Chapter 4
Emulsifier-Carbohydrate Interactions

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Since emulsifiers are amphiphilic molecules, they interact with other polar and nonpolar ingredients commonly present in food (Gaonkar and McPherson, 2005). Interactions with water, carbohydrates, proteins, fats, oils, and flavors have been studied. Interactions may be beneficial, such as retardation of staling in bread, or adverse, such as distortion of a flavor profile. Several mechanisms may be responsible for producing interactive effects: (1) Competition of emulsifiers and ingredients for the interface, (2) Competition for available water, (3) Solubility of ingredients in emulsifiers, (4) Electrostatic interactions between charged species, (5) Nonpolar interactions, or (6) physical or packing interactions, such as entanglement or crystal packing. Since more than one mechanism may be operational in a given food system, explanation of ingredient interactions are often difficult to obtain with a high degree of certainty.

Carbohydrates are ubiquitous in food products. Nutritionally, they serve as sources for rapidly available energy. They also contribute to sensory properties, such as sweetness and texture. Carbohydrates range from low molecular weight simple saccharides to highly complex structures, such as starches and hydrocolloids (Belitz et al., 2004a). Their interactions with food surfactants are extremely important in many foods, such as bakery products. Recently, the epidemics of obesity and Type II diabetes have stimulated reformulation of foods toward lower sucrose and more carbohydrates having lower glycemic indices (Warshaw and Kukami, 2004). Emulsifier carbohydrate interactions may be different in these new formulations.

This chapter will discuss carbohydrate classes where interactions have been thoroughly studied, but will also point out where not enough is known.

4.1 Interactions with Simple Saccharides

Simple saccharides, such as sucrose, fructose, or lactose occur naturally in foods or are added to obtain some benefit. Sugars contribute sweetness in varying degrees depending on their structural configuration. However, they also function as humectants to retain water but reduce water activity, in order to improve microbial stability. For example, water activity has an effect on cell permeability of Staphylococcus

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aureus (Vilhelmson and Miller, 2002). Other ingredients such as glycerol, propylene glycol, and sorbitol, also function as humectants.

Because there are no lipophilic groups in simple saccharides, these molecules have little or no interfacial activity. They do have a strong tendency to form hydrogen bonds, possibly with polar regions of surfactants. Lecithin has a long history of use in the confectionery industry to control viscosity and reduce stickiness (see Chap. 10). Inverse gas chromatography (IGC) has shown that lecithin and polyglycerol polyricinoleate (PGPR) modified the surface of sucrose particles to make it more lipophilic (Rouset et al., 2002). Sugar particles, concentrated in oil dispersions, were found to interact with one another (Bahm et al., 2006). Water bridging and minor components also influence these forces (Gaonkar, 1989; Johansson and Bergenstahl, 1992c). Water vapor permeability through confectionery coatings is also strongly affected by composition (Ghosh et al., 2005). Surfactants, such as lecithin, PGPR, and monoolein inhibit these interactions, resulting in decreased viscosity and sedimentation (Johansson and Bergenstahl, 1992a,b; Servais et al., 2004). Sugar particles may also serve as heterogeneous crystallization nuclei for the confectionery fats (Aronbine et al., 1988; Dhonsi and Stapley, 2006). Recent work has also determined differences in the magnitude of interactive forces in butterfat, cocoa butter, and lauric fats (Dickinson et al., 2005).

Saccharides can compete with mesophase-forming surfactants for available water. Functional properties are often modified by this competition.

4.2 Starch/Surfactant Complexes

Perhaps the most widely studied interactions of food surfactants have been with starch. Linear α-helical regions of starch form inclusion (or clathrate) compounds with single-tailed surfactants. Examples are monoacylglycerols and sodium stearoyl lactylate (SSL). The saturated fatty acids bonded to these ingredients are trapped inside the helices, and are held by lipophile-dipole forces.

Starch molecules are of two types. Amylose has a linear chain structure, while amylopectin has a number of branches. The distribution depends on the vegetable source (Mitolo, 2005) and, for wheat starch; properties depend on fractions obtained from the milling process (Tang et al., 2005). For example, Potato starch is high in amylose, while waxy maize is higher in amylopectin. Amylose forms a left-handed helix with 6 glucosyl units per turn and 0.88 nm between helices (Mikus et al., 1946). Branches on the amylopectin interrupt helix formation and reduce the formation of inclusion complexes with surfactants. Monoacylglycerol complexes were shown to form weaker complexes with amylopectin than amylose (Hahm and Hood, 1987; Lagendiik and Pennings, 1970;, Twillman and White, 1988).

Complexing agents may include any molecule with a lipophilic component, and a structure with a diameter of 4.5–6 Å Iodine (as I_3) forms inclusion complexes with starch. This phenomenon allows starch to be used as an indicator in the titrimetric determination of iodine. Saturated alkyl chains of fatty acids, dimethyl sulfoxide, and linear alcohols may complex inside the helix. Some flavor compounds may be trapped in the α-helix of amylose, resulting in a decreased flavor impact (Rutschmann and Solms, 1990; Maier et al., 1987; Schmidt and Maier, 1987).

In solution by itself, amylose exists as a random coil structure; In the presence of a complexing agent, energy minimization forces the structure into a helix conformation (Neszmelyi et al., 1987). Saturated fatty acid chains are lipophilic and are attracted to the dipole-induced, hydrogen-lined interior of the helix (Krog, 1971). Dipole moments continue to stabilize the complex by effecting a lipophilic solvation in the core. Computer-derived models confirm the stability of the complex based on energy minimization principles (Neszmelyi et al., 1987). Complexing agents compete for available space in the helix and readily undergo reversible interchange (Mikus et al., 1946; Schoch and Williams, 1944). Unit cell packing dimensions and the distance between amylose helices are not affected by the nature of the complexing agent (Raphaelides and Karkalas, 1988). Alkyl lipid chains usually occur as dimers in solution, with the polar head groups held together by hydrogen bonds. For fatty acids, it is the carboxyl group; for monoacylglycerols, glycerol is the polar moiety.

Complexes between amylose and alkyl chains of lipids aggregate into partially crystallized structures. X-ray diffraction shows a V-pattern (Szezodrak and Pomeranz, 1992). These insoluble complexes consist of lamellar mesophases, which are perpendicular to the helices (Raphaelides and Karkalas, 1988). Amylose and Amylopectin complexes with lipids can be differentiated by their physical properties. For example, amylopectin complexes are more soluble in aqueous systems than amylose complexes. Saturated fatty acids have long been used to selectively precipitate amylose from solution (Schoch and Williams, 1944). The relative solubility of amylose and amylopectin complexes can vary with various surfactants (Kim and Robinson, 1979). Iodine may be used to differentiate amylose from amylopectin, since it forms blue complexes with amylose and a red-purple complex with amylopectin.

4.3 Effect of External Lipids on Starch Properties

4.3.1 General

Native fats and oils, used in foods, contain small amounts of surfactants. For example, soybean oil contains low levels of lecithin and mono/diacylglycerols. Surface tension effects have been demonstrated by their removal by adsorption on Florisil (Gaonkar, 1989). These minor constituents may be treated as a constant by product developers, providing the concentrations do not vary significantly from batch to batch. Surfactants that are deliberately added (external lipids) exert a greater effect and may be used to control properties of starches in food formulations. For example, starch/surfactant complexes retard the firming (staling) of bread, prevent stickiness and promote rehydration in instant potato products, and control the texture of extruded foods. Data for high amylose (normal) starches are shown in Table 4.1, while properties for high-amylopectin (waxy) starches are summarized in Table 4.2

Table 4.1 Effect of emulsifiers and complexing agents on properties of nonwaxy starch

Effect of complexation on starch properties	Starch type/Fraction	Complexing agent	Reference(s)
Reduce iodine-binding capacity	Wheat	Sucrose monoesters	Bourne et al. 1960
	Potato	GMS	Conde-Petit and Escher, 1992
	Maize, potato, tapioca, wheat	Sucrose esters	Deffenbaugh, 1990
	Wheat	GMS, SSL	Ghiasi et al., 1982a
	Potato amylose	EMG, polysorbate 60	Kim and Robinson, 1979
	Amylose	MG	Krog, 1971; Krog and Nybo-Jensen, 1970 Krog (1981)
	Tapioca	CTAB, GMS, SLS	Moorthy, 1985
	Amylose	Sucrose esters	Osman et al., 1961
Repress granule swelling and starch solubilization	Wheat	Sucrose monoesters	Bourne et al., 1960
	Maize, potato, wheat	GMS, SSL	Eliasson, 1986b
	Wheat	GMS, SSL	Ghiasi et al., 1982a
	Potato	MG	Hoover and Hadziyev, 1981
	Potato amylose	EMG, polysorbate 60	Kim and Robinson, 1979
	Amylose	MG	Krog, 1971
	Tapioca	MG	Mercier et al., 1980
	Tapioca	CTAB, GMS, SLS	Moorthy, 1985
	Amylose	Sucrose esters	Osman et al., 1961
	Nonwaxy	MG	Strandine et al., 1951
	Wheat flour	MG, SSL	Roach and Hoseney, 1995a,b
	Nonwaxy	MG	VanLonkhuysen and Blankestin, 1974
Increase granule swelling; make gelatinization occur earlier	Maize, potato, wheat	SDS	Eliasson, 1986b
Destabilize granule and increase paste viscosity	Tapioca	SLS	Moorthy, 1985
Decrease starch thickening power <85 °C (before gelatinization)	Wheat	DATEM, MG, SSL	Evans, 1986
	Wheat	GMS, SSL	Ghiasi et al., 1982b
	Potato	MG	Hoover and Hadziyev, 1981
Delay loss of birefrin-gence	Wheat	Sucrose monoesters	Bourne et al., 1960
	Wheat starch	Sucrose monoesters	Ebeler and Walker, 1984

(continued)

Table 4.1 (continued)

Effect of complexation on starch properties	Starch type/Fraction	Complexing agent	Reference(s)
	Wheat	SSL	Eliasson, 1985
	Maize, potato, wheat	GMS, SDS, SSL	Eliasson, 1986b
	Wheat	MG, SSL	Ghiasi et al., 1982a,b
	Wheat flour	Sucrose monoesters	Pomeranz et al., 1969
	Potato	MG	Rilsom et al., 1984
	Various	MG	VanLonkhuysen and Blankestin, 1974
Increase initial pasting temperature, hot paste viscosity, temperature of peak viscosity (i.e. amylograph or RVA) delayed gelatinization	Maize, potato, tapioca, wheat	Sucrose ester	Deffenbaugh, 1990
	Wheat starch	Sucrose monoesters	Ebeler and Walker, 1984
	Wheat	SSL	Eliasson, 1983
	Potato, wheat	SSL	Eliasson, 1986b
	Wheat	DATEM, MG, SSL	Evans, 1986
	Nonwaxy	POEMS	Favor and Johnston, 1947
	Maize	MG	Krog, 1971
	Maize, potato, tapioca, wheat	DATEM, MG, SSL	Krog, 1973
	Pea flour	SSL	
	Wheat flour	Sucrose monoesters	Pomeranz et al., 1969
	Potato	MG	Rilsom et al., 1984
	Masa harina flour	MG	Twillman and White, 1988
Stabilize pasting viscosity and prevent long cohesive texture	Tapioca	GMS, SLS	Moorthy, 1985
Decrease peak viscosity	Waxy maize, potato	POEMS	Favor and Johnston, 1947
Decrease gelatinization enthalpy	Maize, potato, tapioca, wheat	Sucrose ester	Deffenbaugh, 1990
	Potato, wheat	CTAB, saturated. MG, SDS, SSL, lecithin, lysolecithin	Eliasson, 1986a
Increase setback viscosity	Masa harina flour	MG	Twillman and White, 1988
Increase setback viscosity (gelation)	Maize, potato, tapioca, wheat	Sucrose ester	Deffenbaugh, 1990
Depressed G’ and G”; increased temperature of G’ and G”; increased viscous part of visco-elastic response	Maize, potato, wheat	GMS, SLS	Eliasson, 1986b

(continued)

Table 4.1 (continued)

Effect of complexation on starch properties	Starch type/Fraction	Complexing agent	Reference(s)
Induced gelation (increased rigidity of fresh starch gels)	Maize, potato, wheat	CSL, GMS	Conde-Petit and Escher, 1994
Decreased gel volume of heated starch	Wheat	MG, SSL	Eliasson, 1985
Decrease cold paste viscosity	Maize, potato, tapioca, wheat	POEMS	Favor and Johnston, 1947
	Maize	MG	Krog, 1971; Osman and Dix, 1960
	Potato	MG	Hoover and Hadziyev, 1981
	Potato	MG	Rilsom et al., 1984
Decrease retrogradation of starch	Amylose/amylopectin mixtures	CTAB, SDS	Gudmondsson and Eliasson 1990; Krog and Nybo-Jensen, 1970; Lagendiik and Pennings, 1970
	Rice	DATEM, MG, SSL, sucrose esters	Miura et al., 1992
Decrease Amylopectin recrystallization	Maize	Sucrose esters	Matsunaga and Kainoma, 1986
Decreased formulation of resistant starch	Barley, maize, waxy maize	EMG, DATEM, MG, SSL	Szezodrak and Pomeranz, 1992
Reduced gel breaking strength	Maize, potato, wheat	CSL, GMS	Conde-Petit and Escher, 1994
Reduced starch extrudate	Tapioca	MG	Mercier et al., 1980
Solubility and retrogradation	Potato and maize	CSL, MG	Staeger et al., 1988
Reduced *in vitro* enzymolysis	Potato	MG, SSL	Ghiasi et al., 1982a
With β-amylase	Potato amylose	EMG, polysorbate 60	Kim and Robinson, 1979
Reduced *in vitro* amyloglucosidase digestion	Amylose	MG	Eliasson and Krog, 1985
Reduced *in vitro* α-amylase digestion	Amylose	MG	Eliasson and Krog, 1985
	Potato amylose	Lysolecithin	Holm et al., 1983
Decreased glucoamylase digestibility	Maize, potato, tapioca, wheat	Sucrose esters	Deffenbaugh, 1990
	Potato amylose	Lysolecithin	Holm et al., 1983
Slowed rate of *in vivo* α amylase digestion	Potato amylose	Lysolecithin	Holm et al., 1983

CSL calcium stearoyl lactylate, *CTAB* cetyltrimethylammonium bromide, *DATEM* diacetyltartaric acid esters of monoglycerides, *EMG* ethoylated monoglycerides, *GMS* glycerol monostearate, *MG* monoglycerides, *POEMS* polyoxyethylene monostearate, *SDS* sodium dodecyl sulfate, *SLS* sodium lauryl sulfate, *SSL* sodium stearoyl lactylate

Table 4.2 Effect of emulsifiers and complexing agents on properties of waxy starch

Effect of complexation on starch properties	Starch type/fraction	Complexing agent	Reference(s)
Slight reduction in iodine-binding capacity	Amylopectin	MG	Krog, 1971; Krog and Nybo-Jensen, 1970
	Waxy maize	Sucrose esters	Deffenbaugh, 1990
No reduction in iodine-binding capacity	Potato amylopectin	Sucrose monostearate	Bourne et al., 1960
No effect on swelling	Potato amylopectin	Sucrose monostearate	Bourne et al. 1960
Slight delay in peak viscosity	Waxy maize	Sucrose esters	Deffenbaugh, 1990
Viscosity profile not affected	Amylopectin	MG	Hoover and Hadziyev, 1981
	Waxy maize	DATEM, MG, SSL	Evans, 1986
Decreased hot paste viscosity	Waxy maize	POEMS	Favor and Johnston, 1947
Depressed G' and G''; slightly increased temperature of G' and G''; slightly increased viscous part of viscoelastic response	Waxy barley	GMS, SLS	Eliasson, 1986b
Insoluble complex precipitated	Potato amylopectin	Sucrose monostearate	Bourne et al., 1960
	Amylopectin	MG	Batres and White, 1986
No extrudate complex formed	Waxy maize	CSL, MG	Staeger et al., 1988
No complex detected by x-ray diffraction or DSC	Waxy maize	Sucrose esters	Deffenbaugh, 1990
Weak complex suggested by glucoamylase digestion; viscosity profiles, high-performance size exclusion chromatography and NMR	Waxy maize	Sucrose esters	Deffenbaugh, 1990
Complex confirmed by DSC and x-ray diffraction	Potato amylopectin	CTAB, SDS	Gudmundsson and Eliasson, 1990
Reduced amylopectin retrogradation	Waxy maize Amylopectin	CTAB, unsaturated. MG	Eliasson 1988
	Potato amylopectin	CTAB, SDS	Gudmundsson and Eliasson, 1990

CSL Calcium stearoyl lactylate, *CTAB* cetyltrimethylammonium bromide, *DATEM* diacetyltartaric acid esters of monoglycerides, *EMG* ethoylated monoglycerides, *GMS* glycerol monostearate, *MG* monoglycerides, *POEMS* polyoxyethylene monostearate, *SDS* sodium dodecyl sulfate, *SLS* sodium lauryl sulfate, *SSL* sodium stearoyl lactylate

4.3.2 Iodine Binding Capacity

Surfactants, containing fatty acids, reduce the iodine binding capacity (IBC) of nonwaxy starches. This effect is due to the reversible exchange of the alkyl chain and I_3 inside the amylose helix. Little or no reduction of IBC has been observed for waxy, high-amylopectin starches (Table 4.2). The average length of amylopectin branches is 20–26 glucose residues. Fatty acids require 3 turns of a straight helix with 6 residues/turn in order to form complexes. Although significant modification of the properties of waxy starches may be achieved using surfactants, IBC values are low and differences are difficult to detect. (Fig. 4.1) Iodine binding is therefore, not a sufficiently sensitive method for evaluating high-amylopectin starches.

4.3.3 Starch Pasting

Starches and starch-containing ingredients are largely responsible for the texture of many food products. In fat-reduced or fat-free products, starch networks are often used to immobilize free water and prevent syneresis. They may also interact with flavor and aroma molecules (Lopes de Silva et al., 2002; Preininger 2005; Ferry et al., 2006). When starches are heated in the presence of water, the starch granules absorb water and swell. During cooking, the linear amylose starch leaches from the granule. The resulting composition is a mixture of swollen granules, granule fragments, and colloidal starch particles (Olkku and Rha, 1978). The paste viscosity increases dramatically to a peak value during cooking. However, the swollen starch granules are very fragile and will begin to disintegrate. Applied shear forces, mixing for example, will accelerate this disintegration. As this process proceeds,

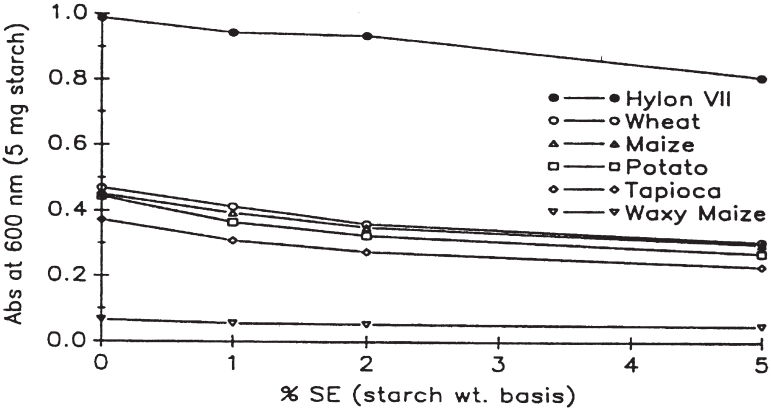

Fig. 4.1 Iodine-binding capacity of starches measured in the presence of a sucrose ester emulsifiers. (From Deffenbaugh, 1990.)

viscosity will rapidly decrease. Added surfactants tend to stabilize the swollen starch granule. Sodium stearoyl lactylate increases cold paste viscosity of wheat, corn, and potato starches (Azizi and Rau, 2005). Addition of shortening increases paste viscosity for wheat and corn starches, but decreases it for potato starch.

4.3.4 Starch Gelatinization

Gelatinization is a process in which crystalline structure is lost during cooking. The process is a first-order, water-mediated melting of the crystalline regions in the starch granule (Donovan, 1979; Zobel, 1984). Maximum swelling and solubilization occur in the presence of excess water (>5 times). Typical formulations meeting this condition are puddings, sauces, and gravies. Incomplete starch hydration occurs in lower-moisture products, such as baked or extruded products. Extremely high viscosities can be achieved in low-moisture systems.

Useful applications in foods have been greatly expanded by using starch/surfactant interactions. Surfactant effects on processing variables can produce cooked starches, or cereal grain products, with significantly modified properties (Lund, 1984). Order of ingredient addition is a critical variable. For example, if monoacylglycerols are added before starch gelatinization occurs, the surfactants penetrate the starch granule and form complexes. This results in a decrease in granule swelling power. Addition of monoacylglycerols after starch gelatinization stabilizes the starch granule against rupture and additional amylose solubilization (Van Lonkhuysen and Blankestijn, 1974). Surfactants, added prior to gelatinization (e.g., polysorbate 60), adsorb to the surface of the starch granule (Kim and Walker, 1992). The surface is rendered lipophilic, which retards the migration of water into the granule.

The effects of surfactants on starch gelatinization can be measured in a number of ways (see Table 4.1). When starch pastes were prepared with glycerol monostearate (GMS) or sodium stearoyl lactylate (SSL), changes in viscoelastic properties coincide with reduced swelling of the granules (Eliasson, 1986b). The granules were less deformable, as indicated by the higher temperatures required to reach peak values for storage modulus (G') and loss modulus (G"). Pasting temperature, hot viscosity, and temperature to peak viscosity for normal starches were increased by surfactants capable of forming inclusion complexes. Obviously, if a starch is added to a food formulation, effects were thought to arise from the improved ability of the starch granule to hold water without rupturing (Mitchell and Zalman, 1951).

Starch, in its native form, displays birefringence when viewed with a polarized light microscope. Gelatinization and melting of the crystalline regions in the starch granule, lead to loss of birefringence and disappearance of the characteristic x-ray diffraction pattern (Eliasson, 1986a). Starch-complexing surfactants slow the rate of gelatinization and, as a result, retard the loss of birefringence.

Some surfactants do not form complexes with starch. Sodium dodecyl sulfate (SDS) has a strong destabilizing effect on starch granule, possibly because of its strong negative charge, detergent power or high potential to form micelles (Eliasson, 1986b; Moorthy, 1985). Destabilization is manifested by a rapid swelling and viscosity increase, followed by granule disruption and viscosity decrease. SDS is a salt of a strong acid and a strong base. Sodium stearoyl lactylate is an ionic surfactant, the salt of a weak acid and a strong base, which forms complexes and stabilizes starch granules. Obviously, when starch is added to a food formulation in order to build viscosity, surfactants, which stabilize the integrity of swollen starch granules, should be selected. In a starch gel, formed from a paste, swollen starch granules are imbedded in, and stabilize an amylose matrix (Ring, 1985). As a starch paste cools, molecules become less soluble and aggregate (Osman, 1967). Cross-linking of the network increases the consistency and the resistance to an applied external force (Zobel, 1984). Some recent work indicates little difference between complexing and noncomplexing surfactants on the gel network structure (Richardson et al., 2004). Gelation is caused by rapid precipitation of amylose while amylopectin tends to crystallize more slowly. Amylopectin requires relatively higher concentrations to undergo precipitation. Amylose forms gels by entrapping water molecules, swollen starch granules, and granule fragments in the helical network. In starch pastes prepared with surfactants, the insoluble complex forms the gel (Conde-Petit and Escher, 1992). Amylose/surfactant complexes accelerate gelation in the first few hours of storage, compared to starch gels made without surfactant (Conde-Petit and Escher, 1994). Gelation of maize, potato, tapioca, and wheat starch is responsible for setback viscosity profiles, as shown in Fig. 4.2 (Deffenbaugh, 1990). Sucrose esters increased setback viscosity by forming complexes that accelerated gelation. Surfactants may be used to induce and control gelation in starch-containing foods (Conde-Petit and Escher, 1992).

4.3.5 Starch Retrogradation

Retrogradation is the formation of ordered, partially crystalline regions in a cooled starch paste. It is a slow process that occurs hours to weeks after pasting and gelation. In high-amylose containing foods, the process may be complete before the product is distributed and consumed. Retrogradation may cause significant deterioration of texture and flavor attributes during shelf life (Miles et al., 1985). Starch-complexing surfactants retard retrogradation of starch, and this is a major application for surfactants in the processed food industry. This effect is due to prevention of side-by-side stacking of starch helices (Miura et al., 1992). Nucleation sites for retrogradation or recrystallization are thereby reduced (Matsunaga and Kainoma, 1986).

Amylopectin retrogradation plays an important role in shelf life stability in some foods. The increase in firmness and loss of flavor in staled bread are caused by retrogradation of the amylopectin fraction of wheat starch (Schoch and French, 1947; Gudmondson and Eliasson, 1990). Control or modification of amylopectin retrogradation by incorporation of surfactants has practical significance.

Interactions between surfactants and amylopectin are more difficult to demonstrate than interactions between surfactants and amylose. Nevertheless, a number of

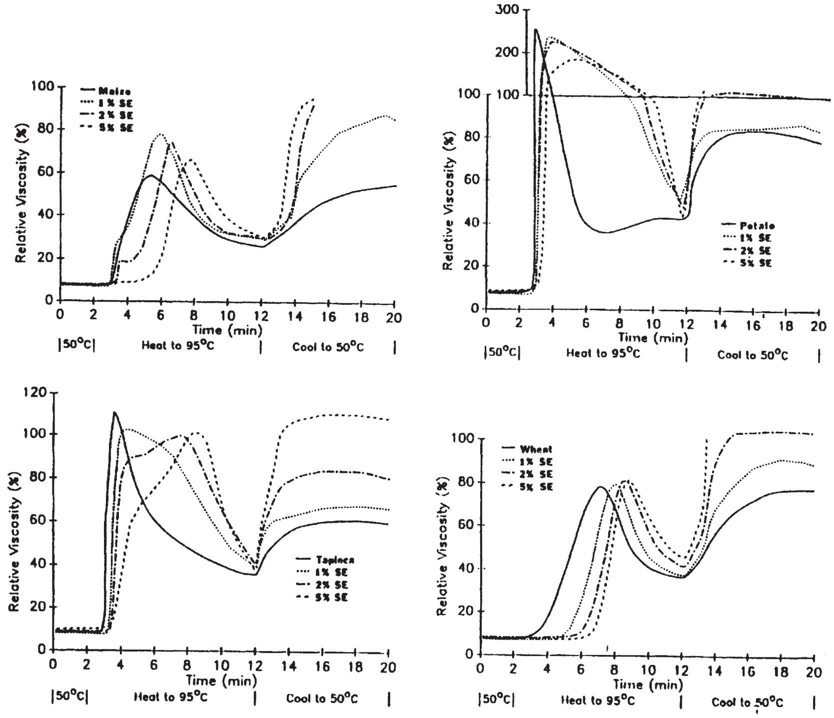

Fig. 4.2 Rapid Visco Analyzer viscosity profiles of maize, potato, tapioca, and wheat starches with 0, 1, 2, or 5% (starch wt basis) of sucrose ester emulsifier. (From Deffenbaugh, 1990.)

reports of indirect evidence in the literature are noted (Evans, 1986; Eliasson and Ljunger, 1988). For example, insoluble complexes between monoacylglycerols and amylopectin have been observed (Batres and White, 1986). Amylase digestion of waxy maize starch was slightly reduced by the presence of surfactant. A delay in viscosity increase during gelatinization also suggests that surfactants interact with amylopectin. Differential scanning calorimetry and x-ray diffraction detected the interaction of monoacylglycerols and other surfactants (Gudmondsson and Eliasson, 1990). These results were correlated with a reduction of amylopectin retrogradation. When amylose and amylopectin are present together, surfactants will preferentially complex with the amylose. As a result, the amylose cannot co-crystallize with the amylopectin and the effect of surfactant on amylopectin is indirect.

4.3.6 Enzymolysis of Starch

Glucoamylase is an enzyme, which cleaves successive glucose units, starting at the nonreducing end of a starch chain. Complex formation with surfactants generally reduces the rate of enzymolysis (see Table 4.1). This effect may be due to steric hindrance, since the surfactants occupy positions between starch helices. For high-amylose starches, the helical chain may be rendered unavailable by precipitation of the complex. Recent studies indicate that in vitro enzymolysis is significantly affected by crystal morphology, resulting from the extent of gelatinization and retrogradation (Slaughter et al., 2001; Chang et al., 2006). Efforts were made to correlate enzyme kinetics with glycemic indices of some starchy foods. However, it has been reported that sucrose esters do not have an appreciable effect on hydrolysis of amylose or amylopectin (Deffenbaugh, 1990). In vivo studies in rats indicated that surfactant/starch complexes did not have a significant effect on the overall digestibility of starch (Holm et al., 1983; Fardet, A., et al.).

4.4 Lipid Adjunct and Surfactant Properties

Since not all surfactants are capable of forming complexes with starch, molecular structure is a critical factor. Single-tailed surfactants with saturated alkyl chains are well suited for comlexation. Binding increases as the alkyl chain length increases (Gray and Schoch, 1962; Hahm and Hood, 1987). Other factors, such as the nature of the polar group and the molecular weight govern the degree of penetration of the alkyl chain into the helix (Miura et al., 1992). In addition to the preceding factors, if the geometry of the starch helix is known, the ratio of lipid/starch required to produce saturation of the helix may be determined by stoichiometry (Karkalas and Raphaelides, 1986).

Solubility of the lipid or surfactant determines the equilibrium concentrations of the complex and the lipid in solution. The more soluble the lipid complexing agent, the greater proportion will be present in the aqueous phase. For example, fatty acids are less soluble than monoacylglycerols. Therefore, a greater proportion of the alkyl chain is forced into the lipophilic core of the starch helix. Differential solubility at higher processing temperatures and storage temperatures should also be considered.

Increased unsaturation in the fatty acid chain reduces the ability of the lipid to form inclusion complexes with starch helices (Lagendiik and Pennings, 1970; Krog, 1971; Hahm and Hood, 1987). The 30° angle of the 9,10 cis(Z) double bond in the fatty acid chain reduces rotational flexibility and produces steric hindrance to insertion into the helix. Similarly, bulky polar groups pose a steric barrier to complex formation (Gray and Schoch, 1962; Krog, 1971; Hahm and Hood, 1987).

4.4.1 Starch Granules

Starch granules may introduce an additional steric barrier to formation of lipid/surfactant complexes. For example, monoacylglycerols exist as micelles or mesophases in an aqueous environment. At low temperatures (<50 °C), these surfactants attach to the surface of the starch granule by simple adsorption (Van Lonkhuysen and Blankestijn, 1974). As the temperature is increased to >80°C, the starch granules swell, and the alkyl chains of the monoacylglycerol penetrate the starch helix. However, some workers have measured strong surfactant/starch complexes at temperatures as low as 60°C, where only slight swelling and gelation were observed (Ghiasi et al., 1982a,b).

4.4.2 Starch Type and Source

Starch is a high molecular weight biopolymer with a molecular structure that varies according to its biological source. As previously discussed, the major variation is the relative proportion of amylose and amylopectin. Structural differences affect the properties of surfactant/starch complexes. For example, glycerol monostearate (GMS) restricted swelling of potato starch granules to a greater extent than it did for maize or wheat starch granules (Eliasson, 1986b).

Some traditional methods of analysis, such as iodine binding capacity and glucoamylase digestion, are not sufficiently sensitive to measure the subtle differences due to differences in starch type. Other methods, such as measurement of viscoelastic properties (Eliasson, 1986b) and viscosity (Deffenbaugh, 1990) are capable of distinguishing different starch types in the presence of surfactant. Viscosity parameters for various starches in the presence of sucrose ester surfactants are shown in Table 4.3 (Deffenbaugh and Walker, 1990). The time to peak viscosity changed more for tapioca than for maize, wheat, and potato starches. The surfactant affected setback viscosity most in wheat starch. Potato and tapioca granules were stabilized by complex formation so that swelling and disintegration were more gradual. Starch-complexing surfactants also stabilize the pasting viscosity of tapioca starch (Moorthy, 1985). Viscosity profiles are convenient for studying complex properties in food systems.

4.4.3 Environmental Conditions

Temperature affects the stability of starch/surfactant complexes and consequently affects, their functionality in food systems. Iodine and fatty acid binding capacities of amylose decrease with increasing temperature (Banks and Greenwood, 1975; Hahm and Hood, 1987). The starch helix becomes more disorganized and its ability to include complexing agents. Increasing temperature may also increase the solubility and mobility of complexing agents in the aqueous phase.

Binding of some fatty aids by amylose is affected by pH via protonation and deprotonation of the carboxyl group (Hahm and Hood, 1987). Palmitic (C-16) and stearic (C-18) acids form dimers below their pK_a values (4.7–5.0) by hydrogen bonding between their protonated carboxyl groups. Twinning of their alkyl chains makes them too bulky to fit into the amylose helix. Above their pK_a, the carboxyl groups are deprotonated, and the dimer dissociates due to electrostatic repulsion.

Table 4.3 Rheological properties of starches with sucrose esters (Deffenbaugh 1990)

Time to Peak (min)				
Starch	0% SE	1% SE	2% SE	5% SE
Maize	5.43^1	5.96^2	6.72^3	7.72^4
Potato	3.03^1	3.64^2	4.08^3	5.15^4
Tapioca	3.67^1	4.26^2	7.23^3	8.33^4
Wheat	7.32^1	8.08^2	8.45^3	8.84^4
Waxy maize	3.45^1	3.54^1	3.86^2	4.16^3
Peak viscosity (%)				
Starch	0%SE	1%SE	2%SE	5%SE
Maize	57.9^1	77.2^2	74.3^2	65.9^3
Potato	256^1	232^2	226^3	183.6^4
Tapioca	113.2^1	104.9^2	99.6^3	$101.32^{2,3}$
Wheat	78.4^1	80.1^1	81.2^1	81.6^1
Waxy maize	88.8^1	101.6^2	98.0^2	89.8^3
Maximum setback viscosity (%)				
Starch	0%SE	1%SE	2%SE	5%SE
Maize	55.0^1	86.0^2	98.8^3	97.4^3
Potato	83.9^1	83.9^1	110.3^2	–
Tapioca	61.5^1	68.1^2	84.8^3	118.0^4
Wheat	78.81^1	90.9^2	129.1^3	166.6^4
Waxy maize	50.2^1	51.0^1	52.6^1	51.3^1

Superscripts 1, 2, 3, 4 indicate significant difference ($p < 0.05$) within starch type

The pH does not affect the binding of lower fatty acids, such as myristic (C-14) or lauric (C-12) that do not form dimmers. Nonionic surfactants, such as monoacylglycerols, are not affected because thee carboxyl group is bonded in an ester linkage and is unavailable for protonation and deprotonation.

The amylose-complexing ability of surfactants containing alkyl chains is affected by their phase behavior (Larsson, 1980). The most effective complexing surfactants have a high degree of freedom in the aqueous phase and exhibit lyotropic mesomorphism. Micelles and vesicles (liposomes) are the mesophases that are the best sources of surfactant monomers for complex formation. Other mesophases (lamellar, hexagonal, cubic) are less effective (Rilsom et al., 1984; Eliasson, 1986a); Lysolecithin, a native single-tail lipid in wheat starch forms a complex with amylose which affects functionality in baking. (Krog and Nybo-Jensen, 1970). Addition of exogenous lysophosphatidylcholine dramatically raised the gelatinization temperature of granular maize starch (Toro-Vazquez et al., 2003).

4.5 Physical Properties of Starch/Surfactant Complexes

Physical properties of starch/surfactant complexes have provided valuable insights into the functionality of surfactants in starch-containing food systems. Techniques, such as x-ray diffraction, differential scanning calorimetry, nuclear magnetic resonance, and electron spin resonance, rheology and microscopy have proven especially useful.

4.5.1 X-Ray Diffraction Patterns

X-ray diffraction was one of the first techniques used to identify starch inclusion complexes (Mikus et al., 1946). This technique yields valuable information about the crystallinity of starch. Clathrates (inclusion complexes) are detected when a powder diffractogram displays a “V-pattern.” X-ray diffraction has been widely used to detect an inclusion complex when starch has been heated in the presence of a native lipid or a surfactant (Hanna and Leliievre, 1975; Hoover and Hadziyev, 1981; Eliasson and Krog, 1985; Biliaderis and Galloway 1986; Eliasson 1988; Deffenbaugh 1990; Rutschmann and Solms, 1990). The helical structure of amylose within the complex was also characterized. X-ray diffraction also displayed V-type patterns for complexes formed between amylopectin and surfactants (Gudmondsson and Eliasson, 1990). Studies also indicated that “free” formed inclusion complexes, while amylopectin in waxy maize starch did not (Evans, 1986; Eliasson, 1988).

X-ray diffraction measurements indicate that the unit cell of the starch helix is essentially the same for all complexes with single-tail surfactants. Surfactants with two or more fatty acid side chains are sterically excluded from penetrating the helix and forming complexes (Osman et al., 1961). Most V-complexes have a pitch of approximately 0.8 nm, indicating that the starch chains are folded so that the alkyl chains are perpendicular to the surface of the lamellae.

4.5.2 Infrared Spectroscopy

Infrared spectroscopy is a useful technique to probe the structure of a surfactant inside the amylose helix. Frequencies for the carboxyl (Osman et al., 1961; Batres and White, 1986), Methyl (Batres and White, 1986), and carbonyl (Hahnel et al., 1995) groups have been investigated. The carbonyl group in glycerol monostearate displays a positive shift inside the complex. This is thought to occur because of electron delocalization inside the helix.

4.5.3 Electron Spin Resonance

Stable free radical fatty acid spin probes may be measured using electron spin resonance (ESR). The line shapes in the spectrum are indicative of the environment surrounding the probe. Reduction in the mobility of the spin probe, due to adsorption or inclusion in a viscous medium, is indicated by line broadening. The technique has been used to study the interactions between fatty acids and starch. The motion of the probe was greatly slowed in the presence of wheat, high amylose maize and waxy maize starches (Pearce et al., 1985). Binding was weaker in waxy maize than in other starches. Results were similar at room temperature, and heating to 90°C and cooling back to room temperature. Binding was thought to occur throughout the granule, since surface adsorption would not account for the amount of probe utilized. The presence of water facilitated binding, presumably by allowing greater penetration into the interior of the granule (Pearce et al., 1985; Nolan et al., 1986). Similar results were found for probes binding to maize and waxy maize starches at room temperature (Johnson et al., 1990). Heating and subsequent cooling were found to destabilize the complex. Heating increases overall spin probe binding by increasing the surface area of the granule and the permeability of the starch granule.

4.5.4 Nuclear Magnetic Resonance

Nuclear Magnetic resonance (NMR) measures chemical shifts for odd-numbered atoms or their isomers (^{1}H, ^{13}C, ^{17}O, ^{31}P). The chemical environment near the nuclei influences the position and shape of the peak in the spectrum, For example, stereochemistry in a molecule may be determined with the Nuclear Overhouser Effect (NOE). ^{13}C NMR can detect changes in the carbon atoms in starch induced by complex formation with surfactants (Jane et al., 1985; Deffenbaugh, 1990).

Downfield shifts were observed for all carbon atoms of starch, which had been converted into an inclusion complex (Jane et al., 1985). However, C-1 and C-4 were the most pronounced, suggesting a rotation of the C-O bond in the glycosidic linkage. ^{13}C NMR of maize starch in solution displayed a downfield shift of C-1 and C-4 at 55–75 °C in the presence of a complexing agent (Deffenbaugh, 1990). At temperatures above 70 °C, no effect was observed. Although the complex was formed during gelatinization, it could not be detected in solution. Waxy maize starch/surfactant complexes could be detected by ^{13}C NMR.

Proton (^{1}H) NMR has also been utilized to study complex formation. The signal intensity of the amylose protons was reduced when sodium palmitate was added. This was interpreted as loss of conformational mobility in the helix due to complex formation, which resulted in extreme line broadening (Bulpin et al., 1982). Signal intensity was restored when the system was heated to >90 °C, apparently due to dissociation of the thermally reversible complex. In a study of cycloheptaamylose, signals for H-3 and H-5 were shifted upfield in the presence of lysolecithin (Kim and Hill, 1985). Since these protons were directed toward the interior of the helix, they experienced a more hydrophobic environment after complex formation with the lipid. No band shifts were observed for complexes between amylopectin and monoacylglycerols (Batres and White, 1986).

Decoupled ^{17}O NMR was used to study the stability of taro pastes toward retrogradation during storage (Lai, 1998). Shifts in signals indicated that water, sugar, and starch mobility were reduced in the presence of monoacylglycerols and sodium stearoyl lactylate.

4.5.5 Differential Scanning Calorimetry

When a sample is heated or cooked while accurately measuring temperature, thermal transitions and enthalpy are detectable by differential scanning calorimetry (DSC). Gelatinization of starch is a water-mediated endothermic melting transition. Starch/surfactant comlexation displays crystallization during heating (Eliasson, 1983; Biliaderis and Galloway, 1986; Evans, 1986; Eliasson, 1986a; Eliasson, 1988; Deffenbaugh, 1990). Data in Table 4.4 show the effect of sucrose esters on gelatinization temperatures and enthalpies of various starches (Deffenbaugh, 1990). Data indicates a delay in gelatinization, consistent with observations made using other methods. However, at transition temperatures of 100–115°C and high moisture levels, melting and crystallization transitions may merge into a single peak.

The gelatinization endotherm is not observed in DSC sample re-scans because the gelatinization process is irreversible. In contrast, starch/lipid complexes melt and recrystallize reversibly. Multiple DSC scans are therefore very useful to confirm the existence of starch/lipid complexes (Hoover and Hadziyev, 1981; Kugimiva and Donovan, 1981; Eliasson, 1988; Staeger et al., 1988; Deffenbaugh, 1990; Szezodrak and Pomeranz, 1992).

Table 4.4 DSC Parameters of starch gelatinization endotherm from thermograms of starch with sucrose ester emulsifier (Deffenbaugh 1990).

T_0 (°C)				
Starch	0% SE	1% SE	2% SE	5% SE
Maize	66.66^1	66.53^1	66.49^1	66.42^1
Potato	59.74^1	59.83^1	59.75^1	59.61^1
Tapioca	63.54^1	63.97^1	64.03^1	63.90^1
Wheat	58.71^1	59.10^1	58.42^1	59.02^1
Waxy maize	69.03^1	68.40^1	68.40^1	68.13^1
T_p (°C)				
Starch	0% SE	1% SE	2% SE	5% SE
Maize	72.83^1	72.59^1	72.69^1	72.66^1
Potato	64.75^1	64.75^1	64.89^1	64.60^1
Tapioca	70.19^1	70.64^1	70.82^1	70.31^1
Wheat	63.69^1	63.72^1	63.30^1	63.67^1
Waxy maize	74.75^1	74.17^1	74.29^1	74.24^1
ΔH (J/g)				
Starch	0% SE	1% SE	2% SE	5% SE
Maize	13.44^1	11.50^2	10.61^2	10.66^2
Potato	16.93^1	16.64^1	$16.26^{1,2}$	15.37^2
Tapioca	18.19^1	15.28^2	13.77^1	11.83^1
Wheat	10.61^1	$9.58^{1,2}$	9.33^2	8.78^2
Waxy maize	16.90^1	17.01^1	16.96^1	16.83^1

Superscripts 1 and 2 indicate significant difference ($p < 0.05$) within starch type

The relative thermal stability of starch/lipid complexes can be measured using DSC. Stability is a function of surfactant and type of starch. The measurements are important because they can predict rheological properties during gelatinization of starch systems (Eliasson, 1986b). Thermal stability and complex-melting enthalpy decrease as the fatty acid chain is interrupted by cis (Z) double bonds (Stute and Konieczny-Janda, 1983; Eliasson and Krog, 1985; Raphaelides and Karkalas, 1988). Chain length of the fatty acid does not affect the melting enthalpy and may or may not affect the thermal stability. Glycerol monostearate (GMS) forms very stable complexes with starch and has very significant effects on starch gelatinization. In Taro paste, sodium stearoyl lactylate showed a larger melting endotherm than monoacylglycerols (Lai, 1998).

Physical properties of starch/surfactant complexes depend on conditions during crystallization. Multiple melting endotherms of complexes or shifting of endotherms during re-scanning indicate the presence of different crystal polymorphic forms. (Paton, 1987; Kugimiva and Donovan, 1981; Bulpin et al., 1982; Biliaderis and Galloway 1986; Eliasson, 1988). At the onset of gelatinization, association of the amylose chain with a ligand provides the conformational order to allow nucleation. Complexation during first heating may be incomplete due to restricted mobility of the amylose chain (Kugimiva and Donovan, 1981). Different polymorphic forms may occur simultaneously within a large crystal, which has folded back on itself (Eliasson, 1988). Complexes in folds or on the surface of the crystal have lower melting temperatures than those further inside the crystal.

4.5.6 Rheological Properties

Rheology is a discipline, which employs mechanical testing to measure the properties of materials under simulated conditions of use. In foods, the tests attempt to discover component interactions, which define the textural attributes, which make foods desirable to consumers (McClements, 2004; Chakrabarti, 2005).

The impact of starch/lipid complexes on rheological properties is often used to manage their functionality in high-starch foods. Important measurements are storage modulus, loss modulus and gel strength. In concentrated potato and wheat starches, dynamic modulus was higher in the presence of GMS and SSL (Kim and Walker, 1992; Keetels et al., 1996). Less gel stiffness occurred with these surfactants during storage. Amylopectin potato starch produced soft shear thinning gels in the presence of GMS and calcium stearoyl lactylate (Nuesslil et al., 2000). The Power Law and the Bird-Leider models were used to determine the effects of triacylglycerol and monoacylglycerol additions to starch pastes (Navarro et al., 1996). Triacylglycerol addition had no effect on wheat starch granules, but increased swelling capacity and decreased amylose leaching in corn starch granules. Waxy maize starch was unaffected by lipid addition. A recent rheological study suggests that amylose/lipid complexes may have utility as controlled lipid release agents (Gelders et al., 2006). Modeling has also been used to investigate starch retrogradation (Farhat and Blanshard, 2001). Rheological measurements also determined functionality in some challenging bakery products, such as cake batter (Sakivan et al., 2004), microwaveable cakes (Seyhun et al., 2003), and frozen bread doughs (Ribotta et al., 2004).

4.5.7 Microstructure of Starch Systems

Observation of structure in model systems by microscopy techniques can provide information about functionality and interactions (Groves, 2005).

The light microscope may be used to examine the gross structure of a food matrix. In principle, objects >200 µm are detectable, but this level of resolution is difficult to achieve in practice. Interactions of surfactants with starch granules were observed in pastilles and yogurts by staining the ingredients (Titoria et al., 2004). Cross-polarized light highlights structures, which display birefringence. Sugar particles show up as white grains while starch granules show up as a chrematistic “Maltese cross.” When starch gelatinizes, the Maltese cross disappears. The rate of gelatinization can therefore be measured in model starch gels or high-starch products (Nuesslil et al., 2000; Lamberti et al., 2004; Seetharaman et al., 2004). Confocal laser scanning microscopy (CLSM) is useful because sectioning of the sample results in a three dimensional image. For example, three dimensional images of corn starch granules were obtained (Bromley and Hopkinson, 2002).

If electrons are used instead of light, much greater resolution of the structure can be obtained. In scanning electron microscopy (SEM), the surface of the sample is observed by scattering of electrons. The sample may be pre-fractured to see interior structure. Transmission electron microscopy (TEM), electrons are passed through a thin section of the sample. Interactions of ingredients may be detected by effects on microstructure (Olsson et al., 2003; Walkenstrom et al., 2003; Tang et al., 2004). The effect of surfactants on microstructure of starch gels, and baked products have been reported (Toro-Vazquez et al., 2003; Ribotta et al., 2004; See-Kang and Suphantharica, 2006). TEM, for example, showed that fine-stranded amylose gels transformed into thicker strands by surfactants, but became spheres at higher surfactant concentrations (Richardson et al., 2004).

4.6 Surfactant/Hydrocolloid Interactions

Hydrocolloids also referred to as gums, have been widely used in the food industry as thickeners and agents for gel formation and particle suspension (Belitz et al., 2004b). They work cooperatively with surfactants to stabilize emulsions against flocculation and coalescence. Surfactants adsorb at the interface to provide steric and electrostatic stabilization. Hydrocolloids, by increasing the viscosity of the aqueous phase, retard the mobility of dispersed phase droplets. For convenience, cellulose will be included in this discussion.

Hydrocolloids have very weak or no surface activity. Some of these products have no lipophilic groups in their molecular structure. However, some gums, such, as guar and arabic, are surface-active because they contain a few percent of proteins, which contain some lipophilic amino acids. Others, such as pectin, contain small lipophilic groups bound to the polymeric chain by ester or ether linkages. Starches and hydrocolloids are chemically modified to include nonpolar functionality (Table 4.5). Surfactant/hydrocolloid interactions may be explained by competition for the interface (Garti et al., 1999).

Polar hydrocolloids may interact with the hydrophilic functional group of a surfactant through ionic or hydrogen bonds (Babak et al., 2000). Some of these complexes have been utilized to reduce total fat and to replace saturated fats with liquid oils (Reimer et al., 1993). The existence of these complexes is more difficult to establish than starch inclusion complexes. SEM and TEM showed significant strand thickening for monoacylglycerol/starch gels but not monoacylglycerol/cellulose gels. The blends, however, did provide texture and flavor advantages in fat-free products (Baer et al., 1991). Surfactant/hydrocolloid compositions are optimized in wheat bread formulations (Fast and Lechert, 1990; Mettler, 1992)

Table 4.5 Some chemically modified polysaccharides

Product	Added group	Typical applications
Starches		
Ethers	$-OCH_2CHROH$	Thickeners for refrigerated and canned foods, pie fillings
Carboxymethyl	$-OCH_2CO_2H$	Instant gelling products
Starch Esters	$-OPO_3H$ $-OCO(CH_2)_nCOO$-	Improved freeze-thaw sta bility, Soups, bakery products, sauces
Cross-linked	Phosphates, Dicarboxylic acids	Products requiring stability at extremes of pH
Celluloses		
Alkylated	$-OCH_3$, $-OCH_2CH_3$, $-OCH_2CH(CH_3)OH$	Viscosity rises with temperature, Batters, dehydrated fruits, coatings
Carboxymethyl	$-OCH_2CO_2H$	Jellies, fillings, ice cream, bakery products, dehydrated foods
Hydrocolloids		
Propylene glycol alginate	$-OCH_2CH(CH_3)OH$	Suspending agent, salad dressings

4.7 Summary

Amphiphicmolecules are capable of interacting with simple saccharides, starches, and carbohydrates. Ionic, hydrogen, and/or hydrophobic bonding may form carbohydrate/surfactant complexes. A special example of hydrophobic (lipophilic) bonding is the formation of starch/surfactant inclusion complexes. These interactions may have a significant impact on the functional properties (such as, stickiness, viscosity, crystallization, or gel strength) of carbohydrates. Modern methods of colloid and emulsion science have led to descriptions of bimolecular interactions. However, correlation of this data to ingredient behavior in complicated food formulations can be quite difficult. This is particularly true when other surface-active agents or polyvalent ions are present. Application of experimental design is a useful tool to explain these effects in real foods.

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