RUBBER CHEMISTRY

J. A. BRYDSON

RUBBER CHEMISTRY

J. A. BRYDSON
Deputy Head, National College of Rubber Technology
The Polytechnic of North London
Holloway, London, UK

APPLIED SCIENCE PUBLISHERS LTD
LONDON

APPLIED SCIENCE PUBLISHERS LTD
RIPPLE ROAD, BARKING, ESSEX, ENGLAND

British Library Cataloguing in Publication Data

Brydson, John Andrew
Rubber chemistry.
1. Rubber chemistry
I. Title
678′.4 TS1892

ISBN 0-85334-779-4

WITH 35 TABLES AND 66 ILLUSTRATIONS

Printed in Great Britain by Galliard (Printers) Ltd Great Yarmouth

PREFACE

The property of rubber elasticity is displayed by an ever increasing range of polymers—hydrocarbon, polar and even inorganic. Such rubbery polymers, however, differ in the way by which they are made, in their chemical and physical properties, in the way in which they form network structures and in the way in which they age. Such differences are due, primarily, to differences in their underlying chemistry and chemical structure.

It is the aim of this monograph to survey, in a single volume, the chemistry of these rubbery polymeric materials and to cover such aspects as their preparative chemistry, relationship of chemical structure to properties, the molecular nature of high elasticity, cross-linking and other chemical modification and ageing. This has been done, not simply because rubbery materials are so fascinating in their own right but also because of their industrial importance. It is therefore hoped that this book will help both the polymerization chemist and the rubber technologist to have a better and broader-based understanding of the materials with which they are concerned and to be able to suggest directions along which developments may proceed.

In order to keep the text to a reasonable size an outline knowledge of polymer chemistry has been assumed. Lists of references are also short when compared with many contemporary publications and have been largely confined to those essential to the narrative, to reviews containing comprehensive reference lists and to more recent work. At least one of the reviews cited has more than 1000 references so no attempt has been made to provide a comprehensive literature survey.

Rubber chemistry is today one of the most active areas of polymer science. In the past few years many new polymers have been introduced whilst there have also been important developments in vulcanization systems and in methods of protection against ageing. The study of network structures requires special techniques, several of which are peculiar to rubber chemistry, and these have been given emphasis. Many of these techniques require certain fundamental assumptions to be made about the nature of rubbery materials, particularly of networks. In collecting material for this book the author has encountered reported observations which do not fit comfortably with conventional theories. Such discrepancies have been pointed out and on occasions the author has been tempted, perhaps rashly but in the hope of stimulating discussion, to offer possible explanations.

Although there are some excellent texts on aspects of rubber science both in book form and in the Rubber Reviews published in association with the journal *Rubber Chemistry and Technology*, there is, as far as the author is aware, no single text covering the subject matter of this book and it is his hope that, with the publication of this book, this deficiency will now be remedied.

J. A. BRYDSON

CONTENTS

Chapter 1

THE HISTORICAL DEVELOPMENT OF RUBBER CHEMISTRY

Chapter 2

THE CHEMICAL NATURE OF THE NATURAL RUBBER MOLECULE

Chapter 3

THE MOLECULAR NATURE OF RUBBER ELASTICITY

Chapter 4

STRUCTURE–PROPERTY RELATIONSHIPS IN RUBBERS

Chapter 5

DIENE HOMOPOLYMER RUBBERS

Chapter 6

DIENE-BASED COPOLYMERS

Chapter 7

REACTIVITY OF DIENE RUBBERS—I

Chapter 8
REACTIVITY OF DIENE RUBBERS—II: CROSS-LINKING PROCESSES

Chapter 9
REACTIVITY OF DIENE RUBBERS—III: OXIDATION AND RELATED PROCESSES

Chapter 10
POLYCHLOROPRENE

Chapter 11
POLYISOBUTENE AND BUTYL RUBBER

Chapter 12
RUBBERS BASED ON ETHYLENE

Chapter 13

FLUORINE-CONTAINING RUBBERS

Chapter 14

ACRYLIC RUBBERS

Chapter 15

RUBBERS PRODUCED BY CONDENSATION AND RING-OPENING POLYMERIZATION MECHANISMS

Chapter 16

POLYURETHANE RUBBERS

Chapter 17

THERMOPLASTIC RUBBERS

Chapter 1

THE HISTORICAL DEVELOPMENT OF RUBBER CHEMISTRY

1.1. INTRODUCTION

Of all the materials provided by nature for man to use as a material of construction, natural rubber is unique. The characteristic of high reversible extensibility fascinates the enquiring mind. As the years have passed since its introduction to the Eastern Hemisphere by Columbus and his fellow explorers the roll of famous men who have studied the material has steadily lengthened. These include Priestley, who coined the word 'rubber'; Faraday, who determined its empirical formula; Weizmann, who in later years became the first president of Israel, and the Nobel Chemistry Prizewinners Staudinger, Flory, Ziegler and Natta.

At the same time there is more than a touch of alchemy imposed on the magic of rubber. The process of mastication was discovered accidentally by Hancock in the 1820s. Only in the late 1940s was it demonstrated that this was due to the rupture of chemical bonds by mechanical means, a discovery which established the science of mechano-chemistry. The discovery of vulcanization, the process that renders rubber less temperature sensitive and also insoluble as well as regenerating high elasticity in masticated rubber, was made totally without understanding of the processes involved. The heating of pieces of rubber in pots of boiling sulphur by Goodyear and others in the early years of the 19th century seems more appropriate to the witches' brews of Shakespeare's Macbeth. Nevertheless some 150 years later sulphur is still the monarch of vulcanizing agents.

There is a further wonder in that the source of natural rubber is a milky sap to be found in many hundreds of species of plants. This milky sap, or latex, when coagulated and dried yields a material which is not only rubbery but in a way crystalline. Today there are many man-made rubbers but the natural product still plays a substantial role on the world's industrial stage, a story very different from that of many other natural materials challenged by synthetics.

On first consideration it may be thought that rubberiness is an invariant property, that rubber is rubber and that is all there is to it. On second thoughts one realizes that the number of products that can be made from natural rubber is very large and that the properties of such products may be very different. One has only to think of a tyre, a toy balloon, an ebonite battery box, an eraser, and a hot-water bottle to appreciate that considerable modification to the rubber may be made by judicious compounding. Indeed it may be argued that greater variation is possible by the selection of additives to the base rubber than by changing the base rubber.

1.2. EARLY YEARS

In the Andalucian city of Seville, between the cathedral, the Alcazar and the banks of the Guadalquivir river is the building of the Archives of the Indies. Amongst the 38 000 papers and documents in these archives are enshrined the first records concerning rubber made by civilised man. The earliest references are said to be in d'Anghiera's *De orbe nuovo decades* of 1530 and in Valdes' *La Historia natural y general de las Indias* published in Seville in the period 1535–37 but further research might well uncover further references.

During the next century a few Spanish chroniclers described a variety of applications of rubber used by the American Indians and indeed by the Spanish settlers in Mexico, as for example the use of latex in rendering capes impermeable to water, but all of this was ignored by a then incurious Europe. It took the travels of Voltaire's friend Charles Marie de la Condamine in South America between 1736 and 1743 for Europe to rediscover the material. It may even be true that only with la Condamine's return to France were the first samples of rubber ever to cross the Atlantic. As a consequence the first real interest by the European in rubber began, in particular by the Frenchmen Fresneau, Herrissent and Macquer. Although they achieved some success in finding a solvent for rubber, in turpentine, they were extremely limited in their ability to manipulate the material.

About 1820 the Scotsman Macintosh rediscovered the process of dissolving rubber and placed the solution between two fabrics which as a result became united, impermeable and without the stickiness of earlier products. His name, or rather a mild corruption of it, mackintosh, has become perpetuated to cover a variety of rainproof outer garments.

Solution of a polymer can barely be considered as a chemical reaction. However the process developed by Macintosh's colleague Thomas Hancock, mastication, can with the knowledge of today be considered as such. Hancock found that if strips of rubber were repeatedly cut, kneaded and re-shredded the material became less elastic and more viscous and capable of flow. We now recognise that this process involves rupture of the rubber molecules to produce materials of lower molecular weight. Hancock recognized that this was a way of facilitating the manipulation of rubber although the product was no longer as elastic as before.

Both raw and masticated rubber were however unsatisfactory for all but a few end uses. The key discovery by the American, Charles Goodyear, in 1839, that heating a mixture of rubber, sulphur and white lead gave a material of far superior properties, is without doubt the most important milestone in the history of rubber. This process, commercially exploited by Hancock, provided the public with an elastic material less liable to become sticky in hot weather and stiff in cold and also insoluble in common solvents. Another of Hancock's friends, Brockeden, termed the process vulcanization—a term used to this day by the rubber technologist and chemist. Today we recognize that this process involves the cross-linking of polymer chains to form network structures which severely limit the ability of the chains to slide past each other. Whilst we now know much more about the requirements of an ideal cross-linking agent and the mechanisms of these reactions, sulphur remains the dominant cross-linking agent of the world's rubber industries.

Whilst Faraday had shown in 1826 that rubber was a hydrocarbon of empirical formula C_5H_8 few further important developments occurred until the closing years of the 19th century when the structure of natural rubber began to be progressively revealed, a process which only became substantially complete about 1930 and which is considered in the next chapter.

1.3. SYNTHETIC RUBBER

Long before the structure of rubber had been established attempts to prepare a synthetic rubber had been made. In 1860 Greville Williams distilled rubber and then fractionated the distillate. From the lowest fraction Williams obtained a liquid boiling at 37–38°C which he called isoprene. Williams further described an experiment involving the exposure to air of isoprene which eventually led to the production of a 'white, spongy elastic mass'. Conceivably this was the first man-made rubber although the 'starting material' isoprene had itself been obtained from natural rubber.

In 1879 F. G. Bouchardat produced a material from isoprene which clearly had many properties akin to the natural product but as with Williams' experiments the isoprene had been obtained from natural rubber. By 1884 W. A. Tilden had prepared isoprene from turpentine and then converted the former to a rubber-like material by methods similar to those used by Bouchardat. At last a rubber had been made by sources independent of natural rubber but it is important to recognize that the product must have differed from the natural polymer in many respects.

At this time it was becoming recognized that conjugated dienes other than isoprene could be converted into elastic substances. In 1881 von Hofmann prepared a rubber from 1,3-pentadiene and in 1892 Couturier polymerized 2,3-dimethyl-1,3-butadiene although he paid little attention to the product.

During the first decade of the 20th century the demand for, and hence the price of, natural rubber was increasing. As a result the Bayer Company in Germany and Strange and Graham in London set up research teams to develop commercial processes for making synthetic rubber. By 1910 both teams had discovered, independently, that polymerization of isoprene could be initiated by metallic sodium and methods were devised for commercial production. The appearance of plantation rubber at about this time led however to a drastic drop in the price of rubber and development work, to all intents and purposes, ceased in England and was severely cut back in Germany.

With the advent of World War I the situation in Germany, as far as the supply of natural rubber was concerned, became acute and renewed research efforts were made. Isoprene was expensive and, although quite a good rubber could be made from it by heat polymerization, yields were poor. Sodium-catalyzed polymerizations gave higher yields but inferior products. Since at that time butadiene was both very difficult and expensive to prepare, dimethyl butadiene became the preferred monomer. In 1917 the Germans commenced the first substantial commercial production of a man-made rubber, from dimethyl butadiene. Two versions were made, Methyl Rubber W, by heat polymerization at about 70°C over a period of five months and

Methyl Rubber H, a hard grade suitable for battery boxes and other ebonite-type uses which was made by a low temperature process operated at 30–35°C and which took about 3–4 months. During the war 2350 tons of Methyl Rubber were produced but, since it was far inferior to natural rubber, production ceased at the end of the war.

For the next few years synthetic rubber research was minimal but two stimuli occurred about 1926. First, Staudinger was establishing the long chain nature of the rubber molecule and secondly the price of rubber was rising once again. The IG Farben Company of which the old Bayer Company had become a part, instituted research which showed the beneficial effects of polymerizing the monomers in aqueous emulsion, particularly in the presence of about 1% benzoyl peroxide. At the same time improvements were made in the sodium-catalyzed polymerization of butadiene and this led to the advent of the Buna rubbers (the name derived from butadiene and natrium, the New Latin term for sodium) production of which went on to the end of World War II.

Whilst the peroxide-initiated emulsion polymerized polybutadiene had disappointing properties it was found in 1929 that copolymerization of butadiene with styrene and in 1930 with acrylonitrile led to the production of interesting materials. The butadiene–styrene rubber, Buna S, was potentially a general purpose rubber but at that time not competitive with natural rubber. On the other hand the butadiene–acrylonitrile rubber, Buna N, now commonly known as nitrile rubber had certain properties such as oil resistance not shown by natural rubber and commercial production was started about 1935. Commercial production of butadiene–styrene rubber did not commence until 1937 and many things were to happen before it became the world's most used rubber.

Whilst the copolymers based on butadiene were being developed in Germany, interesting developments were taking place in the United States. Sometime between 1920 and 1924 J. C. Patrick and N. M. Mnookin had reacted ethylene dichloride with sodium polysulphide by a condensation reaction to produce a novel rubber. This was interesting on two counts. First it showed very good oil resistance and second the polymer contained no carbon–carbon double bonds as did the polymers of isoprene, dimethyl butadiene and butadiene. Commercial production commenced in 1929 and somewhat modified forms are in use today so that these polysulphide rubbers are arguably the oldest synthetic rubber-like materials still in production.

Soon after this the Du Pont company commercially introduced what is still the world's most important special purpose rubber. This had its origin in work on acetylene chemistry started by Niewland in 1906 and which led in the mid-1920s to the development of a process for making vinyl acetylene from acetylene. The addition of hydrogen chloride to the vinyl acetylene yielded 2-chloro-1,3-butadiene, chloroprene, which could be polymerized to form a rubber with good heat, oil and ozone resistance. Initially marketed as Duprene in 1932 the Du Pont company subsequently changed the name to Neoprene. Similar materials are now produced by other organizations in France, Germany, Japan and the USSR.

At about the same time American chemists were also responsible for the development of another elastomer—butyl rubber. In 1930 the Standard Oil Company of New Jersey entered into an agreement with IG Farben in Germany to assist each other in developing chemical products and processes from petroleum. This led the IG company to disclose to the American company that isobutylene could be polymerized to a high molecular weight polymer by a strong Lewis acid catalyst such as boron trifluoride at about −75°C. The management of Standard Oil were initially primarily interested in the use of the material as a fuel additive but two chemists within the company, R. M. Thomas and W. J. Sparks were intrigued by the unusual elastomeric properties of the material. This stimulated work within the American company which led to the production of copolymers containing small amounts of isoprene. The latter provided a few double bonds in an otherwise saturated hydrocarbon which enabled the polymer to be cross-linked using more-or-less conventional vulcanizing systems. Commercial production of this material, known as butyl rubber commenced in 1942.

1.4. HOT AND COLD WAR: HOT AND COLD RUBBER

The IG Farben–Standard oil agreement was to have far greater significance. This was because it provided the American company with technical details of the production of Buna S, the peroxide-initiated emulsion-polymerized copolymer of butadiene and styrene. World War II had started in 1939 and in 1942 the Japanese had taken over Malaya and the then, Dutch East Indies. Supplies of natural rubber to Britain and to the United States were thus severely curtailed. As a direct consequence the US and Canadian governments built between 1942 and 1944 a total of 87 factories with a total annual output capacity of about 1 million tons to produce materials based on the Buna S process. This crash programme played a role in World War II which is difficult to overrate and without which the course of the war would undoubtably have been far different. The product, then known as GR–S, was however, like methyl rubber before it, generally inferior to natural rubber; production dropped sharply at the end of the war and when the writer first became involved in rubber technology in 1949, GR–S, like lunar travel today, was considered a thing of the past.

However, as after World War I, a combination of politico-economic events and a technical development gave a stimulus to the production of man-made general purpose rubbers. The tensions of the so-called cold war between the communist and non-communist worlds had led to the Korean war which served as a reminder that supplies of such an important commodity as rubber should not be dependent on a relatively small geographic area. At the same time development of low temperature polymerization processes gave much better products, known as cold rubbers to distinguish them from the older materials which now became known as 'hot rubbers' in reference to their higher polymerization temperatures. These two factors led to a strong recovery in the use of GR–S which in the mid-1950s was redesignated SBR. With progressive improvements in the product, SBR was eventually to overhaul natural rubber, in tonnage terms, as the world's most important rubber.

1.5. STEREO AND SPECIALITY RUBBERS

Between the early 1930s and the mid-1950s there had been very few really new rubbers introduced and those that had appeared such as the fluoroelastomers and the acrylic rubbers were special purpose materials. Whilst the term synthetic rubber was commonly used to describe the collection of materials then available the term was a misnomer—not even the man-made polyisoprenes possessed the same detailed molecular architecture as the natural product. The German Patent 255 786 taken out by Hans Labhardt of BASF in 1912 had suggested that butadiene and its homologues could be polymerized with the aid of alkali metal alkyls. Familiar with Labhardt's patent, Ziegler and his co-workers in the late 1920s commenced a programme