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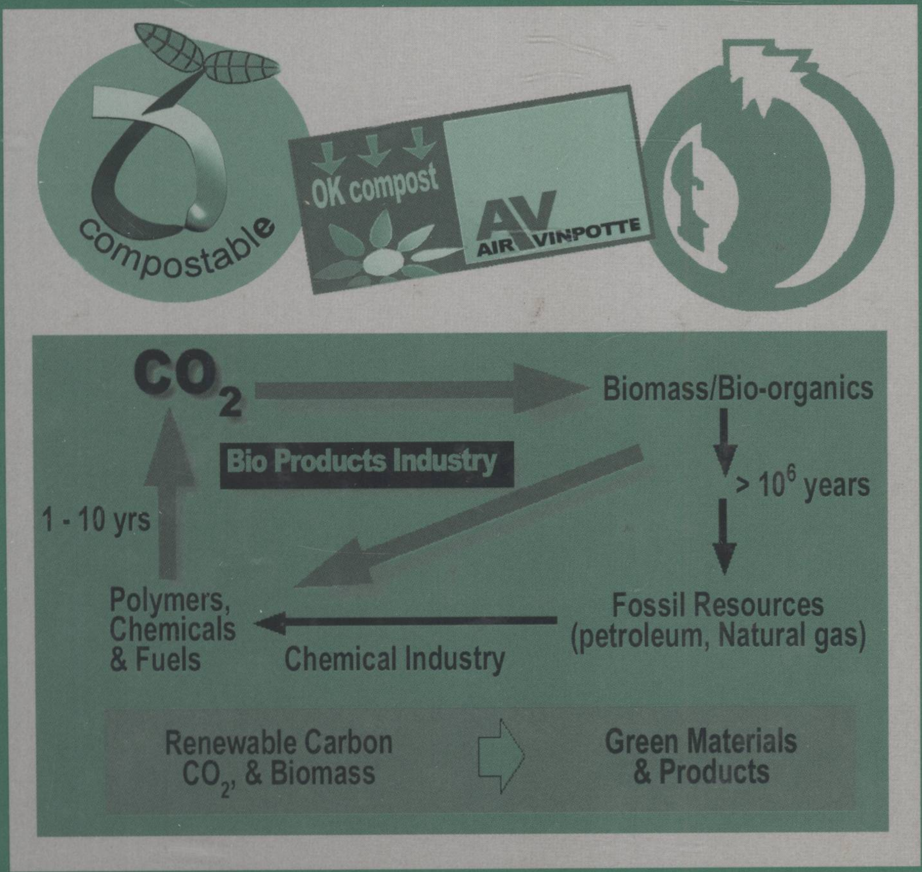
Degradable Polymers and Materials

Principles and Practice



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Degradable Polymers and Materials

Principles and Practice

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Degradable Polymers and Materials

Foreword

The ACS Symposium Series was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of the series is to publish timely, comprehensive books developed from ACS sponsored symposia based on current scientific research. Occasionally, books are developed from symposia sponsored by other organizations when the topic is of keen interest to the chemistry audience.

Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previously published papers are not accepted.

ACS Books Department

Preface

A revolution is in the making in the world, where scientists are working very hard to discover viable biodegradable and natural renewable resource-based alternatives to the fossil-fuel-based, non-degradable polymers and materials. This movement is driven by the growing general awareness among the consumers and governmental agencies in most countries that conventional plastic products, although useful, are doing tremendous damage to their environment, marine and animal life, water supplies, sewer systems, and the rivers and streams. This is further exasperated by the more obvious eyesore of the littering problems that are associated with these non-degradable products, which have created a public outcry that something must be done about it.

The modern petrochemicals-based plastics industry realized more than 20 years ago that it is unsustainable in the long run, because of the limited and rapidly depleting raw material source. Combined with the growing discontent of worldwide plastics-consuming communities with their plastic litter problems, it did not take long before most major plastics manufacturers had launched research programs aimed at developing biodegradable polymers. Although the initial efforts were mostly aimed at making hydrolysable polymers, such as polyesters and polyamides, biodegradable via the use of aliphatic monomers, the recent shift has been toward the use of renewable resource raw materials, such as starches and proteins.

The 22 main chapters in this symposium series book describe various aspects of current research and development related to design, synthesis, properties, processing, applications, degradation, and biodegradation of a variety of novel polymers and materials. This book was developed from the more than 65 papers presented at the spring meeting of the American Chemical Society (ACS) that was held in San

Diego, California in March 2005. The tremendous success of the symposium and the lively discussions that followed every presentation attested to the growing interest in this area. A need for a book such as this was quite apparent at the conclusion of the symposium. Because we were restricted by the size of the book by our publisher, the ACS Books Department, we had to make a careful and judicious selection of symposium presentations that were to be included in this book and that could benefit the R&D community. We sincerely regret that we were unable to include all of the symposium presentations in this book. In the end, we selected chapters that highlight the key areas of activities in this fascinating field. The contributing authors, from all around the world, are recognized leaders in their respective fields.

The authors and the editors of this book sincerely hope that the workers, researchers, scientists and engineers working in this and related fields will find this book very useful and helpful in their work and pursuit of novel, environmentally benign, as well as degradable and biodegradable polymers and materials.

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Overview

People in developed countries have enjoyed a modern, highly industrialized society since the middle of the last century. Many convenient and industrial products are available at low costs. These products (such as synthetic polymers including plastics, fibers, rubber, and other chemicals) are derived mainly from a petroleum source. In such a society, everything is governed by the economic factors for maintaining a convenient daily life. As a result, however, a serious problem arose: an environmental problem of the Earth! This is more or less related with natural resources, energy (including global warming), foods, and population problems, which we now face.

In the area of polymers, the best possible ways to solve the above problem is definitely the use of degradable polymers and related materials. As a simple example, non-degradable waste plastics brought about a serious damage to the environment, which is a white pollution. Reducing the consumption of crude petroleum and other fossil resources will help us to realize a green sustainable society. Recently, many polymer scientists are pursuing studies in this direction and are designing and preparing various degradable polymers. As shown in this book, degradable commodity polymers, ideally derived from renewable resources are expected to gradually replace petroleum-based polymers. A typical example is poly(lactic acid), which is actually used in the packaging industry and in automobiles. Natural polymers will find new practical applications in various ways. Degradable fine polymers will contribute to better materials for biomedical and drug-delivery applications.

Finally, I highly appreciate the organizers for their very timely contributions to this symposium and for the publication of the presented papers. This book suggests to the readers an important direction of future research into polymeric materials. Polymer scientists should always take into account the environmental problems, which are one of the most important and serious problems confronting the 21st century.

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Chapter 1

Introduction

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Introduction

This book describes some recent developments in natural and synthetic degradable and biodegradable polymers and materials, including their synthesis and assembly, characterization and degradation studies, as well as the design and exploration of such materials for specific and alternative eco-friendly and sustainable applications to conventional polymers and materials. The twenty five chapters in this book have been written by world's leading researchers in their respective areas. Here, these chapters have been organized in the order such that they describe advances in natural polymers, natural and synthetic polymers, polymer synthesis, characterization and finally degradation mechanisms.

Several chapters of this book are dedicated to natural polymers, which are inherently biodegradable due to their natural origin. Chemical modifications of natural polymers lead to enhanced properties, typically tailored to specific applications and it is often possible to sustain biodegradability despite chemical conversions of the natural polymers. Since ester bonds readily undergo hydrolysis, various polyesters are considered (bio)degradable and are the focus of many studies that aim at the synthesis of novel, environmentally benign materials, from biomedical materials to lubricants and packaging. In many cases the judicious placement of selected co-monomers within the polyester backbone guarantees a controlled, time-dependent degradability. While it is easy to claim degradability for a particular polymer based on its chemical nature, it is more challenging to actually prove degradability. In particular the question of the degradation timeframe has given rise to arguments and discussions. Polymeric materials can degrade physically due to the influence of heat and/or electromagnetic radiation or biologically under the impact of degrading enzymes. Recently, it became possible to identify biochemical pathways for enzymatically catalyzed polymer degradation. Several chapters are dedicated to the characterization of degradable materials, including rules and legislature that define and govern degradable materials. Known polymer analysis techniques have recently been adopted to detect the early onset of polymer disintegration and to make themselves particularly useful to natural polymers and chemically modified natural polymers.

Plastic materials are used worldwide for a multitude of applications, in fact it is very difficult, if not impossible, to imagine life without plastics today. The application range for plastics is extremely wide and includes such high-performance and high-tech applications as Kevlar in bulletproof vests and low-end applications such as garbage and shopping bags. Some of the manufacturing processes for common polymers that we use on a daily basis are known for more than a century, for instance, the making of polystyrene and polyvinylchloride is known since the 1830's. But it was only after World War II that plastics quickly conquered the materials market. Plastic materials were, and still are, appreciated for their durability, impact and tensile strength, reliability and the ability to adjust their properties to match intended uses and in addition, plastics show virtually no corrosion and age slowly. However, with a worldwide increase of plastic waste build-up, paired with a better understanding of the impact of human action on the environment and new and growing environmental awareness, new demands have arisen for plastic materials, specifically their ability to degrade according to a specific, pre-set timetable. Thus, there is a growing general awareness among consumers and government agencies in most countries around the world that conventional plastic products, although useful, are causing tremendous damage to the environment, water supplies, sewer systems as well as to the rivers and streams. While by no means all currently used plastics ought to be replaced by degradable materials, and certainly no plastics in high-performance applications should be degradable. It is paramount to take into account new procedures for plastics production that are based on renewable resources and/or lead to degradable products especially for materials in single-use applications. This book reflects on the latest developments in the area of degradable materials by summarizing new trends in the synthesis, characterization, physical, chemical and degradation behavior as well as information on legislative regulations.

Every year more than one hundred million tons of plastics are produced worldwide. In 2004, the United States alone produced about 52 million tons of plastics [1,2]. The packaging industry is a major area of interest when considering degradable plastic materials, primarily due to the package's limited life of usage. High and low density polyethylene, polypropylene, polystyrene, polyethylene terephthalate, and polyvinyl chloride and polyvinylidene chlorides cover almost the entire packaging market. While plastics production grew slightly over the past several years, plastics used in the packaging industry stayed constant at approximately 30%, or currently 16 million tons. [2] 70% of all the plastic packaging material, which is roughly 11 million tons, is used for food packaging, thus intended explicitly for short term or single use application. The packaging industry, while it could be the largest consumer of degradable materials, is rather conservative in adopting new technologies. Partially, this is due to the fact that olefin-based polymeric materials have been well established in the industries, both from the manufacturing as well as engineering points of view. Due to the nearly hundred years of process optimization experience, the production of polymers for packaging is highly efficient, stable and hence the resulting polymers are cost-effective and difficult to replace.

By contrast, the manufacturing of naturally derived polymers into packaging materials is a rather novel approach in the industry. Early attempts, dating back to the early 1990's, included embedding of starch granules into polyethylene in an effort to produce a (bio)degradable material. The production of fully biodegradable materials, as defined by the new standards (ASTM D6400, EN 13432, ISO 14855) and certified by agencies such as the Biodegradable Products Institute, the DIN Certico or the AIB Vincotte is still a niche market, with a share of less than 1% of the total market. Some large chemical companies, such as DuPont, Cargill Dow, Monsanto, Eastman and BASF have successfully pursued the development of polyester-based degradable materials. A short list of several biodegradable polymers and their basic properties as well as approximate costs currently available in the market place is given in Table 1.

Smaller and start-up companies, for example Novamont, EarthShell and Plantic are more focused on converting natural renewable resource polymers, such as starch and soy-derivatives, into degradable materials. Due to low volumes and curtailed process optimization, (bio)degradable materials are currently still comparatively expensive as compared to conventional plastics. Whilst consumers in European countries seem to be more agreeable to pay extra price for environmentally friendly products, their American and Japanese

Table 1: Biodegradable polymers and their manufacturers

Producer	Polymer / Class	Product Name	Approx. Price [USD/kg]	Tm [°C]	Tg [°C]	Sp. Gravity [g/cm3]
BASF	Aliphatic-Aromatic Polyester	Ecoflex F Ecoflex S Ecoflex U	4.00	105-115	-33	1.25
Bayer	AliphaticPolyester-amide	BAK 1095 BAK 2195	4.00	125 175		1.15 1.18
Cargill / NatureWorks	Aliphatic Polyester	PLA	3.00	175	57-65	1.25
DuPont	Aromatic **Polyester**	Biomax PET	3.00	208	50	1.35
Eastman Chemical / Novamont	Aliphatic-aromatic Polyester	EastarBio 14766 GP Ultra	4.00	 112 115	 -30 -30	 1.20 1.25
IRe	Aliphatic Polyester	Enpol	5.00	90-150	varies	1.20-1.30
Mitsui Chemicals	Aliphatic Polyester	PLA	4.00	173	74	1.26
Novamont	Starch-Polyester – Blend	Mater-Bi	4.00	61 115	-60	1.20
Showa High Polymer	Aliphatic Polyester	Bionolle	6.00	114 95 102	-30 -35 -4	1.26 1.23 1.30
Solvay	Aliphatic Polyester	PCL	4.00	60	-60	1.20
Union Carbide	Aliphatic Polyester	Tone / PCL	4.00	61	-60	1.20