Low Methylester, Amidated Pectins
Low methylester, amidated pectins are known for their high flexibility, that means their ability to form gels in wide soluble solids and pH-value ranges and with that to offer a very high product safety.

Due to this property there are very different fields of application for low methylester, amidated pectins. It is possible to manufacture products with higher or lower pH-values and in soluble solids ranges between 10 – 80% ss. Such products are, for example, caloriereduced fruit preparations, household gelling agents, nappage, fruit preparations for yoghurt, delicatessen sauces etc.

Therefore low methylester, amidated pectins have to gel in most different products and at the same time they have to meet the very different requirements mainly concerning texture and properties of the final products. Jams, for example, are expected to have an elastic-brittle to elastic-viscous texture, whereas fruit preparations for yoghurt are not intended to show an elastic gelation, but a smooth and viscous texture.

If low methylester, amidated pectins are used for the production of nappage, they should have a setting temperature as low as possible, whereas for use in products with fruit pieces, e.g. jams, a higher setting temperature resp. the forming of a yield point in hot condition for floating prevention is expected.

In order to control the production process as easy as possible and to guarantee a high product safety, the pectin users more and more require the gelling agent to be able to form gels with constant texture in case of recipe modifications (e.g. use of different fruits, alteration of pH-value or soluble solids content).

If in the particular recipe the appropriate low methylester, amidated pectins are used, these requests will be met.

It is also often required to work without the separate addition of calcium salts. This is enabled by the property of low methylester, amidated pectins to form elastic gels already with the natural calcium content of the fruits / raw material under defined conditions.

In order to satisfy these various demands, H&F offer low methylester, amidated pectins which differ in their calcium reactivity. The calcium reactivity here is a measure for the ability to form a gel with a defined setting rate under defined conditions. At the same time the calcium concentration remains constant. Regarding low methylester, amidated pectins this reactivity is decisively influenced by the ratio of degree of esterification and degree of amidation as well as by the raw material used.
Furthermore, low methylester, amidated pectins characterise themselves by their high flexibility and great tolerance towards recipe depending fluctuations and are, with that, easy to process.

With the specific selection of these low methylester, amidated pectins it is possible to manufacture products which meet optimally the consumer demands regarding texture as well as technological demands.

<table>
<thead>
<tr>
<th>Pectin type</th>
<th>Calcium reactivity</th>
<th>Setting rate</th>
<th>Typical degree of esterification</th>
<th>Typical degree of amidation</th>
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</thead>
<tbody>
<tr>
<td>Apple pectin</td>
<td>Citrus pectin</td>
<td></td>
<td></td>
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<tr>
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<td>Amid CF 005</td>
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<td>slow</td>
<td>35%</td>
</tr>
<tr>
<td>Amid AF 010</td>
<td>Amid CF 010</td>
<td>medium</td>
<td>medium</td>
<td>32%</td>
</tr>
<tr>
<td>Amid AF 020</td>
<td>Amid CF 020</td>
<td>high</td>
<td>rapid</td>
<td>30%</td>
</tr>
</tbody>
</table>

Table: Low Methylester, amidated pectins of H&F

The binding happens by complexation of bivalent cations by proximate, free, dissociated carboxyl groups and hydroxyl groups of the respective galacturonic acid units.

The presence of amid groups – in contrast to the low methylester, non-amidated pectins – effect additional bonding zones via hydrogen bonds. The more amid groups are present, that means the more bonding zones are effected, the stronger the resulting gels are.

Regarding low methylester, amidated pectins, the clustering process of the pectin chains happens in a more controlled way than it is the case for low methylester, non-amidated pectins. The reason is that, at comparable degree of esterification, the forming of a gel network due to hydrogen bonds between the amid groups happens slower than the reaction of low methylester pectins with calcium ions.

Gelling mechanisms of low methylester, amidated pectins

The following mechanisms are basic for the gelation of low methylester, amidated pectins:

Comparable to high methylester pectins, the gelation according to the so called „sugar acid gelling mechanism“ results in a network which is formed by hydrogen bonds between the free, undissociated carboxyl groups. At the same time the clustering of the pectin chains is favoured by hydrophobic interactions between the methylester groups. This influence becomes stronger, the higher the degree of esterification of the pectin and the sugar content in the gel are.

Furthermore low methylester, amidated pectins are, like low methylester pectins, also able to form a gel relatively independent from soluble solids content and pH-value if polyvalent cations (e.g. calcium ions) are present („egg box model“).
Influence of calcium ion concentration on the gelation of low methylester, amidated pectins

In the case of low methylester, amidated pectins, the calcium ion concentration which is necessary for gelation, depends on different product parameters such as soluble solids content, pH-value of the product or the buffer concentration.

Already at a low calcium ion concentration the pectin chains start to cluster via calcium bonds. Here the calcium ion concentration which is necessary for gelation, may yet come from the natural calcium content which is brought in by the fruits or the water contained in the recipe.

The amid groups stabilise the network by hydrogen bonds resulting in elastic gel products already at a low calcium ion concentration. Besides the degree of esterification, the amount of amid groups determine the reactivity and with that the calcium need for forming a gel network and the resulting setting temperature.

With increasing the calcium ion concentration the gels become stronger until reaching an optimum, the texture of the gels becomes more elastic and more brittle. As the bondings are additionally stabilised due to the presence of amid groups and with that by the formation of hydrogen bonds, low methylester, amidated pectins are able to gel homogeneously and relatively independent from calcium ion concentration over a wide range (fig. 2).

If the calcium dosage is raised intensely, pre-gelation, that means an over-reaction between the pectin molecules and the calcium ions, occurs. Fine gel particles are formed, the gel arrangement looses its elastic character, the texture becomes pasty and with that the gelling strength is reduced. At mechanical treatment the gel looses water, syneresis occurs. This process of pre-gelation is reversible. If pre-gelled gels made of amidated pectins are heated again to a temperature which is higher than their setting temperature and then cooled down again, an elastic and firm gel will be obtained.
Influence of the raw material on the gelation of low methylester, amidated pectins

Low methylester, amidated pectins can be made from apple pomace as well as from citrus peels.

The raw material used has also an influence on the texture of the manufactured gels. At comparable degree of esterification and degree of amidation, low methylester, amidated apple pectins form elastic-viscous textures which are easy to spread, show a high mouthfeel („body“) and low tendency to syneresis. Gels, which are manufactured with low methylester, amidated citrus pectins, have higher setting temperatures and result in elastic-brittle products.

Gelling properties of low methylester, amidated pectins with differing calcium reactivity

The gelling properties of low methylester, amidated pectins, that means, the setting time / setting temperature and the formation of a particular gel texture, are decisively determined by the calcium reactivity.

Therefore the behaviour of low methylester, amidated pectins in dependence from calcium ion concentration is not only influenced by the fixed recipe parameters such as soluble solids content, pH-value of the product and the amount of present / added buffer salts, but additionally by the particular calcium reactivity of the pectin. Due to this property low methylester, amidated pectins can be specifically selected that, also under most different product parameters, they gel homogeneously and relatively independent from calcium ion concentration for reaching the desired texture in the particular final product.

Reactivity levels of low methylester, amidated pectins:

Low reactivity:
Pectin Amid AF 005, Pectin Amid CF 005  
Medium reactivity:
Pectin Amid AF 010, Pectin Amid CF 010  
High reactivity:
Pectin Amid AF 020, Pectin Amid CF 020
For special applications also H&F pectins with very high reactivity are available. Furthermore, H&F offer tailor-made low methylester, amidated pectins which are already standardized with specific buffer salts to a defined gelling behaviour.

**a) Setting time / setting temperature of low methylester, amidated pectins with differing calcium reactivity**

The higher the calcium reactivity of the low methylester, amidated pectin, the shorter the setting time resp. the higher the setting temperature in a gel preparation, produced with this pectin, is.

The setting temperature of a gel preparation, that means the temperature at which gelation after the boiling process and during the cooling phase starts, is a relevant factor. Here a sol-gel-transit takes place, that means the pectin chains form themselves to a three-dimensional network.

The setting temperature fixes the filling temperature in order to prevent pre-gelation or specifically to cause pre-gelation.

Pre-gelation always occurs if the processing / filling temperature is beneath the setting temperature.

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![Fig. 3: Texture of methylester, amidated pectins in dependence from calcium ion concentration](image-url)

Increasing calcium reactivity  
Decreasing setting time / increasing setting temperature

<table>
<thead>
<tr>
<th>Pectin Amid AF 005</th>
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<tbody>
<tr>
<td>Pectin Amid CF 005</td>
<td>Pectin Amid CF 010</td>
<td>Pectin Amid CF 020</td>
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In this case a gel network is already formed prior to the filling process, which will be destroyed again due to the mechanical stress during the filling process. A partial loss of the maximal obtainable gelling strength and a higher tendency to syneresis result.

b) Gelling properties of low methylester, amidated pectins with differing calcium reactivity at different filling temperature

The texture and the firmness of the final product can be decisively influenced by the selected filling temperature.

By means of two low methylester, amidated pectins with differing calcium reactivity fig. 4 shows, under comparable recipe parameters, the changing of firmness and texture of the final product, if the product was filled at different temperatures.

If a product, for example a fruit preparation (e.g. 45% ss, pH-value 3.3), is manufactured with a reactive pectin and then filled, elastic gels with a constantly high gelling strength will be obtained as long as the filling temperature is higher than the setting temperature of this fruit preparation. If the filling temperature is decreased and reaches a level beneath the setting temperature, pre-gelation will occur resulting in the partial loss of the maximal reachable gelling strength. At the same time the texture of the pre-gelled fruit preparation becomes more and more viscous, the lower the filling temperature is chosen.

Due to the relatively high setting temperature of the fruit preparation manufactured with reactive pectin, the final gelling strength decreases relatively quick with falling filling temperature. If finally this fruit preparation is filled at a low temperature (e.g. 60°C), a pasty texture with higher tendency to syneresis will result due to the pre-gelation occured.

If the same fruit preparation is manufactured with a pectin with less calcium reactivity, the gelling strength will be constant within a wider temperature range as this fruit preparation shows a lower setting temperature. Products which are manufactured with pectins with low calcium reactivity, can therefore also be processed and filled at lower temperatures. The products show only very low tendency to syneresis.

c) Gelling properties of low methylester, amidated pectins with differing calcium reactivity at different product pH-values

The product pH-value has an important influence on the gelling behaviour of low methylester, amidated pectins.

With the example of two pectins with differing reactivity fig. 5 shows the breaking strength in dependence from calcium dosage at three different product pH-values of the gel preparation.

The breaking strength, which is reached by using the pectin with low calcium reactivity in dependence from the calcium dosage, increases for the three product pH-values with increasing calcium ion concentration.
At comparable calcium ion concentration the gel strength decreases from pH 3.2 to pH 3.6 and to pH 4.2 which means that the gels become weaker with rising pH-value, the viscous shares increase.

With rising pH-value of the final product the calcium need increases. That means to obtain comparably firm gels, gels with a higher pH-value need more calcium ions than gels with lower pH-value.

The breaking strength of the gels which are manufactured with a pectin with high reactivity, at first also increases with rising calcium ion concentration.

In comparison, the absolute values in this range are higher than for the pectin with low reactivity. At the same time the texture of the gels which are manufactured with a more reactive pectin, are more elastic at a comparable pH-value.

With a defined calcium ion concentration, however, the gel strength of the gels with a pH-value of 3.2 decreases, as the setting temperature of this gel preparation is high in a way that pre-gelation will occur under the given conditions. With that the texture looses its elasticity and becomes more and more viscous.

In contrast to that, elastic gels are formed over a wide range at pH-values of pH 3.6 and pH 4.2 by using a reactive pectin. The curve progression is plain, that means the breaking strength of these gels changes only little with increasing calcium dosage.

A plain curve progression means to the user, that the working area under these conditions is wide, as the gels are very tolerant towards fluctuations of the calcium content. With that a high flexibility and product safety are guaranteed.
Low methylester, amidated pectins with high reactivity such as Pectin Amid CF 020 or Pectin Amid AF 020 are therefore especially well suited for the use at higher pH-values, whereas for products with lower pH-value rather pectins with a lower reactivity such as Pectin Amid CF 005 or Pectin Amid AF 005 are used.

d) Gelling properties of low methylester, amidated pectins with differing calcium reactivity at different soluble solids content

Besides the pH-value of the product also the soluble solids content is an important parameter for choosing low methylester, amidated pectins.

When altering the soluble solids content, low methylester, amidated pectins show different gelling properties in dependence from their calcium reactivity.

Thus, depending on the product and its soluble solids content, the required gelling behaviour can be reached by choosing the suitable pectin.

The following figures show at the example of three pectins with differing reactivity the breaking strength of gel preparations in dependence from calcium dosage at different soluble solids ranges (20%, 40%, 60% ss).

Fig 5: Breaking strength (Herbstreith Pektinometer Mark IV) of gels (40% ss, 1.0% pectin), manufactured at different pH-values with low methylester, amidated pectins with differing calcium reactivity in dependence from calcium ion concentration.
Gelling behaviour at 20% ss

With rising calcium ion concentration the breaking strength, determined with the Herbstreith Pektinometer Mark IV, increases, the texture of the gels becomes firmer and more elastic.

Over the whole range investigated the high reactive pectin results in firmer gels at comparable calcium ion concentration than pectins with medium resp. low reactivity do.

In order to reach a comparable breaking strength of the gels, pectins with medium and low reactivity require higher calcium dosages than pectins with high reactivity.

To form elastic gels, gel preparations which are manufactured with pectins with medium and low reactivity require a certain amount of calcium ions whereas gels, which are manufactured with a reactive pectin, already form an elastic gel at minor addition of calcium ions which might come from the fruits or the drinking water.

Fig. 6: Breaking strength of gels (20% ss, 1.0% pectin, pH-value 3.2), manufactured with low methylester, amidated pectins with differing calcium reactivity in dependence from calcium ion concentration

In contrast to pectins with low and medium reactivity, the curve progression of pectin with high reactivity is plain and the breaking strength of the gels changes over a wide range only little.

At low soluble solids contents (0 – 20% ss) the reactive pectin requires a certain amount of calcium ions for gelation, however then it shows a high tolerance towards fluctuations of the calcium content resulting in a homogenous gelation over a wide working range.

As a result, low methylester, amidated pectins with high calcium reactivity such us Pectin Amid CF 020 or Pectin Amid AF 020 are excellently suited for the use in products with a low sugar content such as sugar reduced fruit preparations or delicatessen products.

Pectins with very high reactivity such as Pectin Amid CF 025 or Pectin Amid CB 025 are suited among others for glaze, spray nappage or jelly.
Gelling behaviour at 40% ss

If the soluble solids content is raised to 40% ss, low methylester, amidated pectins with medium and higher calcium reactivity will form elastic gels already at a low concentration of calcium ions. Especially for gels which are manufactured with a pectin with medium reactivity, the breaking strength is homogeneously high over a very wide range and relatively independent from calcium ion concentration.

At a defined, relatively high calcium ion concentration the gel strength of gels, which are manufactured with the high reactive pectin, slightly decreases, as here the setting temperature is high in a way, that pre-gelation occurs under the given conditions. Then the texture becomes more and more viscous resulting in falling breaking strength values.

On the contrary, the pectin with low calcium reactivity requires a certain amount of calcium ions to form elastic gels. Then the breaking strength values rise with increasing calcium ion concentration and the gels become firmer.

At comparable gel strength the pectin with high calcium reactivity forms an elastic-brittle texture, whereas gels manufactured with a pectin with low reactivity are elastic-viscous and pasty.

As pectins with high calcium reactivity and especially pectins with medium calcium reactivity show, at a soluble solids content of 40%, a homogeneous gelation over a wide range and with that a high tolerance towards calcium ions, these medium reactive pectins are excellently suited for the use in products in this soluble solids range.

For example, in applications with gelling sugar (2:1) most different fruits are used at approx. 40% ss, which mainly differ regarding their calcium and acid content.

Additionally the household production conditions vary depending from the user. Despite this fact, products with homogeneous gelation and sufficient firmness are expected. Low methylester, amidated pectins with medium reactivity are a guarantee for the successful manufacture of these preparations.

Furthermore, low methylester, amidated pectins with medium calcium reactivity such us Pectin Amid CF 010 or Pectin Amid AF 010 are used for example for calorie-reduced fruit preparations, fruit preparations for yoghurts or to stabilise fruit cream.
Gelling behaviour at 60% ss

At a soluble solids content of 60% pectins with high and medium calcium reactivity already gel without the separate addition of calcium ions. When adding calcium ions, the breaking strength values increase at first, the texture of the gel becomes firmer and more elastic-brittle.

With a further raise of the calcium ion concentration pre-gelation will occur relatively quick and, as a consequence, the gel strength decreases. At a soluble solids content of 60% ss the setting temperature of these pectins increases with increasing calcium ion concentration very intensely, the preparation gels already during the boiling process and the gel can no longer be filled without being destroyed. Due to the pre-gelation, the obtained gels are pasty with decreasing firmness and increased tendency to snyeresis.

As the setting temperature of gels increases with increasing reactivity of the pectins, the calcium ion concentration at which pre-gelation starts, is the lower, the higher the reactivity of the low methylester, amidated pectin is. The pectin with the low reactivity gels at a soluble solids content of 60% already without separate calcium addition. In contrast to pectins with high and medium reactivity, the curve progression of the pectin with low reactivity is plain and the breaking strength of the gels changes only little over a wide range. Even at high calcium dosages pre-gelation will not occur.

Therefore low methylester, amidated pectins with low calcium reactivity such as Pectin Amid CF 005 or Pectin Amid AF 005 are very well suited for the use in products with high sugar content, as for example jams, fruit spreads and fruit preparations for yogurt.

The high setting temperature of the low methylster, amidated pectins with high reactivity such as Pectin Amid CF 020 or Pectin Amid AF 020 can be used for technological reasons to prevent floating. The gelation process starts already during the boiling process and is additionally enhanced by the addition of acid. This gelation results in an increase of viscosity because of which the fruits in the preparation do not separate during the filling process.
Applications areas of low methylester, amidated pectins

- Increasing product pH-value
- Decreasing soluble solids content
- Increasing buffer ion concentration in the product
- Increasing calcium reactivity of the pectin

<table>
<thead>
<tr>
<th>Pectin Amid CF 005</th>
<th>Pectin Amid CF 010</th>
<th>Pectin Amid CF 020</th>
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<tbody>
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<td>Pectin Amid AF 020</td>
<td>Pectin Amid AF 025</td>
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<tr>
<td>Jams</td>
<td>Calorie-reduced fruit preparations (40-50% ss)</td>
<td>Calorie-reduced jams “extra” (30% ss)</td>
<td>Glaze</td>
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<tr>
<td>Fruit spreads (55-60% ss)</td>
<td>Fruit preparations for yoghurt (30-50% ss)</td>
<td>Fruit preparations for diabetics</td>
<td>Spray nappage</td>
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<tr>
<td>Fruit preparations for yoghurt (55-60% ss)</td>
<td>Fruit preparations for cream stabilization</td>
<td>Fruit preparations for fruit milk desserts</td>
<td>Nappage concentrates</td>
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<td>Fruit fillings for bakery products</td>
<td></td>
<td>Delicatessen products</td>
<td>Gelling powder for glaze</td>
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</tbody>
</table>

On request, H&F also offer tailor-made low methylester, amidated pectins for special applications, which are already standardized to a defined gelling behaviour with particular buffer substances.