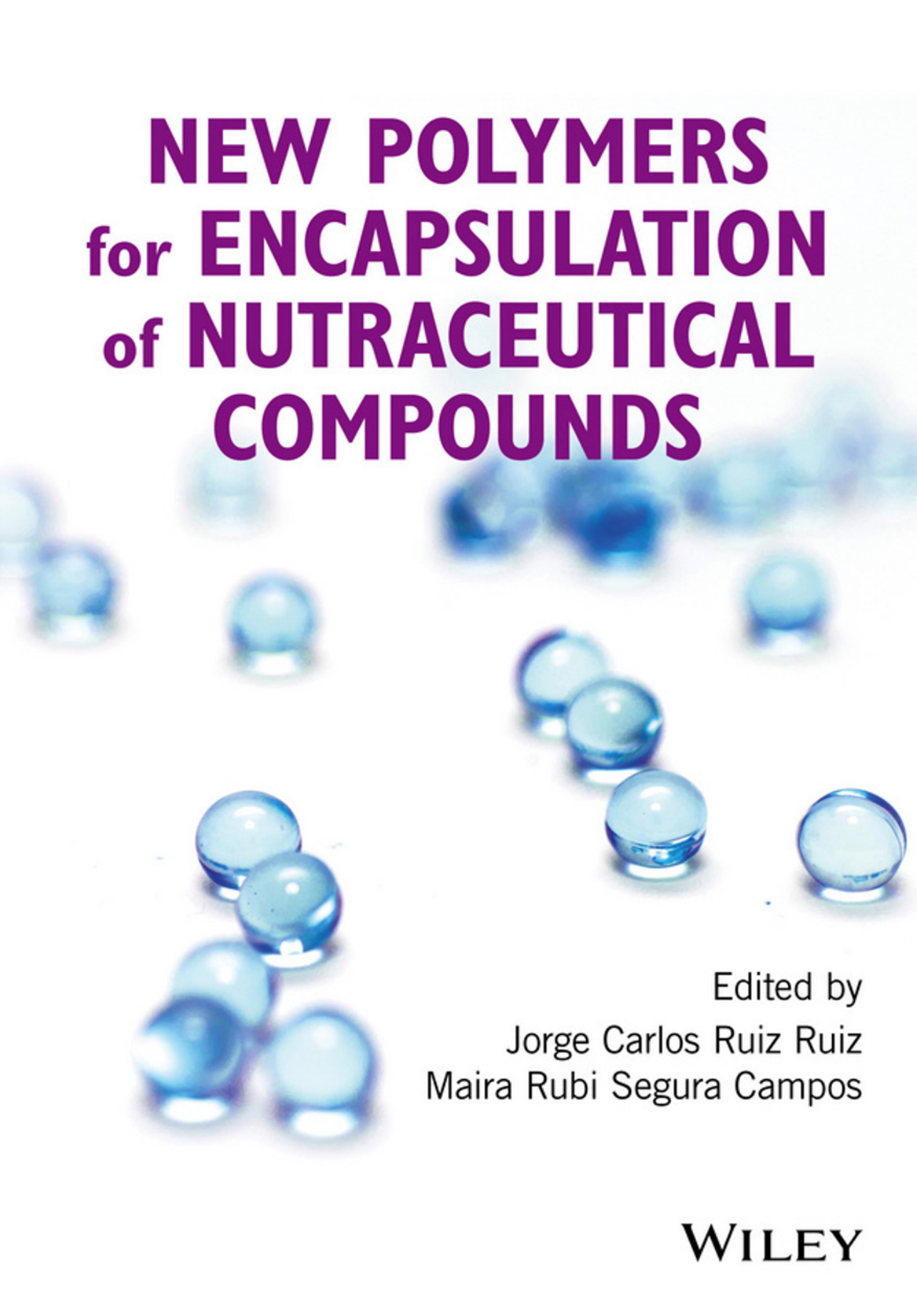


The background of the cover features a collection of translucent blue capsules, likely representing nutraceutical compounds, scattered across a white surface. The capsules are shown in various orientations and depths of focus, creating a sense of depth and highlighting their physical form.

NEW POLYMERS for ENCAPSULATION of NUTRACEUTICAL COMPOUNDS

Edited by
Jorge Carlos Ruiz Ruiz
Maira Rubi Segura Campos

WILEY

New polymers for encapsulation of nutraceutical compounds

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Preface

Microencapsulation has been widely used as a system of controlled release in the pharmaceuticals industry. However, it also has a great potential to be used in the area of functional foods for protecting nutraceutical ingredients. It is an interdisciplinary field that requires knowledge of the field of pure polymer science, familiarity with emulsion technology, and an in-depth understanding of stabilizing bioactive compounds.

In the 21st century, many polymers have been proposed for producing capsules. Examples include the natural polymers alginate, agarose, chitosan, cellulose, collagen, and xanthan and synthetic polymers polyethylene glycol, polyvinyl alcohol, polyurethane, polyether-sulfone, polypropylene, sodium polystyrene sulfate, and polyacrylonitrile-sodium methallylsulfonate. However, the use of novel or nonconvexional polymers as coating materials is a field that still needs study.

The present book provides an approach to the characterization of novel polymers and their use in encapsulation processes, the stability of nutraceutical compounds encapsulated with novel polymers, and the application of encapsulated compounds with novel polymers in functional food systems. These polymers could present many advantages in terms of cost and ability to protect and stabilize the nutraceutical compounds compared to those already used by the food industry to develop functional food systems.

Jorge Carlos Ruiz Ruiz

TOPIC 1

Characterization of modified polymers and their use in encapsulation processes

CHAPTER 1

Tailor-made novel polymers for hydrogel encapsulation processes

Artur Bartkowiak, Katarzyna Sobecka, and Agnieszka Krudos

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1.1 Introduction

Natural polymers are materials of large molecular weight and natural origin such as plants, animals, or microorganisms. They have been known for centuries and have found widespread use in various industries, such as food, cosmetics, pharmaceuticals, textiles, plastics, and paper. They are of considerable importance because they are generally biodegradable and are generally recognized as safe (GRAS), which is a significant advantage, especially in recent times, when “pro-nature” policies and goals to reduce “chemicals” and synthetic materials in our lives, including food, have become popular. This makes the interest in natural polymers unabated and still increasing. One successful way of using these materials is in encapsulation processes, including spray-drying, emulsion techniques, coacervation, and ionotropic gelation. The utility of polymers as encapsulants is determined by their specific properties. These can include film-forming properties, emulsifying properties, high resistance to the environment of the gastrointestinal tract, biodegradability, low viscosity at high solids contents, low hygroscopicity, and availability and low cost (Özkan and Bilek, 2014).

Generally, among the natural polymers two main groups can be distinguished: polysaccharides and proteins. The next section presents the most popular polymers, commonly used as materials to form capsule matrix (Table 1.1 and Table 1.2). Despite the many well-known encapsulants, there is still a need to look for novel polymers and new means to use the old ones in other ways to create ideal capsules with excellent resistance and mechanical properties and wide applicability; this topic is also presented in this chapter.

Table 1.1 Selected carbohydrate polymers commonly used for hydrogel encapsulation processes.

Properties									
Origin/ Isolation	Structures	Solubility in Water	Viscosity	Gel Formation/ Gelation	Synergistic Effects with	Other	Micro- encapsulated Active Substances	Micro- encapsulation Techniques	References
Alginate Mainly from marine brown algae Also from exocellular material of some bacteria	Linear anionic polysaccharide Copolymer with homopolymeric blocks of (1-4)-linked β -D-mannuronate and α -L-glucuronate residues	Depends on the rate of dissociation and the type of the counter-ion Alginic acid: insoluble Salts of alginic acid (sodium alginate): soluble	High viscosity at relatively low concentration Exponential increase with the molar mass Highly dependent on ionic strength	Ionotropic gels in the presence of polyvalent cations (Ca ²⁺ most commonly used) The α -L-glucuronate blocks are responsible for gelation	—	—	Folic Acid (Alginate-Starch)	Coacervation	Madziva <i>et al.</i> (2006)
							<i>Lactobacillus</i> <i>Acidophilus</i> , <i>Bifidobacterium</i> <i>lactis</i> (Alginate/ Hi-Maize Starch) <i>Lactobacillus</i> , <i>Acidophilus</i> (Alginate, CaCl ₂ , chitosan)	Emulsion	Kailasapathy (2006)
Carrageenan Red seaweed (Rhodophyceae) <i>Chondrus</i> <i>crispus</i> , <i>Gigritina</i> , <i>Furcellaria</i> (κ , ι) <i>Eucheuma</i> <i>cottonii</i> (κ) <i>Eucheuma</i> <i>spinosum</i> (ι)	Anionic polyelectrolytes Structure can vary with the source and extraction and purification conditions Three types of carrageenan are commercially available: ι - (iota), κ - (kappa), λ - (lambda) chains contain alternating (1-3)- linked β -D-galactopyranosyl and (1-4)-linked α -D-galactopyranosyl units	Depends on the carrageenan type Solubility in cold/hot water: ι -Carrageenan: Na-salt soluble; K ⁺ , Ca ⁺ , ammonium salts from limited to high swelling/ soluble >70°C κ -Carrageenan: Na-salt soluble; Ca-salts give thixotropic dispersions, soluble >70°C		ι -Carrageenan: thermo-reversible gels during cooling in the presence of specific counter-ions; strongest gels are obtained with Ca ²⁺ Gels are elastic, have high freeze-thaw stability, do not undergo syneresis	Other gums, e.g., κ -carrageenan brittle gels became softened with locust bean gum	—	<i>Bifidobacterium</i> <i>longum</i>	Two-phase (water/oil) system	Adhikari <i>et al.</i> (2003)

Xanthan Produced by bacteria (<i>Xanthomonas campestris</i>) in aerobic fermentation	Some (1-3)-linked units are like the 2- and 4-sulfates Some (1-4)-linked units are like the 2- and 6-sulfates, the 2,6 disulfates, the 3,6-anhydride, the 3,6-anhydride-2-sulfate	λ-Carrageenan: All salts soluble, create viscous, pseudoplastic solutions/soluble	κ-Carrageenan: thermo-reversible gels during cooling in the presence of specific counter-ions; strongest gels are obtained with K⁺ Gels are brittle, have low freeze–thaw stability, undergo syneresis λ-Carrageenan: non-gelling	—	Progressive reduction with increasing shear stress; reversible after eliminating shear stress Stable in a broad range of pHs (2–12) and temperatures Increases after salt addition to a salt-free xanthan solution in concentration >0.15% Increases during heating salt-free xanthan solution	Guar gum: enhancement of viscosity Locust bean gum and konjac mannan: obtain soft, elastic thermo-reversible gels at higher concentration	Undergoes cryogelation Not degraded enzymatically	<i>Bifidobacterium lactis</i>	Extrusion	McMaster et al. (2005)
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Table 1.1 (Continued)

Gum Arabic Obtained from stems and branches of <i>Acacia senegal</i> or <i>Acacia seyal</i>	Branched neutral or slightly acidic compound of arabinogalactan oligosaccharides, polysaccharides, glycoproteins	Highly soluble in cold and hot water to 50wt%	Depends on gum arabic type, pH, ionic strength Maximum viscosity is noted between 6 and 7 pH	—	Majority of plant hydrocolloids, proteins, modified starches Gum tragacanth: lowering the viscosity	Creation of a strong protective film around oil droplets because of presence in the branched structure both protein (hydrophobic) and polysaccharide (hydrophilic) moieties Obtained film/layer protect against, e.g., aggregation, oxidation, evaporation, and moisture absorption	Betacyanin Betalain Lycopene Turmeric Limonene (gum arabic-sucrose-gelatin) <i>Lactobacillus</i> sp/ Linoleic acid	Spray-drying Spray-drying Spray-drying Spray-drying Freeze-drying Interfacial polymerization Spray-drying	Pitalua et al. (2010) Janiszewska & Włodarczyk (2013) Shu et al. (2006) Martins et al. (2010) Kaushik & Roos (2007) Yáñez-Fernández et al. (2008) Fang et al., (2005)
	Composition is highly variable due to climate, source, season, rainfall, etc.								
	Generally the main chain contains β -(1-3)-linked D-galactopyranosyl units								
	Side chains contains two to five β -(1-3)-linked D-galactopyranosyl units combined with the backbone by 1,6-linkages								
	Main and side chains consist of α -L-arabinofuranosyl, α -L-rhamnopyranosyl, 4-O-methyl- β -glucuronopyranosyl								

(Continued)

Table 1.1 (Continued)

Properties							
Origin/ Isolation	Structures	Solubility in Water	Viscosity	Gel Formation/ Gelation	Synergistic Effects with	Other	Micro- encapsulated Active Substances
Gum Karaya (<i>Sterculia Gum</i>)	Dried exudate	Native gum soluble up to 10%	—	—	Other plant	—	—
	Compound partly acetylated polysaccharide received as Ca- and Mg-salts	Up to 30%	—	—	hydrocolloids, carbohydrates, proteins	—	—
<i>Sterculia</i> or <i>Cochlospermum</i> species (e.g., <i>Sterculia urens</i>)	Branched structure	Deacetylated gum soluble up to 90%	—	—	—	—	—
	Main chain contains α -D-galacturonic acid and α -L-rhamnose units	—	—	—	—	—	—
Mesquite Gum	Side chains are linked to the galacturonic acid of the backbone by (1-2)-linkage of β -D-galactose or (1-3)-linkage of β -D-guluronic acid	—	—	—	—	—	—
	Half of the backbone rhamnose units are (1-4)-linked to β -D-galactose units	—	—	—	—	—	—
Obtained from mesquite tree (<i>Prosopis</i> spp.) or shrub	Neutral salt of a composite acidic polysaccharide	Comparable to gum arabic	Increases with concentration	—	—	Good film-forming properties	Cardamom oil
	Branched structure	Possible concentration of solution up to 50%	—	—	—	—	<i>Lactobacillus</i> sp.
	Main chain contains (1-3)-linked β -D-galactose units	—	—	—	—	—	polymerization
	—	—	—	—	—	—	Interfacial polymerization
	—	—	—	—	—	—	Beristain et al. (2001)
	—	—	—	—	—	—	Yáñez-Fernández et al. (2008)

Side chains are linked with backbone by (1-6) bond

Side chains consist of single sugar or oligosaccharide such as L-arabinose (pyranose and furanose ring forms),

I-rhamnose, β -D-glucuronate, and 4-O-methyl β -D-glucuronate

Small amount of proteins

Pectin Main sources: citrus fruits and apples	Hetero-polysaccharide Presents a highly complex, nonrandom structure with linear homo-poly(galacturonic acid) blocks) (smooth regions) and strongly branched blocs (hairy regions) Contains at least 65wt% α -(1-4)-linked D-galacturonic acid-based units units can occur as free acid or salts (Na ⁺ , K ⁺ , Ca ⁺ , ammonium), naturally methanol esterified or as acid amide in amidated pectins	Soluble Possible concentration at range of 6%–12% Most stable at pH 3–4	Low viscosity in comparison with plant gum Close to Newtonian flow at low concentration Pseudoplastic behavior at higher concentration	Depends on the degree of esterification <i>HM pectins:</i> Gel in the presence of sugars and low pH range Gel strength is inversely related to pH level <i>LM pectins:</i> Gel in the presence of calcium ions	Fish oil and fish oil–extra virgin olive oil Lycopene (complex with gelatin)	Spray-drying Coacervation	Polavarapu et al. (2011) Silva et al. (2012)
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Table 1.1 (Continued)

Properties							
Origin/ Isolation	Structures	Solubility in Water	Viscosity	Gel Formation/ Gelation	Synergistic Effects with	Other	Micro- encapsulated Active Substances
	Polymer chain contains some neutral sugars (e.g., L-rhamnose, D-galactose, L-arabinose, D-xylose)			Gelation depends also on the proportion and arrangement of the carboxyl groups in the pectin chain			
	L-Rhamnose unit exists only as (1-2)-linked in the backbone Other sugar units preferably at the rhamnose and galactose residues to the backbone Two types of pectin depending on the esterification degree: high methoxylated (HM) >50% esterification and low methoxylated (LM) <50%			Ca ²⁺ with pectin interaction increases with decreasing esterification degree Amide groups increase the range of the calcium ion concentration where the LM pectins form gel			
Starch							
Produced by most green plants as an energy store	Polymer of α -D-glucose Two architecturally different molecules in the structure: linear (amylose) and branched (amylopectin)	Insoluble in cold water Swelling Swelling power decreases with decrease in granule size and increased amylose content	Amylose is responsible for the solution's high viscosity	MC: Occurs on heating above 50 °C Reversible on cooling substitution	—	—	<i>Bifidobacterium</i> P11 Fish oil Chlorophyll
							Spray-coating, spray-drying Spray-drying Spray-drying Spray-drying
							O'Riordan et al. (2001) Tan et al. (2005) Porrarud and Pranee (2010)

Commercial sources: cereal grain seeds (corn, wheat, rice, sorghum), roots and tubers (potato, tapioca, arrowroot), stems and pith (sago)	Generally the content of amylose is about 20%–30% and amylopectin 70%–80% <i>Amylose</i> contains from 500 to 6000 D-glucose units, which are linked by α-(1-4)-glycosidic bond <i>Amylose</i> occurs in the form of a double helix <i>Amylopectin</i> contains up to 2 million D-glucoses Side chains include about 30 D-glucoses and occur approximately every 20 to 30 glucose units along the chain The point of chain branching has α-(1-6) glycosidic bond Present in small grains of different shapes (spherical or lentil-shaped) and size (e.g., 1–100 μm, 5–900 μm)	Crystalline becomes amorphous in water at 60–70°C <i>Amylose</i>: Specific dissolution behavior because of helical structure Soluble in hot water In dilute solution it can bind with itself in a double helix Undergoes retrogradation and, as a consequence, after drying it becomes insoluble Retrogradation is faster with lower concentration, temperature, molar mass; the fastest is between pH5 and 7 <i>Amylopectin</i>: Insoluble in cold and hot water No tendency to retrogradation and crystallization	Gelation temperature decreases with high degree of substitution <i>HPMC</i>: Creating thermo-reversible gels Gel transition temperature is in range of 50 to 90 °C and depends on the ratio of methyl to hydroxypropyl derivatization Gel texture is changeable with increasing hydroxypropyl substitution
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(Continued)

Table 1.1 (Continued)

Properties							
Origin/ Isolation	Structures	Solubility in Water	Viscosity	Gel Formation/ Gelation	Synergistic Effects with	Other	Micro- encapsulated Active Substances
		<i>Derivatives of native starch:</i> Modification of structure (in chemical, biological, biochemical way) and controlled effect on hydrogen bonding to improve starch properties, e.g., improvement of heat and shear stability, inhibition of swelling, reduction of retrogradation					
Cellulose and Derivatives (Methylcellulose (MC), Hydroxypropyl Methyl Cellulose (HPMC))							
Major structural plants material	Linear polymer of β -D-glucose	Native cellulose:	MC solutions are stable from 3 to 11 PH			MC and HPMC have good film-forming properties	Fish oil/spray-drying
Sources: wood, cotton, straw, flax, jute, hemp	Chain units are bonded by β -(1-4)-glycosidic linkage	Insoluble	Mixture of MC and HPMC exhibit pseudoplastic non-thixotropic flow properties				
Other: acetic bacteria and many algae synthesize cellulose		Crystalline become amorphous in water at 320°C And 25 MPa	Deviation from Newtonian behavior increases with molar mass				
		Derivatives: Swelling and soluble Decreases with increase in polymerization and substitution degrees Solutions are surface active					
							Kolanowski et al. (2007)

From Wandrey et al., 2010; Milani & Maleki, 2012.

