

Modified Starches for the Food Industry

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Within the past few decades, modified starches have broadened the scope of usefulness of starch. Modified food starches provide improved viscosity control over a broad range of processing variables, *e.g.*, pH, temperature, and shear. These products have also provided additives which lengthen the cold storage stability of products, while contributing

to their organoleptic properties. Two techniques of modification, crosslinking, and stabilizing groups and the effects of both on starch properties are discussed. Modified starches provide the food processor with an adaptable tool to meet specific requirements of a variety of food systems.

Starch is used in the food industry in a number of forms, but we shall concern ourselves mainly with its colloidal properties, since these are the main functional properties of starch. If we examine the application of starch as an additive to foods, we find that the greatest use is as a thickener. For years native starch had been used in food systems to a limited degree, and this restriction of use was imposed by the properties of these starches. In general, the dispersions of starches such as corn or wheat which contained amylose were limited in use to systems in which the development of a gel was desirable, whereas with the nonamylose-containing starches such as waxy maize and root starches—tapioca or potato—applications were extremely limited due to the rubbery or elastic texture, which was usually undesirable.

To expand the usefulness of starches, the industry makes use of a variety of techniques for modifying the characteristics which govern the properties of starch. These techniques have given rise to a number of starch derivatives which, during the past two decades, have become a major factor in the food field, where they are used as additives to thicken, stabilize, or provide textural characteristics to a wide variety of food systems, ranging from pie fillings and puddings to salad dressings. In speaking of derivatives today we will limit our remarks to those starches which have been modified by the introduction of substituent groups onto the starch molecule. Modifications by physical means or by chemical or physical means involving reduction of molecular size by scission, as by dextrinization or acid hydrolysis, will not be included since they are a minor factor in the food field. What we will be discussing are those starch derivatives generally prepared in aqueous suspension from which unreacted and water soluble reactants and products are removed.

Most starch derivatives involve the introduction of relatively low levels of substituent groups through the interaction of hydroxyl groups on the molecule with chemicals capable of reacting under relatively mild conditions. The resulting substituent may be introduced onto the starch through ether or ester linkages (Whistler and Paschall, 1967).

The level of substitution of the derivatives used in the food industry is low, the D.S. or degree of substitution ranging from about 0.2 to 0.0001 or less (D.S. is defined as moles of substituent per mole of starch). As a result of this low degree of substitution, most of the anhydroglucose units in the starch are unchanged. Thus, the resulting products usually retain the nutritive values associated with native starch. However, when discussing starches as food additives, we are not primarily concerned with those uses where the main function is to supply caloric values. Our interest is in applications where starch is used as an additive to facilitate processing or impart specific properties to food systems.

While the level of the substituents present in starch derivatives for food use is low, these groups often have a profound effect on the physical properties of the starch. Modified starches have opened up a multitude of new uses in food systems where native starches would either be completely unacceptable or else perform less efficiently.

To put the role of starch modification by derivatization in proper perspective, it is necessary to review certain basic aspects of the starch granule and its molecular structure. Starch is formed from glucose, shown in Figure 1, which is polymerized with the elimination of water and formation of α -glucosidic bonds. The predominant linkage is between the number 1 carbon of one anhydroglucose unit and the 4 carbon of the adjacent one. There are two types of anhydroglucose polymers in starch. One is a linear polymer made up of α -1,4-linked anhydroglucoses. The other is a branched polymer in which the basic 1,4-linkages are supplemented by branches at the 6 position to the 1 carbon.

The linear polymer, known as amylose, is shown in Figure 2. For comparison, cellulose is included to indicate structural difference. In native starch, amylose has a degree of polymerization which varies from about 200–2000, depending upon the plant source. Since it is linear, its molecules have the ability to approach each other closely enough to permit hydrogen bonding to occur. This bonding between molecules leads to a buildup of molecular aggregates having decreased solubility. When this occurs in dilute solution, the associated molecules precipitate. In more concentrated solutions the association is confined to limited portions of the molecule, and a three-dimensional network is built up to form a gel in

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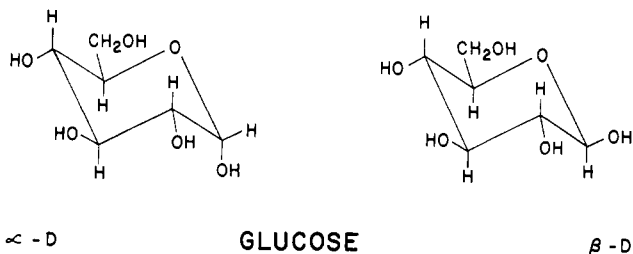


Figure 1. Basic repeating unit of starch

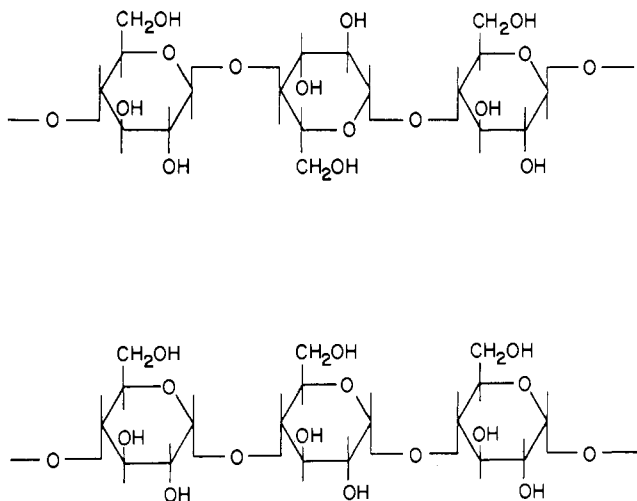


Figure 2. Amylose and cellulose molecules

which the solute (water) is entrapped in the interstices. This is shown in Figure 3. As this occurs, the sol not only solidifies but also loses clarity. The typical gel that forms after a corn starch cook is cooled is caused by this association of amylose molecules. This association and insolubilization of linear molecules and linear segments is commonly called retrogradation (Wurzburg, 1968).

The branched polymer is known as amylopectin and is shown in Figure 4. Its molecules are substantially larger than

amylose molecules, having degrees of polymerization ranging over 200,000. Because of its branches and molecular size, amylopectin molecules lack the mobility of amylose and the ability to approach each other closely enough to permit appreciable hydrogen bonding. As a result, solutions of amylopectin are characterized by excellent stability or resistance to change with age.

Normally, starches contain a mixture of amylose and amylopectin. The composition varies, depending upon the starch source, as is shown in the table below. The highest levels of amylose are found in starch extracted from high amylose corn hybrids. Regular corn starch contains about 24% amylose. The lowest level is found in waxy corn starch, which is essentially pure amylopectin with only traces of the linear component (Whistler and Paschall, 1967).

Amylose Content of Starches

Source	% Amylose
Maize	24
High amylose maize	50
High amylose maize	70
Waxy maize	0-3
Potato	20
Tapioca	17
Wheat	25

The starch molecules are laid down in the plant in the form of minute granules or cells which vary in size and shape with the plant source. Most granules range from about 2 μ on up to 100 μ . The smallest of the commercial starch granules are found in rice and the largest in potato. Corn is intermediate, with granules averaging about 15 μ in diameter.

It is felt that the granule is built up in layers, with the molecules oriented radially, resembling a spherocrystal, as shown in Figure 5. The integrity of the granule is the result of association of linear molecules and linear portions of branched molecules to form regions of crystallinity called micelles. As a result of this association, the starch granule is insoluble in cold water (Meyer, 1950).

Similarly the presence of the amorphous regions imparts to the granule a degree of elasticity, which is reflected in revers-

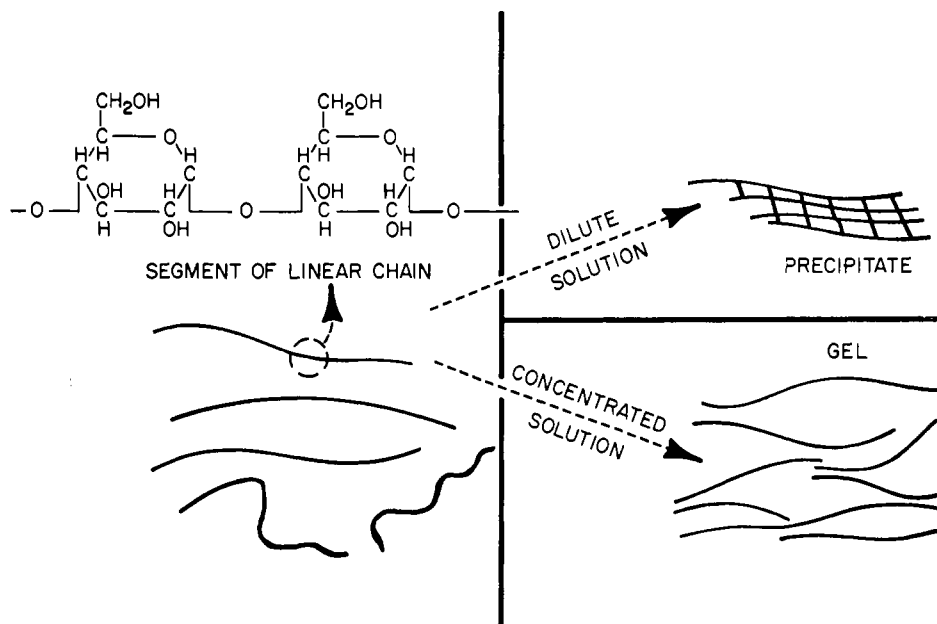


Figure 3. Behavior of amylose molecules in solution

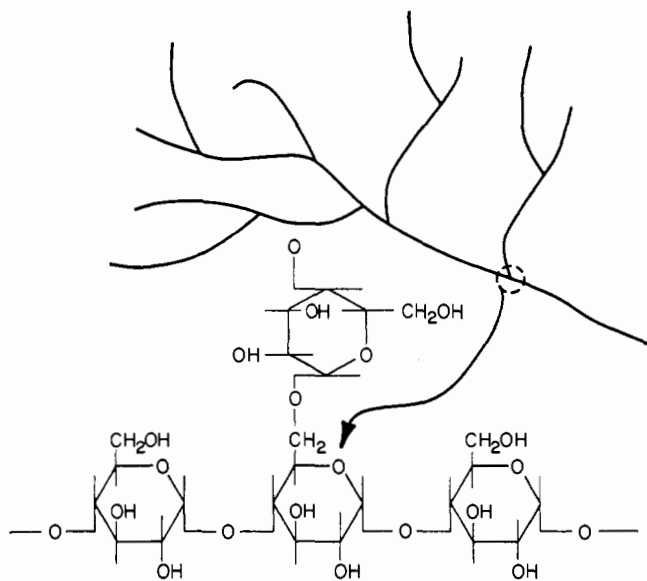


Figure 4. Amylopectin molecule

ible swelling on absorption of moisture. When an aqueous slurry of starch is heated, the granule begins to swell when sufficient energy is used to overcome the cohesive forces. Water penetrates the crystalline regions, the molecules become more mobile, and the granules swell to many times their original volume. Eventually, the granules collapse or rupture to yield dispersions of molecules, associated molecules, and granular fragments (Kerr, 1950). During cooking, the short salve-like properties (desirable for use in many food systems) are developed but these are fugitive and sensitive to heat, pH, shear, and concentration. This texture which is the result of highly swollen starch granules can be maintained by augmenting the granular forces with cross-links between molecules. Crosslinking is one of the basic derivatization techniques used in making specialty food starches. It involves reacting starch in the intact unswollen granule form with di- or polyfunctional reagents capable of reacting with at least two of the hydroxyl groups in neighboring molecules. In this way phosphate and adipate groups are introduced as bridges or crosslinks between neighboring molecules, as shown in Figure 6. These bridges reinforce the hydrogen bonds holding the granule together with strong chemical bonds which resist rupture during the cooking process. Crosslinking is a very effective technique for toughening the granule and maintaining, as well as magnifying, those rheological properties associated with the highly swollen sac. Such properties are considered essential in developing the palatability and texture desired in most thickened food systems.

The properties of crosslinked starches vary widely, depending upon the level of crosslinking, as shown in Figure 7. Here we have Brabender curves showing the viscosity of crosslinked waxy corn starches with different levels of treatment.

As seen in Figure 7, when waxy corn starch is treated with one crosslink per 9000 anhydroglucose units, the rate of cooking is not materially affected. However, after swelling, the granules resist rupture, giving short salve-like pastes in contrast to the elastic phlegmy character associated with broken waxy corn starch granules. At higher levels of treatment, the granules are unable to swell fully. If the degree of crosslinking is high enough, the granules will eventually

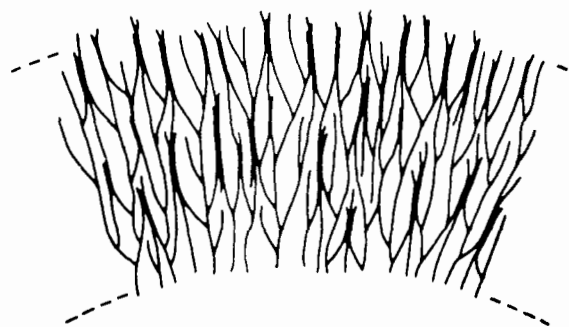


Figure 5. Proposed microstructure of starch granule depicting micellar and amorphous regions

reach a point where they will not cook under normal conditions. Such products, however, are not usually used in foods.

Low pH's accelerate cooking and increase breakdown. By crosslinking the granule, the sensitivity of the granule to pH variations can be reduced. Figure 8 shows the effect of pH on unmodified starch compared to lightly crosslinked starch. Crosslinking, in addition to providing resistance to pH variations, also renders the granule more resistant to high temperatures. Thus, starches can be prepared which will withstand retort temperatures (Wurzburg, 1967).

Pastes of unmodified starch granules when cooked are also sensitive to shear, losing their viscosity readily. Crosslinked starches are more resistant and can be strengthened sufficiently to withstand most processing conditions. The effect of shear on viscosity is shown in Figure 9. Here starches were cooked to the same viscosity and subjected to three rates of shear. The crosslinked starch is more resistant to the shear forces.

By adjusting the degree of crosslinking, starches can be tailored to perform under a wide variety of pH, temperature, or shear conditions encountered in food processing.

While crosslinking improves the stability of hot pastes toward breakdown and loss of viscosity during cooking, it contributes little towards keeping the starch molecules from associating or gelling. Crosslinked starches, as such, provide no advantage in systems where storage stability is essential and even crosslinked waxy starches gel and synerese when subjected to storage at low temperatures. Thus, where clarity or stability of foods stored for prolonged periods of time at refrigerator or freezer conditions is desired, crosslinked products like the unmodified starch thicken or lose their hydrating ability with age. To overcome this problem, starch is treated with monofunctional reagents to introduce stabilizing groups. These groups are clearly substituent groups just as the crosslinking species are, but to differentiate monofunctional from di- or polyfunctional reagents, we chose

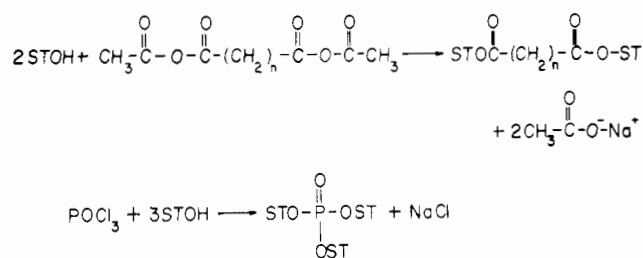


Figure 6. Crosslinking by ester formation

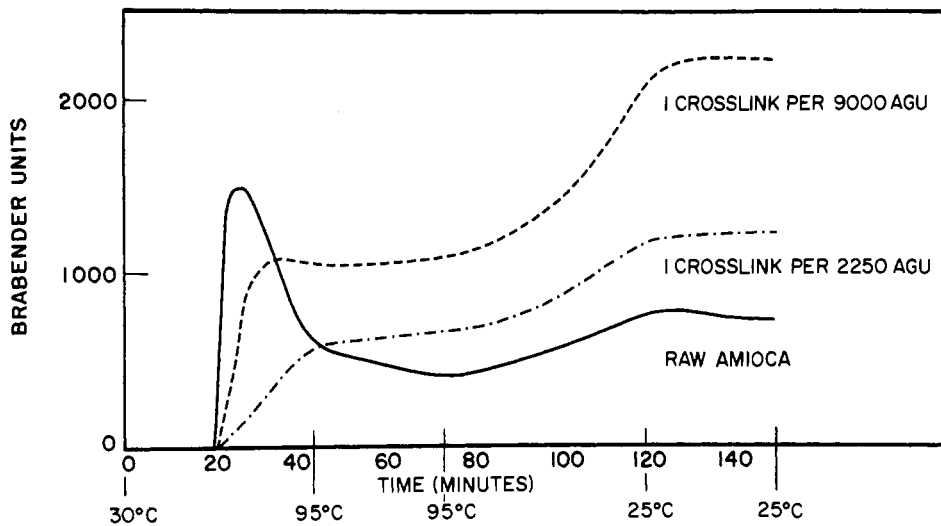


Figure 7. Effect of crosslinking on viscosity of waxy maize starch 5% solids

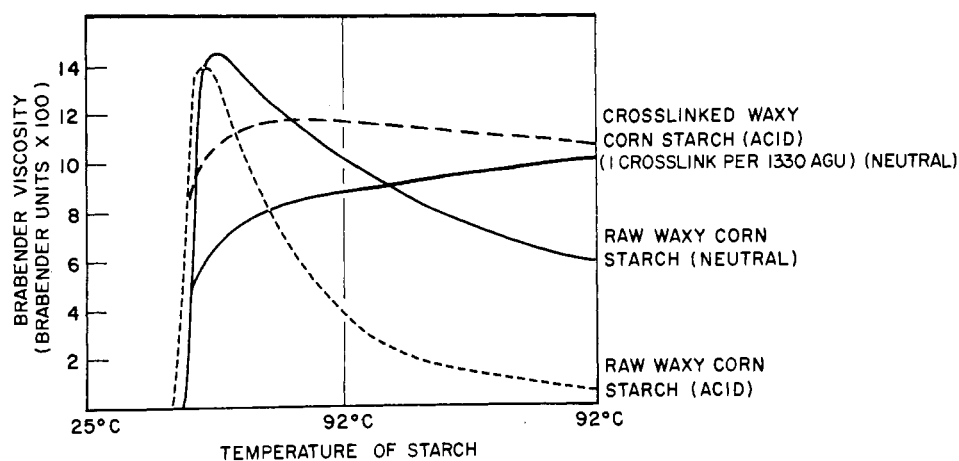


Figure 8. Effect of mild crosslinking on viscosity of waxy maize starch

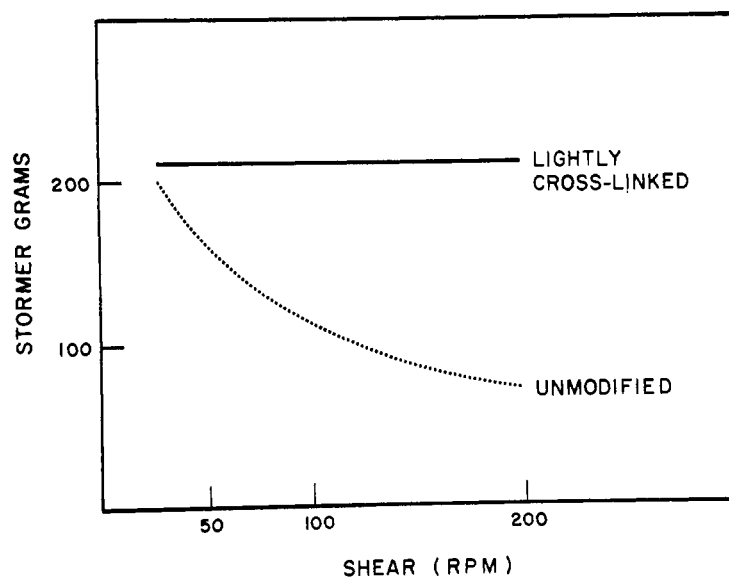


Figure 9. The effect of shear on viscosity of lightly crosslinked and unmodified starch

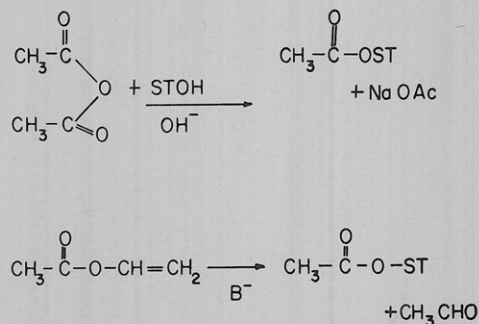


Figure 10. Preparation of starch acetates

to call the monofunctional types stabilizing groups. Further, the percent of treatment with stabilizing groups is usually higher than with crosslinking species, because higher levels of substitution are required to produce clear pastes which are freeze-thaw resistant.

Stabilizing groups cleared for use on starch are hydroxypropyl, phosphate, and acetyl. These are introduced by reacting some of the hydroxyl groups with propylene oxide, orthophosphate, acetic anhydride, or vinyl acetate. Figure 10 shows the reaction occurring when starch is treated with acetic anhydride or vinyl acetate. The influence of varying levels of acetyl substituents in corn starch gels is demonstrated in Figure 11. The samples were cooked at 7% concentration and the sols were poured into molds and left overnight to permit the starch to gel. The unmodified starch forms a rigid gel, while the gelling tendency is reduced with increasing acetyl content. While cold storage of such starches is improved, they are still subject to the variations in processing conditions and generally fail to impart the salve-like textural properties needed. By crosslinking the starch granule and introducing stabilizing groups, products are prepared which show improved stability properties under a variety of conditions. Noteworthy is the reduced tendency of these products to associate or gel on prolonged storage. The effect of these stabilizing groups is marked, despite the low degree of treatment. Their action in promoting the stability of starch dispersions lies in the ability of these groups to interfere with the



Figure 11. The effect of acetyl substitution on cornstarch gel structure

tendency of starch chains to closely align themselves. This reduces the ability to form hydrogen bonds and allows the starch to remain hydrated, clear, and stable (Wurzburg, 1968).

In summary, derivatization for modification provides the starch processor with a tool or tailoring products to meet specific requirements of a variety of food systems. Crosslinking modifies the texture and imparts resistance to processing conditions. Derivatization with monofunctional reagents interferes with the tendency of the molecules to associate and lose their hydrating ability, and imparts clarity and stability to sols made from the modified starches.

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