

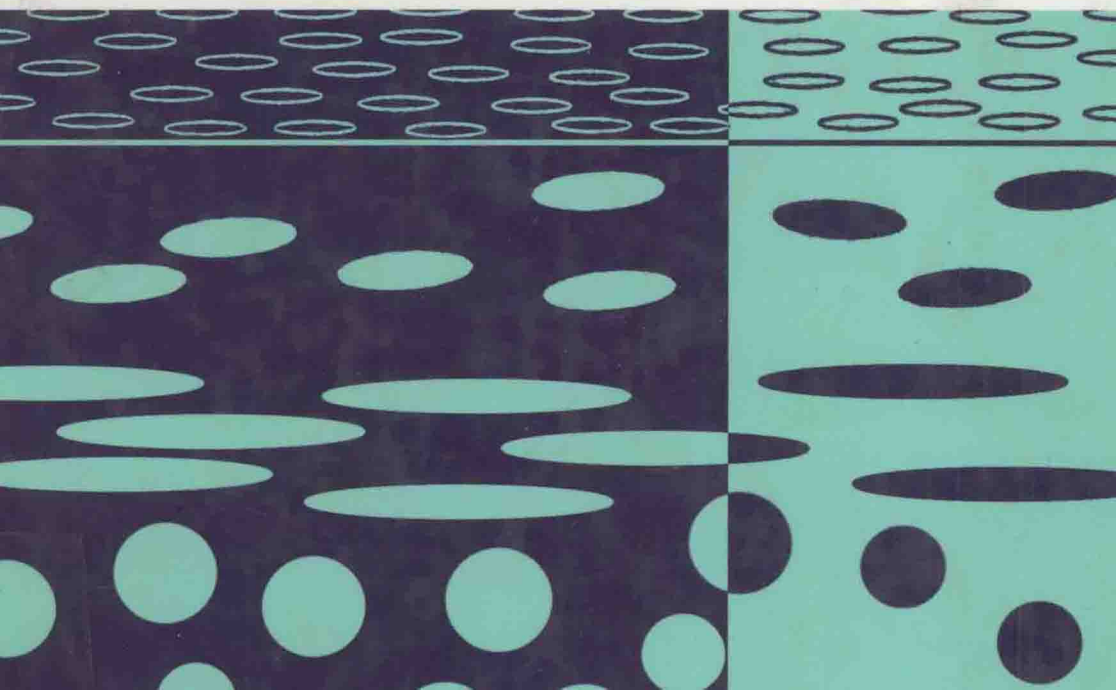
Polymer Blends

Volume 2: Performance

Edited by

D. R. Paul

C. B. Bucknall



POLYMER BLENDS

Volume 2: Performance

Edited by

D. R. Paul

*Department of Chemical Engineering
and Texas Materials Institute
The University of Texas at Austin
Austin, TX 78712-1062*

C. B. Bucknall

*School of Industrial and Manufacturing Science
Cranfield University
Cranfield, Bedford MK43 0AL, United Kingdom*

江苏工业学院图书馆
藏书章



A WILEY-INTERSCIENCE PUBLICATION

JOHN WILEY & SONS

New York / Chichester / Weinheim / Brisbane / Singapore / Toronto

This book is printed on acid-free paper. ©

Copyright ©2000 by John Wiley & Sons, Inc. All rights reserved.

Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Sections 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4744. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 605 Third Avenue, New York, NY 10158-0012, (212) 850-6011, fax (212) 850-6008, E-Mail: PERMREQ @ WILEY.COM.

Library of Congress Cataloging-in-Publication Data:

Polymer blends / D. R. Paul and C. B. Bucknall, editors.

p. cm.

Includes index.

Contents: 1. Formulation –

ISBN 0-471-24825-8 (set : alk. paper). — ISBN 0-471-35279-9 (v. 1). — ISBN 0-471-35280-2 (v. 2)

1. Polymers. 2. Plastics. I. Paul, Donald R. II. Bucknall, C. B.

TP1087.P64 1999
668.9—dc21

99-36533
CIP

Printed in the United States of America.

10 9 8 7 6 5 4 3 2 1

Preface

The field of polymer blends, or alloys, has experienced enormous growth in size and sophistication over the past two decades in terms of both the scientific base and technological and commercial development. It has become clear to us that an appropriate summary of this progress is needed to educate and to guide professionals working in this area into the twenty-first century. This two-volume set is a multiauthored treatise that might be viewed as an updated version of the analogous set edited by Paul and Newman and published in 1978. (See the reading list at the end of Chapter 1.) The book is intended to be a coherent entity rather than a collection of separate chapters, and a great deal of effort has been devoted to coordinating the content and style of the chapters. The editors intended each chapter to be far more than an encyclopedic summary of the literature or a review focusing only on the most recent advances in research. The authors were asked (a) to provide enough background in each chapter to enable beginners to work in the field by reading this book; (b) to sift critically through the literature and present only the most important issues (not every reference deserves mention); and (c) to write clearly but concisely, using carefully selected graphics, in order to make the important conceptual points and capture the attention of the browser.

It is the goal of these two volumes to be the authoritative source that professionals of the next decades will seek out to learn about this important field and use to set directions for future research and product development. The two volumes are roughly equal in length. Volume 1 is subtitled *Formulation* and is largely about the physics, chemistry, and processing issues associated with the formation of polymer blends and the evaluation and control of their structure. Volume 2 is subtitled *Performance* and is primarily concerned with how blends perform in practical situations. Naturally, there is a heavy emphasis on mechanical performance, but several chapters deal with a range of other properties as well. At some risk of oversimplification, it can be said that Volume 1 is about *structure*, while Volume 2 is about *properties*. Thus, the two-volume set provides a broad view of the *structure–property* relationship for polymer blends as seen by experts from around the world.

The editors have been friends and colleagues for many years. Their professional interests have been somewhat different over their careers, but there are many points of intersection. These differences and similarities have been helpful during the course of planning, which started in early 1994, and development of this book. A common view was needed in order to foster agreement on the scope, content, and choice of

authors. The differences in expertise led Don Paul to have primary responsibility for Volume 1 and Clive Bucknall to oversee Volume 2.

We are thankful to many colleagues and friends who have encouraged us and given us advice on many issues.

D. R. PAUL
C. B. BUCKNALL

Contributors, Volume 2

- S. ABDOU-SABET, Advanced Elastomer Systems L.P., Akron, OH 44311
- R. ALEXANDER-KATZ, Depto. de Física, Universidad Autónoma Metropolitana-Iztapalapa, 09340 México, D.F., México
- D. G. BAIRD, Department of Chemical Engineering and the Center for Composite Materials and Structures, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0211
- H. R. BROWN, BHP Steel Institute, University of Wollongong, Wollongong, NSW 2522, Australia
- C. B. BUCKNALL, School of Industrial and Manufacturing Science, Cranfield University, Cranfield, Bedford MK43 0AL, United Kingdom
- X. H. CHEN, Department of Mechanical Engineering, Center for Advanced Materials Technology, University of Sydney, Sydney, NSW 2006, Australia
- C. A. CRUZ-RAMOS, Plastics Additives Research Department, Rohm and Haas Company Research Laboratories, Bristol, PA 19007
- S. DATTA, Baytown Polymers Center, Exxon Chemical Co., Baytown, TX 77522-5200
- J. DU, Department of Materials Science and Engineering, The University of Michigan, Ann Arbor, MI 48109
- T. S. ELLIS, Delphi Automotive Systems Research and Development, Warren, MI 48090
- M. EVSTATIEV, Laboratory for Structure and Properties of Polymers, University of Sofia, 1126 Sofia, Bulgaria
- S. FAKIROV, Laboratory for Structure and Properties of Polymers, University of Sofia, 1126 Sofia, Bulgaria
- K. FRIEDRICH, Institute for Composite Materials Ltd., University of Kaiserslautern, D-67663 Kaiserslautern, Germany
- R. J. GAYMANS, Faculty of Chemical Technology, University of Twente, 7500 AE Enschede, The Netherlands

- F. J. GUILD, Department of Mechanical Engineering, Queen's Building, University of Bristol, Bristol, BS8 1TR, United Kingdom
- J. KARGER-KOCSIS, Institute for Composite Materials Ltd., University of Kaiserslautern, D-67663 Kaiserslautern, Germany
- Y.-W. MAI, Department of Mechanical Engineering, Center for Advanced Materials Technology, University of Sydney, Sydney, NSW 2006, Australia
- M. A. MCLEOD, Department of Chemical Engineering and the Center for Composite Materials and Structures, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0211
- R. A. PEARSON, Department of Materials Science and Engineering, Lehigh University, Bethlehem, PA 18015
- I. G. PLOTZKER, Central Research and Development, Du Pont Company, Wilmington, DE 19880-0323
- L. PRUITT, Department of Mechanical Engineering, University of California at Berkeley, Berkeley, CA 94720
- J. J. SCOBBO, GE Plastics, One Noryl Avenue, Selkirk, NY 12158
- P. M. SUBRAMANIAN, S.P.M. Technologies, Hockessin, DE 19707
- M. D. THOULESS, Department of Mechanical Engineering and Applied Mechanics, The University of Michigan, Ann Arbor, MI 48109
- S.-C. WONG, Department of Mechanical Engineering, Center for Advanced Materials Technology, University of Sydney, Sydney, NSW 2006, Australia
- A. F. YEE, Department of Materials Science and Engineering, The University of Michigan, Ann Arbor, MI 48109

Contributors, Volume 1

- V. ARRIGHI, Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS United Kingdom
- M. BALLAUFF, Polymer-Institut der Universität Karlsruhe, Kaiserstrasse 12, 76128 Karlsruhe, Germany
- J. M. BRADY, Plastics Additives Research Department, Rohm and Haas Company Research Laboratories, Bristol, PA 19007
- C. B. BUCKNALL, School of Industrial and Manufacturing Science, Cranfield University, Cranfield, Bedford MK43 0AL, United Kingdom
- D. G. BUCKNALL, Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, United Kingdom
- M. M. COLEMAN, Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802
- C. A. CRUZ-RAMOS, Plastics Additives Research Department, Rohm and Haas Company Research Laboratories, Bristol, PA 19007
- J. R. DORGAN, Chemical Engineering Department, Colorado School of Mines, Golden, CO 80401
- B. D. FAVIS, Department of Chemical Engineering, University of Montréal, Ecole Polytechnique, Montréal, Québec H3C 3A7, Canada
- W. W. GRAESSLEY, Department of Chemical Engineering, Princeton University, Princeton, NJ 08544
- G. GROENINCKX, Department of Chemistry, Laboratory of Macromolecular Structural Chemistry, Catholic University of Leuven, B-3001 Heverlee, Belgium
- S. Y. HOBBS, General Electric Company, Research and Development Center, Schenectady, NY 12301
- S. D. HUDSON, Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106
- T. INOUE, Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552, Japan

- A. M. JAMIESON, Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106
- D. S. KALIKA, Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY 40506
- T. KYU, Institute of Polymer Engineering, University of Akron, Akron, OH 44325
- C. J. T. LANDRY, Imaging Research Laboratories, Eastman Kodak Company, Rochester, NY 14650
- D. J. LOHSE, Corporate Research Labs, Exxon Research & Engineering Co., Annandale, NJ 08801
- B. MAJUMDAR, GE Plastics, Selkirk, NY 12158
- G. D. MERFELD, General Electric Co., Research and Development Center, Schenectady, NY 12301
- P. C. PAINTER, Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802
- J. P. PASCAULT, Institut National des Sciences Appliquées, Laboratoire des Matériaux Macromoléculaires, 69621 Villeurbanne Cedex, France
- D. R. PAUL, Department of Chemical Engineering and Texas Materials Institute, The University of Texas at Austin, Austin, TX 78712
- J. P. RUNT, Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802
- I. C. SANCHEZ, Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712
- M. SARKISSOVA, Department of Chemistry, Laboratory of Macromolecular Structural Chemistry, Catholic University of Leuven, B-3001 Heverlee, Belgium
- M. T. STONE, Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712
- S. THOMAS, Department of Chemistry, Laboratory of Macromolecular Structural Chemistry, Catholic University of Leuven, B-3001 Heverlee, Belgium
- V. H. WATKINS, General Electric Company, Research and Development Center, Schenectady, NY 12301
- R. J. J. WILLIAMS, Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICE), 7600 Mar del Plata, Argentina

Contents

Preface	vii
Contributors, Volume 2	ix
Contents, Volume 1	xi
Contributors, Volume 1	xiii
MECHANICAL PROPERTIES AND FRACTURE RESISTANCE	
19 Quasielastic Mechanical Properties	1
<i>F. J. Guild</i>	
20 Application of Fracture Mechanics for Characterization of Toughness of Polymer Blends	17
<i>Y.-W. Mai, S.-C. Wong, and X.-H. Chen</i>	
21 Characterizing Toughness using Standard Empirical Tests	59
<i>C. B. Bucknall</i>	
22 Deformation Mechanisms in Rubber-Toughened Polymers	83
<i>C. B. Bucknall</i>	
23 Strengthening Polymer–Polymer Interfaces	119
<i>H. R. Brown</i>	
24 Core–Shell Impact Modifiers	137
<i>C. A. Cruz-Ramos</i>	
25 Toughening Semicrystalline Thermoplastics	177
<i>R. J. Gaymans</i>	
26 Toughening of Epoxies	225
<i>A. F. Yee, J. Du, and M. D. Thouless</i>	
27 Fatigue-Crack Propagation in Polymer Blends	269
<i>R. A. Pearson and L. Pruitt</i>	

BLENDING FOR SPECIFIC PERFORMANCE

28 Transmission and Reflection of Light in Multiphase Media	301
<i>R. Alexander-Katz</i>	

29 Thermomechanical Performance of Polymer Blends	335
<i>J. J. Scobbo, Jr.</i>	

30 Barrier Materials by Blending	359
<i>P. M. Subramanian and I. G. Plotzker</i>	

REINFORCED BLENDS

31 Reinforced Polymer Blends	395
<i>J. Karger-Kocsis</i>	

32 Liquid Crystalline Polymer Blends	429
<i>D. G. Baird and M. A. McLeod</i>	

33 From Polymer Blends to Microfibrillar Reinforced Composites	455
<i>S. Fakirov, M. Evstatiev, and K. Friedrich</i>	

ELASTOMERIC BLENDS

34 Elastomer Blends	477
<i>S. Datta</i>	

35 Thermoplastic Vulcanizates	517
<i>S. Abdou-Sabet and S. Datta</i>	

RECYCLING

36 Recycling of Polymer Blends and Mixtures	557
<i>T. S. Ellis</i>	

Index	583
--------------	------------

Contents, Volume 1

Preface	vii
Contributors, Volume 1	ix
Contents, Volume 2	xi
Contributors, Volume 2	xiii
1 Introduction	1
<i>D. R. Paul and C. B. Bucknall</i>	
THERMODYNAMICS	
2 Statistical Thermodynamics of Polymer Solutions and Blends	15
<i>I. C. Sanchez and M. T. Stone</i>	
3 Polymer–Polymer Interactions Based on Mean Field Approximations	55
<i>G. D. Merfeld and D. R. Paul</i>	
4 Hydrogen Bonding Systems	93
<i>P. C. Painter and M. M. Coleman</i>	
5 Polymer Blends as Viewed by Analogue Calorimetry	141
<i>C. J. T. Landry</i>	
6 Crystalline Polymer Blends	167
<i>J. P. Runt</i>	
7 Fundamentals of Blends of Rigid-Chain (Liquid Crystal) Polymers	187
<i>M. Ballauff and J. R. Dorgan</i>	
8 Thermodynamics of Polyolefin Blends	219
<i>D. J. Lohse and W. W. Graessley</i>	
CHARACTERIZATION	
9 Morphology Characterization by Microscopy Techniques	239
<i>S. Y. Hobbs and V. H. Watkins</i>	

10 Viscoelastic Characterization of Polymer Blends	291
<i>D. S. Kalika</i>	
11 Optical Characterization: Light Scattering, Birefringence, and Ellipsometry	319
<i>T. Inoue and T. Kyu</i>	
12 Neutron Scattering and Polymer Blends	349
<i>D. G. Bucknall and V. Arrighi</i>	
STRUCTURE FORMATION	
13 Formulation and Characterization of Thermoset–Thermoplastic Blends	379
<i>J. P. Pascault and R. J. J. Williams</i>	
14 Chemical Reactions in Blends Based on Condensation Polymers: Transreactions and Molecular and Morphological Characterization	417
<i>G. Groeninckx, M. Sarkissova, and S. Thomas</i>	
15 Morphology and Properties of Blends Containing Block Copolymers	461
<i>S. D. Hudson and A. M. Jamieson</i>	
16 Factors Influencing the Morphology of Immiscible Polymer Blends in Melt Processing	501
<i>B. D. Favis</i>	
17 Reactive Compatibilization	539
<i>B. Majumdar and D. R. Paul</i>	
18 Processing Aids	581
<i>J. M. Brady and C. A. Cruz-Ramos</i>	
Index	595

19 Quasielastic Mechanical Properties

FELICITY J. GUILD

Department of Mechanical Engineering
University of Bristol
Queen's Building
University Walk
Bristol BS8 1TR
United Kingdom

I. Introduction	1
II. Analytical Methods	2
A. Classical Mechanics	2
B. Finite-Element Analysis	3
III. Microstructural Characterization	4
IV. Particle-Distribution Models	5
A. Regular Models	5
B. Random Models	5
V. Elastic Properties	7
A. Hard Particles	7
B. Soft Particles	11
C. More Complex Morphologies	12
VI. Conclusions	14
VII. Acknowledgements	14
VIII. References	14

I. INTRODUCTION

The development of polymer technologies, allowing an ever-increasing range of particulate-filled (rigid or soft) polymers, is leading to increasing need for predictive modeling. The full experimental investigation of all possible materials is becoming

uneconomic, so predictive modeling is becoming more important as a cost-effective method of material investigation; with predictive modeling, elastic properties can be predicted and failure mechanisms can be investigated. This chapter is principally concerned with the prediction of quasielastic properties. Although such simulation can never entirely replace experimental investigation, its importance as an investigative tool is becoming readily apparent.

The analytical methods for simulation are first considered. It is notable that the earliest attempts to model the elastic properties of composite materials are found in the literature of the 19th century; even today, this subject is under investigation. Consideration of the methods of analytical modeling demonstrates the need for microstructural characterization of multiphase materials and for suitable particle-distribution models. Finally, the elastic properties of some filled polymers are presented, divided into overall categories based on the type of particle.

II. ANALYTICAL METHODS

Numerous analytical models have been proposed for the description of both the overall elastic properties of multiphase materials and the stress distributions within them. Some of the different methods of analysis and the main assumptions underlying them are presented in this section.

A. Classical Mechanics

The stress distributions within the matrix around an isolated spherical or cylindrical inclusion, made up of a void or a linearly elastic material, were first obtained by Goodier [1]. Later, the self-consistent approach, based on the theory of elasticity, was used to find the stress distributions around rigid spheres [2] or elastic spheres, or ellipsoids [3], embedded in an infinite elastic matrix. Eshelby's theory was generalized to include the interaction of filler particles, and expressions for elastic constants were derived by Chow [4]. Identical equations for materials containing spherical particles were obtained independently by Kerner [5]. These analyses are based on modeling the composite as an assembly of elements, each consisting of a spherical filler particle embedded in a spherical shell of the matrix, which is itself surrounded by an infinite matrix of material possessing properties of the "composite." Thus, it is inherent in this self-consistent approach that interparticle interactions are ignored.

Further analyses, producing bounds on elastic moduli, are based on the determination of the first-order moments of the random stress and strain fields in the heterogeneous solid. The exact stress fields around heterogeneities can be found as analytical solutions only in cases that allow the definition of regular unit cells. These "classical" analytical methods are based on the assumption of a defined unit cell surrounding each filler particle. The bounds generally arise from the assumption of conditions of equal stress or equal strain within the different unit cells. These approaches are well known in the analysis of continuous-fiber composites, where these simple averages are used to predict the values of longitudinal and transverse stiffness

of the overall composite [6, 7]. These analyses are essentially based on parallel or series spring models in which interactions between neighboring fibers are ignored.

The bounds obtained from some of these analyses are widely spaced. Paul [8] produced bounds for the bulk modulus and shear modulus by incorporating variational principles, but his analysis involved averaging the stress fields. These bounds were improved by Hashin and Shtrikman [9] using the variational principle. This approach is based on the idea of a homogenous reference medium that allows the definition of reference values of stress and strain. It can be shown that the bounds due to Paul [8] arise from the extreme values of the trial stress field. A full derivation of the Hashin and Shtrikman bounds was later given by Willis [10].

The various models were considered by Ishai and Cohen [11], leading to the derivation of the most closely spaced bounds to apply to a particle-filled material. The (cubic) particles were assumed to be regularly arranged in perfect cubic packing. Bounds were derived only for values of tensile moduli; lateral contractions were ignored, so these bounds do not include the full elastic properties of the composite material. The interactions between neighboring particles were not fully taken into account. These bounds are compared with experimental values of tensile moduli for filled polymers containing hard and soft particles later in this chapter.

An alternative analytical approach is based on an effective medium approximation. Such approaches rely on the assumption that the second phase occupies only a small fraction of the volume of the composite material, such that the overall changes in the elastic constants between the matrix material alone and the composite are relatively small. The effective elastic constants can then be calculated using perturbation theory. As is apparent from the use of perturbation theory, these methods are applicable only to materials containing low concentrations of the second phase. Further assumptions include that the “ligament” lengths—that is, the distance between particles—are treated as independent variables; in other words, the value of one interparticle distance is unaffected by the values of other interparticle distances. This assumption is obviously erroneous for a distribution of particles. The perturbation method has been applied to describe elastic properties of particulate-filled materials (e.g., [12, 13]).

B. Finite-Element Analysis

The limitations of the aforementioned analytical methods are apparent. Many of these limitations are overcome by the use of numerical methods. In recent years, the finite-element-analysis method has become increasingly accessible to nonspecialist users through the development of numerous graphical interfaces for both preprocessing and postprocessing and through the increasing power of “desktop” workstations for the processing of solutions. However, it is important to emphasize that increasing accessibility and increasing computer power do not necessarily correlate with increasing accuracy of the resulting solutions. It remains the responsibility of the analyst to make the correct choice of the many parameters required for the analysis, including the overall geometry to be analyzed, the element type (including formulation and integration), the mesh density, the material model, and the boundary conditions.

This list is not exhaustive, but the number of available parameters points to the care that must always be exercised when approaching this method of analysis.

Numerical models include the derivation of lateral contractions; in other words, values of Poisson's ratio ν are obtained. Assuming that the material is macroscopically isotropic, the values of shear modulus G and bulk modulus K can be calculated simply from the values of Poisson's ratio and Young's modulus E , using the following well-known expressions for isotropic elastic solids:

$$G = E/[2(1 + \nu)] \quad (19.1)$$

$$K = E/[3(1 - 2\nu)]. \quad (19.2)$$

The importance of this full description of the elastic properties of filled polymers is becoming increasingly important as the range of their applications is growing.

The choice of overall geometry to be analyzed is the initial step in carrying out any numerical analysis. The calculations are always based on the analysis of a unit cell that is representative of the overall structure. The choice of the unit cell is dependent on the materials model chosen, as discussed in Section IV. The boundary conditions imposed on the cell reflect its interactions with its neighboring cells. Similarly, some choices regarding element type—for example, whether two-dimensional, three-dimensional, or axisymmetric elements are required—arise directly from the definition of the unit cell. Further details regarding the elements used to create the mesh, such as the integration or formulation required for a given problem, and the most suitable mesh density to be used are beyond the scope of this chapter, but may be found in several texts (e.g., [14–16]).

The models chosen to represent the properties of the different constituents must also be considered. Since this chapter is concerned with the quasielastic properties of multiphase materials, the material property models considered here are generally based on linear elasticity. All analyses carried out using “classical” methods, described in the previous section, are based on linear elastic behavior. Further finite-element simulations of these materials can now include sophisticated material property models using either the models provided in the package or new ones written specifically for the application; some of the material property models available have been reviewed recently [17].

III. MICROSTRUCTURAL CHARACTERIZATION

Quantitative descriptions of the spatial arrangement of particles can now be obtained using automatic image analysis. The quantitative methods described here generally lead to descriptions of the microstructure that may be used directly in analytical techniques, such as finite-element analysis. Other methods used for the description of particle arrangement may be described as functional methods; the microstructure is described by some parameter or function. The spatial distribution of the parameter is measured using a specialized image analyzer or software package, and the data are often transferred (for example, to a PC) for further computation. These functional