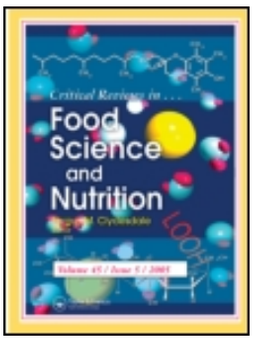

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On the Molecular Characteristics, Compositional Properties, and Structural-Functional Mechanisms of Maltodextrins: A Review

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ABSTRACT: Compositional, physicochemical, and structural properties of maltodextrins and the most important advances that have been made are critically reviewed. Individual topics focuses on the maltodextrin production, carbohydrate composition, and dextrose equivalent determination, factors that alter the polysaccharide properties, the molecular arrangement, the mechanisms and complex physicochemical changes of maltodextrins such as water interaction (hygroscopicity, precipitation, turbidity, bound and free water) and the role of molecular interactions for a network formation. Of particular importance is the information concerning the network structure of maltodextrins gels (degree of crystallinity, crystallite size, aggregation) and the involvement of linear and branched chains for the network formation. Rheological properties have become a desirable tool to predict and understand their structural and functional properties, in single and in mixed systems with other macromolecules. These advances are assessed together with the structural development of food products and processes. Their main food applications, particular advantages, recent commercial directions, and modifications together with potential problems are also discussed. As food ingredients, maltodextrins are a valuable production tool, but still with considerable promises. Nevertheless, a more detailed knowledge of the properties of maltodextrins is necessary in order for their use to be considered as sufficiently effective and desirable in a number of known food applications and for novel development purposes.

KEY WORDS: maltodextrins, processing, water interactions, network microstructure, viscoelasticity, gelation, functional properties, reduced-fat foods, and reduced-calorie foods.

I. INTRODUCTION

Hydrolysis of starch by means of heat and acid,[97] or specific enzymatic treatments,[46] or combined acid and enzyme hydrolysis,[63] yields a spectrum of depolymerized oligomers. The hydrolyzed products mainly consists of D-glucose, maltose, and a series of oligosaccharides and polysaccharides (such as maltose oligosaccharides, maltotriose, and maltotetraose mixtures). The wide range of hydrolyzates available are described in terms of their 'dextrose equivalent' (DE) value, which is a measure of the total reducing power of all sugars present relative to glucose as 100 and expressed on a dry weight basis. Therefore, a degradation product with a high dextrose equivalent has been subjected to a greater degree of hydrolysis than one of a lower DE.

Maltodextrins are hydrolysis products of starches with DE lower than 20 (for DE > 20 the term syrup solids or dextrins is used). They represent a mixture of saccharides with a broad molecular weight distribution between polysaccharides and oligosaccharides and are available as white powders mostly or concentrated solutions. In contrast to native starches, the maltodextrins are soluble in water.

The addition of maltodextrins as food additives has been introduced the last 25 years. Maltodextrins can be classified as carbohydrate-based bulking macromolecular replacements123 (like glucose polymers, modified sugars, and mixed hydrocolloids), and substituted on an equal-weight basis provide 4 kcal or 16.8 kJ/g.[6] Maltodextrins with low DE values are claimed to display in part the desirable organoleptic characteristics of fat, and from the mid to late 1980s they have received considerable attention for developing fat- and calorie-reduced products. Some of their important functional properties include bulking, gelling, crystallization prevention, promotion of dispersibility, freezing control, and binding.[18]

The intent of this article is to briefly review the current knowledge and recent research developments regarding maltodextrins. The article focuses on factors that affect the physicochemical properties, the struc-

tural-functional behavior, and the quality of maltodextrins. The considerable effort on their processing conditions, product applications, and food developments processes and their specific advantages are presented. It can contribute to bridge relations and gaps between maltodextrins properties and their behavior in real food systems. It could provide ideas and introduce areas where it may be necessary to design and perform detailed studies.

II. DESCRIPTION OF MALTODEXTRIN SYSTEM

A. Production

According to Alexander,[3,4] the present technology involving starches and other carbohydrates probably originates with the early work of Richter and co-workers, who were issued patents in 1976. Several types of proprietary equipment and modern installations are used today for a desirable conversion of starch. These aspects have been reviewed recently.[5,18,78]

The acid conversion process consists of treating a suspension of purified starch with a small amount of strong acid at a fairly high temperature.113 Hydrochloric acid 0.02 to 0.03 *M* is usually used and temperatures of 135 to 150°C for 5 to 8 min are applied. Measurement of pH (range 1.6 to 2.0) is not a very sensitive means of controlling acid addition and is normally performed volumetrically or by conductivity measurements, while adjustment of DE is carried out by varying the reaction temperature in a normally fixed time.[18] When sufficient saccharification has taken place, the acid is neutralized, and the mixture is filtered, decolorized and concentrated to the required solids content. In modern methods, the conditions are arranged to keep the time of conversion as short as possible in order to minimize side reactions with partial degradation resulting in bitter taste, off colors and dextrin haze (retrogradation) on storage.[18] Today, the acid hydrolysis is particularly recommended for production of dextrins with DP < 5 (glucose syrups).

In order to have a full continuous hydrolysates production process, the use of continuous conversions catalyzed by enzymes or combinations of acid and enzymic processes are placed. The actual process used for the production of maltodextrin is often patented, and typically involves mixing enzyme and starch slurry, heating at the gelatinization temperature of starch (~75°C) holding there for a fixed time, and then heating to a higher temperature (~105°C) or acidifying the product (pH ~ 3.5) to inactivate the enzyme.[5,16] The optimum conditions (i.e., temperature, pH) for a particular enzyme frequently depend on the organism from which it is produced. Finally, the soluble material is separated from the insoluble fibers by centrifugation and neutralized for subsequent spray drying under vacuum.

Enzyme-catalyzed conversion with mostly a-amylase (1,4-α-D-glucan glucanohydrolase, EC 3.2.1.1) from *Bacillus subtilis* and pullulanase (pullulan 6-glucanohydrolase, EC 3.2.1.41) are now used for production of gelling maltodextrins.[18,48,73,76,129] α-Amylase is an endo-acting enzyme hydrolyses the (1→4)-linkages in α-d-glucans but cannot hydrolyze α-(1→6)-linkages at the branch points. As a result, maltodextrins produced by α-amylase, an extensive hydrolysis of amylose but only a partial hydrolysis of amylopectin, takes place.[18] However, a low amount of high-molecular-weight amylose still remains.[21] The maximum activities of the α-amylases are usually in the acid region between pH 4.8 and 6.5, but the activity-pH profile and location of the pH optima differ depending on the enzyme source, with examples of pH optima ranging from pH 3.5 to pH 9.0. The pH optimum for plant and microbial α-amylases is generally lower than for the animal α-amylases.[76]

Pullulanase is specific for 1→6 linkages in α-D-glucans and therefore acts as a debranching enzyme to provide a series of (1→4) linked -α-D-glucopyranose oligosaccharides. Most pullulanases have pH optima between pH 5.0 and 7.0 and usually temperature optima of 45 to 50°C.[76]

Enzyme catabolized or a combination of acid and enzymic hydrolysis of starch have distinct advantages compared with the acid process. The hydrolysis obtained is more specific, depending on the enzyme or the combination of enzymes selected, and a greater flexibility in the final composition of the product is usually achieved. Enzymic processes provide a greater amount of fermented sugars and less formation of undesirable components from thermal processing, while there is no need to remove salts formed during acid neutralization.[131] It can be conducted at wider pH values and lower temperatures and pressures (an economic advantage of requiring less energy), while the processes are easier to control. Nevertheless, the use of enzymes for starch hydrolyzate is not a completely continuous process, and several attempts have been made to use enzymes insoluble by immobilization techniques.[38,76] In addition to the practical problems using immobilized form of the enzymes on porous matrices, an economic question also arises. Improved characteristics of enzymes can be expected to expand with the use of genetic engineering.

B. Compositional Characteristics

As a digestion product from starch, maltodextrins contain linear amylose and branched amylopectin degradation products (Figure 1). Maltodextrins, therefore, are considered as D-glucose polymers in which the individual α-D-glucopyranosly residues are joined by (1→ 4)-linkages to give linear chains with a degree of (1→ 4, 1→6)-linked or (1→ 6)-linked branch points. The *Dextrose Equivalent* is an inverse measure of the number of anhydro α-D-glucose units, thus, for instance, a maltodextrin of DE 5 corresponds to a polymeric species of 20 glucose molecules (degree of polymerization, DP). However, varying the DE among maltodextrins polysaccharides does not necessarily mean that they differ only in dextrose content. Moreover, maltodextrins with the same DE value can have very different properties, that reflect the composition of the components rising from the hydrolysis reactions. The type of starch (maize, oats, rice, tapioca, potato, etc.) is also an important factor determining the molecular segments of maltodextrins. The ratio of linear amylose chain molecules to branched amylopectin varies according to the source of starch. The majority of starches contain between 15 and 35% of amylose.[76] Wheat and rice starch have characteristics generally similar to those of maize sources. On the other hand, waxy straches differ and are made up entirely of branched amylopectin molecules. As a result, maltodextrins derived from waxy maize starch consist exclusively of amylopectin, contain very little linear amylose, and do not exhibit the retrogradation phenomena typical of common corn starch oligosaccharides.[90] These maltodex-trins have an average molecular weight comparable to other polysaccharides and much less than that of conventional amylopectin. Stability to retrogradation due to some characteristics (size and impurities) of the amylose that inhibits its reassociation is present in starch from potato.[18] Alkali-modified cassava starch[105] is also a good source of maltodextrins of DE.[20–23] In addition, native starches differ in water content, and in addition amylose and amylopectin several noncarbohydrate components are present, such as lipids, proteins, and minerals.

C. Dextrose Equivalent (DE) Determination

Any method for reducing sugar determination can be used; however, traditionally

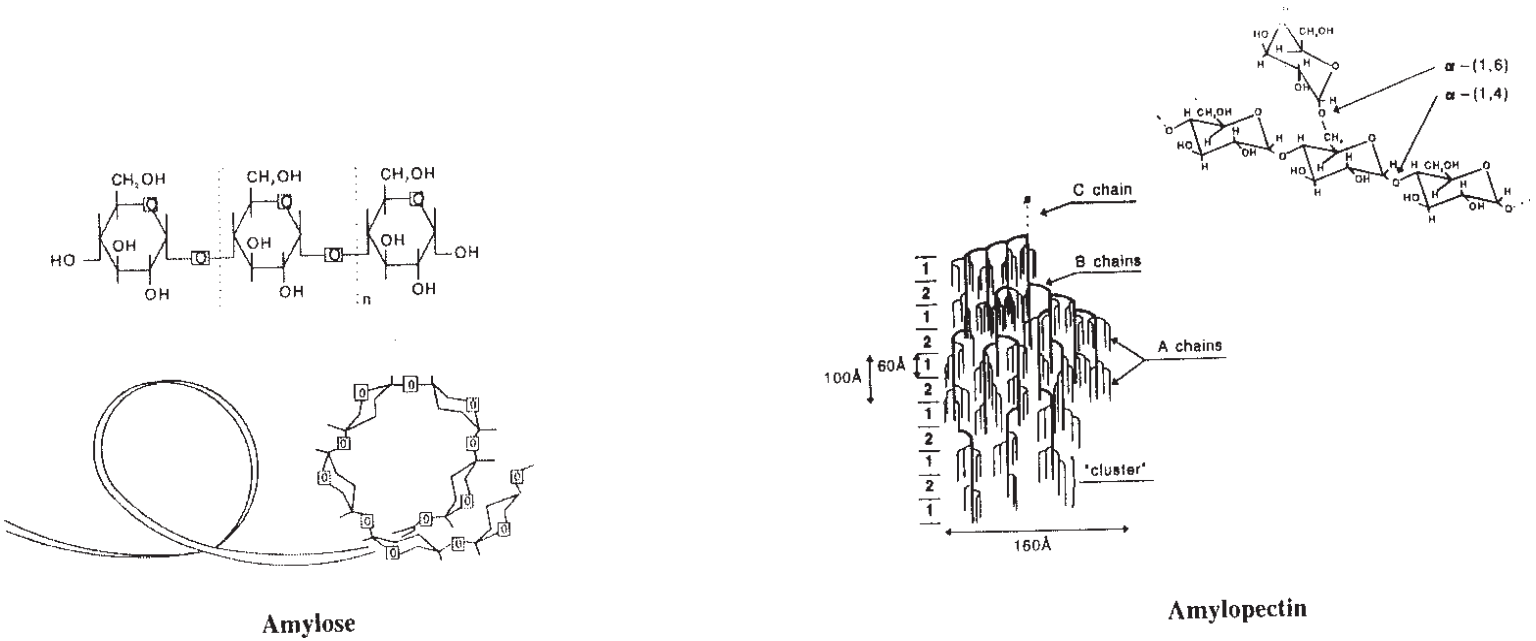


FIGURE 1. (a). Amylose is a linear or sparsely branched polymer of a molecular mass in the range 105 to 106 g/mol linked primarily by 1→4 bonds. The chains form a spiral-shaped single or double helix. (b). Amylopectin is highly multiple-branched with a molecular mass of 107 to 109 g/mol. It also contains 1→4 linked glucose units, but in addition has 1→6 glucosidic branching points occurring every 25 to 30 glucose units. It is generally agreed that the chains are assembled in a 'cluster structure'. However, the fine structure of amylopectin, the nature of the branching and the relative proportions of side chains remains a matter of some discussion (see extensive reports and literature in Ref. 76).

the Lane and Eynon titration[83] has been used to determine the content of reducing sugars and still is the method of choice for some industrial applications. It is a non-stoichiometric reaction in which approximately 5.0 equivalents of cupric ions are required to oxidize 1.0 mol of reducing sugar. Their concentration is monitored titrimetrically, compared with a reference to standard tables, and calculated as a percentage of the dry substance.[127] Careful control of the heating is required, and for the most accurate analysis two titrations are necessary. Table alterations have also been reported improving the original method.[42] The exact procedure has been published by the Corn Refiner Association (Method E-26).[18] However, because the reaction is not entirely stoichiometeric, the theoretical DE of saccharides is always lower that the observed with DE under certain conditions with other main disadvantages being the time consumed, the standardized reagents, and the expertise required.

Rapid determination of dextrose equivalent of maltodextrins (and glucose syrups) could be made by cryoscopy, which is a measurement of freezing point depression.[44] The cryoscopic approach is a response to the number of moles of material in solution. It is unaffected by the presence of high-molecular-weight materials such as residual enzymes, proteins, etc. It can be affected by the presence of low-molecular-weight inorganic salts (i.e., ash).

Nevertheless, the use of oligosaccharide fractionation by gel permeation chromatography is now recommended as the best method for characterization of starch hydrolysates, and the determination of dextrose equivalent is based on the actual composition of oligosaccharides.[80] Fractionation of starch and its hydrolysis products using Bio-Gel P-2,[126] microsperical cellulose,[43] and porous glass beads (CPG-10)[81] have been also reported. Additionally, a number of specific assay methods have been developed for the quantitation of individual oligosaccharides, among colorimetric methods, which is used for the gross determination of total carbohydrate content or total reducing sugar content.[77] Such assays use alkaline 3,5-dinitrosalicylic acid,[17] alkaline ferricyanide,[79] or alkaline picric acid.[96]

1H-NMR studies could also be involved. The anomeric proton region of a maltodextrin spectrum usually comprises four doublets assigned to H(1), the anomeric protons at 1,6 branch points and 1,4 linkages (their ratio cangive the degree of branching), and reducing end groups in the α and β configurations. The DE values of maltodextrins can be determined from the combined intensity of the resonances from α and β reducing end-groups relative to the total anomeric signal.[53]

III. PROPERTIES

A. Physicochemical Characteristics

As a digestion product of starch, the maltodextrins contain linear and branched amylose and amylopectin degradation products the size of which extends from oligomers to macromolecules. In the sol state these molecules are hydrated and expanded, and the extended helical regions are interrupted by short, disordered regions. At high concentrations helices aggregate, forming crystalline domains. Therefore, maltodextrins have a significant portion of average chain length long enough to form thermally reversible gels. The sol-gel transition is a slow process accompanied by dehydration and combined with the growth of helices of sufficiently long molecular chains or chain segments.[107] The transition depends on the temperature, concentration, time, and structural peculiarities.

The gelation of maltodextrins is a weakly cooperative process, with the standard Gibbs free energy of gelation not strongly influenced by the degree of cooperativity.[120] Con-

sidering the low entropic effect, small changes in enthalpy result in the formation of thermodynamically stable gel structures. Low elasticity, small mechanical stability, high rigidity and turbidity are characteristics of these gels. Despite the high rigidity of the maltodextrin gels the heat changes associated with the melting of gels are small.[132] A particular characteristic of the gel matrix is the unbound state of the greater part of the water.

Acetylated maltodextrins do not give 'solid' NMR signals and melting peak in differential scanning calorimetry, as observed in the formation of highly ordered domains of the gel network.[29,121] Hence, acetylation stabilize the maltodextrins in solution and no aggregation or gelation have been observed.

Variations in DE values results in maltodextrins with varying physicochemical properties. Hygroscopicity, solubility, osmolality, and their effectiveness to reduce the freezing point increase with increasing DE, while viscosity, cohesiveness and coarse-crystal prevention increase as DE decreases.[92] It is possible, however, by altering the temperature of hydrolysis to produce malto-dextrins preparations that have similar DE values but different proportions of high-and low-molecular-weight saccharides.[57] Differences in these saccharide profiles are expected to yield maltodextrins with different physicochemical properties. In particular, solubility and solution stability will be influenced by high-molecular-weight components, while viscosity, crystallization, and sweetness will depend on the amount of low-molecular-weight components.

Maltodextrins are suitable ingredients to replace fat in foods[59,60,123] and contribute and/or reproduce the fat like mouthfeel in a variety of products. This sensation presumably originates from the three-dimensional network of submicron particles in structured water layers, that function as the structure of fat. The network is loosely associated and the particle gel structure has a large surface area and high degree of water immobilization. For instance, acid hydrolyzed starch under specific conditions can form crystallites that are essentially intact and organized laterally.[47] This system has low degree of association and the aggregates are very small particles (about 0.02 μm). In a continuous oil phase this loosen association linked to the fat crystals and deform similarly.[123] As well, the particle size of irregularly shaped maltodextrin aggregates are 3 to 5 μm in diameter, approximately the same size as the fat crystals[8,99] which presumably contribute to the fat-like mouthfeel. Maltodextrins have the capacity to participate in Maillard reactions and can be used as nonbrowing carriers for drying sensitive products.[82,92,136]

B. Polymer–Water Interaction of Maltodextrins

1. Hygroscopicity and Storage

Hygroscopicity is one of the most important properties determining the shelf-life and storage stability of maltodextrins. The effect of different relatives humidities (varying from 40 to 95%) has been investigated.[104] Samples exposed to environments of 75% relative humidity and more behave pastry in texture even after 6 days, while at lower relative humidities (40 to 60%) samples attained equilibrium moisture level after 18 days of storage without undergoing any visible textural changes. According to Radosta and co-workers,[101] if the maltodextrins are stored above a definite critical water activity they stick together and change their state from powder to a 'sorption gel'. Thus, the maltodextrins have to be stored under such conditions to prevent the change from powder to sorption gel (Table 1).

Absorption of moisture is well accepted in maltodextrins; however, the reason is not quite solved[104] and more analysis is required.

TABLE 1
Critical Water Activity of the Transition from Powder to Gel Under Sorption Conditions

	Water activity			
$\bar{P}n$	0.45	0.66	0.79	0.93
240	P	P	P	P → G
16	P	P	P → G	G
9	P	P → G	G	S

Note: $\bar{P}n$: the molecular composition of the maltodextrin. P: powder, G: 'sorption gel', S: syrup, P → G: transition from powder to sorption gel.

From Ref. 101 with permission.

Donuelly,[40] after studying the hydroscopicity of different D-glucose polymers, suggested that the presence of compounds like maltotriose and maltotetraose imparts high hygroscopicity to sugar mixtures. On the other hand, individual studies[71] suggest that moisture absorption increases smoothly with decreasing molecular weight, while sugars containing a high-molecular-weight fraction achieved equilibrium moisture sooner than the corresponding low-molecular-weight fraction.

2. Turbidity

Turbidity is considerably important because it influences the film-forming property capable of good retention of volatile compounds during the spray-drying process, which is preferable for flavor encapsulation. Samples with the same level of DE showed substantial differences in their dispersibilty in water, while the low DE values display a relatively low turbidity.[104] Mainly, the greater tendency of amylose to retrograde comparing with amylopectin led to the formation of haze or precipitation at higher concentrations. Factors that influence haze formation are the type of starch used and the methodology adopted for liquefaction for maltodextrins preparations. The use of turbidity measurements is also a suitable method for the determination of the rate of formation of the precipitate.[75]

3. Precipitation

The precipitation of maltodextrins solutions at various temperatures is important for the storage stability, shelf-life, product processing, and obviously the final quality of food preparations. Kennedy and co-workers have extensively investigated the stability of aqueous solutions of maltodextrins (DE 14, 18, 15–25) required for clinical feed preparations.[73] They found that the stability is frequently poor, with precipitation occurring at 25° to 4°C at a rate that shows a negative temperature coefficient.[73,74] The particle distribution is non-Gaussian, with approximately 90% of the particles having diameters less than 3.5 μm, the spherical particles ranging from 1.0 to 8.5 μm and the mean diameter was found to be 2.4 μm. In order to promote the storage stability of such aqueous maltodextrins, the presence of inorganic ions should be avoided by the use of distilled water rather than water purified by ion exchange.[74] The addition of D-glucose and surfactants, despite the fact that they affect retrogradation of starch and amylose, show only a limited degree of improvement in storage stability. Furthermore, the adjustment of pH of the product in intervals of 3.0 to 3.5 by citric acid provides a valuable stabilization effect.

Analysis of the precipitate formed from solutions of maltodextrins (DE 14,18) show that oligosaccharides with degrees of polymerization of 11 and above are the major components, with no evidence for the presence of small oligosaccharides with degrees of polymerization up to 7, while the fraction with DP values above 20 diminishes slightly with storage time.[75] This is in agreement with the results by Gidley et al., who ob-

served that amyloses with mean DP values lower than 110 were particularly unstable and precipitated/retrograded faster than molecules having larger molecular weights (i.e., mean DP values 250, 300) that tend to give turbid suspensions or gels, while the minimum DP required for precipitation is 8 to 9.[54]

The above studies[74] support that precipitation arises through a mechanism similar to that which causes retrogradation in amylose, namely, alignment of linear molecules, via hydrogen bonding, to give aggregates that ultimately precipitate. Branched structures interfere with the formation of these aggregates, prevent retrogradation, and increase the stability of maltodextrin solutions. The precipitation on storage of maltodextrins solutions was increased after extended hydrolysis time and temperature or increased enzyme concentration using α-amylase.[73] This is simply explained as α-amylase will tend to attack the highly branched starch material readily to liberate linear oligosaccharides, and a greater degree of hydrolysis will result in more linear structures present in solution.These investigations also found that a combined use of α-amylase and pullulanase enzymatic treatments can produce better products in terms of oligosaccharide composition and by selection of the reaction times, and storage stability.

The use of DE as a method for describing maltodextrins is not appropriate as well as in the prediction of storage stability.[74] An alternative method of defining maltodextrin materials in terms of their oligosaccharide component composition obtained by gel filtration chromatography was not a full proof method for predicting the shelf-life. Samples with similar oligosaccharide component spectra can have very different precipitation times and storage behavior varying from 1 day to more than 2 years.[74]

However, it has been suggested that amylopectin may play an important role in starch retrogradation via interaction of its branched chains that have average chain lengths in excess of the minimum DP required for retrogradation.[54] Therefore, maltodextrins precipitation is more complex and arises from a mechanism that facilitates both linear and branched fractions. Such effects are discussed extensively at the precipitation from potato maltodextrin-gelatin mixed solutions.[67] The amount of malto-dextrin precipitated (M) was proportional to the square of its initial concentration and to the first power of gelatin concentration ($M = k\,[\text{maltodextrin}]^2\,[\text{gelatin}]$), indicating that gelatin drives substantially self-association and aggregation of maltodextrins when both polymers are present in a single liquid phase. This dependence support reasonably for the initial rate of a two-coil to double helix transition for linear maltodextrin chains in the presence of gelatin. These helices act as nuclei for ordering of shorter segments that also grow significantly by the addition of branched species. Furthermore, 1H NMR studies show that the precipitated maltodextrin is higher in molecular weight and in the degree of branching than the material remaining in solution while it redisolves at about 80°C, behavior that obviously has come from the amylopectin fraction of the original starch.

In summary, the following model for the extent precipitation of maltodextrin from mixed solutions was proposed:[67] the presence of another polymer will drive conversion of maltodextrin from the disordered state to the more compact helical conformation. Within the maltodextrin rapid phase growth of large aggregates by the addition of branched material to the linear helices will continue (a kind of 'synergistic' interactions) until the ordered core becomes totally screened by the disordered fringe. Finally, phase-separation and macroscopic precipitation will occur in mixed solutions promoted by large branched aggregated clusters. Phase separation and precipitation may have also occurred when both polymers con-

centrations are high, before any significant ordering.

4. Free and Bound Water

During gel formation a certain amount of water is absorbed in the system. The part of the water that underlies maltodextrin-water interactions can be characterized as 'bound' water, while the remaining, which does not interact with the polymer, could be denoted as pure 'free' water. These interactions are influenced by the chemical composition, the chemical modification of maltodextrins (crystallinity, ratio between linear and branched molecules), the concentration, the sol gel transition, the temperature, and the other undissolved substances and show characteristic peculiarities. Information for the content and distribution of water in maltodextrins has been provided from NMR, differential scanning calorimetry, water vapor sorption isotherm techniques, infrared spectroscopy, and ESR spectroscopy studies.[90,101,102] The non-freezability of a portion of the water in maltodextrin solutions and gel was taken as a measure for polysaccharide-water interactions. A comprehensive review about polymer-water interactions of maltodextrins is given elsewhere,[103] and only the main findings will be mentioned here (Figure 2).

1. The quantity of polysaccharide-water interactions is largely influenced from the concentration of the maltodextrin. As for starches, the portion of bound water in relation to total water content rises with increasing maltodextrin concentration. Therefore, as the structuring effect of the maltodextrin on water increases, the number of structural elements or aggregates increases, but without changing their micro-structure.
2. It is characteristic that the physical micro-structure or the state of aggregation of the polysaccharide (powder, xerogels, solutions, sol-gel transitions, gels) do not influence the water interactions and the hydration states. They all contain the same amount of bound water at equal polysaccharide concentrations. A very weak modification of the free water results due to the transition from solution to gel. The aggregation state (size and shape of the matrix components) does not change the amount of bound water and the molecular mobility of water. Linear or branched structures of the molecules influence insignificant the polysaccharide-water interactions.
3. The mean molecular mass composition and distribution of molecular masses in maltodextrins are also responsible for the physical properties of water. At high concentrations the interactions between high molecular mass polysaccharides and water dominate, while at more diluted and liquid systems the interaction between oligosaccharides and water increase. The higher the degree of polymerization the higher the bound water at high polysaccharide concentrations. In low molecular mass maltodextrin fractions this relation is reversed with decreasing polysaccharide concentrations. Thus, the oligosaccharides stabilize the water interactions in solutions and gels, whereas the polysaccharides increase the polymer-polymer interactions. However, high molecular maltodextrin fractions contain amounts of bound water that are independent on concentration.
4. With increasing temperature (1 to 60°C) a slight decrease of bound water was found. Structuring of maltodextrin solutions at low temperatures did not result in detectable change in the amount of bound water.

Maltodextrins gels are able to include up to 9 g water/g dry mass inside the gel matrix;

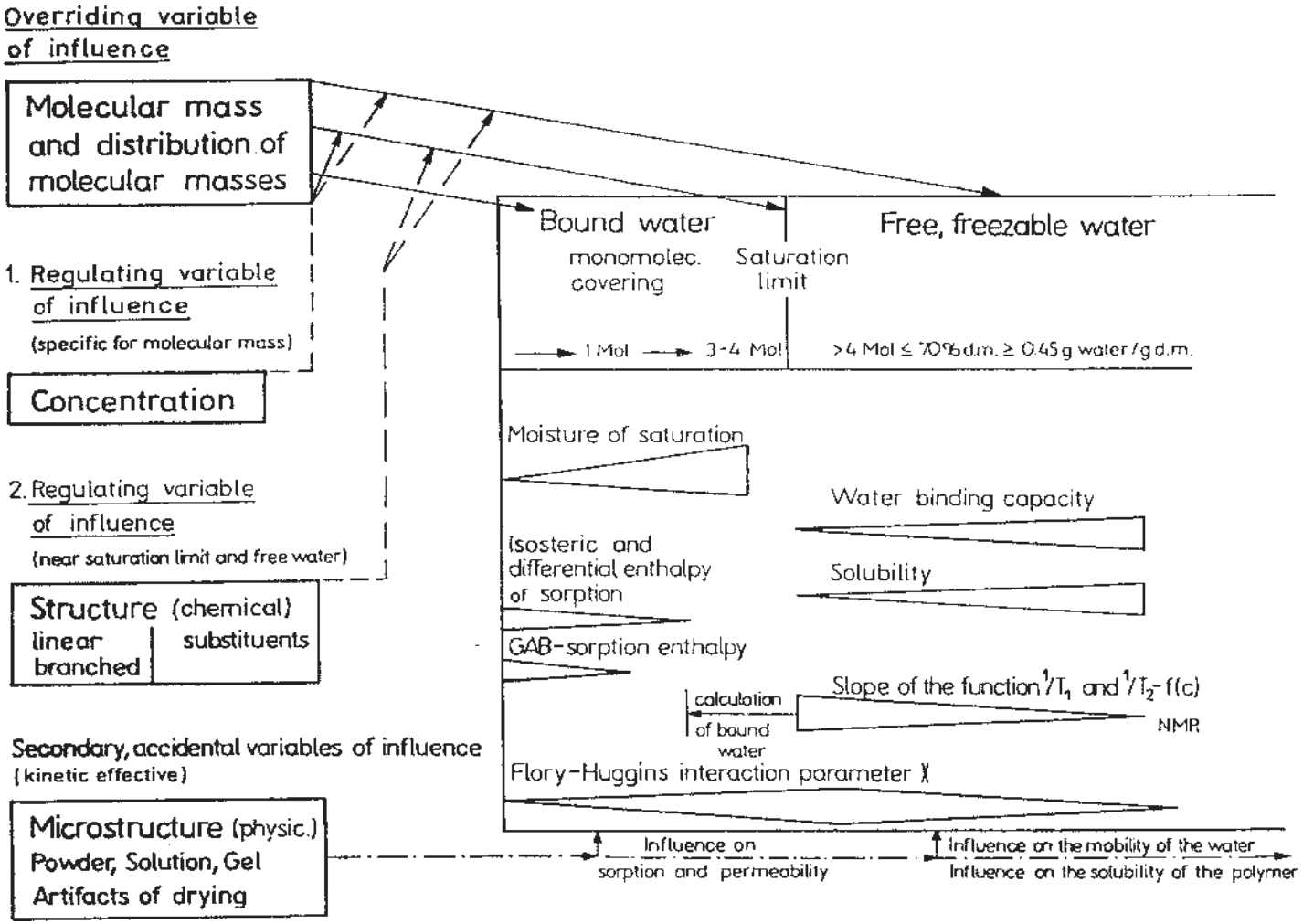


FIGURE 2. Influential variants on polymer-water interactions and their effect in different states. (From Ref. 103 with permission.)

nevertheless, the water that shows real interaction with maltodextrin amounts is much less only 0.3 to 0.5 g/water/g dry mass (water binding capacity).[101,102,103] Hence, the main part of the water in a maltodextrin gel must be located within the gel matrix. Conclusively, the binding of water molecules by maltodextrins gel network is weak, permitting a very high molecular mobility of bound water and fast exchange with free water.

It has been found that the degree of hydration of the starches depends on the source from which they were isolated and increases in the series of hydrolyzed starch maltodextrin < pea starch < wheat starch < maize starch.[50,51] As the degree of maltodextrin hydration is lower and the mobility of the water molecules in the bound state is higher, the probability of forming stable clusters is higher. These clusters act as nuclei for the formation of the maltodextrins gel network.

IV. MECHANISM OF NETWORK FORMATION OF MALTODEXTRINS GELS

The mechanism of network formation (or precipitation, as discussed previously) for maltodextrins can be inferred from the gelation of starch that is based on the creation of co-axial double helices by 1,4-linked α-D-glucan chains and the lateral aggregation of these intermolecular associations.[29,34,67,89,119,120] Maltodextrin gels result from coupling interactions between soluble amylose molecules and sufficiently branched and linear chains of amylopectin molecules.[29,67,89,119,120] The hydrated linear amylose fractions that have a conformation characterized by extended helical regions and interrupted by short disordered regions are responsible for the initiation and acceleration of the gelation. In pure amylose gels conformational ordering occurs from the helicaljunctions of chains with average an helix length longer than 50 to 70 residues, while shorter oligomers than DP 6 have been found to co-crystallize with longer chains.[34] Long outer linear segments of branched amylopectin molecules also interact with the amylose chains. These helical species aggregate to form crystalline domains, which are embedded in a polymer solution with disordered chain segments. Because a portion of the molecule is sufficiently long and can be involved in the formation of several crystalline domains, at proper concentrations an aggregated network in such domains represents the junction zones of the polysaccharide.[108] The junction zones extend over very small dimensions and despite the heterophase state the mechanical properties of the maltodextrin gels corresponded to those of a single phase system.

This 'synergistic' interaction mechanism between different fractions is consistent with studies where the importance of high molecular weight stable helices capable of forming ordered domains as essential constituents of the three-dimensional network have been established, as well as the formation of shorter structures by cooperatively associating with the oligomers.[29,67] Analogous effects have been observed from proton NMR and differential scanning calorimetry by Schierbaum and co-workers.[120,121] Dea and co-workers also similarly confirmed that maltodextrin gels are apparently composed of a network of high-molecular-weight branched molecules further stabilized by interactions with short linear chains.[21] Debranching of maltodextrin gels and the analysis of the different fragments by size-exclusion chromatography shows that the high-molecular-weight fraction was fully excluded (minimum DP ≈ 60) and composed entirely of branched molecules derived from partial depolymerisation of amylopectin.[21] The low-molecular-weight fraction (approximate DP range 10 to 60) contain principally

linear chains, presumably originating from amylose and the outer chains of amylopectin. The high-molecular-weight fraction of maltodextrins is capable of forming gels, unlike the amylopectin from which it derived. The gelation of pure amylopectin occurs more slowly than the gelation of amylose and seems to involve formation and subsequent crystallization of helices over a length of DP.[15,34,54,112] Such studies clearly indicate that the linear low-molecular-weight fraction must be sufficiently involved in the network structure of the polysaccharide and can facilitate structuring of branched species. Finally, the initial phase of the interactions between linear and branched molecules, the rapid aggregation, and the network formation are generally followed by a long period of slow structural rearrangements, strongly dependent on concentration and chain length (Figure 3).[121]

The above conclusions deviate from the models presented on pure high-molecular-weight amylopectin-amylose systems,[89] where incompatibility has been shown. Other authors, therefore, attribute the gelation properties of maltodextrins to the mutual incompatibility between linear and branched chains as are amylose and amylopectin chains.[41] The composition of maltodextrins, however, and the interacting components, deviate from the model results on the pure mixtures. It is also known that amylopectin in the amylose-amylopectin water system can favor the formation of amylose aggregates, which are the structural elements for maltodextrin gels.[52,121] Earlier suggestions also deduce that the structural elements inmaltodextrin hydrogels are connected to weak, unstable structures by secondary forces.[19]

It should be noted that the association between specific side chains, aggregation

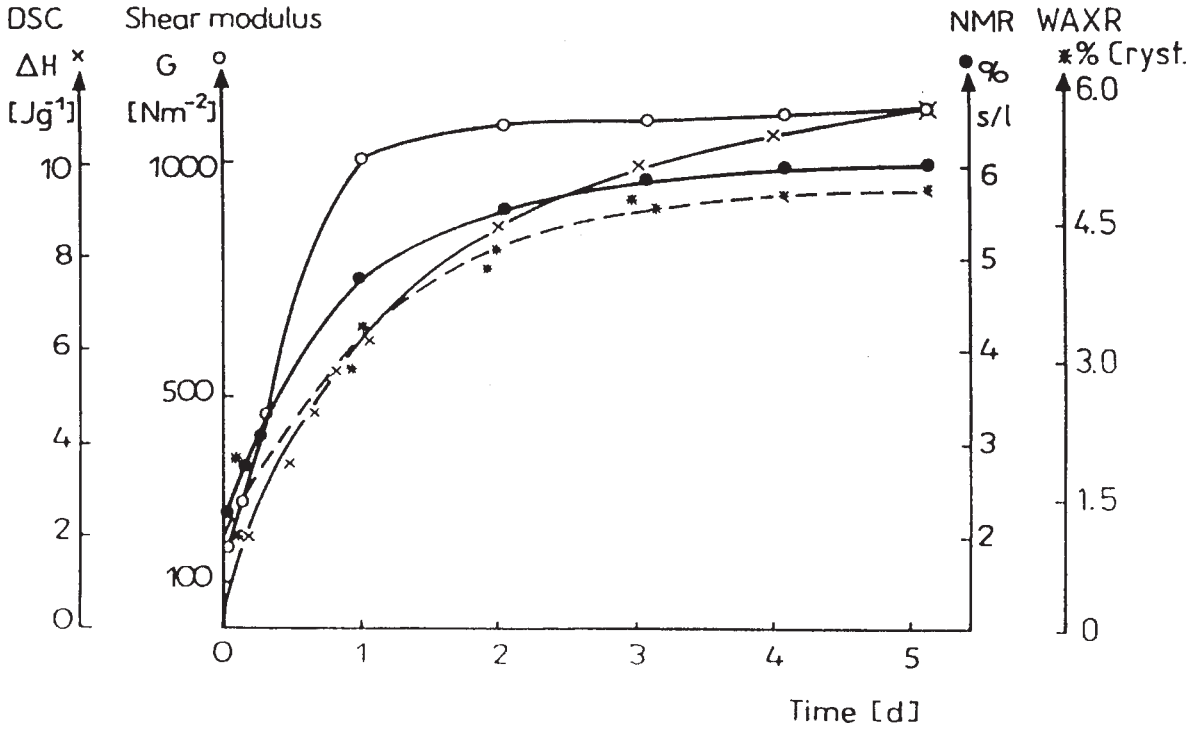


FIGURE 3. Time dependence of sol-gel transition of maltodextrin-solution as characterized by low-resolution NMR (●), wide angle X-ray scattering (*), shear modulus (○), (20% w/w), and DSC-measurements (8% w/w) (x). (From Ref. 121 with permission.)

production, and gel formation was accelerated in the presence of partially disintegrated amylose, rather than in the presence of amylopectin disintegration products.[119,121] The effect is more pronounced in the low concentration systems, while in the nongelling solutions amylose as well initiates the formation of a gel structure. These observations confirm the suggestion that the linear fraction in the dissolved state is responsible for initiation and acceleration of gel formation. It seems reasonable then to conclude that 'compatibility' between soluble amylose and branched chain molecules resulting in the formation of a mixed maltodextrin gel structure.

The peculiar gelling properties of maltodextrins were attributed to preferential α-amylase action in the amorphous region of the starch granule, leading to extensive hydrolysis of amylose but only to a partial hydrolysis of amylopectin.[21] Hydrolysis by α-amylase before and during gelatinization of starch is likely to occur preferentially in the amorphous regions of the granule because of the protection provided by self-association of chains in the crystalline regions. In addition, low cooperativity of interactions as well as low molecular α-glucosidic chains may be responsible for this type of gel behavior.[22,29,54,120]

V. MICROSTRUCTURE ORGANIZATION OF MALTODEXTRINS NETWORK

As provided by small and wide-angle X-ray scattering, the maltodextrin gels, independent of DE and carbohydrate profile, contain crystalline structures. The regions have the same crystalline structure as B-polymorph seen in naturally occurring starches of tubers and roots, including samples of aggregated so-called retrograded starch.[49,107,108,120] The crystalline regions in starches are generally supposed to be due to the crystallinity of the amyloses, which also applies for maltodextrin gels. These crystalline domains consist of right-hand-ordered double helices aggregated into disc-like electron density inhomogeneities with maximum diameter of 280 nm, height (thickness) between 28 and 36 nm, and radius of gyration 89 nm (Figure 4).[107] The anhydroglucose units in these double helical arrangements packed in a hexagonal unit cell ($a = b = 1.85$ nm, c (fiber repeat) = 1.04 nm, $a = b = 90°$ $\gamma = 120°$).[115]

Nevertheless, the crystalline domains in the disk-like regions are not consist of ideal crystals, but lattice distortions exist in the interior of the inhomogeneities that are composed of many microcrystallites. Approximately 10 to 16% of the carbohydrate chains may be involved in these crystallites,[121] which are 16 to 17 μm in size, independent of concentration.[49] Branching of the polysaccharide chains should cause such lattice distortions. The crystallites are embedded in a phase containing the noncrystallising parts of maltodextrins, which contain amorphous polymer chains and water. The majority of the water between the crystalline domains is bound water. However, in spray-dried maltodextrin powder and in the nongelling systems crystalline structures cannot be detected.[108] Other conclusions support that amylopectin makes up the crystalline regions of the maltodextrins, as they are in a less-degraded form than amylose molecules.[21]

With increasing concentration of maltodextrin, a higher order is developed in the gel. Nevertheless, the crystallite sizes and the crystallinity of maltodextrin gels as calculated from two different reflections of X-ray diffraction measurements do not depend on the concentration of the polymer (Table 2).[51] Therefore, increasing the content of maltodextrin in the system should not modify the concentration and the structure of aggregates but further increases only the number of structural elements.[58] As previously discussed, the mobility of water inside

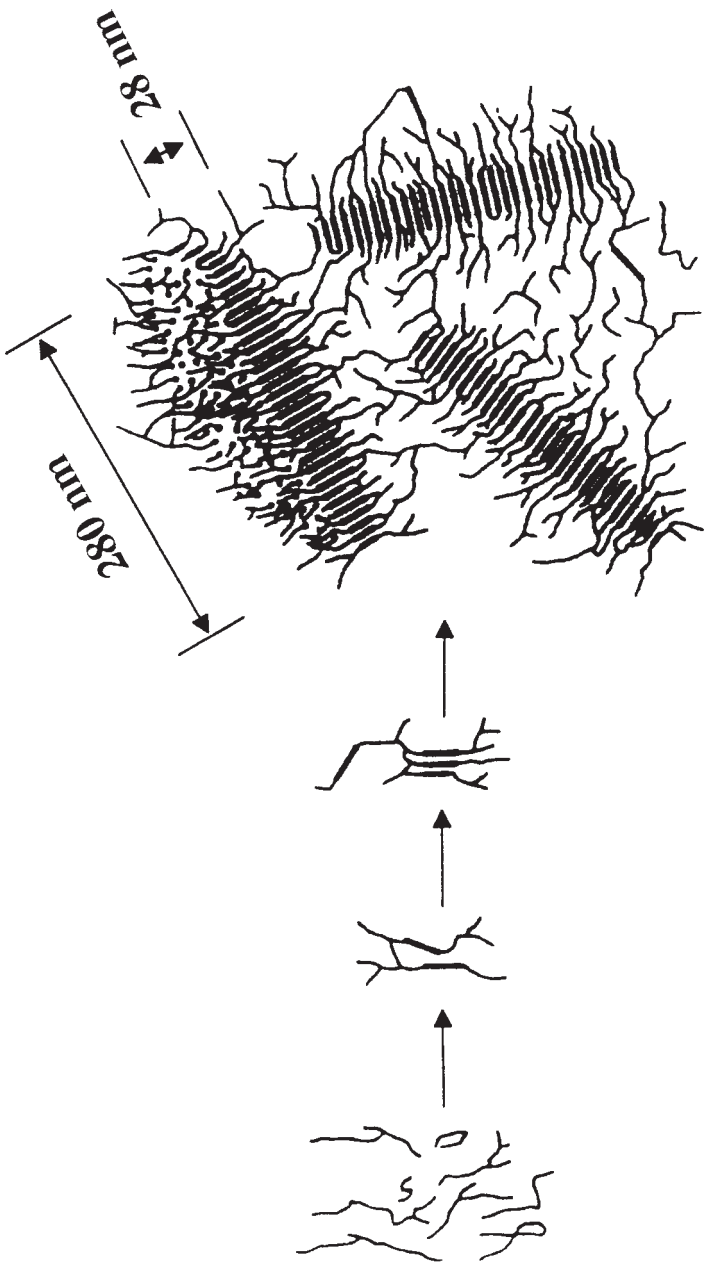


FIGURE 4. Structural model of the maltodextrin gel (the discs are drawn in profile). (From Ref. 107 with permission.)

TABLE 2
Crystallite Size *L(hkl)* Calculated from Two Different Reflections and Crystallinities (β) of Maltodextrin Gels of Different Concentrations as Observed from X-Ray Diffraction Measurements

%w/w concentration	*hkl*	*L*, nm	β, arbitrary units
30.2	100	12.0	1.00
	121	8.4	
30.7	100	12.0	1.05
	121	7.7	
34.0	100	12.0	1.10
	121	8.4	
36.9	100	14.0	1.25
	121	8.4	
38.8	100	12.0	1.30
	121	7.7	
39.4	100	12.0	1.45
	121	8.4	
43.5	100	12.0	1.45
	121	7.7	

From Ref. 51 with permission.

and outside these aggregates is different, while such aggregates may interact with each other to give rise to structures of higher order. Information on the shape of gel-forming molecules was also obtained by the measurements of electron microscopy (Table 3). The structural elements seem to have the form of rotary ellipsoids, whereas substructures have a globular form.[50,118]

VI. RHEOLOGICAL PROPERTIES

A. Single Systems

1. Low-Amplitude Oscillatory Studies

The relatively low molecular weight of maltodextrins makes them very soluble, and solutions can be prepared at 50% w/w solids. Depending on the concentration and the DE value, preparations range from opaque solutions and pastes to thermally reversible gels.[117] Recently, the gelation of malto-dextrins as a function of DE, setting temperature, and polymer concentration have studied.[29,88,66-69] It was found that the temperature dependence for the formation of a self-supporting gel was effectively independent of DE, thus suggesting a similar pattern of intermolecular bonding for the network-forming chains. By contrast, a sharp increase in the concentration dependence of gel formation with decreasing degree of polymerization emphasized the necessity for long, linear macromolecular chains, serving as nucleation sites, for the development of a continuous structure.

Using a theoretical approach developed by Clark and Ross-Murphy,[32] the network formation of various maltodextrins has been studied. By this method the modulus can be fitted with the concentration by the following mathematical expression of the cascade formalism:[33]

$$G' = g\frac{cRT}{M}\left[f\alpha(1-\nu)^2(1-\beta)/2\right] \quad (1)$$

In this equation g = 1 for an ideal rubber,[45] and the factor takes higher values for biopolymer systems where there is a sub-

TABLE 3
Structure Forming of Maltodextrins-Solutions As Revealed by Transmission Electron Microscopy

	Concentration		
State	**15%**	**20%**	**25%**
80°C-solution	Without any structure, single microspheres 40 to 60 μm		
3 h/6°C weak gel	Microspheres Very small chains	Microspheres ~50 μm chains, incomplete combs	Microspheres ~20 nm comb-like structure 0.6 to 2 nm
24 h/6°C gel	Microspheres 30 to 40 μm incomplete combs and clusters 2 nm	Microspheres 20 to 30 μm combs and clusters 3 to 5 nm	Microspheres 20 to 30 μm thick-walled combs and clusters 2 to 3 nm

Note: The differences of the crystallite sizes in accordance with the vlues from previous Table 2 was attributed to different sample preparations techniques.

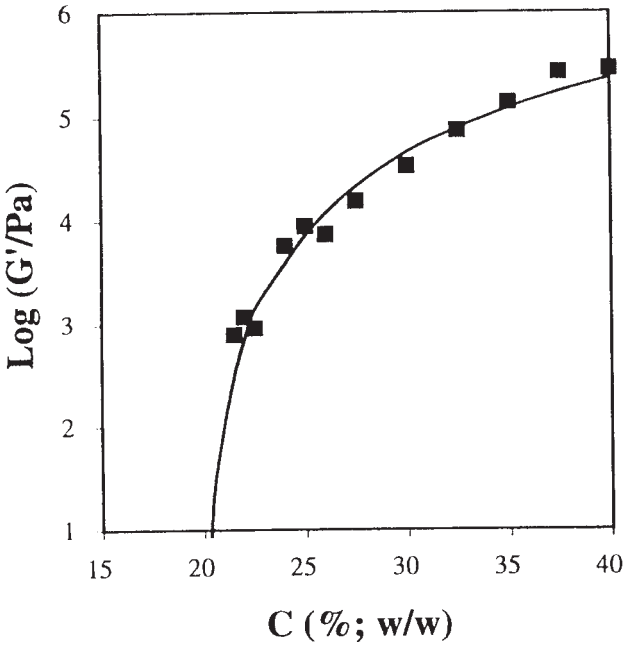
From Ref. 118 with permission.

stantial enthalpic contribution to the elasticity of the network.[32] The term RT refers to the change of entropy per mole of network chains, and the ratio of c to M is the number of moles of polymer per unit volume. The theory also assumes that only a fraction (α) of the available bonding sites (functionality, f) will react, and of those a proportion (extinction probability, ν) will be unable to support the imposed stress, with the parameter β being a function of α, fm and ν. Furthermore, the thermal reversibility of physical cross-links was taken into account by introducing a dimerization reaction between free and associated sites, determined by an equilibrium constant K, and a minimum critical gelling concentration (co) below which the biopolymer is unable to form an infinite network:[61]

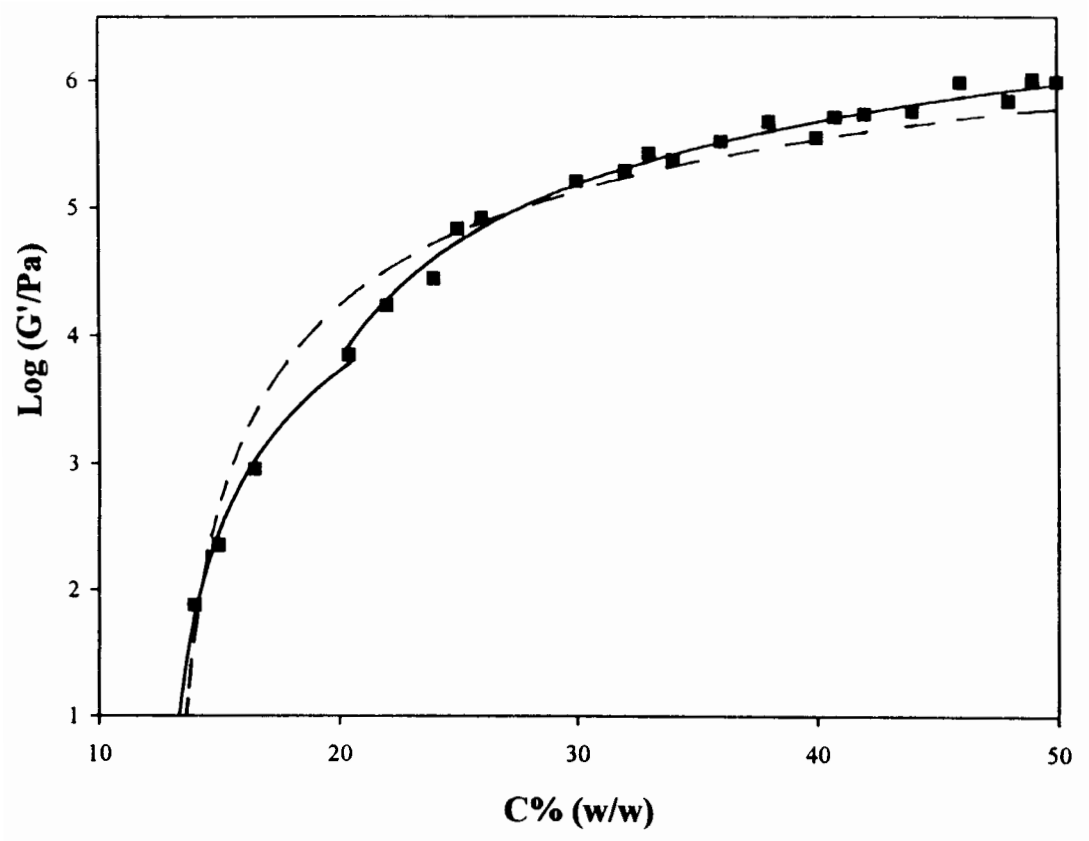
$$c_o = M(f-1)/Kf(f-2)^2 \qquad (2)$$

The least squares fit to the experimental points is shown as a solid line in Figure 5a. A good quality cascade fit for the SA-2 gels produces a high value of co (about 20.2%), a result that is expected due to the short polymeric chains(DP ≈ 35). In accordance with the small degree of polymerization of maltodextrin chains, the application of cascade model suggests that there are on average 2.7 functional points per molecule, a value that is well below the functionality ($f \geq 10$) used to describe the network formation of high-molecular-weight gelatin or agarose samples.[31] On the other hand, the interplay of entropic-enthalpic forces in the malto-dextrin associations produces a highly enthalpic network (g = 3.8), when compared with the more entropic nature of other biopolymer gels.[28,29,66] Overall, the highly ordered enthalpic aggregates, whose microstructure bears no resemblance to that of an entropic rubber network, are in agreement with the idea of crystalline domains in a maltodextrin gel.[107]

The molecular weight distribution is also determining the concentration dependence and the rheological properties of maltodextrins. A commercial potato maltodextrin sample (Cerestar, 1906) where the chromatogram shows that there is a core of high



A



B

FIGURE 5. (a) Concentration dependence of G′ (0.1 rad/s) for SA-2 maltodextrin gels at 5°C. The solid line traces a cascade fit with the following parameters: g = 3.8, f = 2.7, and c_o = 20.2%. (From Ref. 88 with permission.) (b) The blending of two cascade treatments in a concentration-storage modulus continuum for the maltodextrin gels. The dashed line shows an earlier attempt to fit the full set of points with a single cascade treatment. (From Ref. 29 with permission.)

molecular weight chains (about 6% between 2×10^5 and 5×10^6) was also investigated under dynamic oscillation measurements.[29] These chains are capable of forming ordered nuclei for the development of a three-dimensional network. Shorter chains are not likely to participate in the initialization of multifunctional junction zones, with an average helix length of about 70 residues being required for commencing of the nucleation process.[34] However, it was found that linear oligomers with a MW down to 1000 can crystallize with segments of preformed helices thus contributing to the mechanical strength of the network.[54] Therefore, the effect of addition of short species is significant for this batch of potato maltodextrin because it contains about 32% more material than the typical preparation within the MW range from 1000 to 5000, that is, for molecules of 7 to 35 glucose units. The two-step development of shear modulus as a function of concentration in Figure 5b is due to the transition from high-molecular-weight assemblies to large aggregates comprising long helices, and short linear and branched chains. The algorithm of the cascade model (Eq. 1) also fit the two curves. These experimental and calculated evidences are entirely consistent with the proposal of thermally stable long helices acting as the structural units of this maltodextrin network, which, however, encourages at high levels of solids the close packing of shorter, thermally metastable segments around the central core of helices.

The length and therefore the stability of these associations is limited by the length of the shorter partner, which converted to the disordered state at lower temperatures than their longer counterparts, hence producing the two-tiered melting profile of Figure 6. Along these lines, the first wave of structural

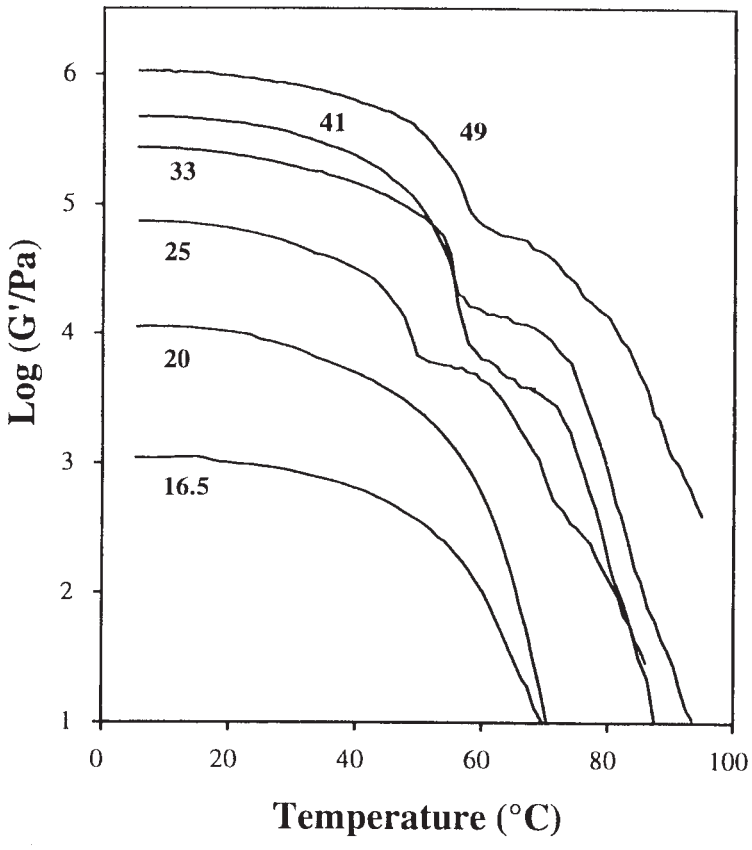


FIGURE 6. Controlled heating of maltodextrin gels (% w/w) from 5 to 95°C at a scan rate of 1 deg/min (frequency of 1.6 Hz; 1% strain). (From Ref. 29 with permission.)

loss during a heating run abolishes the bulk of peripheral associations leaving intact the intermolecular associations of long strands. Therefore, networks at the beginning of the second melting process should comprise sparsely cross-linked structures of high-molecular-weight chain segments in the manner envisaged for maltodextrin concentrations of 20% and below.

In another commercial sample, like Paselli SA-6, Lycadex, and Optagrade maltodextrins, the elastic moduli (G′) has been found to vary linearly with the concentration (do not follow the cascade algorithm).[30,66] Probably, shorter SA-6 chains (compared with the higher average chain length of SA-2) create a network in a different way by agglomeration of aggregated helices with dominant frictional forces between adjacent particles of aggregated helices ($c_o \approx 10\%$ w/w). The data for Optagrade is also entirely different in form. Network development was not obtained at concentrations below ≈13% w/w, and the concentration dependence with the logarithm of the elastic modulus could be fitted by two different straight lines.[30] A possible interpretation of this difference arises from the fact that Optagrade is a mixture of maltodextrin and corn starch. Extended chains create the long range structure by agglomeration of aggregated helices among the short helices and starch granules, producing a more heterogeneous arrangement. Similarly a nondendric structure may be presumed for the Lycadex maltodextrin but the critical gelling concentration is much higher (27% w/w).[30] The botanical origin may be also responsible for differences found in gelation kinetics. For instance,[41] Paselli SA-2 (DE 2.8) from potato starch and N-Oil II maltodextrin (DE 3-5) from tapioca starch are clearly true gels with comparable properties, however, the kinetics of gelation was dramatically different. Thus, under the same conditions and dispersions concentrations, SA2 maltodextrin show gelling behavior after 35 h, while for N-Oil II was after 15 h. The cloudness observed was attributed to a liquid-liquid phase separation between linear and branched chains due to mutual incompatibility that appeared relatively quickly in both systems. Individual studies also found linearity between the dependence of shear modulus with a concentration of maltodextrin for only a limited range (15 to 25%). Beyond this limiting concentration there is a maximum aggregate density, whereas the number of structured crystallite components are increased further.[132]

As a final point, it is evident that the botanical origin and the production procedures are particularly responsible for the differences in the structural and functional properties of maltodextrins networks that drastically related to the final product properties. Further studies are needed in order to understand the factors determining the differences in the gel structure and in the viscoelastic properties of various origin maltodextrin systems.

2. Creep and Stress Relaxation Measurements

Under creep studies maltodextrins show a typically relaxation behavior of thermally reversible polysaccharide and proteins gels. Nevertheless, two different patterns of behaviour observed on passing from concentrated to dilute gels.[51,52] In very concentrated gels the rate of relaxation process are identical, independent of the concentration (the irreversible deformation amounts to about 2%). In this case an increase in the content of polysaccharide in the system results only in an increase in the number of structure elements, while the concentration within each element stays unchanged.[51] In dilute gels the rate of relaxation depends on the concentration (the extent of irreversible deformation is about 7%) and indicates that the systems become more uniform at lower

concentrations. Such differences cannot be detected from the NMR data, possibly due to differences in the volume of the structure elements, which determine the rate of relaxation in these methods. The same relaxation properties were observed for amylopectin-amylose-water mixtures at ageing times of 2 and 48 h after the preparation of gels.[52] In particular, the mechanical-relaxation rates of a constant 5.5% w/w amylose mixture containing increasing concentrations of amylopectin (0 to 40% w/w) were studied. At concentrations of amylopectin in the range 0 to 5.8% and above 12%, there is little concentration-dependence, while at the same time that the concentration of amylopectin ranges from 5.8 to 12% the relaxation rates increases. Such differences in relaxation time could be explained as the result of a variation in the interaction between aggregates, the structural elements of the system. A similar complex character was also obtained in amylose, amylopectin, and their mixtures from the spin-spin relaxation time of water molecules using pulse NMR.[52] Nevertheless, the level of molecular structure that is involved in the relaxation of stress or creep effects cannot be established yet.

3. Large Deformation Properties

Variation of gel strength under compression of maltodextrins show a rapid increase in yield stress with increasing concentration.[21] Below a certain concentration (i.e., 25% w/w) the gels remain elastic after compression, while at higher concentrations the gels are increasingly more brittle and fragment after compression. This is indeed another indication that at higher concentrations part of the polysaccharide is acting as a filler within the gel network, rather than being involved in the tertiary structure, as previously addressed. Generally, higher concentrations of maltodextrins tend to be more brittle, while lower concentrations have a 'slimmy' rather than a creamy character. Their short, pseudoplastic texture was attributed to the low degree of association among the aggregates of submicron particles (about 0.02 μm), when compared with continuous, polymer gel networks that many gums form.[108]

Nevertheless, investigation of the behavior of maltodextrins under compression testing in existent food systems is more complicated. The processing of various product applications (dairy mixtures, low-fat spreads, etc.) is usually achieved within the temperature range of 60 to 75°C from which the polymeric ingredients dissolve or denature without undue depolymerization.[93,94] However, recent work on water continuous low-fat spreads, in which maltodextrins are used as structuring ingredients, suggests that the aforementioned thermal treatment cannot properly dissolve the starch hydrolysates.[27] Checking the effect of temperature on hydration at various maltodextrins dispersed in water at 75°C, it was found that the polymer content was 75 ± 2% of the original maltodextrin concentration. This may even explain why inconsistent results were obtained among HTST-treated maltodextrins (90°C for 15 s), with samples left for 5 min at 85°C. During cooling spreads from the second preparation are stronger (almost by 5 kPa) than those cooled directly to ambient temperature, because additional stress-bearing maltodextrin chains become soluble.

The mechanical properties of the dissolved fraction of maltodextrin chains and their contribution to the overall network strength were evaluated by analyzing them after compression testing. As shown in Figure 7, samples showed very weak structures, reminiscent of thick viscous products. It seems that the polymeric fraction dissolved at 75°C is comprised of low-molecular-weight maltodextrin chains that do not adequately develop the elastic component of a

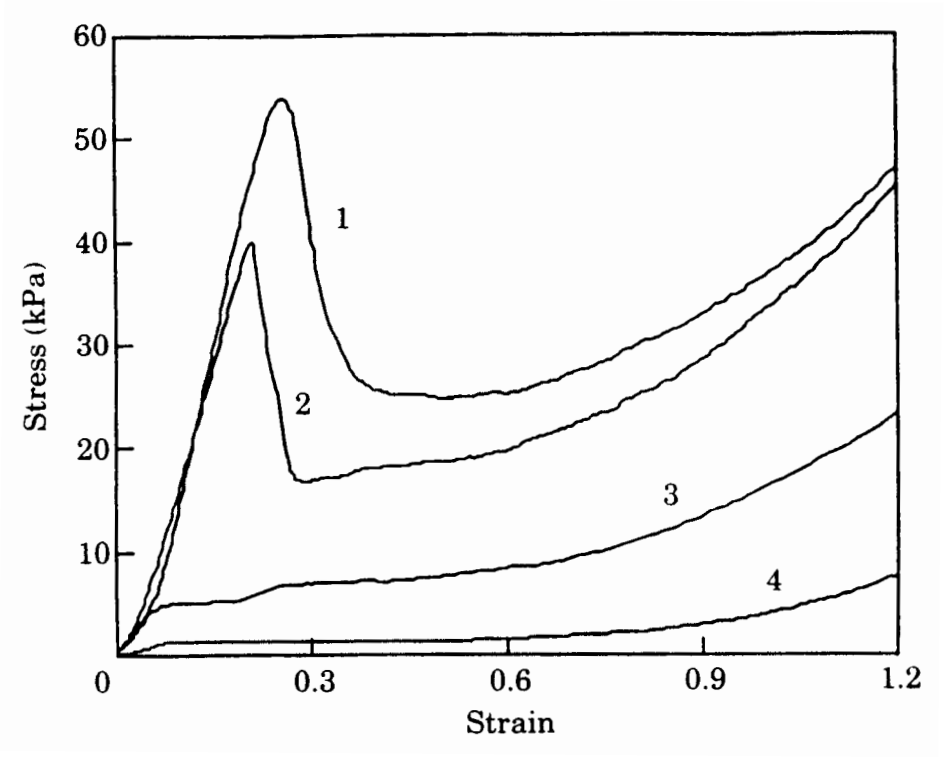


FIGURE 7. Force-deformation profiles of 250 g/kg maltodextrin samples dissolved at 95°C for 15 min (1), dispersed at 75°C and HTST treated (2), dispersed at 75°C and centrifuged (3450 g, 30 min) to produce a precipitate (3), and a supernatant (4). Before the compression analysis samples were left at 5°C for 24 h. (From Ref. 27 with permission.)

network structure. The tightly packed swollen particles of the precipitate, however, show some structure that clearly distinguishes them from the liquid-like response of the supernatant, with the matrix managing to withstand compression up to ≈7 kPa in a rather discontinuous breaking pattern due to the absence of a homogeneous network. By contrast compression of the samples, which have been completely dissolved at 95°C, gives the sharp breakdown profile typical of strong biopolymer gels, thus emphasizing the importance of the remaining 25% of undissolved maltodextrin to the formation of an integral network. Further attempts to see if pasteurization (HTST treatment) reclaims any of the undissolved polymer indicate that maltodextrins are not dissolved completely by this process (only about 74% of the structure is recovered in Figure 7).

Incomplete dissolution of maltodextrin during commercial production, however, might have a beneficial effect on the rate of structure formation on cooling. As discussed previously, it has been shown that retrograded amylose can accelerate gelation of hydrolyzed potato starch, with its linear chains facilitating nucleation and then cooperative association with the branched, shorter structures of amylopectin.[119] Because a fraction of the maltodextrin sample remains undissolved during a conventional HTST treatment, its appropriateness as a seeding material in product development was also investigated.[27] The presence of ordered structure in a maltodextrin solution reduces the gelation time dramatically, by almost 50%. However, it remains to be seen if inclusion of a small amount of seeding amylose or maltodextrin in the aqueous phases becomes

an extra help in the product development and how this factor could be involved in product applications.

B. Steric Exclusion Phenomena in Mixed Maltodextrin-Biopolymers Systems

The studies of maltodextrin with systems such as gelatin, sodium caseinate, and milk protein have been investigated extensively in order to gain a better understanding of the macromolecular organization and the phase structure of binary systems relevant to the food industry.[29,68,69,88] Mixed solutions show signs of bulk phase separation after centrifugation at temperatures where the individual components remain stable as disordered coils. Thus, concentrated preparations resolve into two liquid layers at equilibrium whose composition defines a cloud point curve, or produces an insoluble maltodextrin precipitate.

1. Blending Laws

Recently, some progress has been made in the understanding of how biphasic gels behave in terms of phase continuity, phase inversion, and, above all, solvent distribution between the two phases.[25] It is based on the assumption that either bulk phase separation to equilibrium takes place first with gelation then occurring subsequently and independently in each phase or the fastest gelling component does so prior to the establishment of a true thermodynamic equilibrium with subsequent gelation of the second, slower gelling species. A number of theoretical treatments from the realm of synthetic polymers were adapted for use in biopolymer networks, namely, (1) the application of blending laws to the phase separated biopolymer gels was attempted, taking into account the complication of solvent presence as a third component that can partition itself between the two polymer constituents, (2) the modulus development as a function of concentration (cascade formalism) was derived from the relationship between equilibrium shear modulus and number of elastically effective network chains considering that gel formation due to noncovalent interactions between biological macromolecules is described by a monomer-dimmer equilibrium, and (3) the Flory deswelling theory was applied to biopolymer gels assuming permanent networks on the basis of stress relaxation and dynamic oscillatory evidence.

The mathematical modeling of small deformation modulus of binary gels has been attempted initially, as a function of changing polymer composition in the blend, by Clark and co-workers.[31] It related the mechanical properties of the composite and bulk components via the equations of the Takayanagi "blending laws":

$$G_c = \phi G_x + (1-\phi) G_y \qquad (3)$$

$$1/G_c = \phi/G_x + (1-\phi)/G_y \qquad (4)$$

where G_c, G_x, and G_y are the moduli of the composite, X-phase and Y-phase polymers, respectively, and f is the volume of phase X. For $G_x > G_y$ and the polymer X forming the supporting matrix the above approach gives an isostrain or upper bound behavior (Eq. 3), whereas phase inversion in the system, with the polymer X being now the discontinuous filler, results in the so-called isostress or lower bound model (Eq. 4). The analysis also measured the "relative affinity" of two polymers for water in a composite gel, assuming a thermodynamic equilibrium between the two gelled phases, and uses a parameter p that divides the ratio of solvent fraction in one phase (Sx) to the original (nominal) concentration of the appropriate polymer (x) by the corresponding ratio of the other polymer ($1- S_{x,y}$):

$$p = \left(S_x / x\right) / \left(\left[1 - S_x\right] / y\right) \qquad (5)$$

However, if a permanent gel network is formed at one concentration and then taken to a different concentration by introduction or removal of solvent (swelling or deswelling), the initial and final moduli (Gi and Gf) are related to the initial and final concentrations (ci and cf) by:

$$G_i / F_f = \left(c_i / c_f\right)^{2/3} \qquad (6)$$

The relevance of this behavior to analysis of mixed gel moduli is that unless the system has already separated into discrete phases in the sol state, the first component to gel will do so at its original, nominal concentration across the whole system. Subsequent gelation of the second component within the pores of the existing gel will then create a separate (discontinuous) phase, making a portion of the solvent unavailable to the polymer in the original (continuous) network. This removal of solvent can be regarded as 'deswelling' of the continuous network, raising its modulus, but to a value substantially lower than would have been attained if phase separation to the same phase volumes had occurred prior to gelation.

2. Gelation and Distribution of Water in Binary Systems

Recent investigations on systems of direct practical relevance, which one component of is maltodextrin, has shown evidence of formation of biphasic gels by both mechanisms as discussed above (i.e., phase separation followed by gelation and formation of a second phase within an existing network).

From Figure 8 it is evident that low protein concentrations in the blend allow the maltodextrin to form a weak network surrounding the stronger inclusions of protein particles, whereas at higher levels of sodium caseinate (above 12.5%) a weak protein structure is created that is capable of suspending the stronger maltodextrin particles.[88] In Figure 9 the calculated bounds and the experimental results from Figure 8 have been replotted as a function of the parameter p using Eq. 5. Modeling of the rearrangement of water between the two polymeric constituents has demonstrated that the water partition values are profoundly affected by the phase inversion in the co-gels. Clearly, the amount of water held in each phase changes dramatically as the system goes through a phase inversion. With maltodextrin as the continuous phase, the polysaccharide keeps one and a half times more solvent than the protein ($\log p \approx 0.17$; $p \approx 1.5$). When the macromolecular maltodextrin assemblies are incorporated in a discontinuous arrangement (filler); however, the caseinate molecules manage to invert the solvent-to-polymer distribution in each phase ($\log p \approx -0.19$; $p \approx 0.6$). In particular, the proportion of solvent associated with the maltodextrin phase is reduced, as it ceases to be the supporting phase and becomes the discontinuous filler. Obviously, water diffuses in the anisotropic medium seeking osmotic equilibrium, but the decline in the amount of solvent kept in the maltodextrin phase with the reduction in its surface-to-volume ratio (following phase inversion) argues for mixed gels trapped kinetically from equilibrium solutions. Otherwise, the equilibrium value of 'relative affinity' of the two polymers for water should not be affected by the geometrical rearrangement of their phases in a binary mixture.

The theoretical postulate of initial phase separation and subsequent gelation of the two components separately in their own phases has been shown to describe well the steric exclusion phenomena between a commercial milk protein and maltodextrin.[29] The formation of milk protein or maltodextrin continuous gels allowed the resolution of two different patterns of water distribution in the blend. Solvent fractions derived from

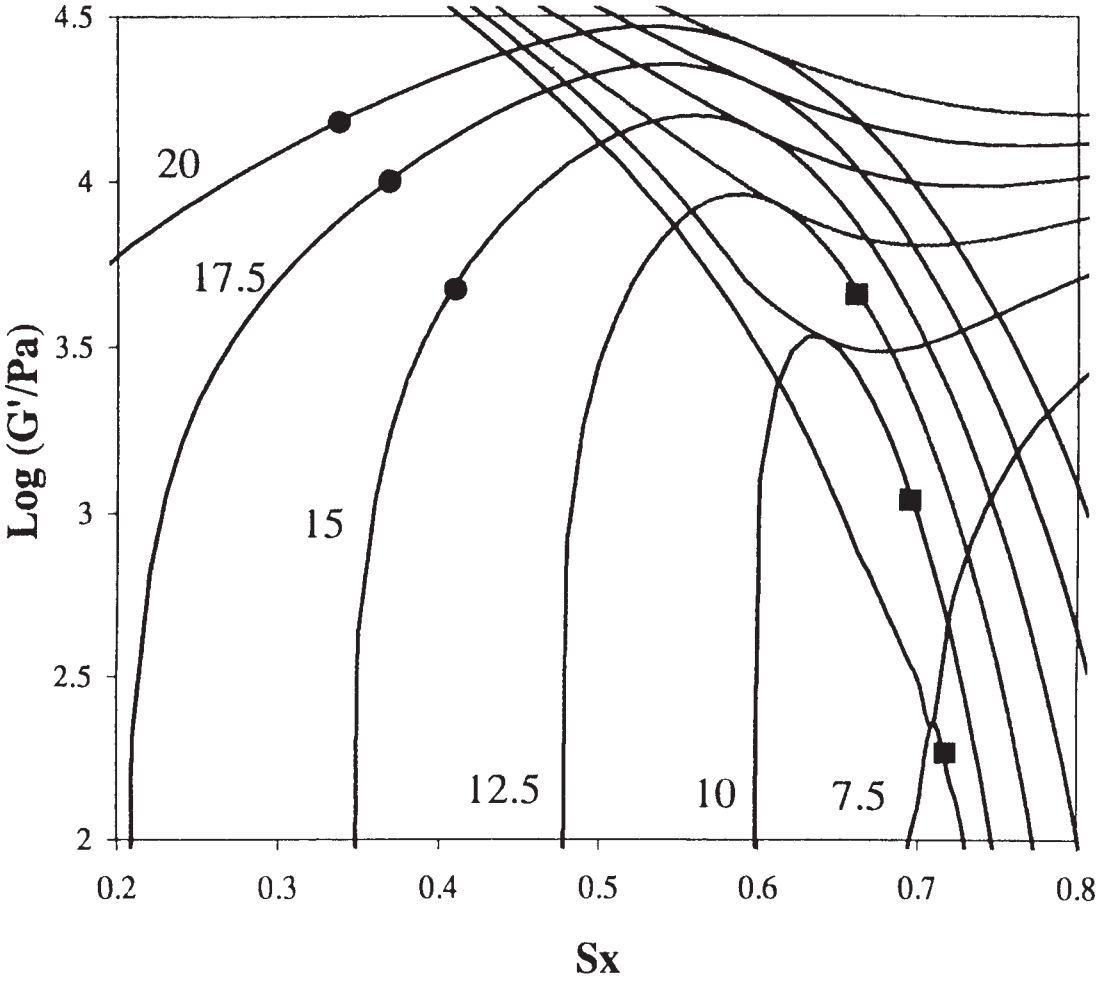


FIGURE 8. Reproduces the computerized output of calculated bounds for the 15% w/w SA-2 maltodextrin series with sodium caseinate (SC) plotted against the solvent fraction in the SA-2 phase (polymer X). Composite bounds of a maltodextrin continuous network run from the top left to the bottom right corner of the graph, whereas composite curves for a caseinate continuous phase stretch from the bottom left to the top right corner of the same figure, with both traces crossing at a single point ($G_x = G_y = Gc$). Experimental points are marked on the maltodextrin (■) and sodium caseinate (●) continuous bounds. (From Ref. 88 with permission.)

the calculated upper and lower bounds were used for analysis of water partition between the two phases, yielding $p \approx 1.7$ ($\log p \approx 0.23$) for the intercepts in the milk-continuous systems, whereas the data beyond the phase inversion point (maltodextrin-continuous systems) are better fitted with a value of $p \approx 1.1$ ($\log p \approx 0.04$). In particular, the proportion of solvent associated with the milk protein phase is reduced as it ceases to be the supporting phase and becomes the discontinuous filler. A simple explanation of this behavior is that the water-binding capacity is not only a reflection of the individual properties of each polymer, but also depends on the geometrical organization of the composite's microstructure. Because it has been demonstrated that the maltodextrin inclusions are spherical (Figure 10), it has been proposed that the increase in the amount of solvent associated with the maltodextrin phase is due to phase inversion, and the ensuing increase in its surface-to-volume ratio as the water tries to diffuse in the anisotropic

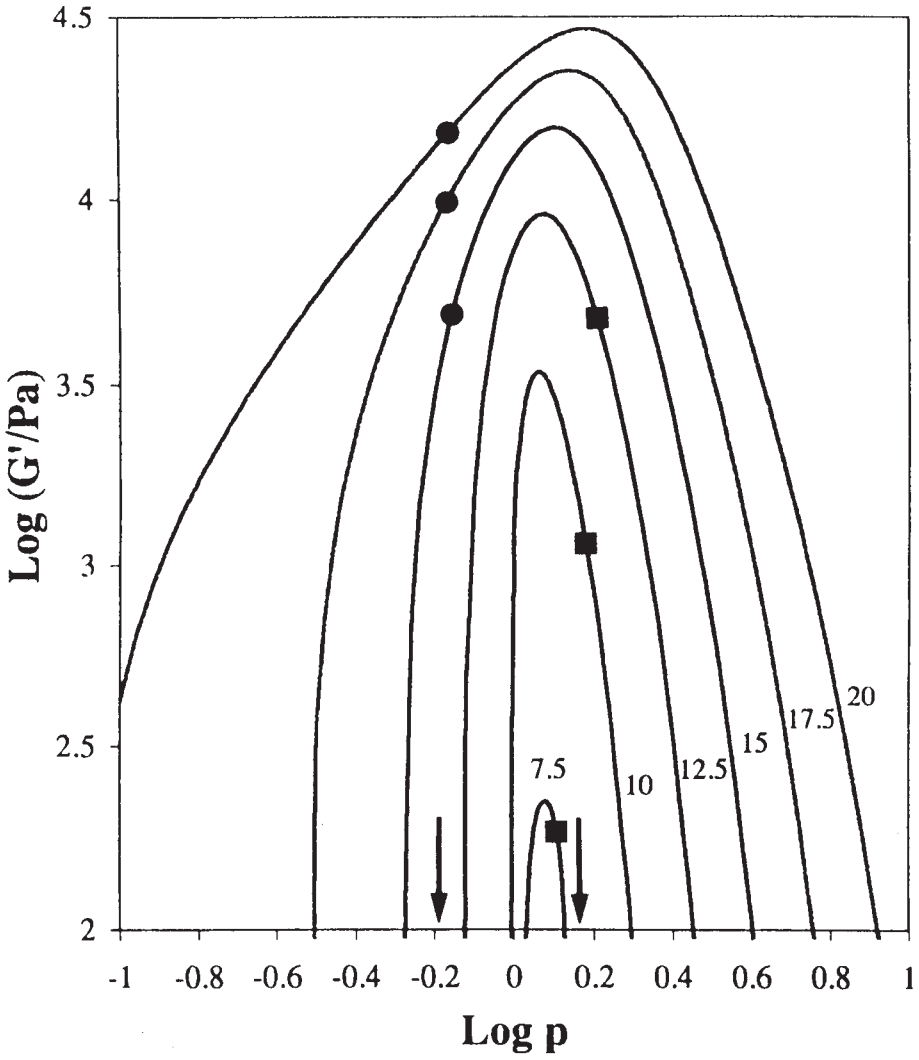


FIGURE 9. Calculated lower bounds for the composite mixtures of 15% w/w maltodextrin series as a function of log p, with the concentrations of sodium caseinate (%) plotted to the right of the corresponding bounds. Experimental moduli are plotted on the maltodextrin (■) and sodium caseinate (●) continuous bounds and relative values of solvent partition at both sides of the phase inversion point are indicated by the arrows. (From Ref. 88 with permission.)

medium.[29] Obviously, by accepting diffusion to osmotic equilibrium as the mechanism behind water rearrangement, the approximately round-shaped filler would expose relatively less surface for a given volume, thus reducing its 'intrinsic' relative power of attraction for solvent. Moreover, it follows that the difference in p values is the result of phase-separated gels trapped away from equilibrium conditions, because the equilibrium value of "relative affinity" of the two polymers for water should not be affected by the geometrical rearrangements of their phases in a binary mixture.

Furthermore, the kinetic ('deswelling') approach to explicit analysis of water partition between two demixed polymers has been utilized to describe the cold-setting aqueous preparations of thermally processed gelatin/maltodextrin[68,69] and that, in the hydration state, form similar species of comparable functionality.

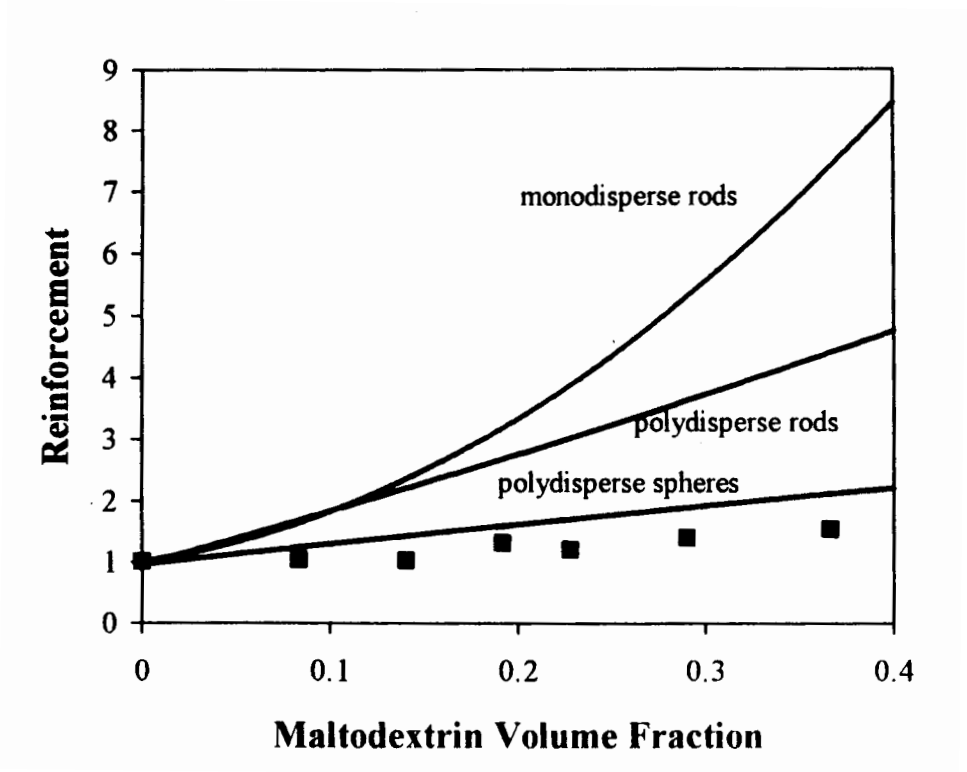


FIGURE 10. Reinforcement (Gcomposite to Gmatrix) of maltodextrin at concentrations between 0% and 12% embedded in a milk protein gel matrix. Comparison of the experimental results (■) with the predicted behavior obtained from the Kerner equation for spherical, plate, and rod-like inclusions of maltodextrin filler in the composite gel. (From Ref. 29 with permission.)

Overall, the appearing picture of the effect of polymer conformation on the state of phase separation in binary mixtures relevant to the food industry has as follows:[24,29,68,69,88] conformationally similar species in solution like the disordered coils of gelatin and maltodextrin tolerate each other at low concentrations in a monophasic solution. During cold-setting, the faster-gelling polymer in each mixture develops its continuous network prior to ordering of the second component. Maltodextrin after ordering claim extra solvent and as a result deswell to a certain extent the protein network, but the systems remain under kinetic control with slow diffusion of water from the faster to the slower setting component with time. In both systems, at higher concentrations (i.e., at combinations above the phase inversion point) the kinetic effect is swamped by the enthalpic disadvantage of polymer segments being surrounded by others of a different type and phase separation occurs in solution. This persists in the gel state and produces a single pattern of water partition throughout the concentration range, but it is difficult to say if the systems have now reached thermodynamic equilibrium.

Dealing with the question of kinetic influences vs. thermodynamic equilibrium, it has been demonstrated that thermodynamic incompatibility between the conformationally dissimilar species of thermally unfolded globular molecules of milk protein and disordered chains of maltodextrin promotes an early phase separation in solution and then in the gel state, that is, at both sides of the phase inversion point. As a result, there is an immediate reinforcing effect of the maltodextrin filler on the milk protein gel that was not observed in the case of gelatin and maltodextrin, where composite values

below the phase inversion point remain close to that of the continuous gelatin network at its nominal concentration. Hence, above all, both deswelled and phase-separated networks seem to be under kinetic control with the solvent continuously seeking (but not achieving within the experimental time constraints) osmotic equilibrium.

Moreover, phase separation occurs more easily with mixed maltodextrins systems with uncharged polymers (i.e., at low locust bean gum concentration), compared with the case of a charged polymer, that is, maltodextrin/carboxymethylcellulose.[7] Thermodynamic incompatibility of maltodextrins (DE 12, 17, 19) with the presence of proteins is responsibile as well for reducing the heat stability of caseinate-stabilized emulsions.[36] Enhancement of thermodynamic incompatibility was more evident at higher temperatures or at higher molar mass of polysaccharide.

The mixed gel phase continuity, phase inversion, and solvent distribution in non-equilibrium arrangements should be heavily governed by the thermal history that the blend is subjected to. Recent studies found that different rates of gelation reveal a trend in the partition of solvent between the constituent structures in the development of composite modulus, and in the polymer composition at which phase inversion occurs.[70] Rheological measurements and light microscopy work on the gelation and phase separation of gelatin-maltodextrin solutions (quench cooling and controlled cooling) confirms the shift in the phase inversion point when slow gel rates are employed. The gradual cooling diminishes the competition between gelation and steric exclusion and makes the rate of phase separation faster than that of gelation. Again, to what extent this state of equilibrium had been disturbed by gelation during cooling of the phase-separated protein solution remained largely unresolved.

Obviously, there is a straightforward positive relationship between 'performance' characteristics of the biopolymer networks and maltodextrin polysaccharide that can be used to manipulate the rheological behavior and water immobilization of one gelling agent at the expense of the other. A good understanding of the above blending laws and of the technical approaches involved will also assist the food scientist in placing the development of novel products on a sound technological basis.

3. Large Deformation Properties of Low-Fat Spreads Using Maltodextrins

The mechanical strength and the gelation rate of a maltodextrin structure on low-fat spreads depends on the molecular weight of the polymer and the heat treatment. Thus, the effect of gelling hydrolysate chainlength on the mechanical properties of water continuous spreads was recently briefly investigated by gradually replacing the control product formulation (DE ≈ 3), with lower molecular weight homologues (DE ≈ 6 or ≈8 or ≈12). The systems were further weakened in accordance with the additional reduction in the overall chain length of the maltodextrin blend (30%, 60%, and almost total loss of cohesion, respectively).[27] Moreover, it was shown that products hydrolyzed at the same dextrose equivalent (e.g.,1906 Cerestar and N-LiteD, DE ≈ 3) have a different degree of branching in the molecule and form dissimilar gel networks and dissimilar products at the same material concentrations.[30] The partition, length, and stability of less tightly packed swollen particles, that interfere in a such way that the intermolecular structure, among the contributions of high-molecular-weight fraction determine their performances.

Some background understanding of the phase behavior and rheology of the milk protein-maltodextrin low-fat spreads with and without thickening agents (such as xanthan,

locust bean gum, guar gum, fibers) and at different homogenization conditions was as well attempted.[27,30] It seems that the two gelling components exclude each other from their phases, thus forming a composite of a milk protein continuous network penetrated by the maltodextrin inclusions. It appears also to be a critical ratio of surface area to polymer concentration where the interaction between maltodextrin (and carbohydrates in general) and milk protein switches from being unfavorable (destruction of protein structure) to being favorable (enhancement of protein network) by binding flocculation.

VII. FOOD APPLICATIONS

A number of health-related organizations have issued recommendations on reducing fat and cholesterol intake levels. As a result, sales of full-fat products in EU and U.S. have been declining steadily and increased the demand for new low-fat, low-calorie products.[35,133]

Maltodextrins have the ability to form gels and retain water, and therefore are used in the food industry as a texture modifier, either for gelation, retention of water, and to a certain extent substitution of fat.[3] They perform multifaceted functions in food systems,[123] including (1) bulking, (2) providing resistance to caking, (3) adding texture and body, (4) forming films, (5) binding flavor and fat, (6) serving as oxygen barriers, (7) giving surface sheen, (8) aiding dispersibility and solubility, (9) freezing control and preventing crystallization, and (10) as product extenders. Maltodextrins are also cheaper in comparison with other major edible hydrocolloids, and their solutions have a bland flavor and smooth mouthfeel. Despite their multifunctional performance, usually the addition of hydrolyzed starch is not enough to provide the proper texture, sensory qualities, and satisfy consumers desires without the addition of other carbohydrates and proteins.

Reductions in blood cholesterol levels may be achieved by dietary changes other than replacing animal fat. For example, maltodextrin made from oats, by the action of its component beta-glucan, increases high-density lipoprotein cholesterol and decreases low density lipoprotein cholesterol. In addition, malto-dextrins are easily digested in the intestinal tract, more quickly than starch and somewhat slower than glucose, tending to elevated blood glucose levels.

Certainly, it is not in the scope of this article to give a full description of all the applications of maltodextrins in the market of food industry, thus only a brief categorized summary is given below, while more information has given elsewhere.[5,87,92,123,130] Some of the main applications are to formulate salad dressings, fillings and gravies, rehydration drinks, dairy products (including frozen desserts), meat analogues, baked goods (pastries, snacks, cakes), confectioneries, encapsulation of flavors and colorants, and in a variety of specific other products.

Maltodextrins can be used to replace oils in low-calorie salad dressings. In certain pourable and spoonable dressings, maltodextrins have combined with natural and synthetic gums such as xanthan and cellulose-based gums. A 25% maltodextrin solution can replace 30 to 50% of oil in a 30% oil spoonable salad dressing, or the malto-dextrin can be dry blended and added to the liquids in the paste portion of the formula.[123,128] Maltodextrins are easily miscible with nutritive fats and oils and give emulsions that are stable under refrigerator conditions. Lower DE maltodextrins result in a better fat binding. In frozen desserts, maltodextrins in combination with cellulose gums prevent large ice crystals from forming during freezing process and control crystallization and melt-down. Higher viscosities, higher consistency indices but less air was incorporated in ice creams with maltodextrin-based formulations.[122] Such properties might be useful in creating new

types of frozen dairy desserts. In the production of low-calorie yoghurt, organoleptic assessments conclude an acceptable quality of the products, independent of the habital frequency of consumption.[13,14]

The reduction in the amount of fat initially saw the development of spreadable products with half the amount of fat found in traditional embodiments (80% in butter and margarine), and then the formulation of dispersions with a 20% fat content. Today, very low-fat preparations have been launched to the market with a fat phase as low as 3 to 0% of the product. Naturally, to preserve the solid-like appearance of low-calorie substitutes, maltodextrins were introduced to structure the increasingly larger aqueous phase. Obviously, the disproportionate aqueous phase came to dominate the textural properties of products. The gelling maltodextrins possess brittle or elastic textural properties, food manufactures turned to mixtures of proteins or fibers with maltodex-trins.[2,20,23,30,37,84,93,94,95] The idea there was to intelligently manipulate the exclusion phenomena between polymers and to form micron-sized homogenous phases that alternate through thin interfaces in the mixture and creating a so-called plastic dispersion that imitates the smooth texture and creamy mouthfeel required.[29,30,70]

Early work by Schiavello[116] describe that maltodextrins could replace dried milk in meat analogues without a disadvantage to taste or aroma. A slight decrease in the pH values (from 5.9 to 5.5), which is obtained by this substitution favored stability of color and flavor. More recent investigations[98] have also proven that maltodextrins and dextrins interfere with meat protein gelation and produced dense, low-yielding sausages compared with textural studies of sausages containing crosslinked starches and starches with substituted and oxidized modifications. Their effects vary according to the origin of the starch, induced modifications, conditions of use, and the nature of the product to which they are added.[56,65,72] On the other hand, there are no specific investigations about the properties of mixed meat proteins with malto-dextrins.

Incorporation of maltodextrins to the 'light' bakery products (can be a gram-for-gram fat replacement) does not yet satisfactory mimic the range of functions of fat; nevertheless, this depends on the degree to which consumers accept the loss of typical characteristics.[9,10,62,123,133,134] Setser and coworkers found thick, leathery crusts in cakes containing high levels of an 18-DE corn maltodextrin and also in the combinations of maltodextrins with polyols.[123]

Maltodextrins have been proven useful to reduce Maillard reactions and used in microencapsulation of food components such as fat and oils, vitamins, minerals, and colorants.[78,85,106,114,124,125] The microencapsulated materials (core) are covered by a film coating material (wall) that protects the core but releases the contents under the desired conditions. Maltodextrins reveal important matrix forming properties in wall systems. Their surface active characteristics, however, and the low viscosity of their solutions do not promote emulsification of oil-like materials.[78] High DE molecules protected encapsulated orange peel oil against oxidation,[1] suggesting the importance of DE to the functionality of the wall system. A recent work evaluates squid oil capsule's protection from oxygen as well their thermal stability.[86] It has been suggested that capsules containing a wall material from a mixture of malto-dextrin as stabilizer, egg yolk lecithin, gelatin and caseinate show optimal protection against oxidation. The thermal stability is greater and the self-life is longer than free squid oil and encapsulated squid oil prepared without them.

The effect of maltodextrins in protecting encapsulated flavors from oxidation varied greatly. Typically, maltodextrins do not result in good retention of volatile compounds during the spray drying process, origi-

nated from their poor film-forming ability[106,111] and from their properties such as turbidity and hygroscopicity.[104] Bangs and Reineccius[11] reported that retention of volatile flavor compounds decreases as malto-dextrin DE increased, although other individual studies showed that samples having DE between 10 to 20 could be satisfactory utilized as wall material for flavor encapsulation.[104] Combinations of whey proteins and high DE maltodextrins (DE 5-15) are effective wall systems for microencapsulation of volatiles.[125] Such wall systems provide high volatile retention levels and limit the proportion of solvent extractable core. This proportion was reduced with increasing DE value of carbohydrate. When low DE maltodex-trins are incorporated at a high proportion into whey-containing wall systems, they adversely affected the emulsion characteristics and caused structural defects in the dry product.

VIII. FUTURE DIRECTIONS

The fat replacer market was about $100 million in 1991 and would grow to $305 million by 1996 in the U.S.[3] According to the continuing development of links between diet and health, the technology of maltodextrins production will continue to advance considerably. A large number of different maltodextrins are already available and valuable, enlarging the list of additives for application in the food industry (Table 4). Product applications and the development of new methods for specific formulations will continue to expanded further.[3,4]

Studies on starch have provided a background to gain a better understanding of the maltodextrin properties; however, it is clear that their properties and use have unusual and unique characteristics. Although the different starch types may partially account for the differences in processing, structural and functional properties of maltodextrins, the exact causes for such variations remain poorly understood. Careful selection or grouping the raw materials based on the starch types would probably maximize and improve their specific applications.

There is further potential for developing the technology for an effective and controlled production of maltodextrins on a commercial scale. The use of enzymatic hydrolysis methods must be expanded as the requirements of purity and yield become more pressing. The recent developments in genetic engineering can as well be considered, providing ways for a production of highly active microorganisms to improve the existing processes.

More work needs to be done in relating maltodextrin composition to different functionality parameters. However, because of the apparent heterogeneity of maltodextrins this is not as simple as in other polysaccharides. There is a need for greater use of the fractionation and reconstitution approach in order to give fundamental information on the relationships between the proportions of the main groups of polysaccharides and functional parameters (e.g., gelation time and strength). Additional attention is requisite in order to establish evaluation methods between the functional properties of maltodextrins, the preconditions for network structure in connection with the physical attributes of processed products.

There is a need to develop theoretical models that predict structural-functional properties at a fundamental molecular level, such as based on Eq. 1. Knowledge of the dependence of different functional parameters on the molecular weight of maltodextrin would be of great value for the formation of desired maltodextrin networks. The properties of mixed systems containing maltodextrins and the relative effect of kinetics on the physical properties of foodstuffs comprise maltodextrins, still await answers. These considerations appear to place constraints on the range of the use of maltodextrins, nevertheless, the recent advances have not

TABLE 4
Commercially Available Maltodextrins Used in the Food Industry

Type of starch	Tradename (developer)	Molecular weight and/or dextrose equivalent	Conc. used %	Method for preparation	Special features
Corn maltodextrin	Lycadex 200 (Roquette)	DE < 5	10–20	Blend with cold water	Enzymatically hydrolyzed; nongelling for use in sauces salad dressings
Corn Maltodextrin	Maltrin M040 Maltrin M050 Maltrin M100 10 DE Maltrin M150	20000 5 DE 15 DE	35	Blend with cold water	Functional properties depend on DE
Potato maltodextrin	Paselli SA2 (Avebe America)	150000 3 DE	>20	Blend with warm water	Enzymatically hydrolyzed used in wide variety of products
Potato maltodextrin	Lycadex	DE < 5 100 (Roquette)	25	Blend with cold water	Enzymatically hydrolyzed; used as gel in bakery products, frozen desserts, and spreads
Whole rice maltodextrin	Rice*trin 3 Complete (Zumbro/IFP)	3 DE	>20	Blend with cold water	Hydrolyzed by α-amylase contains 10% protein as 1 to 5 μm particles; used in frozen desserts, bakery products, salad dressings
Tapioca maltopdextrin	Instant N-Oil II (National Starch and Chemical)		30–40	Blend with cold water	Pregelatainized; recommended for HTST processing and stable for low-temperature storage
Agglomerated waxy corn maltodextrin	Star-Dri (A. E. Staley LoDex (American Maize Peoducts)				Available as DE 1, 5, 10, or 15; high bulking ability
Waxy corn	N-lite B maltodextrin (National Starch and Chemical)		25–30	Use as dry powder or as gel prepared by heating to 88°C with high-speed agitation	Used for laminated doughs to to extend shelf life and replace up to 100% shortening

From Ref. 123 with permission.

received the most interest. It is necessary to predict and understand the effect and performance of maltodextrins on the flavor components, shelf life, long-term storage conditions (at or below ambient temperatures), and browning reactions in food systems. They must be correlated, if possible, with the commercial DE characterization or with other more powerful methodology. Correlation between the mechanical properties with their sensory response and the structure of multicomponent gels is essential to be achieved.

Despite the wide range of advantages as fat substitutes, maltodextrins particles can partly imitate the texture of fat and overcome the detrimental effects caused by fat reduction (i.e., flavor release). Thus, another aspect that little is known is the nature and the mechanism of how they contribute to the sensation of fat components. Neither reliable qualitative nor quantitative data are available on their behavior in the presence of alternative fat mimetics. Nutritional aspects like their ability for gradual absorption (i.e., via osmosis) of the liquids into body cells, is an essential topic for study. It would be interesting to know whether the genetic material will be responsible for such absorption or is the entire way of processing will be also involved.

The resistant starch recently introduced is defined as a highly retrograded maltodextrin that also contains about 30% total dietary fiber. This material has a small particle size and low-water-holding capacity, particularly useful for extruded cereal products. To develop new carbohydrates based on resistant starch is a new unexplored area with particular challenges.

The above discussion only briefly examines some of the maltodextrins properties and demonstrates their complexity. It also shows that maltodextrins are a valuable tool to tune up the properties of food products and to improve food quality. Adequate accomplishment of future tasks should be possible with the already known properties of the system. The availability of economically produced maltodextrins would greatly accelerate the step at which fundamental and practical studies can be exploited.

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