MATERIALS CHARACTERIZATION SERIES

SERIES EDITORS: **C. Richard Brundle** and **Charles A. Evans, Jr.**

材料表征原版系列丛书

聚合物的表征

CHARACTERIZATION OF Polymers

Ned J. Chou
Stephen P. Kowalczyk
Ravi Saraf
Ho-Ming Tong

Mc Graw Hill Education

哈爾濱工業大學出版社
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Ho-Ming Tong, Stephen P. Kowalczyk, Ravi Saraf, and Ned J. Chou

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C. Richard Brundle and Charles A. Evans, Jr.

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We dedicate this volume to the memory of our dear colleague, Ned J. Chou, who passed away during the course of this project. Ned's kindness and wisdom will be greatly missed by all who have known him.

Preface to the Reissue of the Materials Characterization Series

The 11 volumes in the *Materials Characterization Series* were originally published between 1993 and 1996. They were intended to be complemented by the *Encyclopedia of Materials Characterization*, which provided a description of the analytical techniques most widely referred to in the individual volumes of the series. The individual materials characterization volumes are no longer in print, so we are reissuing them under this new imprint.

The idea of approaching materials characterization from the material user's perspective rather than the analytical expert's perspective still has great value, and though there have been advances in the materials discussed inl each volume, the basic issues involved in their characterization have remained largely the same. The intent with this reissue is, first, to make the original information available once more, and then to gradually update each volume, releasing the changes as they occur by on-line subscription.

C. R. Brundle and C. A. Evans, October 2009

Preface to Series

This Materials Characterization Series attempts to address the needs of the practical materials user, with an emphasis on the newer areas of surface, interface, and thin film microcharacterization. The Series is composed of the leading volume, *Encyclopedia of Materials Characterization*, and a set of about 10 subsequent volumes concentrating on characterization of individual materials classes.

In the *Encyclopedia*, 50 brief articles (each 10 to 18 pages in length) are presented in a standard format designed for case of reader access, with straightforward technique descriptions and examples of their practical use. In addition to the articles, there are one-page summaries for every technique, introductory summaries to groupings of related techniques, a complete glossary of acronyms, and a tabular comparison of the major features of all 50 techniques.

The 10 volumes in the Series on characterization of particular materials classes include volumes on silicon processing, metals and alloys, catalytic materials, integrated circuit packaging, etc. Characterization is approached from the materials user's point of view. Thus, in general, the format is based on properties, processing steps, materials classification, etc., rather than on a technique. The emphasis of all volumes is on surfaces, interfaces, and thin films, but the emphasis varies depending on the relative importance of these areas for the materials class concerned. Appendixes in each volume reproduce the relevant one-page summaries from the *Encyclopedia* and provide longer summaries for any techniques referred to that are not covered in the *Encyclopedia*.

The concept for the Series came from discussion with Marjan Bace of Manning Publications Company. A gap exists between the way materials characterization is often presented and the needs of a large segment of the audience—the materials user, process engineer, manager, or student. In our experience, when, at the end of talks or courses on analytical techniques, a question is asked on how a particular material (or processing) characterization problem can be addressed the answer often is that the speaker is "an expert on the technique, not the materials aspects, and does not have experience with that particular situation." This Series is an attempt to bridge this gap by approaching characterization problems from the side of the materials user rather than from that of the analytical techniques expert.

We would like to thank Marjan Bace for putting forward the original concept, Shaun Wilson of Charles Evans and Associates and Yale Strausser of Surface Science Laboratories for help in further defining the Series, and the Editors of all the individual volumes for their efforts to produce practical, materials user based volumes.

C. R. Brundle *C. A. Evans, Jr.*

Preface to the Re-issue of *Characterization of Polymers*

There were 22 authors originally involved in writing this volume, which presents an integrated overview of the surface, interface, and thin film properties of polymers, coupled with the analysis methods used to characterize these properties. In addition to the introductory chapters on polymer structure, synthesis, and fabrication, the areas of chemical composition, morphology, surface modification, adhesion, interface chemistry and reactivity, and friction and wear, are all addressed, together with the appropriate techniques to characterize them. Of course, there have been advances in all these areas since the volume was originally published, but the underlying principles and the basics of the characterization techniques and methodology remain valid. Following the reissue of the volume in close to its original form, it is our intention that updates covering advances made will be released as they become available.

C. R. Brundle and C. A. Evans, December 2009

Preface

Although a polymer specialist typically has the background needed to appreciate the subtleties of the polymer which are important for its application, he or she may not have the training to extract all the information available from the analysis of the polymeric material. Often, a polymer analyst has the opposite strengths and weaknesses. As a result, it is important for both the specialist and analyst to understand some aspects of the work of the other. But, whereas there are a number of books on surface and interfacial analysis written for the polymer analyst, there are few books written for the polymer specialist with a focus on surface and interfacial properties rather than the analysis. This series of books by Manning Publication Co., copublished with Butterworth-Heinemann, is intended to rectify this situation for polymers as well as ceramics, metals, semiconductors, and other materials.

The present volume, *Characterization of Polymers*, is intended for general polymer scientists and engineers without much experience in analysis but who have to deal with polymer surface and interface problems on a day-to-day basis. Because of the aforementioned focus on properties, and because many of the analytical techniques used for different types of materials are the same, this volume does not emphasize the characteristics of different techniques; this is accomplished in the lead volume of this Series, *Encyclopedia of Materials Characterization*. Instead, the present volume uses a case study approach to illustrate the importance of polymer problems and how they have been solved using surface and interfacial analyses. Each case study is carefully selected so that the whole range of important properties of polymers is adequately covered. The objective of this volume is not to make the reader an expert in analysis, but to get him or her started to become one. More importantly, the volume provides the reader with the knowledge to select appropriate characterization techniques which will help solve the problems at hand, and to plant questions and new ideas in the mind of the expert analyst with whom he or she is working. The techniques chosen are widely accepted techniques; novel techniques which have a high chance of acquiring wide acceptance in the near future are also mentioned.

Scope and Organization

The first two chapters give an overview of polymer chain structure and synthesis and fabrication techniques encountered commercially. The next five chapters discuss surface properties and modification techniques in the order of chemical composition, microstructures and related properties, structures and morphology of interfaces and thin films, thermodynamics, and surface modification. These are followed by four chapters dealing with interfacial properties involving at least one polymer.

Topics covered are adhesion, polymer–metal, polymer–ceramic, and polymer–polymer interfaces, as well as friction and wear pertaining to polymer damages caused by two contacting materials in relative motion. Chapter 7, on surface modification, bridges these two parts of the book because such techniques affect both surface and interfacial properties. Finally, in Chapter 12, references (e.g., books and handbooks) are given to aid in future studies. A brief description of all chapters is provided below to assist the reader in planning his or her studies:

Chapter 1, on chain structures and polymer synthesis, describes the chain structures in natural and synthetic polymers and the various routes of polymer synthesis. Also included is a brief description of polymer surface structure. Emphasis is placed on commodity structural polymers, engineering thermoplastics, high-temperature polymers, typical copolymers, and polymer blends.

Chapter 2 gives an overview on commercial polymers, their applications, and commonly used fabrication techniques for their processing. Polymer fabrication techniques discussed include foam processing, film forming/casting, composite processing, extrusion, and molding. Examples on the application of various fabrication techniques are described in some detail. When applicable, analytical methods are mentioned as they pertain to property studies or tailoring. The effects of processing on surface properties and others (e.g., mechanical and physical properties) are also discussed.

Chapter 3, on chemical composition, discusses the techniques and methodologies used to characterize the chemical composition of polymers. The main techniques used to determine chemical composition are summarized, and the types of information obtained from each are described. Chemical composition aspects that are addressed include degree of stoichiometry, functionality determination, completeness of reactions, reactive moieties, contaminations, dopants, surface segregation, and multilayer integrity.

A critical review of various microscopy techniques to measure the morphology of polymer surface and thin films is given in Chapter 4. This chapter describes contrast mechanisms and optics for various microscopy techniques, with specific examples from mesomorphic polymer systems to give an appreciation of the techniques. Apart from visualization, the chapter explains microscopy as a tool to obtain quantitative structural information when complemented with other methods. Recent scanning probe techniques such as atomic force microscopy and scanning tunneling microscopy, and modern developments in scanning and high-resolution electron microscopy, are also covered.

Surface morphology study using scattering methods is described in Chapter 5. The chapter outlines the theoretical and experimental aspects of the methods to provide an appreciation of their limitations and advantages. Less common methods such as surface wave probes and surface second-harmonic-generation methods that are established techniques but are not commonly used on polymer interfaces are also covered to highlight recent developments. Moreover, other surface methods such as grazing incidence X-ray scattering, reflectivity, and optical wave guiding covering length scale form 10^3 μm to 1 nm are covered.

Chapter 6, on surface thermodynamics, discusses the physical chemistry of polymer surface in terms of specific and dispersive interactions. This chapter outlines the theory of wetting and (work of) adhesion in terms of acid–base and London attraction. It provides the details on contact angle measurement techniques, adsorption isotherm methods and calorimetry, which are important in obtaining quantitative information on surface energy of interfaces with polymers. The chapter also touches upon ellipsometry serum replacement, inverse gas chromatography and infrared spectroscopy for the characterization of polymer surfaces.

Surface modification of polymers is covered in Chapter 7. Surface modification is an indispensable processing tool for the fabrication of a wide variety of polymer and plastic products. This chapter covers surface modification by mechanical means, by wet chemical treatments, and by dry processing techniques. This chapter also describes how surface modifications are monitored, as well as some of the tools that are employed in dry processing.

The successful application of polymers is quite often dependent on their adhesion to other materials. Chapter 8, on adhesion, reviews the basic concepts of adhesion. Some of the techniques to measure adhesion are described, along with their pitfalls. This chapter also discusses the issues of locus of failure, surface modification, and environmental stability.

Chapter 9, on primarily polymer–metal and polymer–ceramic interfaces, deals with the chemistry involved at these interfaces. Besides addressing the reactivity of these interfaces, the chapter deals with thermal stresses and interfacial fracture. These properties are particularly important for multilevel structures such as would be found in multichip modules important in microelectronics.

Chapter 10 details various techniques to characterize polymer–polymer interfaces. This chapter discusses the relevance of concentration profile of the polymers across the interface—a crucial property for adhesion and other interfacial properties. It also describes techniques such as forward recoil spectroscopy, neutron reflectivity, and dynamic SIMS nuclear reaction for quantitatively measuring interfaces of compatible and incompatible polymer systems.

In the preceding three chapters, ensuring strong adhesive bonding between materials is the aim. Chapter 11, on friction and wear, addresses how to minimize polymer damages caused by two contacting materials in relative motion. This chapter discusses the mechanisms and measurement of tribological properties and correlations between these properties with chemical, physical, and mechanical properties.

Chapter 12 provides readers with references for their future studies in the various subject areas covered by this book. Also given are references dealing with the investigation of polymers in general, polymer characterization and test methods, the advances in the use of computers for polymer research, and environmental effects on polymers. These references are included to help the reader formulate a well-rounded approach even though they may not be specifically related to polymer surfaces and interfaces.

We take this opportunity to thank the authors of the present volume, as well as Dr. Marjan Bace, Ms. Lee Fitzpatrick, and the editorial staff at both Manning Publications Co. and Butterworth-Heinemann for making this volume a reality. Thanks are also due to Dr. Richard Brundle, one of the two series editors, for many stimulating and informative discussions.

Ho-Ming Tong, Steven P. Kowalczyk, Ravi Saraf, and *Ned J. Chou*

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