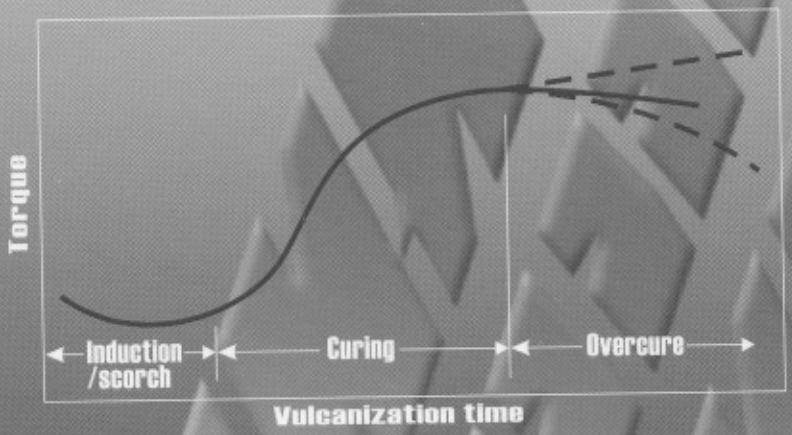
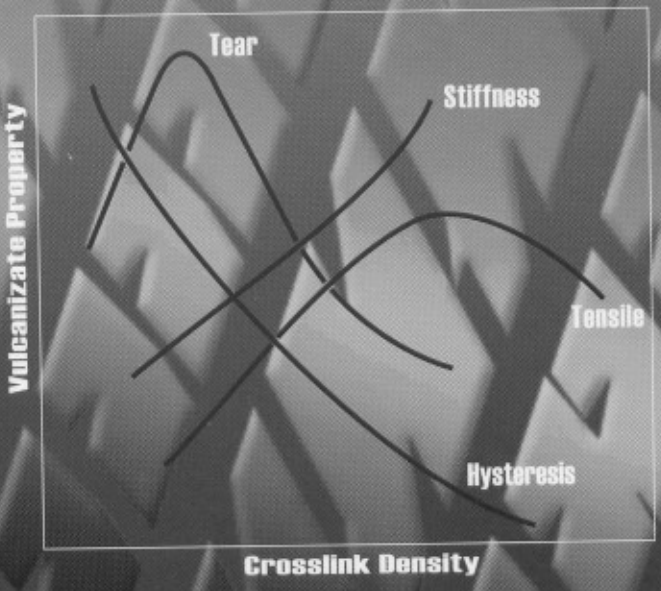
Basic Elastomer Technology

Edited by **KRISHNA C. BARANWAL**
HOWARD L. STEPHENS





RUBBER DIVISION

CHAPTERS

1. RUBBER COMPOUNDING—HISTORICAL PERSPECTIVE

BENJAMIN KASTEIN

2938 OVERLOOK RD., CUYAHOGA FALLS, OHIO 44224

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I. RUBBER APPRECIATION

Rubber is a fascinating, marvelous material with a unique combination of properties. The compounder originates recipes to optimize one, several, or all of rubber's inherent capabilities to provide a compound that will be molded or formed into the desired useful marketable produce.

A rubber band is an example that utilizes the stretch nature of rubber. A tire tread needs to be primarily flexible and abrasive resistant. A special inner-liner of the tire has amazing resistance to air permeation while rubber boots need to be water proof. These are only a few examples of the usefulness of rubber; the list is almost endless.

The compounder has to know what materials are available for his purpose. And regardless of how many years of experience he/she can rely on, there is never any end to the accumulation of new knowledge. The compounder's knowledge and talents concoct a recipe that provides the desired physical properties required in the end product for satisfactory service and performance. In addition, attention is directed to give to the recipe ingredients to achieve ease and safety of processing behavior of the compound during mixing, extrusion and calendering in the factory prior to the forming, molding and curing of the product. Premature scorch, set-up or curing during processing, must be avoided.

To be a rubber compounder is a challenging assignment. To have the title "Rubber Compounder" is to receive recognition for a professional achievement. Com-

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2.A. ELASTOMER TECHNOLOGY OVERVIEW

HOWARD L. STEPHENS
EMERITUS PROFESSOR OF POLYMER SCIENCE AND CHEMISTRY, DEPARTMENT OF POLYMER SCIENCE, THE UNIVERSITY OF AKRON, AKRON, OH 44325-3909

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I. INTRODUCTION

Anyone new to the rubber industry should have a background in the fundamentals involved in the selection, preparation, and testing of the materials used to prepare useable products. It is the purpose of this chapter to describe the nomenclature, classification and the methods used for the preparation of synthetic elastomers and their molecular structure and size. The remaining chapters will describe in detail how these elastomers are prepared, modified, tested and utilized in the rubber industry.

For this purpose, the author assumes that everyone has had some background in their training, either in grade school or high school or perhaps in college courses, and is acquainted with the concept of atoms, elements and molecules. The general terms used in this regard are defined in Table I.

The special terminology used in this chapter is given in Table II. These definitions are from the American Society for Testing and Materials (ASTM) publication Book of Standards, Volume 9.01 on Rubber, Natural and Synthetic, Method D 1566. This volume and others from the same source are used extensively by our industry, and one should be aware of these test methods and specifications.

2.B. RUBBER SCIENCE AND TECHNOLOGY PUBLICATIONS

JOAN C. LONG
RUBBER DIVISION ACS LIBRARY, THE UNIVERSITY OF AKRON, AKRON, OHIO
44325-3907

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Although the literature of the science and technology of rubber is not as abundant as that of polymer science and technology, a number of significant books and handbooks have been published in the last decade. On the following pages, the books relating to rubber science and technology have been classified according to those that are more general in nature, and those that cover the aspects of compounding and processing, properties and engineering, and testing. Special categories have been included for books on rubber blends, natural rubber and latices, scrap rubber, thermoplastic elastomers and for the history of rubber. Abstracting and indexing services are included as well as information on conference proceedings and papers, standards, the major periodicals that cover rubber science and technology, and sources of information on industry trade and statistics.

A number of publications, particularly databases, handbooks and directories, have become available as CD-ROMs as well as in printed format, and some publications are available on the worldwide web. These additional formats are indicated

3. INTRODUCTION TO RUBBER COMPOUNDING

KRISHNA C. BARANWAL
AKRON RUBBER DEVELOPMENT LABORATORY, 2887 GILCHRIST ROAD, AKRON, OH 44305

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I. INTRODUCTION

Rubber compounding includes selection of proper ingredients to enable one to process compound and vulcanize to give desirable physical and chemical properties, especially after aging. Elastomers by themselves are not useful until they are properly mixed with the proper ingredients and cured. Depending on the type of rubber products, various ingredients are used. Each ingredient has specific function in imparting desired properties.

Compounding of rubber involves several steps. First is the recipe selection with proper ingredients and correctly weighing each ingredient. The selected formulation should be easily processable, *i.e.*, mixing, calendering and extrusion with maximum scorch safety. It can be then molded and cured within a reasonable time period to produce a specific product with desired properties. These steps should be performed at the lowest possible cost. Thus, rubber compounding has three very important criteria, which the author calls three P's; they are processing, properties and price.

In this chapter, the discussion includes the basic steps of compounding, functions of major ingredients, some common properties and selected test methods. The purpose of this chapter is to acquaint a new compounder with basics of compounding. Other chapters in this book provide more detailed information on elastomers, fillers, processing aids, curing agents, test methods and properties.

4. FILLERS—
A. CARBON BLACK

MICHEL GERSPACHER AND WESLEY WAMPLER

SID RICHARDSON CARBON CO., 4825 N. FREEWAY, FORT WORTH, TEXAS 76106

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I. INTRODUCTION

Carbon black is a material that has been known and produced since antiquity but only found its widespread manufacture and use in the last century when it was discovered that when mixed into rubber it improves its mechanical properties. The

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4. FILLERS—
B. NON-BLACK

JOHN T. BYERS

DEGUSSA–HÜLS CORPORATION, AKRON, OH

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5. PROCESSING METHODS IN THE RUBBER INDUSTRY

PETER S. JOHNSON
PROCESSING CONSULTANT, 1098 HAGLE STREET, SARNIA, ONTARIO, CANADA N7V4B1

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I. INTRODUCTION

Raw rubber as received from the manufacturer, or from the plantation in the case of natural rubber, has few uses as such. It has to be mixed with various compounding ingredients, shaped, and vulcanized to give a useable end product. These three components, mixing, shaping, and curing, together, constitute rubber processing.

Mixing is central to rubber processing. If the base compound is inadequately mixed, problems cascade down through the subsequent processes or shaping and curing into the end product. There are three general shaping processes: extrusion, calendering and molding—compression, transfer, or injection type.

Rubber is a difficult material to process because it has both viscous and elastic properties. But, even more than this, because of the infinite variety of possible compounds that can be prepared from any grade of rubber, it is difficult to predict mixing, molding, or extrusion behavior of a compound based on the properties of the raw rubber alone. Depending on the type and quantity of carbon black, plasticizer, other fillers, etc. used, the resulting compound may be difficult, or easy, to mix, shape, and cure. However, a compound is formulated, first and foremost, to meet end-application requirements, not merely to process well. The processing plant has to adjust its process to suit the compound, not the other way around. However, it is of no value to present the plant with a compound impossible to mix or process. Therefore, there has to be an integration between the compound,

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6. TESTING RUBBER DURING PROCESSING AND VULCANIZATION

ROBERT I. BARKER
166 MELODY DR., AKRON, OH 44321
AND
ALFRED B. SULLIVAN
396 HIGHPOINT DR., WADSWORTH, OH 44281
AND
R. WARREN WISE
12982 KEDLESTON CIRCLE, FT. MYERS, FL 33912

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I. INTRODUCTION

A. HISTORICAL PERSPECTIVE

From the beginnings of the rubber industry there have been major problems with the determination of the processibility and uniformity of elastomeric materials. An excellent review article by White and Soos[1] details the history of processibility

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7. VULCANIZATION OF RUBBER—A. SULFUR AND NON-PEROXIDES

CHARLES P. RADER
ADVANCED ELASTOMER SYSTEMS, L.P., 288 SOUTH MAIN ST., AKRON, OHIO 44311

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I. DEFINITION

Vulcanization is the process by which rubber is changed from essentially a plastic material to either an elastic or a hard material. As a plastic material unvulcanized rubber readily undergoes permanent deformation; whereas, vulcanized rubber is highly elastic and resistant to plastic deformation. Elastomeric rubber is much more commercially important than hard rubber (ebonite) and differs only in its lower content (0.5–6%) of vulcanizing agent. (Figure 1).

Rubber is normally vulcanized by heating with a vulcanizing agent (usually sulfur plus an accelerator) at a temperature between 120 and 200°C in a mold of the desired shape and size. Vulcanized rubber is thermosetting since it cannot be remolded, in contrast to a thermoplastic material (*e.g.*, polyethylene) which can be. The properties of rubber are improved dramatically by vulcanization. This improvement has made it an extremely important industrial process, enabling the economical

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7. VULCANIZATION OF RUBBER—B. PEROXIDES

J. B. Class and Peter R. Dluzneski

Hercules Incorporated, 500 Hercules Road, Wilmington, DE 19808

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I. HISTORY

Benzoyl peroxide was first made in 1858 by Brodie[1], but commercial interest in this compound did not begin until the early 1900s after it was observed to be an effective bleaching agent for edible oils and flour.[2] In 1915, Ostromislenski[3] discovered that benzoyl peroxide could be used to vulcanize rubber. The peroxide curing mechanism was further elucidated by Fisher and Gray[4] who found that the unsaturation in the rubber was not affected by this vulcanization process. It was then assumed that peroxide crosslinking does not depend on double bonds.

Despite its ability to cure rubber, benzoyl peroxide was not widely used because it was observed that peroxide-cured rubber had low strengths and poorer aging properties than sulfur vulcanizates.[5] With the advent of polyethylene in the 1930s, benzoyl peroxide enjoyed renewed interest since sulfur was ineffective in vulcan-

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8. PHYSICAL TESTING OF RUBBER

R. J. Del Vecchio
Technical Consulting Services, 5228 Beckwyck Dr.,
Fuquay-Varina, North Carolina 27526

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I. INTRODUCTION

Everyone understands the need for testing. Whether it is a Law School graduate being required to take the Bar exam or a batch of antibiotic being checked for biological activity or an O-ring rubber compound undergoing compression set testing, the effort and expense of testing are borne in order to create a level of confidence that some function will be fulfilled as intended/needed. Society does not want to

9. GENERAL PURPOSE ELASTOMERS— B. STYRENE BUTADIENE RUBBERS (SBR)

BENJAMIN KASTEIN

2938 OVERLOOK ROAD, CUYAHOGA FALLS, OH 44224

AND

KRISHNA C. BARANWAL

AKRON RUBBER DEVELOPMENT, INC, 2887 GILCHRIST ROAD, AKRON, OH 44305

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I. HISTORY

A. EMULSION SBR

Production of Government Rubber-Styrene, GR-S, began as a war time emergency to provide a material suitable to replace natural rubber in the many products where the unique properties of natural rubber were essential. To list only a few would include passenger, truck and aircraft tires, tank treads and many non-tire uses such as insulation for wire and cable, hoses and gaskets.

Scientists for years had tried to find a replacement for natural rubber but most efforts have attempted to duplicate the major monomer of natural rubber, isoprene. Two German scientists, Drs. Tschunker and Bock,[1] made an elastomer by the then unusual procedure of polymerizing in emulsion, two dissimilar monomers, butadiene

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10. SOLVENT RESISTANT ELASTOMERS—A.I. NITRILE RUBBER (NBR)

M. S. JONES

ZEON CHEMICALS, L.P., P.O. BOX 37620, LOUISVILLE, KY 40233-7620

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I. INTRODUCTION

A. HISTORY

The very earliest record of nitrile rubber in the literature is found in a French patent issued in 1931. Nitrile rubber (NBR) was first commercially produced in Germany in 1935. Domestic production was begun in January 1939 by The B.F. Goodrich Co.[1]. The earliest nitrile polymers were what today are considered hot polymers (polymerized at 30°C and above). Drawing from information obtained in 1945 from captured German synthetic rubber plants, the production of cold

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11. TEMPERATURE RESISTANT ELASTOMERS—A. POLYSULFIDE RUBBER

CINDY HANSON

ROHM AND HAAS COMPANY, 1275 LAKE AVE., WOODSTOCK, IL 60098

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I. INTRODUCTION

There are several definitions for polysulfide type polymers. The Condensed Chemical Dictionary defines polysulfide as "a synthetic polymer in either solid or liquid form obtained by the reaction of sodium polysulfide with organic dichlorides...alone or mixed with ethylene dichloride."[1] Lucke defines polysulfide as "...pre-polymers of aliphatic molecule segments, which are linked together...by two or more sulfur atoms and which contain mercaptan end-groups...."[2] Mercaptan-terminated polymers that do not contain disulfide bridges or sulfur in the backbone of the polymer but have reactive mercaptan end groups and monosulfide linkages in the backbone are called polymercaptan polymers. This chapter will review the class of materials that have disulfide linkages in the backbone of the polymer.

Polysulfide polymers are characterized by their excellent resistance to various fuels, oils, solvents, their low temperature properties, excellent weathering properties, and vapor impermeability. They have moderate physical properties and compression set resistance, a strong odor, and can be difficult to process. They can be blended with other elastomers which helps overcome some of the negative characteristics without severely effecting the solvent resistance and low temperature flexibility.

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12. LATEX AND FOAM RUBBER

ROBERT F. MAUSSER*

38 SPORTSMAN DR., SHELTON, CONNECTICUT 06484

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I. BACKGROUND AND INTRODUCTION

The production of articles from latex can be considered as both the older and newer of rubber technologies. The older because natives of South and Central America were the first persons to produce and use rubber goods. Goods such as water-proof clothing, water bottles, balls, and shoes were fabricated from natural latex. Excavations indicate that natives used rubber products in religious ceremonies as early as the 6th century A.D.[1]

Christopher Columbus was the first European to discover rubber goods: during his second voyage to the "New World" he found Haitian natives playing with rubber balls. It was he and other early explorers who introduced rubber products to Europe. The first samples of "dry" rubber were sent to France from Peru by Charles de la Condamine[2] in the year 1736. Attempts were made to produce rubber articles from "dry" rubber both at home and in Europe during the late 18th and early 19th centuries. The goods were generally of poor quality and durability. It was not until Charles Goodyear (USA) 1839 and Thomas Hancock (UK) 1842–43, working independently, discovered the process of vulcanization (use of sulfur and heat to cure rubber) that quality durable goods could finally be produced from

* Deceased, Feb. 1999. The Editors wish to thank his widow, Lillian Mausser, and family for supporting the completion of this chapter. It represents a tribute for his many contributions to latex technology and the rubber industry in general.

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13. THERMOPLASTIC ELASTOMERS

GEOFFREY HOLDEN
HOLDEN POLYMER CONSULTING, INCORPORATED, PMB 473, 1042 WILLOW CREEK ROAD, A101, PRESCOTT, AZ 86301-1670

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I. INTRODUCTION

The use of thermoplastic elastomers has significantly increased since they were first produced about thirty-five years ago. A recent article[1] estimates their worldwide annual consumption at about 1,000,000 metric tons/year in 1995 and this is expected to rise to about 1,400,000 metric tons/year in 2000. Three books have covered this subject in detail: one mostly deals with the scientific aspects[2]; another is an introduction to the subject[3]; and the last book concentrates on the end uses of these materials.[4]

The properties of thermoplastic elastomers in relation to other polymers are summarized in Table I.

TABLE I
COMPARISON OF THERMOPLASTIC ELASTOMERS WITH CONVENTIONAL PLASTICS AND RUBBERS

Type elastomer	Thermosetting	Thermoplastic
Rigid	Epoxies Phenol–formaldehyde Urea–formaldehyde	Polystyrene Polypropylene Poly(vinyl chloride) High density polyethylene
Flexible	Highly filled and/or highly vulcanized rubbers	Low density polyethylene EVA Plasticized PVC
Rubbery	Vulcanized rubbers (NR, SBR, IR, etc.)	Thermoplastic Elastomers

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14. RECYCLING OF RUBBER

KRISHNA C. BARANWAL
AKRON RUBBER DEVELOPMENT LABORATORY, 2887 GILCHRIST ROAD, AKRON, OH 44305

AND

WILLIAM K. KLINGENSMITH
AKRON CONSULTING CO., P.O. BOX 19009, AKRON OH, 44319

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I. INTRODUCTION

In the late 1980s and early 1990s, there was a movement on a national and international scope to deal with and address a perceived scrap rubber problem. For example, with U.S., what to do with the 270–280 million scrap tires a year along with associated 300–500 million pounds of scrap rubber produced in the manufacture of rubber goods. With the passage of the Intermodal Surface Transportation Efficiency Act (ISTEA), numerous companies, often with state's treasury funding much of the project, were created. The act required the incorporation of rubber crumb into asphalt road paving on all federally funded road project. A bonanza

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