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Fundamentals and Applications

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Preface

Beads made from Egyptian faience have been excavated from grave deposits (c. 4000–3100 BC), together with beads of glazed steatite (a soft rock) and of semi-precious stones such as turquoise, carnelian, quartz, and lapis lazuli. Information on these and many more ancient beads used for ornaments and jewelry, ritual ceremonies, as art artifacts and gifts for amorous women throughout history, and descriptions of the raw materials (e.g., glass, bone, precious and other stones) and manufacturing technologies used for their production can be located in many references. Many books are devoted to the description of beads that are not of water-soluble polymer origin, techniques for their production, their art, value, and distribution, reflecting the wealth of information existing in this field of science and art. On the other hand, there are no books fully devoted to the fascinating topic of hydrocolloid (polymeric) beads and their unique applications. A few books contain scattered chapters and details on such topics, while emphasizing the possibility of locating fragments of information elsewhere; however, again, there is no book that is solely devoted to hydrocolloid beads and their versatile applications. In the meantime, the use of water-soluble hydrocolloid beads is on the rise in many fields, making a book that covers both past and novel applications of such beads, as well as their properties and ways in which to manipulate them, crucial. The aim in writing this volume was to present, in an easy-to-follow sequence, a description of bead production methods and of techniques which can be used to estimate, and modify, their physical and chemical properties. This book offers a full description of not only traditional and recent developments and applications of beads in the fields of agriculture, biotechnology, environmental studies, medicine, and food, but also topics which have never been covered in the literature, making it of the utmost importance to industry and academia.

Chapter 1: Physical Properties of Beads and Their Estimation

In Chapter 1, the criteria used to describe the shape and size of beads are explained. In particular, sections on roundness, sphericity, measurement of axial dimensions, and resemblance to geometric bodies are included. A special section is devoted to the methods used to estimate average projected area, volume, and density, including specific gravity balance and pycnometric methods. Other sections are devoted to bead surface area and specific surface in porous media, e.g., dried beads. Also covered are image processing and its utilization for hydrocolloid beads. Finally, the chapter discusses the structure of hydrocolloid beads, their density, and their porosity.

Chapter 2: Bead Formation, Strengthening, and Modification

This chapter begins with a brief overview of the typical polymeric materials used for bead creation and their limitations. A full description is then provided of procedures to construct different bead forms, e.g., from cylindrical to almost perfectly spherical, by changing both the molds and the media into which the molten or dissolved hydrocolloid preparation is dropped or transferred. Also, some information on dropping methods, changing drop size and distribution, and liquid sprays is provided, affording a measure of control over bead size and distribution. The various water-soluble polymers that can be used for bead formation are discussed at length. The properties of gel beads prepared from agar/agarose κ-carrageenan, alginate, celluloses, chitosan, and to a lesser extent polyacrylamide and other synthetic polymers, among many others, are described. The use of crosslinking agents for both creation and strengthening of several bead types is thoroughly covered. Special methods to modify the porosity of the formed beads are also described, as are methods of slow dissolution of crystals by acid to facilitate better growth of embedded cells via pH regulation. A special section is devoted to beads prepared from proteins, ways to increase their stability (with, for example, glutaraldehyde), and their influence on the cells embedded within them. Since a combination of alternative methods may well provide a good means of overcoming the evident shortcomings of current bead-formation techniques, at the end of this chapter, a few approaches are presented, such as adding epoxy-resin reagent and curing agent to alginate for matrix stabilization, and other less known approaches for bead stabilization, as well as less traditional ways of producing and modifying beads.

Chapter 3: Methods and Mathematical Models for the Drying of Polymeric Beads

Water-soluble polymer beads can be dried for a variety of purposes (described in full in Chapter 6). In general, after drying, the texture is porous. In many cases, the bead is capable of retaining its integrity even after immersion in water for long periods. In addition, and in contrast to wet gel beads, porosity facilitates the liberation of gases during fermentation without harming the dried bead's integrity. This chapter covers methods for drying polymeric beads, including air-drying, fluidized-bed and microwave-assisted fluidized-bed drying, and freeze-drying, and freeze-dried biological products are fully described. Sections also include drying of dosage forms made of drug dispersed in a polymer, mathematical and numerical models to analyze the drying, and a discussion of special cases such as drying a polymer bead with shrinkage.

Chapter 4: Food and Biotechnological Applications for Polymeric Beads and Carriers

The immobilization of microorganisms or cell suspensions in beads for a variety of biotechnological and food purposes is described—information which is hard to find in currently available books. Examples include amino acid (e.g., L-aspartic acid, L-alanine, and L-phenylalanine) production, organic acid (e.g., citric acid, malic acid, gluconic acid, lactic acid) fermentation and conversion, special uses in ethanol, wine, vinegar, and sake production such as malolactic fermentation, removal of urea from sake and wine by immobilized acid urease, beer brewing using an immobilized yeast bioreactor system, and uses in soy sauce production. Other uses related to miscellaneous flavor materials and aroma compounds are also discussed. These include, but are not limited to, biotransformation from geraniol to nerol, production of limonin, β-ionone, naringin, blue cheese flavor, vanillin, and Japanese seasoning. Special beads that serve for immobilization and are used in the milk industry, e.g., for hydrolysis of lactose in milk, are also detailed. Miscellaneous applications also include production of oligosaccharides, preservatives and bacteriocins, xylitol, carotenoids and leucrose, and *cis,cis*-muconic acid. Less known uses of enzymes immobilized within beads for food applications are also described. Various industrial options such as fuel ethanol production, application of gels for separation matrices, bioartificial organs, and insect-cell immobilization are included. In general, the chapter attempts to touch upon all of the novel applications of bead-immobilized cells for the food and biotechnology industries, such as the production of aroma compounds, the microbial production of bioflavors and their biotransformation.

Chapter 5: Medicinal Applications of Hydrocolloid Beads

This chapter gathers together information culled from many sources. It describes the use of cells encapsulated in hydrogels, stem cells in bead environments, charged hydrogel beads as new microcarriers for cell culture, as a potential support for endothelial cells, and for vaccine delivery. Other sections provide information on crosslinked chitosan beads for different medicinal purposes: mucoadhesive beads and their applications for eyes and the alimentary system and polyelectrolyte complexes. Additional sections describe novel approaches to cell encapsulation for improved biocompatibility and immunoisolation. Emphasis is placed on methods using alginate–polylysine alginate for encapsulation, and a glimpse is provided of the art and science of artificial cells, encapsulated enzymes for the clinical laboratory, and encapsulation of living cells and tissues for biomedical purposes.

Chapter 6: Dry Bead Formation, Structure, Properties, and Applications

The drying of hydrocolloid beads results in cellular moieties, and this chapter therefore deals with cellular solids. A few manufacturing methods for hydrocolloid cellular solids are described. They include, but are not limited to, drying bicarbonate-containing gels after acid diffusion and cellular solids produced by fermentation and enzymatically. A special section deals with the inclusion of oils in gels and their influence on the properties of the resultant dried cellular solid. Several methods, e.g., compression studies, are described for evaluating the mechanical properties of the dried beads. The chapter also details the models used for describing these beads' stress–strain behavior. The structure and acoustic properties of such cellular solids as a result of production method are also addressed. The applications of dried beads have never been thoroughly reviewed. This chapter attempts to redress this by describing their use as carriers for vitamins, as study models, and for separation and includes special dry beads for water treatment and matrices entrapping hydrocolloid cellular beads. Hydrocolloid cellular carriers for agricultural uses are also presented, e.g., the preservation of biocontrol agents in a viable form by dry cellular bead carriers and the carriers' capacity to protect these agents against UV radiation. The chapter ends with a discussion on the textural features of dried hydrocolloid beads.

Chapter 7: Liquid-Core Beads and Their Applications in Food, Biotechnology, and Other Fields

In 1971, Maddox's patent on soft gelatin capsules was approved. In 1980, Lim and Sun published their hallmark study in which microencapsulated islets were used as a bioartificial pancreas. In that manuscript, alginate–polylysine liquid-core capsules were produced and described. In the food area, Sneath's patent (1975) and later our group contributed to the manufacture and study of liquid-core hydrocolloid capsules. This chapter describes these liquid-core capsules, both natural and synthetic, and the procedures used to produce them. Methods for including oil within these capsules are also provided, along with an overview of their biotechnological and special food applications. Additional biotechnological applications of liquid-core capsules include growth of microorganisms and activity of enzymes within them, and food applications include the manufacture of unique specialty foods and fruit products and the encapsulation of aroma and health compounds, among others. The chapter also describes agricultural and environmental uses of liquid-core capsules and illustrates some special applications: aids to quitting smoking, in the beauty industry for removal of body hair, and in the paper industry.

Chapter 8: Beads as Drug Carriers

Beads are often used as drug carriers in passive, as well as active drug targeting, making this a highly relevant topic in today's research. Major general topics covered in the first part of this chapter include controlled drug release, gels in drug-delivery systems, dual drug-loaded beads, and drug release from the beads. Throughout, issues such as methods of drug incorporation, bead properties, extent and nature of crosslinking and the physicochemical properties of the drug, interactions between the drug and the matrix material, concentration of the matrix material and release environment (e.g., the presence of enzymes) are discussed. Described beads include albumin beads, alginate beads, alginate beads reinforced with chitosan, calcium alginate/PNIPAAM beads, different chitosan beads (e.g., chitosan–tripolyphosphate beads, chitosan microspheres in treating rheumatoid arthritis, carboxymethyl chitosan beads), gelatin beads and those crosslinked with dextran, modified starch microspheres, dextran beads, gellan beads, guar beads, pectin beads for colon-specific drug delivery, pectin–chitosan beads, and modified poly(vinyl alcohol) microspheres. The chapter also summarizes information on achieving controlled production of the beads, such as preparation of biodegradable hydrogels based on polyesters, hydrogels with degradable crosslinking agents and those crosslinked with small molecules, azo reagents or albumin, and hydrogels with biodegradable pendant chains. The chapter finishes with a description of the more unique beads, such as those with floating ability and those made from xyloglucan.

Chapter 9: Beads and Special Applications of Polymers for Agricultural Uses

The concept of bead encapsulation has become highly relevant to agriculture. Beads can encapsulate microorganisms for use in the field of bacterial inoculation technology. Immobilized plant cell suspensions and single seed products have proven to be easy to produce, store, and handle during industrial operation. This chapter describes the goals of encapsulation in agriculture, e.g., to temporarily protect the encapsulated microorganisms from the soil environment and microbial competition and to release them gradually for the colonization of plant roots. Special cases for enlarging populations in which the entrapped bacterial biomass is low are described; other cases in which, for example, immobilized fungi are used as biocontrol agents against soil-borne pathogens are thoroughly detailed; survival of bead-entrapped populations is compared with that of populations encapsulated in peat, and the influence of special additives on bacterial survival is described. In addition, timing and methods for the application of bacterial inoculants are delineated. In particular, topics such as carriers for the slow release of bacteria that affect plant growth, inoculation of seedlings and plants with beads containing fungal inoculum, joint immobilization of plant growth-promoting bacteria and green microalgae, cryopreservation by encapsulation/dehydration technique, and controlled release of agricultural chemicals are discussed at length. The chapter also supports the reader with a list of biotechnological applications such as gene-delivery systems using beads, bioactive bead methods for obtaining transgenic plants and in synthetic seed technology and describes unique applications of polymers, including superabsorbent polymers and seed coating.

Chapter 10: Beads for Environmental Applications

This chapter focuses on the use of beads to immobilize microorganisms for pollutant biodegradation. Special emphasis is placed on chemically contaminated water, soil, and air. Water treatments are reviewed, and wastewater treatment by anaerobic fixed bed reactor or using immobilized microorganisms is discussed, along with the more specific examples of arsenic removal from water, chitosan and the removal of heavy metal ions, and water denitrification. The chapter lists the advantages of using encapsulated bacterial cells for soil applications, describes the preparation of such beads, and gives information on the protection of encapsulated cells from environmental stress. Another topic is the use of beads to protect against toxicity and the related issues of soil treatments, agrochemicals, controlled release of pesticides into soils, and sustained release of fungicide. Because these beads are introduced into soils, a special section is devoted to release from these beads in the soil environment. In addition to discussing the advantages of beads for environmental applications, the chapter tries to account for the limitations of such technologies, such as the problem of substrate diffusion into immobilized preparations. Other covered issues include air pollution and sampling and the determination of trace contaminants in air by concentration on porous polymer beads. Finally, the chapter discusses miscellaneous applications such as biodegradation and removal by microalgae.

In addition to covering the numerous types of hydrocolloid beads, this book describes their many traditional and non-traditional uses, developed in many hydrocolloid R&D laboratories all over the world, including ours. The book addresses many important industries and as such is designed to capture the interest of those who are looking for new applications in the fields of agriculture, food, environmental quality control, biotechnology, and medicine; it will be of interest to the polysaccharide chemist, as well as to academic and other researchers and authorities in the fields of food, chemistry, medicine, and biotechnology.

My hope is that this book will assist all levels of readers. It is dedicated not only to the academic community but also to the broader population of industrialists and experimenters who will find this book to be not only a source of knowledge but also a launching pad for novel ideas and inventions. In particular, this book is expected to be of interest to personnel involved in food formulation, food scientists, food technologists, industrial chemists and engineers, pharmaceutical staff and medical doctors, and those who deal with drug delivery from beads. Potential readers also include both professional and dedicated non-professional environmentalists, farmers, agriculturalists, and those working on the development of novel beads and their applications. Finally, it is hoped that this book will find a prominent place in the traditional university and research institute libraries where food science, chemistry, agriculture, environmental studies, and other theoretical and practical industrial topics are taught and studied.

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Acknowledgments

This book was written over the course of 2 years. It contains a description of polymer macro- and micro-gel beads, their properties, and applications. It also includes their many traditional and non-traditional uses, developed in our and many other hydrocolloid laboratories worldwide. My hope is that this manuscript will assist readers who are in search of comprehensive knowledge about the fascinating field of beads, as well as those seeking up-to-date information on the very different current and past uses and applications of polymer beads in many areas. Comments and questions from these readers will be very much appreciated.

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