THE PHYSICS OF RUBBER ELASTICITY

BY

L. R. G. TRELOAR

THIRD EDITION

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General Editors

PREFACE TO THE THIRD EDITION

THE preparation of the Third Edition of this book has presented problems which were not encountered either with the First or with the Second Edition. The expansion of the subject during the last 16 years has involved a problem in the selection and arrangement of material to which there is no completely satisfactory solution. As a guiding principle I have assumed that the primary objective should be to provide a logical and reasonably detailed presentation of the main developments in the field of the *equilibrium* elastic properties of rubber (including the photoelastic and swelling properties), together with the associated theoretical background. In consequence it has been necessary to eliminate the last two chapters of the Second Edition, dealing respectively with stress-relaxation and flow and dynamic properties. The two chapters relating to crystallization have also been removed, though some references to this subject have been included in an enlarged Chapter 1. Despite its great inherent interest, particularly in relation to the historical development of the physics of rubber elasticity, the subject of crystallization in rubber is now seen to be incidental rather than fundamental to the main theme of this book, and its proper treatment would require an extensive discussion of crystallization in polymers other than rubber. A number of authoritative treatments of this wider subject are already in existence.

The main advances in more recent years have been in the thermodynamic analysis of rubber elasticity and in the essentially separate development of the phenomenological (i.e. non-molecular) approach to the subject. To take account of the former it has regrettably been necessary to divide the treatment of the thermodynamics into two parts, the first (elementary) being contained in Chapter 2, and the second (advanced) in the final chapter. The previous Chapter 8 (on phenomenological theory) has been expanded into three separate chapters (Chapters 10, 11, and 12), of which Chapter 11 contains essentially new material.

Inevitably these changes will to some extent reduce the attractiveness of the book for the student who wishes to acquire a broad knowledge of the whole range of physical phenomena associated with rubber. It can only be hoped that this loss will be more than offset by the greater value of the book as a critical review of the subject of rubber elasticity in the more restricted sense, in which field no comparable work is readily available.

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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.

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Welwyn Garden City

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CONTENTS

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GENERAL PHYSICAL PROPERTIES OF RUBBERS

1.1. What is a rubber?

THE original material of commerce known as rubber (or more precisely 'india-rubber') is obtained in the form of latex from the tree *Hevea Braziliensis.* The more expressive term 'caoutchouc', derived from the Maya Indian words meaning 'weeping wood', in reference to the exudation of the latex from a wound in the bark (Le Bras 1965), has been retained by the French, and transliterated into other European languages. The word *rubber* is derived from the ability of this material to remove marks from paper, to which attention was drawn by the chemist Priestley in 1770 (Memmler 1934, p. 3). In current usage the term rubber is not restricted to the original natural rubber, but is applied indiscriminately to any material having mechanical properties substantially similar to those of natural rubber, regardless of its chemical constitution. The more modern term *elastomer* is sometimes employed in relation to synthetic materials having rubber-like properties, particularly when these are treated as a sub-class of a wider chemical group. 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 more restricted 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 the scientific standpoint to define a 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 those 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.

The most obvious and also the most important physical characteristic of the rubber-like state is of course the high degree of deformability exhibited under the action of comparatively small stresses. A typical force–extension curve for natural rubber is shown in Fig. 1.1; the maximum extensibility normally falls within

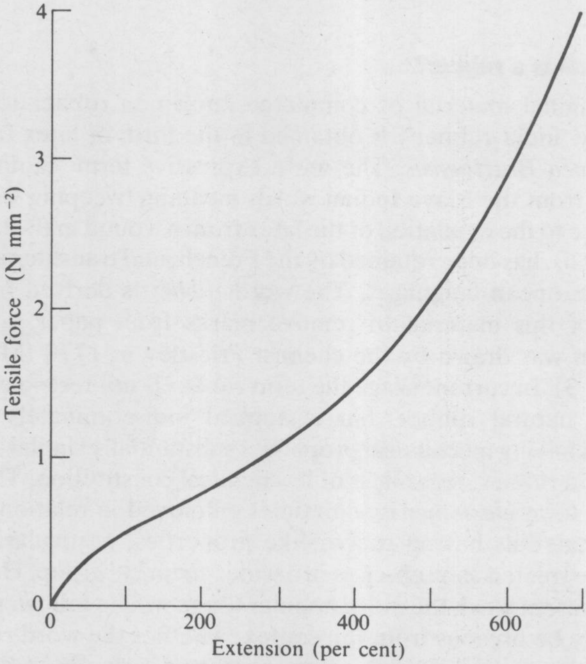


FIG. 1.1. Typical force–extension curve for vulcanized rubber.

the range 500–1000 per cent. The curve is markedly non-linear (i.e. Hooke's law does not apply), hence it is not possible to assign a definite value to Young's modulus except in the region of small strains. In this region its value (represented by the tangent to the curve at the origin) is of the order of $1{\cdot}0\ \mathrm{N\ mm^{-2}}$. These properties—high extensibility and low modulus—are to be contrasted with the properties of a typical hard solid (e.g. steel), for which the value of Young's modulus is $2{\cdot}0\times10^{5}\ \mathrm{N\ mm^{-2}}$ and the corresponding maximum elastic (i.e. reversible) extensibility about 1·0 per cent or less. There is thus an enormous difference between rubbers on the one hand and ordinary hard solids (crystals, glasses, metals, etc.) on the other.

Thermoelastic effects

In addition to these familiar mechanical properties rubber also possesses a number of other less well-known properties, namely, the thermal or thermoelastic properties, which are of even greater scientific significance. The study of these properties dates from the beginning of the last century, when Gough (1805) made the following two observations, i.e.

(1) that rubber held in the stretched state, under a constant load, contracts (reversibly) on heating; and
(2) that rubber gives out heat (reversibly) when stretched.

Gough's conclusions were confirmed some 50 years later by Joule (1859), who worked with the more perfectly reversible vulcanized rubber which had become available since the time when Gough's original experiments were carried out. The two effects referred to are usually known as the Gough–Joule effects. An example of the second, taken from Joule's publications, is reproduced in Fig. 2.10 (p. 38); this shows the rise of temperature due to the evolution of heat on stretching up to an extension of 100 per cent.

These thermoelastic effects are not peculiar to natural rubber, but are characteristic of the rubber-like state, being observed in a wide variety of synthetic rubbery polymers.

1.2. Chemical constitution of rubbers

Natural rubber is essentially a hydrocarbon, whose constitution was established by Faraday (1826) to be consistent with the formula $(C_5H_8)_n$. The rubber exists in the latex in the form of small globules, having diameters in the range 0·1–1·0 μm, suspended in a watery liquid or serum, the concentration of the rubber being about 35 per cent. The rubber particles would coalesce, of course, 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

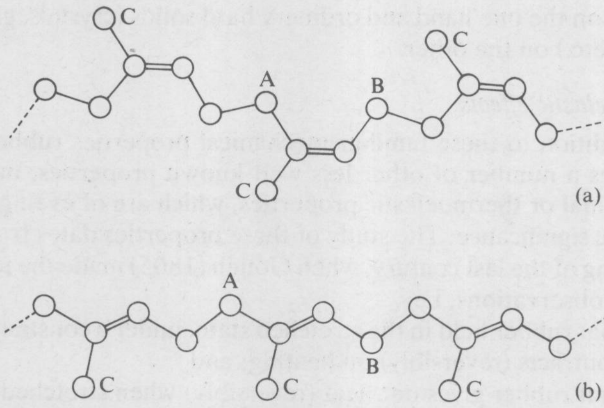


FIG. 1.2. The structure of the molecule of (a) *Hevea* rubber and (b) gutta-percha. A–B = isoprene unit. C = methyl group.

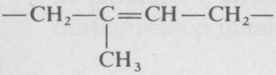
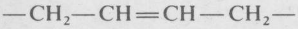
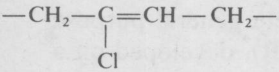
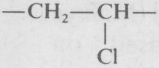
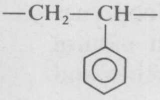
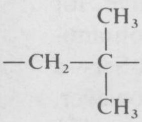
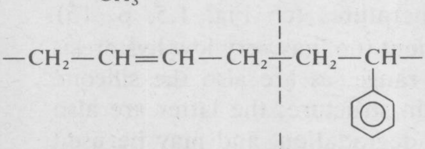
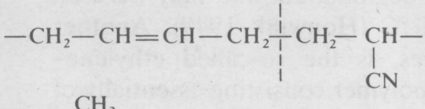
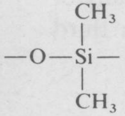
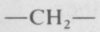
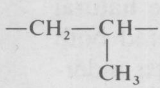
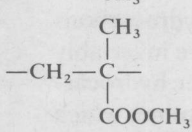
structure shown in Fig. 1.2. The succession of isoprene units in the chain is perfectly regular, with every fourth carbon atom in the chain carrying the methyl (CH_3) side-group. The presence of the double bond is very significant, since it is this that largely determines the chemical reactivity of the molecule and its ability to react with sulphur or other reagents in the vulcanization process. The double bond is also responsible for the susceptibility of the rubber molecule to oxidation or other degradative reactions leading to a deterioration of physical properties (aging).

The structure of gutta-percha, the other natural polymer of isoprene, differs slightly but significantly from that of rubber. As will be seen from Fig. 1.2, the difference lies solely in the arrangement of the single C—C bonds with respect to the double bonds in the chain backbone. In rubber the single bonds lie on the *same* side of the double bond, forming the so-called *cis*-configuration, whilst in gutta-percha they lie on opposite sides of the double bond, giving the *trans*-configuration. One consequence of this difference is that gutta-percha crystallizes more readily than rubber; it is in fact crystalline at room temperature, becoming rubber-like only when heated above the crystal melting point, namely, 65 °C.

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

TABLE 1.1

Structural formulae of some typical rubbers and related materials

	Polyisoprene (natural rubber, gutta-percha)
	Polybutadiene
	Polychloroprene (Neoprene)
	Polyvinyl chloride
	Polystyrene
	Polyisobutylene (basis of 'butyl' rubber)
	†Butadiene-styrene (BSR) rubber
	†Butadiene-acrylonitrile ('nitrile') rubber
	Polydimethyl siloxane (silicone rubber)
	Polyethylene (polythene)
	Polypropylene
	Polymethyl methacrylate (Perspex)

† In these copolymers the respective monomer units occur in a random sequence along the chain.