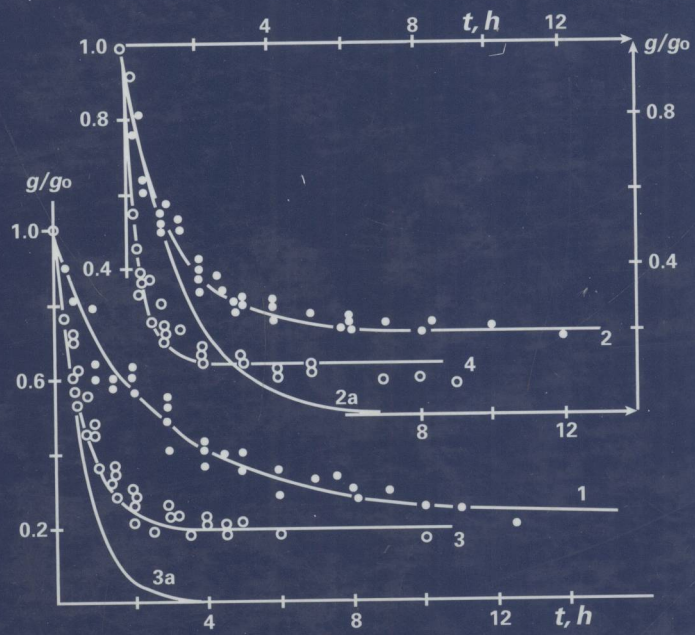
Handbook of Polymer Degradation

Second Edition, Revised and Expanded



edited by
S. Halim Hamid

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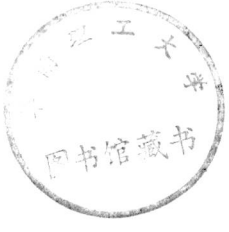
King Fahd Institute of Petroleum & Minerals
Dhahran, Saudi Arabia



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Handbook of Polymer Degradation

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To H. E. Dr. Bakr Abdullah Bakr
my mentor, who always inspires me to take challenges

Preface to the Second Edition

Since the publication of the first edition of the *Handbook of Polymer Degradation* in 1992, a multitude of developments in the manufacturing, processing, application, and use of polymers have occurred. Keeping this in view and encouraged by the success of the first edition, it was decided to bring out the revised and expanded second edition, covering a broad spectrum of topics in this ever-developing and broadening field of polymer degradation and stabilization. Focusing on the basics of photo- and biodegradability, as well as on environmental issues engendered by increased use of polymers in many industries, this edition exhaustively examines the life cycles of polymers from the most current theoretical and practical perspectives.

The present volume is composed of 20 contributions from over 30 experts of international repute. It contains a wealth of up-to-date information on polymer degradation and stabilization for environmental, health, and materials scientists; polymer, plastics, and chemical engineers; and upper-level undergraduate and graduate students in these disciplines. The broad spectrum of authorship from 11 countries represents the global nature and concerns of the subject matter. Each chapter attempts to achieve balance between theory and applications. The reader may find some overlap in theoretical aspects between chapters, but this is useful and necessary from the point of view of completeness.

One of the significant features of this volume is the authorship of several chapters by world authorities who have provided the essence of lifelong investigations of their subjects. For example, François Gugumus' chapter on polyolefin and agricultural greenhouse film stabilization presents an excellent blend of theoretical background and real-life application of polymeric film stabilization for extended lifetime. Peter Klemchuk's chapter on photodegradable polymers is the culmination of long years of theoretical and practical experience accumulated during his association with Ciba-Geigy. The list goes on, but I would also like to mention Jan Pospíšil, Guennadi Efremovich Zaikov, Ann-Christine Albertsson, Norma D. Searle, and Jacques Verdu.

For the sake of clarity, the contributions have been organized into four broad parts. The first part, "Additives and Stabilizers in Polymers," contains six chapters covering this important topic. The following part, "Mechanisms of Polymer Degradation and Stabilization," contains two chapters—one by George and Celina, and the other by Zaikov and coworkers. Six special topics have been covered in the chapters presented in Part III, "Controlled Degradation and Stabilization." The last part, "Wavelength Sensitivity of Polymers" was introduced in this edition to respond to the emerging questions of radiation effects, particularly in the light of ozone depletion and increased UV radiation with shifting wavelength.

The aim of this book is to present an up-to-date account of polymer degradation and stabilization. This volume is obviously an important reference monograph for researchers studying the stability of polymers for outdoor use, producers, end-users, quality controllers, environmentalists, and students who want to apply their knowledge in practical conditions.

I acknowledge the support of the King Fahd University of Petroleum & Minerals (KFUPM) for this project. I wish to express my gratitude to the Rector of KFUPM, H. E. Dr. Abdulaziz A. Al-Dukhayyil, for his encouragement. I would particularly like to thank Nihal Ahmad for his many suggestions and invaluable assistance, which helped me immensely in the successful completion of this project. I wish to express my appreciation to all the staff of Marcel Dekker, Inc., who did their jobs with utmost professionalism. Finally, to my wife and children, I give my deepest thanks for their understanding and forbearance during the development and completion of this book.

S. Halim Hamid

Preface to the First Edition

The subject of polymer degradation and stabilization is becoming increasingly complex because of its dedication to specialized polymeric applications. Rapid advances of polymer applications into new fields inevitably leave a significant gap between demand and inherent polymer limitations. We have made an attempt to include a chapter on each application detailing the behavior of polymers in a specific environment. This handbook contains 19 chapters on varied topics by internationally known authorities who have shared their experiences in the application of polymers to specialized fields.

Chapters were chosen primarily to cover the complete spectrum of polymer degradation and stabilization from the point of view of polymer producers, processors, end users, additives producers, designers, and environmentalists. In each chapter, wherever possible, theory is outlined to provide the user with a broad perspective on a particular topic. It is anticipated that the major users of this handbook will be researchers, but students and professors will also find it a unique and helpful reference book.

This handbook has been divided into three parts—general topics, degradability, and specialized topics. In the first part, we begin with a chapter on degradation and stabilization of polypropylene that discusses the structure and morphology of polypropylene and how these are influenced by radiation-induced degradation. Next, we turn to the susceptibility of polymers to UV radiation, which is well known. We focus on stratospheric ozone depletion, which generally has detrimental effects because of increased UV radiation. This chapter introduces new data and clarifies various aspects of the effects of increased UV radiation on polymers and includes measures to reduce these effects. In Chapter 3, chemical degradation of polymers is discussed in detail with emphasis on various modes of chemical degradation and its impact on applications. Polymer blends are gaining popularity because of economical and technical advantages. Chapter 4 includes various aspects of degradation of polymer blends. Next, artificially accelerated weathering and its relationship to natural weather are authoritatively explained by Musa Kamal and Bing Huang. Following this is a rather detailed treatment of the general concepts of photodegradation of polymers, which is vital to the understanding of weathering and its effects. Weather cannot be changed but polymers can be made compatible with weather. This topic is covered at length with experimental results in Chapter 7. Following this, various aspects of polymer stabilization are very well explained for different polymers by A. J. Chirinos-Padrón and N. S. Allen. Synergism and antagonism of stabilizers are included in Chapter 9.

In Part II, special attention has been accorded to the subject of environmental aspects and waste management of polymers because this is always a difficult

concept to explain. Chapter 10 presents a critical review of photo- and biodegradable plastics. A.-C. Albertsson's authoritative viewpoint on biodegradation of polymers is presented in this section. The material covered in Chapter 12 demonstrates various aspects of starch-based degradable plastics. The increased significance of environmental toxicology of plastics has required a chapter on this subject and includes legislative issues.

The chapters in Part III, on specialized topics, introduce new topics that are not currently available from other single literature sources. F. Henninger of Ciba-Geigy has contributed an excellent chapter on aspects of greenhouse film formulations. The durabililty of geomembranes and geotextiles is covered in Chapter 15. The chapter on application of polymers as a coating material, by George Mills, includes a rather complete discussion of polymer durability in various industrial applications. Medical and biomedical fields are incorporating polymers in a number of applications. We have included two chapters—one by experts from industry (Boehringer Mannheim) and the other from academia (Case Western Reserve University)—to provide a general view of polymer degradation in medical application and biodegradability of biomedical polymers. Polymeric insulators are replacing conventional ceramic insulation; however, the lifetime of polymeric insulators is dependent on weather-induced as well as electrical stresses. Chapter 18 covers different aspects of polymer degradation in insulation of high-voltage transmission.

We owe special thanks to the contributors for their enthusiastic support. This effort would not have been possible without their willingness to share valuable knowledge and experiences. As editors who have reason to know and appreciate the cost of their contributions in time and effort, we join with others in the profession in acknowledging our indebtedness to them and to the universities, companies, and organizations they serve.

We would like to take this opportunity to express our sincere thanks and appreciation to Dr. Bakr A. Bakr, Rector of KFUPM, for his encouragement and personal interest in this project. Our thanks are also due to Dr. Abdallah Dabbagh, Director of the Research Institute, for his constant support. With sincere appreciation we acknowledge the assistance of the administrative affairs department of our institute, particularly its past and present managers. Mr. Mahmoud Sourani and Mr. Hamza Garatly. Abdullah Aitani's critical observations helped in improving the final product, and we thank him for his comments. Our special thanks and appreciation go to Nihal Ahmad, without whose persistent help and long hours this book could not have taken final shape.

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I
ADDITIVES AND STABILIZERS IN POLYMERS

Contents

1

Polyolefin Stabilization: From Single Stabilizers to Complex Systems

FRANÇOIS LOUIS GUGUMUS
Ciba Specialty Chemicals Limited, Basel, Switzerland

I. INTRODUCTION

Polypropylene (PP) needs protection in every stage of its life cycle. It starts with storage, immediately after manufacturing. Then, a small amount of a phenolic antioxidant usually gives sufficient protection. It continues with processing, during which an adequate stabilization is a prerequisite for minimizing degradation of PP in the molten state at temperatures between 200° and 300°C. It ends with a suitable stabilization for the application foreseen. This is a stabilization against thermal oxidation only, if PP is not to be exposed to light. It will be a stabilization against photothermal oxidation if ultraviolet (UV) light exposure is involved. The requirements for polyethylene (PE) are similar to those for PP, but the stabilizer levels are usually lower because PE is inherently less sensitive to oxidative attack than PP.

Processing stabilization is usually achieved with combinations of high molecular mass phenolic antioxidants with phosphites or phosphonites. These aspects will not be developed here. For details the reader is referred to other publications (1–4). Further developments in this respect have been reported more recently (5,6).

Long-term heat stabilization traditionally involved high molecular mass phenolic antioxidants. More recently, it was recognized that high molecular mass or polymeric hindered amine light stabilizers (HALS) are even more efficient for thermo-oxidative stabilization of polyolefins in the solid state. In the following, the evolution of UV stabilization of polyolefins from the beginning to the actual trends will be documented. Then, some aspects of thermal stabilization with HAS will be developed.

The polymers used were either unstabilized commercial resins stored in a refrigerated room to minimize oxidation, or polymers already containing a small