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"Food Packaging"

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Introduction

"Food Packaging" is the seventh volume of Nanotechnology in the Agri-Food Industry, a series aimed at bringing together the most recent and innovative applications of nanotechnology in the agriculture and food industries and to present future perspectives in the design of new or alternative foods. The volume "Food Packaging" presents the development of novel nano-bio-materials and the enhancement of barrier performance of nondegradable and biodegradable plastics in industrial packaging. Like the rest of the series, the book is edited by Dr Alexandru Mihai Grumezescu at the Department of Science and Engineering of Oxide Materials and Nanomaterials, Politehnica University of Bucharest, Romania, who is an experienced and widely published researcher and editor in the field of nano- and biostructures.

The book comprises 20 independent chapters authored by academics from 17 countries. Each chapter reviews recent developments in a chosen area of food packaging. Altogether, the book gives a full account of the efforts made by scientists across the world starting from the 1990s but mostly in the first 15 years of the 21st century in developing advanced polymer packaging materials for food, by adopting the approaches of nanotechnology and biomaterials, and progress made, particularly in the following areas:

- Barrier properties
- Ecofriendly and/or cost effective packaging
- Active packaging
- Intelligent packaging.

Although the book itself is not structured into different sections, this review covers all 20 chapters by categorising them into the above listed themes.

Nanotechnology and Improvement of Barrier Properties

Good barrier properties are key requirements for food packaging materials. Compared to glass, metal and ceramics, the barrier properties of polymer materials to gases and liquids are inferior and enhancement is often needed. Nanotechnology has emerged as a successful approach. Improvement of barrier performance is the central topic of many of the chapters in this book and nanotechnology is extensively discussed.

Chapter 1 by Iman Soltani *et al.* (North Carolina State University, USA) concentrates on the fundamental aspects of nanotechnological strategies for high barrier polymer food packaging materials. Two strategies are presented: applying inorganic coatings to the surface of plastics and developing nanocomposites. Starting with classifying coatings according to the number of layers, a clear overview of the inorganic coating approach is provided. The history and technology of applying a single layer (10–100 nm) of metal and oxide/nitride coating to the surface of polymers with physical (for example thermal or sputtering) vapour deposition (PVD), chemical vapour deposition (CVD) and atomic layer deposition (ALD) methods are described. For multilayer coatings, the authors focus on relatively recently developed layer-by-layer assembly (LBL) coating. The evolution of LBL technology, including the interaction and layer building mechanism employed, the range of materials used for fabrication, from the original multilayer of oppositely charged polymer to charged particles (for example globular protein) and charged platelets (exemplified by exfoliated natural clays such as montmorillonite, MMT), and the fabrication methods from simple dipping to spraying and spin coating, is accounted.

The ability to improve barrier properties is presented and the shortcomings of coating methods, which are defects and adhesion issues, are explained. The authors introduce the polymer nanocomposites (PNC) strategy to overcome these drawbacks and focus on polymer clay nanocomposites (PCNs). Methods to prepare and characterise PCNs are summarised. The well-recognised four typical morphologies of layered silicates polymer micro/nanocomposites: phase separated, exfoliated, intercalated and intercalated plus flocculated are cited and depicted (**Figure 1**). These correlate directly to the barrier enhancement effect. Following a theoretical discussion of molecular transport in polymers and nanocomposites, case studies are included to provide a clear comparison of the barrier enhancement abilities of the routes discussed. Typically, improvement of up to 3, 3, 4 and 1 order of magnitude (against O_2) can be achieved relative to the base polymer materials for PVD/CVD, ALD, LBL coating and PCNs, respectively. The authors highlight the commercial importance of PCNs for their facile processability, mechanical robustness and lengthy stability, despite their relatively modest barrier efficacy.

Nanocomposites are no doubt the most appreciated nanotechnology in this book and are discussed by many authors separately in the

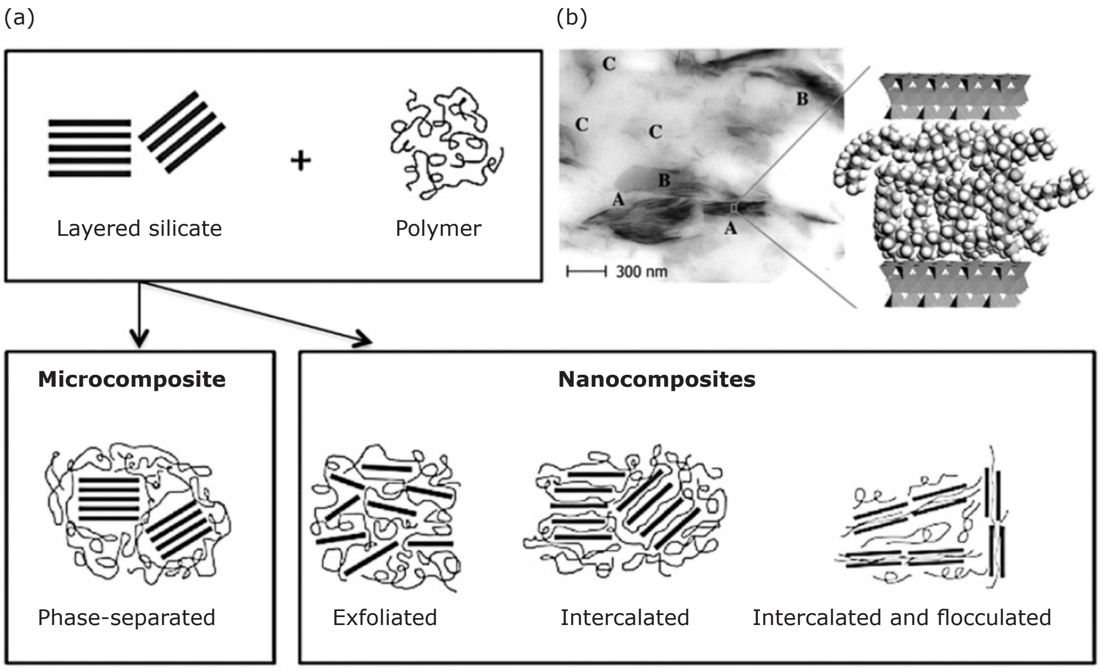


Fig. 1 (a) Schematic illustration showing the results of incorporating layered silicates into polymeric matrices to yield either phase-separated microcomposites or different types of nanocomposites (labelled), depending on the level of dispersion achieved; (b) TEM image of a nanocomposite composed of dispersed clay platelets in a PP matrix. Here, **A**, **B**, and **C** identify intercalated stacks, disordered intercalated tactoids and exfoliated platelets, respectively. A schematic representation of an intercalated clay stack is included wherein parallel platelets are separated by PP chains. (**A**) Adapted from (1). Reproduced from (2), copyright the Materials Research Society other 16 chapters, as a key solution to improve not only the barrier performance but other properties as well.

Studies of a special type of polymer nanocomposites, polymer/graphene nanocomposites are specifically reviewed in Chapter 20 by Ahmad Allahbakhsh (Tarbiat Modares University and Islamic Azad University, Iran). In outlining the concept of substituting nanoclay with graphene in polymer nanocomposites for barrier and reinforcement, the author underlines the use of functionalised or oxidised graphene (graphene oxide (GO)) instead of pure graphene in polymer nanocomposies for achieving dispersibility and compatibility of the nanoparticles. The preparation (through chemical oxidation and micromechanical exfoliation of graphite) and the properties of GO and its covalent and non-covalent interaction with polymers are discussed, which pave the way to review studies of nanocomposites of GO with a number of polymers: polypropylene, polyethylene, polyethylene terephthalates, polyvinylalcohol, polylactide and pullulan. The preparation of nanocomposites by melt compounding, *in situ* polymerisation and solution blending routes plus LBL techniques, and the effective reduction of permeation to gases are described.

Chapter 8 by Agustín González *et al*. (Universidad Nacional de Córdoba, Argentina) discusses the structure-property relationship of nanocomposites from the viewpoint of reinforcement. The literature of nanocomposites composed of various nanoparticles (starch and cellulose nanocrystals, chitosan nanoparticles, inorganic lamellar fillers, cellulose nanofibres and nanowhiskers and carbon nanotubes) are thoroughly examined for the mechanical reinforcement of biopolymers. Additional effects of nanocomposites such as magnetic and electric functions are also briefly reviewed.

Chapter 14 by J. Rodolfo Rendón-Villalobos *et al.* (Instituto Politécnico Nacional, Mexico) concisely reviews the development of nanocomposites and presents them as the ideal barrier material. The authors provide an overview of the technology of polymer multilayer (generally 3–9 layers) films and coatings based on a discussion of gas permeability and material barrier properties and the barrier properties that multilayer films can offer, with a focus on bioplastics.

Chapter 18 by Karolth Espinosa *et al*. (UNS-CONICET, Argentina) deals specifically with polypropylene/talc nanocomposites. Through a detailed description and a review of their processing, including film blown technology, and the morphology, mechanical properties and barrier performance of the final films, the authors present the feasibility of using polypropylene/talc nanocomposites as low cost improved barrier materials as well as the scalability challenge.

The enhancement of barrier properties is further studied by other authors in depth in Chapters 2, 5, 12, 13 and 20. In Chapter 5, Xueyan Yun *et al*. (Inner Mongolia Agricultural University, China) discuss the fabrication of high barrier plastics and their application for food packaging. In addition to nanocomposites, coating and LBL assembly technologies, the authors provide an overview of more traditional technologies such as polymer orientation/stretching and blending. The authors also discuss using organic coatings to enhance barrier properties, for example polyvinylidene chloride on polyethylene terephthalate. Improved preservation of various foods by enhanced polymer films, including meat products, chilled meat, cheese, salad sauce, seafood and agricultural products, is demonstrated by case studies. As the basis of the discussion, fundamentals of food packaging, such as the impact on the shelf life of factors such as light, oxygen, carbon oxides and moisture through the mechanisms of oxidation and photooxidation, degradation of protein and vitamins, colouration, growth of microorganisms and other physical or chemical reactions are provided.

Bio-nanocomposites and Ecofriendly Packaging

Judging by the market size and the huge volume of materials consumed, the packaging industry may be seen as a materials intensive industry. There has been extensive research on ecofriendly packaging to minimise the impact on the environment. A solution is using bioplastics – biodegradable polymers or polymers made from renewable resources. This book follows the trend with 14 chapters discussing natural, bio-polymer or biodegradable polymer packaging.

Renewability is a big advantage in bioplastics. This is exemplified in Chapter 7 by Ana Sofia Lemos Machado Abreu *et al*. (University of Minho, Guimarães, Portugal). The authors discuss bioplastics from agro-wastes for food packaging applications. An overview of a number of petroleum based biodegradable polymers and polymers from renewable resources is provided. It is interesting that the authors enlist polyethylene as a biodegradable polymer for its hydro/oxodegradation ability and the possibility to blend it with well-known biodegradable polymers. Cellulose is highlighted as a polymer which is available from plants, bacterial processes and in particular from agro-wastes. In presenting renewable cellulose and its derivatives as potential food packaging materials, studies on extracting cellulose from agro-wastes, physical blending of cellulose with other biodegradable polymers, chemical modification of cellulose in ionic liquids and graft polymerisation of cellulose are reviewed.

Nanocomposites play a significant role in bio-polymer packaging. Chapter 10 by Ana Sofia Lemos Machado Abreu *et al*. (University of Minho, Guimarães, Portugal) discusses biodegradable polymer nanocomposites for packaging applications. The chemistry of various natural polymers including soy, corn-zein, starch, cellulose, chitosan and other polysaccharides and synthetic or bacterial-based polyesters including polycaprolactone, polylactic acid and polyhydroxyalkanoates are summarised. Studies on nanocomposites of these polymers are reviewed. A short discussion of the biodegradation process and its limitations is provided. A few examples of commercial biodegradable polymer food packages are given by the authors. In Chapter 3, Sushama Talegaonkar *et al*. (Jamia Hamdard, India; Mendel University, Czech Republic, and University of Natural Resources and Life Sciences, Austria) thoroughly review the research on the commonly used nanoparticle fillers including nanoclay, nano-cellulose, silicon dioxide, carbon nanotubes, silver dioxide, zinc oxide, titanium dioxide and the nanocomposites of common natural polymer cellulose, starch and chitosan. The authors attempt to look at bio-nanocomposites from the angle of active and intelligent packaging.

Chapter 19 by Aleksandra R. Nesic and Sanja I. Seslija (University of Belgrade, Serbia) focuses on the influence of nanofillers on the properties of polysaccharide based nanocomposites. Following an overview of food packaging materials (materials type, criteria and trends), the authors review polymer nanocomposites research by type of nanofillers. The characteristics of the nanofillers and the properties and functions of the respective nanocomposites are summarised. Next the authors provide comprehensive knowledge about the sources of extraction, physical structure and physical-chemical properties of nine commonly seen polysaccharides and their application including food packaging materials *via* a nanocomposites route. A further hurdle to overcome for commercialising polysaccharide nanocomposite packaging materials is identified by the authors at the end of the chapter.

ZnO nanocomposites with polyhydroxyalkanoates are further discussed in Chapter 6 by Ana M. Díez-Pascual (Alcalá University, Spain). The synthesis, structure, properties and applications of polyhydroxyalkanoate polymers and ZnO nanoparticles are detailed. Studies on nanocomposites of ZnO with two specific polyhydroxyalkanoates: polyhydroxybutyrate and polyhydroxybutyrate-co-valerate are reported.

The barrier properties of bio-nanocomposites of biodegradable polymers with nanofillers are thoroughly discussed in a number of chapters, particularly in Chapters 2, 12 and 13. Chapter 2 by Giulio Malucelli (Politecnico di Torino, Alessandria, Italy) provides a literature survey of biocomposites containing nanofillers of different morphology (three-dimensional (3D) spherical and polyhedral particles, two-dimensional (2D) nanofibers and one-dimensional (1D) platelets) and of different chemistry (for example colloidal silica, polyhedral oligomeric silsesquioxanes, carbon black, nanoclays and starch nanocrystals). An improvement of barrier properties by tens of percent can be seen. The authors also dedicate one section to the LBL method, highlighting its advantages such as effective barrier property improvement, imparting of other additional functions, process simplicity and eco-friendliness.

Chapter 12 by Marina Patricia Arrieta *et al*. (Institute of Polymer Science and Technology, Madrid and Polytechnical University of Valencia, Alcoy, Spain) aims at elucidating the role of nanoparticles in improving the barrier properties of bioplastics and assessing the impact of the shape of nanoparticles to barrier properties. The research of bio-nanocomposites of biodegradable polymers (polylactide, polycaprolactone, polyhydroxy butyrate, polyhydroxy butyrate-co-valerate, plasticised starch and polyvinyl alcohol) with MMT, cellulose nanocrystals and ZnO nanoparticles as representative 1D, 2D and 3D geometry nanofillers is described in detail. The additional influence of factors such as surface properties of nanoparticles and their interaction with components of the bioplastics, adhesion and crystallisation on barrier properties is discussed. The extra antimicrobial benefits of nanocomposites containing ZnO is also specified.

Chapter 13 by Kateryna Fatyeyeva *et al*. (Normandie University and University of Rouen, France) focuses on high barrier biopolymer/clay nanocomposites. The authors clearly outline the background on nanocomposites, government regulation, biopolymers, clays and biopolymer/clay nanocomposites. Mechanistic understanding and the barrier properties of nanocomposites formed by nanoclay with polysaccharides, proteins, aliphatic polyesters and mixtures of polymers are reviewed in detail. As well as enhancing the concept of improving barrier properties by clay nanocomposites, a full picture of the influence of the biopolymer and nanoclays themselves as a component to the final nanocomposites is provided. The future development of biopolymer/clay nanocomposites is discussed. The barrier properties of bioplastics are also a focus of Chapter 14.

Despite the potentials of bioplastics and some examples of commercial products, more research and development is needed to make bioplastics more comparable to traditional petroleum based polymers in properties and performance to achieve full commercialisation success in food packaging. This is highlighted by many authors in the above chapters. The authors also look at future directions for development.

Active Packaging

A significant step in food packaging is active packaging, which can proactively extend the shelf life, maintain or even improve the condition of packaged food. Functional nanocomposites, nanocomposites of physically, chemically or biologically active nanoparticles play vital roles and have become an important route for active packaging. This book records the progress in active packaging, in particular nanocomposites for active packaging.

Active packaging including antimicrobial packaging and modified atmosphere control is highlighted as a trend in Chapter 19. In Chapter 8, readers can learn how metals and metal oxides, carbon nanotubes and biopolymer nanoparticles are incorporated into polymers to impart antimicrobial, UV-blocking and anti-oxidant functionalities. In Chapter 3, several commercial product examples of atmosphere control packaging (for moisture, oxygen and carbon dioxide) are briefly described.

Antimicrobial and antibacterial packaging is well addressed in this book. Both Chapter 15 by Iva Rezić *et al*. (University of Zagreb, Croatia) and Chapter 16 by Majid Montazer *et al*. (Amirkabir University of Technology, Iran) are dedicated to antimicrobial nanocomposites. Together the two chapters present essential information about the antimicrobial properties of a list of nanoparticles including metals (silver, copper, iron), metal oxides (titania, ZnO, copper oxide, ferrous oxide, magnesium oxide), carbon nanotubes, nanoclays, biopolymers (chitosan, nisin, alginate) and their composites with polymers. Chapter 16 concentrates on bio-nanocomposites. It is worth mentioning that toxicological properties of nanoparticles and the health, ethical and regulatory issues related to antimicrobial packaging are well discussed in the two chapters. The antimicrobial properties for ZnO-based bio-nanocomposites are also discussed in Chapters 6 and 12.

Nanodiamond is a special class of bioactive nanoparticles. Chapter 9 by Katarzyna Mitura *et al*. (Koszalin University of Technology, PLASTMOROZ Sp. z o.o. Sp. and Koszalin University of Technology, Poland) presents a complete report of bioactive packaging with nanodiamond particles. A full account of nanodiamonds, including their sources of origin, preparation, modification, morphology, properties, antimicrobial, antioxidant and biomedical activity, cyto-toxicology and their increasing application in coatings and nanocomposites is provided. Readers are shown the ways in which nanodiamonds differ from metals and metal oxides deriving from their electronic structure and zeta potential.

An interesting type of active packaging is provided by flavour and aroma. Chapter 17 discusses nanoencapsulation of flavour and aroma for food packaging. The science of flavour and aroma is summarised in the chapter. Natural aromatic substances are often synthesised by living organisms as a defense mechanism or as secondary metabolites and have antioxidant, antibacterial and antifungal properties. By incorporating these into food packaging they can reduce the most common spoilage pathogens and prevent deterioration of food quality. A proven effective process is for flavours and aromas to be micro- or nano-encapsulated into capsules and incorporated as particles into packaging materials. Encapsulation technology and the materials used for encapsulation, and studies of largely successful incorporation of nanoencapsulated flavours into polymer films for food packaging, are reviewed.

In Chapter 11, Mythili Prakasam *et al*. (University of Bordeaux, France) discuss flexible packaging for nonthermal decontamination by high hydrostatic pressure, which may be classed as a special type of active packaging. High hydrostatic pressure processing technology is described, including the materials requirements, the working mechanism and its impacts on physical, chemical, mechanical, barrier and active migration properties of packaging materials particularly multilayer packaging.

Intelligent Packaging

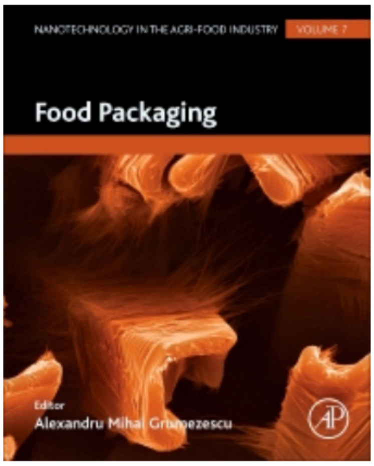
Intelligent packaging communicates information on the state of the package and packed goods to owners and customers. It has been a target of research and development and several types of intelligent packaging are emerging. Chapter 4 by Viviane Dalmoro *et al*. (Federal University of Rio Grande do Sul and Polymer Technology Center at Triunfo, Brazil) describes some developments in the area of encapsulation of sensors for intelligent food packaging. Commercial interest in intelligent packaging is assessed by the authors at the beginning of the chapter and readers are shown that the market is growing in size. A few products currently on the market or in development such as freshness, integrity and time-temperature indicators, radio frequency identification tags and embedded sensors are then described. An overview of the chemistry and processing technology of current and emerging packaging materials is made in the context of encapsulating sensors. The authors highlight the sol-gel method as a versatile way to encapsulate and develop packaged sensors. Sol-gel chemistry, in particular silane chemistry, is discussed and the development of sol-gel encapsulated sensors, for example dyes or indicators, and their application in packaging to detect amine, formaldehyde and pH changes for food quality monitoring are reviewed. A summary of the current regulation status of intelligent and active packaging in Europe and the USA is included.

Intelligent packaging is also discussed in some other chapters of the book. Chapter 8 mentions the development of nanocomposites containing nanoparticles as intelligent indicators, for example TiO_2 as a UV-activated oxygen indicator, chiral nematic nanocrystalline cellulose as a humidity indicator, Ag/Cu nanoparticles and carbon nanotubes as freshness indicators and quantum dots as microorganism growth indicators. In Chapter 3, a commercial product indicating oxygen levels is briefly described.

Conclusions

As with similar books, the volume is primarily a collection of reviews published in scientific journals and little patent literature is included, although in some chapters brief summaries of the commercial technology are provided. Many readers, especially those researchers from industry, may be interested to learn more about the commercial status of the technologies discussed in this book. As the book is written by many groups of independent authors, inevitably readers may find that there is some overlap in content between some of the chapters. There appear to be some plain language errors easily spotted in parts of the current edition.

Nevertheless, the book has succeeded in presenting readers with the frontiers of food packaging materials science. The state-of-the-art in developing high barrier and multifunctional food packaging materials using nanotechnology and biodegradable or renewable polymers is well documented, as well as fundamental knowledge, scientific background and insights into the future development of packaging materials. The book provides a comprehensive reference for the design of food packaging materials, development of technology and the manufacturing of food packaging products, and thus will certainly appeal to professionals working on food packaging from both industry and academia. The book will also interest general readers including graduate and undergraduate students in materials science and engineering.



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