

THE PHYSICS
OF
RUBBER
ELASTICITY

SECOND EDITION

L. R. G. TRELOAR

THE PHYSICS OF RUBBER ELASTICITY

BY

L. R. G. TRELOAR

BRITISH RAYON RESEARCH ASSOCIATION

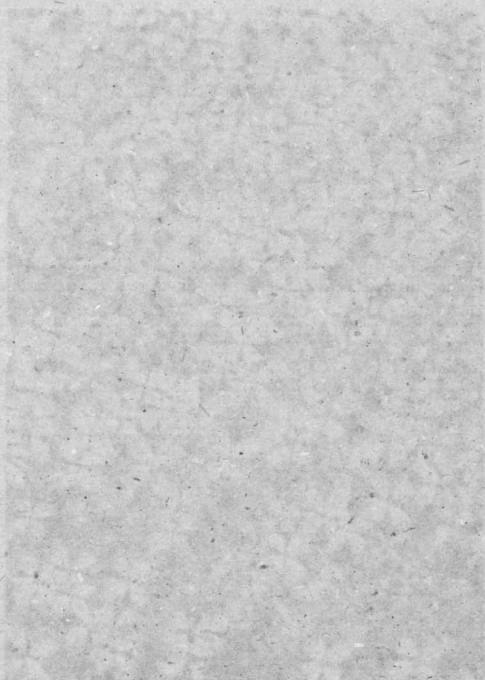
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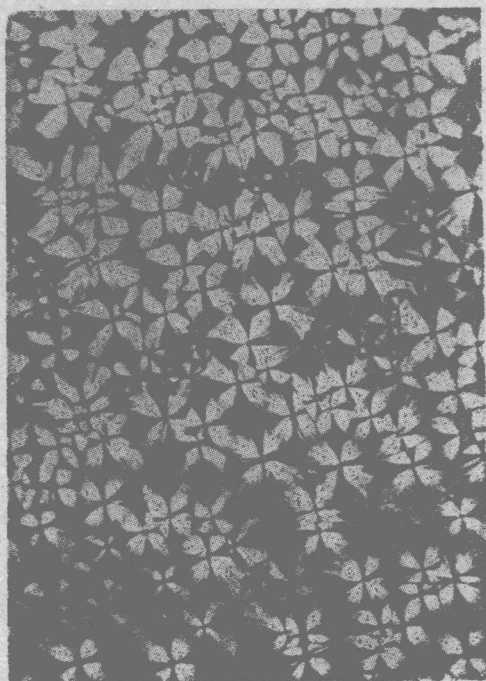
MONOGRAPHS ON THE PHYSICS AND CHEMISTRY OF MATERIALS

General Editors

WILLIS JACKSON H. FRÖHLICH N. F. MOTT
E. C. BULLARD



Printed in Great Britain by the University Press, Cambridge.
The paper used in this volume is of the highest quality.
The binding is of the best material available.



Film of polyethylene viewed between crossed Nicols,
showing 'spherulitic clusters' of crystallites.
(Bunn and Alcock)

PREFACE TO THE SECOND EDITION

THOUGH the basic concepts of the statistical-thermodynamic theory of rubber elasticity remain unchanged, their detailed development and application has continued to make progress since the appearance of the First Edition, and in the same period a large amount of new experimental material relevant to the subject has appeared. To do justice to these new developments has necessitated a complete revision and rearrangement of the text. In the present edition separate chapters have been given to the phenomena of swelling, previously only briefly referred to, and to the estimation of the degree of cross-linking, in which important new methods of investigation are discussed. Chapter X (Photo-elastic properties) and Chapter XIV (Dynamic properties) have been extensively modified, and the two chapters in the First Edition dealing respectively with 'Deviations from the statistical theory' and 'The solution of problems involving large elastic strains' have been amalgamated into a new chapter entitled 'Phenomenological theory of large elastic deformations'.

I should like to express my thanks to Mr. J. Wilson, Director of Research, British Rayon Research Association, for providing me with every facility for the preparation of this work, and to my many colleagues who have given me the benefit of their advice and criticism on particular subjects.

L. R. G. T.

*British Rayon Research Association
Manchester*

PREFACE TO THE FIRST EDITION

It is sometimes considered unnecessary for those engaged in the practical development of industrial processes to concern themselves with the so-called theoretical aspects of their subject. On examination, it is usually found that exponents of this point of view are not entirely consistent, for in any type of work involving experimentation it is impossible to get along without some sort of theory, however limited or *ad hoc* it may be. My excuse for doing the work which I do (of which this book is one aspect) is that I always believe that if one is going to have a theory at all one may as well take some trouble to find the one which most nearly represents the known facts.

In the subject of rubber elasticity it is not easy to discover from the mass of literature, often of a rather mathematical character, what are the generally accepted theories. In this book I have therefore attempted to convey (in not too mathematical language) the fundamental concepts of the subject, and to present the whole in a more or less consistent form. In this task I have admittedly given expression to my own point of view, and I have drawn freely on the work of my associates at the British Rubber Producers' Research Association. I cannot hope to acknowledge the many who have helped me by the discussion of particular sections, but I should like to mention particularly Dr. G. Gee, Director of the B.R.P.R.A., who read and criticized the manuscript in detail, my colleague Mr. R. S. Rivlin, who gave me the benefit of his unpublished ideas and works, and Dr. K. Weissenberg, with whom I was able to discuss the final chapter.

I should also like to thank the Board of the B.R.P.R.A. for encouraging me to undertake this work, and for the provision of facilities for its execution.

L. R. G. T.

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Welwyn Garden City*

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SHOWING 'SPHERULITIC CLUSTERS' OF CRYSTALLITES. Magnifica-
tion $\times 250$. (Bunn and Alcock, *Trans. Faraday Soc.* 1945, 41,
317) *Frontispiece*

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CHAPTER I

GENERAL PHYSICAL PROPERTIES OF RUBBERS

1. Introduction

THE word 'rubber' is used in two different senses. Originally it meant 'india-rubber', the natural product of the tree *Hevea Brasiliensis*, of which the chief chemical constituent is the rubber hydrocarbon $(C_5H_8)_n$ or polyisoprene. The only other rubber then known was *gutta-percha* or *balata*, another natural product represented by the same empirical formula $(C_5H_8)_n$, but differing slightly in the structural form of the molecule. Recent years have seen the development of a very large number of synthetic rubbers having a wide variety of chemical constitutions, and the term 'rubber' is now commonly employed to include any material comparable with natural rubber in possessing the physical property of large elastic extensibility. Some writers prefer to restrict the word to its original usage, and to employ some other term, such as 'synthetic elastomer', to designate members of the more general class. However, in the present work the more popular usage will be followed. It will generally be obvious from the context whether the word rubber is used in the general or in the particular sense; in cases where confusion might arise, it will be sufficient to refer to *natural* or *Hevea* rubber.

The reasons for this choice are not entirely verbal. It is at least equally justifiable from a scientific point of view to define rubber in terms of its physical properties as in terms of its chemical constitution. Indeed, in the present work we shall be concerned very much more with the fundamental structural aspects in which all rubbers may be considered to be essentially the same, than with the more detailed specific features in which they differ from one another. The emphasis will be placed mainly on *rubber-like elasticity* as a phenomenon associated with the *rubber-like state of matter*, a state which, as we shall see, is

closely related to a certain rather special type of molecular structure.

The most obvious, and also the most important, characteristic of the rubber-like state is, of course, a high degree of elastic deformability under the action of comparatively small stresses.

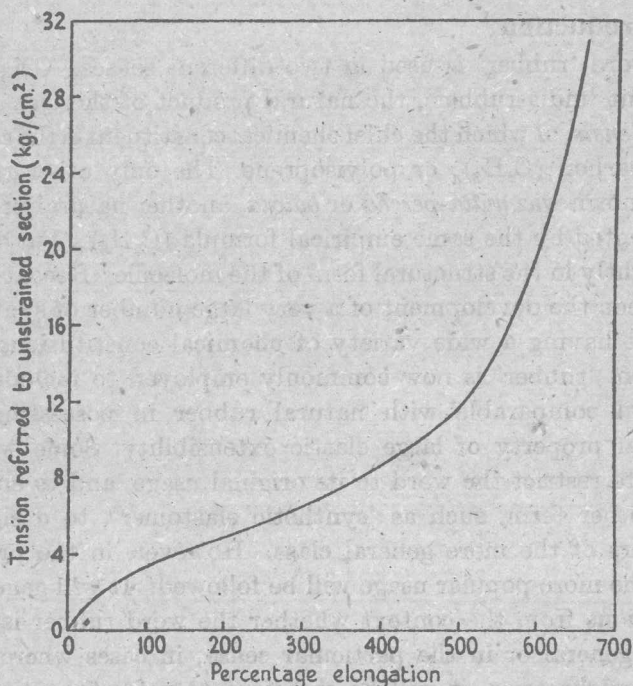


FIG. 1.1. Typical force-extension curve for vulcanized rubber.

A typical stress-strain curve for rubber is shown in Fig. 1.1; the maximum extensibility normally falls within the range 500 to 1,000 per cent., while the value of Young's modulus (in the region of small extensions) is of the order of 10 kg./cm.² or 10⁷ dynes/cm.² By way of contrast it may be mentioned that Young's modulus for typical hard solids is in the region of 10¹² dynes/cm.², while their maximum elastic (i.e. reversible) extensibility seldom exceeds 1 per cent. There is thus an enormous difference between rubbers on the one hand and ordinary hard

solids (e.g. of a crystalline or glassy nature) on the other. The interpretation of this difference is the principal question with which this book will be concerned.

2. Chemical constitution of rubbers

As already stated, natural rubber is essentially a hydrocarbon having the empirical formula $(C_5H_8)_n$. The hydrocarbon exists

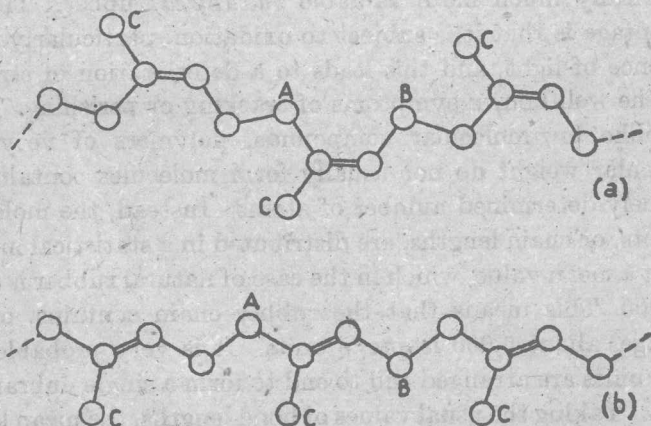




FIG. 1.2. The structure of the molecule of (a) *Hevea* rubber, and (b) *gutta-percha*. *AB*—isoprene unit. *C*—methyl group.

in the original latex in the form of small globules of mean diameter about 0.5μ ($5 \cdot 10^{-5}$ cm.) suspended in a watery medium or serum, the concentration of hydrocarbon being about 35 per cent. of the total weight. The hydrocarbon particles would, of course, coalesce, were it not for a layer or sheath of non-rubber constituents, principally proteins, which is adsorbed on their surfaces and functions as a protective colloid. From this latex the solid rubber may be obtained either by drying off the water or by precipitation with acid. The latter treatment yields the purer rubber, since it leaves most of the non-rubber constituents in the serum.

Chemically, the rubber hydrocarbon is a polymer of isoprene (C_5H_8), built up in the form of a continuous chain, having the structure shown in Fig. 1.2 (a). Every fourth bond in the chain

is a double bond, and every fourth carbon atom has attached to it the methyl (CH_3) group, in a perfectly regular manner. The presence of the double bond is very significant, since it is this that largely determines the chemical reactivity of the molecule. It leads at once to the principal advantage and also to the principal disadvantage of natural rubber. The advantage is that it may readily be combined with sulphur to form the technically much more valuable *vulcanized* rubber. The disadvantage is that it is subject to oxidation, particularly in the presence of light, and this leads to a deterioration of strength and the well-known symptoms of cracking or perishing.

Unlike low-molecular compounds, polymers of very high molecular weight do not usually form molecules containing a uniquely determined number of atoms. Instead, the molecular weights, or chain lengths, are distributed in a statistical manner about a mean value, which in the case of natural rubber is about 350,000. This means that the rubber chain contains, on the average, about 5,000 isoprene units. It is very probable that these units are arranged end to end to form a single unbranched chain. Taking the usual values of bond lengths, the mean length of the molecule on this basis is found to be about $2 \cdot 10^{-4}$ cm.

The structure of gutta-percha differs but slightly from that of rubber. As will be seen from Fig. 1.2(b), the difference lies solely in the arrangement of the single C—C bonds adjacent to the double bond. In natural rubber these single bonds both lie on the *same* side of the double bond, thus , forming the so-called *cis*-configuration, whilst in gutta the single bonds lie on opposite sides of the double bond, thus , to form the *trans*-configuration. This difference leads to certain differences in physical properties—notably in the phenomena of crystallization—between the two compounds.

Although the two single bonds adjacent to the double bond remain permanently fixed in a single plane (whether in the *cis*- or *trans*-configuration), the remaining single bonds are not thus fixed but are subject to rotation out of the plane formed by neighbouring bonds, as will be discussed in detail later. The structural forms shown in Fig. 1.2 are thus to a certain extent

schematic; in practice the molecule does not lie all in one plane, as there suggested.

Synthetic rubbers

It is not the purpose of this book to discuss the peculiarities of synthetic rubbers in any detail, but this introduction would not be complete without some reference to this important and expanding group of industrial materials.

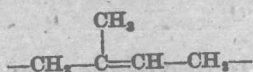
The chemical structure of a few of the more important synthetics is shown in Table I. Polychloroprene is a special-purpose rubber, which has the property of not swelling to any serious extent in hydrocarbon oils, which makes it particularly useful for engine mountings and similar purposes. It is also very resistant to deterioration by oxygen in the presence of light. Polyvinyl chloride is harder and less extensible than natural rubber; it is widely used in articles of clothing and drapery, where it has the added advantage of showing up coloured pigments very favourably. It is also frequently employed in cable insulation. Butyl rubber, based on polyisobutylene, has the advantage of a lower permeability to gases than natural rubber, which makes it useful for the inner tubes of tyres; against this, however, it does not retain its elasticity at low temperatures so well as natural rubber. GR-S rubber, the general purpose synthetic produced in very large quantities in America during the war, is a mixed polymer of butadiene and styrene.

The silicone rubbers, based on the silicon-oxygen chain, are chemically in a different class from hydrocarbon rubbers. They are generally more resistant to chemical attack and thermal degradation, and may therefore be used at comparatively high temperatures. They are also highly resistant to water absorption. They retain their elasticity over a wide range of temperature, from -55° to $+300^{\circ}$ C., and may be used continuously in air at 150° C. Their tensile strength is, however, rather low (Houwink, 1949).

The formulae in Table I represent only short segments of the molecules, which in all cases have the form of very long chains containing many thousands of monomer units.

TABLE I

Structural formulae of some typical rubbers and related materials



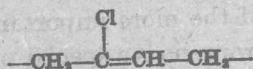
Polyisoprene (natural rubber, gutta-percha)



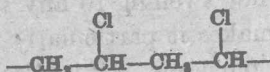
Polyethylene ('Polythene')



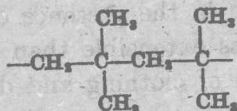
Polytetrafluoroethylene ('Teflon')



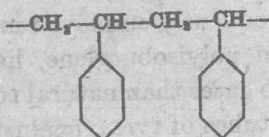
Polychloroprene ('Neoprene')



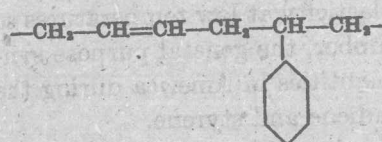
Polyvinyl chloride



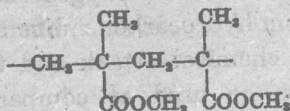
Polyisobutylene (basis of 'Butyl' rubber)



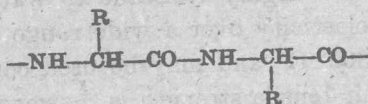
Polystyrene



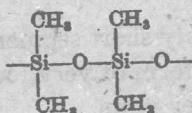
Butadiene-styrene copolymer (German 'Buna-S', American 'GR-S')



Polymethyl methacrylate ('Perspex')



Protein (gelatin, wool, silk, etc.)



Polymethyl siloxane (Silicone rubber)

3. Early theories of rubber elasticity

Reference was made in § 1 to the very wide gap between the elastic properties of rubbers and those of an ordinary hard solid—a difference amounting to a factor of about 100,000 in rigidity and about 1,000 to 10,000 in extensibility. To those who first began to study the reason for these differences it seemed that the only means available for explaining such a large elastic extensibility without departing from classical conceptions of the nature of elasticity was to postulate some sort of open structure which would permit of comparatively large bulk displacements being obtained with only small strains in the structural elements. Familiar examples of such structures are the coil spring and certain types of lattice (or cellular) structures. Theories of rubber elasticity based on models of this kind were proposed, for example, by Ostwald (1926), and by Fikentscher and Mark (1930). Ostwald imagined the outer sheath of the latex globule to be comprised of a sort of network of micelles or molecular aggregates containing protein and resin which was suspended in low-molecular rubber hydrocarbon of a more or less fluid character. The elasticity of the rubber was supposed to be due to the micellar network of non-rubber constituents. Fikentscher and Mark postulated a spiral configuration of the molecule of the rubber hydrocarbon in which the tendency to retract was considered to be due to residual forces between neighbouring turns of the spiral, associated particularly with the double bonds.

A rather similar theory proposed by Mack (1934) envisaged a folded configuration of the polyisoprene molecule maintained by the agency of forces between hydrogen atoms. This model permitted an extension of 300 per cent. in passing from the closely packed to the fully extended form of the chain by rotation about single bonds. In addition, a further extension of the bulk rubber was introduced by turning of the extended molecules into the direction of the strain, bringing the maximum extensibility of the rubber up to 600 per cent.

Mack's theory came very close to current conceptions of elasticity firstly in drawing attention to the possibility of a more

or less irregularly kinked form of molecular chain resulting from rotations about single bonds, and secondly by the significance attached to the turning of the molecules into the direction of the extension. The theory was inadequate, however, in regarding the interatomic forces as fundamentally responsible for the elasticity.

4. The kinetic theory of elasticity

These theories, and others of a similar character, sought to explain long-range elasticity in terms of the constitution of the only example of a rubber available at that time, namely natural (polyisoprene) rubber. It is significant that the proper understanding of the phenomenon owed much to the recognition of the very close connexion between natural rubber and many other materials, e.g. gelatin, muscle, silk, etc., of widely diverse chemical composition. Thus, for example, Wöhlisch (1926) drew attention to the similarity between the contraction on heating of tendons (collagen) and the contraction of stretched (crystalline) raw rubber, which he sought to explain in terms of the thermal movements of crystals, micelles, or rod-like molecules. Later there arose a realization of the possible significance of the *internal vibrations and rotations of long-chain molecules* in connexion with the problem of high elasticity. Such considerations represented a departure from the more usual idea of a molecule as an essentially rigid structure whose form is determined by purely static forces. In 1931, for example, Haller calculated the effect of thermal vibrations on a chain of the paraffin type, represented as a planar zigzag (Haller, 1931). The energy required to deform the valence angles and to stretch the bond lengths was compared with the thermal energy of the atoms, and it was shown that this thermal energy would lead on the average to a considerable curvature. However, this calculation ignored the much more important consideration of rotations of the bonds.

The first exponents of the now generally accepted theory of rubber elasticity were Meyer, von Susich, and Valko (1932), and Karrer (1932, 1933), though the latter author was thinking

primarily of muscle. Meyer, von Susich, and Valko based their theory on the consideration that the thermal energy of the atoms of a long-chain molecule will lead to greater amplitudes in the direction perpendicular to the chain than in the direction of the chain, since the forces tending to restrict vibrations and rotations in the lateral direction are much weaker than the primary valence forces in the longitudinal direction. The effect of this dissimilarity will be to produce a repulsive pressure between parallel or extended chains, which repulsive pressure will tend to draw the ends of the chains together and may thus be regarded as equivalent to a longitudinal tension. Under the influence of the lateral repulsive pressure the stretched rubber will therefore retract 'until an irregular, statistically-determined arrangement of the molecules and their parts is brought about, in which condition molecular impacts no longer have a resultant directional effect'. The quotation shows that Meyer, von Susich, and Valko clearly appreciated the relation between elasticity and the ability of the chain to take up an irregular or statistically determined form by virtue of the interchange of energy between its constituent elements and surrounding atoms. This is the fundamental concept of the now generally accepted theory of rubber elasticity.

The authors showed that their kinetic theory of elasticity led to the conclusion that the tension in a piece of stretched rubber should be directly proportional to the absolute temperature. This result they were able to confirm experimentally in work published at a later date.

Though using as an argument in favour of their theory the similarity in elastic properties exhibited by various materials (gelatin, cellulose, silk, etc.), Meyer, von Susich, and Valko appreciated the difference in degree of elasticity shown by different materials and drew attention to the significance of crystallization as a factor determining the range of elastic extensibility and other mechanical properties.

Karrer attempted to explain the properties of muscle on very similar lines and, like Meyer, von Susich, and Valko, regarded muscle as a member of a class of long-chain structures which