

## ABOUT STARCH MODIFICATION

There are a number of chemical modifications made to starch to produce many different functional characteristics. Most modifications take place in reaction vessels wherein the necessary reagents, heat and pressure are applied to the starch. When the desired chemical result is reached the reaction is halted by the addition of other reagents. The modified starch complex is then washed to remove ash, salts and other impurities and finally dried to about 12% moisture and packaged.

Starches are modified to change the properties of unmodified starch. Unmodified starch in its granular state is insoluble in water. It will swell when mixed with water and can be heated to form a paste. The paste is not stable when stressed by shear, acid or freezing. Under those stresses, syneresis (or water release) will occur as the starch retrogrades or degrades. The released water makes the food preparation very susceptible to microbacteriological contamination.

The properties of unmodified starch, however, can be altered by chemical modification. Chemical modification begins by separating the starch molecules from each other by heating, shearing, or mixing it with certain chemical reagents in the presence of water - the most common is heat.

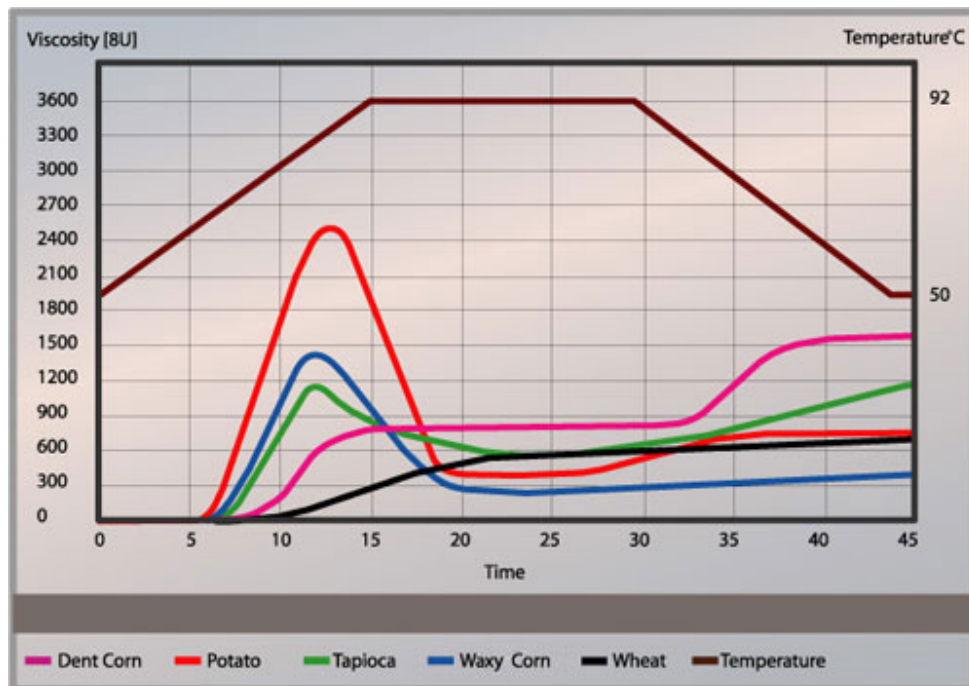
When heat is applied to a starch slurry at a particular temperature the granule will start to expand rapidly. This granule expansion is called gelatinisation. Table 1 shows the gelatinisation temperatures of the main unmodified starch types. During gelatinisation the bundles of starch molecules separate as the granule absorbs water. As water is absorbed the viscosity of the starch slurry increases to a peak at which point the granular state of the starch has largely disappeared and been replaced by an amorphous mass of starch and water bound together called a gel. The gelatinisation process is irreversible.

**Table 1**

Starch	Gelatinisation Temp(°C)
Waxy Corn	62 - 72
Waxy maize	63 - 72
Wheat	52 - 63
Tapioca	59 - 70
Potato	56 - 66
High amylose maize	110 - 120

When the heated starch slurry cools the starch molecules start to realign which causes a second rise in viscosity. This second rise is called set-back. Generally the higher the amylose content the greater the set-back. Figure 1 (below) illustrates the changes in viscosity of a variety of unmodified starches during the gelatinisation process

**Figure 1**



The phenomenon of gelatinisation can be duplicated by shear which physically separates the starch molecules in the granule allowing water to be absorbed.

Gelatinisation can also occur by the addition of an alkaline reagent such as a hydroxide or hypochloride. The alkaline reagents initiate oxidation of the starch molecules thereby disrupting the composition of the starch granule enabling some water absorption.

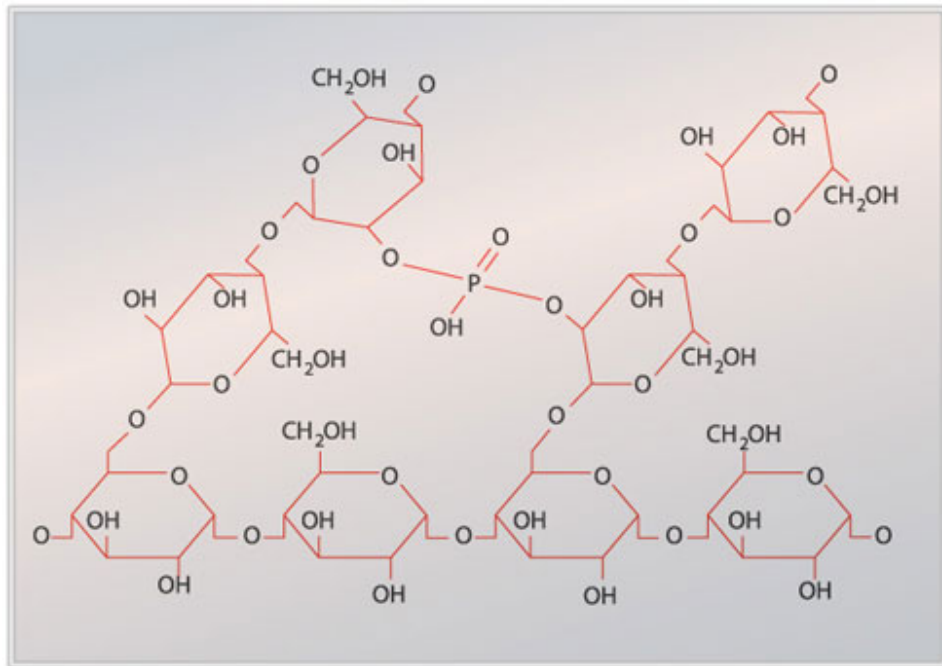
Once cooled to an ambient temperature gelatinised starches form either a firm gel or a flowing paste. The tendency to setback increases directly in proportion to the amylose content. Regular maize or wheat starch with 25% amylose will setback, whereas a waxy maize with no amylose forms a long stringy gel will not setback.

When a gel is formed the starch is considered to have retrograded. During retrogradation the starch molecules start to realign and form hydrogen bonds and in doing so tend to squeeze out or release water. This release of water is called syneresis and in a food product with a long shelf life it is a major problem. Fortunately, the risk of syneresis can be lessened by chemically modifying the starch to form esters with chemical bonds that restrict the starch molecule's tendency to retrograde.

### Cross-Linking

Starches with relatively high levels of amylose have a tendency to retrograde, that is realign after cooking and cooling. Retrogradation creates syneresis, which is a problem in food products with long shelf lives because of the risk of microbacteriological contamination. One way of reducing the tendency of a starch to retrograde is to use a starch with little amylose. Grains have been bred with almost no amylose - these are called waxy grains. Waxy maize is the most common and it is 100% amylopectin.

### Cross-Linking



Unfortunately, whilst they do not normally retrograde, in an unmodified form amylopectin forms long and stringy pastes, which do not feel palatable in the mouth. Moreover, most cooked unmodified starch pastes or gels are vulnerable to degradation from shear, or the effects of other chemicals such as acids. A solution has been found whereby chemically modifying the amylopectin reduces its tendency to degrade and significantly alters its paste properties.

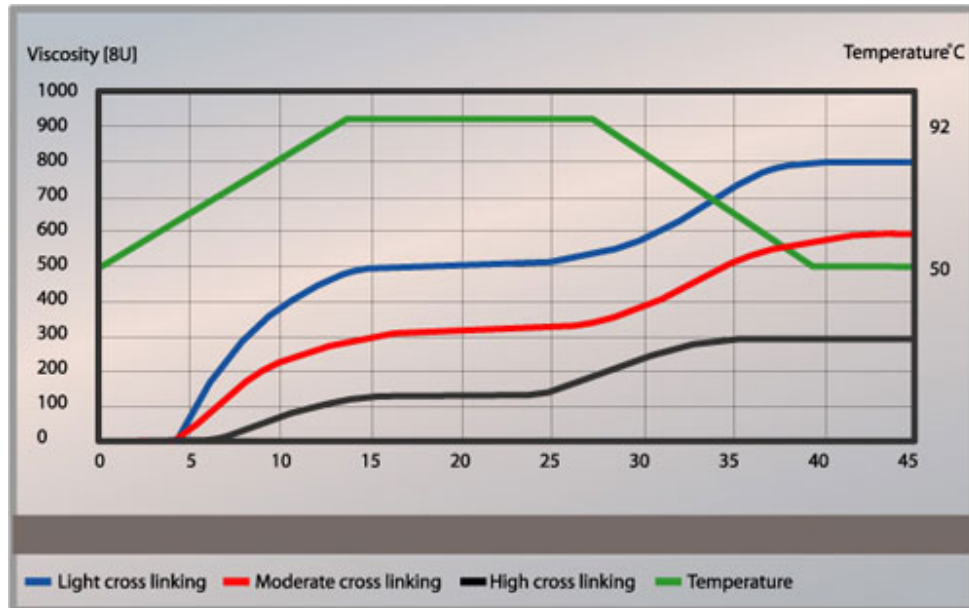
The chemical modification is called cross-linking because it involves building ester links between the branches of the large amylopectin molecule. The ester links are most commonly formed by mixing phosphorous oxychloride, or sodium trimetaphosphate with a starch slurry that has been partially swollen by an alkaline agent. The result is amylopectin retained as a granule with phosphate ester links built between branches of the starch molecule. The compound is known as a starch ester or a di-starch phosphate.

Cross-linking alters the gelatinisation of the starch granule. As expected more energy is required to separate the starch molecules, thus increasing the gelatinisation temperature. The hot peak viscosity is higher because the starch retains its molecular structure and there is little or no set-back on cooling. The stability of the molecular structure of the starch also makes it more resistant to shear and acid hydrolysis or cleaving of the starch molecule.

Importantly, it also makes the cooked paste noticeably shorter in texture, thus overcoming the mouthfeel and appearance problems of unmodified waxy maize.

The number of phosphate bridges can be varied depending on the application of the starch. The more modified the more resistant to shear and acid hydrolysis the starch becomes. Figure 2 shows the different viscosity profiles of starches with different levels of cross-

linking.

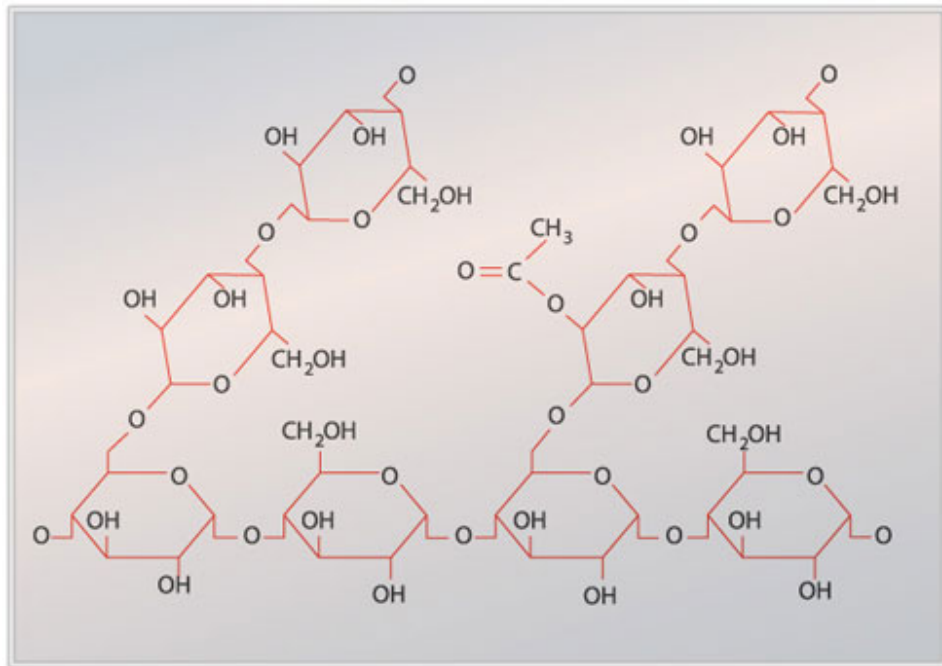


Cross-linked starches are prone, however, to degradation if the paste is cooled to very low temperatures such as below the freezing point of water. Degradation caused by freezing can be overcome by a second chemical modification in addition to the cross-linking. The second modification involves molecular substitution of a hydroxide molecule for a short chain hydrocarbon within the starch molecule.

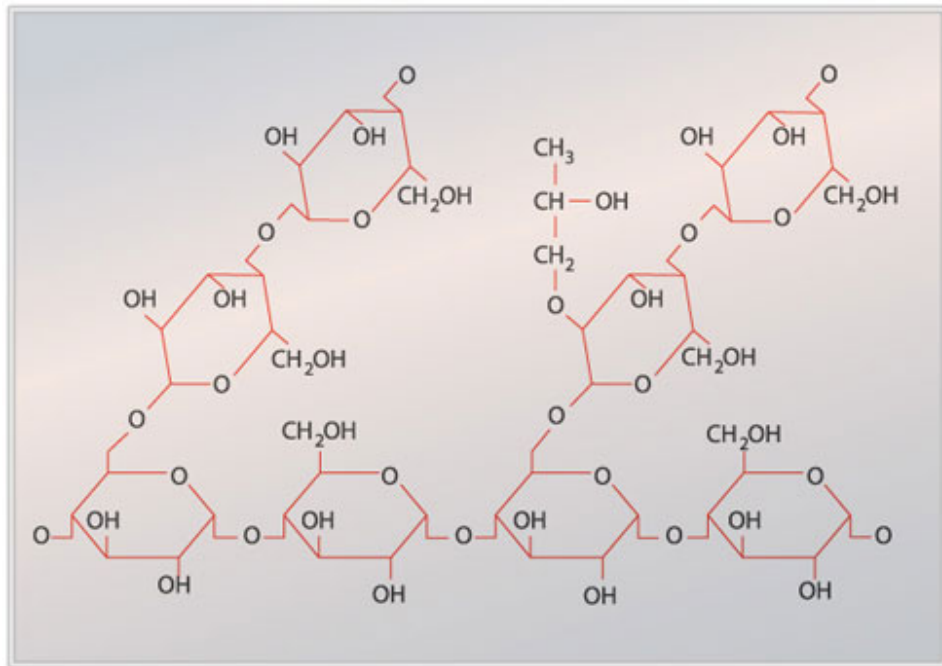
### Acetylation & Hydroxypropylation

Degradation of a cross-linked starch by freezing can be inhibited by substituting the hydroxides on the starch polymer with chemical groups unlikely to form hydrogen bonds with nearby starch molecules. Substituting conducted with cross-linking produces a double modified starch whereby the likelihood of degradation is significantly reduced. The two most common hydrocarbon groups added are acetyl or hydroxypropyl molecules.

### Acetylation with Acetic Anhydride



### Hydroxypropylation



The usual procedure entails mixing starch in alkaline conditions with either acetic anhydride or alkylene oxide depending on the substitution. The substitution takes place and the starch is neutralised, filtered, washed and dried.

The effect of substitution is to significantly separate the starch molecules within the granule.

Water absorption is made easier and the gelatinisation temperature is lowered by approximately 2-10°C, depending on the level of substitution.

Double modified starches of these types will not degrade, even at temperatures below the freezing point of water, whilst retaining the short texture and shear and acid resistance of cross-linked starches.

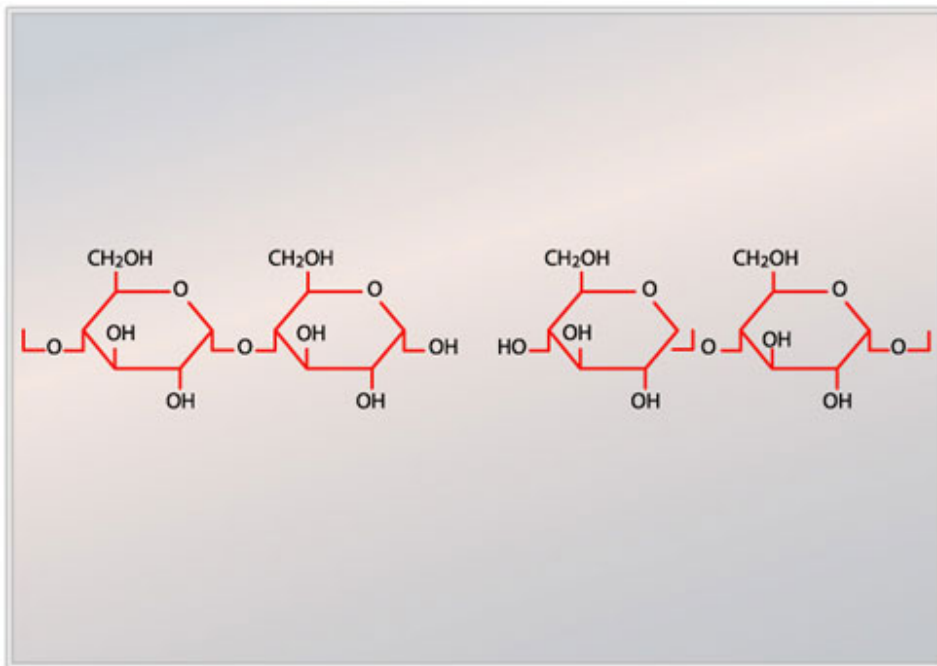
### Acid Hydrolysis

Cross-linking and substitution (described above) do not radically alter the molecular weight of the starch molecule. There are other modifications that aim to shorten the starch polymers because shorter chain molecules have important and beneficial functional properties.

A common type of chemical change of this type is acid hydrolysis.

Unlike acid hydrolysis in glucose manufacturing the aim here is to keep the starch granule relatively intact. The aim in glucose production is to gelatinise the starch granules fully. Acid hydrolysis is conducted by adding acid to a starch slurry heated to just below its gelatinisation temperature. The most common acids used are hydrochloric and sulphuric acid. The heat separates the starch molecules sufficiently to allow the acid access into the starch granule. Once within the starch granule the acid cleaves the linkages between the dextrose molecules within the starch polymer. The reaction is neutralised and the starch filtered, washed and dried.

### Hydrolysis



The acid hydrolysed starch has a lower hot peak viscosity when gelatinised because the smaller starch polymers in the granules swell significantly less than unmodified starches.

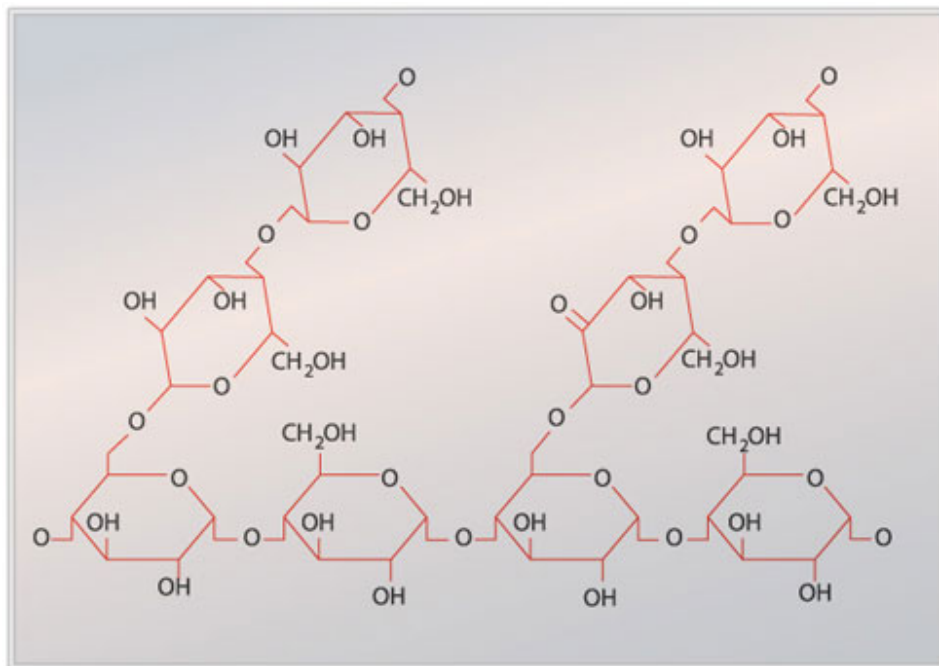
Hence, acid hydrolysed starches are commonly called thin boiled starches. The starch can be gelatinised at much higher levels of solids. The higher solids impart greater gel strength on cooling and stable water retention

### Oxidation

A second major type of starch chemical modification that involves reducing the size of the starch polymer is oxidation. Oxidation involves mixing sodium hypochlorite in starch slurry. The result after washing and drying is a very complex mixture of chemicals.

The hypochlorite cleaves the links within the starch polymer as well as the carbon to carbon bonds in the dextrose molecule to produce carboxyl and carbonyl groups. The starch chains are now much shorter and the large carboxyl and carbonyl groups reduce the tendency of the starch to retrograde.

### Oxidation



The short chains limit the starch's ability to absorb water so they can be heated at higher solids and their viscosity remains relatively low. The carboxyl and carbonyl groups give the starches a stickiness that is beneficial for coating foods and in batters. They also make the starches more stable than acid hydrolysis starches.

The level of chlorine used in the oxidation process determines whether or not the starch is classified as oxidised or bleached. A bleached starch made using sodium hypochlorite must use less than 0.82% active chlorine relative to dry starch. Higher levels of sodium hypochlorite are classified as oxidised starches.

