# FOOD HYDROCOLLOIDS

Structures, Properties, and Functions

Edited by Katsuyoshi Nishinari and Etsushiro Doi

# **Food Hydrocolloids**

### Structures, Properties, and Functions

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## **Food Hydrocolloids**

Structures, Properties, and Functions

#### PREFACE

It is now well recognised that the texture of foods is an important factor when consumers select particular foods. Food hydrocolloids have been widely used for controlling in various food products their viscoelasticity, emulsification, gelation, dispersion, thickening and many other functions. An international journal, FOOD HYDROCOLLOIDS, launched in 1986 has published a number of stimulating papers, and established an active forum for promoting the interaction between academics and industrialists and for combining basic scientific research with industrial development.

Although there have been various research groups in many food processing areas in Japan, such as fish paste (kamaboko, surimi), soybean curd (tofu), agar jelly dessert, kuzu starch jelly, kimizu (Japanese style mayonnaise), their activities have been conducted in isolation of one another. The interaction between the various research groups operating in the various sectors has been weak. Symposia on food hydrocolloids have been organised on several occasions in Japan since 1985. Professor Glyn O. Phillips, the Chief Executive Editor of FOOD HYDROCOLLOIDS, suggested to us that we should organise an international conference on food hydrocolloids. We discussed it on many occasions, and eventually decided to organise such a meeting, and extended the scope to include recent development in proteinaceous hydrocolloids, and their nutritional aspects, in addition to polysaccharides and emulsions.

The international conference in Tsukuba was organised by the Japanese Society of Food Hydrocolloids under the auspices of many relevant societies and organisations. It was an epoch-making-event for Japanese researchers as well as overseas participants working in the field of food hydrocolloids. Many of the participants who know each other through their publications, could benefit from face-to-face discussions during tea time, lunch time, poster sessions and

industrial exhibitions. The social and scientific exchange was so fruitful that all the participants felt very pleased to be there. We are particularly grateful for the overwhelming response to the success of the meeting. As a result, it has been decided to organise the 2nd International Conference on Food Hydrocolloids at Ohio State University in USA during the first week of September 1994.

This book we trust will convey the essence and enthusiasm of the conference. Papers included in this book are classified into the following six groups:

- \* Polysaccharides
- \* Functional Properties
- \* Proteins
- \* Emulsions
- \* Interactions
- \* Nutrition and Physiology

The information collected in this book supplies valuable scientific information and provides suggestions for further developments which will further assist our understanding and utilisation of food hydrocolloids.

Katsuyoshi Nishinari Etsushiro Doi

#### **CONTENTS**

#### POLYSACCHARIDES

Structural Aspects of Some Functional Polysaccharides
On the Relation Structure-Properties of Some Polysaccharides Used in the Food Industry
Gelation of (Some) Seaweed Polysaccharides
The Specification of the Gum Arabic of Commerce
Hydrogels of Chitin and Chitosan
Molecular Weight Dependence of Antimicrobial Activity by Chitosan Oligomers
Characteristics and Applications of a Polyfructan Synthesized from Sucrose by Aspergillus Sydowi Conidia
Alginates and Gellan Gum: Complementary Gelling Agents
Gellan Gum: Production and Properties
Conformation and Physical Properties of Two Unusual Microbial Polysaccharides: Rhizobium Trifolii CPS and Levan

Rheological and Thermal Properties of Gellan Gum Gels
Selection of Gum Producing <i>Alcaligenes</i> sp. Strains
Molecular Association and Dissociation in Formation of Curdlan Gels
Food Applications of Curdlan
Rheology and DSC of Curdlan-DMSO-Water Systems
Studies on Xanthan Structure by Scanning Tunnelling Microscopy 131 Wilkins, M., Davies M.C., Jackson, D.E., Roberts, C.J., Tendler, S.J.B., Mitchell, J.R., and Hill, S.E.
Xanthan Gum: A Multifunctional Stabiliser for Food Products(135 Challen, I. A.
ESR Study on Spin-Labeled Xanthan Gum
Xanthan Gum Production from Brazilian Strains
Effect of Soluble Soybean Polysaccharide on Dispersion Stability of Acidified Milk Protein
"AI-GEOK", A Unique Gel-Forming Polysaccharide of Ficus awkeotsang: Structure, Gelation Mechanism and Utilization of the Oligosaccharides
Gelling Properties of Acid-Modified Starches
The Effect of Low Levels of Antioxidants on the Swelling and Solubility of Cassava Starch
Physical Properties of Starch Pastes

Effects of Saccharides on Stabilities of Rice Starch Gels-Correlation between Structure of Saccharides and Stabilizing Effects on Gel Structure
Effects of Molecular Weight on the Retrogradation of Amylose 179 Kitamura, S., Hakozaki. K., and Kuge, T.
Effect of DMSO on the Gelation of Amylose
Physicochemical Characterisation of Alginate from Malaysian Brown Seaweeds
Rheological Properties of Aqueous Solutions of Aubasidan
Influence of Small Additives of Aubasidan on Gel Formation in Aqueous Solutions of Red Seaweed Polysaccharides
FUNCTIONAL PROPERTIES
Rheological and Organoleptic Properties of Food Hydrocolloids(201) Morris, E. R.
Food Hydrocolloids in the Dairy Industry
Rheological Studies of Fish Proteins
Critical Behavior of Agarose Near the Sol-Gel Transition Point 235 Fujii, T., Kumagai, H., and Yano, T.
Small-Angle Neutron Scattering Studies of Proteoglycan from Shark Fin Cartilage
Preparation of a Polyelectrolyte Complex Gel and Its pH-Dependent Swelling Behavior
Mechanical Properties of Foods in the Vicinity of Gelation Point 251 Kumagai, H., Inukai, T., Fujii, T., and Yano, T.
Interaction between Polyelectrolyte Inhibitors of Calcium Phosphate Formation and Calcium Ion

The Sol-Gel Transition of Food Macromolecules under High Pressure 259 Gekko, K.
Utilization of High Hydrostatic Pressure to Make Alginate Gels 265 Shioya, T., Hirano, R., and Tobitani, A.
Coagulation Behavior of Egg PC Vesicles with Different Particle Sizes
Functionality of Different Protein Products in Meat Emulsions with Reduced NaCl Content
Gelation of Low Density Lipoprotein (LDL) from Hen Egg Yolk during Freezing and Thawing
Effect of Starch on the Evaluation of Surimi Gels Made from Various Kinds of Fish Species
The Use and Control of Chemical Reactions to Enhance Gelation of Macromolecules in Heat Processed Foods
Mechanism of Wall Effect on Fluidity of Milk in a Capillary 295 Nakamura, T., Yamamoto, A., Sakanishi, K., and Mineshita, T.
Measurement of Fluid Viscosity and Gel Setting Point by a Hot-Wire Method
Effect of the Addition of High Methoxy Pectin on the Rheology and Colloidal Stability of Acid Milk Drinks
Changes in Firmness of Strawberry Fruit during Growth and Partial Purification of Its Polygalacturonase
PROTEINS
Heat-Induced Transparent Gels of Globular Proteins
Thermodynamic Aspects of Food Protein Functionality

NMR Study on Lysophosphatidylcholine-Protein Interactions and Their Functional Properties
Emulsifying Properties of Bovine Serum Albumin and Its Enzymatic Hydrolyzate
Enhanced Emulsifying Ability of Food Surfactants by Addition of Lysophospholipids
INTERACTION
Mixed Polysaccharide Gels Formed between Xanthan Gum and Glucomannan
Large Deformation Rheology of Mixed Gels of Konjac-Kappa-Carrageenan
Rheological Study on a Mixed System of Konjac Glucomannan and Carrageenan: Effects of Molecular Weight of Konjac Glucomannan (57) Kohyama, K., Iida, H., Ochi, T., Ohashi, S., and Nishinari, K.
Influence of Xanthan Gum Addition on Frozen Starch Paste Properties
Features of Protein-Starch Granule Conjugates
Rheology and DSC of Gellan-Agarose Mixed Gels
PHYSIOLOGY AND NUTRITION
Physiological Aspects of Food Hydrocolloids
Evaluation of Short-Chain Fatty Acid Production in the Cecum of Fiber Fed Rats
Dietary Fiber-Induced Changes in Bile Acid Conjugation and Taurine Metabolism in Rats

Anti-Hypertensive Substances in Viscous Material of Fermented
Soybean (Natto)
Okamoto, A., Hanagata, H., Matsumoto, E., Kawamura, Y.,
and Yanagida, F.
Beneficial Effect of Dietary Fiber on Iron Bioavailability
in Rats
Kishida, T., Shimizu, Y., and Kiriyama, S.
Index

#### STRUCTURAL ASPECTS OF SOME FUNCTIONAL POLYSACCHARIDES

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#### INTRODUCTION

Carbohydrate polymers are widespread in nature, and play important roles in all life-stages of the organisms. Biological, physiological and other functions of natural polysaccharides are summarized in Table 1. Although in a nutritional point of view, the most important function of carbohydrate must provide biological fuel, which is reserved in the form of starch or glycogen, some undigestible polysaccharides, either plant hemicelluloses or microbial polysaccharides, have recently attracted attention because of the physiological effect as dietary fibers. In the field of food science and technology, pectic substances in plant cell wall matrix, and a variety of gum exudates, have long been used as emulsion stabilizers, water absorption agents, gelling and thickening agents. In addition, some microbial polysaccharides having unique properties, elaborated extracellularly in abundant amounts, have recently been utilized as a gel-forming agent or a food-packing film. In Table 2 natural polysaccahrides as food hydrocolloids are classified according to their biological sources. Although functionality of individual polysaccharides are closely related to their own molecular shapes, we must first look into the primary structure of the building units, i.e. the carbohydrate components, mode of linkages and their sequential arrangements. In this symposium structural correlations with functionality of some plant and microbial polysaccharides, important food hydrocolloids, are discussed.

#### Biological functions

- a) Cell wall architecture (plants and microorganisms)
- b) Hydration or gelation of intracellular fluids
- c) Cell-cell recognition (cell surface)
- d) Stimulation of host defense

#### Physiological functionality

- a) Nutrition (biological fuel)
- b) Dietary fiber
- c) Source of functional oligosaccharides

#### Functionality as food hydrocolloid

- a) Stabilizer
- b) Thickener
- c) Gelling agent
- d) Water-holding agent

### GENERAL MOLECULAR STRUCTURE OF NATURAL POLYSACCHARIDES AND METHODS FOR STRUCTURAL ANALYSIS

The rheological characteristics of natural polysaccharides are principally related to their molecular conformations, which may be regulated by the sequences of carbohydrate chains. Therefore, it must be necessitated to know their chemical structure, especially, the mode of glycosidic linkages in the building units. Even in homoglycans, there are wide varieties in modes of glycosidic linkages, arrangements of glycosyl residues, and molecular shape, either a linear or branched molecule. For example, there are a variety of glucose polymers occurring in nature as classfied:

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	Glucosidic linkage	Name	Occurrence
$\alpha$ -D-GLUCANS;	$(1\rightarrow 4)$ linear	amylose	plant
	$(1\rightarrow 4)$ 1, 6 branch.	amylopectin	plant
	$(1\rightarrow 4)$ 1, 6 branch.	glycogen	mammal
	$(1 \rightarrow 4)_3(1 \rightarrow 3)$	elsinan	Elsinoe sp.
	$(1\rightarrow 6)$ 1, 3 branch.	dextran	L. mesenteroides
	$(1\rightarrow 3)$ 1, 6 branch.	(mutan)	Str. mutans
	$(1\rightarrow 3)G(1\rightarrow 4)$	nigeran	Asp. niger
$\beta$ -D-GLUCANS;	$(1\rightarrow 4)$ linear	cellulose	plant cell wall
	$(1\rightarrow 4)_nG(1\rightarrow 3)$	cereal gum	endosperm
	$(1\rightarrow 4)_2G(1\rightarrow 3)$	lichenan	lichen
	$(1\rightarrow 3)$ linear, DP 30	laminaran	seaweed
	$(1\rightarrow 3)$ linear	curdlan	Alc. faecalis
	$(1\rightarrow 3)$ less branch.	The same of the sa	yeast cell wall
	$(1\rightarrow 3)$ 1, 6 branch.		fungi, mushroom
	(1→2) cyclic		Arg. tumefaciens

These plant and microbial glucans of either  $\alpha$  - or  $\beta$ -configuration, with different linkages, exhibit their specific properties and functionality. For instance, amylose and cellulose, both linear molecules build up with  $(1 \rightarrow 4)$ -linked D-glucose residues, but with different anomeric linkages ( $\alpha$ -, or  $\beta$ -), giving different physical properties and enzymic

```
PLANT POLYSACCHARIDES
  Starch and its modified products
  Seed gums
     Cereal gums (1, 3/1, 4-\beta - Glucan)
     Galactomannans (Guaran, Locust bean, Tara bean etc.)
     Xyloglucan (Tamarind)
  Tuber gums
     Glucomannan (Konjac), Inulin
  Cell wall constituents
     Cellulose (chemical modified)
     Fucoxyloglucan
      Arabinoxylan (monocot), Arabinogalactan (dicot)
     Pectinic substances (Rhamnogalacturonan, Galacturonan etc.)
  Exudate mucilages
     Gum arabic, Gum tragacanth, Karaya gum and others
SEAWEED EXTRACTS
     Agar (Gal., 3,6-AnhydroGal)
     Carrageenan (sulfated Gal), Fucoidan
     Alginic acid (Guluro-mannuronide)
     Laminaran
MICROBIAL POLYSACCHARIDES
  Neutral polymers
     Dextran (\alpha-1, 6 glucan)
     Pullulan (\alpha-1,6/1,4); low viscosity, film sheet
     Elsinan (\alpha - 1, 3/1, 4); high viscosity, film sheet
     Curdlan (\beta-1,3); heat-gelation
     Screloglucan (6-0-branched<sub>\beta</sub>-1, 3)
     Levan (2,6-fructan)
  Acidic polymers
     Xanthan (GlA, Pyruvate, Man, 4Glc<sub>8</sub>-); synergistic gelation effect
     Gellan (\rightarrow 361c_{\beta} \rightarrow, \rightarrow 461A_{\beta} \rightarrow, \rightarrow 4Rha_{\alpha} \rightarrow, \rightarrow 461c_{\beta} \rightarrow); gel forming
  Others having potential utilization
     Welan gum (Kelco)
     Rhamsan gum (Kelco)
     B. polymyxa acidic Ps
     PS 1004 from methnol (Ga, Man, Al, GlA)
     T. fuciformis acidic PS (G1A, \rightarrow3Man\alpha\rightarrow)
     Acetobacter sp. acidic PS (G1A, Ga1, \rightarrow 4G1c_{\beta} \rightarrow)
```

susceptibilities. In a similar way,  $(1\rightarrow 3)$ -linked  $\alpha$ - and  $\beta$ -D-glucans possess significantly different conformations from each other, shown in Fig. 1. For instance, curdlan, a gel-forming bacterial glucan¹, and the backbone moiety of many antitumor, branched  $\beta$ -D-glucans, e.g., scleroglucan, lentinan, schizophyllan and other fungal glucans, consist of  $\beta$ - $(1\rightarrow 3)$  glucosyl chains. They are mostly present as a triple helical strands, which are most likely responsible for their host-mediated antitumor activity². In contrast, the  $(1\rightarrow 3)$ - $\beta$ -D-glucosyl chain, which forms a backbone of the dental cariogenic  $\alpha$ -glucan ("mutan"), elaborated by Strept. mutans may have a ribbon-like single-

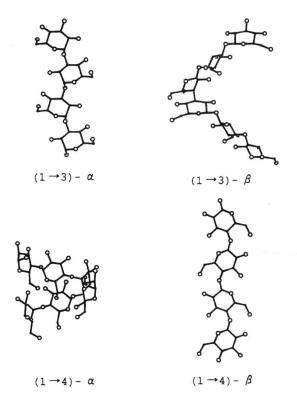


Fig. 1 Crystalline conformation of  $\alpha$  - and  $\beta$  -D-glucans. (Courtesy of Dr. K. Ogawa, RIAT, University of Osaka Prefecture)

chain conformation, which may give an insolubility characteristic; the adhesive characteristic may be exhibited by  $\alpha$  -(1 $\rightarrow$ 6)-linked D-glucosyl side chains.

Many of natural polysaccharides, currently used as potent food hydrocolloids, such as, emulsion stabilizer, water-holding, thickening or gelling agents, are obtained from various tissues of plants, *i.e.* seeds, tubers, and exuded mucilages, and also from seaweed extracts (see, Table 2). Dextran was introduced into pharmaceutical industry as a blood plasma substitute after the second world war. Then, xanthan and pullulan, and recently gellan gum have also been put on commercial market, and some other microbial polymers have attracted attention because of their potential utilizations, as will be discussed later.

Most of these polysaccharides are heteropolysaccharides comprising different carbohydrate components. Some contain charged groups, e.g., carboxyl, sulfonyl, or amino groups. Their unique rheological characteristics are basically attributable to the molecular shapes as well as localization of the charged groups. Fig. 2 shows viscosities of aqueous solutions of typical natural gums. For instance, galactomannans, e.g., guar and locust bean gum, give high viscosity, most probably due to the characteristic features as the linear chain of the  $\beta$ - $(1\rightarrow 4)$ -linked mannan and solubility property may be attributed to the presence of regularly arranged  $\alpha$ -galactosyl branches. On the other hand, gum Arabic, a multiply branched acidic heteropolysaccharide, shows extremely