid groups in the pectin molecule is substituted by more than 50% methyl ester groups, the pectin is known as high ester (HE). If this number is less than 50%, the pectin is called low ester (LE) (see figure 5).

As some LE pectins contain amide groups, LE pectins are subdivided into amidated pectins (LA) and non-amidated or conventional pectins (LC).

HE pectins

The typical degree of esterification (DE) for commercial HE pectins ranges from 50% to more than 80%.

HE pectins are characterised as being able to gel in aqueous systems with more than 55% soluble solids and a pH ranging from 2.8 to 3.5. The higher the number of ester groups, the faster the pectin will gel. This forms the basis for classifying high ester pectin from rapid set to extra slow set.

High ester pectins are also widely used for their protein stabilisation properties. In this application, the details of the molecular structure and especially the distribution of the ester groups on the galacturonic acid backbone are key factors. Through raw material selection and process technology, Danisco is able to produce high ester pectins with a highly controlled molecular structure to ensure consistent performance in the application.

High ester pectins are standardised according to their application: SAG grade, gel strength, setting temperature, viscosity and protein stability are the main parameters used for standardisation purposes.

LC pectins

LC pectin, like HE pectin, consists of a linear chain of partially esterified galacturonic acid units.

The DE of LC pectins is below 50% and typically ranges from 30% to 50%.

With this low level of ester groups, the number of carboxyl groups is significant for the formation of calcium cross-links resulting in gel formation. Therefore, LC pectins are characterised according to their degree of calcium reaction.

LC pectins are standardised according to their application, typically in terms of

<table>
<thead>
<tr>
<th>PECTIN TYPE</th>
<th>DE RANGE (%</th>
<th>SETTING TIME (SECONDS)</th>
<th>TYPICAL SETTING TEMPERATURE (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extra slow set</td>
<td>58 - 62</td>
<td>260 - 330</td>
<td>55</td>
</tr>
<tr>
<td>Slow set</td>
<td>63 - 67</td>
<td>170 - 225</td>
<td>70</td>
</tr>
<tr>
<td>Medium rapid set</td>
<td>67 - 71</td>
<td>120 - 160</td>
<td>75</td>
</tr>
<tr>
<td>Rapid set</td>
<td>&gt; 70</td>
<td>&lt; 110</td>
<td>83</td>
</tr>
</tbody>
</table>

Table 1. Typical setting time and temperature of HE pectins.

Note: Setting times and temperatures are highly dependent on the recipe used, especially soluble solids level and pH.

Figure 2. Pectin is derived from the fibrous and pulpy parts of the fruit.

Figure 3. Typical pectin flow process.
gelling, setting temperature and calcium tolerance.

LA pectins differ from LC pectins as a number of amide groups are situated in the pectin molecule, partially substituting methyl ester groups. Legislation limits the degree of amidation to 25%. Like LC pectins, LA pectins form intermolecular calcium cross-links, resulting in gel formation.

No direct comparison can be made between calcium reactions of LA and LC pectin, as the amide groups in LA pectins interfere with the gelling mechanism of the pectin (see functional properties below).

LA pectins are standardised according to their applications, typically gel strength, setting temperature and calcium tolerance.

**CHEMICAL AND PHYSICAL PROPERTIES**

**Solubility**

Pectin is soluble in water but insoluble in most organic solvents. The solubility rate in water is related to the degree of polymerisation and the number and distribution of methyl ester groups. The pH, temperature and ionic strength of the solution are of great importance to the rate of pectin dissolution. The calcium content of the water used to dissolve the pectin is particularly relevant as high water hardness will often result in incomplete pectin dissolution.

Like any hydrocolloid, pectin grains swell before going into solution. If pectin grains are not well separated upon dispersion in water (high shear mixing, dry blending with other material), the swelling of the grains will cause them to agglomerate, forming lumps. These lumps are extremely difficult to dissolve once they are formed. For this reason, it is of great practical importance to the industrial user to obtain a good pectin dispersion in water (see table 2).

**Rheology of pectin solutions**

Pectin solutions are viscous, which means pectin is widely used to add viscosity, especially to juice and soft drinks.

Dilute pectin solutions are almost Newtonian and only slightly affected by the presence of calcium. However, solutions with more than 1% pectin exhibit pseudo-plastic behaviour and are strongly affected by calcium. The texture starts as water and then develops through thixotropic solutions with yield value to stiff gels depending on the pectin type and concentration, level of calcium and pH.

**Stability**

High ester pectins are stable at pH levels of 2.5 to 4.5. Above a pH level of 4.5, β-elimination will occur, depolymerising the galacturonic acid chain. This mechanism requires an esterified carboxyl group next to the glycosidic bond to be cleaved (figure 6) so low ester pectins are more stable at higher pH values.

The pectin molecular structure is quite resistant to heat. When pH is around 3.5, pectin is only marginally depolymerised.

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**Table 2. Practical ways to dissolve pectin.**

<table>
<thead>
<tr>
<th>METHOD</th>
<th>PROCEDURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution after dry blending with sugar</td>
<td>Dry blend pectin with 5 parts sugar. Add to hot water (80-90°C) and mix for a few minutes.</td>
</tr>
<tr>
<td>Direct solution</td>
<td>Add the pectin slowly to hot water (80-90°C) during vigorous agitation.</td>
</tr>
<tr>
<td>Syrup dispersion</td>
<td>Disperse the pectin into sugar syrup. The pectin will only hydrate if the soluble solids are brought below 25% at a later stage of the process.</td>
</tr>
<tr>
<td>Direct addition</td>
<td>Dry blend the pectin with 5 parts sugar. Add directly to the product mix when soluble solids are below 25% and boil for min. 3 minutes.</td>
</tr>
</tbody>
</table>

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**Figure 6. β-elimination mechanism.**
at high temperatures. The heat stability of pectin is greatly improved when the water activity of the system is lowered following the addition of sugar.

**FUNCTIONAL PROPERTIES**

Pectins are used in a broad variety of food and pharmaceutical products. Their principal properties are gel formation, viscosity build up and protein stabilisation. As methods develop for obtaining a better understanding of pectin's molecular structure, pectin is likely to be attributed new functional properties in the future.

Gelling of high ester pectins

**Gelling mechanism**

It is generally accepted that a high ester pectin gel is formed by cross-linking the polymer in junction zones, in which mainly hydrogen bonds but also hydrophobic attractions between the methyl ester groups play a part. Calcium bridges may also participate, especially if the esters are distributed in blocks, leaving large parts of the molecule as free acids.

As the pectin chains carry negative charges, they will tend to repel each other. This repulsion can be directly correlated to the pH of the medium and the number of free galacturonic acids of the pectin. The higher the pH and lower the degree of esterification, the higher the charge density and, hence, the stronger the repulsion.

This repulsion and, more importantly, the impossibility of forming hydrogen bonds between ionised pectin chains are the reasons why a low pH is required for high ester pectin gelling. At a low pH, typically below 3.5, the repulsion is low enough for the distance between the pectin chains to be sufficiently reduced so hydrogen bonding can occur. In order to achieve sufficient hydrophobic interactions to stabilise the molecular network, the water activity of the system also has to be decreased. Sugars are usually added for this purpose.

Upon storage of a cooled gel, it is typical that the texture will still develop into a stronger final gel. This corresponds to a slow reorganisation of the network involving the creation of new junction zones or an enlargement of the existing junctions between the pectin molecules (see figure 7).

**Parameters influencing gelling**

The gelling and final gel structure of high ester pectins are influenced by a great number of parameters, the main ones being the pectin concentration, degree of esterification and molecular weight of the pectin molecule, and the pH, ionic strength, water activity, sugar type and cooling rate of the gelling medium.

**Pectin concentration**

The concentration of high ester pectin will increase the final gel strength of the system due to a larger number of active junction zones. An increase in molecular weight would have the same effect. In addition to this expected effect, the gelling rate is also increased with an increasing pectin concentration and a power law can be calculated between the two parameters.

**Degree of esterification**

The degree of esterification of the galacturonic acids affects both the charge density of the polymer and the number of sites for hydrophobic interaction. As pectin molecules with a high degree of esterification are less charged, they can form gels at a higher pH and will also start gelling at a higher temperature.

**pH and ionic strength of the gelling system**

The lower the pH, the lower the repulsion between the pectin molecules and, thus, the easier it will be for them to interact. This means a low pH will lead
to faster gelling in high ester pectins. However, below a critical level, the gel strength will actually be reduced as the gelling process is too fast to obtain a well-organised polymer network and precipitation can occur. The optimum pH for gelling is controlled by the pectin’s degree of esterification as well as the soluble solids content of the medium (see figure 8).

Water activity and sugar types
Water activity and sugar types both affect the way hydrophobic interactions can develop between the pectin molecules. As water activity is reduced, the hydrophobic interactions are easier to form, causing faster gelling to occur and the final gel strength to be increased. The most common way to reduce water activity in a food system is through the use of sugars. The effect of sugars on hydrophobic interaction and, thus, on gel structure is specifically linked to their molecular conformation and interaction with the neighbouring water molecules (see figure 9).

Influence of cooling rate and storage temperature
As the cooling rate is increased, the gelling rate increases accordingly. However, during rapid cooling and with a low storage temperature, gelling can actually become very slow, reflecting the difficult development of hydrophobic interactions in these conditions. With an intermediate cooling rate and temperature range, hydrogen bonds and hydrophobic interactions together can contribute to the build-up of a network with maximum elasticity. The final firmness is typically not affected by the cooling rate.

Properties of high ester pectin gels
Due to the nature of the molecular interactions involved in high ester pectin gelling, gels made with these pectins will typically be non thermo-reversible and non shear-reversible.

When submitted to mechanical stress, the broken gel will then show a high level of syneresis.

Gelling of low ester pectins
Low ester pectin has traditionally been used to gel food products when the conditions required to achieve a gel with high ester pectin were not met. Recently, however, low ester pectins have also found applications in high sugar and low pH systems because of their specific texture characteristics.

Though the same basic mechanism applies, low ester conventional and amidated pectin differ in their gelling properties and offer a broad range of functional properties.

Gelling mechanism
The gelation of low ester pectin is mainly the result of calcium bridges between carboxylic groups from two pectin chains with the participation of hydrogen bonding. The most commonly accepted model of association is the egg box model (figure 10). Even though a number of positive ions can bridge pectin molecules, especially magnesium and potassium, calcium is particularly effective at forming complexes with carbohydrates.

The exact calcium requirements to obtain a gel highly depend on the pectin’s degrees of esterification and amidation, the recipe and process parameters such as the rate of cooling.

An optimum calcium level can be defined for a given pectin in specific conditions. Above this optimum level,
pre-gelation will occur, i.e. gelling will occur at temperatures too high to obtain a coherent gel structure (figure 11).

The typical gelling mechanism of high ester pectin, with hydrogen bonds and hydrophobic interactions, can also contribute to the final texture of low ester pectin gels, especially at a low pH and with high soluble solids.

**Parameters influencing gelling**

Although the availability of calcium is a critical factor in the gelling of low ester pectins, other parameters in relation to the pectin molecule and media have a significant influence on gelling and the final structure obtained. The main parameters are the number and distribution of ester and amide groups, as well as the molecular weight of the pectin molecule and the pH, ionic strength and water activity of the gelling system.

**Influence of esterification**

Because calcium bonds can only occur in esterification-free zones, gel strength increases with a decreasing degree of esterification. For low ester pectin with an average DE of above 30%, the distribution of the esters may be highly important as this controls the length of possible junction zones and influences the gelling temperature, final gel strength and texture.

**Influence of amidation**

Pectin amidation was developed in the 1940s as a means of modifying the functional properties of low ester pectins in order to achieve better gelling control. The exact involvement of amides is not fully clear. However, gels made with amidated pectins are typically firmer and require less calcium. They are also more thermo-reversible than those made with low ester conventional pectins.

**Influence of molecular weight**

As for any polymer gel, the length of the polymer governs the number of junction zones required to achieve a coherent network. Low ester pectins with a high molecular weight exhibit a higher gelling rate, lower calcium requirements for gelling and an overall more cohesive and elastic gel structure with a reduced tendency towards syneresis.

**Influence of pH**

With a low sugar content, pectin molecules are neutralised with protons as pH decreases, reducing the probability of junction zones forming with calcium. This translates into higher calcium requirements and a looser gel texture at a low pH (see figure 12). On the other hand, when the water activity of the system is decreased by the addition of sugar, the gelling mechanism of high ester pectin starts to play a significant part in gelling and the calcium requirements are then actually decreased when the pH is lowered. In standard food systems, the availability of the natural calcium will also be increased at a lower pH, reducing the need for extra calcium addition.

**Influence of ionic strength**

An increase in gel strength can be observed at a higher ionic strength. This is usually explained by the neutralisation of the polymers by the extra ions, allowing the chains to be closer and leading to a more organised and cohesive gel.

**Influence of water activity**

As the solids level increases, calcium requirements decrease. However, for most pectins, a higher solids level accelerates gelling and increases the setting temperature and final gel strength. It also reduces the optimum calcium window, thus increasing the risk of pre-gelation. In practice, this leads to a choice of pectin with a higher degree of esterification (less calcium reactive) at a higher solids level.

**Properties of low ester pectin gels**

The properties of low ester pectin gels are very dependent on the type of pectin used (conventional or amidated) along with the procedure and formulation employed to make the gel. Typically, they are thermo-reversible and show a high degree of thixotropy.

In specific conditions it is, however, possible to obtain heat resistant or very brittle gels with no shear reversibility.

**Protein stabilisation with high ester pectin**

In acidified conditions, casein and, more generally, food proteins tend to agglomerate and sediment if the viscosity of the system is low enough. In these conditions the proteins are also very sensitive to dehydration and the product can easily become sandy after heat treatment.

With the rapid development of acidified dairy beverages worldwide, now expanding with other protein sources such as soy, the need for effective protein
stabilisers in a low pH environment is growing fast. High ester pectin has proven a very useful stabiliser in these conditions.

**Mechanism**

It is generally accepted that, at sufficient pectin concentrations, the adsorption of the carboxyl blocks of the pectin molecule to the protein surface will stabilise the protein system through steric repulsion (figure 13). Both the pectin’s degree of esterification and the actual distribution of the esters on the polymer affect its stabilisation properties. Excessively large blocks of carboxyl groups tend to interact with the ions present in the system, such as calcium, rather than with the protein, an interaction leading to an increase in viscosity or even gelation. This explains why only high ester pectin with a fairly high degree of esterification is useful in this application.

**Conditions**

Through its role in the ionisation of the protein and pectin molecules, pH is the most significant factor affecting the electrostatic pectin-protein interactions. It also plays a very significant role in the protein structure and the way the proteins interact in a complex system such as milk.

The optimum pH range for interaction between high ester pectin and casein is 3.6 to 4.5. At a lower pH, the block structures of the high ester pectin will not be sufficiently ionised for proper protein binding as the pH is too far below the pKa of the pectin. Above the isoelectrical point of the protein, the protein-polysaccharide complex is very weak or non-existent.

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<th>FUNCTION</th>
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<td>GRINDSTED® Pectin AMD series</td>
<td>Acidified protein drinks</td>
<td>Protein stabilisation</td>
</tr>
<tr>
<td>GRINDSTED® Pectin CF series</td>
<td>Confectionery Bakery fillings</td>
<td>Gelling with low setting temperature</td>
</tr>
<tr>
<td>GRINDSTED® Pectin SF series</td>
<td>Low sugar jams and jellies</td>
<td>Gelling with good syneresis control</td>
</tr>
<tr>
<td>GRINDSTED® Pectin YF series</td>
<td>Fruit preparations Bakery fillings</td>
<td>Texture and yield value Texture and bake stability</td>
</tr>
</tbody>
</table>

Table 4. The main Danisco pectin series.

**DANISCO PECTIN SERIES**

In addition to standard high ester and low ester pectins, Danisco has developed pectin tailored to specific applications. In each case, the pectins are tested and standardised in specific systems representative of the application.

The main pectin series are outlined in table 4.

**AVAILABLE LITERATURE**

Danisco offers a comprehensive range of technical literature on pectin related topics.

- TM 4002: GRINDSTED® Pectin for reduced sugar jam, jelly and fruit spread
- TM 4004: GRINDSTED® Pectin for yogurt fruit preparations
- TM 2032: Determination of stability index for GRINDSTED® Pectin AMD products
- PB 2001: GRINDSTED® Pectin AMD protein stabilisers for acidified beverages
- PB 3501: GRINDSTED® Pectin for sugar confectionery
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