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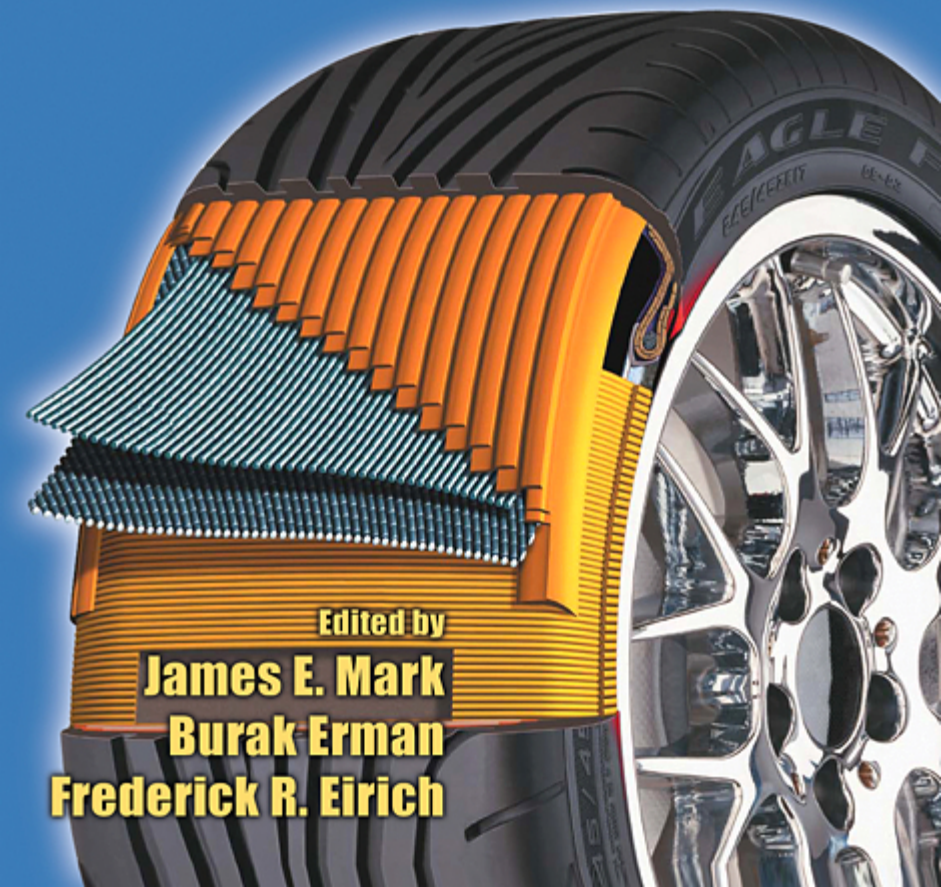
THIRD EDITION



Edited by
James E. Mark
Burak Erman
Frederick R. Eirich

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Edited by

James E. Mark

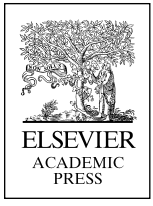
Department of Chemistry
The University of Cincinnati
Cincinnati, Ohio

Burak Erman

Department of Chemical and Biological Engineering
Koc University
Istanbul, Turkey

Frederick R. Eirich

Polytechnic University
Brooklyn, New York



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Academic Press is an imprint of Elsevier

Elsevier Academic Press
30 Corporate Drive, Suite 400, Burlington, MA 01803, USA
525 B Street, Suite 1900, San Diego, California 92101-4495, USA
84 Theobald's Road, London WC1X 8RR, UK

This book is printed on acid-free paper.

Library of Congress Cataloging-in-Publication Data
Science and technology of rubber / [edited by] James E. Mark, Burak Erman.
p. cm.
Includes bibliographical references and index.
ISBN 0-12-464786-3
1. Rubber. I. Mark, James E., 1934– II. Erman, Burak.
TS1870.S35 2005
678′.2–dc22 2005042048

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

ISBN: 0-12-464786-3

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Printed in the United States of America
05 06 07 08 09 10 9 8 7 6 5 4 3 2 1

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Contributors

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

R. J. Ceresa (497), Chemistry and Polymer Technology Department, Polytechnic of South Bank, London, England

Stuart L. Cooper (555), Department of Chemical and Biomolecular Engineering, The Ohio State University, Columbus, Ohio 43210

Aubert Y. Coran (321), A. Y. Coran Consulting, Longboat Key, Florida 34228

Emmanuel Custodero (367), Manufacture Française des Pneumatiques Michelin, 63040 Clermont-Ferrand Cedex, France

Sudhin Datta (529), ExxonMobil Chemical Co., Baytown, Texas 77520

Jean-Baptiste Donnet (367), ENSCMu-UHA, 68093 Mulhouse Cedex, France

Burak Erman (157), Department of Chemical and Biological Engineering, Koc University, Rumelifeneri Yolu, Sariyer 34450, Istanbul, Turkey

A. N. Gent (1, 455), The University of Akron, Akron, Ohio 44325-3909

Brian P. Grady (555), School of Chemical Engineering and Materials Science, The University of Oklahoma, Norman, Oklahoma 73019

A. F. Halasa (497), Research and Development, The Goodyear Tire & Rubber Company, Akron, Ohio 44305

Avraam I. Isayev (663), Institute of Polymer Engineering, The University of Akron, Akron, Ohio 44325-0301

James E. Mark (157), Department of Chemistry, The University of Cincinnati, Cincinnati, Ohio 45211-0172

Jean Marie Massie (497), Lexmark International, Lexington, Kentucky 40511

K. L. Ngai (183), Naval Research Laboratory, Washington, D.C. 20375-5320

Deanna L. Gomochak Pickel (29), Research Laboratories, Eastman Chemical Company, Kingsport, Tennessee 37662-5150

Donald J. Plazek (183), University of Pittsburgh, Pittsburgh, Pennsylvania 15261

Roderic P. Quirk (29), The Maurice Morton Institute of Polymer Science, The University of Akron, Akron, Ohio 44325-3909

Brendan Rodgers (401, 619), ExxonMobil Chemical Company, Houston, Texas 77520-2101

C. M. Roland (105), Naval Research Laboratory, Chemistry Division, Code 6120, Washington, D.C. 20375-5342

Walter Waddell (401, 619), ExxonMobil Chemical Company, Houston, Texas 77520-2101

James L. White (237), Department of Polymer Engineering, University of Akron, Akron, Ohio 44325-0301

Preface to the Third Edition

The basic purpose of this new edition is to update the material in the second edition, which is now more than 10 years old. As a result, the 14 chapters in that earlier edition have been revised and expanded, and a new chapter on the recycling of rubbers has been added.

It is again hoped that this book will provide the type of broad overview of elastomers and their mechanical properties that will be useful to the polymer science and engineering community in general.

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 to 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 Division'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 of 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 crosslinking 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 10 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.

1 Rubber Elasticity: Basic Concepts and Behavior

A. N. GENT
The University of Akron
Akron, Ohio

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.

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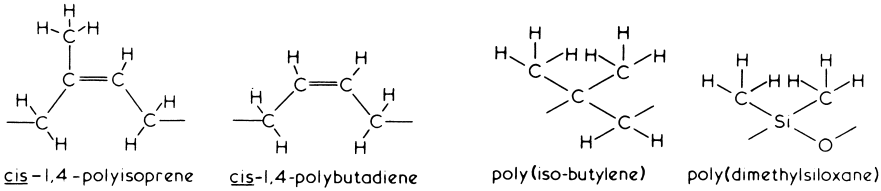

FIGURE 1 Repeat units for some common elastomer molecules.

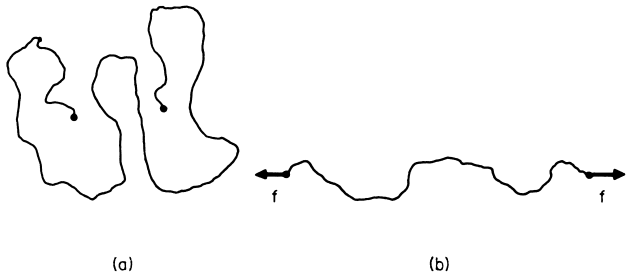

FIGURE 2 (a) Random chain and (b) oriented chain. (From Gent [37].)

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 noncolinear 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,[1] governed by three factors: the statistics of random processes; a preference for certain

[1]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.

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. 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[2] [2], 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 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,

$$f = Ar \tag{1}$$

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,

$$A = 3kT/r_0^2 \tag{2}$$

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

$$r_0^2 = nl^2 \tag{3}$$

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.

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

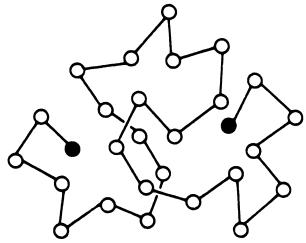

FIGURE 3 Model chain of freely jointed links.

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

$$r_0^2 = C_\infty n l^2 \tag{4}$$

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 on the chemical structure of the molecule and also on 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, 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

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

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

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

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

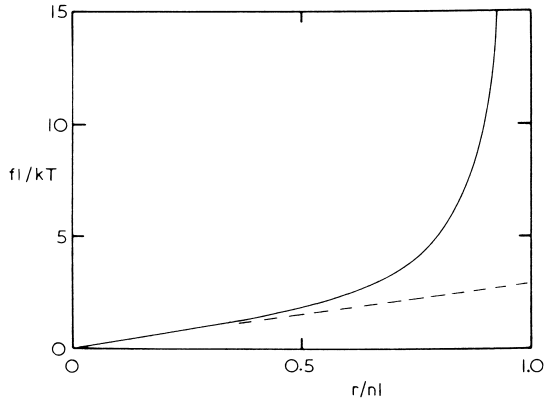

FIGURE 4 Tension–displacement relation for a freely jointed chain [Eq. (5)], ---, Gaussian solution [Eq. (1)]. (From Gent [37].)

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 [3].

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 [4]. In this way, a general semiquantitative 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 met by incorporating a small number of intermolecular chemical bonds (crosslinks) to make a loose three-dimensional molecular network. Such crosslinks are generally assumed to form in the most probable positions, so that the long sections of molecules between them have the same spectrum of end-to-end lengths as a similar set of uncrosslinked 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

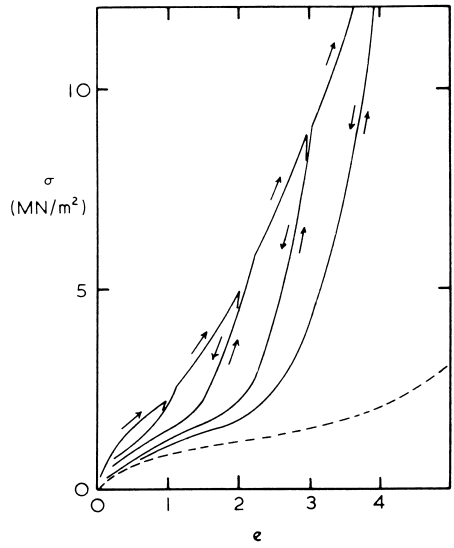

FIGURE 5 Stress-induced softening of a carbon black-filled vulcanizate of a copolymer of styrene and butadiene (25:75); ---, stress–strain curve of a corresponding unfilled vulcanizate. (From Tobolsky and Mark [5].)

the crosslink 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 intertwining, with a spacing (in the bulk state) characteristic of the particular molecular structure [6]. 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 crosslinked rubber, many of these entanglements are permanently locked in (Fig. 6), the more so the higher the degree of crosslinking. If they are regarded as fully equivalent to crosslinks, 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 crosslinks, respectively, where

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

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 crosslinks, respectively. The efficiency of entanglements in constraining the participating chains is, however, somewhat uncertain, particularly when the number of chemical crosslinks is relatively small [7–9]. Moreover, the

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(isobutylene)	17,000
cis-1,4-Polybutadiene	7,000	Poly(dimethylsiloxane)	29,000
cis-1,4-Polyisoprene	14,000	Polystyrene	35,000

[a]Obtained from flow viscosity measurements.

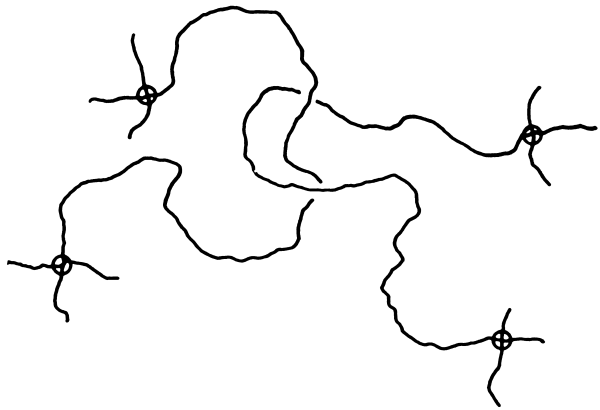

FIGURE 6 Sketch of a permanent entanglement. (From Gent [37].)

force–extension relation for an entangled chain will differ from that for a crosslinked chain [10], being stiffer initially and nonlinear in form. The effective number N of molecular chains which lie between fixed points (i.e., crosslinks 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

$$w = Ar^2/2 \tag{7}$$

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 [11]

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

where r_f^2 denotes the mean square end-to-end distance between chain ends (crosslink 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 random crosslinking 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 on the number of molecular chains and not on 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 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, 9].

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}.

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

$$\lambda_1 \lambda_2 \lambda_3 = 1 \tag{9}$$

As a result, the stress–strain relations become

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

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

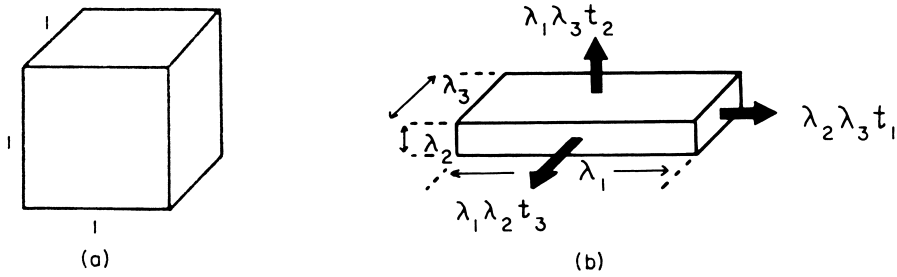

FIGURE 7 (a) Undeformed and (b) deformed states.

$$t_1 - t_2 = (NAr^2/3)(\lambda_1^2 - \lambda_2^2) \tag{10}$$

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,

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

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 on 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

$$t_{12} = G\gamma, \qquad G = NAr^2/3 \tag{12}$$

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 linear only for quite small extensions (Fig. 8), so that Young's modulus is applicable only for extensions or compressions of a few percent.

All of the stress relations given above are derived from Eq. (8). They are therefore valid only for moderate deformations of the network, i.e., for deformations sufficiently small for the chain tensions to be linearly related to their

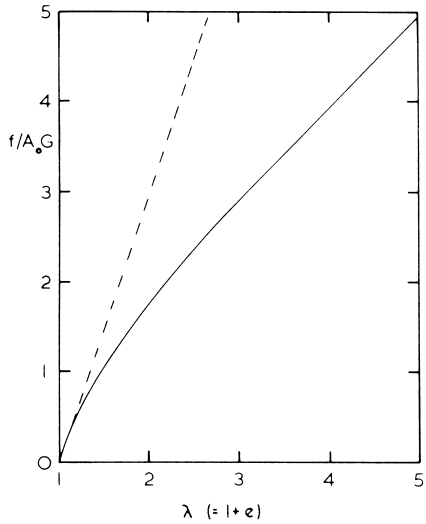

FIGURE 8 Force–extension relation for simple extension. ---, Linear relation obtaining at infinitesimal strains. (From Gent [37].)

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 [12].

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 becoming zero at a swelling ratio of about 5. Thus, the "C_2 stress" appears to reflect a non-Gaussian characteristic of network chains, which is important only at small values of the chain end-to-end distance r. Indeed, Thomas [13] has shown that the magnitude of the C_2 stress and its complex dependence on type and degree of strain, and on 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

$$2w = Ar^2 + Br^{-2} \tag{13}$$

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 on temperature 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. 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 [9].

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 crosslink sites [7–9]. Prager and Frisch [10] 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.

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 calculated from the chemistry of crosslinking. This discrepancy may be due to an error in the theoretical treatment as given here. James and Guth [14] arrived at stresses only half as large as those given in Eq. (10), from a somewhat different theoretical standpoint.

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.

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 on 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 on 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 [15, 16], 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

$$\mathrm{J}_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3$$
$$\mathrm{J}_2 = \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2 - 3$$
$$\mathrm{J}_3 = \lambda_1^2\lambda_2^2\lambda_3^2 - 1$$

where λ_1, λ_2, λ_3 are the principal stretch ratios (the ratios of stretched to unstretched lengths, Fig. 7). Moreover, for an incompressible material, J_3 is identically zero, and hence only two independent measures of strain, J_1 and J_2, remain. It follows that the strain energy density W is a function of these two variables only:

$$W = f(J_1, J_2) \tag{14}$$

Furthermore, to yield linear stress–strain relations at small strains, W must be initially of second order in the strains e_1, e_2, e_3. Therefore, the simplest possible form for the strain energy function is:

$$W = C_1J_1 + C_2J_2 \tag{15}$$

where C_1 and C_2 are elastic coefficients with a sum $2(C_1 + C_2)$ equal to the small-strain shear modulus G. Equation 15 was originally proposed by Mooney [17] and is 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 is identified with $Nar^2/6 = \frac{1}{2}NkT\,(r/r_0)^2$.

On expanding Eq. (15) as a power series in strains e, where $e = \lambda - 1$, it is found to include all terms in e^2 and e^3. Thus it necessarily gives good agreement with experiment at small strains, say for values of e up to 10 to 20%, where higher powers of e are negligibly small. However considerable confusion has arisen from its application at larger strains, for values of e of 100% or more, when it no longer holds. It is rather unfortunate that experimental stress–strain relations in simple extension appear to be in accord with Eq. (15) up to moderately large strains. This fortuitous agreement arises because the particular strain energy function obeyed by rubber, discussed later, depends

on strain in such a way that the two stress–strain relations in tension are similar in form. Relations for other types of strain are quite different, even at modest strains [18].

A. Stress–Strain Relations

Stresses can be obtained from the derivatives of the strain energy function W:

$$t_1 = \lambda_1(\partial W/\partial \lambda_1) - p \tag{16}$$

Rewriting Eq. (16) in terms of the generic derivatives $\partial W/\partial J_1$ and $\partial W/\partial J_2$ yields

$$t_1 = 2[\lambda_1^2 \partial W/\partial J_1 - (1/\lambda_1^2)\partial W/\partial J_2] - p, \qquad \text{etc.} \tag{17}$$

The functions $\partial W/\partial J_1$ and $\partial W/\partial J_2$ are denoted W_1 and W_2 hereafter.

Experimental measurements indicate that W_1 is approximately constant. However, the second term is far from constant even at moderate strains. Good agreement is obtained when it is expressed as a logarithmic function of J_2 [19]:

$$W = C_1 J_1 + C_2' Ln[(J_2 + 3)/3] \tag{18}$$

where C_2' is a constant. This form of the second term is in reasonably good numerical agreement with the predictions of Thomas's additional term in the strain energy function for a single chain, Eq. (13), and simpler in form.

Values of C_1 and C_2' are similar in magnitude, 0.25 to 0.5 MPa, for typical soft rubber vulcanizates. However, whereas C_1 is approximately proportional to the number of network strands per unit volume, C_2' appears to be rather constant, independent of the degree of crosslinking, and thus it is relatively more important for lightly crosslinked materials. As mentioned earlier, it appears to reflect physical restraints on molecular strands like those represented in the "tube" model of restricted configurations in the condensed state [9]—restraints that diminish in importance as the deformation increases or the strands become more widely separated.

Strain-Hardening at Large Strains

Rubber becomes harder to deform at large strains, probably because the long flexible molecular strands that comprise the material cannot be stretched indefinitely. The strain energy functions considered up to now do not possess this feature and therefore fail to describe behavior at large strains. Strain-hardening can be introduced by a simple modification to the first term in Eq. (18), incorporating a maximum possible value for the strain measure J_1, denoted J_m [20]:

$$W = -C_1 J_m Ln(1 - J_1/J_m) + C_2' Ln[(J_2 + 3)/3] \tag{19}$$

Equation 19 reduces to Eq. (18) when the strains are relatively small, i.e., the ratio J_1/J_m is small. Thus Eq. (19) is probably the simplest possible strain energy function that accounts for the elastic behavior to good approximation over the entire range of strains [21]. It requires three fitting parameters, two of which are related to the small-strain shear modulus G:

$$G = 2[C_1 + (C_2'/3)] \tag{20}$$

The molecular theory of rubberlike elasticity predicts that the first coefficient, C_1, is proportional to the number N of molecular strands that make up the three-dimensional network. The second coefficient, C_2', appears to reflect physical restraints on molecular strands like those represented in the "tube" model [9] and is in principle amenable to calculation. The third parameter, J_m, is not really independent. When the strands are long and flexible, it will be given approximately by $3\lambda_m^2$, where λ_m is the maximum stretch ratio of an average strand. But λ_m^2 is inversely proportional to N for strands that are randomly arranged in the unstretched state [11]. J_m is therefore expected to be inversely proportional to C_1. Thus the entire range of elastic behavior arises from only two fundamental molecular parameters.

Considerable success has also been achieved in fitting the observed elastic behavior of rubbers by strain energy functions that are formulated directly in terms of the extension ratios λ_1, λ_2, λ_3 instead of in terms of the strain invariants I_1, I_2 [22]. 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.

At moderate strains, the value of J_2 is often large enough for terms involving W_2 to be neglected. Some stress–strain relations are now derived using this approximation to illustrate how such calculations are carried out and to deduce under what conditions the deformations become unstable. Instabilities are interesting from a theoretical point of view because they occur suddenly, at a well-defined deformation, and they are often unexpected on the basis of classical elasticity theory. Moreover, a comparison of the observed onset of instability with the predictions of various strain energy functions W provides, at least in principle, a critical test for the validity of a proposed form for W. From a practical standpoint, unstable states are quite undesirable because the deformation becomes highly non-uniform, leading to premature failure.

Inflation of a Thin-Walled Tube

Inflation of a tube is described by extension ratios of λ_1 in the circumferential direction and λ_2 in the axial direction, with the wall thickness h becoming $h/\lambda_1\lambda_2$ because the rubber volume remains constant. The inflation pressure P gives rise to stresses in the circumferential and axial directions:

$$t_1 = \lambda_1^2\lambda_2 r\,P/h$$
$$t_2 = \lambda_1^2\lambda_2 r\,P/2h \tag{21}$$

where r is the tube radius in the unstrained state.

From Eq. (21), on putting the stress $t_3 = 0$, the undefined pressure p is obtained as:

$$p = -2W_1/\lambda_1^2\lambda_2^2 \tag{22}$$

[In a thin-walled tube of large radius the inflating pressure P is much smaller than the stresses t_1 and t_2 that it generates, and thus P can be neglected in comparison with the stress t_3 in determining p.] Inserting this result for p in Eqs. (21) and (22) yields a relation between the extension ration λ_2 and the expansion ratio v (= $\lambda_1^2\lambda_2$) of the internal volume of the tube:

$$2\lambda_2^3 = (v^2+1)/2v^2 \tag{23}$$

The relation between inflating pressure P and internal volume of the tube is then obtained as:

$$Pr/hC_1 = 2(v^2-1)[2v/(v^2+1)]^{1/3}/v^2[1-(J_1/J_m)] \tag{24}$$

This relation is plotted in Fig. 9 for various values of the limiting strain measure J_m. The inflating pressure is seen to pass through a maximum at a volume expansion ratio between about 58 and 66%, depending on the value assumed for J_m. This feature suggests that larger expansions will be unstable. Indeed, thin-walled tubes undergo a strikingly non-uniform deformation at a critical inflation pressure, shown schematically in Fig. 10. One portion of the tube becomes highly-distended as a bubble or aneurysm while the rest is lightly inflated. The two stable deformations that can coexist at the same inflation pressure after the critical state is reached are shown schematically by the horizontal broken line in Fig. 9. However, when J_m is infinitely large, the aneurysm is unbounded and failure would then occur immediately on reaching the critical pressure.

Inflation of a Thin-Walled Spherical Balloon

In this case, if the balloon radius expands by a factor λ, equibiaxial extensions of ratio λ will be set up in the balloon, with a shrinkage ratio $1/\lambda^2$ of the

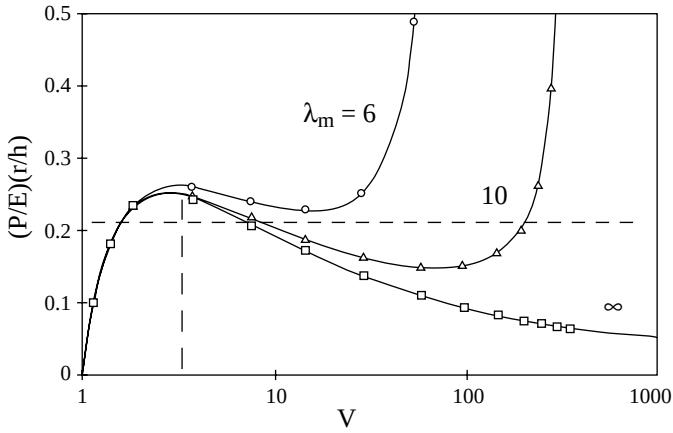

FIGURE 9 Pressure–volume relations for a thin-walled tube from Eq. (24) using various values for the maximum possible extension ratio λ_m. The vertical broken line denotes the onset of instability. ($E = 6\ C_1$.)

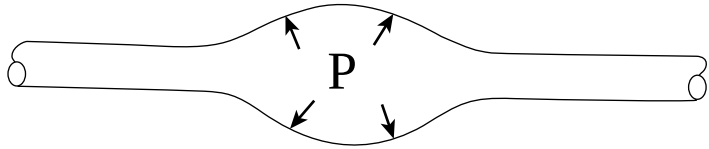

FIGURE 10 Sketch of an aneurysm in an inflated tube.

wall thickness to maintain the rubber volume constant. The circumferential stresses t_1 and t_2 are equal and given by:

$$t_1 = t_2 = 2W_1(\lambda^2 - \lambda^{-4})/[1-(J_1/J_m)] \tag{25}$$

from Eq. (17), when the stress $t_3 = 0$ and $W_2 = 0$. The inflation pressure P is then given by:

$$Pr/hC_1 = 4(\lambda^{-1} - \lambda^{-7})/[1-(J_1/J_m)] \tag{26}$$

where r and h are the unstrained radius and wall thickness of the balloon. In this case the potential instability occurs even earlier, at a radial expansion ratio between 38 and 50% depending on the value chosen for J_m. In practice, the deformation becomes quite complex (Fig. 11). The balloon remains roughly spherical in shape but one part is lightly stretched while the remainder is highly stretched. The two states of strain resemble the two deformations that are predicted at a given pressure after the critical point is reached.

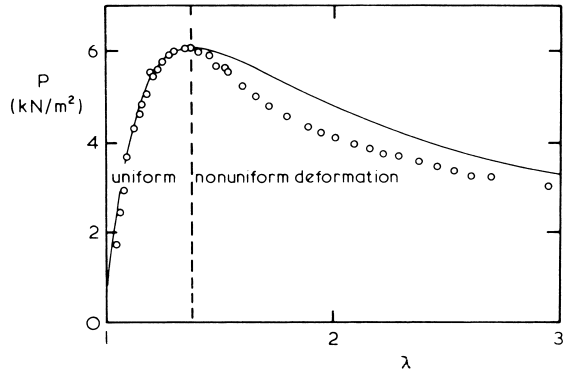

FIGURE 11 Inflation of a thin-walled spherical rubber balloon. Solid curve: Eq. (26) with $J_m = \infty$. (From Gent [37].)

Inflation of a Thick-Walled Spherical Shell

The internal pressure P required to inflate a small spherical cavity in the center of a thick block can be obtained by integrating the contributions from concentric shells (thin-walled balloons) given in the preceding section. The result is [23]

$$P/C_1 = 4\lambda_0^{-1} + \lambda_0^{-4} - 5 \tag{27}$$

for an infinitely extensible rubber ($J_m = \infty$), where λ_o is the biaxial stretch ratio at the surface of the cavity. This relation does not exhibit a maximum and thus does not indicate that the deformation is unstable. However, at high values of λ_o the pressure P asymptotes to a constant value of about $5C_1$, i.e., about $5G/2$, where G is the small-strain shear modulus. For typical rubbery materials where G is about 0.5 MPa, the maximum pressure is thus about 1.2 MPa, or about 12 bar. Any small cavity will expand greatly at this rather modest inflation pressure. Internal fracture is therefore likely to occur in soft rubbery solids at inflation pressures or equivalently, triaxial tensions, of this amount. In practice, all rubbery solids are found to develop internal fractures when supersaturated with gases or liquids at pressures or triaxial tensions about equal to $5G/2$ [23, 24].

Note that the initial radius of the spherical cavity does not appear in Eq. (27). Thus, cavities of all sizes are predicted to inflate equally. However, we have neglected surface energy contributions that will tend to stabilize small cavities. When they are taken into account it appears that only cavities having radii greater than about 100 nm will expand dramatically at the low pressures predicted by Eq. (27). Internal fractures suggest that vulcanized rubber must contain many precursor cavities of this effective size or larger.

Surface Instability of Compressed or Bent Blocks

Biot [25] showed that the surface of an elastic half-space will become unstable at critical values of strain ratios λ_1, λ_3 set up in two perpendicular directions in the surface. The critical condition is

$$\lambda_1^2 \lambda_3 = 0.2956 \tag{28}$$

When the block is subjected to unidirectional compression parallel to the surface, with free expansion permitted in the other two directions, then $\lambda_3 = 1/\lambda_1^{1/2}$ and Eq. (28) yields a critical value for λ_1 of 0.444. A large block of rubber in simple compression is therefore predicted to show a surface instability at a compression of 55.5%. (Beatty [26] noted that various buckling and bulging modes of deformation are generally encountered before this, depending on the slenderness of the block.) If the block is subjected to equi-biaxial compression parallel to the surface, then $\lambda_3 = \lambda_1$ and the critical compression becomes 33.3%.

When a thick elastic block (cuboid) is bent, the inner surface becomes compressed while the extension ratio λ_3 along the width is largely unchanged (at unity). Thus, from Eq. (28) an instability would be expected on the inner surface when λ_1 is 0.544, i.e., when the surface is compressed by about 46%. Experimentally, sharp folds or creases appear suddenly in the inner surface of a bent block at a critical degree of bending [27], see Fig. 12. However, the critical compression of the inner surface was considerably smaller than predicted by Biot's theory, 35% instead of 46%. It is not known why the instability occurred so much sooner than expected. Although rubber follows a more complex strain energy function than the simple form assumed here, it is unlikely that the difference would have such a large effect.

Rubber articles are often subjected to rather severe bending deformations, for example, in tires. Folds and creases in the interior may pass undetected. Nevertheless, they represent lines of high stress concentration and sites of possible failure. Folds ("Schallamach waves") also appear when soft rubber slides over a rigid countersurface [28]. They appear to be Biot creases caused by frictional compression of the surface.

Resistance of a Compressed Block to Indentation

When a block is subjected to a sufficiently large equibiaxial compression in the surface plane it becomes unstable to small indentations. Green and Zerna [29] expressed the relation between indentation force N and amount of indentation d as:

$$N/G = (8/3)R^{1/2} d^{3/2} f(\lambda) \tag{29}$$

where G is the shear modulus of the half-space material, R is the radius of the indentor, and $f(\lambda)$ is a function of the equibiaxial compression ratio λ, given by

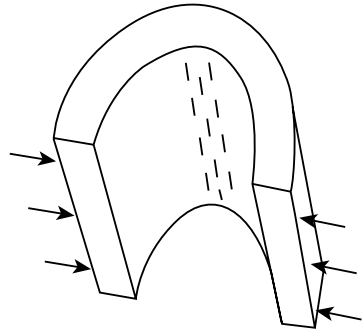

FIGURE 12 Sketch of a bent block showing creases that appear on the inner surface where the compressive strain is greatest.

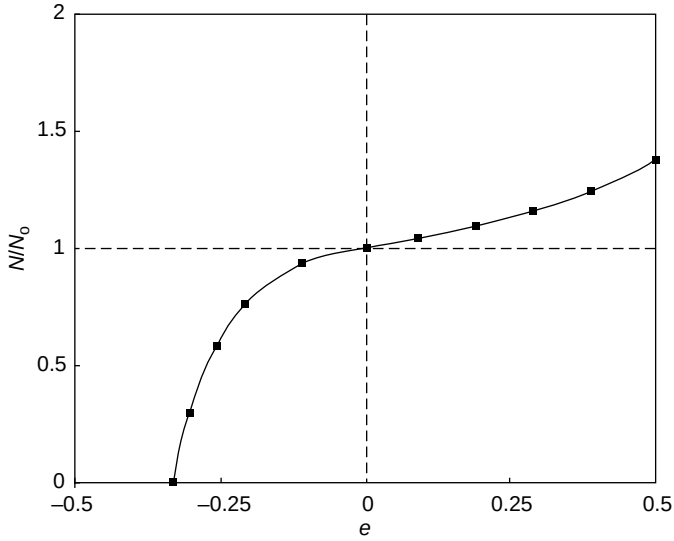

FIGURE 13 Force N for a small indentation vs. equibiaxial strain e parallel to the surface of a half-space. N_o denotes the force when $e = 0$. (From Green and Zerna [29].)

$$f(\lambda) = (\lambda^9 + \lambda^6 + 3\lambda^3 - 1)/\lambda^4(\lambda^3 + 1) \tag{30}$$

Values of indentation force N for a given small indentation, from Eq. (27), are plotted in Fig. 13 against the equibiaxial strain e parallel to the surface, where $e = \lambda - 1$. [N_0 denotes the value for an initially unstrained block, when $f(\lambda) = 2$.] The resistance to indentation is seen to decrease sharply as the compressive strain is increased, becoming zero at a compressive strain of 0.333, in agreement with Biot's result.

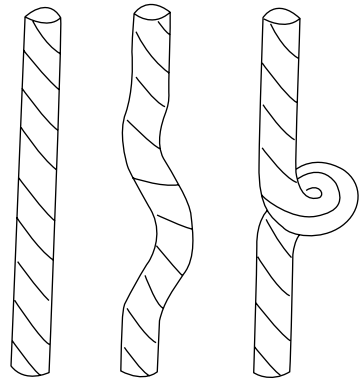

FIGURE 14 Sketch of a "kink" that appears on twisting a stretched rubber rod (From Gent and Hua [30].)

Torsional Instability of Stretched Rubber Rods [30]

Another unstable state is encountered when a stretched rubber rod is subjected to large torsions. A kink suddenly appears at one point along the rod, Fig. 14, and more kinks form on twisting the rod further.

Minimization of the total elastic strain energy suggests that the rod will become unstable at a critical amount of torsion: part of the rod will unwind and form a tight ring while the remainder of the rod will become slightly more stretched. A simple criterion can be derived on this basis for the onset of "kinks." For a neo-Hookean material, Eq. (8), the condition for forming a kink becomes:

$$4(1-1/\lambda^3) = -(a^2\phi^2/\lambda) + 2\pi(a^2\phi^2/\lambda)/[\pi - (a\phi/\lambda^{1/2})] \tag{31}$$

where ϕ is the critical amount of torsion at which uniform torsion becomes unstable, in terms of the imposed extension ratio λ and the rod radius a. Measured values for rods of different radius, stretched to extensions of up to 250%, were found to be in reasonably good agreement with Eq. (31), indicating that the sudden formation of kinks in twisted rubber rods is, indeed, a consequence of an elastic instability.

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 on the square and higher powers of strain, rather than the simple pro-