RUBBER COMPOUNDING

PRINCIPLES, MATERIALS, AND TECHNIQUES

FRED W. BARLOW

Rubber Compounding

Principles,
Materials.

江海山山南岛岛南部
萩 书章

Fred W. Barlow Rubber Consultant Stow, Ohio

Library of Congress Cataloging in Publication Data

Barlow, Fred W.

Rubber compounding: principles, materials, and techniques / Fred W. Barlow.

p. cm. -- (Plastics engineering; 20)

Includes bibliographies and index.

ISBN 0-8247-7851-0

1. Rubber. 2. Elastomers. 3. Rubber chemicals. I. Title.

II. Series: Plastics engineering (Marcel Dekker, Inc.); 20..

TS1890.B268 1988

678'.23--dc19

87-37208

CIP

Copyright © 1988 by MARCEL DEKKER, INC. All Rights Reserved

Neither this book nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage and retrieval system, without permission in writing from the publisher.

MARCEL DEKKER, INC. 270 Madison Avenue, New York, New York 10016

Current printing (last digit): 10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

Preface

Long ago someone described a book's preface as the author's excuse for writing the book. So I'll start by giving mine. Currently, there are few books that deal exclusively with rubber compounding. There are many courses on rubber compounding available to those in the rubber industry. These courses consist mostly of lectures on rubber-compounding materials by experts, usually from supplier companies. Although the material presented is generally excellent and up to date, deficiencies or difficulties encountered with the ingredients may be understated, and there is not an ongoing attempt to weave the information together to show how compounds are built up. This book is an attempt to fill those voids.

iv PREFACE

The author has at one time or another worked with the compounding of all the polymers described here. But obviously no comprehensive book on compounding can be written from the experience and remembrances of one person. Accordingly, the voluminous technical literature has been freely consulted and used. A constant problem has been judging what would be most useful to include. Certainly carbon blacks and accelerators cannot be excluded but what about fire retardants and mold release agents? This book contains brief notes on fire retardants but mold release agents have been omitted.

It is inevitable in a book of this kind that errors will creep in and for these the author takes sole responsibility. Although rubber technology is not changing as fast as some other technologies, it is changing and this means the information will change in time. It cannot be too strongly urged that compounders keep in close touch with their suppliers, environment officials, customers, and the technical literature to make sure they stay close to the "cutting edge."

Successful compounding!

Fred W. Barlow

Contents

Preface	9	iii
One: I	ntroduction to Compounding	1
I.	Scope	1
II.	Demands and Rewards	3
III.	Classification of Materials	3
IV.	Training for Compounding	4
Two: E	Elastomers: Natural and Styrene-Butadiene Rubber	11
I.	Scope	11
II.	Chemical Structures	12
III.	Natural Rubber	17

vi CONTENTS

IV.	Styrene-Butadiene Rubber	31
Refe	erences	44
Three:	Elastomers: Polybutadiene and Chloroprene Rubber	45
I.	Scope	45
II.	Polybutadiene Rubber	46
III.	Chloroprene Rubber	51
	erences	58
10010	7.011000	00
Four:	Elastomers: Butyl and Ethylene Propylene Rubbers	59
I.	Scope	59
II.	Butyl (IIR) Rubber	60
III.	Ethylene Propylene Rubbers (EPM and EPDM)	66
Refe	erences	72
Five: E	Elastomers: Nitrile, Polysulfide, and Reclaimed Rubbers	75
I.	Scope	75
	Nitrile Rubber	76
III.	Polysulfide Rubber	84
	Reclaimed Rubber	87
Refe	erences	94
Six: V	ulcanizing Agents	97
I.	Introduction	97
	Sulfur Curing Systems	101
	Peroxide Curing Systems	103
	Urethane Crosslinkers	108
V.	Metallic Oxides	111
Refe	erences	112
Couran	Aggalaratava	445
	Accelerators	115
I.	Introduction	115
	Theory of Use	118
III.	Types and Applications	121

CONTENTS	vii

IV.	Special Applications	127
Ref	erences	129
e		
Eight:	Activators and Retarders	131
I.	Activators	131
II.	Retarders	134
Ref	Cerences	136
Nine:	Reinforcers: Carbon Blacks	137
I.	Introduction	137
	Properties	138
	Reinforcement	143
	Manufacture	144
	Grading Carbon Blacks	148
	Compounding	149
Ref	erences	166
Ten: N	Ion-Black Fillers	169
I.	Introduction	169
	Clay	171
	Silica and Silicates	178
	Calcium Carbonate	183
Ref	erences	185
Eleven	: Processing Aids	187
I.	Peptizers	187
II.	Semipeptizers	190
III.	Processing/Dispersing Agents	190
	Compounding with Processing Aids	193
Refe	erences	194
Twelve	e: Plasticizers and Softeners	197
I.	Introduction	197
	Petroleum-Based Softeners	199
III.	Pine Products	209

viii CONTENTS

IV.	Synthetic Resins	211
V.	Esters	213
VI.	Natural Fats and Oils	214
Refe	erences	215
Thirtee	en: Age Resisters	217
I.	Introduction	217
II.	Theories on Oxidative and Ozone Attack	219
III.	Effects of Oxygen and Ozone Attack	220
IV.	Antioxidant and Antiozonant Types	222
V.	Antioxidant and Antiozonant Protective Mechanisms	224
VI.	Using Age Resisters in Compounding	226
Refe	erences	232
Fourte	en: Miscellaneous Ingredients	233
I.	Introduction	233
II.	Blowing Agents	234
	Rubber Chemical Dispersions	236
	Flame Retardants	238
V.	Colorants	240
VI.	Bonding Agents	245
Refe	rences	248
Fifteer	n: Compound Development—Part 1	249
I.	General Principles	249
	Illustrative Examples	259
Sixtee	n: Compound Development—Part 2	271
Ref	erences	278
Sevent	een: Testing and Specifications	281
I.	Testing	281
II.		290
_	Specifications Serences	294

Appendixes:	
One: Unit Volume and Density	295
Two: Abbreviations	299
Three: Weights, Measures, and Conversion Factors	303
Four: Density and Unit Volume of Compounding	
Materials	309
Five: Principal Physical Properties of Rubber and	
their Coefficients of Change	313
Index	317

One | Introduction to Compounding

SCOPE

This book was written to provide a guide to modern compounding, to describe the materials involved as well as why and how they are used to build up a compound. Many technologists would agree that rubber compounding is still more of an art than a science, so the emphasis is on simplicity, common usage, and understanding. However, where scientific study is providing answers, pertinent material is included or noted. The book is fashioned to serve the needs of the beginning compounder as well as providing a useful reference for those more advanced or who serve the rubber goods industry as suppliers, for example.

The compounding, mixing, and testing of rubber stocks covers a formidable array of materials and technics. To attempt to cover all would mean a cumbersome and disjointed work. Accordingly this text is only concerned with six general-purpose rubbers and two specialty rubbers. The six general-purpose rubbers are natural, styrene-butadiene, polybutadiene, butyl, ethylene-propylene, and neoprene. These are called general-purpose rubbers because of their usage in a wide variety of products. The two specialty rubbers are butadiene-acrylonitrile and polysulfide rubbers. These rubbers are primarily chosen for their solvent resistance, especially petroleum-derived solvents, and find use in such applications as gasoline and paint spray hose tubes. A section on reclaimed rubber is included. The above rubbers would include over 96% of the world's consumption.

Although they have different shades of meaning, the terms polymers, elastomers, and rubbers will be used interchangeably in this book to avoid repetition. No matter what term is used the compounder does have a mountain of these to work with. In 1985 the International Rubber Study Group estimated that 13,325,000 metric tons of rubber was produced. Of this 32.6%, 4,340,000 tons was natural; the remaining 67.4% synthetic. Production of all rubbers usually follows consumption closely and growth in the last 5 years has been slow. Production of all rubbers in 1985 was only about 6% above that of 1980.

The variety of rubber compounds used is enormous. One company with which the writer was associated — a mechanical rubber goods producer — had formulas for 800 compounds, although normal inventories consisted of only a fraction of that number. Considering the variety of rubber products and the number of manufacturers, it would appear that thousands of compounds are available if not in regular use. Whether such large numbers are necessary is questionable. The smaller the number of compounds a manufacturer can satisfy his customers with, the greater the savings in cost accounting, longer mixing runs, warehousing, loss from storage hardening, and quality control costs.

INTRODUCTION 3

II. DEMANDS AND REWARDS

Good compounding means formulas are developed which are environmentally safe, factory-processable, provide a satisfactory service life, and are cost-competitive to other compounds used in the same application. These requirements put considerable demands on the compounder. That person must have at least extensive knowledge of materials as diverse as carbon black and paraffin wax, sulfur, and ester plasticizers. There must be sufficient familiarity with rubber-processing equipment for reasonable assurance the compounds can be processed without difficulty. Costs are always a major concern and constantly increasing environmental safety regulations must not be overlooked. A heavy endowment of unflappability and detective ability is required when a hitherto smooth-running compound seems to be causing an unacceptable percentage of rejects just when there is a rush order from a valued customer. But the rewards are great, there are no safety hazards to anyone, and the customer is satisfied with goodquality product. With low scrap losses, reduced energy consumption from less reworking of bad compound, and a cost-competitive compound, factory profit possibilities are enhanced. All of this gives a satisfying sense of accomplishment to the compounder.

III. CLASSIFICATION OF MATERIALS

It is customary when discussing compounding to classify the materials used by the function they serve. Some materials, such as zinc oxide, can behave in more than one way. In this book the following classifications will be used:

- 1. Elastomers
- 2. Vulcanizing or cross-linking agents
- 3. Accelerators
- 4. Activator/retarders
- Process aids
- 6. Softeners and plasticizers

- 7. Reinforcers-black
- 8. Reinforcers/fillers non black
- 9. Age resisters
- 10. Miscellaneous materials

A chapter (two in the case of elastomers) is devoted to each class in turn and the remainder of the book is devoted to how this information is used for commercial compounding.

IV. TRAINING FOR COMPOUNDING

Training for rubber compounding is usually on-the-job training in the United States with entry level jobs often taken by science or engineering graduates. Not infrequently the latter are from chemistry or chemical engineering courses rather than physics. This is somewhat strange for although chemical problems exist in such areas as vulcanization and aging, it is the physical properties of rubber that are most appreciated in its service applications.

In some countries rubber technology is taught as a college level course. One of the best known is the London School of Polymer Technology (formerly known as the National College of Rubber Technology) in England. A licentiateship course is offered which is roughly equivalent to a high-school leaving level; a more rigorous course is the associateship level, equivalent to a bachelor of science degree. Because of its high reputation the school attracts students world wide. As a good illustration of what compounding is about and the knowledge needed to be a successful compounder, two recent examinations are reproduced below.

A typical compound for a first grade conveyor belt cover is shown in Table 1.1. Compounds do not always require material from each of the classes above. This compound indicates in a very general way the amount of each class of these materials usually used. With certain classes of materials, such as age resisters, there are many nongeneric materials and trademarked materials are specified. A common convention among compounders is to base formulations on 100 parts of elastomers and to list the elastomer

INTRODUCTION 5

Table 1.1 Conveyor Belt Cover Compound

Material	Parts	Functional class
Natural rubber (SMRCV)	100,0	Elastomer
N 220 Carbon black	45.0	Black reinforcer
Zinc oxide	4.0	Activator
Stearic acid	2.0	Activator
Rubber process oil	4.0	Softener
Agerite Resin D ^a	2.5	Age resister
Paraffin wax	1.0	Age resister
CBSb	0.5	Accelerator
Sulfur	2.5	Vulcanizing agent
	161.5	

aVanderbilt Company trade name.

first. Less widely observed but useful is placing the accelerators and vulcanizing agent at the end of the compound so that curative systems can be quickly identified.

In rubber technology English, metric and SI units are commonly encountered in the literature. Appendix III, Weights, Measures, and Conversion Factors, gives the various relations and illustrates a method for more fool-proof conversions from units of one type to another.

^bAbbreviation for n-cyclohexylbenzothiazole-2-sulfenamide.

National College of Rubber Technology Licentiateship Course in Polymers 1981

Paper 3R: Rubber Chemistry and Technology (Rubber option candidates only)

Answer FIVE questions

- 1. Compare the raw material, processing and vulcanizate properties of natural rubber and emulsion polymerized SBR.
- 2. Suggest an appropriate rubber for each of the following applications:
 - (a) car windscreen seal;
 - (b) tyre inner tube;
 - (c) petrol tank seal;
 - (d) car engine mounting.

Give reasons for your choice in each case. For one of the products suggest a mix formulation, paying particular attention to the curing system. Briefly outline any special features of mixing and moulding procedures for the formulation selected.

- 3. Survey the developments over the last 70 years, in rubber compounding ingredients.
- 4. Write notes on TWO of the following:
 - (a) the main effects of filler characteristics on vulcanizate properties;
 - (b) the various types of aging of rubbers and means of limiting such aging;
 - (c) colouring materials for non-black rubber compounds.
- 5. You are given a hydrocarbon rubber compound. Describe what steps you would take to separate and estimate the components of the compound.

A rubber compound (2.032 g) was extracted with acetone and 0.407 g of extract obtained. A portion of the extract-

This test and the one that follows are reproduced with the permission of the London School of Polymer Technology, London, England.

INTRODUCTION 7

ed rubber (0.972 g) was heated in a porcelain boat at 550°C in a nitrogen atmosphere and 0.595 g remained. This was further heated in a furnace at 550°C and 0.105 g remained. Determine in parts per hundred of rubber polymer:

- (a) the acetone extract;
- (b) the carbon black content;
- (c) the mineral filler content.
- 6. Describe how ozone causes cracking in a rubber. Name one antiozonant and describe its mode of action.
- 7. What do you understand by the term S-B-S triblock polymers? Describe the physical nature of these materials at:
 - (a) -120°C;
 - (b) 20°C;
 - (c) 140°C.

Give reasons for the differences. What are the main applications of the polymers?

 Compare the properties of vinylidene fluoride-hexafluoroprene copolymers, ethylene-methyl acrylate copolymers and polydimethylsiloxanes as heat resisting rubbers. Include in your answer references to mechanical and chemical properties.