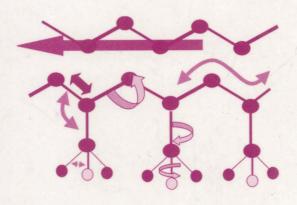
HANDBOOK OF PLASTICS ANALYSIS



edited by Hubert Lobo Jose V. Bonilla HANDBOOK OF PLASTICS ANALYSIS

江苏工业学院图书馆

Hubert Lobo

DatapointLats

Itchaca, New York

edited by

藏书章

Jose V. Bonilla

ISP Chemicals Calvert City, Kentucky



Although great care has been taken to provide accurate and current information, neither the author(s) nor the publisher, nor anyone else associated with this publication, shall be liable for any loss, damage, or liability directly or indirectly caused or alleged to be caused by this book. The material contained herein is not intended to provide specific advice or recommendations for any specific situation.

Trademark notice: Product or corporate names may be trademarks or registered trademarks and are used only for identification and explanation without intent to infringe.

Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress.

ISBN: 0-8247-0708-7

This book is printed on acid-free paper.

Headquarters

Marcel Dekker, Inc., 270 Madison Avenue, New York, NY 10016, U.S.A.

tel: 212-696-9000; fax: 212-685-4540

Distribution and Customer Service

Marcel Dekker, Inc., Cimarron Road, Monticello, New York 12701, U.S.A.

tel: 800-228-1160; fax: 845-796-1772

Eastern Hemisphere Distribution

Marcel Dekker AG, Hutgasse 4, Postfach 812, CH-4001 Basel, Switzerland

tel: 41-61-260-6300; fax: 41-61-260-6333

World Wide Web

http://www.dekker.com

The publisher offers discounts on this book when ordered in bulk quantities. For more information, write to Special Sales/Professional Marketing at the headquarters address above.

Copyright © 2003 by Marcel Dekker, Inc. All Rights Reserved.

Neither this book nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage and retrieval system, without permission in writing from the publisher.

Current printing (last digit):

10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

HANDBOOK OF PLASTICS ANALYSIS

PLASTICS ENGINEERING

Founding Editor

Donald E. Hudgin

Professor Clemson University Clemson, South Carolina

- 1. Plastics Waste: Recovery of Economic Value, Jacob Leidner
- 2. Polyester Molding Compounds, Robert Burns
- Carbon Black-Polymer Composites: The Physics of Electrically Conducting Composites, edited by Enid Keil Sichel
- 4. The Strength and Stiffness of Polymers, edited by Anagnostis E. Zachariades and Roger S. Porter
- Selecting Thermoplastics for Engineering Applications, Charles P. Mac-Dermott
- Engineering with Rigid PVC: Processability and Applications, edited by I. Luis Gomez
- 7. Computer-Aided Design of Polymers and Composites, D. H. Kaelble
- 8. Engineering Thermoplastics: Properties and Applications, edited by James M. Margolis
- 9. Structural Foam: A Purchasing and Design Guide, Bruce C. Wendle
- Plastics in Architecture: A Guide to Acrylic and Polycarbonate, Ralph Montella
- 11. Metal-Filled Polymers: Properties and Applications, edited by Swapan K. Bhattacharya
- 12. Plastics Technology Handbook, Manas Chanda and Salil K. Roy
- 13. Reaction Injection Molding Machinery and Processes, F. Melvin Sweeney
- 14. Practical Thermoforming: Principles and Applications, John Florian
- Injection and Compression Molding Fundamentals, edited by Avraam I. Isayev
- 16. Polymer Mixing and Extrusion Technology, Nicholas P. Cheremisinoff
- High Modulus Polymers: Approaches to Design and Development, edited by Anagnostis E. Zachariades and Roger S. Porter
- Corrosion-Resistant Plastic Composites in Chemical Plant Design, John H. Mallinson
- 19. Handbook of Elastomers: New Developments and Technology, edited by Anil K. Bhowmick and Howard L. Stephens
- Rubber Compounding: Principles, Materials, and Techniques, Fred W. Barlow
- Thermoplastic Polymer Additives: Theory and Practice, edited by John T. Lutz. Jr.
- 22. Emulsion Polymer Technology, Robert D. Athey, Jr.
- 23. Mixing in Polymer Processing, edited by Chris Rauwendaal
- 24. Handbook of Polymer Synthesis, Parts A and B, edited by Hans R. Kricheldorf

- 25. Computational Modeling of Polymers, edited by Jozef Bicerano
- 26. Plastics Technology Handbook: Second Edition, Revised and Expanded, Manas Chanda and Salil K. Roy
- 27. Prediction of Polymer Properties, Jozef Bicerano
- 28. Ferroelectric Polymers: Chemistry, Physics, and Applications, edited by Hari Singh Nalwa
- 29. Degradable Polymers, Recycling, and Plastics Waste Management, edited by Ann-Christine Albertsson and Samuel J. Huang
- 30. Polymer Toughening, edited by Charles B. Arends
- 31. Handbook of Applied Polymer Processing Technology, edited by Nicholas P. Cheremisinoff and Paul N. Cheremisinoff
- 32. Diffusion in Polymers, edited by P. Neogi
- 33. Polymer Devolatilization, edited by Ramon J. Albalak
- 34. Anionic Polymerization: Principles and Practical Applications, *Henry L. Hsieh and Roderic P. Quirk*
- 35. Cationic Polymerizations: Mechanisms, Synthesis, and Applications, edited by Krzysztof Matyjaszewski
- Polyimides: Fundamentals and Applications, edited by Malay K. Ghosh and K. L. Mittal
- 37. Thermoplastic Melt Rheology and Processing, A. V. Shenoy and D. R. Saini
- 38. Prediction of Polymer Properties: Second Edition, Revised and Expanded, Jozef Bicerano
- 39. Practical Thermoforming: Principles and Applications, Second Edition, Revised and Expanded, *John Florian*
- 40. Macromolecular Design of Polymeric Materials, edited by Koichi Hatada, Tatsuki Kitayama, and Otto Vogl
- 41. Handbook of Thermoplastics, edited by Olagoke Olabisi
- 42. Selecting Thermoplastics for Engineering Applications: Second Edition, Revised and Expanded, Charles P. MacDermott and Aroon V. Shenoy
- 43. Metallized Plastics: Fundamentals and Applications, edited by K. L. Mittal
- 44. Oligomer Technology and Applications, Constantin V. Uglea
- 45. Electrical and Optical Polymer Systems: Fundamentals, Methods, and Applications, edited by Donald L. Wise, Gary E. Wnek, Debra J. Trantolo, Thomas M. Cooper, and Joseph D. Gresser
- 46. Structure and Properties of Multiphase Polymeric Materials, edited by Takeo Araki, Qui Tran-Cong, and Mitsuhiro Shibayama
- 47. Plastics Technology Handbook: Third Edition, Revised and Expanded, Manas Chanda and Salil K. Roy
- 48. Handbook of Radical Vinyl Polymerization, *Munmaya K. Mishra and Yusuf Yaqci*
- 49. Photonic Polymer Systems: Fundamentals, Methods, and Applications, edited by Donald L. Wise, Gary E. Wnek, Debra J. Trantolo, Thomas M. Cooper, and Joseph D. Gresser
- 50. Handbook of Polymer Testing: Physical Methods, edited by Roger Brown
- 51. Handbook of Polypropylene and Polypropylene Composites, edited by Harutun G. Karian
- Polymer Blends and Alloys, edited by Gabriel O. Shonaike and George P. Simon
- Star and Hyperbranched Polymers, edited by Munmaya K. Mishra and Shiro Kobayashi
- 54. Practical Extrusion Blow Molding, edited by Samuel L. Belcher

- Polymer Viscoelasticity: Stress and Strain in Practice, Evaristo Riande, Ricardo Díaz-Calleja, Margarita G. Prolongo, Rosa M. Masegosa, and Catalina Salom
- 56. Handbook of Polycarbonate Science and Technology, edited by Donald G. LeGrand and John T. Bendler
- 57. Handbook of Polyethylene: Structures, Properties, and Applications, *Andrew J. Peacock*
- Polymer and Composite Rheology: Second Edition, Revised and Expanded, Rakesh K. Gupta
- Handbook of Polyolefins: Second Edition, Revised and Expanded, edited by Cornelia Vasile
- 60. Polymer Modification: Principles, Techniques, and Applications, edited by John J. Meister
- 61. Handbook of Elastomers: Second Edition, Revised and Expanded, edited by Anil K. Bhowmick and Howard L. Stephens
- Polymer Modifiers and Additives, edited by John T. Lutz, Jr., and Richard F. Grossman
- 63. Practical Injection Molding, Bernie A. Olmsted and Martin E. Davis
- 64. Thermosetting Polymers, Jean-Pierre Pascault, Henry Sautereau, Jacques Verdu, and Roberto J. J. Williams
- 65. Prediction of Polymer Properties: Third Edition, Revised and Expanded, *Jozef Bicerano*
- 66. Fundamentals of Polymer Engineering: Second Edition, Revised and Expanded, *Anil Kumar and Rakesh K. Gupta*
- 67. Handbook of Polypropylene and Polypropylene Composites: Second Edition, Revised and Expanded, edited by Harutun G. Karian
- 68. Handbook of Plastics Analysis, edited by Hubert Lobo and Jose V. Bonilla

Additional Volumes in Preparation

Preface

Plastics are one of the enabling technologies of the 20th century. They are among the most complex engineering materials being used in the world today, with amazing properties that have revolutionized the way in which products are manufactured. They are used in almost every walk of life, ranging from the mundane to high-end applications in which no other material could serve as a replacement. In each of these applications, it has been crucially important to understand their behavior through various parts of their product life, from manufacture to utilization and eventually their reclaim or disposal. The tools and techniques used to develop this understanding are referred to as plastics analysis.

Plastics analysis can be broadly grouped into two main categories. *Physical analysis* refers to the evaluation of the physical behavior of the material. Properties such as strength, thermal behavior, and flow properties fall into this category, as do failure and morphological characteristics. *Chemical analysis* seeks to evaluate the compositional characteristics of the polymer. The combination of these two broad approaches has been used successfully to correlate the behavior of plastics to their composition.

A wide variety of modern tools are available to the plastics analyst. As the range of available tools continue to expand, it is necessary for the analyst to keep abreast of all these technologies so as to be able to apply the most appropriate technique to the solution of a particular problem. This handbook seeks to highlight the most prominent tools in use by providing information on these diverse techniques and their application, and provides guidelines on the analysis and interpretation of results. It also provides a ready source of detailed references to readers interested in a more complete understanding of the subject matter.

iv Preface

In order to maintain a practical focus, the book concentrates on an approach that is more phenomenological than theoretical. While not going into detailed derivations, the book sets forth the basic governing equations where necessary to provide a good theoretical understanding of the techniques. Through the use of case studies and illustrations, the reader will be aided in the understanding of possible outcomes of each analysis technique.

A number of plastics analysis techniques are currently standardized to national and international norms. The book lists these norms in the form of reference tables and provides brief descriptions where necessary.

The chapters contain:

Introduction of the technique and a brief scientific basis; governing equations if applicable

Illustrations of test instruments along with schematics to aid in the understanding of the techniques

Detailed descriptions, including measurement method(s), highlighting differences in technique(s), if relevant, including merits and deficiencies of the technique

Images of typical outcomes of the analysis

A listing of applicable national and international standards

Applications with typical case studies and corresponding results; these are intended to aid in the analysis and interpretation of results from the analysis

Discussions

Conclusion, including information on the latest advances in the field (noncommercial) so as to provide an indication of future potential of the technology

References and additional reading

The handbook will serve as a concise reference to practitioners in the industry, providing technical information about plastics analysis and descriptions of the technology used to perform the measurements. It is aimed at laboratory personnel who need to have a working knowledge of plastics analysis techniques and would like to keep abreast of the latest developments in the field. These will include laboratory managers, supervisors, and engineers.

The book will also serve as a basic reference to research engineers and scientists who may be looking for techniques to solve problems or investigate behavioral phenomena.

Hubert Lobo Jose V. Bonilla

Contributors

Jose V. Bonilla ISP Chemicals, Calvert City, Kentucky, USA

Anita J. Brandolini William Paterson University of New Jersey, Wayne, New Jersey, USA

John Coates Consulting, Newtown, Connecticut, USA

Gary J. Fallick Waters Corporation, Milford, Massachusetts, USA

Robert Falcone ICI Fluoropolymers, Bayonne, New Jersey, USA

Kenneth J. Fielder PerkinElmer Instruments LLC, Shelton, Connecticut, USA

Galina Georgieva GE Medical Systems, Waukesha, Wisconsin, USA

Scott Kinzy ICI Fluoropolymers, Bayonne, New Jersey, USA

John Lemmon GE Corporate Research, Schenectady, New York, USA

Hubert Lobo DatapointLabs, Ithaca, New York, USA

Kevin P. Menard PerkinElmer Thermal Laboratory, Materials Science Department, University of North Texas, Denton, Texas, USA

Rick Nielson Waters Corporation, Milford, Massachusetts, USA

viii Contributors

Burke Nelson Goettfert USA, Rock Hill, South Carolina, USA

Koichi Nishikida Thermo Electron Corporation, Madison, Wisconsin, USA

Philip Plantz Microtrac, Inc., Largo, Florida, USA

Andrew W. Salamon PerkinElmer Instruments LLC, Shelton, Connecticut, USA

Contents

Preface Contributors		iii vii
1.	General Introduction to Plastics Analysis Hubert Lobo and Jose V. Bonilla	1
2.	Capillary Rheometry Burke Nelson	43
3.	Practical Uses of Differential Scanning Calorimetry for Plastics Andrew W. Salamon and Kenneth J. Fielder	79
4.	Thermogravimetric Analysis of Polymers Scott Kinzy and Robert Falcone	111
5.	Thermal Conductivity and Diffusivity of Polymers Hubert Lobo	129
6.	Thermomechanical and Dynamic Mechanical Analysis Kevin P. Menard	155
7.	Infrared and Raman Analysis of Polymers Koichi Nishikida and John Coates	201
8.	Plastics Analysis by Gas Chromatography Jose V. Bonilla	341

vi		Contents
9.	Nuclear Magnetic Resonance of Polymeric Materials Anita J. Brandolini	403
10.	Inorganic Analyses of Polymers John Lemmon and Galina Georgieva	511
11.	Liquid Chromatography of Polymers Gary J. Fallick and Rick Nielson	549
12.	Particle Size Measurement of Plastics and Polymers Using Laser Light Scattering <i>Philip Plantz</i>	593
Appendix: ASTM Methods for Analysis of Plastic and Rubber Materials		613
Index		629

General Introduction to Plastics Analysis

Hubert Lobo

DatapointLabs, Ithaca, New York, USA

Jose V. Bonilla

ISP Chemicals, Calvert City, Kentucky, USA

INTRODUCTION

Plastics have undoubtedly been the wonder materials of the last century. They have fundamentally revolutionized the manner in which we conceptualize and implement new products. They are ubiquitous in today's environment, appearing in ways that range from mundane to high-tech, from indispensable to completely wasteful. The manner in which these materials have been used has shaped our impressions of plastics as necessary evils as well as miracle materials.

A lot of the negative impressions have come from the fact that the world was not prepared for materials of this complexity. In many ways, our inability to understand plastics affected the manner in which we used or misused them. Before the arrival of plastics, most materials were relatively simple, or if complex, natural. In both cases, either by the application of existing science or by long historical knowledge of their use, it was possible to use these materials in an effective manner. In the case of plastics, the converse occurred. The arrival of plastics heralded the onset of one of the most comprehensive periods of discovery in material science. The very nature

2 Lobo and Bonilla

of plastics has demanded significant advances in our ability to understand polymers, analyze their composition, and characterize this behavior. These technologies, collectively termed plastics analysis techniques, have come a long way in helping us design novel materials for a better tomorrow.

Our impression of plastics as miracle materials has also stemmed from an incomplete understanding of their complexity. Plastics analysis has allowed us to apply the rigorous application of scientific technique to deepen our knowledge of their behavior, replacing our previous wonder with a deep-rooted scientific understanding that permits us to truly appreciate the capabilities of these materials. Indeed, it is this knowledge that will shape our use of these truly amazing materials in the new millennium.

The introduction of plastics requires us to apply a wide range of techniques to understand their behavior. Plastics exhibit complex molecular characteristics. From our understanding of molecular structure, we are now able to attempt to correlate behavior to structure. This ability, however, is still, far from an exact science. The complex manner in which polymer molecules interact still prevents us from developing strong structure-property relationship theories. Indeed, the disconnection between our understanding of molecular-level behavior and macro-level characteristics is one of the sharpest dividing lines between classical material science and polymer science. In the case of metals, it has been relatively easy to apply our atomic-level understanding of the material and its microstructure to its behavior. In sharp contrast, polymer molecules vary widely in molecular weight. The manner in which polymer molecules interact with each other depends to a great extent on the pendant groups that are attached to the chain. Most frustrating of all, even though we are able to understand these aspects, this still does not permit us to apply our knowledge to understand macro-level behavior. This has forced the simultaneous development of both chemical analysis and physical analysis to grapple with the problem.

Chemical analysis techniques permit us to analyze molecular composition and molecular weight to allow us to characterize plastics precisely. Physical methods allow us to look at the behavior of plastics in response to a variety of influences such as temperature, pressure, and time. This understanding helps us to say how the plastics will behave in their lifetime. Plastics analysis may include identification and chemical composition, thermal properties, mechanical properties, physical properties, electrical properties, and optical properties, among others. Chemical analysis may include material identification and characterization by techniques including FTIR, NMR, GC, GC/MS, HPLC, and GPC. Thermal analysis does provide information such as melting point, glass transition, flash point, heat deflection temperature, melt flow rate, and Vicat softening point. Mechanical properties, on the other hand, provide critical information such as tensile

properties, flexural strength, impact strength, hardness, compressive strength, modulus, and fatigue. Recent advances in microscopy also permit us to peek into molecular structure. The atomic force microscope, for example, has truly revolutionized our ability to probe molecular behavior, promising us a startling new understanding of plastics.

The past few years have been characterized by a large growth in development of new polymers and composite materials. Modern research and developments of high-technology materials have also driven the development of new analytical equipment and analytical technologies. As materials become more and more sophisticated and complex, so also must become the analytical techniques required for materials testing and materials characterization.

Innovative, accurate, easy-to-use, performance, and reliability are the requirements that describe instrumentation needed in modern laboratories involved in materials research or materials manufacturing facilities. Instrumentation of this type is needed in order to deliver outstanding performance to downstream customers. Modern instruments, hardware, and software products are designed to support such requirements.

This book covers some of the most significant techniques used in modern analytical technology to characterize plastic and composite materials. A short general introduction to some of them is provided here to the topics covered in more detail in later chapters. A general introduction is also given to other techniques that are not covered in extensive detail in this book but that are of significant use in characterization of certain critical properties of plastic materials.

Much of plastics testing is done by methodology developed and validated in-house by analytical scientists to meet specific needs. There are also a large number of official testing methods developed by agencies such as the American Society for Testing Materials (ASTM). A reference list of ASTM methods used for analysis of plastic and plastic-related materials is included as an appendix at the end of this book.

There are many applications of plastics analysis. It is useful to examine these applications using a life-cycle viewpoint. In each area, one is then able to see the importance of these vital techniques to the understanding and proper application of plastic materials in our lives and the environment.

PLASTICS AND PRODUCT DESIGN

Historically, product developers have had a great deal of difficulty working with plastics. They simply did not behave in the conventional manner. None of the conventional rules of behavior applied either in the manner in which the product was made or in the manner in which it behaved once it was

4 Lobo and Bonilla

produced. There were serious contradictions to conventional design philosophies—for example, the concept that making it thicker did not necessarily make it stronger, or that once it was made, it did not necessarily want to stay that way. Factors such as stress relaxation and residual stresses played havoc with first-generation plastic products, giving plastics the bad reputation that years of continuous improvement have not been able to erase. A lot of improvement can be attributed to our current understanding of physical behavior.

Plastics exhibit large nonlinear stress—strain behavior. Large recoverable deformation is, in fact, one of the defining characteristics of a plastic. This characteristic has been used unfairly to portray plastics as weak materials because they lack the stiffness and strength of metals. In fact, it means that a plastic part can undergo a large amount of recoverable deformation before it breaks. This characteristic has been exploited, for example, in the replacement of the metal automotive bumper with TPO. The stress—strain relationship of a plastic shows a continuously decreasing stiffness with larger strain. This is because, in contrast to metals, plastics do not undergo complete instantaneous recovery upon unloading. When the plastic is unloaded, the response is viscoelastic, with partial instantaneous "elastic" response and a component of "viscous" time-based recovery. The introduction of the dimension of time is therefore a serious complicating factor, presenting essentially a fourth dimension to be considered in design. Viscoelasticity, creep, and stress relaxation are some of the measures used to characterize this behavior.

PLASTICS AND MANUFACTURING

In conjunction with the injection molding process, plastics have revolutionized the manufacturing process over the past 20 years. Major economies in assembly were achieved by molding in features and incorporating subcomponents into a single part. For a very long time, however, injection molding was perceived to be a "black art" because of the extreme difficulty of making good parts. It took significant research in areas of polymer rheology, thermal properties, and mechanical behavior to develop the scientific understanding that guides modern injection molding. Other plastics processing methods have also benefited from these advances. Characterizations of viscoelastic behavior and extensional rheology guide modern blow molding and thermoforming, transforming this industry into a producer of high-quality engineering products.

PLASTICS AND THE ENVIRONMENT

Just as steel rusts and wood rots, plastics degrade in the environment. This is in stark contrast to the picture of the 1960s, which presented plastic as both