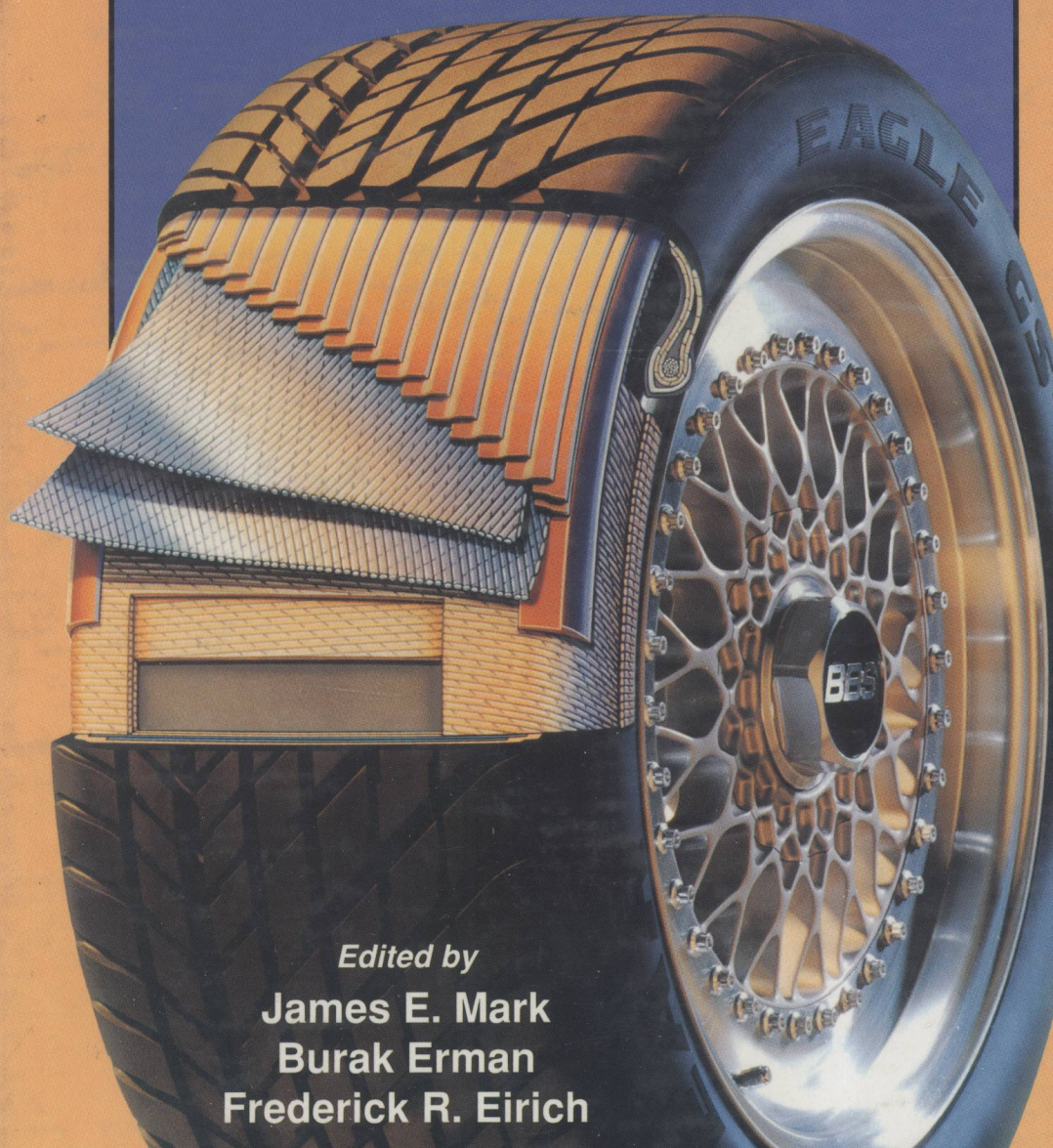


SECOND EDITION

# Science and Technology of

# RUBBER



*Edited by*

**James E. Mark**

**Burak Erman**

**Frederick R. Eirich**

# Science and Technology of **RUBBER**

**Second Edition**

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Science  
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**RUBBER**

Second Edition



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## Preface to the Second Edition

The goals of the new edition of this book are much the same as those described in the Preface to the First Edition, namely a broad overview of elastomers and rubberlike elasticity. Again, the emphasis is on a unified treatment, ranging from chemical aspects such as elastomer synthesis and curing, through theoretical developments and characterization of equilibrium and dynamic properties, to final applications (including tire manufacture and engineering).

Although the material has been divided into the same 14 chapters, advances in the field since the first edition appeared in 1978 required the addition of a great deal of new material. As a result of this extensive updating, the chapters are now generally 20–30% longer.

During the past 15 years, a number of the original contributors passed away, retired, or moved into different areas of research or into entirely different nonresearch areas. Of the 23 authors contributing to this second edition, nearly half are new to this editorial project.

The editors, coauthors, and publishers all hope this new edition will find an enthusiastic response from readers in the polymer science and engineering community in general, and from those in the elastomers area in particular.



## Preface to the First Edition

The continuing success of the American Chemical Society Rubber Divisions's correspondence course, based on Professor Morton's "Rubber Technology" persuaded the Division's Educational Committee to introduce a second, more advanced course. This editor was commissioned to assemble a number of chapters on the graduate to postgraduate level, stressing the continuous relation between ongoing research in synthesis, structure, physics, and mechanics and rubber technology and industry. This collection of chapters covering, to various depths, the most important aspects of rubber science and technology, and the list of authors, all leading authorities in their fields, should be of vital interest not only to those who want to expand their formal education or update and supplement their experience in the field, but to anyone interested in the unusual chemistry and physics and the outstanding properties and farflung usefulness of elastomers. The intermediate level of presentation, a mixture of theory, experiment, and practical procedures, should offer something of value to students, practitioners, and research and development managers.

It has been the bias of this editor, based on many years of teaching at Polytechnic's Institute of Polymer Chemistry, that the most successful way of teaching and learning polymer subjects is to refer continually to the special features of macromolecules. For elastomers, in particular, it is most instructive to derive the unique features of high elasticity from those of long flexible chain molecules in their matted and netted state and the changes imposed by large deformations, including the key role played by the internal viscosity as a function of temperature and rate. Swaying the authors to lean to this approach inevitably caused some overlap but, at the same time, allowed synthesis and structure, elasticity and flow, blending, filling, and cross-linking to be treated in different contexts; a more integral composition without too frequent a need for cross references to other chapters became possible. For the same reason, some variation in nomenclature was allowed, especially if it reflected differing uses in the literature.

Particular concerns in preparing this composite book have been the combination of information and instruction, and the sequence and correlation of the chapters' contents. The first ten chapters take the reader from an



introduction through synthesis characterization, mechanical behavior, and flow to the major processing steps of filling, compounding, and vulcanization and to the theories and measurement of elastomeric performance, leaning strongly on the "materials" approach. The next three chapters deal with the ever broadening fields of blended, modified, and thermoplastic elastomers, while the last chapter, for reasons of space, is the only representative of the chapters originally planned on manufacturing, possibly the forerunner of another volume. All chapters, while presenting theory, mechanism, and the author's overview of the internal consistency of the material's pattern of behavior, serve also as substantial sources of data and as guides to the relevant literature and to further self-study. As such, this book should be suitable not only as a basis for the new course, but also as an instrument of instruction for students, teachers, and workers in all fields of polymer and, indeed, of material science.

This, in any case, was the intent of all the authors whose extensive, conscientious, and patient cooperation made this book possible. Special thanks are due to Dr. A. Gessler and the Exxon Corporation, Linden, New Jersey, and Dr. E. Kontos, Uniroyal Chemical Division, who conceived the idea of a second course and of the nature of this book and to Dr. H. Remsberg, Carlisle Tire and Rubber Company, then Chairman of the Division's Educational Committee, without whose firm backing and continuous understanding this effort could not have been concluded. Drs. Gessler, Kontos, and Remsberg were further instrumental in gathering many of the authors and offering a number of early revisions of the manuscripts.



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# 1

# Rubber Elasticity: Basic Concepts and Behavior

**A. N. GENT**

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- I. Introduction
- II. Elasticity of a Single Molecule
- III. Elasticity of a Three-Dimensional Network of Polymer Molecules
- IV. Comparison with Experiment
- V. Continuum Theory of Rubber Elasticity
- VI. Second-Order Stresses
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## I. INTRODUCTION

The single most important property of elastomers—that from which their name derives—is their ability to undergo large elastic deformations, that is, to stretch and return to their original shape in a reversible way. Theories to account for this characteristic high elasticity have passed through three distinct phases: the early development of a molecular model relating experimental observations to the known molecular features of rubbery polymers; then generalization of this approach by means of symmetry considerations taken from continuum mechanics which are independent of the molecular structure; and now a critical reassessment of the basic premises on which these two quantitative theories are founded. In this chapter, the theoretical treatment is briefly outlined and shown to account quite successfully for the observed elastic behavior of rubbery materials. The special case of small elastic deformations is then discussed in some detail because of its technical importance. Finally, attention is drawn to some aspects of rubber elasticity which are still little understood.



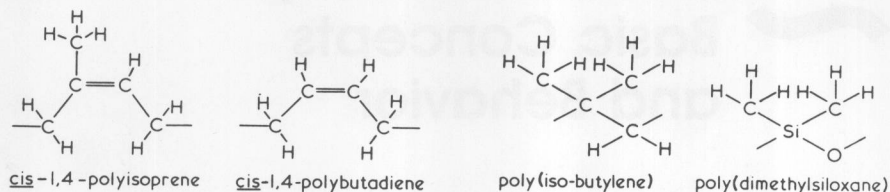


FIGURE 1 Repeat units for some common elastomer molecules.

## II. ELASTICITY OF A SINGLE MOLECULE

The essential requirement for a substance to be rubbery is that it consist of long flexible chainlike molecules. The molecules themselves must therefore have a "backbone" of many noncollinear single valence bonds, about which rapid rotation is possible as a result of thermal agitation. Some representative molecular subunits of rubbery polymers are shown in Fig. 1; thousands of these units linked together into a chain constitute a typical molecule of the elastomers listed in Fig. 1. Such molecules change their shape readily and continuously at normal temperatures by Brownian motion. They take up random conformations in a stress-free state but assume somewhat oriented conformations if tensile forces are applied at their ends (Fig. 2). One of the first questions to consider, then, is the relationship between the applied tension  $f$  and the mean chain end separation  $r$ , averaged over time or over a large number of chains at one instant in time.

Chains in isolation take up a wide variety of conformations,<sup>1</sup> governed by three factors: the statistics of random processes; a preference for certain sequences of bond arrangements because of steric and energetic restraints within the molecule; and the exclusion of some hypothetical conformations which would require parts of the chain to occupy the same volume in space. In addition, cooperative conformations are preferred for space-filling reasons in concentrated solutions or in the bulk state.

Flory [1] has argued that the occupied-volume exclusion (repulsion) for an isolated chain is exactly balanced in the bulk state by the external (repulsive) environment of similar chains, and that the exclusion factor can therefore be ignored in the solid state. He has also pointed to many experimental observations which indicate that cooperative effects do not significantly affect the distribution of chain end-to-end distances in bulk or the relation between tension and distance. It is noteworthy, for example, that modest swelling by simple liquids (say  $< 50\%$ ) does not make rubbers much

<sup>1</sup>Although the terms *configuration* and *conformation* are sometimes used interchangeably, the former has acquired a special meaning in organic stereochemistry and designates specific steric structures. *Conformation* is used here to denote a configuration of the molecule which is arrived at by rotation of single-valence bonds in the polymer backbone.