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ELASTOMERS AND RUBBER COMPOUNDING MATERIALS

Manufacture, Properties and Applications

edited by
I. FRANTA

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Preface

Elastomers form a special class of materials characterized by a unique combination of useful properties, such as elasticity, flexibility, toughness and impermeability. The uses of elastomers include both typical industrial and engineering applications, such as seals, hoses, insulators or tyres, and special applications, such as medical aids, various implants or artificial hearts.

The properties of rubber products depend not only on the characteristics of elastomers, but also on the various additives and ingredients mixed into the basic elastomer to form a rubber compound.

The selection of additives and their incorporation into the rubber to improve the properties of a basic elastomeric material, or rubber compounding, is still based more on experience and art than on a rational or scientific approach.

This book surveys the properties of elastomers and particular groups of rubber compounding ingredients and chemicals to help the rubber technologist to rationalize the very complex task of rubber compounding. The reader will find in this book fundamental information on the production, properties and application of all basic materials used for formulating rubber compounds, i.e. elastomers, vulcanization chemicals, fillers, stabilizers, plasticizers, blowing agents and textile reinforcing materials. Chapters on the history of the rubber industry, the general properties of rubbers, and the principles of production of synthetic polymers are also included.

It was the intention of the authors to provide the reader with a book offering both technical information and specifications of particular compounding materials, and to present an explanation of the structure-property relationships as a starting point for more rational rubber compounding and hence application of the rubber products. The book will be useful to those in the rubber industry but will also serve as a reference and explanatory text for students of polymer science and rubber technology.

This volume is the third edition and is based on the second Czech edition of the text published in 1979. Some parts of the book have been completely rewritten and the whole text has been updated and revised for the English translation.

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Special gratitude is due to the late Prof. Dr. I. Franta, who conceived the idea of the project and formed the team of authors whose cooperation made this book possible. After the death of Prof. Franta the team of authors further cooperated on the preparation of the English edition of the book and the main portion of the editorial work was assumed by one of the co-authors, Dr. Petr Vondráček, whose effort helped the English version to come true.

The authors

CHAPTER 1.

Introductory part

Ivan Franta

1.1 BRIEF HISTORY OF RUBBER

1493–1496: The first European to see caoutchouc, i.e. rubber, was Columbus; during his travels in South America and Haiti he saw natives playing with balls made of the dried juice of some trees.

1736: The French scientist Charles Maria de la Condamine sent the first samples of rubber to Europe from his journey through equatorial and South America (he also pointed out the possibilities of its use).

1770: J. Priestley gave the name "rubber" to caoutchouc, when he used it as an eraser of pencil marks.

1791: S. Peal obtained the first patent in the field of rubber; his discovery consisted in the impregnation of textile material with a solution of rubber in turpentine oil. Fourcroy in France found that latex can be stabilized with ammonia.

1811: In Vienna the first factory for the processing of natural rubber in Europe was founded.

1820: T. Hancock discovered that natural rubber can be converted into a plastic state by mechanical shearing. From his first apparatus, called "pickle", the rubber industry two-roll mill (Chaffee, 1836) and the roller mixing machine were developed (Banbury, 1916).

1823: C. Macintosh obtained a patent for the raincoat fabric consisting of a layer of rubber sandwiched between cloth and introduced mineral oil as a cheap solvent for rubber.

1826: M. Faraday determined the empirical formula of caoutchouc as C_5H_8.

1832: F. W. Ludersdorf found that if turpentine oil is evaporated from a solution of rubber and sulphur, the rubber loses its adhesive power.

1837: T. Hancock proposed a coating machine.

1839: Charles Goodyear in America discovered hot vulcanization of rubber with sulphur (patent from 1841).

1843: Independently, T. Hancock discovered in England hot vulcanization of rubber with sulphur.

1845: R. W. Thompson proposed the idea for the production of tyres.

1846: A. Parkes discovered cold vulcanization with sulphur monochloride.

1849: H. G. Tyer introduced the use of zinc carbonate, zinc oxide and other zinc compounds in rubber mixes.

1858: H. L. Hall obtained the first patent for the regeneration of waste rubber.

1860: C. G. Williams isolated a light fraction from the products of dry distillation of rubber, to which he gave the name isoprene.

1876: H. A. Wickham imported a batch of seeds from the tree *Hevea brasiliensis* from Brazil to London; the young plants cultivated from them in Kew Gardens were sent to Ceylon (Sri Lanka) and Malaysia; thus the plantation production of rubber was founded. This plantation method was developed by H. V. Ridley.

1879: G. Bouchardat expressed the view that isoprene is the fundamental component (unit) of rubber; on reaction with hydrochloric acid he prepared a substance similar to rubber from isoprene obtained by dry distillation of rubber.

1881: N. C. Mitchel obtained a patent for the elimination of textile material from rubber waste by treatment with sulphuric acid.

1884: W. A. Tilden prepared a rubber-like material from isoprene obtained by pyrolysis of turpentine oil.

1885: I. L. Kondakov prepared synthetic isoprene for the first time.

1888: I. Mariuca prepared dimethylbutadiene and discovered its ability to polymerize.
The first 500 kg of rubber were prepared from plantations.

1893: J. F. Palmer patented weftless fabric for racing bicycle tyres; the principle spread to all types of tyres.

1895: Tyres for motor cars were used for the first time for the Bordeaux–Paris race.

1899: I. L. Kondakov observed polymerization of dimethylbutadiene over sodium.

1900: I. L. Kondakov polymerized dimethylbutadiene to a leathery mass similar to rubber by heating it with a solution of potassium hydroxide.

1902: C. O. Weber published his theory of vulcanization.

1906: G. Oenslager discovered organic accelerators.

1908: L. M. Kucherov observed the polymerization effect of sodium on isoprene.

1909: S. V. Lebedev found that butadiene may be polymerized to a mass similar to rubber. He formulated a general rule for the polymerization of unsaturated hydrocarbons and showed that the tendency to polymerize, leading to rubber-like substances, is strong in diene hydrocarbons with a conjugated system of double bonds and published a paper on thermopolymerization.
F. C. Mathews demonstrated the reinforcement of rubber with carbon black; this was utilized industrially in 1912.

1910: C. Harries proved the structure of polyisoprene by ozonolysis.

1911: I. I. Ostromyslenskii proposed a method of producing butadiene from ethanol, via acetaldehyde, aldol and butylene glycol.

1912: Carbon black was used for the first time for the reinforcement of tyre treads (J. Tew and G. Oenslager).

1914: Instead of cross textiles, cord fabric was used for tyres. The production of methylrubber in Germany, the first industrial production of synthetic rubber. Proposition for the construction of low-pressure balloon tyres.

1915: I. I. Ostromyslenski reported the synthesis of butadiene from ethanol and acetaldehyde.

B. V. Byzov made a patent application for the production of butadiene from the gases formed during the processing of mineral oil.

1916: I. I. Ostromyslenski discovered vulcanization with trinitrobenzene. F. H. Banbury invented the internal mixer.

1918: S. J. Peachey discovered vulcanization by consecutive treatment with SO_2 and H_2S.

1919: Introduction of thiuram as an accelerator of vulcanization.

1920: Introduction of mixing in the Banbury mixer.

1921: G. Bruni and Romani discovered vulcanization of rubber by means of thiuram without sulphur.

W. C. Geer and W. W. Evans introduced the method of accelerated ageing of rubber in hot air. Introduction of Denax as an accelerator.

P. Schidrovitz obtained a patent for the production of Vultex, a prevulcanized latex.

A. Pfeiffer obtained a patent for the principle of radial tyres.

1923: Production of concentrated latices by centrifugation introduced.

1925: Introduction of a test of accelerated ageing in oxygen, according to Bierere-Davies.

Introduction of Kaptax as an accelerator.

1928: S. V. Lebedev developed the synthesis of butadiene from ethanol.

1929: Industrial production of Thiokol.

Industrial production of balloon tyres.

Industrial production of foam rubber from latex.

1931: Industrial production of chloroprene rubber (Dupren). Introduction of latex concentration by evaporation (Revertex).

1932: Industrial production of polybutadiene SKB.

1935: Industrial production of Buna 85 and 115.

1937: Industrial production of Buna S and Perbunan.

1938: Use of viscose silk for cords.

1940: Industrial production of butyl rubber.

1945: Production of silicone rubber.

1946: Industrial production of radial tyres.

1948: Use of polyamide for the production of cords. Cold styrene-butadiene rubber.
1950: Industrial production of tubeless tyres.
1952: Production of oil-extended rubber.
1955: Production of chlorosulphonated polyethylene. For the first time a product similar to natural caoutchouc, i.e., *cis*-1,4-polyisoprene, was prepared by polymerization of isoprene.
1959: Production of ethylene-propylene rubber.
Production of polyurethane rubbers.
Production of *cis*-1,4-polyisoprene.
1963: Production of ethylene-propylene terpolymer.
1965: Production of thermoplastic rubbers.
Production of epichlorohydrin elastomers.
1966: Production of technically specified natural rubber (SMR).
1967: Development of the production of tyres with new constructions (bias belted, radial tyres, etc.).
Polyester cords extensively used in tyre production.
Production of chlorinated polyethylene rubbers.
1970: Production of elastomeric perfluoroolefin copolymer.
1971: Industrial production of bromobutyl rubber.
1972: Introduction of polyether-polyester thermoplastic rubber (Hytrel).
Production of carboxylated nitrile rubber.
Introduction of "improved" carbon black.
Steel wire cords extensively used in tyre production.
1975: Production of norbornene rubber.
Production of ethylene acrylic rubber.
Introduction of polyphosphazene rubber.
1976: Aromatic polyamide cords used in special applications.
1978: Production of polyurethane tyres.
1980: Introduction of thermoplastic polyolefin vulcanizates.
1985: Introduction of oil-resistant thermoplastic rubber.
Production of hydrogenated nitrile rubber.
1988: Industrial production of fully hydrogenated nitrile rubber.

1.2 INTRODUCTION AND GENERAL DESCRIPTION OF RUBBERS

Rubber has been imported into Europe for more than 200 years, but it became a technically important material only after the discovery of vulcanization by Charles Goodyear in 1839. Gradually it penetrated into all fields of human