



SCIENCE AND TECHNOLOGY OF RUBBER

Edited by
FREDERICK R. EIRICH

Under the Auspices of the
Rubber Division of the American Chemical Society

ACADEMIC PRESS, INC.
A Subsidiary of Harcourt Brace Jovanovich, Publishers

SCIENCE AND TECHNOLOGY OF RUBBER

Contributors

J. R. BEATTY

R. J. CERESA

STUART L. COOPER

A. Y. CORAN

P. J. CORISH

JOHN D. FERRY

A. N. GENT

F. J. KOVAC

OLE KRAMER

GERARD KRAUS

MAURICE MORTON

MITCHEL SHEN

M. L. STUDEBAKER

G. VER STRATE

JAMES C. WEST

JAMES LINDSAY WHITE

SCIENCE AND TECHNOLOGY OF RUBBER

Edited by

FREDERICK R. EIRICH

*Polytechnic Institute of New York
Brooklyn, New York*

Under the auspices of the

RUBBER DIVISION OF THE
AMERICAN CHEMICAL SOCIETY



ACADEMIC PRESS New York San Francisco London 1978

A Subsidiary of Harcourt Brace Jovanovich, Publishers

COPYRIGHT © 1978, BY ACADEMIC PRESS, INC.
ALL RIGHTS RESERVED.
NO PART OF THIS PUBLICATION MAY BE REPRODUCED OR
TRANSMITTED IN ANY FORM OR BY ANY MEANS, ELECTRONIC
OR MECHANICAL, INCLUDING PHOTOCOPY, RECORDING, OR ANY
INFORMATION STORAGE AND RETRIEVAL SYSTEM, WITHOUT
PERMISSION IN WRITING FROM THE PUBLISHER.

ACADEMIC PRESS, INC.
111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by
ACADEMIC PRESS, INC. (LONDON) LTD.
24/28 Oval Road, London NW1 7DX

Library of Congress Cataloging in Publication Data

Main entry under title:

Science and technology of rubber.

Includes bibliographies.

1. Rubber. 2. Elastomers. I. Eirich, Frederick
Roland, Date

TS1890.S315 678'.2 77-80783

ISBN 0-12-234360-3

PRINTED IN THE UNITED STATES OF AMERICA

Contents

LIST OF CONTRIBUTORS

xi

PREFACE

xiii

Chapter 1 Rubber Elasticity: Basic Concepts and Behavior

A. N. Gent

I.	Introduction	1
II.	Elasticity of a Single Molecule	2
III.	Elasticity of a Three-Dimensional Network of Polymer Molecules	6
IV.	Comparison with Experiment	11
V.	Continuum Theory of Rubber Elasticity	12
VI.	Second-Order Stresses	14
VII.	Elastic Behavior under Small Deformations	16
VIII.	Some Unsolved Problems in Rubber Elasticity	19
	References	20

Chapter 2 Polymerization

Maurice Morton

I.	Introduction	24
II.	Classification of Polymerization Reactions and Kinetic Considerations	25
III.	Functional Group Polymerization	27
IV.	Chain Addition Polymerization by Free Radical Mechanism	29
V.	Emulsion Polymerization	34
VI.	Copolymerization	43
VII.	Addition Polymerization by Cationic Mechanism	48
VIII.	Addition Polymerization by Anionic Mechanism	54
IX.	Stereospecific Polymerization and Copolymerization by Coordination Catalysts	61
X.	Graft and Block Copolymerization	65
	References	71

Chapter 3 **Structure Characterization in the Science and Technology of Elastomers**

G. Ver Strate

Introduction	75
I. Chemical Composition and Repeat Unit Structure (Table I)	76
II. Compositional and Sequence Distribution of Copolymers; Additives (Tables IIA, IIB)	79
III. Molecular Weight and Its Distribution (MWD); Branching; Gel (Tables III)	82
IV. Rubber–Glass and Other Secondary Transitions (Table IV)	112
V. Crystallinity (Table V)	116
VI. Morphology (Table VI)	122
General References	126

Chapter 4 **The Molecular and Phenomenological Basis of Rubberlike Elasticity**

Mitchel Shen

I. Introduction	155
II. Statistics of a Polymer Chain	157
III. Rubberlike Elasticity of a Polymer Network	162
IV. Applications of Rubberlike Elasticity Theories	172
References	177

Chapter 5 **Dynamic Mechanical Properties**

Ole Kramer and John D. Ferry

I. Introduction	180
II. Definitions of Dynamic Mechanical Properties and Viscoelastic Functions	181
III. Zones of Dynamic Viscoelastic Behavior and Their Qualitative Molecular Interpretation	184
IV. The Transition Zone	187
V. The Plateau Zone	197
VI. Practical Aspects of Dynamic Properties	201
VII. Dynamic Properties in Large Deformations	209
VIII. Experimental Methods and Apparatus for Measurements and Tests	215
References	220

Chapter 6 **Rheological Behavior of Unvulcanized Rubber**

James Lindsay White

I. Introduction and Historical Background	224
II. Basic Concepts	226

III.	Rheological Measurements	245
IV.	Molecular Structure and Rheological Properties of Uncompounded Elastomers	255
V.	Flow of Blends and Compounds	265
VI.	Rheological Applications to Processing	270
	References	281
 Chapter 7 Vulcanization		
<i>A. Y. Coran</i>		
I.	General Considerations	292
II.	Sulfur Vulcanization	295
III.	Accelerated Sulfur Vulcanization	297
IV.	Vulcanization by Phenolic Resins, Quinone Derivatives, or Maleimides	315
V.	Vulcanization by Metal Oxides	322
VI.	Vulcanization by Peroxides	325
VII.	Cross-Linking by Chain Extension Reactions	330
VIII.	Thermoplastic Elastomers	333
	References	335
 Chapter 8 Reinforcement of Elastomers by Particulate Fillers		
<i>Gerard Kraus</i>		
I.	Introduction	339
II.	Carbon Black	340
III.	Filler Morphology and Its Characterization	341
IV.	Physical and Chemical Interactions at the Filler Surface	344
V.	The State of the Filler in the Rubber Mix	348
VI.	The State of the Rubber in the Filled Composite	349
VII.	Properties of Unvulcanized Rubber-Filler Mixes	350
VIII.	Mechanical Behavior of Filled Rubber Vulcanizates at Small and Moderate Strains	352
IX.	Large Deformation Behavior	355
X.	Failure Properties	359
	References	364
 Chapter 9 The Rubber Compound and Its Composition		
<i>M. L. Studebaker and J. R. Beatty</i>		
I.	Introduction	367
II.	Selection of Ingredients	368
III.	Compounding Costs	406
IV.	Mixing	408
V.	Resistance to Aging	410

VI.	Summary	416
	References	417
 Chapter 10 Strength of Elastomers		
<i>A. N. Gent</i>		
I.	Introduction	419
II.	Initiation of Fracture	420
III.	Crack Propagation	433
IV.	Tensile Rupture	440
V.	Abrasive Wear	451
	References	452
 Chapter 11 The Chemical Modification of Polymers		
<i>R. J. Ceresa</i>		
I.	Introduction	455
II.	Esterification, Etherification, and Hydrolysis of Polymers	456
III.	The Hydrogenation of Polymers	459
IV.	Dehalogenation, Elimination, and Halogenation Reactions in Polymers	461
V.	Other Addition Reactions to Double Bonds	464
VI.	Oxidation Reactions of Polymers	467
VII.	Miscellaneous Chemical Reactions of Polymers	468
VIII.	Block and Graft Copolymerization	470
	References	487
	Bibliography	487
 Chapter 12 Elastomer Blends		
<i>P. J. Corish</i>		
I.	Introduction	489
II.	Elastomer/Elastomer Blends	492
III.	Elastomer/Plastic Blends	514
IV.	General Correlations and Conclusions	524
	References	525
 Chapter 13 Thermoplastic Elastomers		
<i>James C. West and Stuart L. Cooper</i>		
I.	Introduction	531
II.	Morphology of Thermoplastic Elastomers	535
III.	Behavior in the Transition Temperature Range	544
IV.	Orientation	550
V.	Mechanical Properties	559

CONTENTS

ix

VI.	Application of Thermoplastic Elastomers	563
	References	564

Chapter 14 Tire Manufacture and Engineering

F. J. Kovac

I.	Introduction	569
II.	Tire Engineering	573
III.	Tire Manufacture	599
	Bibliography	606

AUTHOR INDEX	609
--------------	-----

SUBJECT INDEX	633
---------------	-----

This page intentionally left blank

List of Contributors

Numbers in parentheses indicate the pages on which the authors' contributions begin.

- J. R. BEATTY (367), The B. F. Goodrich Research & Development Center, Brecksville, Ohio 44141
- R. J. CERESA (455), Chemistry & Polymer Technology Department, Polytechnic of South Bank, London, England
- STUART L. COOPER (531), Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706
- A. Y. CORAN* (291), Monsanto Industrial Chemicals Company, Rubber Chemicals Research Laboratories, Akron, Ohio 44313
- P. J. CORISH (489), Dunlop Research Centre, Birmingham, England
- JOHN D. FERRY (179), University of Wisconsin, Madison, Wisconsin 53706
- A. N. GENT (1, 419), Institute of Polymer Science, The University of Akron, Akron, Ohio 44325
- F. J. KOVAC† (569), Tire Reinforcing Systems, The Goodyear Tire and Rubber Company, Dayton, Ohio
- OLE KRAMER (179), University of Copenhagen, Copenhagen, Denmark
- GERARD KRAUS (339), Phillips Petroleum Company, Bartlesville, Oklahoma 74004
- MAURICE MORTON (23), Institute of Polymer Science, The University of Akron, Akron, Ohio 44325
- MITCHEL SHEN (155), Department of Chemical Engineering, University of California, Berkeley, California 94720
- M. L. STUDEBAKER (367), Phillips Chemical Company, Stow, Ohio 44224
- G. VER STRATE (75), Elastomers Technology Division, Exxon Chemical Company, Linden, New Jersey 07036
- JAMES C. WEST* (531), Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706
- JAMES LINDSAY WHITE (223) The University of Tennessee, Knoxville, Tennessee 37916

*Present address: 260 Springside Drive, Akron, Ohio 44313.

†Present address: Goodyear International Tire Technical Center, Colmar-Berg, Grand-Duchy of Luxembourg.

*Present address: Allied Chemical, Morristown, New Jersey.

This page intentionally left blank

Preface

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 selfstudy. 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 of 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.

Chapter 1

Rubber Elasticity: Basic Concepts and Behavior*A. N. GENT*

INSTITUTE OF POLYMER SCIENCE
 THE UNIVERSITY OF AKRON
 AKRON, OHIO

I. Introduction	1
II. Elasticity of a Single Molecule	2
III. Elasticity of a Three-Dimensional Network of Polymer Molecules	6
IV. Comparison with Experiment	11
V. Continuum Theory of Rubber Elasticity	12
VI. Second-Order Stresses	14
VII. Elastic Behavior under Small Deformations	16
VIII. Some Unsolved Problems in Rubber Elasticity	19
Acknowledgments	20
References	20

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 upon 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.

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 will 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 will take up a wide variety of conformations,* 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 will be 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 softer [2], although it would certainly reduce any packing constraints. Also, direct observation of single chain dimensions in the bulk state by inelastic neutron scattering gives values fully consistent with unperturbed chain dimensions obtained for dilute solutions in theta solvents† [3, 4], although intramolecular effects may distort the local randomness of chain conformation.

Flory has again given compelling reasons for concluding that the chain end-to-end distance r in the bulk state will be distributed in accordance with

* 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.

† These are (poor) solvents in which repulsion between different segments of the polymer molecule is balanced by repulsion between polymer segments and solvent molecules.

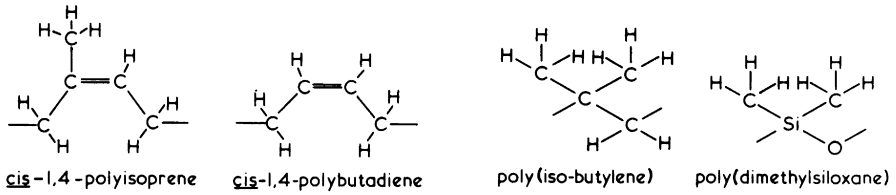


Fig. 1. Repeat units for some common elastomer molecules.

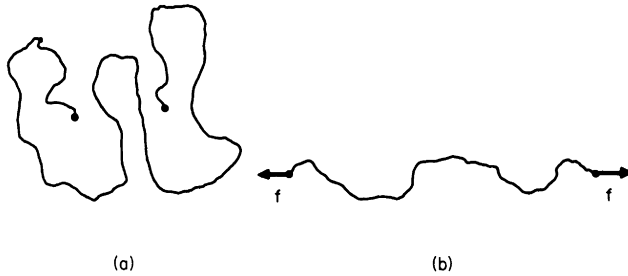


Fig. 2. (a) Random chain and (b) oriented chain. (From Gent [46].)

Gaussian statistics for sufficiently long chains, even if the chains are relatively stiff and inflexible over short lengths [1]. With this restriction to long chains it follows that the tension–displacement relation becomes a simple linear one:

$$f = Ar \quad (1)$$

where f is the tensile force, r is the average distance between the ends of the chain, and A is inversely related to the mean square end-to-end distance r_0^2 for unstressed chains;

$$A = 3kT/r_0^2 \quad (2)$$

where k is Boltzmann's constant and T is the absolute temperature.

If the real molecule is replaced by a hypothetical chain consisting of a large number n of rigid, freely jointed links, each of length l (Fig. 3), then

$$r_0^2 = nl^2 \quad (3)$$

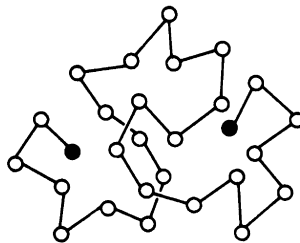


Fig. 3. Model chain of freely jointed links.

In this case r_0^2 is independent of temperature because completely random link arrangements are assumed. The tension f in Eq. (1) then arises solely from an entropic mechanism, i.e., from the tendency of the chain to adopt conformations of maximum randomness, and not from any energetic preference for one conformation over another. The tension f is then directly proportional to the absolute temperature T .

For real chains, consisting of a large number n of primary valence bonds along the chain backbone, each of length l ,

$$r_0^2 = C_\infty n l^2 \quad (4)$$

where the coefficient C_∞ represents the degree to which this real molecule departs from the freely jointed model. C_∞ is found to vary from 4 to 10, depending upon the chemical structure of the molecule and also upon temperature, because the energetic barriers to random bond arrangements are more easily overcome at higher temperatures [1]. $C_\infty^{1/2}l$ may thus be regarded as the effective bond length of the real chain [5], a measure of the "stiffness" of the molecule.

Equation (1) is reasonably accurate only for relatively short distances r , less than about one third of the fully stretched chain length [2]. Unfortunately, no good treatment exists for the tension in real chains at larger end separations. We must therefore revert to the model chain of freely jointed links, for which

$$f = (kT/l)L^{-1}(r/nl) \quad (5)$$

where L^{-1} denotes the inverse Langevin function. An expansion of this relation in terms of r/nl [2],

$$f = (3kTr/nl^2)[1 + (3/5)(r/nl)^2 + (99/175)(r/nl)^4 + (513/875)(r/nl)^6 + \cdots] \quad (6)$$

gives a useful indication of where significant departures from Eq. (1) may be expected.

Equation (5) gives a steeply rising relation between tension and chain end separation when the chain becomes nearly taut (Fig. 4), in contrast to the Gaussian solution, Eq. (1), which becomes inappropriate for $r > \frac{1}{3}nl$. Rubber shows a similar steeply rising relation between tensile stress and elongation at high elongations. Indeed, experimental stress-strain relations closely resemble those calculated using Eq. (5) in place of Eq. (1) in the network theory of rubber elasticity (outlined in the following section). The deformation at which a small but significant departure is first found between the observed stress and that predicted by small-strain theory, using Eq. (1), yields a value for the effective length l of a freely jointed link for the real molecular chain. This provides a direct experimental measure of molecular stiffness. The values obtained are relatively large, of the order of 5–15 main-chain bonds, for the only polymer which has been examined by this method so far, *cis*-1,4-polyisoprene [6, 7].

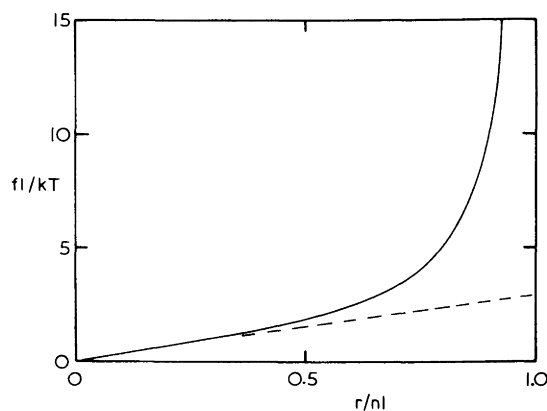


Fig. 4. Tension-displacement relation for a freely jointed chain (Eq. (5)): (---), Gaussian solution (Eq. (1)). (From Gent [46].)

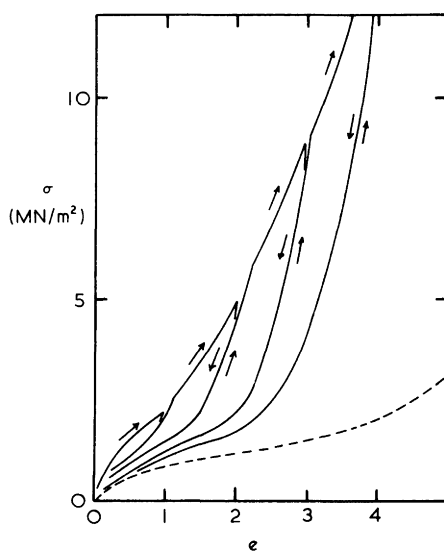


Fig. 5. Stress-induced softening of a carbon-black-filled vulcanizate of a copolymer of styrene and butadiene (25/75); (---), stress-strain curve of a corresponding unfilled vulcanizate. (From Tobolsky and Mark [7a].)

Equation (5) has also been used to estimate the force at which a rubber molecule will become detached from a particle of a reinforcing filler, for example carbon black, when a filled rubber is deformed [8]. In this way, a general semi-quantitative treatment has been achieved for stress-induced softening (Mullins effect) of filled rubbers (shown in Fig. 5).

III. Elasticity of a Three-Dimensional Network of Polymer Molecules

Some type of permanent structure is necessary to form a coherent solid and prevent liquidlike flow of elastomer molecules. This requirement is usually met by incorporating a small number of intermolecular chemical bonds (cross-links) to make a loose three-dimensional molecular network. Such cross-links are generally assumed to form in the most probable positions, i.e., so that the long sections of molecules between them have the same spectrum of end-to-end lengths as a similar set of uncross-linked molecules would have. Under Brownian motion each molecular section takes up a wide variety of conformations, as before, but now subject to the condition that its ends lie at the cross-link sites. The elastic properties of such a molecular network are treated later. We consider first another type of interaction between molecules.

High molecular weight polymers form entanglements by molecular intertwinning, with a spacing (in the bulk state) characteristic of the particular molecular structure. Some representative values of the molecular weight M_e between entanglement sites are given in Table I. Thus, a high molecular weight polymeric melt will show transient rubberlike behavior even in the absence of any permanent intermolecular bonds.

In a cross-linked rubber, many of these entanglements are permanently locked in (Fig. 6), the more so the higher the degree of cross-linking [9, 10]. If they are regarded as fully equivalent to cross-links, the effective number N of network chains per unit volume may be taken to be the sum of two terms N_e and N_c , arising from entanglements and chemical cross-links, respectively, where

$$N_e = \rho N_A / M_e, \quad N_c = \rho N_A / M_c$$

and ρ is the density of the polymer, N_A is Avogadro's number, and M_e and M_c denote the average molecular weights between entanglements and between cross-links, respectively. However, the efficiency of entanglements in constraining the participating chains is somewhat uncertain, particularly when the number of chemical cross-links is relatively small [11-13]. Moreover, the force-

TABLE I
REPRESENTATIVE VALUES OF THE AVERAGE MOLECULAR WEIGHT M_e BETWEEN
ENTANGLEMENTS FOR POLYMERIC MELTS^a

Polymer	M_e	Polymer	M_e
Polyethylene	4,000	Poly(iso-butylene)	17,000
<i>cis</i> -1,4-Polybutadiene	7,000	Poly(dimethylsiloxane)	29,000
<i>cis</i> -1,4-Polyisoprene	14,000	Polystyrene	35,000

^a Obtained from flow viscosity measurements.

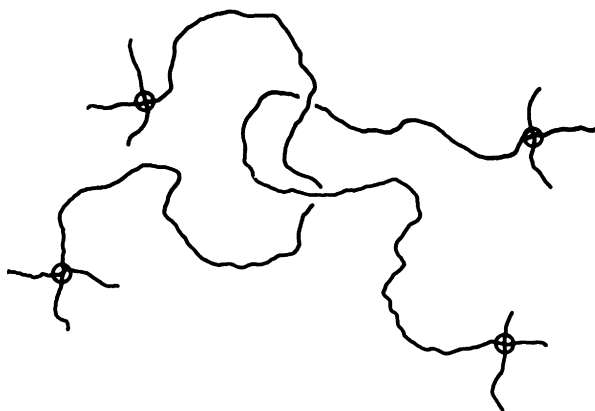


Fig. 6. Sketch of a permanent entanglement. (From Gent [46].)

extension relation for an entangled chain will differ from that for a cross-linked chain [14], being stiffer initially and nonlinear in form. The effective number N of molecular chains which lie between fixed points (i.e., cross-links or equivalent sites of molecular entanglement) is therefore a somewhat ill-defined quantity, even when the chemical structure of the network is completely specified.

It is convenient to express the elastic behavior of the network in terms of the strain energy density W per unit of unstrained volume. The strain energy w for a single chain is obtained from Eq. (1) as

$$w = Ar^2/2 \quad (7)$$

For a random network of N such chains under a general deformation characterized by extension ratios $\lambda_1, \lambda_2, \lambda_3$ (deformed dimension/undeformed dimension) in the three principal directions (Fig. 7), W is given by [2]

$$W = NAr_f^2(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3)/6 \quad (8)$$

where r_f^2 denotes the mean square end-to-end distance between chain ends (cross-link points or equivalent junctions) in the undeformed state. The close similarity of Eqs. (7) and (8) is evident, especially since $r^2 = (r_f^2/3)(\lambda_1^2 + \lambda_2^2 + \lambda_3^2)$.

For a random cross-linking process r_f^2 may be assumed to be equal to r_0^2 , the corresponding mean square end-to-end distance for unconnected chains of the same molecular length. Because A is inversely proportional to r_0^2 (Eq. (2)), the only molecular parameter which then remains in Eq. (8) is the number N of elastically effective chains per unit volume. Thus, the elastic behavior of a molecular network under moderate deformations is predicted to depend only upon the number of molecular chains and not upon their flexibility, provided that they are long enough to obey Gaussian statistics.

Although r_f^2 and r_0^2 are generally assumed to be equal at the temperature of network formation, they may well differ at other temperatures because of

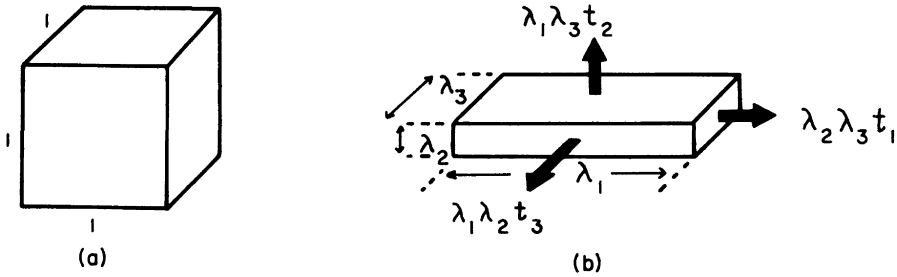


Fig. 7. (a) Undeformed and (b) deformed state.

the temperature dependence of r_0^2 for real chains (Eq. (4)). Indeed, the temperature dependence of elastic stresses in rubbery networks has been widely employed to study the temperature dependence of r_0^2 , as discussed elsewhere [1, 15–17].

Another way in which r_f^2 and r_0^2 may differ is when the network is altered after formation. For example, when the network imbibes a swelling liquid, r^2 for the swollen network will be increased by a factor λ_s^2 in comparison to its original value, where λ_s is the linear swelling ratio. At the same time the number of chains per unit volume will be decreased by a factor λ_s^{-3} . Thus, the strain energy density under a given deformation will be smaller for a swollen network by a factor λ_s^{-1} [2].

From the general relation for strain energy, Eq. (8), the elastic stresses required to maintain any given deformation can be obtained by means of virtual work considerations (Fig. 7),

$$\lambda_2 \lambda_3 t_1 = \partial W / \partial \lambda_1$$

with similar relations for t_2 and t_3 . Because of the practical incompressibility of rubbery materials in comparison to their easy deformation in other ways, the original volume is approximately conserved under deformation. The extension ratios then obey the simple relationship

$$\lambda_1 \lambda_2 \lambda_3 = 1 \quad (9)$$

As a result, the stress–strain relations become

$$t_1 = \lambda_1 (\partial W / \partial \lambda_1) - p, \quad \text{etc.}$$

where p denotes a possible hydrostatic pressure (which has no effect on an incompressible solid). Thus, only stress differences can be written explicitly [2],

$$t_1 - t_2 = (N A r^2 / 3) (\lambda_1^2 - \lambda_2^2) \quad (10)$$

For a simple extension, say in the 1-direction, we set $\lambda_1 = \lambda$, and $\lambda_2 = \lambda_3 =$

$\lambda^{-1/2}$ (from Eq. (9)), and $t_2 = t_3 = 0$. Hence,

$$t(= t_1) = (NAr^2/3)(\lambda^2 - \lambda^{-1}) \quad (11)$$

It is customary to express this result in terms of the tensile force f acting on a test piece of cross-sectional area A_0 in the unstrained state, where

$$f/A_0 = t/\lambda$$

The corresponding relation is shown in Fig. 8. It illustrates a general feature of the elastic behavior of rubbery solids: although the constituent chains obey a linear force-extension relationship (Eq. (1)), the network does not. This feature arises from the geometry of deformation of randomly oriented chains. Indeed, the degree of nonlinearity depends upon the type of deformation imposed. In simple shear, the relationship is predicted to be a linear one with a slope (shear modulus G) given by

$$t_{12} = G\gamma, \quad G = NAr^2/3 \quad (12)$$

where γ is the amount of shear, e.g., dx/dy .

Because rubbery materials are virtually incompressible in bulk, the value of Poisson's ratio is close to 0.5. Young's modulus E is therefore given by $3G$ to good approximation. However, the predicted relation between stress and tensile strain (extension) e ($= \lambda - 1$) is only linear for quite small extensions (Fig. 8), so that Young's modulus is only applicable for extensions or compressions of a few percent.

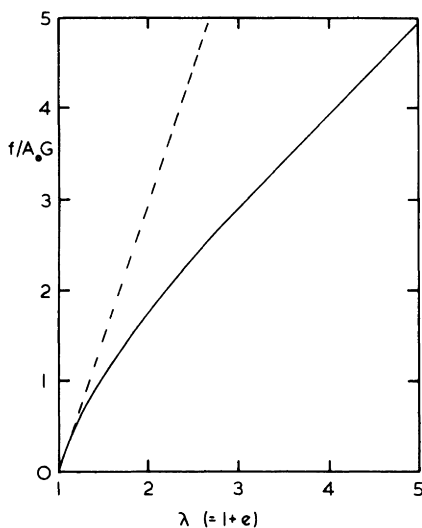


Fig. 8. Force-extension relation for simple extension: (---), linear relation obtaining at infinitesimal strains. (From Gent [46].)

For other deformations, notably the inflation of a thin spherical shell and of a cylindrical tube, the load–deformation relations become so nonlinear that in these cases the inflation pressure P passes through a maximum value when the radial expansion is only 38% and 60%, respectively, above r_0 , the unstrained radius. Thereafter, the pressure decreases continuously on further inflation. This feature indicates a potentially unstable condition. Indeed, it is not possible to inflate a spherical balloon or cylindrical tube uniformly to expansions greater than these amounts because they undergo a transition from a uniform to a nonuniform deformation state at these points.

Experimental measurements for a spherical rubber balloon (initial radius $r_0 = 29$ mm, initial thickness $d_0 = 0.40$ mm, shear modulus $G = 0.35$ MN/m²) are shown in Fig. 9 and compared with the relation obtained from Eqs. (9) and (10):

$$Pr_0/Gd_0 = 2(\lambda^{-1} - \lambda^{-2}) \quad (13)$$

where λ is now the radial expansion ratio r/r_0 . The expansion at which P reaches a maximum value is indicated by a vertical broken line. Up to this point the deformation appears to be uniform and the experimental measurements of inflation pressure are in good agreement with Eq. (13). Beyond this point they diverge from the calculated relation and the balloon undergoes a strikingly nonuniform expansion, as revealed by a grid drawn on it in the unstrained state.

All of the stress relations given above are derived from Eq. (8). They are therefore only valid for moderate deformations of the network, i.e., for deformations sufficiently small for the chain tensions to be linearly related to their end-to-end distances r (Eq. (1)). Unfortunately, no correspondingly simple expression can be formulated for W using Eq. (5), the relationship for large strains of the constituent chains, in which the molecular stiffness parameter reappears. Instead, a variety of series approximations must be used, as in Eq. (6), to give close approximations to the behavior of rubber networks under large strains [2].

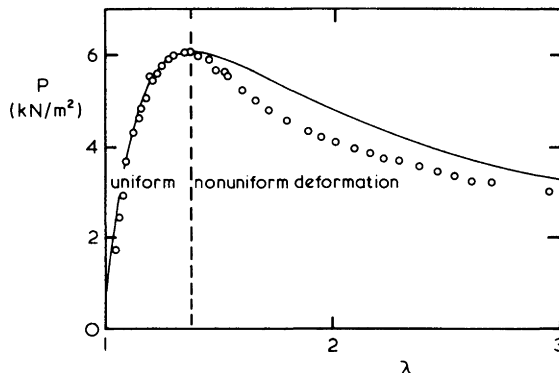


Fig. 9. Inflation of a thin-walled spherical rubber balloon. Solid curve: Eq. (13). (From Gent [46].)

IV. Comparison with Experiment

Although the treatment of rubber elasticity given in the preceding section is generally rather successful, certain discrepancies are found to occur. The first consists of observed stresses higher than predicted, e.g., by Eq. (11), and is often expressed by an additional contribution referred to as the C_2 term. This contribution is relatively large at small strains (although it is always the smaller part of the observed stress) and decreases in importance as the strain increases. It also decreases as the network is dilated by swelling with an inert liquid. Thus, the " C_2 stress" appears to reflect a non-Gaussian characteristic of network chains which is only important at small values of the chain end-to-end distance r . Indeed, Thomas [18] has shown that the magnitude of the C_2 stress and its complex dependence upon type and degree of strain, and upon degree of swelling, can all be accurately described by a simple additional term in the relation for the strain energy w for a single network chain, Eq. (7), which becomes

$$2w = Ar^2 + Br^{-2} \quad (14)$$

The second term clearly becomes insignificant at large values of r .

Further evidence bearing on the physical nature of the discrepancy is provided by two other observations: C_2 does not appear to be strongly dependent upon temperature [19] and therefore does not appear to be associated with the energetics of chain conformations; and it is closely correlated with the tendency of the polymer chains to form molecular entanglements [20, 21]. For example, those polymers that have a high density of entanglements in the bulk state (Table I) yield rubbery networks with a relatively high C_2 stress component.

Finally, there is no evidence that isolated chains in theta solvents fail to conform to Gaussian statistics, so that the C_2 discrepancy appears to arise only when the molecular chains are tied into a network.

These varied aspects of the C_2 stress suggest that it is associated with entangled chains in networks (Fig. 6) and specifically that it arises from restrictions on the conformations available to entangled chains, different from those operating at cross-link sites. Prager and Frisch [14] have pointed out that chains involved in model entanglements are governed by different statistics; their conclusions are quite consistent with what is known of the C_2 stress, but a quantitative comparison is not yet possible.

A second discrepancy between theory and experiment is found when the Gaussian part of the measured stresses is compared with the theoretical result for an ideal network. Numerical differences of up to 50% are obtained between the density of effective chains calculated from the observed stresses and that from the chemistry of cross-linking (e.g., see Bueche [9]). This discrepancy may be due to an error in the theoretical treatment as given here [22]. James and

Guth [23] arrived at stresses only half as large as those given in Eq. (10), from a somewhat different theoretical standpoint. However, up to the present the quantitative aspects of cross-linking and the topology of networks formed by cross-linking have been difficult to measure and to control, so that an accurate test of the theory is not yet feasible.

A third and major discrepancy, already referred to, is found at large deformations when the network chains fail to obey Gaussian statistics, even approximately. Considerable success is achieved in this case by using Eq. (5) in place of Eq. (1) for chain tensions in the network [2].

Notwithstanding these discrepancies, the simple treatment of rubber elasticity outlined in this chapter has proved to be remarkably successful in accounting for the elastic properties of rubbers under moderate strains, up to about 300% of the unstrained length (depending upon the length and flexibility, and hence the extensibility, of the constituent chains). It predicts the general form of the stress-strain relationships correctly under a variety of strains, the approximate numerical magnitudes of the stresses for various chemical structures, and the effects of temperature and of swelling the rubber with an inert mobile liquid upon the elastic behavior. It also predicts novel second-order stresses, discussed later, which have no counterpart in classical elasticity theory. In summary, it constitutes a major advance in our understanding of the properties of polymeric materials.

V. Continuum Theory of Rubber Elasticity

A general treatment of the stress-strain relations of rubberlike solids was developed by Rivlin [24, 25], assuming only that the material is isotropic in elastic behavior in the unstrained state, and incompressible in bulk. It is quite surprising to note what far-reaching conclusions follow from these elementary propositions, which make no reference to molecular structure.

Symmetry considerations suggest that appropriate measures of strain are given by three strain invariants, defined as

$$\begin{aligned} I_1 &= \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \\ I_2 &= \lambda_1^2 \lambda_2^2 + \lambda_2^2 \lambda_3^2 + \lambda_3^2 \lambda_1^2 \\ I_3 &= \lambda_1^2 \lambda_2^2 \lambda_3^2 \end{aligned}$$

Moreover, for an incompressible material I_3 is identically unity (Eq. (9)) and hence only two independent measures of strain, namely, I_1 and I_2 , remain. It follows that the strain energy density W is a function of these two variables only:

$$W = f(I_1, I_2) \quad (15)$$

Furthermore, because the differences between the deformed and undeformed

states $I_1 - 3$ and $I_2 - 3$ are of second order in the strains, e_1, e_2, e_3 , the strain energy function at sufficiently small strains must take the form

$$W = C_1(I_1 - 3) + C_2(I_2 - 3) \quad (16)$$

where C_1 and C_2 are constants. This particular form of strain energy function was originally proposed by Mooney [26] and is therefore often called the Mooney–Rivlin equation. It is noteworthy that the first term corresponds to the relation obtained from the molecular theory of rubber elasticity, Eq. (8), if the coefficient C_1 were identified with $NAr^2/6 = \frac{1}{2}NkT(r^2/r_0^2)$.

Eq. (16) leads to the following stress–strain relation in simple extension or compression,

$$t(= t_1) = 2C_1(\lambda^2 - \lambda^{-1}) + 2C_2(\lambda - \lambda^{-2})$$

in place of Eq. (11). In terms of the tensile or compressive force F acting on a test piece of cross-sectional area A_0 in the unstrained state, this relation becomes

$$F/A_0(\lambda^2 - \lambda^{-1}) = 2C_1 + 2C_2/\lambda \quad (17)$$

Although Eq. (17) is necessarily valid at small strains, considerable confusion has arisen from its application at larger strains, when it no longer holds. It is almost unfortunate that the stress–strain relation obtained in simple extension *appears* to be in accord with the Mooney–Rivlin equation (16), up to moderately large strains. This fortuitous fit arises because the particular strain energy function obeyed by rubber, discussed later, depends upon strain in a certain way [27].

The strain energy function W is determined experimentally from measured stresses in terms of its derivatives $\partial W/\partial I_1$ and $\partial W/\partial I_2$, denoted hereafter W_1 and W_2 . The former is found to be approximately constant, but the latter varies with the strain, primarily as a function of the strain measure I_2 [2, 27–29]. This variation may be described to a good approximation by the simple empirical relation

$$W_2 = K_2/I_2$$

where K_2 is a constant [30]. However, it should be noted that both the small dependence of W_1 and the large dependence of W_2 upon strain are described accurately by Eq. (14), the Thomas modification of Gaussian molecular theory [18].

Considerable success has also been achieved in fitting the observed elastic behavior of rubbers by strain energy functions which are formulated directly in terms of the extension ratios $\lambda_1, \lambda_2, \lambda_3$ instead of in terms of the strain invariants I_1, I_2 [28, 29, 31–35]. Although experimental results can be described economically and accurately in this way, the functions employed are empirical and the numerical parameters used as fitting constants do not appear to have any direct physical significance in terms of the molecular structure of

the material. On the other hand, the molecular elasticity theory, supplemented by a simple non-Gaussian term whose molecular origin is in principle within reach, seems able to account for the observed behavior at small and moderate strains with comparable success.

VI. Second-Order Stresses

Because the strain energy function for rubber is valid at large strains, and yields stress-strain relations which are nonlinear in character, the stresses depend upon the square and higher powers of strain, rather than the simple proportionality expected at small strains. A striking example of this feature of large elastic deformations is afforded by the normal stresses t_{11} , t_{22} , t_{33} that are necessary to maintain a simple shear deformation of amount γ (in addition, of course, to simple shear stresses) [24, 25, 36]. These stresses are predicted to increase in proportion to γ^2 .

They are represented schematically in Figs. 10 and 11 for two different choices of the arbitrary hydrostatic pressure p , chosen so as to give the appropriate reference (zero) stress. In Fig. 10, for example, the normal stress t_{11} in the shear direction is put equal to zero; this condition would arise near the front and rear surfaces of a sheared block. In Fig. 11, the normal stress t_{33} is put equal to zero; this condition would arise near the side surfaces of a sheared block. In each case a *compressive* stress t_{22} is found to be necessary to maintain the simple shear deformation. In its absence the block would tend to increase in thickness on shearing.

When the imposed deformation consists of an inhomogeneous shear, as in torsion, the normal forces generated (corresponding to the stresses t_{22} in Figs. 10 and 11) vary from point to point over the cross section (Fig. 12). The exact way in which they are distributed depends upon the particular form of strain energy function obeyed by the rubber, i.e., upon the values of W_1 and W_2 which obtain under the imposed deformation state [36].

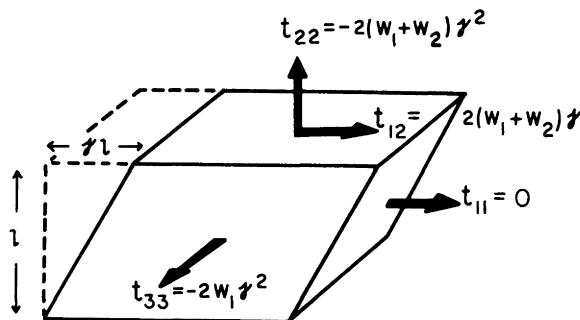


Fig. 10. Stresses required to maintain a simple shear deformation of amount γ . The normal stress t_{11} is set equal to zero. (From Gent [46].)

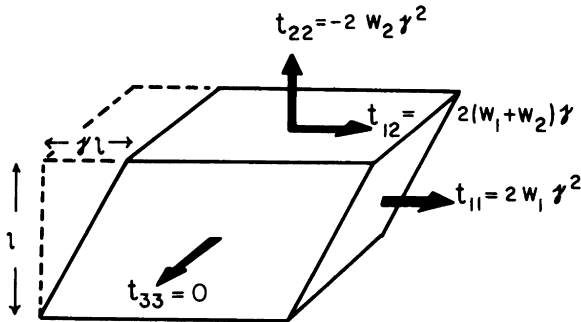


Fig. 11. Stresses required to maintain a simple shear deformation of amount γ . The normal stress t_{33} is set equal to zero. (From Gent [46].)

If a rubber block is subjected to a shearing stress while it is simultaneously compressed against a rigid frictional surface, it may undergo, when the coefficient of friction μ is high, a large shear deformation before sliding begins. If the applied compressive deformation (assumed small) is held constant, the normal stress t_{22} will then increase sharply as the amount of shear increases. Indeed, when the amount of shear γ exceeds a critical value of $(2\mu)^{-1}$ and $W_2(W_1 + W_2)^{-1}(2\mu)^{-1}$ for the stress conditions shown in Figs. 10 and 11, respectively, no sliding is possible, because the greater the applied shear stress t_{12} , the more the compressive stress t_{22} generated by the shear deformation exceeds that necessary to prevent sliding.

We therefore infer that sliding becomes completely inhibited for soft elastic materials held under a small compressive strain of approximately $0.08\mu^{-2}$ [37]. The condition for such frictional "locking" depends upon whether the material under consideration lies near front and rear surfaces of the block, or near the side surfaces, because different stress conditions prevail in these dif-

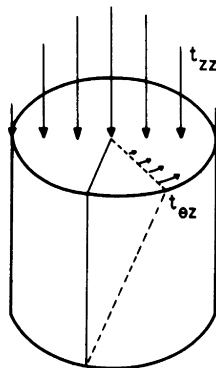


Fig. 12. Sketch of a cylindrical rod under torsion, showing the distribution of normal stress t_{zz} (corresponding to $-t_{22}$ in Figs. 10 and 11) over the cross section of the rod [36].

ferent regions (Figs. 10 and 11). When it does occur, however, the block must undergo frictional tearing, and hence abrasive wear, in order to move over the frictional surface.

These considerations illustrate again the close connection between an understanding of rubberlike elasticity and of other physical properties of rubbery materials.

VII. Elastic Behavior under Small Deformations

Under small deformations rubbers are linearly elastic solids. Because of high moduli of bulk compression, about 2000 MN/m^2 , compared to the shear moduli G , about $0.2\text{--}5 \text{ MN/m}^2$, they may be regarded as relatively incompressible. The elastic behavior under small strains can thus be described by a single elastic constant G . Poisson's ratio is effectively $1/2$, and Young's modulus E is given by $3G$, to good approximation.

A wide range of values for G can be obtained by varying the composition of the elastomer, i.e., by changing the chemistry of cross-linking, oil dilution, and filler content. However, soft materials with shear moduli of less than about 0.2 MN/m^2 prove to be extremely weak and are seldom used. Also, particularly hard materials made by cross-linking to high degrees prove to be brittle and inextensible. The practical range of shear modulus, from changes in degree of cross-linking and oil dilution, is thus about $0.2\text{--}1 \text{ MN/m}^2$. Stiffening by fillers increases the upper limit to about 5 MN/m^2 , but those fillers which have a particularly pronounced stiffening action also give rise to stress-softening effects like those shown in Fig. 5, so that the modulus becomes a somewhat uncertain quantity.

It is customary to characterize the modulus, stiffness, or hardness of rubbers by measuring their elastic indentation by a rigid die of prescribed size and shape under specified loading conditions. Various nonlinear scales are employed to derive a value of hardness from such measurements [38]. Corresponding values of shear modulus G for two common hardness scales are given in Fig. 13.

Many rubber products are normally subjected to fairly small deformations, rarely exceeding 25% in extension or compression or 75% in simple shear. A good approximation for the corresponding stresses can then be obtained by conventional elastic analysis assuming linear relationships. One particularly important deformation is treated here: the compression or extension of a thin rubber block, bonded on its major surfaces to rigid plates (Fig. 14). A general treatment of such deformations has recently been reviewed [39].

It is convenient to assume that the deformation takes place in two stages: a pure homogeneous compression or extension of amount e , requiring a uniform compressive or tensile stress $\sigma_1 = Ee$, and a shear deformation restoring points in the planes of the bonded surfaces to their original positions in these

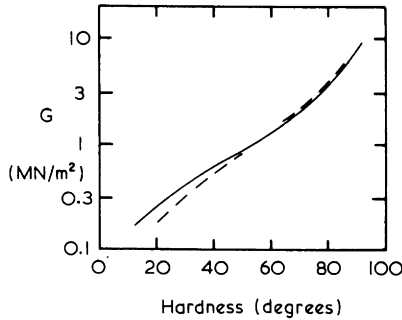


Fig. 13. Relations between shear modulus G and indentation hardness: (—), Shore A Scale; (---), International Rubber Hardness Scale. (From Tobolsky and Mark [7a].)

planes [40]. For a cylindrical block of radius a and thickness h , the corresponding shear stress t acting at the bonded surfaces at a radial distance r from the cylinder axis is given by

$$t = Eer/h$$

This shear stress is associated with a corresponding normal stress or pressure σ_2 , given by

$$\sigma_2 = Ee(a^2/h^2)[1 - (r^2/a^2)] \quad (18)$$

These stress distributions are shown schematically in Fig. 14. Although they must be incorrect right at the edges of the block, because the assumption of a simple shear deformation cannot be valid at these points of singularity, they appear to provide satisfactory approximations over the major part of the bonded surfaces [41].

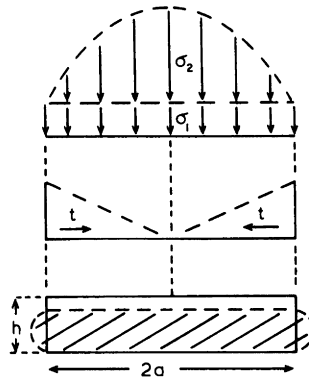


Fig. 14. Sketch of a bonded rubber block under a small compression. The distributions of normal stress σ and shear stress t acting at the bonded surfaces are represented by the upper portions of the diagram. (From Tobolsky and Mark [7a].)

By integrating the sum of the normal stresses $\sigma_1 + \sigma_2$ over the bonded surface, the total compressive force F is obtained in the form [40]

$$F/\pi a^2 e = E[1 + (a^2/2h^2)] \equiv E' \quad (19)$$

Clearly, for thin blocks of large radius the effective value E' of Young's modulus (given by the right-hand side of Eq. (19)) is much larger than the real value E , due to the restraints imposed by the bonded surfaces. Indeed, for values of the ratio a/h greater than about 10, a significant contribution to the observed displacement comes from volume compression or dilation because E' is now so large that it becomes comparable to the modulus of bulk compression [40] (Fig. 15).

When a thin bonded block is subjected to tensile loading, a state of approximately equal triaxial tension is set up in the central region of the block. The magnitude of the stress in each direction is given by the tensile stress, or negative pressure, σ_2 at $r = 0$, i.e., Eea^2/h^2 , from Eq. (18). Under this outwardly directed tension a small cavity in the central region of the block will expand uniformly in size. However, the degree of expansion is predicted by the theory of rubber-like elasticity to become indefinitely large at a critical value of the tension of about $5E/6$ [42]. (This is a type of elastic instability, resembling that observed in the inflation of a balloon or tube.) Thus, if cavities are present in the interior of a bonded block, they are predicted to expand indefinitely, i.e., rupture, at a critical tensile strain e_c , given approximately by

$$e_c = 5h^2/6a^2$$

and at a corresponding critical value of the applied tensile load, obtained by substituting this value of e in Eq. (19).

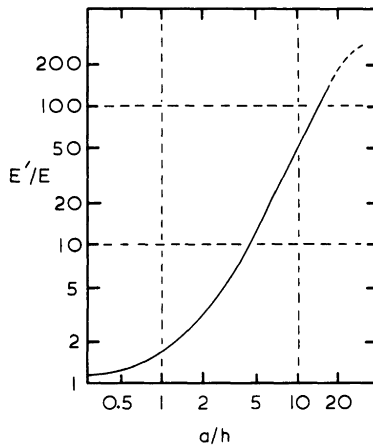


Fig. 15. Effective value of Young's modulus E' for bonded blocks versus ratio a/h of radius to thickness. (From Tobolsky and Mark [7a].)

As discussed in Chapter 10, internal cracks and voids are found to develop suddenly in bonded rubber blocks at well-defined tensile loads, which agree with those predicted by the treatment outlined above [42]. In particular, the loads are found to increase in proportion to Young's modulus E for rubbers of different hardness, in support of the proposed mechanism of fracture due to elastic instability. To avoid internal fractures of this kind it is thus necessary to restrict the mean tensile stress applied to thin bonded blocks to less than about $E/3$.

In compression, on the other hand, quite large stresses can be supported. A stress limit can be calculated by assuming that the maximum shear stress, developed at the bonded edges, should not exceed G , i.e., that the maximum shear deformation should not exceed about 100%. This yields a value for the allowable overall compressive strain of $h/3a$, corresponding to a mean compressive stress of the order of E for discs with ratios a/h between about 3 and 10. However, this calculation assumes that the approximate stress analysis outlined earlier is valid right at the edges of the block, and this is certainly incorrect. Indeed, the local stresses in these regions will depend strongly upon the detailed shape of the free surface in the neighborhood of the edge.

VIII. Some Unsolved Problems in Rubber Elasticity

We turn now to some features of the elastic response of rubbery materials which are still not fully understood:

(a) As normally prepared, molecular networks comprise chains of a wide distribution of molecular lengths. Numerically, small chain lengths will tend to predominate. The effect of this diversity upon the elastic behavior of networks, particularly under large deformations, is not known.

A related problem concerns the elasticity of short chains. They are inevitably non-Gaussian in character and the analysis of their conformational statistics is likely to be difficult. Nevertheless, it seems necessary to carry out this analysis in order to be able to treat real networks in an appropriate way.

(b) Insufficient attention seems to have been paid to problems of network topology, i.e., to the functionality of cross-links, their distribution in space, intramolecular loop formation, and the type and degree of molecular entanglement set up in networks. (See however Alfrey and Lloyd [43], Dusek and Prins [44] and interpenetrating networks [45].)

(c) The effect of mutual interaction between molecular chains in the condensed state, and their probable adoption of cooperative conformations in hydrocarbon rubbers appears to be small, as discussed earlier. However, this is unlikely to be a valid generalization for all networks; some will probably interact strongly and the effect in these cases will presumably be quite significant. No analysis of this effect is known to the author.

(d) Finally, the formulation of a satisfactory general treatment of networks under large deformations, when the chains approach their fully stretched state, would be valuable in the quantitative treatment of work hardening, fatigue, and fracture processes.

ACKNOWLEDGMENTS

The reader is referred to two excellent and authoritative surveys of rubberlike elasticity by Professor L. R. G. Treloar, one of the principal contributors to the subject [2, 16]. The present chapter is an expanded version of an earlier review, prepared on the occasion of Professor Treloar's retirement [46]. Acknowledgment is also due to the Engineering Division of the National Science Foundation for support of a program of research in the course of which this chapter was written. Reference has been made to some recent work carried out in this program [37]. The author's thanks are due to Mr. R. A. Paden for drawing the figures.

REFERENCES

1. P. J. Flory, "Statistical Mechanics of Chain Molecules." Wiley (Interscience), New York, 1969.
2. L. R. G. Treloar, "Physics of Rubber Elasticity," 2nd Ed. Oxford Univ. Press (Clarendon), London and New York, 1958.
3. J. P. Cotton, B. Farnoux, and G. Jannink, *J. Chem. Phys.* **57**, 290-294 (1972).
4. R. G. Kirste, W. A. Kruse, and J. Schelten, *Makromol. Chem.* **162**, 299-303 (1972).
5. W. H. Stockmayer and C. W. Pyun, in "Polymers in the Engineering Curriculum" (H. Markovitz, ed.), pp. 17-61. Carnegie-Mellon Univ. Press, Pittsburgh, Pennsylvania, 1971.
6. L. Mullins, *J. Appl. Polym. Sci.* **2**, 257-263 (1959).
7. M. C. Morris, *J. Appl. Polym. Sci.* **8**, 545-553 (1964).
- 7a. A. V. Tobolsky and H. F. Mark, eds., "Polymer Science and Materials," Chap. 13. Wiley, New York, 1971.
8. F. Bueche, *J. Appl. Polym. Sci.* **4**, 107-114 (1960); **5**, 271-281 (1961).
9. A. M. Bueche, *J. Polym. Sci.* **19**, 297-306 (1956).
10. C. G. Moore and W. F. Watson, *J. Polym. Sci.* **19**, 237-254 (1956).
11. L. Mullins and A. G. Thomas, *J. Polym. Sci.* **43**, 13-21 (1960).
12. J. Scanlan, *J. Polym. Sci.* **43**, 501-508 (1960).
13. N. R. Langley, *Macromolecules* **1**, 348-352 (1968).
14. S. Prager and H. L. Frisch, *J. Chem. Phys.* **46**, 1475-1483 (1967).
15. W. R. Krigbaum and R. J. Roe, *Rubber Chem. Technol.* **38**, 1039-1069 (1965).
16. L. R. G. Treloar, *Rep. Prog. Phys.* **36**, 755-826 (1973).
17. J. E. Mark, *Rubber Chem. Technol.* **46**, 593-618 (1973).
18. A. G. Thomas, *Trans. Faraday Soc.* **51**, 569-582 (1955).
19. T. L. Smith, *J. Polym. Sci., Part C* **16**, 841-858 (1967).
20. G. Kraus and G. A. Moczvember, *J. Polym. Sci., Part A* **2**, 277-288 (1964).
21. C. Price, G. Allen, and F. de Candia, *Polymer* **11**, 486-491 (1970).
22. K. J. Smith, Jr. and R. J. Gaylord, *J. Polym. Sci., Polym. Phys. Ed.* **13**, 2069-2077 (1975).
23. H. M. James and E. Guth, *J. Chem. Phys.* **11**, 455-481 (1943); *J. Polym. Sci.* **4**, 153-182 (1949).
24. R. S. Rivlin, *Philos. Trans. R. Soc. London, Ser. A* **241**, 379-397 (1948).
25. R. S. Rivlin, in "Rheology, Theory and Applications" (F. R. Eirich, ed.), Vol. 1, Ch. 10. Academic Press, New York, 1956.
26. M. Mooney, *J. Appl. Phys.* **11**, 582-592 (1940).