

SYNTHETIC RUBBERS:
Their Chemistry
and Technology

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ARTIFICIAL RUBBERS: Their Chemistry and Technology

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Preface

This book has its origin in a proposal made a few years ago that I should collaborate with Dr H. J. Stern in the production of a third edition of his well-known text-book entitled *Rubber: Natural and Synthetic*. The suggestion was that I should contribute a series of chapters on synthetic rubbers. Although, in the event, it has not proved possible to publish the full book in the form originally planned, it was apparent that, with some restructuring, the material which I had collected would be valuable as an independent summary of the chemistry and technology of synthetic rubbers. It is in this form that the material is now offered.

The primary purpose of this book is to provide a brief up-to-date survey of the principal types of synthetic rubber which have been and are currently available. Two classes of material are included which are regarded by some as being thermoplastics rather than rubbers, namely, plasticised polyvinyl chloride and the thermoplastic synthetic rubbers. The topics which are covered for each main family of synthetic rubbers are (i) the sources of the monomers, (ii) polymerisation procedures and the effects of important polymerisation variables upon the rubber produced, (iii) the types of rubber currently available commercially, (iv) interesting aspects of the compounding of the rubbers, with special reference to such matters as vulcanisation, reinforcement, protection against degradation, and (where appropriate) plasticisation, and (v) an indication of applications. Where appropriate, an attempt has been made to set the development of the various synthetic rubbers into historical context, and to relate the development to economic, political and commercial factors. In dealing with these diverse aspects of the various synthetic rubbers, an attempt has been made to give broad generalisations of widespread validity, rather than a wealth of detailed information pertaining to particular matters. The author is well aware that such broad generalisations can be misleading in particular

instances, but he also knows that it is all too easy to lose the reader in a mass of detail.

The subject of synthetic rubber latices is specifically excluded from this book. It is far too large a subject for inclusion in a book of this type, especially in view of the many additional concepts which would have to be introduced over and above those which are necessary for the treatment of solid synthetic rubbers. In any case, synthetic latices are dealt with in some detail in my book *High Polymer Latices*, thorough revision of which is currently being undertaken.

A difficult decision which faces the author of a broad survey such as this book purports to be concerns the placing of matters of general interest for the subject as a whole. Shall he gather them together in one or more introductory chapters, which will probably be tedious to read because individual materials and processes which exemplify these matters have not yet been encountered? Or shall he insert them as they arise in connection with individual materials and processes? If the latter course were adopted, then the book could have a very fragmented appearance. In fact, a compromise approach has been adopted here. Some general matters, such as the molecular prerequisites for a substance to be rubbery, the basic facts of polymerisation chemistry, and the industrial production of widely used monomers, have been dealt with in the chapters which are essentially introductory to the book as a whole. Other general topics have been dealt with in connection with individual rubbers which exemplify their importance. Examples include the effect of polymerisation temperature upon the structure of rubbers produced by emulsion polymerisation, which is dealt with in connection with styrene-butadiene rubbers; the swelling of elastomer vulcanisates, which is dealt with in connection with acrylonitrile-butadiene rubbers; and the vulcanisation of rubbers by heating with organic peroxides, which is dealt with in connection with ethylene-propylene rubbers. It is hoped that this approach will make for easier reading, at least on the part of the newcomer to the subject.

The audience to whom this book is primarily directed is graduate chemists, physicists and technologists who are employed in the polymer-producing and polymer-using industries and in allied and ancillary industries. Whilst the main intention of this book is to provide a 'free-standing' survey of synthetic rubbers, an important secondary intention is to introduce the reader to the specialised review literature which is available for the various types of synthetic rubber. The volume of primary research literature which now exists for many of the synthetic rubbers is enormous, especially for those rubbers which are used in large tonnage. It would have

been quite impracticable to have provided comprehensive lists of references for each type of synthetic rubber. The policy which has been adopted is to provide for each type of synthetic rubber a general bibliography which gives some of the more important review articles and monographs, as well as literature references for some of the specific matters which are discussed in the text. It will become evident to the reader that considerable use has been made in the course of the preparation of this book of several of the articles which appear in the *Encyclopedia of Polymer Science and Technology*, published by John Wiley and Sons. It is appropriate to acknowledge here the usefulness of this encyclopedia, containing as it does authoritative and readable reviews of many of the subjects which will be of interest to readers of this book. The assistance which has been gained from the series of authoritative reviews of individual synthetic rubbers which has appeared over the years in the journal *Rubber Chemistry and Technology*, published by the American Chemical Society, is also acknowledged. Apart from such intrinsic merits as this present book may possess, it will have performed a useful function if it directs its readers to these authoritative articles and reviews, and to the comprehensive bibliographies covering the respective parts of the subject which they give.

An important matter which calls for some comment is the relationship between this book and the book entitled *Rubber Chemistry* which has recently been written by my colleague and friend John Brydson and published by Applied Science Publishers Ltd. There must inevitably be some overlap of subject matter between this book and that by Brydson, but the overlap is not great. Brydson's book is concerned primarily with the chemical aspects of the behaviour of rubbery materials, including natural rubber, whereas this book is concerned with synthetic rubbers as an interesting and useful family of materials. There is, for instance, much greater emphasis here on the variants of a given type of synthetic rubber which are available, and of the consequences of these variants for applications. It is to be hoped that this book will come to be regarded as essentially complementary to that by Brydson, rather than as one which covers the same ground.

There is one further important matter to which any author writing on a technological subject in these days must draw attention. This concerns the health hazards which may accompany the use of some of the materials which he mentions. We are becoming increasingly aware of these hazards. Seldom, if ever, does the reputation of a substance in this respect improve as a consequence of increased knowledge and wider experience. Usually greater knowledge informs us of the existence of a hazard where none was

thought to exist, or of the existence of a greater hazard than was believed formerly. For various reasons, not the least of which is the rate at which knowledge and opinion are changing in this field, it has been considered inappropriate to deal with this aspect of the subject in this book. Rather it is considered wiser to give a general warning that some of the materials mentioned here are already believed to be deleterious to health and that the remainder are all potentially liable to become suspect in the light of increasing knowledge. Those who propose themselves to make use of the materials mentioned in this book are therefore strongly advised first to seek up-to-date authoritative opinion on likely health hazards. For those who propose to direct others to use these materials, this precaution is obligatory.

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Chapter 1

Introduction

1.1 RUBBERS NATURAL AND SYNTHETIC

Whatever connotations may have attached to the word 'rubber' in the past; this word has for many years now been used to denote the class of materials which display the property of long-range reversible elasticity. Such materials are also now commonly referred to as 'elastomers'; in fact, the words 'rubber' and 'elastomer' are used almost synonymously.

The property of long-range reversible elasticity can be conveniently defined as 'the ability to be able to sustain large reversible extensions without rupture'. By 'large' in this context is meant 'of the same order of magnitude as the linear dimensions of the material sample being deformed'. The lower limit might reasonably be set at 50% linear extension, although in practice the maximum linear extensions which rubbery materials can undergo without rupture are commonly in the range 100-500%. There is no upper limit to the extensibility for the purpose of this definition of a rubber, but in practice the upper limit of reversible elasticity is approximately 1000% linear extension.

The property of large-scale extension without rupture is not itself sufficient to define a rubbery material. Liquids are capable of enduring almost unlimited extension without rupture; gases certainly are. To qualify as a rubber, the extension must be essentially reversible in the sense that, when the stress which is responsible for the deformation is removed, the material rapidly recovers to approximately its original dimensions. There is inevitably some vagueness in this description because we are seeking to encompass the behaviour of a family of real materials, rather than of ideal materials whose behaviour can be prescribed by definition. By 'rapid' in this context is meant that the recovery takes place over a period of a few seconds at the most. The qualification that the material returns to 'approximately'

its original dimensions is necessary because seldom is the return ever to exactly the original dimensions, any more than the recovery ever takes place instantaneously; in fact, the exact extent of the recovery depends upon the time which is allowed for the recovery. By the word 'approximately' in this context is meant that the recovery is such that the linear dimensions of the recovered material do not differ from the corresponding initial dimensions by more than a few per cent.

It is difficult to fit rubbery materials into the normal categories of solid, liquid and gaseous; they are unusual in having affinities with all three of the common states of matter. They are clearly solid in the sense that they feel more-or-less solid and neither flow nor expand spontaneously when left to themselves. They resemble liquids in that they are able to endure large extensions without rupture, although, as has been noted above, unlike liquids the extension is essentially recoverable. The affinity with gases is more subtle, since clearly rubbers do not resemble gases in respect of either very low density, compressibility or tendency to expand spontaneously. The affinity to the gaseous state is revealed by experiments in which the stress required to maintain a strip of rubber at constant extension is measured as a function of temperature, or, alternatively, by experiments in which the extension at constant stress is measured as a function of temperature. Unlike most solid materials, the stress required to maintain a constant extension of a rubber *increases* with increasing temperature if the constant extension is more than a few per cent. Equally unexpectedly — and it is a manifestation of the same phenomenon — the extension at constant stress *decreases* as the temperature increases, provided that the constant stress is such that the extension exceeds a few per cent. If the first of these observations is compared with the fact that the pressure of a gas held at constant volume increases with increasing temperature, then it becomes clear that there is some affinity between rubbers and gases in respect of their thermo-mechanical properties. This affinity is further emphasised by the fact that the elastic properties of rubbers can be explained in general terms by a molecular theory which is in some respects analogous to the kinetic theory of gases.

It will become clear from the final section of this chapter that rubbery materials as normally encountered seldom consist of a single component. Usually they are rather complex mixtures of vulcanising ingredients, fillers, plasticisers, antioxidants, pigments, etc. However, their rubbery character always depends upon the presence in the mixture of one or more base materials which are themselves inherently rubbery in nature, or, in a few cases, become rubbery in the presence of a suitable plasticiser. These base

materials are usually, but not invariably, organic in nature. It is with an important sub-group of these base materials, and with the ways in which these base materials are compounded and processed to form useful materials, that this book is concerned.

The base rubbers which almost all rubbery materials contain to a lesser or greater extent are classified into two broad groups, *natural* and *synthetic*. As the title implies, the concern of this book is exclusively with the latter. By the term *natural rubber* is meant a rubber which occurs naturally as a product of the metabolism of certain trees and plants, notably trees of the *Hevea brasiliensis* species. Although not a pure substance, natural rubber is principally a linear *cis*-1,4-polyisoprene of high molecular weight. By the term *synthetic rubber* is understood a rubber which is produced by man from chemical compounds of low molecular weight (say, less than 500). The meaning of the term is not usually extended to cover rubbery materials which are made by the chemical modification of substances which are initially rubbery, such as natural rubber. The term is, however, commonly regarded as including rubbers which have not been produced *directly* from low-molecular-weight compounds. Thus both chlorosulphonated polyethylene and plasticised polyvinyl chloride are conventionally regarded as being synthetic rubbers, even although the high-molecular-weight intermediates from which they are produced (polyethylene and polyvinyl chloride, respectively) are not usually thought of as rubbers.

What were the motivating forces which led to endeavours to manufacture synthetic rubbers? They were probably at least four in number:

1. a desire, if not necessity, to achieve independence in respect of a product which hitherto had been obtainable from natural sources only;
2. a desire to achieve greater ability to meet increased demands;
3. a desire to obtain rubbers which possess properties which are not possessed by the natural product, such as resistance to swelling in oils, resistance to extremes of temperature and resistance to certain deteriorative influences, notably ozone; and
4. curiosity.

Concerning the first of these motivations, it is self-evident that the more routes one has to a desirable product, the better is one able to meet the changes of circumstance which may arise as a consequence of political or economic causes. Concerning the second, it has to be noted that the development of the rubber industry has paralleled very closely the

development of transportation powered by the internal-combustion engine. It is extremely doubtful whether the demand for rubber for the manufacture of rubber tyres consequent upon the growth of the automotive industry could have been met solely by the producers of natural rubber. Concerning the third of these motivations, the shortcomings of natural rubber in certain applications has led to a requirement for rubbery materials which possess rather different ancillary properties to those possessed by natural rubber. Although the demand for rubbers possessing these properties has never been large compared to the demand for rubber for tyres, the role played by these rubbers has become increasingly important over the years as man has sought to develop his technology in the context of, for example, the aerospace industry. Thus, whereas the early synthetic rubbers were regarded as being substitutes—and 'ersatz' substitutes at that—for natural rubber, several of the newer types permit the application of elastomeric materials in environments where application would scarcely be feasible at all were natural rubber the only rubber available. Concerning the fourth of these motivations, it is the case that many scientists (including prominent scientists such as Michael Faraday) have been very interested in natural rubber and the strange mechanical properties which it possesses. The relationship between rubbery substances on the one hand and low-molecular-weight organic compounds of known structure on the other has often elicited curiosity. The ability to produce rubbery substances from organic compounds of low molecular weight has clearly constituted an important step in the understanding of that relationship.

Consideration of these motivating forces leads immediately to two important observations of a very general nature. The first of these is that synthetic rubbers can be broadly classified into two categories, namely, the *general-purpose types* and the *special-purpose types*. As the names imply, the first category comprises rubbers which are intended for applications, such as the manufacture of tyres and 'general mechanical' products, which call for no properties other than satisfactory mechanical properties at normal temperatures and the ability to retain those properties for satisfactory periods of time under normal service conditions. In the second category are those rubbers which have special properties such as resistance to swelling in oils, and are in consequence intended for specialised applications such as the manufacture of oil seals. Without exception, all the general-purpose synthetic rubbers which have been developed so far have contained only carbon and hydrogen. Likewise, all the special-purpose synthetic rubbers thus far developed have contained other elements besides

carbon and hydrogen; indeed carbon and hydrogen are absent from some of the more exotic types.

The second important observation concerns the relationship between the synthetic rubber molecule and the low-molecular-weight compound from which the rubber was manufactured. The molecules of all rubbery materials are in the general class of those known as *polymers*, that is, they are of high molecular weight and comprise one or more small chemical units repeated many times over. The average molecular weights of raw rubbers are often very high, being typically in the range 10^5 - 10^6 . Assuming, as is usually the case, that the molecular weight of the repeat unit is of the order of 50-100, this will mean that each rubber molecule can contain on average between 10^3 and 2×10^4 repeat units per molecule. In the case of a synthetic rubber, the repeat units in the rubber molecule are derived from the low-molecular-weight compounds—called *monomers*—from which the rubber was manufactured. The chemical reaction by which monomer molecules are converted into polymer molecules is known as *polymerisation*. More will be said of these reactions in Chapter 4. It is sufficient to note at this stage that the majority of synthetic rubbers are manufactured by the process of *addition polymerisation*, in which the monomer units become added to one another without any small molecule being eliminated. A few synthetic rubbers are manufactured by *condensation polymerisation*, in which a small molecule is eliminated during each step of the polymer-building reaction. It may also be noted that (a) the polymerisation reaction may involve a mixture of monomers, in which case the product is known as a *copolymer* because it contains more than one type of repeat unit; and (b) the sequences of repeat units in the molecules of raw synthetic rubbers are essentially linear, or, at least, if branching and crosslinking between the essentially linear sequences do occur, then these are regarded as generally undesirable features.

1.2 MOLECULAR REQUIREMENTS FOR A RUBBERY SUBSTANCE

It is appropriate at this stage to summarise the molecular requirements which must be fulfilled if a substance is to have the mechanical properties which we associate with a rubber. Not only should such a summary be helpful in understanding certain of the matters which will be discussed in subsequent chapters; it should also be helpful in giving some insight into the molecular reasons why certain monomers have achieved great importance in connection with the manufacture of synthetic rubbers.

In addition to the obvious requirement of molecular stability, the molecular requirements which have to be fulfilled if a polymer is to be rubbery in nature and to be utilisable as a rubber in practice are five in number:

1. The segments of the polymer sequence must be capable of moving essentially independently of segments of the same sequence which are some distance away, i.e., the polymer sequence must be flexible.
2. Strong interaction between neighbouring segments must be absent, and so also must high concentrations of bulky substituents which inhibit segmental motion.
3. The polymer must not crystallise to any appreciable extent in the unstrained state nor at low extensions.
4. The molecular weight must be high.
5. The facility must exist for the introduction of a low concentration of crosslinks between neighbouring polymer molecules.

Considering these points in order, the requirement of independent segmental mobility implies (a) that a sufficient proportion of the main-chain bonds of the polymer sequence have the type of flexibility which is depicted in Fig. 1.1, (b) that the polymer sequence is essentially linear, and (c) if branching does occur, it must not be so extensive as seriously to inhibit segmental mobility. The type of flexibility depicted in Fig. 1.1 is rotational flexibility of one bond about its neighbour. The requirement is that rotation should be possible without undue hindrance, notwithstanding that the angle between the two bonds is fixed within narrow limits. It is by means of essentially independent segmental motions of this type that the rubber molecule as a whole can readily move from one conformation to another. An important consequence of rotational segmental flexibility is that, because of purely statistical considerations, the polymer molecule is more likely to adopt a coiled-up conformation than one in which the molecule is extended. It is this feature, together with the ready inter-conversion of molecular conformations, which endows the bulk material with the property of long-range reversible elasticity.

Molecular features which tend to restrict or inhibit independent segmental mobility must either be absent altogether or else be present in insufficient concentration to destroy the ability of the polymer sequence as a whole to pass readily from one conformation to another. Two important molecular features which have a tendency to restrict independent segmental mobility are (a) attractive forces between segments arising from the presence of chemical groupings which have permanent dipoles associated

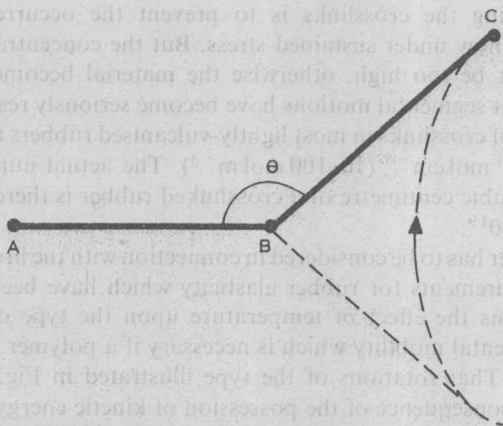


FIG. 1.1. Illustrating type of flexibility which polymer sequence must possess if material is to exhibit rubbery properties in the bulk state. AB and BC are neighbouring segments of the polymer sequence. BC must be able to rotate about AB as shown, without serious hindrance, although the bond angle θ remains essentially unchanged.

with them, and (b) the presence of bulky substituents in the main chain which give rise to steric hindrance.

Another factor which will clearly inhibit independent segmental motions is crystallisation of the polymer segments into a regular lattice, thereby effectively immobilising the segments. Even if the polymer sequence itself is inherently flexible, crystallisation of sections of the sequence can change an otherwise rubbery polymer into a material which is rather more rigid than would be expected. The actual rigidity depends upon the proportion of the polymer which is present in crystalline form. An outstanding example of the effect of segmental crystallisation is to be found in polyethylene. On the basis of inherent segmental mobility, this polymer would be expected to be rubbery at room temperature; in fact, it is a rather rigid plastic because of segmental crystallisation.

The requirement for high molecular weight arises because, if the molecular weight is not sufficiently high, then the polymer molecules are able to move relative to one another in a concerted fashion. The material then behaves as a viscous liquid rather than as a rubber.

However, even if the molecular weight is very high, an uncrosslinked rubber will flow as a very viscous liquid if subjected to a steady stress over a long period of time. It is for this reason that most rubbers have to be lightly crosslinked in order that they may perform satisfactorily in service. The

object of introducing the crosslinks is to prevent the occurrence of irreversible viscous flow under sustained stress. But the concentration of crosslinks must not be too high, otherwise the material becomes rigid because independent segmental motions have become seriously restricted. The concentration of crosslinks in most lightly-vulcanised rubbers is of the order of 10^{-5} – 10^{-4} mol cm $^{-3}$ (10–100 mol m $^{-3}$). The actual number of crosslinks in each cubic centimetre of a crosslinked rubber is therefore of the order of 10^{18} – 10^{19} .

One further matter has to be considered in connection with the first of the five molecular requirements for rubber elasticity which have been listed above. This concerns the effect of temperature upon the type of bond flexibility and segmental mobility which is necessary if a polymer is to be rubbery in nature. That rotations of the type illustrated in Fig. 1.1 do actually occur is a consequence of the possession of kinetic energy by the polymer molecules and their constituent parts. In fact, the extent of the independent segmental motions required for rubbery character in the bulk material, and the ease with which transitions between molecular conformations connected by such motions can occur, is determined by the balance between the kinetic energy of the segments on the one hand and the resistance which exists to the rotation of one interatomic bond about its neighbour on the other. As the temperature of a rubber is lowered, the kinetic energy of the polymer molecules and their constituent parts is reduced. For this reason, if for no other, the ease of rotation of one interatomic bond about its neighbour is reduced. So too, in consequence, is the ease with which independent segmental motions can occur. One practical consequence is that a rubber becomes less rubbery as the temperature is lowered. (This effect, which is really in the nature of a gradual change of physical state, as will become evident below, must not be confused with the fact, to which reference has been made in Section 1.1, that rubbers in the rubbery state become 'stiffer' as the temperature is *increased*.) As the temperature is progressively lowered, there is eventually reached a small range of temperature over which the material changes from what is evidently essentially a rubber to what is essentially a rigid material. The ability of one interatomic bond to rotate about its neighbour is almost completely lost. So too are the independent segmental motions of the several parts of the polymer chain. The polymer molecules are now virtually frozen in position, and transitions between possible different molecular conformations cannot occur with any ease. Further lowering of the temperature merely leads to further embrittlement of the material. These changes can be reversed by raising the temperature. The transition between behaviour as a rubbery material and behaviour as a rigid material,