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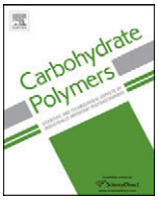

Review

Pasting, paste, and gel properties of starch–hydrocolloid combinations

James N. BeMiller*

Whistler Center for Carbohydrate Research, Department of Food Science, Purdue University, West Lafayette, IN 47907-2009, USA

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ABSTRACT

A review with 267 references. Use of starch–hydrocolloid combinations is widespread, particularly in the food processing industry. Many studies have been conducted with a goal of understanding why the addition of a small amount of a hydrocolloid influences the properties of a starch-based paste, gel, or food product. Multiple variables are encountered in the research reports, including the use of different types of starches and hydrocolloids and different methods of preparation and evaluation of composite pastes and gels. Most commonly, a starch–hydrocolloid composite paste and/or gel exhibited (as compared to the starch alone paste and/or gel) increases in peak and final viscosities, short-term retrogradation, and gel strength and decreases in the temperature of the initial rapid viscosity increase, granule swelling, starch polymer molecule leaching from swollen granules, and long-term retrogradation; but opposite effects have also been observed. Most evidence seems to point towards the following mechanisms: hydrocolloid molecule interaction with leached starch polymer molecules—in some cases increasing network formation and in other cases decreasing or weakening the network formed by starch polymer molecules, changes in starch granule swelling (either positive or negative changes), swollen granule association via depletion flocculation, and phase separation between amylose, amylopectin, and hydrocolloid molecules in the continuous phase. The overall conclusion is that, because of the complexity of the variety of systems, several mechanisms are likely to be operating and the proportions of competing mechanisms likely vary with different specific hydrocolloids, different starches, and different methods of preparation of composite pastes and gels.

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* Tel.: +1 765 494 5684; fax: +1 765 494 7953.
E-mail address: bemiller@purdue.edu

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1. Introduction

Non-starch polysaccharides used in formulated food systems are now usually called hydrocolloids, which is the term used in this review. In the older literature, such carbohydrate polymers are called gums or food gums. Both terms (hydrocolloids and gums) as used in this review refer to water-soluble polysaccharides or polysaccharide derivatives.

Starch–hydrocolloid combinations have been used in processed foods (including confections) since at least about 1950. The reasons for using combinations vary with the product, but can be generalized as follows. Native starches do not generally have ideal properties for the preparation of food products. Most often native starches are chemically modified to improve their tolerance to processing (heat, shear, and acidic) conditions, to improve the texture of pastes and gels made from them, and to provide cold storage and freeze–thaw stability, control water mobility, and other attributes desired by food processors. Addition of the proper hydrocolloid can also overcome the shortcomings of native starches—for example, can protect starch granules against shear during cooking, improve product texture/rheology (Kulicke, Eidam, Kath, Kix, & Kull, 1996), hold moisture, and protect against syneresis. And hydrocolloid–starch combinations may accomplish these things while at the same time providing a "clean label", i.e., avoidance of using the terms modified food starch or food starch modified.

Some starch–hydrocolloid combinations used, or proposed to be used, in high-moisture food products are listed in Table 1 . Until now, an extensive literature and patent search has not been made for these products, however, and many products are made using combinations that have not been described in the patent or other literature.

Four reviews on this subject have been published previously (Appleqvist & Debet, 1997; Funami, 2009; Sikora & Krystyjan, 2008; Sudhakar, Singhal, & Kulkarni, 1996a); but the latter two were not available to this author, the former two did not cover all the available literature, and as the data in Table 2 shows, more than two-thirds of the 150 basic research papers on this subject have appeared since 1997. (This review covers the literature since it was first observed that hydrocolloids affected starch pasting and the nature/behaviors of starch pastes and gels until 30 June 2010.)

There are at least two reasons why this subject has been the subject of so much research. (1) It is practically important. (2) What happens when a starch and a hydrocolloid are heated together is not yet understood to the point that the outcome can be modeled and/or predicted. The latter is not the result of not enough data. There is a plethora of data, so why has it not been possible for researchers to agree on a process or mechanism?

1.1. Variables

Hydrocolloids have a variety of different structures, including differences in branching, flexibility, molecular weight ranges, and ionic charge, all of which influence their behavior and the rheology of their solutions (BeMiller, 2007). For example, phase separation in starch pastes may be greater when charged polymer molecules are added than when neutral ones are added, so a mechanism may be, and probably is, structure specific. Hydrocolloids such as guar gum, locust bean (carob) gum, and tara gum are not pure polysaccharides, but rather are the ground endosperm of the respective seeds and thus contain protein, fiber, ash, etc. (BeMiller, 2007). In this context, Brennan et al. (2006) found marked differences when using purified fenugreek gum (another galactomannan) vs. fenugreek flour. Also, Symons and Brennan (2004) acknowledged that the presence of protein in barley beta-glucan fractions likely affected the obtained results. Methylcellulose and hydroxypropyllcellulose have the unique property of thermogelation that affects starch pasting curves. The commercial carrageenans are not single molecular species, but are mixtures that may be enriched in one type. Commercial carrageenan preparations are often blended to provide specific characteristics for specific applications, often contain added salts (cations), and are often standardized. The structures of all naturally occurring polysaccharides, but particularly of the carrageenans, vary with growing conditions of their source plants.

Starches also differ from each other. Each starch is unique. The differences are in fine structures of the amylose (AM)[1] and amylopectin (AP) molecules and in granule behavior (see, e.g., Ji, Ao, Jane, & BeMiller, 2004). Differences occur not only from species to species, but also from cultivar to cultivar and from growing season to growing season (see, e.g., Inouchi, Ando, Asaoka, Okuno, & Fuwa, 2000; Mica, 1969; Paterson, Hardacre, Li, & Rao, 2001; Sasaki, Yasui, & Matsuki, 2000a; Svegmark et al., 2002; Tester & Karkalas, 2001; Wilkins et al., 2003a, 2003b; Wootton & Mahdar, 1993). Normal rice starch in particular can have a rather wide range of AM contents (see, e.g., Bett-Garber et al., 2001; Fitzgerald et al., 2009).

In addition, like all polysaccharide molecules, hydrocolloid and starch polymer molecules are both polymolecular and polydisperse.

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[1] Abbreviations used are listed at the bottom of Table 3.

Table 1
A partial listing of patents[a] and papers on practical uses of starch–hydrocolloid combinations.

Reference	Claims[b]
Kuchinke and Buchta (1967)	A preparation containing a pregelatinized starch plus agar or LBG that can be used to prepare cold-setting mixes for shape-retaining puddings, sliceable custards, or similar food products.
Société de Produits Chimiques d'AUBY (1966)[c]	Heated and co-precipitated complexes of starch + carrageenan with unique properties.
Decnop (1969)	A cold-water-dispersable, pregelatinized starch product that may contain CMC or another hydrocolloid
Yoder and Bugg (1971)	An ingredient consisting of a blend of pregelatinized wheat flour and/or a pregelatinized starch, an edible hydrocolloid, such as guar gum or CMC, and sodium stearyl fumarate that can be used to prepare food products with improved freeze–thaw stability.
Bahoshy et al. (1971)	A pudding mix composition containing a starch, a modified starch, and a hydrocolloid.
Eskritt et al. (1976)	A dry dessert mix composition containing a pregelatinized starch product and a hydrocolloid.
Christianson and Gardner (1980)	Composites made by heating starch and hydrocolloid together in water then spray drying the dispersion that had improved viscosity building, solubility, and gel-forming properties.
Cheng (1980a)	Products useful for preparing retorted or aseptically packaged puddings or other edible, texturized starch products made by extruding mixtures of a starch and a hydrocolloid.
Cheng (1980b)	LBG-xanthan blends decreased setting times of starch-based confections.
Koho (1980) [c]	Use of xanthan to prevent retrogradation.
Cheng and Wintersdorff (1981)	Products made by gelatinizing starches in the presence of xanthan, then drying the pastes (using a process used to make a pregelatinized starch) have properties similar to those of chemically modified starches.
Fonteneau and Germon (1986)	Sauce and gravy compositions containing rice starch and LBG.
Rapp (1986)	A pudding composition particularly adapted to production of sterile, aseptically packaged pudding products.
Rudin (1986)	An instant yogurt-like food product containing a hydrocolloid and a modified and/or pregelatinized starch product or a cold-water-swelling starch.
Weaver and Steensen (1987)	A sugar-free, instant-type pudding and a hydratable dry mix for its preparation containing a modified starch and/or pregelatinized starch product, κ-type carrageenan, and sodium alginate.
Bielskis et al. (1989)	Starch–hydrocolloid blends produced by heating the two together in the presence of water until the starch is gelatinized and extruding the mixture under minimal shear, but with enough pressure that it expands, that are useful in stabilizing frozen desserts, sour cream, and salad dressings. Polymer molecules are minimally degraded.
Clark and Burgum (1989)	Composite gels made with high-acyl gellan and starch that have textural and functional properties similar to those of gels made with starch alone were used to make fast-gelling food products.
Coffey (1990)	A method of thickening a food product using combinations of starches and methylcelluloses.
Wilson (1991)	A dry mix containing starch and xanthan that develops a thickened sauce during meat cooking processes.
Christianson and Fanta (1995)	Starch–hydrocolloid blends prepared by jet cooking slurries of the two and drum drying the resulting solution that, when placed in water, hydrate rapidly to yield dispersions that are not only smooth and viscous, but also possess considerable lubricity and are useful as thickening agents, suspending agents, and fat replacers. Polymer molecules are degraded.
Kasica and Eden (1995)	A continuous, coupled jet-cooking, spray-drying process to make starch–hydrocolloid blends, particularly those involving a high-amylose starch.
Appleqvist et al. (1996)	Use of hydrocolloids in frozen sauces.
Dunn and Finocchiaro (1997)	Texturizing agents containing a pregelatinized starch and a hydrocolloid that can be used in the preparation of low-fat and fat-free foods.
Marrs (1997)	The presence of xanthan, because of its competition for water, results in more rigid gels.
Carpenter et al. (1998)	An imitation cheese (cheese analog) composition containing a native or modified starch and a hydrocolloid or a combination of hydrocolloids.
Mukprasirt, Herald, Boyle, and Rausch (2000a), Mukprasirt, Herald, and Flores (2000b), Mukprasirt, Herald, Boyle, and Boyle (2001), Mukprasirt, Herald, and Seib (2002)	Rice flour–corn flour-methylcellulose–oxidized corn starch batter compositions.
Wei, Wang, and Wu (2001)	Fruit fillings.
Hawkes and Zeien (2002)	An ingredient made by extrusion cooking of a high-amylose starch and a hydrocolloid.
Sikora, Juszczak, Sady, and Krawontka (2003)[c]	Starch–xanthan blends as thickeners of cocoa syrups.
Mandala et al. (2004b)	Addition of xanthan or LBG changed the rheology and structure of a model white sauce.
Gibiński et al. (2006)	Sweet and sour sauces thickened with oat starch–xanthan and potato starch–xanthan combinations were evaluated.

Table 1 (*Continued*)

Reference	Claims[b]
Dolz, Hernández, and Delegido (2006)	Salad dressings stabilized with a stabilizer and crosslinked starch + xanthan, LBG, or a xanthan–LBG combination were evaluated.
Funami et al. (2006)	Starch–funugreek combinations increase viscosity and suppress or accelerate retrogradation.
Sikora, Kowalski, Tomasik, and Sady (2007b)	Strawberry sauces thickened with oat, potato, and corn starches + xanthan were evaluated.
Sikora, Kowalski, Krystyjan, Krawontka, and Sady (2007a)	Corn starch–xanthan mixtures were optimized for thickening cocoa syrups.
Hernández, Dolz, Delegido, Cabeza, and Dolz (2008)	Formulations containing a crosslinked and stabilized food starch and a HM-pectin or deacylated gellan were used to make salad dressings.
Yamane (2008)	Beverage powders and beverages for people with difficulty swallowing.
Arocas, Sanz, and Fiszman (2009)	Effects of adding xanthan and LBG on freeze–thaw stability of white sauces prepared with corn, waxy maize, potato, and rice starches were determined.
Li, Qiao, Mei, and Wang (2009a)	Starch–xanthan mixtures used to prepare milk puddings.
Li et al. (2009b)[c]	Propylene glycol alginate, pectin, and pregelatinized starch were used in stirred yogurt production.
Arocas, Sanz, Salvador, Varela, and Fiszman (2010)	Xanthan or LBG were added to starch-based white sauces to be frozen, then reheated.

[a] Mostly, but not exclusively, from the patent literature; and mostly, but not exclusively, U.S. patents.

[b] *Abbreviations used*: CMC = carboxymethylcellulose, LBG = locust bean (carob) gum. For the most part, specific hydrocolloids are not identified.

[c] Abstract only available.

Table 2

Research papers published that involve the co-presence of a starch and a hydrocolloid in a system containing a relatively high percentage of water.

Year	No. of papers	Year	No. of papers
1948	1	1995	4
1965	1	1996	9
1973	1	1997	2
1977	1[a]	1998	2
1978	1	1999	8
1980	3	2000	3
1981	3	2001	2
1982	2	2002	8
1986	3	2003	9
1987	1	2004	9
1988	3	2005	7
1989	2	2006	12
1991	2	2007	6
1992	3	2008	20
1993	3	2009	12
1994	2	2010	5[b]

[a] First paper reporting results of experiments designed to determine effects of non-starch polysaccharides on a starch.

[b] Until 30 June 2010.

When an aqueous suspension of starch granules is heated in the presence of a hydrocolloid (even in a RVA or equivalent instrument), pH can make a dramatic difference. Not only does pH affect the rheological behaviors of ionic hydrocolloids, acidic pH values, even those found in food products, will effect hydrolysis of both the starch, resulting in substantial losses in viscosity, and of the hydrocolloid, resulting in both average molecular weight decreases and structural changes. This aspect of starch–hydrocolloid interactions has not been investigated.

Table 3 lists both the starches and the hydrocolloids that have been used in various studies. (In a few cases, isolated AM, isolated AP, and wheat or rice flours were used in the investigations.) Twenty-one different native starches have been used in combination with 32 different hydrocolloids of a wide variety of structures, properties, and molecular sizes. Only a few studies have been done with chemically modified starches, although combinations of modified food starches with hydrocolloids are used by food processors. In the few cases in which modified food starches were used, they were commercial products and were not defined as to the degree of substitution, and/or crosslinking or any other treatment, such as thinning. All the non-starch polysaccharides are water-soluble ones except for a few mentions of water-insoluble pentosans. With one known exception, only peer-reviewed papers were used to construct Table 3.

There are two basic ways to prepare a starch–hydrocolloid composite paste or gel. (1) By substitution/replacement: a 100% starch paste/gel is compared to one made with $(100 - x)\%$ starch + $x\%$ hydrocolloid. Since the hydrocolloid replaces the starch, one that produces a solution of lower viscosity than that of the starch may reduce the viscosity produced by the mixture and vice versa when a hydrocolloid that produces a solution of higher viscosity than an equivalent amount of starch is used. (2) By addition: a 100% starch paste/gel is compared to one made with 100% starch + $x\%$ hydrocolloid. In this case, whether the hydrocolloid is one that produces a solution of lower viscosity than that from an equivalent amount of starch or one that produces a solution of higher viscosity, the hydrocolloid will add to the viscosity of the starch paste/gel. It is not always clear from experimental descriptions whether addition or replacement was used.

There are 3 ways to prepare composite pastes or gels using either the replacement or the addition protocol. (1) A hydrocolloid powder and a starch powder are mixed and added together to water, and the suspension is heated. (2) A solution of a hydrocolloid is prepared and a starch is added to it. The suspension is then heated. Different temperatures and shear regimes (up to jet cooking) have been used with methods 1 and 2. (3) A solution of the hydrocolloid is prepared. A starch paste is prepared separately, and the two solutions are mixed. All three preparations will give different results; see, for example, Mandala and Bayas (2004). Together, there are at least 6 different basic ways to prepare composite pastes and gels, and the method of preparation does affect the results (Section 2.6).

Different instruments and techniques have been used. Most often, a starch was added to a hydrocolloid solution and the suspension was heated in a Rapid Visco-Analyzer (RVA) (the specific program parameters used were not always specified), but other ways of cooking the starch have also been used. Different instruments for determining viscosity have been used, as have different mechanical spectrometers, different geometries, and different programs for oscillatory rheological analyses. Gels have been prepared under different conditions, and different instruments, geometries, and programs have been used for compression tests. Different techniques have been used to determine degrees of syneresis, freeze–thaw stability, and amounts of retrogradation. When determining gelatinization parameters by DSC, different water contents and rates of heating have been used. Finally, different techniques

Table 3
Summary of studies on the effects of hydrocolloids on starch pasting and paste and gel properties.

Reference	Starch(es)[a]	Hydrocolloid(s)[b]	Some findings and conclusions[b]
Crossland and Favor (1948)	Corn Waxy maize Wheat Potato Tapioca Wrinkled pea	Sodium alginate CMC	Hydrocolloids enhanced the observed first-stage swelling of wheat starch, i.e., produced two stage swelling/pasting curves for wheat starch.
Sandstedt and Abbott (1965)	Corn Waxy maize Wheat Potato	CMC	Used CMC solutions to obtain pasting curves.
Miller et al. (1973)	Wheat	CMC	Used CMC (8% of starch weight) to obtain pasting curves.
Kim and D'Appolonia (1977)	Wheat flour[c]	Wheat-flour pentosans	Water-soluble pentosans slowed rate of AP retrogradation in starch gels. This effect was more pronounced than was that with water-insoluble pentosans. Water-insoluble pentosans slowed rate of retrogradation of both AM and AP. Neither affected gelatinization or the basic mechanism of retrogradation. Both decreased rate of setback.
Bean and Yamazaki (1978)	Wheat	CMC	An earlier increase in viscosity is observed in the presence of CMC.
Hoek (1980)[d]		LBG	Synergism
Howling (1980)[d]		Gum arabic	Precipitation of starch occurred in the presence of a high concentration of gum arabic in a confection. Believed to be due to the non-availability of water.
Lii and Chen (1980)[d]		Hsin-tsao leaf gum	Hydrocolloid interacts strongly with non-ionic, non-waxy type starches and forms resilient gels.
Christianson et al. (1981)	Wheat	Guar gum Xanthan CMC	Earlier onset of viscosity increase. Substantial increase in peak viscosity.
Longton and LeGrys (1981)	Wheat	Wheat flour pentosans	Addition of pentosans did not change significantly the kinetics of aging (AP retrogradation) of 50% starch gels.
Sanderson (1981)			Addition of xanthan resulted in a reduction in the temperature at which the initial rapid increase in viscosity occurred.
Ghiasi, Varriano-Marston, and Hoseney (1982)	Wheat	CMC	CMC (30% of weight of starch) used so that the two stages of granule swelling/pasting could be seen.
Christianson (1982)	Corn Wheat	Guar gum Xanthan CMC	The presence of xanthan made corn starch gels much more rigid (so that their shape was retained), but reduced gel strength. Its effect in reducing retrogradation upon gel aging was much more pronounced in corn starch gels than in wheat starch gels and its effect was much greater than was that of guar gum, the gels containing which were only a little different than control gels. CMC had no effect on gel characteristics.
Kalichevsky et al. (1986)	Smooth-seeded pea amylose	Dextran	Amylose and dextran in solution were incompatible and segregated.
Descamps et al. (1986)	Corn Waxy maize Modified waxy maize Modified potato Modified tapioca	κ-, ι-, and λ-Type carrageenans	Only ι-type carrageenan showed synergism and that was strong and varied with the type of starch used.
Sajjan (1986)	Wheat	Guar gum LBG Xanthan	Hydrocolloids reduced the blue value of starch and inhibited syneresis of starch gels.
Sajjan and Rao (1987)	Wheat	Guar gum LBG Xanthan	Hydrocolloids increased pseudoplasticity of starch paste in the order xanthan > guar gum > LBG
Michniewicz and Jankiewicz (1988)	Wheat Rye	Water-soluble rye pentosans	Complexes were formed that involved mainly AP.
Yoshimura et al. (1988)	Corn	Konjac glucomannan (KG)	KG promoted retrogradation during its early stages and then retarded it slightly during long-term storage and reduced syneresis.
Tye (1988)	Corn Modified corn	κ- and ι-Type carrageenans	ι-Type carrageenan showed syngergism; κ-type did not.
Allonce et al. (1989)	Corn Wheat	Guar gum LBG	Both gums reduced the temperature at which the initial rapid increase in viscosity occurred and increased peak viscosity, with guar gum having the greatest effects.

Table 3 (*Continued*)

Reference	Starch(es)[a]	Hydrocolloid(s)[b]	Some findings and conclusions[b]
Kuhn, Elsner, and Gräber (1989)	Corn	LBG Xanthan Gum arabic Carrageenan	A concentration-dependent interaction between corn starch and xanthan as a result of cooking extrusion of mixtures was evident.
Gudmundsson et al. (1991)	Corn Waxy maize Amylomaize Wheat Potato	Water-soluble arabinoxylan from rye flour (WS-AX)	WS-AX had little effect on gelatinization. It did extend the phase transition temperature range and decreased enthalpy of gelatinization (ΔH) for the wheat starch, but had no effect on waxy maize starch. The effect that a hydrocolloid has on the gelatinization process is a function of the type of starch employed. WS-AX increased retrogradation. Effects on retrogradation were independent of the AM:AP ratio. Potato starch + WS-AX gels were softer initially, but more rigid, more elastic, and more cohesive after storage.
Alloncle and Doublier (1991)	Corn	Guar gum LBG Xanthan	Hydrocolloids produced a significant increase in viscosity. Viscoelastic properties of hot pastes and gels were less affected by galactomannans than by xanthan. Hydrocolloids made the gels less elastic. They also effected a more rapid initial increase in gel firmness, but a decrease in firmness upon extended storage. G' values of gels containing guar gum increased initially upon aging, but then reached a plateau, while G' values of gels containing LBG increased continuously without reaching a plateau. LBG increased G' values in conc. dependent manner.
Kohyama and Nishinari (1992)	Sweet potato	CMC(H^+) MC[e]	Little effect on temperature or enthalpy of gelatinization. MC prevented retrogradation.
Sudhakar et al. (1992)	Corn Waxy amaranth	CMC	Waxy amaranth starch–CMC systems had greater viscosities than did corn starch–CMC systems. CMC improved freeze–thaw and processing conditions stability.
Liu and Lelievre (1992)	Rice	Gellan LBG + gellan	Under small-strain oscillatory conditions, the presence of starch granules in either gel increased G', i.e., reinforced the gel matrix. Under large-deformation conditions, both native and gelatinized granules in the gel matrix caused the stress and strain at failure to decrease.
Ferrero et al. (1993a, 1993b), Ferrero et al. (1994)	Corn (Wheat flour)	Xanthan	Xanthan reduced AM retrogradation during freezing and thawing, but had no effect on AP retrogradation. Syneresis was reduced because of water-holding capacity of xanthan.
Cameron et al. (1993)	Wheat	HPC[e]	HPC had little or no effect on gelatinization of the starch. The presence of the starch prohibited precipitation of HPC.
Bahnassey and Breene (1994)	Corn Waxy maize Wheat Tapioca Amaranth	Guar gum LBG Xanthan Gellan Konjac flour	Increased peak viscosity, especially with LBG and especially with wheat and corn starches. Setback increased as a function of hydrocolloid concentration.
Eidam et al. (1995)	Corn	Guar gum LBG Xanthan CMC κ- and ι-Type carrageenans	Partial substitution of starch by a hydrocolloid sometimes resulted in lower G' values and higher G'' values than a starch alone paste at equal total concentration. Gelation was accelerated by the hydrocolloids in the order CMC > LBG > guar gum > κ-type carrageenan > xanthan, but final gel strength decreased. ι-Type carrageenan retarded gelation and increased gel strength. Formation of the normal starch polymer network was inhibited by xanthan.
Sudhakar et al. (1995a)	Corn	Guar gum Xanthan	The increase in pasting temperature effected by increases in sucrose concentration is counteracted by the apparent decrease in pasting temperature effected by the addition of a hydrocolloid.
Sudhakar, Singhal, and Kulkarni (1995b)	Corn	Xanthan	Addition of salts affected final viscosities and pasting temperatures.
Rayment et al. (1995)	Rice	Guar gum	Rice starch granules (ungelatinized) were used as particulate inclusions in guar gum solutions. As the amount of filler increased, the viscosity of the composite became more shear-rate dependent until the Newtonian plateau was eliminated.
Liehr and Kulicke (1996)	Corn Waxy maize Potato Waxy rice Modified waxy maize	LBG Tara gum ι-Type carrageenan	LBG and ι-type carrageenan produced the best freeze–thaw stability.

Table 3 (*Continued*)

Reference	Starch(es)[a]	Hydrocolloid(s)[b]	Some findings and conclusions[b]
Ferrero et al. (1996)	Corn	Guar gum LBG Xanthan CMC Alginate	All T_{gel} parameters, increased, especially T_c and the phase transition temperature range. The effect was greater for ionic hydrocolloids.
Fanta and Christianson (1996)	Corn Waxy maize Amylomaize Wheat Potato Tapioca	Guar gum LBG Xanthan CMC Carrageenan Konjac glucomannan (KG)	Hydrocolloids and starch were cooked together by jet cooking, then drum dried. Composites of corn starch with guar gum and KG did not form gels. Other composites produced soft gels. Properties of the composites depended both on the starch–hydrocolloid ratio and on the particular starch–hydrocolloid combination.
Kulicke et al. (1996)	Waxy rice	Guar gum LBG	With increasing amounts of galactomannan, the elasticity of the gel decreased, i.e., G'/G'' decreased, and the properties of the system became less frequency dependent. Viscoelastic behaviors changed continuously as the starch–hydrocolloid ratio changed.
Sudhakar et al. (1996a)	Corn Waxy amaranth	Guar gum LBG	Both hydrocolloids increased the peak viscosities, hot-paste viscosities, and final viscosities of pastes of both starches. Both hydrocolloids decreased the temperature of rapid viscosity increase of corn starch, but had little or no effect on this parameter for amaranth starch. Both hydrocolloids decreased syneresis and improved freeze–thaw stability.
Sudhakar et al. (1996b)	Corn	Guar gum	Both salts and the hydrocolloid made the pastes more pseudoplastic.
Abdulmola et al. (1996)	Waxy maize Crosslinked and stabilized waxy maize	Xanthan	(Under the ionic and temperature conditions used [mild, 80 °C], xanthan molecules were stabilized in a rigid, ordered conformation and the integrity of granules was maintained.) The presence of xanthan did not change granule swelling. Increased G' with increasing concentrations of starch.
Yoshimura et al. (1996)	Corn	Konjac glucomannan (KG)	Addition of the hydrocolloid increased T_o, T_p, and T_c but had no effect on ΔH. KG promoted corn starch retrogradation short term, but slightly retarded it long-term.
Sekine (1996)[d]		Xanthan	Starch granules heated in a solution of xanthan swelled, but did not disintegrate. Viscoelasticity of the resulting gels and the effects of starch conc. on the viscoelasticity varied with the type of starch.
Biliaderis et al. (1997)	Waxy maize Wheat	Guar gum Xanthan Wheat flour arabinoxylan (native and crosslinked) Oat β-glucan	Concentrated (40%, w/w of starch) gels were studied. Hydrocolloids did not affect peak gelatinization temperatures, but increased the phase-transition temperature range and ΔH. Hydrocolloids retarded G' development and network formation, but enhanced the crystallization rate in concentrated waxy maize starch gels. Hydrocolloids increased development of both short- and long-range order in concentrated waxy maize starch gels. The rheology of concentrated wheat starch gels was little affected by hydrocolloids.
Conde-Petit et al. (1997)	Potato	Xanthan	Studies of interactions between potato starch and complex-forming emulsifiers in the presence of xanthan, revealed that, while the incompatibility between starch molecules and xanthan molecules did not affect formation of starch–emulsifier complexes, it did hinder the gelation process induced by complexation of starch and emulsifier and reduced the firmness of the resulting gels. When dispersions of starch and xanthan molecules were mixed, an antagonistic effect was observed.
Liu and Eskin (1998)	Pea Acetylated pea	LBG Yellow mustard mucilage (YMM)	Onset of viscosity increase occurred at a lower temperature, but there was no change in T_{gel}. Final viscosities increased. YMM increased the pseudoplastic shear-thinning of pastes.
Mohammed et al. (1998)	Waxy maize (crosslinked and stabilized)	Agarose	A system of crosslinked and stabilized waxy maize starch granules trapped in an agarose gel matrix was used as a model for composite gels. It was concluded that composite moduli derived by the isostrain and isostress blending laws of Takayanagi, Harima, and Iwata (1963) were in good agreement with those determined experimentally. At a starch conc. of $\sim$2%, swollen granules were present within a continuous agarose (agaran) network. At starch conc. of 3–5%, a bicontinuous network formed. At a starch conc. of 6%, starch has become the dominant component.
Rojas et al. (1999)	(Wheat flour)	Guar gum Xanthan Sodium alginate LM-pectin κ-Type carrageenan HPMC[e]	Onset of viscosity increase at a lower temperature, especially with alginate. Alginate, xanthan, and HPMC increased the viscosity at 95 °C, while guar gum, LM-pectin, and κ-carrageenan decreased it. Each hydrocolloid affected pasting properties in a different way. T_o increased. ΔH decreased.

Table 3 (*Continued*)

Reference	Starch(es)[a]	Hydrocolloid(s)[b]	Some findings and conclusions[b]
Closs et al. (1999)	Waxy maize Amylopectin	Guar gum	Phase separation The preparation method influenced the rheological properties of composite pastes. Structural strength of pastes from blends was greater than that of individual components.
Tecante and Doublier (1999)	Crosslinked and stabilized (adipate-acetate) waxy maize	κ-Type carrageenan κ-Type carrageenan + K^+	Shear-thinning systems were produced. Pastes of this crosslinked and stabilized waxy maize starch prepared in the presence of a κ-type carrageenan (without K^+) exhibited greater hot-paste viscosities than starch alone pastes. However, such hot pastes (with or without K^+) did not exhibit an enhancement of viscoelastic properties. Upon cooling, the behavior of pastes of starch + κ-carrageenan (without K^+) changed considerably. Gels were predominantly solid-like and elastic. Granules were more swollen in the presence of hydrocolloid.
Yoshimura et al. (1999)	Corn	Tamarind xyloglucan	G' and G'' of composite gels were greater than the respective values for the controls and increased with increasing hydrocolloid conc. and storage time.
Kim and Wang (1999)	Waxy maize	Guar gum	T_p of melting of starch in the presence of a limited amount of water was increased when guar gum was added.
Chao and Lai (1999a, 1999b)[d]	Wheat	Hsian-tsao leaf gum	Dynamic rheological characterization indicated a "weak gel". Storage and loss moduli and hardness increased and tan δ decreased with increasing salt concentration up to a point. Salts facilitated formation of junction zones.
Lai et al. (1999)	Rice Modified potato and waxy maize	κ- and ι-Type carrageenans Agarose	When combinations of gelatinized rice starch and agarose (agaran) solutions were examined, the combinations (as compared to agarose solutions alone) exhibited a decrease in G'_{max}, initial rate of G' increase, and gel-melting temperature (T_m). In contrast, adding gelatinized starches to κ-carrageenan solutions increased T_{gel}, G'_{max}, the initial rate of G' increase, and T_m values. Composites containing ι-carrageenan behaved similarly to those containing κ-type carrageenan except for the temperature of gelation, which was slightly increased over that of the control (no starch) with κ-type carrageenan and substantially increased over the control when ι-type carrageenan was used. Gelation of κ-carrageenan was accelerated by adding starches. Gelation of ι-carrageenan may be either retarded by the addition of rigid starch granules or accelerated by addition of soluble starch molecules.
Sasaki et al. (2000b)	Wheat	Non-starch polysaccharide (NSP) of wheat flour	NSP addition increased peak viscosity and breakdown. Adding NSP to low-AM starch increased gel rigidity and varied with the ratio of water-insoluble to water-soluble NSP. Adding NSP to a wheat starch with a normal AM content reduced the amount of dissolved starch/AM, reducing G' of gels. Suggested that ratio of water-soluble NSP to water-insoluble NSP affects its water-binding capacity and physical properties, resulting in differing dynamic viscoelastic properties of composite gels.
Lo and Ramsden (2000)	Corn Wheat Rice	LBG Xanthan	Hydrocolloids increased freeze–thaw resistance of gels.
Lai and Chao (2000)	Wheat	Hsian-tsao leaf gum	The setting and melting temperatures of composite gels shifted to higher temperatures with increasing conc. of added salts. The appearance of two exothermic peaks in the cooling curve (DSC) suggested the formation of junction zones with different binding energies or rotational freedoms.
Liao and Lai (2001)[d]	Corn Wheat Tapioca	Decolorized hsian-tsao leaf gum	Composite gels with wheat starch had higher gel–sol–gel transition temperatures and enthalpies than those with corn or tapioca starches.
Ahmad and Williams (2001)	Sago	Guar gum LBG	Hydrocolloids had little effect on gelatinization temperature or enthalpy. Hydrocolloids improved freeze–thaw stability. Effects of hydrocolloids on rheology were dependent on the MW of the polysaccharide. For higher MW materials, G' increased, but G'' increased to a greater extent. There was a reduction in gel elasticity and phase separation.
Shi and BeMiller (2002)	Corn Waxy maize Wheat Potato Tapioca Rice Waxy rice	Guar gum Xanthan CMC HPMC[e] Sodium alginate ι- and κ-Type carrageenans	Shapes of viscosity vs. temperature curves as starch granules in hydrocolloid solutions were heated through their gelatinization and pasting temperatures were a function of specific hydrocolloid-starch combinations. Peak viscosity of potato starch was greatly decreased by the presence of negatively charged hydrocolloids (which altered the granule gelatinization/pasting process). T_{gel} was not affected.

Table 3 (*Continued*)

Reference	Starch(es)[a]	Hydrocolloid(s)[b]	Some findings and conclusions[b]
Mandala, Palogou, and Kostaropoulos (2002)	Acid-thinned potato	Xanthan	Hydrocolloid increased rigidity of gels stored at low temperatures.
Lai and Liao (2002a, 2002b)	Corn Wheat Tapioca	Decolorized hsian-tsao leaf gum	Hydrocolloid effected an increase in G'. Marked increase in viscosity and G' values upon cooling and eventually gelation. For the gels, $G' > G''$, and both moduli were almost frequency independent throughout the studied range. Therefore, the gels were elastic gels. Tapioca starch contributed more to the viscous property of composite gels, while wheat and corn starch contributed more to their elasticity.
Autio et al. (2002)	Amylomaize VII	κ-Type carrageenan (Ca^{2+})	Gelation of the hydrocolloid and the AM occurred at the same temp., but a two-stage melting behavior was observed. The two components separated into their own phases, and two reversible networks were formed, i.e., κ-carrageenan and AM gelled separately in their own phases. AM-rich domains in composite gels increased as the ratio of carrageenan to amylomaize VII increased. κ-Carrageenan neither accelerated nor retarded AM gel formation. The rigidity of composite gels was dependent on the starch–hydrocolloid ratio.
Tecante and Doublier (2002)	Potato amylose	κ-Type carrageenan	A particle-/granule-free system was studied. The two polysaccharides have slight incompatibility without phase separation in the liquid state. Gel properties depended on hydrocolloid concentration. At low conc., AM aggregation occurred rapidly and rigidity of the gels increased as a result of phase separation. At higher conc., a sharp decrease in G' as occurred, suggesting phase inversion with the hydrocolloid forming the continuous phase. At still higher conc., G' steadily increased (a predominance of carrageenan gel properties). G' increased rapidly with storage time at 25 °C, then reached plateau values, with the increased being as the conc. of hydrocolloid increased. Properties of these gels are also determined by the presence or absence of K^+.
Lee et al. (2002)	Sweet potato	Guar gum LBG Xanthan CMC Sodium alginate Gellan Gum arabic κ-Type carrageenan	Xanthan reduced paste viscosity; guar gum and alginate increased it. Freeze–thaw induced retrogradation was reduced by hydrocolloids, with sodium alginate being more effective than xanthan or guar gum.
Gonera and Cornillon (2002)	Corn Waxy maize Potato	Guar gum Xanthan	Guar gum did not affect the T_{gel} of corn starch. In contrast, xanthan decreased both T_1 and T_2 relaxation times.
Freitas et al. (2003)	Waxy maize Amylomaize	Galactoxyloglucan	Hydrocolloid addition increased both paste viscosity and thermal stability of the gel.
Tester and Sommerville (2003)	Corn Waxy maize Wheat	Guar gum Xanthan κ-Type carrageenan Pectin Gum arabic	When starch was heated in hydrocolloid solutions (gum arabic, 5%; pectin, 2%; guar gum, 0.5%; carrageenan, 0.2%; xanthan 0.2%) at high starch:hydrocolloid ratios and to temperatures around the T_{gel} of the starch, starch granule swelling and gelatinization was restricted and the extent of hydrolysis by α-amylase reduced. The effect on starch hydrolysis at equal conc. (0.2%) was κ-type carrageenan > xanthan > pectin > gum arabic > guar gum. Little effect of the hydrocolloids on T_o or T_p was found, but T_c increased, particularly for higher starch conc. Gelatinization enthalpy decreased.
Lai and Lii (2003)[d]		κ-Type carrageenan Agarose	Incorporation of starch (either soluble or insoluble) into agarose (agaran) gels reduced G' and increased $\tan\delta$. In contrast, starch-κ-carrageenan composite gels had increased G' values and reduced $\tan\delta$ values, i.e., more rigid gels were formed. Effects were a function of the type of starch.
Mali et al. (2003)	Yam	Guar gum Xanthan	Viscosity increased in the presence of hydrocolloids with guar gum giving a larger increase than did xanthan. Xanthan addition resulted in less syneresis upon refrigerated storage. G' values increased with storage time at 4 °C, but less so when xanthan was present.
Peressini et al. (2003)	Corn	MC[e]	Increased shear thinning
Krüger et al. (2003)	Corn	Guar gum Xanthan Sodium alginate	Granule swelling was reduced by presence of hydrocolloids. Hydrocolloids shifted T_{gel} to higher temperatures and reduced gelatinization rate constants.
Mandala and Palogou (2003)	Potato	Xanthan	Addition of xanthan accelerated gel formation, but not further structure building.
Liu et al. (2003)	Wheat Rice	Yellow mustard mucilage (YMM) YMM + LBG (9:1)	Addition of YMM increased both peak and final viscosities. The presence of YMM did not affect T_p, but increased ΔH (slightly) and the phase transition temperature range.

Table 3 (*Continued*)

Reference	Starch(es)[a]	Hydrocolloid(s)[b]	Some findings and conclusions[b]
			The presence of YMM increased hardness, adhesiveness, chewiness, and springiness of gels. YMM + LBG (9:1) increased viscosity, but decreased gel hardness. Addition of either YMM or YMM + LBG (9:1) lowered the temperature of initial rapid viscosity increase. The presence of YMM decreased swelling power and leaching of starch polymer molecules. Addition of YMM did not decrease retrogradation in wheat starch gels until after 15 days. It decreased syneresis in both wheat and rice starch gels in a concentration-dependent manner.
Lai et al. (2003)	Corn Wheat Tapioca	Hsin-tsao leaf gum	Firmness of composite gels increased with increasing hydrocolloid concentration to a point, then decreased with further concentration increases. The effectiveness of starches in forming gels (as determined by viscosity, firmness, and G') was wheat > corn > tapioca.
Symons and Brennan (2004)	Wheat	Barley β-glucan	Substitution of the starch with the hydrocolloid at a 1% level increased peak and final viscosities and breakdown, but substitution of 5% of the starch with the hydrocolloid reduced peak and final viscosities and breakdown. There was no change in T_o, T_p, or T_c, but there was a reduction in ΔH of gelatinization.
Mandala et al. (2004a)	Wheat	Xanthan	Sodium chloride addition resulted in a transparent upper zone, an intermediate turbid zone of AM aggregates, and an opaque lower zone of granules and/or AM aggregates. Xanthan dominates the overall viscoelastic behavior and accelerates AM aggregation.
Mandala and Bayas (2004)	Wheat	Xanthan	Different preparation conditions for the composite systems gave different results. Xanthan enhanced granule swelling at 75 °C. Xanthan increased AM leaching at temperatures <80 °C, but reduced it at higher temperatures. Xanthan induced folding of A-type granules. Composite systems exhibited shear-thinning behavior.
Brennan et al. (2004)	Waxy maize	Xanthan	Xanthan increased final viscosity and improved freeze–thaw stability.
Juszczak et al. (2004a)[d]	Rye	Guar gum LBG Gum arabic	Guar gum and LBG increased viscosities during pasting and increased shear stress during flow, with LBG producing the greatest increases. Gum arabic decreased the apparent viscosity during pasting.
Juszczak et al. (2004b)	Wheat	Guar gum LBG	Freeze-dried gels were studied. Addition of both hydrocolloids resulted in increases in apparent viscosity of shear stress during flow, with guar gum being more effective.
Korus et al. (2004)	Triticale	Guar gum Xanthan Gum arabic	Guar gum and xanthan increased peak viscosity and shear stress. Gum arabic reduced viscosity. Guar gum reduced thixotropy hysteresis.
Naruenartwongsakul et al. (2004)[d]	(Wheat flour)	MC (different molecular sizes)[e] HPMC	MW of MC had little effect on initial increase in viscosity. Increases in MW of MC increased peak viscosity and lowered peak temperature up to a point.
Munhoz et al. (2004)[d]	Amylomaize (71% AM)	Guar gum Xanthan	Both hydrocolloids reduced gel strength (120-h storage)
Funami et al. (2005a)	Wheat	Guar gum LBG Tara gum Konjac glucomannan	Peak viscosity increased in the order LBG > tara gum > guar gum. (Molecular size order guar gum > tara gum > LBG). Tan δ increased during short-term storage; therefore, retrogradation was retarded. Effect was related to molecular size and not to the amount of leached AM. Retrogradation rate constant decreased with addition of hydrocolloids, an effect that was related to molecular size. Galactomannans with fewer galactosyl units were more effective in reducing long-term retrogradation. Hydrocolloid addition had no effect on swollen granule size. Hydrocolloid addition reduced AM leaching.
Funami et al. (2005b)	Corn Waxy maize Amylomaize	Guar gum (different molecular sizes)	Increases in MW lowered the temperature of initial viscosity increase and increased peak viscosity. During storage at 4 °C, G' rose rapidly, then reached plateau values with the increases being reduced when guar gum of any MW was added.
Funami et al. (2005c)	Corn Waxy maize Amylomaize	Guar gum (different molecular sizes)	After cold storage for 24 h, tan δ of pastes containing guar gum increased; therefore, short-term retrogradation was retarded. Related to amount of AM leached from granules.

Table 3 (*Continued*)

Reference	Starch(es)[a]	Hydrocolloid(s)[b]	Some findings and conclusions[b]
			The higher the MW of guaran, the lower the amount of AM leached up to a point. Guar gum also retarded retrogradation during long-term storage, but even higher-MW guaran was required. Long-term retrogradation may be promoted by low-MW guaran.
Aguirre-Cruz et al. (2005)	Whole corn	Xanthan CMC	Corn kernels were nixtamalized. A hydrocolloid was added to the masa, which was then freeze-dried and powdered. The hydrocolloids increased the T_p of gelatinization independent of structure or conc. and decreased ΔH (conc. dependent). Composite gels showed reduced ΔH (of retrograded starch melting). Samples of composites gave higher peak, trough, and final viscosity values (dependent on hydrocolloid structure and concentration). Hydrocolloids decreased both G' and G'' of gels.
Chaisawang and Suphantharika (2005)	Cationic tapioca	Guar gum Xanthan	Both hydrocolloids increased peak and final viscosities. Xanthan delayed the rapid initial increase in viscosity and increased setback. Guar gum increased swelling power and the solubility index, while xanthan inhibited granule swelling and the leaching of AM. Both hydrocolloids promoted granule-granule associations, probably by bridging. Additions of hydrocolloids increased T_o (T_p and T_c were unchanged) and decreased ΔH and the phase transition temperature range. Both hydrocolloids increased G', with xanthan being the more effective. Xanthan addition decreased $\tan\delta$ more than did addition of guar gum. (Not surprisingly, an interaction between xanthan [anionic] and the cationic starch was proposed [author].)
Yoo et al. (2005)	Rice	Guar gum LBG	Composite pastes had shear-thinning behavior with yield stress. Addition of the hydrocolloids lowered the activation energy of apparent viscosity, with LBG being the more effective, indicating that hydrocolloid addition made the pastes less temperature dependent. G' and G'' of composite pastes increased with an increase in frequency, while complex viscosity (η^*) decreased. The magnitudes of G' and G'' increased with an increase in hydrocolloid conc. $\tan\delta$ values, which indicated that composite pastes were more elastic than viscous, increased with increases in hydrocolloid conc., i.e., the pastes became less elastic and more viscous with increases in hydrocolloid conc.
Temsiripong et al. (2005)	Tapioca	Tamarind seed xyloglucan	Gelatinization parameters were little changed by the presence of the hydrocolloid. Neither did the hydrocolloid have a significant influence on the apparent pasting temperature. Presence of the hydrocolloid promoted continued retrogradation upon long-term storage. The hydrocolloid lowered the gelation temperature of composite pastes in a conc.-dependent manner. Presence of the hydrocolloid suppressed the increase in paste viscosity during storage. Presence of the hydrocolloid increased G' and G'' in a conc.-dependent manner. $\tan\delta$ of composite pastes increased with increasing hydrocolloid content. G' of stored pastes was reduced by the presence of the hydrocolloid while G'' increased with increasing hydrocolloid conc. G' increased slightly with gel storage time, then reached plateau values in a conc.-dependent manner. The hydrocolloid provided shear stability during gel storage.
Du Toit et al. (2006)[d]	Carboxymethyl-starch	κ-Type carrageenan	Presence of the hydrocolloid increased gel compressibility, adhesiveness, and viscosity. When K^+ was present, dense, turbid, syneresing gels were produced.
Kim and Yoo (2006)	Rice (20.3% AM)	Xanthan	Composite systems had high shear-thinning flow behavior. Consistency index, apparent viscosities, G', G'', and gelation rate constants increased with increases in conc. of xanthan. G' increased rapidly during short-term storage, then reached plateau values.
Liu et al. (2006)	Pea Buckwheat	Yellow mustard mucilage (YMM)	Presence of YMM effected increases in peak viscosity, G', G'', and η^*, but decreased $\tan\delta$ and produced an earlier onset of viscosity increase. Presence of YMM increased hardness, adhesiveness, and chewiness of composite gels, but decreased resilience. YMM decreased the swelling of both starches. YMM decreased the solubility of buckwheat starch.
Song et al. (2006)	Rice	Guar gum Xanthan Gum arabic Gellan *Sphingomonas chungbukensis* DJ77	Apparent swelling power of starch was reduced at low hydrocolloid conc. and increased with increasing conc. due to less effective centrifugation in viscous media. All hydrocolloids, except that of *Sphingomonoas chungbukensis* DJ77, increased apparent viscosity, consistency index (K), and trough and final viscosities. All except guar gum reduced peak viscosity.

Table 3 (*Continued*)

Reference	Starch(es)[a]	Hydrocolloid(s)[b]	Some findings and conclusions[b]
			Retrogradation appeared not to be affected by hydrocolloids at low conc. because setback was unchanged.
Tischer et al. (2006)	Corn Waxy maize Amylomaize Yam	ι-Type carrageenan	Each starch-ι-carrageenan mixture produced a paste/gel with different characteristics. Synergism with yam starch resulted in increased thermal stability and softer yet more solid and more elastic gels. (Yam starch AP has a lower degree of branching and shorter ave. chain lengths, compared to maize starches).
Sae-kang and Suphantharika (2006)	Tapioca	Xanthan	Phase separation.
Khanna and Tester (2006)	Corn Waxy maize Amylomaize Potato	Konjac glucomannan (KG)	Enthalpy (ΔH) of gelatinization decreased and T_c increased as conc. of hydrocolloid increased. KG retarded long-term retrogradation and, as a result, increased the amount of digestible starch in stored systems.
Chaisawang and Suphantharika (2006)	Tapioca Tapioca phosphate	Guar gum Xanthan	Hydrocolloids increased peak, breakdown, and final viscosities of native tapioca starch, with the effect of guar gum being greater than that of xanthan. Guar gum had similar effects on phosphorylated tapioca starch, but xanthan had the opposite effect. Hydrocolloids increased T_o and T_p. Xanthan covered the surface of granules. In contrast, guaran formed sheet structures in the continuous phase. Hydrocolloids increased swelling power of starches at temperatures > 80 °C. Hydrocolloids increased G' but decreased tan δ and, therefore, increased the solid nature of pastes.
Rodríguez-Hernández et al. (2006)	Waxy maize	Deacylated gellan (Ca^{2+})	When waxy maize starch (3%) was heated in gellan solutions (0.005–0.05%) at 75 °C and 90 °C, the two pasting temperatures produced different rheological properties and paste/gel ultrastructures. At 75 °C, swollen and partially disrupted granules were observed. At 90 °C, granule remnants were the dominate features of pastes/gels. Below 0.02% conc. of gellan, swollen and disrupted granules were surrounded by compact, slightly interconnected networks of gellan molecules. Above 0.02% conc., gellan networks dominated the viscoelastic behavior because of more evenly distributed gellan networks on which swollen granules and granule fragments exerted a weakening effect.
Achayuthakan et al. (2006)	Waxy maize Crosslinked waxy maize Cold-water-swelling corn	Xanthan	Addition of xanthan affected granule size distributions of waxy maize and crosslinked waxy maize starch granules when they were heated in a hydrocolloid solution, but did not change the granule size of cold-water-swelling corn starch granules. Xanthan had a synergistic effect on the yield stress of waxy maize and cold-water-swelling corn starch pastes. It had an antagonistic effect on the yield stress of crosslinked waxy maize starch pastes.
Kim et al. (2006)	Rice (20.3% AM)	Guar gum LBG	G' and G'' values increased with increases in hydrocolloid conc. G' and G'' values in composite gels containing LBG were generally greater than those of gels containing guar gum. G' values of composite gels containing guar gum increased rapidly during early stages of storage at 4 °C, then reached a plateau. G' values of composite gels containing LBG increased steadily without reaching a plateau during 4 °C storage. Tan δ values decreased during gel aging, indicating that the gels became more elastic with aging. However, tan δ values of composite gels after aging were much greater than that of the starch-alone gel, indicating that they were more viscous than the starch-alone gel. Hydrocolloid molecules retarded retrogradation.
Brennan et al. (2006)	Wheat Wheat flour	Fenugreek gum	Addition of the hydrocolloid increased peak and final viscosities in a conc.-dependent manner. Addition of the hydrocolloid increased gel hardness, but hardness decreased as the content of hydrocolloid increased. Addition of the hydrocolloid increased G', G'', and tan δ in an conc.-dependent manner.
Huang et al. (2007)	Rice Waxy rice	κ-Type carrageenan Konjac glucomannan (KG) Gellan (high-acyl)	A low conc. of carrageenan and a high conc. of gellan produced gels with increased hardness and adhesiveness. Rice starches containing AM formed gels with the greatest hardness, adhesiveness, and chewiness. KG had no effect on any kind of rice starch.

Table 3 (*Continued*)

Reference	Starch(es)[a]	Hydrocolloid(s)[b]	Some findings and conclusions[b]
Hongsprabhas et al. (2007)	Tapioca Mungbean (Rice flour)	Sodium alginate Carrageenan	With mungbean starch, alginate increased the time required to reach peak viscosity, increased peak and final viscosities, and reduced setback. Alginate also affected the shear-thinning characteristics of mungbean starch, but not those of corn starch. Rice flour in the presence of either alginate or carrageenan produced the least setback and most shear-resistant pastes. Carrageenan induced aggregation of AM in rice flour pastes. All effects were dependent on the conc. of the hydrocolloid. In gelatinized mung bean and tapioca starch granules, protein had migrated towards the outer surface.
Ptaszek and Grzesik (2007)	Corn	Guar gum	The guar gum-corn starch system exhibited microphase separation (AFM). Change in temperature did not change proportions of two phases. Only their mechanical properties changed.
Lafargue et al. (2007)	Modified pea	κ-Type carrageenan + K^+	Addition of hydrocolloid (with K^+) produced a dramatic increase in viscosity and gel strength and resulted in higher gel setting and melting temperatures. G' values increased rapidly with time, then reached plateau values.
Satrapai and Suphantharika (2007)	Rice (30% AM)	β-Glucan	Addition of β-glucan (from spent brewer's yeast) gave significant increases in peak and final viscosities, breakdown, and setback. Addition of the hydrocolloid reduced the temperature of initial rapid viscosity increase. T_o, T_p, and T_c increased significantly, but ΔH decreased, as the conc. of the hydrocolloid increased. The phase transition temperature range was unchanged. T_c values were lower than the apparent pasting temperatures. The hydrocolloid reduced the rate of retrogradation during storage in a conc.-dependent manner. The retrogradation rate was greatest during the first week of storage. Magnitudes of G' and G'' increased with increases in hydrocolloid conc. G' and G'' of stored composite gels decreased with increasing hydrocolloid conc. Tan δ values increased with increasing hydrocolloid conc. Tan δ values decreased with storage time, indicating that the gels became more solid-like during storage. Therefore, the hydrocolloid promoted retrogradation initially, then retarded it during longer storage times.
Khondkar, Tester, Hudson, Karkalas, and Morrow (2007)	Waxy maize	LM-pectin	It was attempted to crosslink waxy maize starch molecules and LM-pectin molecules with STMP after pasting the waxy maize starch in a solution of LM-pectin. However, no evidence was presented of the extent of starch molecule–starch molecule crosslinking, pectin molecule–pectin molecule crosslinking, intramolecular reactions, or reactions that produced monoesters. Also, although it is stated that LM-pectin is an excellent gelling and thickening agent, there is no evidence that the required Ca^{2+} ions were present. Accordingly, this paper cannot be used in any analysis of starch–hydrocolloid interactions.
Kaur et al. (2008)	Corn Waxy maize Amylomaize Potato Crosslinked waxy maize	Cassia gum	(Cassia gum polysaccharide is a galactomannan with a Man–Gal ratio of 5:1.) Freeze-dried composite pastes had quite different appearances (SEM) than those of starch alone pastes. The former had a shrunken and tighter arrangement of granule remnants and a significant reduction in remnant sizes. For corn and waxy maize starches, in general, peak and final viscosities increased and breakdown decreased with increasing hydrocolloid conc.; setback trends were mixed for corn starch, but decreased with increasing hydrocolloid conc. for waxy maize starch. For potato starch, peak viscosity and breakdown decreased and final viscosity increased with increasing hydrocolloid conc.; setback increased significantly from 0% to 1% hydrocolloid conc., than decreased as the conc. was raised to 5%. High-AM corn starch did not cook out under RVA conditions. G' and G'' values for corn and waxy maize starch pastes (measured during temperature sweeps [heating]) increased upon replacement of 1% of the starch with the hydrocolloid, then decreased to values below that of the control paste at a replacement level of 5%. Again, high-AM corn starch did not paste in the RVA. G' and G'' values of potato starch pastes decreased with increasing hydrocolloid content. T_{gel} increased as the hydrocolloid conc. increased for corn and potato starches, but T_{gel} of waxy maize starch was unchanged. Tan δ values increased as the hydrocolloid conc. increased for corn, waxy maize, and potato starch gels. Addition of cassia gum led to greater G' and G'' values for all stored gels short-term, with the increase in G'' being greater than the increase in G'.

Table 3 (*Continued*)

Reference	Starch(es)[a]	Hydrocolloid(s)[b]	Some findings and conclusions[b]
Achayuthakan and Suphantharika (2008)	Waxy maize	Guar gum Xanthan	Hydrocolloids increased peak, breakdown, final, and setback viscosities. Pastes containing xanthan had higher G' values and lower tan δ values, indicating that they were more structured and more solid-like than the controls. Pastes containing guar gum were thixotropic. Those containing xanthan were less so and became antithixotropic at higher xanthan conc.
Song et al. (2008)	Corn Wheat	Guar gum Xanthan Gum arabic Gellan	Guar gum and gellan increased peak viscosities. Xanthan and gum arabic reduced them. Gel hardness was a function of specific starch–hydrocolloid combinations. Starch–gellan composite gels had dense and stable network structures.
Muadklay and Charoenrein (2008)	Tapioca	Guar gum LBG Xanthan Konjac glucomannan (KG)	Amount of syneresis after freezing and thawing was used as a measure of retrogradation. Effectiveness was in the order of xanthan, LBG, KG, guar gum, with the latter increasing the amount of syneresis.
Savary et al. (2008)	Modified waxy maize	κ-Type carrageenan LM-pectin	Even continuous phase was heterogeneous.
Tan et al. (2008)[d]		Soluble soybean polysaccharides	The presence of the polysaccharides slowed the aging process of starch gels.
Weber et al. (2008)[d]	Corn Waxy maize Amylomaize	Guar gum Xanthan	The presence of xanthan in corn and amylomaize starch gels improved the texture and minimized the effects of retrogradation. Xanthan also improved the texture of waxy maize starch gels, with lesser amounts being needed. The presence of guar gum had no effect on amylomaize starch gels. Gel strengths of corn and waxy maize starch gels containing guar gum varied.
Baranowska, Sikora, Kowalski, and Tomasik (2008)	Potato	Guar gum LBG Xanthan κ-Type carrageenan ι-Type carrageenan Gum arabic Gum karaya	Studied (by NMR) molecular dynamics of water molecules (conformation changes in hydrocolloids and gelatinization of starch granules) as a function of temperature.
Nagano et al. (2008)	Corn	Guar gum	Hydrocolloid had little effect on granule swelling behavior, but did inhibit leaching of starch molecules from granules as a function of conc. and/or MW of the guaran. The resulting gels had more viscous characteristics (increased tan δ).
Tran et al. (2008)	Tapioca Modified tapioca (6 types)	Guar gum Xanthan CMC HM-pectin LM-pectin Agar	Only xanthan and CMC significantly reduced freezable water.
Choi and Yoo (2008)	Sweet potato	Guar gum LBG	The presence of either galactomannan increased the consistency index (K), apparent viscosity, and Casson yield stress. The presence of the hydrocolloids increased G', G'', and η^* in a conc.-dependent manner. Increases in tan δ were small. Tan δ values of composite gels containing guar gum were much lower than those of composite gels containing LBG. Tan δ values of pastes containing LBG increased with increases in hydrocolloid conc., while increases in guar gum content decreased tan δ values. Therefore, it was concluded that tan δ of composite gels was strongly influenced by the structure of hydrocolloid and hydrocolloid conc., that the starch–guar gum composite gels were more elastic than the starch–LBG composite gels, and that the elastic nature of sweet potato starch gels can be reduced by addition of LBG.
Sikora et al. (2008)	Corn Potato Tapioca Oat	Xanthan	Viscosity was a function of AM content and MW of the starch polymers. No phase separation during setback. Addition of hydrocolloid reduced the shear stress of the potato starch gel. Shear stress of starch–hydrocolloid composite gels were only slightly dependent on shear rate. The presence of the hydrocolloid lowered the temperature of initial rapid viscosity increase for all 4 starches in a conc.-dependent manner. The presence of xanthan continuously increased the peak viscosity in a conc.-dependent manner for corn and tapioca starch pastes. The presence of a small amount of xanthan (9:1 starch–xanthan ratio) in potato starch pastes reduced the peak viscosity to <2% of that of the starch-alone paste, but the peak viscosity value steadily increased from that value as the xanthan content increased. For oat starch pastes, the peak viscosity first increased, then steadily decreased as the xanthan content increased. Presence of xanthan reduced initial shear stress in corn, tapioca, and oat starch pastes, but increased it in potato starch pastes.

Table 3 (*Continued*)

Reference	Starch(es)[a]	Hydrocolloid(s)[b]	Some findings and conclusions[b]
Kowalski, Sikora, Tomasik, and Krystyjan (2008)[d]	Corn Potato Tapioca Oat	Guar gum LBG Xanthan κ-Type carrageenan Gum arabic Gum karaya	Avoiding phase separation is crucial for formation of gels with high viscosity. Therefore, the hydrocolloid used with an anionic starch (potato) should be nonionic (a galactomannan), unless the hydrocolloid has a low MW and/or high polydispersity (gum karaya). Nonionic starches “combine” (reviewer’s quotation marks) with hydrocolloids regardless of whether they have an ionic change. Generally, gum arabic, xanthan, and carrageenan reduced viscosity. Presence of hydrocolloids reduced elasticity of composite gels.
Pongsawatmanit and Srijunthongsiri (2008)	Tapioca	Xanthan	Addition of xanthan increased pasting temperature and peak and final viscosities and decreased setback. Pastes were shear thinning. Addition of xanthan reduced syneresis in freeze–thaw stability tests.
Viturawong et al. (2008)	Rice (33.0% AM)	Xanthan	Addition of xanthan increased peak and final viscosities, breakdown, and setback either in the presence or absence of salts. The initial increase in viscosity was unaffected. T_{gel} was unaffected. All pastes were thixotropic. Addition of xanthan decreased hysteresis loop areas. Gel rigidity was reduced with addition of xanthan. Rheological properties of normal rice starch pastes and gels were changed to a much greater degree by the addition of xanthan than were the gelatinization properties of the starch and were a function of the MW of the xanthan.
Techawipharat et al. (2008)	Rice (11.9% AM) Waxy rice	CMC MC[e] HPMC[e] κ-, ί-, and λ-Type carrageenans	Peak and final viscosities were increased in the orders MC > CMC and λ-type > ί-type > κ-type carrageenans. Both were slightly decreased when HPMC was the added hydrocolloid. Tan δ values of normal rice starch pastes were increased upon addition of hydrocolloids, indicating that the pastes were less structured and less solid-like than the control pastes. Tan δ values for waxy rice starch–hydrocolloid composite pastes were unchanged. Consistency coefficient (K) and apparent viscosity values increased, following the same trend observed during pasting; the opposite trend was observed for flow behavior index values. The swelling power and solubility index values of normal rice starch increased significantly when hydrocolloids were added; the values for waxy rice were much less affected. Starch–hydrocolloid pastes exhibited a phase-separated microstructure in which AM- and AP-rich domains were dispersed in a hydrocolloid-rich continuous phase.
Chaudemanche and Budtova (2008)	Corn	κ-Type carrageenan	AM and κ-carrageenan molecules show only slight incompatibility, without any phase separation in the liquid state, but did separate into phases upon gelation. There is strong phase separation between κ-carrageenan and AP molecules in solution. Swollen granules and/or granule fragments have an affect on solution and gel properties. In such a complicated system, rheological responses depend on the state of the composite and its composition. In a semi-dilute regime, the viscosity and elasticity values for a 3% mixture at 60 °C were higher than the calculated additive values. At 20 °C, practically no increase in G' was found.
Funami et al. (2008a)	Corn (15%, w/v)	Fenugreek gum	The onset of viscosity increase was delayed, the peak viscosity increased, and the T_{gel} peak temperature increased with increasing conc. and/or MW of the hydrocolloid. The enthalpy of gelatinization did not change. No evidence of phase separation or that the hydrocolloid altered the gelatinization process. Long-term retrogradation was inhibited. Coil overlap values were determined.
Funami et al. (2008b)	Corn (5%, w/v)	Fenugreek gum	Addition of higher-MW fractions of the hydrocolloid increased peak viscosity and decreased the temperature of rapid viscosity increase. In gels that had been stored at 4 °C (short-term), the hydrocolloid increased tan δ, the effect of the added hydrocolloid being less for higher-MW fractions because of a decrease in the amount of AM leached in their presence. That structural hardening of the composite paste was reduced was also indicated by another rheological parameter. Presence of the hydrocolloid reduced G' with lower-MW fractions being more effective. Lower-MW fractions also increased syneresis of stored gels. Higher-MW fractions decreased syneresis. Coil overlap values were determined.

Table 3 (*Continued*)

Reference	Starch(es)[a]	Hydrocolloid(s)[b]	Some findings and conclusions[b]
Funami et al. (2008c)	Wheat	Gum arabic Soluble soybean polysaccharide	Both polysaccharides decreased peak viscosity, shifted the onset of viscosity increase to lower temperatures, decreased the leaching of AM, reduced the incidence of granule ghosts, increased the rate constants for short-term retrogradation, and decreased G'. Swollen granule diameters were unchanged.
Huang (2009)	Potato Yam Yam bean Sweet potato Taro	Guar gum LBG	Addition of hydrocolloids increased peak and final viscosities, breakdown, and setback. Changes in gelatinization enthalpies were mixed. Only small changes were found for swelling power values and solubilities.
Weber et al. (2009)	Corn Waxy maize Amylomaize (71% AM)	Guar gum Xanthan	With corn starch, the presence of guar gum increased peak and final viscosities, breakdown, and pasting temperature, generally in conc.-dependent manners. With corn starch, the presence of xanthan decreased peak and final viscosities, breakdown, and setback and increased gel stability, generally in conc.-dependent manners. With waxy maize starch, the presence of guar gum had no effect on breakdown or retrogradation but increased peak and final viscosities and peak time, generally in conc.-dependent manners. With waxy maize starch, the presence of xanthan had no effect on peak and final viscosities but increased peak time and the time of initial rapid viscosity increase.
Banchathanakij and Suphantharika (2009)	Rice (29% AM)	Curdlan Oat, barley, and yeast β-Glucans	All 4 β-glucans increased peak and final viscosities, breakdown, and setback. Only curdlan and oat β-glucan reduced the temperature of the initial rapid increased in viscosity. None of the hydrocolloids had an effect on T_o, T_p, or T_c of gelatinization, but they all decreased ΔH slightly. All 4 β-glucans reduced long-term retrogradation, with the soluble ones (oat and barley β-glucans) being more effective than the insoluble ones (curdlan and yeast β-glucan).
Bárcenas et al. (2009)	Wheat	Gum arabic HM-pectin HPMC[e]	Hydrocolloids had little effect on RVA parameters.
Wang et al. (2009)	Waxy maize	Xanthan	Addition of both xanthan and sucrose increased apparent viscosity, G', and G''. Xanthan increased the solid-like properties of gels, while sucrose decreased them. The presence of xanthan made gels more thermostable while the presence of sucrose made gels less thermostable.
Choi and Yoo (2009)	Sweet potato	Xanthan	The presence of xanthan increased the consistency index (K). The effect of temperature on the apparent viscosity of composite pastes was described by the Arrhenius equation; E_a increased with increasing conc. of xanthan. Composite pastes had high shear-thinning behavior, with yield stress and steady-shear properties being a function of the hydrocolloid conc. G', G'', and η^* values of composite gels increased and $\tan\delta$ values decreased as the conc. of xanthan increased, indicating that the hydrocolloid contributed to the elastic properties of the gels. G' of gels increased with time, then reached plateau values.
Wasserman et al. (2009)	Wheat	Guar gum Xanthan	Properties of wheat-starch pastes/gels depended on the structure and conc. of the hydrocolloid. Gels had a heterogeneous morphology. A 65:35 (w/w) mixture of guar gum and xanthan produced an optimum increase in rigidity and strength of composite gels.
Ptaszek et al. (2009)	Waxy maize	Guar gum Xanthan CMC	Composite systems were heterogeneous.
Ravindran and Matia-Merino (2009)	Corn	Fenugreek	The temperature of initial rapid viscosity increase was lowered by the presence of the hydrocolloid, but only at higher replacement levels. Peak viscosity time, setback, and final viscosity increased with increasing content of the hydrocolloid. Breakdown decreased with increasing content of the hydrocolloid. G'' and $\tan\delta$ increased as starch was replaced with hydrocolloid.
Chen et al. (2009)	Tapioca	Decolorized hsian-tsao leaf gum (dHG)	A synergistic interaction between dHG and tapioca starch that resulted in network formation and increased the apparent viscosity value, G' and G'' and decreased $\tan\delta$ as the conc. of dHG increased.
Kim et al. (2009)[d]	Waxy rice	Guar gum Xanthan	Addition of both hydrocolloids increased apparent viscosity (η_a, 100) and consistency index (K) values. The flow behavior index (n) values decreased with increases in conc. of xanthan.

Table 3 (*Continued*)

Reference	Starch(es)[a]	Hydrocolloid(s)[b]	Some findings and conclusions[b]
			G', G'', and η^* values increased with increases hydrocolloid conc. Addition of xanthan produced higher dynamic moduli and lower $\tan\delta$ values than did guar gum.
Kaur et al. (2009)[d]	Corn Asmylomaize	Cassia gum	Addition of cassia gum changed the morphology and reduced the size of granule remnants. Peak and final viscosity values increased. G' and G'' values increased.
Chantaro and Pongsawatmanit (2010)	Tapioca	Xanthan	Addition of sucrose increased T_{gel} and ΔH whether or not xanthan was present. Addition of sucrose increased peak and final viscosities, pasting temp., breakdown, and setback of composite pastes in a conc.-dependent manner. While setback values of composite pastes increased with the addition of sucrose, they decreased significantly with increasing xanthan conc. The presence of xanthan enhanced the thermal stability of steady shear viscosities of pastes with and without sucrose.
Vriesmann, Silveira, Petkowicz, and de (2010)	Cupuassu	Water-soluble pectic fraction	Evidence was presented that starch and the water-soluble pectin fraction formed gels cooperatively.
Sikora et al. (2010)	Potato	Guar gum LBG Xanthan κ- and λ-type carrageenans Gum arabic Gum karaya	All hydrocolloids, with the exception of gum arabic, decreased the temp. of initial rapid viscosity increase.
Liu, Bailey, and White (2010)	Oat flour	β-Glucan	The β-glucan content of oat flour made a considerable contribution to the pasting and paste properties of the flour, especially to the final viscosity.
Shanavas, Moorthy, Sajeev, Misra, and Sundazeem (2010)[d]	Tapioca	Konjac glucommannan	Incompatibility is suggested

[a] Corn = normal maize starch; most modified starches are not identified by the specific type of modification in this table.

[b] *Abbreviations used*: AFM = atomic force microscopy, AM = amylose, AP = amylopectin, CMC = carboxymethylcellulose (sodium salt), G' = elastic (storage) modulus, G'' = viscous (loss) modulus, HPC = hydroxypropylcellulose, HPMC = hydroxypropylmethylcellulose, LBG = locust bean (carob) gum, HM-pectin = high-methoxyl pectin, LM-pectin = low-methoxyl pectin, MC = methylcellulose, MW = molecular weight, NMR = nuclear magnetic resonance, SEM = scanning electron microscopy, STMP = sodium trimetaphosphate, $\tan\delta$ = loss tangent, T_c = conclusion temperature (of melting), T_{gel} = gelatinization temperature, T_o = onset temperature (of melting), T_p = peak temperature (of melting), T_1 = spin–lattice relaxation time, T_2 = spin–spin relaxation time, ΔH = enthalpy, η^* = dynamic (complex) viscosity.

[c] Wheat flour and rice flour are also included in this table although they are not pure starches.

[d] Abstract only available.

[e] HPMC and MC solutions increase in viscosity or gel and HPC precipitates upon heating as opposed to the behavior of other hydrocolloids.

have been used to determine starch granule swelling and solubilities.

In spite of this overwhelming variability in the way data was obtained, an analysis of it will be attempted. A synopsis of some results is given in Table 3. In a complete analysis of the available information, results of each starch–hydrocolloid combination under the different conditions of preparation and measurement would be evaluated and compared. Therefore, this review should serve as a guide for the location of papers that should be studied for details of the methods used, results obtained, thinking in analyzing the results, and comparison with previous works.

1.2. Characteristics of starch pastes and gels

The characteristics of starch granule swelling, breakdown, and retrogradation during processing and of retrogradation during storage in large part determine the textures and stabilities of high-moisture starch-based foods and are properties that are attempted to be modified and/or controlled by the addition of hydrocolloids. It is important, therefore, to understand the mechanisms of pasting and paste and gel formation of starches (in the absence of hydrocolloids). A cursory description follows. Three recent reviews of the structures of amylose and amylopectin molecules and their arrangement in starch granules have appeared (Jane, 2009; Perez, Baldwin, & Gallant, 2009; Pérez & Bertoft, 2010). The physical properties of starch granules and pastes and the nature of pastes and gels have also been reviewed (Morris, 1990; Parker & Ring, 2001).

Aspects of starch granules that pertain to this review are gelatinization, pasting, setback/retrogradation as hot pastes cool, and retrogradation in starch gels. During the past three decades, a greater and greater understanding of these processes has developed. In the majority of investigations of the properties of starch–hydrocolloid mixtures, the mixtures were heated together in excess water in a RVA or a Brabender Visco-Amylograph, this discussion will approach the characteristics of composites from the perspective of heating starch in excess water in one of these instruments.

The system resulting from the cooking of a starch in excess water is a complex system-even without an added hydrocolloid. Its properties are determined by the AM:AP ratio of the starch (Sasaki et al., 2000a), the fine structures and molecular weight distributions of the AM and AP molecules, the amount and nature of the protein and lipid present, the amount of available water, and the time, temperature, and shear of the cooking/heating process.

When starch granules are heated in excess water, they undergo a process called gelatinization (Ratnayake & Jackson, 2009; Sablani, 2009), which has been described as follows: when a mixture of starch granules in an excess of water is heated to temperatures above what is known as the initial gelatinization temperature, the granules swell as hydrogen bonds in amorphous regions are disrupted and water, which acts as a plasticizer, is absorbed. As the temperature increases, more hydration and more swelling occurs in amorphous regions, pulling apart crystallites, which regions also eventually undergo hydration and melt. This disruption of amorphous and crystalline structures results in an irreversible loss of crystalline, double-helical (Cooke & Gidley, 1992), lamellar, and orientational orders (Parker & Ring, 2001) and granule properties related to that order. Leaching of starch polymer molecules, especially amylose also occurs. The loss of crystalline order involves melting of the crystallites of amylopectin and is dependent on the crystalline polymorph present, its degree of perfection, and the amount of water present (Parker & Ring, 2001). Water is the plasticizer for starch granules. In fact, amorphous regions are plasticized by water into a rubbery state even at ambient temperature (Waigh, Gidley, Komanshek, & Donald, 2000). Loss of order in amorphous regions is a non-equilibrium, glass transition process (Slade & Levine, 1993).

Because gelatinization involves different kinds of loss-of-order transitions and because granules in a population from a single source are heterogeneous (see, e.g., Ji et al., 2004) with regards to many measurable characteristics including (it can be assumed) perfections of crystallites, gelatinization occurs over a temperature range. The gelatinization (phase-transition) temperature range not only varies from granule to granule within a population of granules from a single source, but also from botanical source to botanical source (see Fredriksson, Silverio, Andersson, Eliasson, & Åman, 1998; Ji et al., 2004). And as already mentioned (Section 1.1), the specific nature of a given kind of starch can vary with the cultivar and the growing location and conditions.

Starch granules swell during the process of gelatinization, and starch polymer molecules (primarily amylose molecules) leach from the swollen granules (Shi, Seib, & Lu, 1991), with leaching of the starch polymer molecules becoming easier and easier as the granules swell (Doublier, 1981; Zeleznak & Hoseney, 1987). Swollen granules from which considerable starch polymer molecules have leached are known as granule ghosts (Atkin, Abeysekera, & Robards, 1998).

The process of pasting follows gelatinization. The process of pasting occurs with continued heating of starch granules in the presence of excess water and involves continued granule swelling, additional leaching of dissolved starch polymer molecules, and disruption of the fragile, swollen granules. The result is a viscoelastic mass (called a paste) consisting of a continuous phase that is a molecular dispersion of once dissolved starch polymer molecules that now form a network and a discontinuous phase of swollen granules, granule ghosts, and granule fragments. In the RVA or Brabender instruments, pasting occurs with continued heating (normally to a 95 °C hold temperature) under the shear of the instrument after all order is lost in granules. During pasting, considerable continued granule swelling and leaching of starch polymer (primarily amylose) molecules occurs. A peak viscosity, primarily resulting from swollen granules, is reached. During the 95 °C hold, the fragile swollen granules disintegrate under the shear conditions of the instrument, and the viscosity decreases to a trough viscosity (a process called breakdown). The degree of fragmentation depends on the shear rate, shear time, and nature of the starch granules. At this point, what is known as a hot paste results.

In the work reported in this review, the distinction between a paste and a gel is not always clear. In starch science, a paste usually refers to the hot, freshly cooked system and a gel is the system after cooling and often subsequent storage. Both are viscoelastic materials. A hot paste is composed of a continuous phase of dissolved and partially dissolved starch polymer molecules (primarily amylose and low-molecular weight amylopectin molecules) and a discontinuous phase of swollen granules (from which different amounts of amylose and amylopectin molecules will have leached) and granule fragments (Alloncle & Doublier, 1991; Hermansson & Svegmark, 1996; Morris, 1990). Paste properties are determined by the sizes and natures (primarily rigidity) of the particles in the discontinuous phase (Rao, Okechukwu, Da Silva, & Oliveira, 1997; Rao & Tattiyakul, 1999), the composition and nature of the continuous phase (sizes and fine structures of the amylose and amylopectin molecules and their degrees of interaction), and interactions between the two phases. It has been proposed that the behaviors of pasted starch systems were determined primarily by the phase volume of swollen granules and their deformability (Evans & Lips, 1992). Indeed, it is known that the viscosity of starch pastes is substantially reduced as swollen starch granules disintegrate under shear (a process known as breakdown). However, Lii, Tsai, and Tseng (1996) and Tsai, Li, and Lii (1997) concluded that the major factors influencing the rheological properties of starch pastes and gels were both the rigidity of the swollen granules and the hot-water soluble components of the continuous phase. Within the continuous phase, there is phase separation between amylose and amylopectin molecules (Kalichevsky & Ring, 1987). The reasonably concentrated hot pastes produced in one of the instruments used to quantify pasting and paste properties are usually viscous, free-flowing fluids.

As the hot pastes, especially of amylose-containing starches, begin to cool, they become more elastic and develop distinct solid properties, i.e., gelation occurs. (Although the transition from a viscous fluid to an elastic gel can be determined by determination of the storage [elastic; G'] and the viscous [loss; G''] modulii, the literature often simply assumes that the hot, somewhat fluid system is a paste, i.e., a viscoelastic liquid, and the cooled, more solid-like system is a gel.) The transition from a viscous liquid to a gel, when determined by one of the instruments, is called setback; the molecular process that produces setback is known as retrogradation (Atwell, Hood, Lineback, Marston, & Zobel, 1988).

Retrogradation is a non-equilibrium, polymer crystallization process (Slade & Levine, 1987, 1991). At low AM concentrations, precipitation of AM due to retrogradation occurs; higher concentrations, which are more common, result in gel formation and are discussed here. The first (short-term) phase of retrogradation occurs as the paste cools and involves network formation (entanglements and/or junction zone formation) between amylose molecules (Doublier & Choplin, 1989; Eidam, Kulicke, Kuhn, & Stute, 1995; Ellis & Ring, 1985; Gidley, 1989; Silverio, Svensson, Eliasson, & Olofsson, 1996), forming an elastic gel. This short-term phase may last up to 48 h. Embedded within the network are granule ghosts and remnants (Keetels, van Vliet, & Walstra, 1996a, 1996b; Miles, Morris, Orford, & Ring, 1985; Ring, 1985), making the gel a filled gel, i.e., a network forming the continuous phase filled with dispersed particles (Zasypkin, Braudo, & Tolstoguzov, 1997). Some amylopectin entanglements may be involved, but primarily retrogradation of amylopectin is a much slower process that may proceed for several weeks (Ring et al., 1987; Silverio et al., 1996), depending on the storage temperature. In starches that do not contain amylose, amylopectin molecules can associate to form weak gels (Cameron, Durrani, & Donald, 1994; Durrani & Donald, 1995). The chain lengths affect the rate of retrogradation of amylopectin molecules, with longer chain lengths resulting in faster retrogradation rates (Kalichevsky, Orford, & Ring, 1990).

Because of the reduced energy in chain segments and whole molecules, phase separation probably increases as pastes cool, resulting in increased network formation and even particles of amylose in an amylopectin matrix (Jacobson, Obanni, & BeMiller, 1997). However, there is evidence that at least partial co-crystallization of AM and AP molecules of at least some starches can occur (Gomand, Lamberts, Visser, & Delcour, 2010; Miles et al., 1985).

Because both particles and solubilized starch molecules have roles in the behaviors of starch pastes and gels, the method of paste and gel preparation affects their properties.

In a food system, many other ingredients (e.g., sugar and other water-soluble solutes, salts, and surfactants/emulsifiers) influence the processes of gelatinization, pasting, breakdown, and retrogradation/setback. These are not covered here, but it should be mentioned that especially does AM complex with polar lipids, which complexes can either accelerate or retard gelatinization and/or retrogradation (Eliasson, 1998; Mira, Eliasson, & Persson, 2005), the primary effect most often being an inhibition of granule swelling and leaching of amylose. In addition to the nature of the starch, the starch concentration is important as it impacts the relative importance of the continuous and discontinuous phases of pastes and gels (Doublier, Llamas, & Le Meur, 1987; Ellis, Ring, & Whittam, 1989). Also affecting the rate of retrogradation/gelation is the water content during storage (Jang & Pyun, 1997; Liu & Thompson, 1998) and the storage temperature (Jang & Pyun, 1997; Kim, Kim, & Shin, 1997).

Starch pastes, in general, are strongly thixotropic and shear thinning (Nguyen, Jensen, & Kristensen, 1998). Even cooled starch gels are in metastable, non-equilibrium states (Biliaderis & Zawistowski, 1990; Slade & Levine, 1987) and, as a result, undergo further chain aggregation and partial crystallization upon storage (Morris, 1990). G' and G'' of normal corn and waxy maize starch dispersions increase to maximum values upon initial heating ($G' > G''$), then decrease with further heating (Hsu, Lu, & Huang, 2000; Kaur, Singh, Singh, & McCarthy, 2008), in agreement with the description of gelatinization and pasting under shear described above. Peak G' and G'' values decrease in the order potato starch > waxy maize starch > corn starch (Kaur et al., 2008). Both G' and G'' values increase upon cooling of hot pastes with the increases in G'' values being in the order potato starch ≫ corn starch > waxy maize starch. Changes in tan δ values are small. During short-time storage, G' and G'' values increase and tan δ values decrease, indicating that the gels become firmer.

The addition of a hydrocolloid to a starch paste or gel makes an already complex system even more complex. It can be assumed that cooked starch–hydrocolloid systems are systems of various particles originating from swollen starch granules suspended in mixed polymer solutions or polymer networks of varying rheological properties and that the contributions of the dispersed and continuous phases to the properties of the overall system vary with factors such as relative concentrations of starch and hydrocolloid, preparation conditions, and interactions between and/or compatibilities of the various polymer molecules present.

2. Results

2.1. Early results on the influence of hydrocolloids on starch pasting

Having hypothesized that use of a viscous medium would magnify small increases in granule swelling, Crossland and Favor (1948) did find that, when solutions of sodium alginate or CMC were used as the aqueous medium in which to determine Brabender ViscoAmylograph pasting curves, wheat starch showed two-stage swelling. This was in agreement with the large (A) granules having a lower pasting temperature than the small (B) granules (Sahlstrom, Baevre, & Brathen, 2003; Shinde, Nelson, & Huber, 2003). The same procedure was used by Sandstedt and Abbott (1965) and Miller, Derby, and Trimbo (1973).

2.2. Importance of specific combinations of a starch and a hydrocolloid and hydrocolloid concentration

Christianson, Hodge, Osborne, and Detroy (1981), Descamps, Langevin, and Combs (1986), Sajjan and Rao (1987), Alloncle and Doublier (1991), and Eidam et al. (1995) alluded to the fact that the properties of composite pastes/gels were a function of the specific starch–hydrocolloid combination and the ratio of the two components, a conclusion first stated clearly by Fanta and Christianson in 1996. The concept was then seconded by Autio, Vesterinen, and Stolt (2002), Song, Kim, and Shin (2008), and Chaudemanche and Budtova (2008). Shi and BeMiller (2002) added that viscosity vs. temperature profiles created as starches in solutions of hydrocolloids were heated through their gelatinization and pasting temperatures were also a function of specific starch–hydrocolloid combinations.

A nice case in point is the interaction of wheat starch with hsin-tsao leaf gum (native and decolorized) (Chao & Lai, 1999a, 1999b; Chen, Kuo, & Lai, 2009; Lai & Chao, 2000; Lai & Liao, 2002a, 2002b; Lai, Liu, & Lin, 2003; Liao & Lai, 2001; Lii & Chen, 1980). Hsin-tsao leaf gum will interact with any starch containing AM, but forms the strongest, most resilient gels with wheat starch (Liao & Lai, 2001); the same type of gel is not formed with other hydrocolloids. The combination is used, among other things, to make a gel called grass jelly. Pieces of grass jelly are consumed in a beverage.

Hongsprabhas, Israkarn, and Rattanawattanaprakit (2007) and Sikora, Kowalski, and Tomasik (2008) concluded, in addition, that effects of a hydrocolloid on a starch upon which it has an effect are dependent on the concentration of the hydrocolloid. Yoo, Kim, and Yoo (2005) and Wasserman et al. (2009) agreed. Temsiripong, Pongsawatmanit, Ikeda, and Nishinari (2005), Brennan et al. (2006), Satrapai and Suphantharika (2007), and Kaur et al. (2008) found that changes in hydrocolloid concentration affected several paste and gel properties (reported in other sections of this review).

2.3. Effects of the type of starch on the composite paste or gel

Many noticed that the properties of composite pastes and gels differed depending on the type of starch used, but special mention of the phenomenon was made by Christianson (1982), Gudmundsson, Eliasson, Bengtsson, and Åman (1991), Sudhakar, Singhal, and Kulkarni (1992), Sudhakar et al. (1996a), Cameron, Sansom, and Donald (1993), Bahnassey and Breene (1994), Sasaki, Yasui, and Matsuki (2000b), Liao and Lai (2001), Lai and Liao (2002a, 2002b), Lai and Lii (2003), Liu, Eskin, and Cui (2006), Tischer, Noseda, de Freitas, Sierakowski, and Duarte (2006), Hongsprabhas et al. (2007), and Sikora et al. (2008). Lai et al. (2003) reported that the effectiveness of starches in forming gels with hsin-tsao leaf gum was in the order wheat > corn > tapioca. (AM is required.) Sasaki et al. (2000b) and Techawipharat, Suphantharika, and BeMiller (2008) also found that the amount of AM in the starch made a difference in gel properties in the composite systems they used. However, Gudmundsson et al. (1991) reported that the effect of a hydrocolloid on retrogradation was independent of the amount of AM in the starch. Tischer et al. (2006) related gel properties to the structure of the AP in the starch. Shi and BeMiller (2002) found that negatively charged gums greatly restricted the granule swelling, gelatinization, and pasting processes of potato starch (negatively charged due to monostarch phosphate ester groups) and greatly reduced peak viscosity.

2.4. Effects of the type of hydrocolloid on the composite paste or gel

That different hydrocolloids would have different effects on the pasting and paste properties of a given starch is not surprising since they are so structurally (chemical structures, ionic charges, shapes, stiffness/flexibility, molecular weight ranges) diverse and exhibit a range of properties such as intrinsic viscosity (volumes swept out by individual molecules) and degrees of associations with other molecules of the same hydrocolloid and other molecules, including water molecules. Since the report of a difference in the effect of water-soluble and water-insoluble pentosans on retrogradation in wheat flour gels (Kim & D'Appolonia, 1977), there have been many reports of differences in effects of water-soluble polysaccharides (hydrocolloids) on pasting, paste, and gel properties of starches (Eidam et al., 1995; Fanta & Christianson, 1996; Ferrero, Martino, & Zaritzky, 1996; Kim, Lee, & Yoo, 2006; Rojas, Rosell, & Benedito de Barber, 1999; Sasaki et al., 2000b; Shi & BeMiller, 2002; Techawipharat et al., 2008; Yoo et al., 2005) with the general conclusion paralleling that of Rojas et al. (1999) that each hydrocolloid affected pasting and paste properties in a different way. Wasserman et al. (2009) concluded that properties of wheat starch pastes and gels depended on both the structure and the concentration of the hydrocolloid. Banchathanakij and Suphantharika (2009) reported that soluble beta-glucans were more effective than insoluble ones in retarding retrogradation.

Several have compared the effects of guar gum and locust bean gum (LBG), both galactomannans, but with different branching patterns (BeMiller, 2007) for obvious reasons. Alloncle, LeFebvre, Llamas, and Doublier (1989) found that guar gum had the greater effect on increasing the viscosity of corn[2] and wheat starch pastes, while Bahnassey and Breene (1994) reported the opposite. Juszczak, Witczak, Fortuna, and Banachowicz (2004) reported that LBG had the greater effect on increasing the viscosity of rye starch pastes during pasting, while Juszczak, Fortuna, Witczak, and Dymel (2004) reported the opposite with triticale starch pastes. Funami et al. (2005a) found that the effects on increasing peak viscosity were in the order LBG > tara gum > guar gum, which is inverse to the order of molecular size and the degree of branching. Muadklay and Charoenrein (2008) found that LBG was the more effective in reducing syneresis after freezing and thawing and concluded that it was the more effective at reducing retrogradation. Huang (2009) studied the effects of the two hydrocolloids on five starches and reported that changes in gelatinization enthalpies were mixed. Sajjan and Rao (1987) and Sudhakar et al. (1996a) attributed differences in the effects of guar gum and LBG on starches to guaran molecules being more extended and LBG polysaccharide molecules being more coiled, allowing the former to hydrogen bond to AM molecules. A more recent examination of the molecular structures of guaran and LBG resulted in the conclusion that guaran molecules are indeed more extended than are LBG molecules, which coil and form intermolecular hydrogen bonds (Morris et al., 2008), which would result in less interaction of LBG molecules with AM molecules.

The effects of guar gum and xanthan have also been frequently compared because both guaran and xanthan are high-MW polymers and both produce highly viscous solutions; however, the molecules of guaran are neutral while those of xanthan are anionic and molecules of guaran are flexible while those of xanthan are rather rigid. Christianson (1982) found that xanthan had a marked effect on gel rigidity (increased) and gel strength (decreased), while guar gum had only a small effect and CMC had essentially no effect. Alloncle and Doublier (1991) reported that the viscoelastic properties of corn starch pastes and gels were less affected by galactomannans than by xanthan. Mali et al. (2003), Chaisawang and Suphantharika (2006), and Weber, Clerici, Collares-Queiroz, and Chang (2009) found that guar gum increased viscosities more than did xanthan, while Lee, Baek, Cha, Park, and Lim (2002) reported that xanthan actually reduced paste viscosity. Chaisawang and Suphantharika (2005) found that xanthan increased G' of composite gels more than did guar gum.

Comparisons have also been made of the effects of the three types of carrageenans. Tye (1988) reported that iota-type carrageenan gave a synergistic effect while kappa-type did not. Eidam et al. (1995) found that κ-type carrageenan accelerated gelation of corn starch and decreased final gel strength, while ί-type carrageenan had opposite effects and that its effects were different from those of all other hydrocolloids. Techawipharat et al. (2008) found that peak and final viscosities increased in the order lambda-type > iota-type > kappa-type. Shi and BeMiller (2002) found that the presence of iota-type carrageenan had little effect on the viscosity of corn starch pastes and that neither type had much of an effect.

Eidam et al. (1995) reported that gelation was accelerated and gel strength decreased by hydrocolloids in the order CMC > LBG > guar gum > κ-type carrageenan > xanthan and that ί-type carrageenan had the opposite effect, i.e., retarded gelation and increased gel strength. Tester and Sommerville (2003) found that the effect on alpha-amylolysis in composite gels was in the order κ-type carrageenan > xanthan > pectin > gum arabic > guar gum. Muadklay and Charoenrein (2008) found that effectiveness in reducing syneresis following freezing and thawing was xanthan > LBG > konjac glucomannan > guar gum.

An aspect of the use of galactomannans in these studies that should be considered is that these gums/hydrocolloids are powdered endosperm of the respective seed and contain, in addition to the 73–87% polysaccharide (guaran in the case of guar gum), 3–6% protein and 1–4% insoluble fiber, both of which could influence behaviors of the starch with which it is used. However, from a practical point of view, use of the unpurified, i.e., commercial, hydrocolloid is appropriate.

When a kappa-type carrageenan was employed in a composite system containing K^+ ions, Ca^{2+} ions, or milk, even more complex gelling systems with different gel characteristics resulted (Therkelsen, 1993). In them, gel strength and other behaviors were dominated by the carrageenan gel system if the concentration of the hydrocolloid was high enough.

2.5. *Effects of hydrocolloid molecular size*

Funami et al. (2005b) reported that the temperature of the initial rapid viscosity increase decreased and peak viscosity increased as the average MW of guar gum fractions increased. Funami et al. (2005c) concluded that low-MW guar gum fractions promoted long-term retrogradation, but that high-MW fractions retarded it. Nagano, Tamaki, and Funami (2008) found that guar gum inhibited leaching of starch molecules from corn starch as a function of concentration and/or MW. In a comparison of the effects of guar gum, LBG, and tara gum, Funami et al. (2005a) found that the extent of peak viscosity increase and both short- and long-term retrogradation decrease followed the order of galactomannan molecular size (guar gum > tara gum > LBG) (but there are fine structural differences as well [reviewer's note]). Funami et al. (2008b) also examined the effects of another galactomannan, fenugreek gum, as a function of MW and found that higher-MW fractions increased peak viscosity and decreased the temperature of rapid viscosity increase, syneresis, and amylose leaching, while lower-MW fractions had a greater effect on increasing the loss tangent (tan δ).

Naruenartwongsakul, Chinnan, Bhumiratana, and Yoovidhya (2004) reported that the MW of methylcellulose (MC) had little effect on the initial rapid increase in viscosity, but that as the MW increased, peak viscosity increased and peak temperature decreased up to a point. Viturawong, Achayuthakan, and Suphantharika (2008) found that the effects of xanthan in increasing peak and final viscosities, breakdown, and setback and in decreasing gel rigidity became more pronounced as its MW increased.

2.6. *Effects of method of paste/gel preparation*

Closs, Conde-Petit, Roberts, Tolstoguzov, and Escher (1999) recognized that the preparation method influenced the rheologi-

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[2] In this review the term corn starch is used rather than normal maize starch.

cal properties of composite systems. This concept was confirmed by Lai, Huang, and Lii (1999), Mandala and Bayas (2004), and Rodríguez-Hernández, Durand, Garnier, Tecante, and Doublier (2006). The effects are significant.

2.7. Effects of hydrocolloids on the onset of rapid viscosity increase

A decrease in the time/temperature of the rapid viscosity increase of heated starch suspensions in hydrocolloid solutions (RVA or Brabender) for specific starch–hydrocolloid combinations was recognized early and has been erroneously attributed to a decrease in either gelatinization temperature or pasting temperature. Neither is true. However, in a paper as late as 2010, the initial temperature of rapid viscosity increase recorded with a Brabender Viscograph was called the onset temperature of gelatinization.

Kim and D'Appolonia (1977) first reported that neither water-soluble nor water-insoluble pentosans affected gelatinization of wheat starch. Liu and Eskin (1998) also reported that, although the onset of viscosity increase occurred at a lower temperature, there was no change in the gelatinization temperature, a finding confirmed by Shi and BeMiller (2002). Bean and Yamazaki (1978), Christianson et al. (1981), Alloncle et al. (1989), Sudhakar, Singhal, and Kulkarni (1995a), Sudhakar et al. (1996a), Rojas et al. (1999), Liu, Eskin, & Cui (2003), Liu et al. (2006), Satrapai and Suphantharika (2007), Funami et al. (2008b), Funami, Nakauma, et al. (2008), Ravindran and Matia-Merino (2009) (only at higher replacement levels), and Sikora, Tomasik, and Krystyjan (2010) found that addition of a hydrocolloid caused the rapid viscosity increase to occur at lower temperatures (as compared to the starch alone), but this was not always the case. Xanthan was reported to delay the rapid initial increase in viscosity in both native tapioca starch (Pongsawatmanit & Srijunthongsiri, 2008) and cationic tapioca starch (Chaisawang & Suphantharika, 2005) suspensions. Likewise, Funami et al. (2008a) reported that fenugreek gum delayed the onset of viscosity increase in heated corn starch suspensions. Kaur, Singh, Singh, and McCarthy (2009) found the same phenomenon when another galactomannan, cassia gum, was used. (It is possible that delays in the apparent pasting, i.e., increases in the apparent pasting temperature, could have been due to reduced heat transfer in the more viscous system, which would increase the lag between the recorded temperature and the temperature inside the canister [reviewer].) Viturawong et al. (2008) found that the addition of xanthan to rice starch suspensions had no effect on the onset of viscosity increase. Temsiripong et al. (2005) concluded that xyloglucan had little or no effect on either gelatinization or the apparent pasting temperature of tapioca starch. Banchathanakij and Suphantharika (2009), in comparing the effects of two soluble and two insoluble beta-glucans, found that one soluble and one insoluble beta-glucan reduced the temperature of initial rapid increase in viscosity, while the other two had no effect.

2.8. Effects of hydrocolloids on gelatinization of starch granules

Although it was found that, at least in most cases, hydrocolloids had little or no effect on gelatinization temperatures (Section 2.7) (see also Ahmad & Williams, 2001; Cameron et al., 1993; Gonera & Cornillon, 2002; Gudmundsson et al., 1991; Kohyama & Nishinari, 1992; Liu et al., 2003; Symons & Brennan, 2004; Techawipharat et al., 2008; Viturawong et al., 2008), changes have been reported. Ferrero et al. (1996) reported that all gelatinization parameters increased when a hydrocolloid was present, especially the conclusion temperature (T_c) and the phase transition temperature range with the effect being greater for anionic hydrocolloids. Yoshimura, Takaya, and Nishinari (1996) found that addition of a hydrocolloid increased the onset (T_o), peak (T_p), and conclusion (T_c) temperatures of gelatinization, but had no effect on the melting enthalpy (ΔH). Biliaderis, Arvanitoyannis, Izydorczyk, and Prokopowich (1997) reported that hydrocolloids did not affect T_p, but increased the phase-transition temperature range and ΔH. Rojas et al. (1999) found that T_o increased, but ΔH decreased. Kim and Wang (1999) found that a hydrocolloid increased T_p when a limited amount of water was present. Tester and Sommerville (2003) reported that T_c increased, ΔH decreased, and T_o and T_p were little changed. Krüger, Ferrero, and Zaritzky (2003) found that hydrocolloids increased T_{gel}. Aguirre-Cruz, Méndez-Montealvo, Solorza-Feria, and Bello-Pérez (2005) found that hydrocolloids increased T_p and decreased ΔH. According to Khanna and Tester (2006), the presence of a hydrocolloid decreased ΔH and increased T_c. Chaisawang and Suphantharika (2006) found that hydrocolloids increased T_o and T_p. Satrapai and Suphantharika (2007) found that a hydrocolloid increased T_o, T_p, and T_c significantly but decreased ΔH as the hydrocolloid conc. increased. In summary, all studies found an increase in T_c while T_o and T_p either increased or were essentially unchanged. In most cases, ΔH was reduced. Effects on the phase-transition temperature range were mixed.

2.9. Effects of hydrocolloids on paste viscosity and/or gel strength

A common result of starch–hydrocolloid combinations is an increase in paste viscosity or gel strength over that produced by the starch alone. Those who reported an increase in paste viscosity were Hoek (1980), Christianson et al. (1981), Descamps et al. (1986) and Tye (1988) (only iota-type carrageenan of the carrageenans), Alloncle and Doublier (1991), Bahnassey and Breene (1994), Sudhakar et al. (1996a), Rojas et al. (1999) (only certain hydrocolloids), Tecante and Doublier (1999), Sasaki et al. (2000b), Freitas, Gorin, Neves, and Sierakowski (2003), Mali et al. (2003), Liu et al. (2003), Brennan, Tan, Kuri, and Tudorica (2004), Juszczak, Witczak, et al. (2004), Korus, Juszczak, Witczak, and Achremowicz (2004), Funami et al. (2005a) (in reverse order of molecular size for galactomannans), Aguirre-Cruz et al. (2005), Chaisawang and Suphantharika (2005), Chaisawang and Suphantharika (2006), Liu et al. (2006), Song, Kwon, Choi, Kim, and Shin (2006), Brennan et al. (2006) (concentration-dependent), Hongsprabhas et al. (2007), Lafargue, Lourdin, and Doublier (2007), Satrapai and Suphantharika (2007), Achayuthakan and Suphantharika (2008), Sikora et al. (2008), Song, Kim, and Shin (2008) (certain hydrocolloids only), Pongsawatmanit and Srijunthongsiri (2008), Viturawong et al. (2008), Techawipharat et al. (2008), Funami, Nakauma, et al. (2008), Huang (2009), Wang et al. (2009), Chen et al. (2009), and Kaur et al. (2009). Ravindran and Matia-Merino (2009) found that peak viscosity time, setback, and final viscosity increased and breakdown decreased with increasing content of the hydrocolloid. Closs et al. (1999) reported that the structural strength of composite pastes was greater than that of individual components. Uniformly, gum arabic is reported to decrease paste viscosity (Funami, Nakauma, et al., 2008; Juszczak, Witczak, et al., 2004; Korus et al., 2004; Song et al., 2006, 2008) (but as mentioned, this may be the result of replacing starch with a hydrocolloid that produces less viscosity [reviewer]). Occasionally, xanthan was reported to decrease viscosity (Song et al., 2006, 2008), which may be a reflection of the procedure used to prepare the composite paste. Kaur et al. (2008) and Sikora et al. (2008) found that the effect of a hydrocolloid on a starch was a function of both the starch used and the conc. of the hydrocolloid. Bárcenas, De la O-Keller, and Rosell (2009) reported that gum arabic, high-methoxyl pectin, and hydroxypropylmethylcellulose had little effect on RVA parameters. Symons and Brennan (2004) found that substitution of a starch with a hydrocolloid at a low level (1%) increased viscosity and breakdown, while substitution at a higher level (5%) reduced viscosity and breakdown. Yoo et al. (2005) reported that the viscous nature of composite pastes increased with increases in hydrocolloid concentration, although pastes were more elastic than viscous overall.

2.10. Effects of hydrocolloids on granule swelling and starch polymer leaching

That granules became more swollen when heated in a hydrocolloid solution was reported by Tecante and Doublier (1999), Mandala and Bayas (2004), Chaisawang and Suphantharika (2005) (guar gum vs. xanthan), Chaisawang and Suphantharika (2006) (both guar gum and xanthan at 80 °C), and Techawipharat et al. (2008). Sekine (1996) reported that wheat starch granules heated in a solution of xanthan swelled but did not disintegrate. Tester and Sommerville (2003), Krüger et al. (2003), Liu et al. (2003, 2006), and Song et al. (2006) reported that granule swelling was reduced. Shi and BeMiller (2002) found a specific inhibition of potato starch granule swelling by anionic hydrocolloids, a phenomenon attributed to repelling forces between the phosphate groups in potato starch granules and the negative charges on the hydrocolloid molecules. Funami et al. (2005a), Funami, Nakauma, et al. (2008), Nagano et al. (2008), and Huang (2009) reported little if any change in swelling power.

Abdulmola, Hember, Richardson, and Morris (1996) first reported that xanthan maintained the integrity of waxy maize starch granules. (A similar finding was reported in the same year by Sekine (1996), but this reviewer was unable to determine the type of starch used.) Gonera and Cornillon (2002) found that xantan molecules became associated with the surface of granules. Chaisawang and Suphantharika (2006) also observed that, in contrast to guar gum, xanthan molecules coated starch granules. Inhibition of granule swelling, if it occurs, could be important because starch granules (swollen or unswollen) as particulate inclusions in hydrocolloid dispersions and gels changes their nature (Chaudemanche & Budtova, 2008; Rayment, Ross-Murphy, & Ellis, 1995), in fact, they reinforce the gel matrix (Liu & Lelievre, 1992). Swelling inhibition may be related to the reports that xanthan reduced peak viscosity (Song et al., 2006). However, it has also been reported that xanthan enhanced granule swelling at 75 °C and induced folding of A-type wheat starch granules (Mandala & Bayas, 2004).

Granule swelling is likely related to dissolution and leaching of starch polymer molecules. Liu et al. (2003) found that a hydrocolloid decreased the solubility of starch polymer molecules within swollen granules, while Techawipharat et al. (2008) reported a significant increase in solubility. Those that reported that hydrocolloid addition inhibited starch polymer (primarily amylose) leaching also included Funami et al. (2005a, 2008b), Funami, Nakauma, et al. (2008) and Nagano et al. (2008). Mandala and Bayas (2004) found that xanthan increased the leaching of amylose from wheat starch at temperatures <80 °C, but reduced it at higher temperatures. Funami et al. (2005c) found that guar gum reduced the leaching of amylose from corn starch, with higher-MW fractions being more effective.

2.11. Starch–hydrocolloid incompatibility

Thermodynamic incompatibility and phase separation has been proposed as a mechanism for the changes observed in composite pastes and gels over those of starch pastes and gels (Section 3.11). Kalichevsky, Orford, and Ring (1986) found that polymer molecules segregated in a composite solution of amylose and dextran. Others claiming direct or inferred evidence of phase separation were Alloncle and Doublier (1991), Conde-Petit, Pfirter, and Escher (1997), Closs et al. (1999), Ahmad and Williams (2001), Autio et al. (2002), Tecante and Doublier (2002) (in gels only), Mandala and Bayas (2004), Kim and Yoo (2006), Sae-kang and Suphantharika (2006), Ptaszek and Grzesik (2007), Techawipharat et al. (2008), and Chaudemanche and Budtova (2008) (strong phase separation between kappa-type carrageenan and corn amylopectin molecules in solution, but separation between kappa-type carrageenan and corn amylose molecules occurred only upon gelation), Wasserman et al. (2009), and Ptaszek et al. (2009). On the other hand, Sikora et al. (2008) and Funami et al. (2008a) found no evidence of phase separation. Lai et al. (1999) reported that gelation of kappa-type carrageenan was accelerated by the addition of a starch. Mohammed, Hember, Richardson, and Morris (1998), using waxy maize starch and agarose (agaran) found that, at a starch concentration of ∼2%, swollen granules were present within a continuous hydrocolloid network. At a starch concentration of 3–5%, a bicontinuous network formed; and at a starch concentration of 6%, starch became the dominant component.

2.12. Starch–hydrocolloid co-polymer network formation

Associated with the idea of a synergistic interaction between starch and hydrocolloid polymer molecules is the hypothesis of co-polymer network formation. As mentioned earlier, this concept is exemplified by the interaction of starch, especially wheat starch, with hsin-tsao leaf gum (Chao & Lai, 1999a, 1999b; Chen et al., 2009; Lai & Chao, 2000; Lai & Liao, 2002a, 2002b; Lai et al., 2003; Liao & Lai, 2001; Lii & Chen, 1980). Lai and Chao (2000) concluded that the appearance of two exothermic peaks in the DSC cooling curve suggested the formation of junction zones with different binding energies or rotational freedoms. A composite network was seconded by Chen et al. (2009). Other evidence for composite network formation is less direct. Rather, several concluded that whether a continuous network was formed from starch polymer molecules or from polymer molecules of a gel-forming hydrocolloid depended on the relative concentrations of the two and that swollen granules and granule fragments exert a weakening effect (Rodríguez-Hernández et al., 2006). Michniewicz and Jankiewicz (1988) concluded that complexes of starch polymer (primarily AP) molecules with water-soluble pentosans were formed (see also Sections 2.14 and 3.7).

2.13. Effects of hydrocolloids on retrogradation, setback, gelation, freeze–thaw stability, and syneresis

Related to the question of whether there is a synergistic interaction between starch polymer molecules and hydrocolloid polymer molecules (Section 2.12) is the degrees of setback, retrogradation, gel formation, freeze–thaw stability, and syneresis and dynamic viscoelastic behaviors (Section 2.14). These related behaviors are summarized here, but it is not easy to draw general conclusions because this is an example of different means of paste/gel preparation, different temperatures of storage, different measurement times, and different measurement techniques being employed. Kim and D'Appolonia (1977) reported that water-soluble pentosans slowed the rate of amylopectin retrogradation in wheat starch gels and that water-insoluble pentosans slowed the rate of retrogradation of both amylose and amylopectin in the same gels. Agreeing that hydrocolloids slowed or prevented retrogradation or gelation were Kohyama and Nishinari (1992), Funami et al. (2005a, 2005c), Kim et al. (2006), Tan, Li, Li, Dong, and Qin (2008), Weber, Queiroz, and Chang (2008), and Pongsawatmanit and Srijunthongsiri (2008). Liu et al. (2003) reported that a hydrocolloid did not decrease retrogradation in wheat starch gels until after 15 days. Chantaro and Pongsawatmanit (2010) found that setback of tapioca starch gels containing sucrose decreased significantly with increasing xanthan conc.

In contrast, Gudmundsson et al. (1991), Bahnassey and Breene (1994), Mandala, Michon, and Launay (2004a), Chaisawang and Suphantharika (2005), Kim and Yoo (2006), Viturawong et al. (2008), and Ravindran and Matia-Merino (2009) reported an increase in setback/starch polymer aggregation (early-stage retrogradation) upon addition of a hydrocolloid, while Longton and LeGrys (1981) and Song et al. (2006) concluded that hydrocolloids had no effect on setback/retrogradation. Michniewicz and Jankiewicz (1988) and Biliaderis et al. (1997) reported that hydrocolloids increased the retrogradation of amylopectin, while Ferrero, Martino, and Zaritzky (1993a, 1993b, 1994), found no effect of xanthan on retrogradation of corn and wheat starch amylopectins. Ferrero et al. (1993a, 1993b, 1994) (from the same study) reported a decrease in retrogradation of amylose, while Mandala and Bayas (2004) reported that xanthan increased retrogradation of wheat starch amylose. Eidam et al. (1995) reported that five hydrocolloids accelerated gelation of corn starch and decreased final gel strength, while ι-type carrageenan produced opposite effects. Hongsprabhas et al. (2007) also found that the effect of a hydrocolloid on retrogradation/gelation/setback was function of the specific starch–hydrocolloid combination. Temsiripong et al. (2005) concluded that the presence of xyloglucan lowered the gelation temperature of tapioca starch pastes and suppressed the usual increase in paste viscosity during storage, but not because of a reduction in retrogradation.

A possible explanation of those contradictions is found in the reports of Yoshimura, Takaya, and Nishinari (1988), Yoshimura et al. (1996), Alloncle and Doublier (1991), and Funami et al. (2008a), Funami, Nakauma, et al. (2008) who reported that the presence of hydrocolloids promoted short-term retrogradation (presumably due primarily to amylose-amylose aggregation) and retarded long-term retrogradation (presumably due primarily to amylopectin-amylopectin associations). Satrapai and Suphantharika (2007) agreed and added that the effects of the hydrocolloid were concentration dependent. Khanna and Tester (2006) also found that the presence of a hydrocolloid retarded long-term retrogradation.

The degree of instability of gels, i.e., the amount of syneresis during their storage or following, freeze–thaw cycles, has often been used as a measure of the extent of retrogradation. Those that found that hydrocolloids decreased syneresis of pastes/gels during long-term storage were Sajjan and Rao (1987), Yoshimura et al. (1988), Liu et al. (2003), and Muadklay and Charoenrein (2008). Those that found that hydrocolloids improved freeze–thaw stability (which is very poor for the pastes/gels of native starches) were Ferrero et al. (1993a, 1993b, 1994), Sudhakar et al. (1996a), Lo and Ramsden (2000), Ahmad and Williams (2001), Lee et al. (2002), Brennan et al. (2004), and Pongsawatmanit and Srijunthongsiri (2008). However, as pointed out earlier, syneresis may have been reduced because of the water-holding capacity of the hydrocolloid (Ferrero et al., 1993a, 1993b, 1994).

2.14. *Effects of hydrocolloids on dynamic moduli*

Most starch pastes and gels containing hydrocolloids not only generally exhibit higher viscosities, they also usually have increased dynamic moduli compared to pastes prepared without addition of a hydrocolloid. The increases in dynamic moduli are often not as dramatic as are the increases in viscosity, but they are more indicative of the processes occurring within the pastes and gels. When considering determinations of dynamic viscoelastic behaviors, it must be remembered that the nature of a starch gel changes with storage time, i.e., as it undergoes short-term and then long-term retrogradation, with temperature, and especially when using a gel-forming hydrocolloid, with the ratio of starch to hydrocolloid. Those that reported an increase in G' (an indicator of network formation, i.e., the elastic component of the sample) were Lai and Lii (2003), Chaisawang and Suphantharika (2006), and Achayuthakan and Suphantharika (2008). Yoo et al. (2005) reported an increase in both G' and G'' (with one exception – a low concentration of one hydrocolloid) in a concentration-dependent manner. Increases in G' and G'' (an indicator of the fluid nature of the composite) in a hydrocolloid concentration-dependent manner were also reported by Yoshimura, Takaya, and Nishinari (1999), Ahmad and Williams (2001), Temsiripong et al. (2005), Kim and Yoo (2006), Liu et al. (2006), Kim et al. (2006), Brennan et al. (2006), Satrapai and Suphantharika (2007), Choi and Yoo (2008, 2009), Wang et al. (2009), Kim, Lee, and Yoo (2009), and Kaur et al. (2009). Ravindran and Matia-Merino (2009) reported an increase in G''. Satrapai and Suphantharika (2007) reported that the magnitudes of G' and G'' increased with increases in hydrocolloid concentration in freshly prepared gels, then decreased with storage time, also in a concentration-dependent manner. Temsiripong et al. (2005) reported a decrease in G' in stored pastes. They concluded that the hydrocolloid provided shear stability during gel storage. Kaur et al. (2008) found that G' values for corn and waxy maize starch pastes first increased as starch was replaced with cassia gum, then decreased as the hydrocolloid content increased, while G' and G'' values for potato starch pastes decreased with increasing hydrocolloid conc. Eidam et al. (1995) reported decrease in G' and an increase in G'', while Chaisawang and Suphantharika (2005) reported increases in both G' and G''.

Because of these differences, the more important parameter may be G''/G' ($\tan\delta$, the loss factor), but even then different values have been reported. Eidam et al. (1995), Ahmad and Williams (2001), Funami et al. (2005a, 2005c), Yoo et al. (2005), Nagano et al. (2008), and Ravindran and Matia-Merino (2009) reported an increase in the value—an indication of a less rigid, more viscous, less structured material. To the contrary, Lai and Lii (2003), Chaisawang and Suphantharika (2005, 2006), Liu et al. (2006), Achayuthakan and Suphantharika (2008), Funami et al. (2008b), Funami, Nakauma, et al. (2008), Choi and Yoo (2009), and Kim et al. (2009) reported a decrease in $\tan\delta$—an indication of a more rigid, more solid-like material. Kim et al. (2006) found that $\tan\delta$ values decreased during aging of composite gels, indicating that the gels became more elastic, but that $\tan\delta$ values of the composite gels after aging were much greater than that of the starch-alone gel, indicating that the composite gels were more viscous than the starch-alone gel. Temsiripong et al. (2005) and Satrapai and Suphantharika (2007) found that $\tan\delta$ values increased with increasing hydrocolloid conc., but decreased with storage time. Juszczak, Witczak, et al. (2004) and Juszczak, Fortuna, et al. (2004) reported an increase in shear stress during flow, while Sikora et al. (2008) reported a decrease in this parameter. What these results taken together seem to indicate is that different paste and gel characteristics are obtained with different specific starch–hydrocolloid combinations, methods of gel preparation before measurement, and conditions during measurement. The interaction of starches with hsian-tsao leaf gum, which may be a special case of synergistic molecular interactions resulting in network formation and gelation, produces gels with increases in both G' and G'', with $G' > G''$, and a decrease in $\tan\delta$, indicating formation of a strong, but elastic, gel. Variables that present problems in interpreting these and other results were presented in Section 1.1.

The following reported shear-thinning of starch–hydrocolloid composite pastes: Peressini, Bravin, Lapasin, Rizzotti, and Sensidoni (2003), Kim and Yoo (2006), and Pongsawatmanit and Srijunthongsiri (2008). Sajjan and Rao (1987), Sudhakar, Singhal, and Kulkarni (1996b), Liu and Eskin (1998), and Mandala and Bayas (2004) reported that the shear-thinning behavior was the pseudoplastic type, while Alloncle et al. (1989), Achayuthakan and Suphantharika (2008), Hongsprabhas et al. (2007), and

Viturawong et al. (2008) reported that it was thixotropic behavior. Tecante and Doublier (1999) concluded that the shear thinning was "anti-thixotropic". Hongsprabhas et al. (2007) found that pastes containing granules or granule fragments exhibited rheopectic behavior.

Sikora et al. (2008) reported that the presence of xanthan reduced the initial shear stress in corn, tapioca, and oat starch pastes, but increased it in potato starch pastes.

2.15. *Effects of hydrocolloids on starch paste and gel textures*

The textures of starch–hydrocolloid composite pastes and gels are, of course, related to their viscoelastic characteristics reported in the previous section. In addition, Du Toit, Pillay, and Danckwerts (2006) reported that the presence of κ-type carrageenan increased gel compressibility, adhesivity, and viscosity. Liu et al. (2003, 2006) reported that the presence of yellow mustard mucilage increased gel hardness, adhesiveness, and chewiness; other effects on texture depended on the nature of the starch. Lafargue et al. (2007) reported that the presence of a kappa-type carrageenan and potassium ions increased gel strength and gel setting and melting temperatures. Wasserman et al. (2009) found that addition of a 65:35 (w/w) combination of guar gum and xanthan produced an optimum increase in rigidity and strength of wheat starch gels. Song et al. (2008) reported that gel hardness was determined by the specific starch–hydrocolloid combination. Sasaki et al. (2000b) also reported that different combinations resulted in gels with different dynamic viscoelastic properties, and Kulicke et al. (1996) concluded that viscoelastic behaviors of gels changed as the starch–hydrocolloid ratio changed. According to Ferrero et al. (1994), Krüger et al. (2003), Munhoz, Weber, and Chang (2004), and Viturawong et al. (2008) hardness/rigidity of cereal starch gels was reduced upon addition of xanthan. Munhoz et al. (2004) reported that guar gum had the same effect. Eidam et al. (1995) reported that most hydrocolloids accelerated gelation but reduced gel strength; to the contrary iota-type carrageenan retarded gelation and increased gel strength. (Gel strength could be related to the amount of leached amylose [reviewer].) Wang et al. (2009) reported that the presence of xanthan made starch gels more thermostable. Chantaro and Pongsawatmanit (2010) found that the presence of xanthan increased the thermostability of steady shear viscosities of tapioca starch gels.

3. Proposed mechanisms

Some of what are listed as proposed mechanisms in Table 4 are conclusions/hypotheses based on the authors' data and some are assumptions based on an earlier, published conclusion or hypothesis. (In constructing Table 4, the author largely used expressions of the original authors.) What Sections 2 and 3 together illustrate is that collecting data in this area is not as difficult as interpreting it.

3.1. *Increased viscosity due to increased work required for paste flow*

Crossland and Favor (1948) first proposed that viscosity increases resulting from addition of a hydrocolloid were due to an increase in the work required to move swollen starch granules past each other in the more viscous medium (as compared to water alone or water containing dissolved/leached starch polymer molecules). Hongsprabhas et al. (2007) modified this concept by suggesting that the increase in peak visocosity could arise just from the friction of stabilized swollen granules moving past each other. In contrast, Christianson et al. (1981) and Christianson (1982) suggested that an increase in viscosity of the continuous phase (due to the hydrocolloid) would result in an increase in shear force exerted on swollen granules which would bring about their breakdown and a decrease in viscosity. Satrapai and Suphantharika (2007) also suggested this possibility.

3.2. *Alterations in granule shape and/or swelling and leaching*

Bean and Yamazaki (1978) attributed a viscosity increase in a wheat starch paste containing CMC to the fact that the granules were more swollen. Rojas et al. (1999) and Song et al. (2006) also concluded that low concentrations of hydrocolloid increased granule swelling and thereby peak and trough viscosities. However, Alloncle et al. (1989) concluded that hydrocolloids did not affect granule swelling when used in the concentrations studied, and even more researchers concluded that granule swelling was restricted by the presence of a hydrocolloid (Achayuthakan & Suphantharika, 2008; Biliaderis et al., 1997; Funami et al., 2005a, 2008b; Temsiripong et al., 2005; Tester & Sommerville, 2003). Granules that are more swollen are susceptible to breakdown under heat and shear forces (Funami et al., 2005b).

Viscosity could increase due to reduced granule swelling (as it does with slightly chemically crosslinked granules) due to less granule disintegration/breakdown (Achayuthakan & Suphantharika, 2008). Funami et al. (2005a), Symons and Brennan (2004), Khanna and Tester (2006), and Satrapai and Suphantharika (2007) reasoned that reduced swelling might be due to a reduction in water molecules being available to the granules. Another effect which might move the viscosity in the opposite direction would be a reduction in the dissolution/leaching of amylose (Bahnassey & Breene, 1994; Biliaderis et al., 1997; Funami et al., 2005a, 2005b; Funami, Nakauma, et al., 2008; Hongsprabhas et al., 2007; Huang, Kennedy, Li, Xu, & Xie, 2007; Weber et al., 2009), leaching of low-molecular-weight amylopectin (Bahnassey & Breene, 1994), or leaching of starch polymer molecules in general (Funami et al., 2008b). Retention of amylose in starch granules was proposed to strengthen them (Aguirre-Cruz et al., 2005; Biliaderis et al., 1997; Conde-Petit et al., 1997; Lai et al., 2003) and reduce their disintegration. Christianson et al. (1981) and Christianson (1982) conjectured that the presence of hydrocolloid molecules increased starch paste viscosity due to increases in granule size (swelling) and changes in their shape during swelling, making the forces exerted on them much greater, resulting in more granule disintegration and greater dissolution of starch polymer molecules. Likewise, Sandstedt and Abbott (1965) determined that CMC altered the shape of corn and wheat starch granules during their swelling. Chaisawang and Suphantharika (2006) concluded that the characteristics of composite pastes are determined by at least three factors, one of which was the degree of granule swelling in the system. Closs et al. (1999) concluded that differences in granule swelling and disintegration are responsible, in part, for differences in the structural strengths and viscoelastic behaviors of composite systems. (See also Sections 3.3 and 3.5.)

3.3. *Changes in gelatinization of granules*

(These proposed mechanisms are related to those in Sections 3.2 and 3.5.) As already mentioned, several erroneously reported that hydrocolloid addition lowered the gelatinization temperatures of starches, mistaking the temperature of the observed rapid increase in viscosity with the gelatinization temperature. Liu and Eskin (1998) stated that the apparent lower pasting temperature is not due to a change in gelatinization parameters. This conclusion was seconded by Shi and BeMiller (2002) (Section 2.7). However, whether or not there is a change in the gelatinization process seems to be related to the amount of water in the system. Ahmad and Williams (2001), Tester and Sommerville (2003), and Khanna and

Table 4
Summary of proposed mechanisms.

Reference	Mechanism[a]
Crossland and Favor (1948)	Concluded that viscosity increases were not the result of a specific interaction between the starch and the hydrocolloid, but rather that the work required to move swollen granules past each other was magnified in more viscous media.
Sandstedt and Abbott (1965)	CMC altered the shape of corn and wheat starch granules during swelling.
Kim and D'Appolonia (1977)	Pentosans reduce retrogradation by reducing the availability of the starch polymer molecules for crystallization. Water-soluble pentosans had the greatest effect on AM and water-insoluble pentosans mainly influenced AP, thereby reducing the amounts of starch polymers available for retrogradation.
Bean and Yamazaki (1978)	Wheat starch granules swollen in the presence of CMC were larger.
Christianson et al. (1981)	Two explanations were offered: (1) earlier onset of viscosity increase was attributed to associations between solubilized (leached) AM molecules and hydrocolloid molecules during the second stage of wheat starch granule swelling. (2) The presence of hydrocolloid molecules increased paste viscosity due to increases in granule size and changes in their shape during swelling, making the forces exerted on them much greater which resulted in more granule disintegration and starch polymer molecule solubilization.
Christianson (1982)	The synergistic increase in paste viscosity effected by hydrocolloids might be the result of at least two effects: (1) interaction between leached AM and low-MW AP molecules and hydrocolloid molecules and (2) forces exerted on granules in the shear field are much larger than those encountered in starch–water suspensions of equal starch conc. due to the thickening effect of the hydrocolloid. Hydrocolloid molecules might absorb onto, extend into, and cover the surface of granules, restricting their swelling and the leaching of starch molecules from them. When wheat starch granules are heated in a hydrocolloid solution (as opposed to water) with shear, the changes in shape they undergo are different, again as a result of the increase in shear force in the more viscous medium. Xanthan and guar gum molecules form complexes with AM molecules.
Yoshimura et al. (1988)	It was concluded that konjac glucomannan did not interact synergistically with corn starch. Promotion of retrogradation of corn starch pastes/gels over short storage times was due to an increase in the effective concentration of starch effected by immobilization of water by the hydrocolloid.
Tye (1988)	The increase in viscosity upon cooling was due to the formation of "complexes" between carrageenan molecules and leached molecules of AM and low-MW AP.
Alloncle et al. (1989)	Hydrocolloids are excluded from granules. Therefore, their concentration in the continuous phase increases as granules take up water and swell and viscosity increases. Hydrocolloids do not affect granule swelling (at least not in the combinations studied). Amylose and galactomannan molecules are thermodynamically incompatible.
Gudmundsson et al. (1991)	Water-soluble arabinoxylan increases retrogradation by decreasing the amount of water available to the starch. Phase separation favors interactions between like molecules.
Alloncle and Doublier (1991)	Viscoelastic properties of pastes and gels are primarily a function of the volume occupied by swollen particles. Changes in viscoelastic behaviors can be ascribed to phase separation phenomena due to hydrodynamic incompatibility of dissimilar polysaccharides. Due to the increased viscosity of the continuous phase, phase separation between AM and AP molecules could not be completed, resulting in less AM in the gel network than in gels without added hydrocolloid and, therefore, long-term gel rigidity was reduced.
Liu and Lelievre (1992)	Weakening of a gellan or LBG + gellan gel by the presence of starch granules was probably caused by stress conditions which led to failure in the vicinity of the particles. At relatively high concentrations, gelatinized granules strengthened the composites, perhaps due to both adhesion between the dispersed phase and the continuous phase and depletion of water in the continuous phase. Phase separation of dissolved starch and hydrocolloid molecules.
Ferrero et al. (1993a, 1993b)	Amylose–hydrocolloid intermolecular associations compete with amylose–amylose associations, decreasing the probability of retrogradation.
Cameron et al. (1993)	A single layer of HPC coated wheat starch granules, reducing its effective conc. in solution.
Ferrero et al. (1994)	Xanthan associates with dissolved AM, but does not affect crystallization of AP.
Bahnassey and Breene (1994)	Viscosity increase was due to dissolution of AM and low-MW AP molecules and their association with hydrocolloids.
Eidam et al. (1995)	Effects of most hydrocolloids on corn starch are non-specific (for the most part) and a result of thermodynamic incompatibility between the hydrocolloid molecules and starch molecules. The increased viscosity due to hydrocolloid addition restricts the mobility of AM molecules and allows self-associations to occur. This process is also enhanced by phase separation due to thermodynamic incompatibilities that result in the AM molecules being close to each other, so initial gelation is accelerated. However, addition of hydrocolloids results in network defects that result in a weakening of the gel network and in the final gel being more viscous and less elastic than the starch-alone gel. In particular, xanthan inhibited formation of the normal starch polymer network. ί-Type carrageenan molecules, in contrast, interact with starch molecules, presumably AM, contributing to and reinforcing the three-dimensional network structure.
Liehr and Kulicke (1996)	Freeze–thaw stability of pastes/gels was improved by a combination of network crosslinking and an exclusion effect.
Ferrero et al. (1996)[b]	The fact that xanthan did not prevent retrogradation of AP was attributed to xanthan remaining outside granules while AP was inside them. The fact that all T_{gel} parameters increased as the conc. of hydrocolloid increased was attributed to a reduction in available water.
Kulicke et al. (1996)	Composite gels of galactomannans and waxy rice starch are composed of a mixed polymer network containing more permanent junction zones (starch molecules) and temporary entanglements (galactomannans) that contribute individually to the network structure and gel characteristics because galactomannan and starch polymer molecules are incompatible. Galactomannans weaken network structures due to a reduced number of segments of starch molecules capable of association.

Table 4 (*Continued*)

Reference	Mechanism[a]
Abdulmola et al. (1996)	The dominant effect of xanthan is the promotion of association of swollen native and modified waxy maize starch granules, possibly by a depletion flocculation mechanism, but bridging flocculation cannot be ruled out.
Yoshimura et al. (1996)	The effective starch conc. increased as a result of immobilizing water molecules.
Biliaderis et al. (1997)	In the case of concentrated (40%, w/w of starch) waxy maize starch (amylopectin) gels, added hydrocolloids interfere with the formation of intermolecular associations and reduce the connectivity of the network structure. Opposing mechanisms may be operating in concentrated wheat starch gels: (1) hydrocolloids may decrease granular swelling and retard the leaching of amylose, resulting in granule stiffening. (2) Hydrocolloid molecules in the continuous phase may reduce contacts between swollen granules and interrupt the amylose network.
Conde-Petit et al. (1997)	The high viscoelasticity of the starch–xanthan pastes/gels is a result of a reduced degree of starch granule disintegration. Xanthan neither interfered with the AM fraction nor induced aggregation of AM molecules. Incompatibilities exist between starch molecules and xanthan molecules that promote formation of microphase-separated domains where AM, AP, and xanthan molecules are mutually excluded. Phase separation favors interactions between like molecules, but this effect may be masked by starch–xanthan intermolecular interactions. Xanthan interfered with the gelation process resulting from complexation of AM with an emulsifier, weakening the structure and forming a phase-separated network. The rapid gelation caused by complexation of AM with an emulsifier reduces the extent of phase separation.
Liu and Eskin (1998)	The apparent lower pasting temperature was not due to a change in gelatinization properties. A stable complex between pea starch polymers and yellow mustard mucilage produced synergistic effects.
Mohammed et al. (1998)	Hydrocolloid promoted granule association via depletion flocculation.
Rojas et al. (1999)	The presence of a hydrocolloid increases the capacity of granules to swell.
Closs et al. (1999)	Granule swelling and granule disintegration, along with polymer degradation, result in systems of different structural strength and viscoelastic behaviors. Phase separation.
Tecante and Doublier (1999)	Two types of systems were produced from waxy maize starch adipate/acetate + κ-type carrageenan with and without K^+: (1) particles suspended in a polymer solution and (2) particles suspended in a network matrix (when K^+ was present). Composite gels contain various types of particles suspended in solutions of various rheological properties. The overall behavior of the system depends on the amounts and properties of each phase. A depletion flocculation mechanism may be involved.
Yoshimura et al. (1999)	The effective conc. of starch molecules in the continuous phase increases as a result of mutual exclusion of starch molecules and hydrocolloid molecules based on their thermodynamic incompatibility. There was no synergistic interaction resulting in network formation.
Chao and Lai (1999a, 1999b)	Wheat-starch + hsian-tsao leaf gum formed junction zones whose formation was facilitated by the presence of salts.
Lai et al. (1999)	Potential interactions between red algal polysaccharides and starches depend on the kind of starch (or modified starch), the specific hydrocolloid, and the method used to prepare the composites. Properties of agarose–starch composite gels are governed by interference of soluble starch polymers with gelation of the hydrocolloid. Properties of κ-carrageenan-containing composite gels are governed by the exclusion effect of swollen granules. There may be an association between κ-carrageenan molecules and soluble starch polymer molecules that results in an acceleration of hydrocolloid gelation.
Sasaki et al. (2000b)	Water-soluble polysaccharides may reduce amount of water available for starch gelatinization and prevent both dissolution and association of AM.
Ahmad and Williams (2001)	Hydrocolloid affects the gelatinization process by reducing the amount of available water. Phase separation in pastes. The rate of amylose molecule aggregation is increased by galactomannan molecules of high MW at high conc. The rapid rise in G' of gels with time and the development of a pseudoplateau region are attributed to the aggregation of AM molecules. Hydrocolloid decreases AM-AM and/or AM-AP associations during freezing.
Shi and BeMiller (2002)	Specific interactions between certain leached molecules, primarily AM, and certain hydrocolloids are responsible for viscosity increase before granule pasting. Repelling forces between charges on negatively charged gums and phosphate groups on potato starch inhibit granule pasting.
Mandala et al. (2002)	Xanthan formed phase-segmented domains that were concentrated around granule fragments and ghosts.
Lai and Liao (2002a)	Synergistic interaction between decolorized hsian-tsao leaf gum and starches is a function of the AM content of the starch.
Lai and Liao (2002b)	Starch polymer network formation is reinforced by polysaccharide.
Tecante and Doublier (2002)	Whether dissolved starch polymer molecules or hydrocolloid molecules form the continuous phase is determined by their relative concentrations. At conc. of κ-carrageenan <0.3%, a potato AM – κ-carrageenan system consists of a continuous phase formed by AM in which a solution of the hydrocolloid (or a macromolecular network of the hydrocolloid when K^+ is present) is dispersed. At conc. of 0.3–0.5%, AM is the dispersed phase and κ-carrageenan the continuous phase. At a conc. >0.5%, the phases remain the same, but the hydrocolloid has a greater influence on the rheological properties.
Gonera and Cornillon (2002)	Xanthan became associated with the external granule surface where it absorbed water from the surrounding environment and the granule and strengthened granules up to their breaking point.
Freitas et al. (2003)	The increase in viscosity and thermal stability of gels is due to intermolecular interactions, primarily between AM molecules and hydrocolloid molecules.

Table 4 (*Continued*)

Reference	Mechanism[a]
Tester and Sommerville (2003)	Hydrocolloids restrict swelling of starch granules around their T_{gel}. There is a direct relationship between the volume fraction of water and T_c. Gums moderate the gelatinization process by binding and immobilizing water molecules. There is even less water available after most granules have gelatinized, so T_c is elevated. The effect of hydrocolloids on the gelatinization process is reduced by reducing the volume fraction of water in the system.
Mali et al. (2003)	Network formed by hydrocolloid prevents alignment of AM molecules.
Peressini et al. (2003)	Entangled polymer chains in composite solutions and gels.
Krüger et al. (2003)	Reduced heating rates and water molecule diffusivities (as a result of increased viscosity) are likely responsible for the increased T_{gel}.
Liu et al. (2003)	Yellow mustard mucilage may form a strong entanglement with dissolved AM molecules or interact with granule ghosts (increasing viscosity). The hydrocolloid might increase the effective starch concentration by immobilizing water molecules, might have its concentration increased in the continuous phase around starch granules as they swell, or may form hydrogen bonds with the starch polymer molecules in swollen granules. Interaction of the hydrocolloid with starch polymer molecules may occur within granules, the result being inhibition of swelling and dissolution.
Lai et al. (2003)	Each polymer promotes self-association of the other, resulting in, not only phase separation, but also limited disintegration of gelatinized granules and the promotion of a network from solubilized AM.
Symons and Brennan (2004)	The reduction in viscosity at higher levels of substitution of the starch with a hydrocolloid is likely a result of a reduction of starch available for gelatinization, which in turn is a result of (a) less water being available to the starch granules and (b) a reduction in the concentration of starch in the pastes. Reduction in available water results in less granule swelling.
Mandala et al. (2004a, 2004b)	The main effect of starch in a wheat starch–xanthan system is to increase the effective conc. of xanthan by excluded volume phenomena.
Mandala and Bayas (2004)	No evidence of wheat starch–xanthan interaction in the continuous phase.
Funami et al. (2005a)	Possible inhibition of granule swelling as a result of less water being available for swelling. Galactomannan molecules interact with long, exterior chains of solubilized AP molecules, leading to an increase in paste viscosity, galactomannans with fewer galactosyl units being more effective. Galactomannans decrease amount of AM leached by increasing the viscosity of the continuous phase, but do not form a network that gels. Galactomannans increase the effective concentrations of AM and AM-like components in the continuous phase through a viscosity increase and an acceleration of short-term retrogradation. Hydrocolloids strengthen the gel network formed short-term which might impede further structural ordering, i.e., crystallization of AM or co-crystallization of AM and AP, upon long-term storage, with galactomannans with fewer galactosyl units being more effective.
Funami et al. (2005b)	In the presence of high-MW guaran, granules become less resistant to heat and mechanical shear. Guaran molecules interact with both AM and AP molecules. The interactions become greater with increasing MW of the guaran molecules up to a critical MW. Interactions between guaran molecules and AM molecules might be responsible for the earlier onset of viscosity increase, while interactions between guaran molecules and AP molecules with longer external chain lengths might be responsible for the increase in peak viscosity.
Funami et al. (2005c)	Mechanisms of and effects of AP chain length on short- and long-term retrogradation differ as does the affect of guaran MW. Inhibition of short-term retrogradation is due to a decrease in the amount of AM leached. There is a specific linear chain length of AM molecules that participates in interactions with guaran molecules.
Aguirre-Cruz et al. (2005)	The increase in T_p of gelatinization was attributed to intermolecular interactions producing more stable structures. Hydrocolloids prevent retrogradation to some degree. Hydrocolloids interfere with formation of the network structures of starch pastes/gels.
Yoo et al. (2005)	Guar gum showed a greater synergism with rice starch than did LBG because of its greater hydration capacity. Hydrocolloid molecules become concentrated in the continuous phase. The rheological behavior of composite pastes is a function of the characteristics of the starch, whose molecules form a network with permanent junction zones, and the characteristics of the hydrocolloids, whose molecules form temporary entanglements in the network.
Temsiripong et al. (2005)	The observed rheological stability when xyloglucan is incorporated into tapioca starch pastes is not due to a retardation or prevention of retrogradation. Granule starch swelling may be suppressed by the hydrocolloid. The hydrocolloid appeared to be concentrated in the continuous phase, dominating the liquid-like behavior of composite pastes and gels and inhibiting the formation of a network structure.
Kim and Yoo (2006)	The effect of xanthan on increasing the rate of gelation of rice starch appeared to be attributable to phase separation.
Liu et al. (2006)	The earlier onset of viscosity increase is due to hydrocolloid interaction with a small amount of leached AM, when such is present. Interactions of YMM molecules with leached AM, and perhaps AP, molecules also give rise to increased viscosity. The network structure of gels can be enhanced by the addition of a hydrocolloid, which could be due either to an association between the hydrocolloid and AP and/or AM or to an incompatibility that increases the effective concentrations of both starch and hydrocolloid polymer molecules.
Song et al. (2006)	Hydrocolloids at low conc. increased granule swelling and thereby peak and trough viscosities.
Khanna and Tester (2006)	Hydrocolloid may act as a physical barrier (through hydrogen bonding) that prevents AP retrogradation, restricts amylose–starch polymer contact, and contributes to continuous phase viscosity that affects polymer mobility. The presence of hydrocolloids reduces the volume fraction of water available for granule swelling and gelatinization.

Table 4 (*Continued*)

Reference	Mechanism[a]
Chaisawang and Suphantharika (2006)	Pasting and paste characteristics of starch–hydrocolloid mixtures are affected by at least 3 factors: (1) the characteristics of the hydrocolloid in the continuous phase, (2) granule swelling in the composite system, (3) any electrostatic interactions between starch granules and hydrocolloid molecules. Xanthan totally enveloped starch granules while guar gum did not, allowing the granules to paste freely.
Rodrı́guez-Hernández et al. (2006)	The rheological properties of waxy maize starch–gellan pastes/gels are determined by the hydrocolloid conc. (whether it forms a continuous network) and the temperature of cooking (the amounts of swollen granules and granule fragments present).
Achayuthakan et al. (2006)	In general, xanthan reduced the amount of inter-particle bonding with a concomitant increase in the contribution of the system's mixed polymer network.
Kim et al. (2006)	Phase separation due to thermodynamic incompatibility resulted in network structures of like polymers being favored over those between different polymers. The thickening effect of hydrocolloids restricts the mobility of AM molecules resulting in interactions between AM molecules occurring more easily and quickly. Acceleration of gelation may also be due to an increase in the effective conc. of starch polymer molecules in the continuous phase. Hydrocolloids retarded retrogradation in an AM-containing starch, but the hydrocolloid molecules do not interact with starch polymer molecules to form ordered structures.
Huang et al. (2007)	κ-Type carrageenan and high-acyl gellan were involved in forming a network with AM-containing rice starches. Pasting and paste characteristics of starch and flour suspensions are a function of the exclusion effects of swollen granules, maintenance of the rigidity of swollen granules, restriction of AM leaching, molecular incompatibilities, and aggregation of AM molecules.
Hongsprabhas et al. (2007)	Alginate and carrageenan, both anionic hydrocolloids, effected retention of AM with swollen granules and maintained the granular structure of amylose-rich, more rigid swollen granules or induced their aggregation in a conc.-dependent manner. The rate of viscosity increase and the increase in peak viscosity could arise from friction of the swollen granules. The differences in granule rigidity/deformability from starch to starch are likely due to the location of AM and its migration in granules during gelatinization and pasting. Concentration of granular protein in the granule envelope could help maintain its integrity and keep starch polymer molecules, including amylose molecules, inside granules, decreasing their swelling power and increasing their resistance to shear.
Ptaszek and Grzesik (2007)	Guar gum-corn starch system phase separated in a temperature-independent manner. Changes in temperature did change the mechanical properties of the microdomains.
Lafargue et al. (2007)	Greater viscosity and gel strengths were attributed to excluded volume effects between κ-type carrageenan and starch resulting in a increased conc. of the hydrocolloid in the network. When a stabilized (non-gelling) starch was used, it was proposed that the κ-carrageenan molecules excluded from the volume occupied by the much more concentrated modified starch molecules formed a finely structured, continuous-phase network filled and reinforced with a solution of modified starch molecules.
Satrapai and Suphantharika (2007)	The increase in peak viscosity was attributed to the hydrocolloid (β-glucan) forming a network which entrapped granules. The hydrocolloid reduced the availability of water for granule swelling. The increased viscosity could increase the shear forces exerted on the swollen granules, increasing breakdown. Associations between starch polymer molecules and hydrocolloid molecules could be responsible for increases in setback and final viscosity. An increase in T_{gel} was interpreted as being due to reduced heating rates and mobility of water molecules. The melting of starch crystallites in excess water precedes the first rise in viscosity. Acceleration of gel formation was attributed to an increase in the effective conc. of starch polymer molecules as a result of immobilization of water by the hydrocolloid molecules, the result being easier and faster local interactions between AM molecules. Hydrocolloid molecules bound water, reduced the mobility of the starch chains, and thereby retarded retrogradation long-term. The presence of hydrocolloid molecules was believed to reduce the number of "permanent crosslinks" (author) between AP molecules.
Kaur et al. (2008)	It was concluded that the decrease in viscosity breakdown of potato starch pastes upon addition of hydrocolloid might have been due to less granule swelling. The hydrocolloid might have reduced the number of starch polymer–starch polymer junction zones or the number of these junction zones could have been lower because of phase separation. The decrease in tan δ of gels upon cooling might have been due to retrogradation of leached starch molecules and interactions between starch polymer molecules remaining inside swollen granules, resulting in a reinforcement of the gel structure.
Achayuthakan and Suphantharika (2008)	Agreed that the volume of the aqueous phase accessible to the hydrocolloid was reduced due to granule swelling during pasting (Alloncle et al., 1989), that the resulting increase in viscosity (due to an increased conc. of hydrocolloid in the continuous phase) increased the shear forces exerted on the swollen granules, effecting a decrease in viscosity (breakdown) (Christianson et al., 1981), that xanthan was particularly effective in increasing peak viscosity due to its coating of granules (Gonera & Cornillon, 2002; Chaisawang & Suphantharika, 2006) which restricted granule swelling and disintegration and promoted granule-granule association, and that the increase in T_{gel} could be due to reduced heating rates and water diffusivities in the more viscous systems (Krüger et al., 2003).
Song et al. (2008)	Starch–gellan composite gels contain stable network structures.
Savary et al. (2008)	Gelling polysaccharides and crosslinked and stabilized waxy maize starch resulted in unevenly distributed close-packed swollen granules as the discontinuous phase and a polysaccharide network as the continuous phase, but some of the polysaccharide molecules were found inside swollen granules.
Tran et al. (2008)	Because of the linear decrease in freezable water as the hydrocolloid conc. increased, it was concluded that there was no interaction between the starches and the hydrocolloids.
Choi and Yoo (2008)	Modification of the dynamic rheological properties was due to a network structure in which interactions between molecules of the same type are favored over those between molecules of different types. Therefore, rheological behaviors of composite pastes and gels are determined by the characteristics of the starch, which forms "permanent" (author) junction zones in the network and the characteristics of the hydrocolloid, which forms temporary entanglements in the network.

Table 4 (*Continued*)

Reference	Mechanism[a]
Sikora et al. (2008)	Gelation of starch in composite pastes proceeds under conditions of water deficiency.
Techawipharat et al. (2008)	Starch–hydrocolloid pastes have a phase-separated microstructure in which starch-rich domains are dispersed in a hydrocolloid continuous phase.
Chaudemanche and Budtova (2008)	In the liquid state, properties are determined by the hydrocolloid (κ-carrageenan). An increase in the hydrocolloid concentration results from an excluded volume effect when swollen granules and/or granule fragments are present. They effect an increase in viscoelastic characteristics in the liquid state and a decrease in the gelled state.
Funami et al. (2008a)	Suggested that fenugreek gum of relatively large MW or conc. may be involved in molecular associations between AM molecules or AP molecules with long exterior chain lengths, either as leached molecules or associated with swollen starch granules. Lower-MW hydrocolloid molecules may result in reduced peak viscosity because of an inhibition of granule swelling and leaching of starch polymer molecules. Inhibition of long-term retrogradation is attributed to interactions between the hydrocolloid and AP. In stored gels, not only the volume fraction of swollen granules, which seems to be the most important factor, but also the ability of the hydrocolloid to bind water molecules required for starch polymer crystallization, should be considered. The results suggest that the effects of galactomannan chain length (MW) are greater than those of the galactose side units on the pasting and paste properties of the starch, while the opposite is true for long-term retrogradation.
Funami et al. (2008b)	Rheological changes may be due to polymer molecule incompatibility, i.e., phase separation that increases the effective concentration of AM in the continuous phase, although there was not direct evidence for this.
Funami et al. (2008c)	Composite systems are less ordered (as compared to the starch-only system). Hydrocolloids inhibit leaching of amylose molecules without affecting granule swelling. Molecular associations between hydrocolloid molecules and leached AP molecules, especially those with long external chains, not only effect a viscosity increase, but may also be responsible for the reduction in leaching of AM molecules (rather than phase separation). Some hydrocolloids promote short-term retrogradation (where amylose gelation predominates) without any molecular associations that contribute to structural ordering. An increase in gel syneresis effected by low-MW fractions of the hydrocolloid may be due to promotion of AM crystallization.
Weber et al. (2009)	The presence of xanthan appeared to delay swelling of both corn and waxy maize starch granules. The delay in swelling of corn starch granules meant less leaching of AM and a significant reduction in retrogradation/setback.
Choi and Yoo (2009)	The initial rapid increase in G' with gel aging was interpreted as being due to an increase in the effective conc. of AM in the continuous phase.
Ravindran and Matia-Merino (2009)	The hydrocolloid promoted early-stage retrogradation, possibly due to intermolecular associations between AM and the hydrocolloid or to an increase in AM content and/or phase separation in the continuous phase that favors AM network formation. Dynamic rheological properties are also consistent with phase separation or intermolecular interactions.

[a] For abbreviations, see Table 3 (footnote b). Also, conc. = concentration(s).

[b] Only abstract available to the reviewer.

Tester (2006) concluded that hydrocolloids modify the gelatinization process by reducing the volume fraction of water in the system. Tester and Sommerville (2003) further point out that there is even less and less available water as granules gelatinize, which results in an elevated conclusion temperature (T_c). However, Aguirre-Cruz et al. (2005) attributed the increase in peak temperature of gelatinization to intermolecular interactions that produced more stable structures, and Krüger et al. (2003), Satrapai and Suphantharika (2007), Achayuthakan and Suphantharika (2008) suggested that the apparent increase in gelatinization temperature might be due to reduced heating rates and water diffusivities in the more viscous system. Satrapai and Suphantharika (2007) further observed that the melting of starch crystallites in excess water preceded the actual pasting temperature (which is what would be expected for all starches with or without added hydrocolloid [reviewer]).

3.4. Synergistic interactions between hydrocolloid and starch polymer molecules

(These proposed mechanisms are related to those in Sections 3.3, 3.7 and 3.10.) (The term synergism used by many conducting the reported investigations refers generally to viscosity increases greater than what would be obtained by adding the viscosity of the hydrocolloid solution and/or to increases in dynamic moduli compared to that of the starch paste alone.) Christianson et al. (1981) and Christianson (1982) proposed that the observed earlier onset of viscosity increase was due to associations between solubilized/leached (primarily amylose) molecules and hydrocolloid molecules that occurred before granule pasting. Evidence for this phenomenon (largely on the basis of rheological/viscoelastic data) was claimed by Sajjan and Rao (1987), Alloncle et al. (1989), Alloncle and Doublier (1991), Bahnassey and Breene (1994), Eidam et al. (1995), Abdulmola et al. (1996), Liu and Eskin (1998), Shi and BeMiller (2002), Freitas et al. (2003), Liu et al. (2006), and Funami et al. (2005b, 2008b). Satrapai and Suphantharika (2007) suggested that associations between starch and hydrocolloid molecules could be responsible for increases in final viscosities. Those that concluded that there was not an interaction between starch and hydrocolloid molecules were Crossland and Favor (1948), Yoshimura et al. (1988), and Tran, Thitipraphunkul, Piyachomkwan, and Sriroth (2008). The differences are probably an indication that only specific hydrocolloid–starch polymer molecules form complexes.

Others went even further, concluding that hydrocolloid–starch polymer (especially amylose) interactions resulted in network formation and/or crosslinking. They include Liehr and Kulicke (1996), Kulicke et al. (1996), Chao and Lai (1999a, 1999b), Lai et al. (1999), Lai and Liao (2002b), Freitas et al. (2003), Funami et al. (2005a), Liu et al. (2006), Achayuthakan, Suphantharika, and Rao (2006), Huang et al. (2007), and Song et al. (2008). Liu et al. (2003) suggested that polymer entanglements might be the cause of the viscosity increase. Funami et al. (2005a, 2005b, 2005c, 2008b) concluded that there is a specific linear chain length of amylose and amylopectin molecules that interacts with guaran molecules and an optimum molecular weight of guaran molecules and degree of galactomannan branching for such interactions. (Increases in setback/retrogradation may be due more and more interactions, i.e., network formation, as the paste cools and molecules have less energy. On the other hand, breakdown may be less affected since interactions are less likely in hot systems [reviewer].) In contrast, Peressini et al. (2003) concluded that the properties of pastes and gels containing hydrocolloids was only due to entangled polymer chains; Yoshimura et al. (1999) and Mandala and Bayas (2004) concluded that there was no synergistic interaction resulting in network formation. Eidam et al. (1995) concluded that most hydrocolloid molecules effect network defects that weaken the gel and make in more viscous and less elastic compared to the starch gel alone, but that iota-type carrageenan molecules interact with leached starch molecules and both contribute to and reinforce the network structure–once again indicating that different combinations result in different behaviors. Biliaderis et al. (1997) also concluded that hydrocolloids interfere with the formation of intermolecular associations and reduce the connectivity of network structures. Yoo et al. (2005) agreed that the presence of hydrocolloid molecules disrupts the starch polymer network.

Interactions between hydrocolloid and amylose molecules that compete with amylose–amylose intermolecular interactions have been proposed as the reason for reduced retrogradation (Aguirre-Cruz et al., 2005; Ferrero et al., 1993a, 1993b, 1994). Funami et al. (2008a) suggest that intermolecular associations may be responsible for reduced leaching of amylose molecules, which would mean less retrogradation. Ferrero et al. (1994) concluded that xanthan does not affect retrogradation of amylopectin, then (Ferrero et al., 1996) attributed this phenomenon to amylopectin remaining inside swollen granules (while xanthan was outside). However, Khanna and Tester (2006) suggest that reduction in retrogradation of amylopectin may be due to hydrogen bonding with hydrocolloid molecules. Changes in rates of retrogradation may also be due to phase separations (Section 3.11). Kim et al. (2006) concluded that guar gum and LBG retarded retrogradation in an AM-containing starch but that the hydrocolloid molecules did not interact with starch polymer molecules to form ordered structures.

Liu and Lelievre (1992) and Funami et al. (2008b) suggest a possible association between hydrocolloid molecules in the continuous phase and swollen granules.

If intermolecular interactions are important in network formation, their contribution would be that of an average value for the specific concentrations of the polymer molecules in the paste or gel. However, amylose, amylopectin, and hydrocolloid preparations are comprised of spectra of molecules that are both polymolecular and polydisperse and whose compositions vary from source to source. A method of measuring the binding force between two individual polysaccharide molecules has been developed (Takemasa, Sletmoen, & Stokke, 2009). However, Takemasa et al. (2009) point out that the differences in fine structure occurring within populations of molecules mean that a large number of molecular pairs from specific sources would have to be tested to get an average value.

3.5. *Granule strengthening*

Biliaderis et al. (1997) proposed that hydrocolloids may decrease granule swelling, retard the leaching of amylose, and thereby effect granule stiffening (as compared to starch granules alone). In the same year, Conde-Petit et al. (1997) reported that xanthan reduced the degree of potato starch granule disintegration, and Appleqvist and Debet (1997) reported that ί- and κ-type carrageenans protected starch systems against shear, confirming an earlier report of Tye (1988). In the latter case, evidence of a specific mechanism was not given; however, Appleqvist et al. (1996) had proposed that protection against shear damage might be due to restricted granule swelling and, therefore, less granule fragility. Tester and Sommerville (2003) agreed that hydrocolloids restrict swelling of starch granules (around their T_{gel}). Liu et al. (2003) suggested that a hydrocolloid might form hydrogen bonds with starch polymer molecules within swollen granules (assuming that hydrocolloid molecules could penetrate into granules—a phenomenon for which there is some evidence (see Savary, Handschin, Conde-Petit, Cayot, & Doublier, 2008) and thereby inhibit swelling and starch polymer dissolution. Hongsprabhas et al. (2007) agreed that the presence of certain hydrocolloids could result in maintenance of the granular structure of certain starches. The latter concluded that strengthening resulting in granules being more resistant to heat and shear occurred only in granules containing amylose and that differences in granule rigidity were likely due to the location of amylose molecules and their migration in granules during gelatinization and pasting. Aguirre-Cruz et al. (2005) concluded that an increase in the peak temperature of gelatinization was due to molecular interactions that produced more stable structures. Christianson (1982) first suggested that hydrocolloid molecules could absorb onto the surface of granules and form a coating around them. Gonera and Cornillon (2002) presented evidence that xanthan molecules became associated with the external granule surface and hypothesized that the hydrocolloid absorbed water from both the surrounding environment and the granule and strengthened the granule. Chaisawang and Suphantharika (2006) and Achayuthakan and Suphantharika (2008) agreed that xanthan had this unique property. However, Krüger et al. (2003) attributed an increase in (apparent [reviewer]) gelatinization temperature when a hydrocolloid was present to a reduction in heating rates and water molecule diffusivities as a result of increased viscosity. Likewise, Sasaki et al. (2000b) said that the reduced swelling may be the result of less water being available to the starch granules.

To the contrary, Bean and Yamazaki (1978), Rojas et al. (1999), and Song et al. (2006) concluded that the presence of a hydrocolloid increases the capacity of granules to swell, and Funami et al. (2005b) found evidence that, in the presence of high-MW guaran molecules, granules became less resistant to heat and shear. Together, there is little doubt that differences in granule swelling, strength, and disintegration resulting from different starch–hydrocolloid combinations result in systems of different structural strengths and viscoelastic behaviors (Closs et al., 1999). (See also Section 3.2.)

What makes the data particularly difficult to interpret is the fact that a decrease in viscosity, for example, could result from a decrease in granule swelling or from an increase in swelling accompanied by greater breakdown.

3.6. *An increase in hydrocolloid concentration in the continuous phase*

Alloncle et al. (1989) were the first to suggest that, because hydrocolloids were excluded from granules, their concentration in the continuous phase would increase as granules take up water and swell and that the increase in hydrocolloid concentration in the continuous phase would increase viscosity. This possibility was embraced by Liu and Lelievre (1992), Lai et al. (1999), Liu et al. (2003), Mandala et al. (2004a), Mandala, Savvas, and Kostaropoulos (2004b), Yoo et al. (2005), Huang et al. (2007), Lafargue et al. (2007), Achayuthakan and Suphantharika (2008), and Chaudemanche and Budtova (2008). Rodríguez-Hernández et al. (2006) and Savary et al. (2008) added that properties of composite pastes and gels were also a function of whether the concentrated hydrocolloid molecules could form a network. [This reviewer adds that it has not been established that hydrocolloid and other water-soluble polymer molecules are excluded from the volume of swollen granules. One could ask the question “If molecules the size of amylose molecules and lower-MW amylopectin molecules can diffuse out of swollen granules, cannot hydrocolloid molecules of a similar size diffuse into them?” As a matter of fact, Savary et al. (2008)

found some hydrocolloid molecules inside swollen granules, but unequivocal evidence that water-soluble polymer molecules can penetrate unswollen or swollen granules is lacking.] Temsiripong et al. (2005) concluded that, because the hydrocolloid molecules were concentrated in the continuous phase, they dominated the liquid-like behavior of composite pastes and gels.

3.7. An increase in the effective concentration of starch molecules in the continuous phase

Yoshimura et al. (1988) suggested that short-term retrogradation of corn starch was promoted by hydrocolloids as a result of an increase in the effective concentration of starch molecules (primarily AM molecules) resulting from immobilization of water molecules by the hydrocolloid molecules. This concept was also invoked as a possibility by Yoshimura et al. (1996), Liu et al. (2003), Kim et al. (2006), and Satrapai and Suphantharika (2007), Choi and Yoo (2009), and Ravindran and Matia-Merino (2009). Lai et al. (2003) said that each polymer promoted self-association of the other, resulting in phase separation (Section 3.11), limited disintegration of gelatinized granules, and formation of an amylose network.

Sikora et al. (2008) concluded that gelation of starch in composite pastes proceeded under conditions of water deficiency.

3.8. Prevention of starch-polymer molecular associations

Alloncle and Doublier (1991) suggested that, due to the increased viscosity of the continuous phase, phase separation between amylose and amylopectin molecules could not be completed resulting in less amylose in the gel network and reduced long-term gel rigidity. Kim and D'Appolonia (1977) concluded that pentosans interacted with the starch polymer molecules and reduced their availability for intermolecular associations/retrogradation, with water-soluble pentosans having a greater effect on amylose molecules and water-insoluble pentosans having the greater effect on amylopectin molecules. Ferrero et al. (1993a, 1993b), Eidam et al. (1995), Biliaderis et al. (1997), Mali et al. (2003), Aguirre-Cruz et al. (2005), and Yoo et al. (2005) also concluded that hydrocolloids could interfere with network formation by leached amylose molecules. Conde-Petit et al. (1997) concluded that xanthan interfered with the gelation process resulting from complexation of amylose molecules with an emulsifier. Funami et al. (2008a) said that the ability of hydrocolloids to stabilize or to bind water molecules required for starch polymer crystallization (Lee et al., 2002) should be considered (but it was not suggested why non-starch polymer molecules at low conc. should be so much more effective in this regard than starch polymer molecules and swollen granules [reviewer]). Satrapai and Suphantharika (2007) suggested that hydrocolloid molecules reduced retrogradation by binding water molecules and reducing the mobility of starch polymer chains. Ahmad and Williams (2001) concluded that hydrocolloids decrease amylose–amylose and/or amylose–amylopectin intermolecular associations during freezing. Temsiripong et al. (2005) concluded that the hydrocolloid inhibited network structure formation (without freezing).

To the contrary, Ahmad and Williams (2001) concluded that the rate of amylose molecule aggregation was promoted by galactomannan molecules of high MW, and Funami et al. (2008b) said that low-MW fractions of a galactomannan promoted amylose retrogradation. Funami et al. (2005a) concluded that galactomannans increase the effective concentration of amylose and amylose-like molecules in the continuous phase and accelerate both short-term and long-term retrogradation. Finally, Conde-Petit et al. (1997) stated that xanthan neither promoted nor retarded aggregation of uncomplexed amylose molecules. (See also Section 3.4.)

Funami, Nakauma, et al. (2008) concluded that composite systems were less ordered than were starch-only systems.

3.9. Differences between interactions of hydrocolloid molecules with the starch polymer molecules

(This mechanism is related to the co-operative mechanism [Section 3.4].) Ferrero et al. (1994) concluded that xanthan molecules interact with dissolved AM molecules, but not with AP molecules. Lai and Liao (2002a) and Huang et al. (2007) concluded that synergistic interactions resulting in gel formation were a function of the AM content of the starch. Shi and BeMiller (2002) concluded that the earlier onset of viscosity increase was due to interactions between hydrocolloid molecules and leached AM molecules. Liu et al. (2006) concluded that the general increase in viscosity was due to interactions of hydrocolloid molecules with leached AM, and perhaps AP, molecules and that interactions of AP and/or AM molecules with hydrocolloid molecules might result in network formation. Funami et al. (2005a) concluded that galactomannan molecules interact with long, exterior chains of dissolved AP molecules with galactomannans with fewer galactosyl units being more effective in increasing paste viscosity; Yoo et al. (2005) agreed. Funami et al. (2005b) concluded that guaran molecules interact with both AM and AP molecules, the interactions increasing as the MW of the guaran molecules increased up to a critical MW. They then suggested that interactions with AM molecules might be responsible for the earlier onset of viscosity increase while interactions with AP molecules might be responsible for the increase in peak viscosity. Funami et al. (2008a) attributed reductions in long-term retrogradation to interactions between hydrocolloid molecules and AP molecules. Funami et al. (2005c) also concluded that the effects of AP chain length on both short- and long-term retrogradation differ with the MW of guaran and that the MW of a galactomannan affected the pasting and paste properties of a starch more than did the degree of branching, while the degree of branching had the greater effect on long-term retrogradation. Ferrero et al. (1996) attributed the fact that xanthan did not prevent retrogradation of AP to the AP molecules remaining inside the swollen granules. Yoo et al. (2005) concluded that the rheological behavior of composite pastes is a function of the characteristics of the starch, whose molecules form a network with permanent junction zones (permanent being a relative term [reviewer]), and the characteristics of the hydrocolloids, whose molecules form temporary entanglements in the networks.

3.10. Starch molecule interference with hydrocolloid gelation

Lai et al. (1999) concluded that properties of agarose-starch composite gels are related to interference of dissolved starch molecules with gelation of the hydrocolloid. (This concept obviously applies only to gel-forming hydrocolloids [reviewer].) (See also Sections 3.3 and 3.4.)

3.11. Incompatibility of starch and hydrocolloid polymer molecules

(In considering this possibility, it needs to be remembered that there is already phase separation between AM and AP molecules in a starch paste [Section 1.2].) Alloncle et al. (1989) suggested that AM and galactomannan molecules are incompatible. Gudmundsson et al. (1991) then pointed out that the resulting phase separation favors interactions between like molecules, and Alloncle and Doublier (1991) pointed out that phase separation was due to hydrodynamic incompatibility of dissimilar polymer molecules. The latter also concluded that, due to the increased viscosity of the continuous phase, phase separation between AM and AP molecules were incomplete resulting in less AM in the gel network composite systems. Agreeing with the proposition that apparent synergistic effects were due to mutual exclusion of hydrocolloid molecules and starch polymer molecules as a result of thermodynamic incompatibility which results in AM molecules being close enough to each other that association occurs were Liu and Lelievre (1992), Eidam et al. (1995), Kulicke et al. (1996), Biliaderis et al. (1997), Conde-Petit et al. (1997), Closs et al. (1999), Sasaki et al. (2000b), Ahmad and Williams (2001), Lai et al. (2003), Kim and Yoo (2006), Liu et al. (2006), Huang et al. (2007), Ptaszek and Grzesik (2007), Techawipharat et al. (2008), Funami, Nakauma, et al. (2008), and Ravindran and Matia-Merino (2009). Eidam et al. (1995), Kulicke et al. (1996), and Choi and Yoo (2008) concluded that, because interactions between molecules of the same type are favored over interactions between different-type molecules, the dynamic rheological behaviors of composite pastes and gels are function of the characteristics of the starch, which forms "permanent" (reviewer added quotation marks) junction zones, and the characteristics of the starch which may form temporary entanglements in the network. To the contrary, Eidam et al. (1995) and Kim et al. (2006) suggested that the thickening effect produced by hydrocolloids restricted the mobility of AM molecules, resulting in local interactions between AM molecules occurring more easily and quickly. The results of Ahmad and Williams (2001) and Ptaszek and Grzesik (2007) suggest out that incompatibility resulting in macroscopic phase separation would result in the low elasticity found in starch—galactomannan composite gels (Section 2.12).

Funami et al. (2008a) concluded that the effective concentration of starch polymer molecules resulting from a mutual exclusion because of hydrodynamic incompatibility did not occur in 15% corn starch gels.

3.12. Association of swollen granules

Both depletion flocculation and bridging flocculation have been proposed with the most support for depletion flocculation first proposed by Abdulmola et al. (1996) because measurements suggested that the increase in moduli as the starch concentration increased was much too great to be due to an increase in the concentration of the hydrocolloid in the continuous phase (Section 3.6). Mohammed et al. (1998) and Tecante and Doublier (1999) concurred. The argument is the following (Abdulmola et al., 1996): As two starch particles (of any kind) approach each other, a point will be reached at which surrounding polymer molecules, depending on their hydrodynamic volume, will be excluded from the intervening gap, creating a region of lower concentration. Segregating the polymer molecules into regions of high polymer concentration and regions of low polymer concentration results in a loss of entropy which can be offset by the particles moving closer together with a consequent reduction in the volume of the excluded layer. Because of its rigid conformation and high molecular weight, xanthan has a large hydrodynamic volume and should be (and is) particularly effective in promoting association between swollen granules. Hongsprabhas et al. (2007) and Achayuthakan and Suphantharika (2008) supported the idea of depletion flocculation. Bridging flocculation, which involves polymer molecules adhering to the surface of starch particles and tethering them together, has not been ruled out. In this case, a more rigid polymer would also reduce the entropic barrier to particle association. On the other hand, Biliaderis et al. (1997) and Achayuthakan et al. (2006) suggested that hydrocolloid molecules in the continuous phase might reduce contacts between swollen granules or granule particles.

3.13. Influence of particles in composite pastes and gels

Chaisawang and Suphantharika (2006) said that pasting and paste characteristics of starch–hydrocolloid mixtures are affected by at least three factors: (1) the properties of the hydrocolloid solution [or in some cases, intermolecular network (reviewer's addition)] in the continuous phase, (2) granule swelling in the composite system (and the volume occupied by those granules and granule fragments [reviewer's addition; see Sections 3.2 and 3.5], and (3) interactions between the continuous and dispersed phases. Alloncle and Doublier (1991) stated that the viscoelastic properties of composite pastes and gels are primarily determined by the volume occupied by swollen particles. Tecante and Doublier (1999) expanded this concept by concluding that composite gels contain various types of particles suspended in solutions of various rheological properties, giving an overall behavior to the system that depends on the amounts and properties of each phase (and interactions between them [reviewer's addition]). Liu and Lelievre (1992) concluded that the weakening of a LBG-gellan gel by native and swollen starch granules at relatively low concentrations was probably the result of stress-induced failure in the vicinity of the particles, but they also stated that, at relatively high concentrations, swollen granules strengthened the composites, perhaps due to adhesion between the dispersed and continuous phases. Chaudemanche and Budtova (2008) agreed that starch granules and granule fragments weakened the gel structure of a gel-forming hydrocolloid. Rodríguez-Hernández et al. (2006), Savary et al. (2008), and Funami et al. (2008b) agreed that volume fraction occupied by particles is an important contribution to gel properties.

3.14. Effect of the specific starch–hydrocolloid combination and method of paste/gel preparation

Lai et al. (1999) stated that interactions between hydrocolloids and starches depend on the specific starch and the specific hydrocolloid used and the method used to prepare the composite paste/gel. Tecante and Doublier (2002) then pointed out that whether starch polymer (AM) molecules or hydrocolloid molecules form the continuous phase is determined by their relative concentrations (which would be a function of the degree of dissolution of starch polymer molecules [reviewer's addition]).

4. Conclusions

Some general conclusions supported by the majority of data are the following:

- Viscosity vs. temperature profiles, viscosity vs. shear profiles, and properties of composite pastes/gels are a function of the specific starch–hydrocolloid combination and the ratio of the two components.
- Pasting and paste/gel properties of starches with a specific added hydrocolloid often vary with the type of starch used. Amylose content, the fine structure of amylopectin molecules, and ionic charge [potato starch] may be factors.
- Different hydrocolloids often have different effects on the pasting and paste properties of a given starch. Factors may be the ability to interact with a starch polymer (primarily amylose) due to differences in hydrocolloid structural characteristics such as the degree of branching, molecular weight, molecular flexibility, and presence and type of an anionic charge. In general, effects of a particular hydrocolloid increased as its molecular weight increased.
- The presence of a hydrocolloid often resulted in increases in
    - ○ Conclusion temperature of gelatinization

  - Peak viscosity
  - Overall paste viscosity
  - Short-term retrogradation
  - Gel strength
  - Apparent freeze–thaw stability
- and decreases in
  - The temperature of the initial rapid viscosity increase
  - The enthalpy of gelatinization
  - Granule swelling
  - Starch polymer molecule leaching/solubility
  - Long-term retrogradation
- Sometimes opposite effects were observed. At other times, no effect was observed. Where effects were seen, they were often related to the hydrocolloid concentration. Opposite effects have been observed in
  - Granule swelling
  - Retrogradation
  - G' (network formation)
  - G'' (the viscous nature of gels)
  - Tan δ
- The preparation method may influence the rheological properties of composite systems.

What these results seem to indicate is that different pastes and gel characteristics are obtained with different specific starch–hydrocolloid combinations, methods of preparation, and conditions during measurement.

Many mechanisms have been proposed to account for the changes in pasting and paste and gel characteristics that occur when a hydrocolloid is used together with a starch. It seems to be clear that pasting and paste/gel characteristics of starch–hydrocolloid mixtures are likely influenced by

- The properties of the hydrocolloid–starch solution in the continuous phase.
- The volume occupied by swollen granules and granule fragments.
- The natures of swollen granules and granule fragments in the system.
- Interactions between swollen granules and/or granule fragments.
- Interactions between starch and hydrocolloid molecules in the continuous phase and particles in the dispersed phase.

Specific mechanisms that have been proposed and most often used to explain the data are the following:

- Viscosity increases might be due to the increased work required to move swollen granules past each other (in a more viscous medium).
- The increased shear force exerted on the swollen granules brings about their disintegration (breakdown) and a decrease in viscosity.
- Some hydrocolloids appear to reduce/restrict granule swelling, which also reduces breakdown and leaching. Reduced swelling might be due to less water being available to granules.
- Phase separation due to molecular incompatibility of polymer molecules occurs. Phase separation favors interactions between like molecules, i.e., phase separation results in amylose molecules being sufficiently close to each other that associations are favored. Differences in the degrees of phase separation may be related to the relative concentrations of the starch polymer and hydrocolloid molecules.
- Some hydrocolloid molecules interact with leached starch polymer molecules resulting in an earlier onset of viscosity increase and network formation (increased viscosity in general). It has also been suggested that the presence of hydrocolloid molecules results in less starch polymer (amylose) network formation due to less phase separation between AM and AP molecules because of either increased viscosity of the continuous phase and a reduction in mobility of starch polymer chains or less water molecules being available for starch polymer molecule crystallization. In a third variation, it was suggested that the presence of hydrocolloids results in amylose network defects, reducing viscosity and weakening the gel. All three interpretations may be correct and reflect what happens in different starch–hydrocolloid combinations.
- Granule swelling probably plays an important role. Some concluded that the presence of a hydrocolloid increases granule swelling. Others concluded that certain hydrocolloid molecules strengthen granules and restrict granule swelling. Especially is it believed by some that xanthan molecules can associate with the external granule surface and, thereby, strengthen granules, i.e., increase their rigidity. Other hydrocolloids that appear to reduce granule swelling may do so by reducing the amount of water available to granules. Here again, different conclusions may be the result of different specific starch–hydrocolloid combinations and/or preparation conditions.
- Restriction of granule swelling, when and if it occurs, probably reduces the leaching of AM molecules and, thereby, their availability for network formation.
- The properties of composite pastes and gels are a function, at least in part, of the fact that hydrocolloid molecules are excluded from even swollen granules. As a result, their concentration in the continuous phase increases as granules take up water and swell. The result is an increase in viscosity and network formation if a gel-forming hydrocolloid is used. Others have suggested that there is an increase in the effective concentration of starch polymer molecules in the continuous phase due to binding of water molecules by the hydrocolloid molecules.
- Promotion of associations between swollen granules by hydrocolloids through depletion flocculation.

The ultimate conclusion that can be drawn is probably that, because of the complexity of the systems (starch + hydrocolloid + water, even without other ingredients) and the variety of structures of starch granules, starch polymer molecules, and hydrocolloid molecules, several mechanisms are likely to be operating and proportions of competing mechanisms likely vary with different specific hydrocolloids, different starches, and different methods of preparation of the composite pastes and gels.

5. Not covered in this review

Not covered in this review are the following: non-food applications of starch–hydrocolloid composites; interactions of other water-soluble polymers, including gelatin and other proteins, with starches; use of carrageenans, especially kappa-type carrageenans in milk systems; additions of hydrocolloids to doughs used for baking (in which they are incorporated in attempts to make acceptable gluten-free products or to retard staling); use of hydrocolloids in other low-moisture starch-based products such as confections, pasta, tortillas, and extruded snack foods; use of starch–hydrocolloid combinations in meat products; investigations of the use of polydextrose, maltodextrins, and other low-molecular-weight products of polysaccharide hydrolysis; starch–hydrocolloid composite films; or dry heating starch–ionic hydrocolloid mixtures to produce new ingredients. Neither have the effects of sugars, salts, or other ingredients on starch–hydrocolloid pastes and gels been analyzed in detail (see Sudhakar et al., 1996a, 1996b). They are, however, included in Table 4.

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