Microhardness of polymers

This book deals with the micromechanical characterization of polymer materials. Particular attention is given to microhardness measurement as a technique capable of detecting a variety of morphological and textural changes in polymers. A comprehensive introduction to the microhardness of polymers is provided, including descriptions of the various testing methods in materials science and engineering. The book also includes the micromechanical study of glassy polymers and discusses the relevant aspects of microhardness of semicrystalline polymers. It is demonstrated that microhardness, in combination with other techniques such as microscopy, differential scanning calorimetry and X-ray scattering can be very helpful in better understanding structure–property relationships, and in doing so can contribute to the improvement of physical and mechanical properties, manufacturing processes and design of parts made from polymeric materials. This book will be of use to graduate level materials science students, as well as research workers in materials science, mechanical engineering and physics departments interested in the microindentation hardness of polymer materials.

Born in 1936, Professor BALTÁ CALLEJA was educated in Spain where he obtained his first degree in physics at the University of Madrid. In 1958 he started his research work at the University of the Sorbonne in Paris on pioneering NMR studies of organic liquids relating to intermolecular effects. In 1959 he moved to the H.H. Wills Physics Laboratory in Bristol to work on crystallization and morphology of synthetic polymers. In 1962 he obtained a PhD in physics at the University of Bristol. In 1963 he was appointed Adjoint Professor of Electricity and Magnetism at the University of Madrid. Since 1970 he has led a group on macromolecular physics at the Spanish Research Council. Presently, he is Professor of Physics and Director of the Institute for Structure of Matter, CSIC, in Madrid. He is Chairman of the Macromolecular Board of the European Physical Society and has also been chairman of the Solid State Physics Group of the Spanish Royal Society of Physics. He was awarded both the Humboldt Research Award and the DuPont Research Award in 1994. He is, or has been, a member of the editorial boards of *Acta Polymerica*, *Journal of Macromolecular Science – Physics* and *Journal of Polymer Engineering*. He is the author of more than 280 papers and has contributions in several books. He is the author of the book *X-ray Scattering of Synthetic Polymers*, Elsevier, 1989.

Born in 1936, Professor FAKIROV was educated in Bulgaria where he obtained his first degree in chemistry at the University of Sofia in 1959. In 1960 he was appointed Assistant Professor at the same university. In 1962 he moved to the Lomonosov State University, Moscow, obtaining his PhD degree in chemistry in 1966. In 1972 he was appointed Associate Professor at Sofia University. In 1987 he was appointed full Professor of Polymer Chemistry at the same university. He has spent many years as Visiting Professor in various international institutions. Since 1984 he has led a group on the structure and properties of polymers at the University of Sofia. He has been Vice President of Sofia University. He was given the Award of the Union of Bulgarian Scientists and the Honour Award '100 Years of the University of Sofia'. He is a member of the editorial boards of *Applied Composite Materials* and *Advances in Polymer Technology*, and Associate Editor of the *International Journal of Polymeric Materials*. He is presently a fellow of the Foundation for Science and Technology, Portugal, and has also been a fellow of many other international institutions. He is the author of more than 220 papers, has contributions in several books as editor and coauthor, and holds nine US patents. He is the author of the book *Structure and Properties of Polymers*, Martinus Nijhoff, Int., 1985.

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To our wives
Sabine and Galina,
for their year-long
patience, understanding and support

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Contents

Preface

The search for quantitative structure–property relationships for the control and prediction of the mechanical behaviour of polymers has occupied a central role in the development of polymer science and engineering. Mechanical performance factors such as creep resistance, fatigue life, toughness and the stability of properties with time, stress and temperature have become subjects of major activity. Within this context microhardness emerges as a property which is sensitive to structural changes.

The microindentation hardness technique has been used for many years for the characterization of such 'classical' materials as metals, alloys, inorganic glasses, etc. Its application to polymeric materials was developed in the 1960s. The potential of this method for structural characterization of polymers was developed and highlighted to a large extent by the studies carried out in the Instituto de Estructura de la Materia, CSIC, Madrid.

Nowadays, the microhardness technique, being an elegant, non-destructive sensitive and relatively simple method, enjoys wide application, as can be concluded from the publications on the topic that have appeared during just the last five years – they number more than 100, as is shown by a routine computer-aided literature search. In addition to some methodological contributions to the technique, the microhardness method has also been successfully used to gain a deeper understanding of the microhardness–structure correlation of polymers, copolymers, polymer blends and composites. A very attractive feature of this technique is that it can be used for the micromechanical characterization of some components, phases or morphological entities that are otherwise not accessible for direct determination of their microhardness.

Since the 1940s studies of the microhardness of metals and ceramics have furnished a well established picture of the basic mechanisms involved, as recognized by the First International Workshop on Indentation held in Cambridge in 1996. However, the investigation of the microhardness of polymers is more recent and has so far been restricted to aspects of rather technical interest. The test has been used to examine: the correlation of rheological properties with microhardness, the comparison of yield stress from hardness and tension tests, the determination of internal stresses in the surface of plastics, lacquer coatings, the curing of resins and the diffusion of water through nylons. However, the lack of fundamental knowledge of the influence of the structure (lamellar thickness, crystallinity, chain orientation, etc.) on microhardness has only been recently recognized.

The microhardness technique has been established as a means of detecting a variety of morphological and textural changes in crystalline polymers and has been extensively used in research. This is because microindentation hardness is based on plastic straining and, consequently, is directly correlated to molecular and supermolecular deformation mechanisms occurring locally at the polymer surface. These mechanisms critically depend on the specific morphology of the material. The fact that crystalline polymers are multiphase materials has prompted a new route in identifying their internal structure and relating it to the resistance against local deformation (microhardness).

After an introductory chapter highlighting the value of microhardness in science and engineering, the techniques for the determination of microhardness of polymeric materials together with data evaluation are discussed in Chapter 2. Chapter 3 is devoted to the study of glassy polymers and attention is focused on glass transition temperature determination, ageing of glassy polymers and micromechanics studies of amorphous polymers with applications to the study of crazing in polymer glasses. Chapter 4 deals with the microhardness of crystalline polymers. The effects of various crystal parameters such as the degree of crystallinity, crystal size, surface energy, etc., as well as the influence of the molecular weight are discussed. The detection of polymorphic transition is also discussed. In this chapter examples showing the possibility of following the crystallization kinetics by means of microhardness are also given. The relationship between hardness and macroscopic mechanical properties is briefly presented in the light of various mechanical models. Chapter 5 covers the microhardness of polymer blends, copolymers and composites – all of which are multicomponent and/or multiphase systems and, therefore, showing often some peculiar behaviour in comparison to the homopolymers. In Chapter 6 more recent data on microhardness under strain are summarized and the concept of reversible microhardness is introduced. Finally, in Chapter 7 examples are given of the application of the microhardness technique for the characterization of polymeric materials including the influence of processing conditions, the characterization of natural polymers and biopolymers, weathering tests, the characterization of modified polymer surfaces and others.

It is noteworthy that, in contrast to some other books in the same series of Cambridge University Press, the present one is based not on a lecture course but mainly on the systematic investigations carried out during the 1980s and 1990s at the Instituto de Estructura de la Materia, CSIC, Madrid. We wish to record our appreciation here to Drs F. Ania, M.E. Cagiao, T.A. Ezquerra, A. Flores and D.R. Rueda for their many helpful discussions, comments and suggestions and for their invaluable participation in much of the work described in this volume. The book also has another peculiarity. Although it does not pretend to review all the publications on microhardness of polymers, it is based on our own studies on polymer structure in which have been involved a great many of the leading polymer scientists world-wide, including, to name only some: Professors A. Keller, I.M. Ward and D.C. Bassett from England; H. Kilian, H.G. Zachmann, E.W. Fischer, G.H. Michler, R.K. Bayer and N. Stribeck from Germany; A. Peterlin, R.S. Porter and J.C. Seferis from the USA; T. Asano and M. Hirami from Japan; H.H. Kausch from Switzerland. Furthermore, it has been the goal of the authors to stress the correlation between the microhardness of polymers and their structure using both their own research experience and results from many other workers in the field. Nevertheless, the authors hope that the book will be not only of interest to scientists and engineers but also useful for students reading for BSc or BEng degrees in materials science and materials engineering.

We would like to thank the many friends and colleagues who have allowed us to use examples from their work and also their publishers who have given us permission to reproduce photographs and diagrams. Acknowledgement is made to various firms for the provision of illustrations of their microhardness testing devices. The majority of the work on microhardness and the structure–property relationship of polymers, performed in the IEM, CSIC, Madrid, has been supported by the Dirección General de Investigación Científica y Técnica (DGICYT) and the New Energy Industrial Development Organization (NEDO), Japan. This support has been, and still is, invaluable and is warmly acknowledged.

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