

John S. Dick

# How to Improve Rubber Compounds

1800 Experimental Ideas for Problem Solving



2<sup>nd</sup> Edition

HANSER

Dick

## **How to Improve Rubber Compounds**



John S. Dick

# How to Improve Rubber Compounds

1800 Experimental Ideas for Problem Solving

2<sup>nd</sup> Edition

Hanser Publishers, Munich

**HANSER**  
Hanser Publications, Cincinnati

*The Author:*

John S. Dick,  
2915 Stanley Rd., Fairlawn, OH 44333, USA  
John.Dick@dynisco.com  
www.rubberchemist.com

Distributed in North and South America by:  
Hanser Publications  
6915 Valley Avenue, Cincinnati, Ohio 45244-3029, USA  
Fax: (513) 527-8801  
Phone: (513) 527-8977  
www.hanserpublications.com

Distributed in all other countries by  
Carl Hanser Verlag  
Postfach 86 04 20, 81631 München, Germany  
Fax: +49 (89) 98 48 09  
www.hanser-fachbuch.de

The use of general descriptive names, trademarks, etc., in this publication, even if the former are not especially identified, is not to be taken as a sign that such names, as understood by the Trade Marks and Merchandise Marks Act, may accordingly be used freely by anyone. While the advice and information in this book are believed to be true and accurate at the date of going to press, neither the author nor the editors nor the publisher can accept any legal responsibility for any errors or omissions that may be made. The publisher makes no warranty, express or implied, with respect to the material contained herein.

Library of Congress Cataloging-in-Publication Data

Dick, John S.

How to improve rubber compounds : 1800 experimental ideas for problem solving / John S. Dick. -- 2nd edition.

pages cm

ISBN 978-1-56990-533-3 (hardcover) -- ISBN 978-1-56990-534-0 (e-book) 1. Rubber. 2. Rubber, Artificial. I. Title.

TA455.R8D53 2014

678:23--dc23

2013037811

Bibliografische Information Der Deutschen Bibliothek

Die Deutsche Bibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliografie; detaillierte bibliografische Daten sind im Internet über <<http://dnb.d-nb.de>> abrufbar.

ISBN 978-1-56990-533-3

E-Book ISBN 978-1-56990-534-0

All rights reserved. No part of this book may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying or by any information storage and retrieval system, without permission in writing from the publisher.

© Carl Hanser Verlag, Munich 2014

Production Management: Steffen Jörg

Coverconcept: Marc Müller-Bremer, [www.rebranding.de](http://www.rebranding.de), München

Coverdesign: Stephan Rönigk

Typesetted by Manuela Treindl, Fürth

Printed and bound by Kösel, Krugzell

Printed in Germany

# Disclaimer

The information contained in this book is experimental in nature and is directed towards individuals with advanced scientific training and rubber compounding experience. The author, review panel members, editors, and publisher make no representation or warranties, either expressed or implied, with respect to the accuracy, currency, completeness, or suitability of the information contained in this book and will not be liable for any damages, costs or liability arising out of any use of material contained in this book for any purpose including, without limitation, technical inaccuracies and typographical errors.



# Preface

Rubber compounding is an art as well as a science. This book is intended to be a companion for the earlier book titled *Rubber Technology: Compounding and Testing for Performance*. As indicated in the preface of the earlier edition of this book, the art in rubber compounding is to achieve the best trade-offs in properties and to be able to meet product performance requirements at acceptable production costs.

The objective of this book is to provide the experienced and well-trained rubber compounder with new experimental ideas, which he or she may be able to use to improve certain specific rubber compound properties. Of course, when compounders are considering implementing some of these general experimental ideas for their specific compounds, not only should they thoroughly check out the effects on the target compound property, but also how this change will be affecting other compound properties as well. Generally, any specific change in a rubber compound will certainly affect a wide range of other properties for better or for worse. There always appear to be a wide range of “unintended consequences,” which have to be thoroughly checked out through laboratory testing, factory trials, controlled field evaluations, and so forth. All companies should have a formal approval process and sign-off procedures before any compounding change is allowed in production. Many times, the effective improvement of a rubber compound requires not just one change but an intelligent selection of multiple changes in order to achieve the best overall compromise (best trade-off) in compound properties to more effectively meet the product’s performance requirements.

The new edition now contains over 1800 experimental ideas to improve specific rubber compound properties, which are organized in five chapters covering improving cured physical properties, degradation resistance, measurable processability properties, qualitative processing attributes, and tire performance properties. In addition, this book includes an appendix on rubber blends commonly used for specific product applications and an appendix on commonly used cure systems. The majority of these experimental ideas were

found from a thorough review of the general rubber literature. Another set of experimental ideas was obtained from the companion book mentioned above. Also, a very important source of additional experimental ideas from the first edition was the contributions of the eighteen-member Review Panel for this book (listed in Section 1.6). The additional ideas published in the 2nd edition are the result of an extensive review of over one thousand recent journal articles and conference presentations from rubber societies in the United States, Europe, China, and India.

The experimental ideas given in this book may not work in all specific situations. Changes to improve one target compound property will certainly affect other properties as well, for better or for worse, and this book does not purport to show how these other properties are affected. Also, this book does not purport to address safety and health issues. The information contained in this book is experimental in nature and is meant for individuals with advanced scientific training and rubber compounding experience.

September 2013, John S. Dick

*www.rubberchemist.com*

# Contents

Disclaimer .....	V
Preface .....	VII
<b>1 Introduction .....</b>	<b>1</b>
1.1 Complexity of Compound Ingredient Selection .....	1
1.2 Industrial Complexity.....	3
1.3 Complexity of Ingredient Property Relationships .....	3
1.4 Experimental Ideas .....	6
1.5 Sources of Ideas .....	7
1.6 Review Panel.....	8
<b>2 Improving the Physical Properties of Cured Rubber Compounds.....</b>	<b>9</b>
2.1 Increasing Tensile Strength .....	9
2.2 Increasing High-Temperature Tensile Strength .....	23
2.3 Increasing Ultimate Tensile Elongation .....	25
2.4 Increasing Hardness and Modulus.....	30
2.5 Reducing Set, Under Compression and/or Tension.....	43
2.6 Increasing Rebound and Decreasing Hysteresis .....	52
2.7 Increasing Tear Resistance.....	69
2.8 Increasing Hot Tear Resistance.....	79
2.9 Improving Low-Temperature Properties.....	83
2.10 Increasing Electrical Conductivity .....	90
2.11 Increasing Thermal Conductivity.....	98
2.12 Decreasing Coefficient of Friction .....	101
2.13 Decreasing Air Permeability .....	102
2.14 Increasing Rubber-to-Metal Adhesion .....	105
2.15 Improving Rubber-to-Fabric Adhesion.....	110
2.16 Improving Flame Retardance.....	111
2.17 Reducing Compound Cost.....	115

3	Improving Degradation Resistance of Cured Rubber Compounds .....	125
3.1	Improving Hot Air and/or Heat Aging Resistance .....	125
3.2	Improving Ozone Resistance .....	144
3.3	Improving Flex Fatigue Resistance and/or Cutting and Chipping Resistance .....	153
3.4	Improving Abrasion and/or Wear Resistance .....	170
3.5	Improving Oil and/or Solvent Resistance .....	183
3.6	Improving Staining and Discoloration Resistance .....	192
3.7	Improving Weathering Resistance .....	194
3.8	Improving Hydrolysis Resistance .....	196
4	Optimizing Measurable Processability Properties .....	197
4.1	Reducing Viscosity .....	197
4.2	Increasing Shear Thinning .....	203
4.3	Reducing Elasticity (Nerve) .....	205
4.4	Increasing Tack .....	207
4.5	Reducing Stickiness to Metal Surfaces .....	212
4.6	Increasing Percent Dispersion of Carbon Black and Fillers .....	214
4.7	Increasing Green Strength .....	222
4.8	Increasing Scorch Safety Time .....	228
4.9	Increasing Cure Rate .....	239
4.10	Reducing Reversion .....	247
4.11	Reducing Marching Modulus .....	253
4.12	Reducing Cold Flow .....	254
5	Minimizing Adverse Processing Attributes .....	255
5.1	Reducing or Eliminating Porosity, Bubbles, or Voids in Both the Uncured and the Cured State .....	255
5.2	Mixing: Reducing Filler or Black Incorporation Times (BITs) .....	262
5.3	Mixing: Decrease Total Mixing Time .....	264
5.4	Mixing: Reducing or Eliminating Lumps in Dumped Batches .....	268
5.5	Mixing: Reducing Bagging on the Mill .....	269
5.6	Mixing: Reducing Back Rolling on the Mill .....	270
5.7	Extrusion: Reducing Die Swell (Improving Dimensional Stability) .	271
5.8	Extrusion: Improving Smoothness of the Extrudate Surface .....	276
5.9	Extrusion: Increasing Extrusion Rate Without Loss of Quality .....	281
5.10	Calendering: Eliminating Blisters .....	287
5.11	Calendering: Improving Calender Release .....	289
5.12	Raw Material and Mixed Stock Bin Storage: Lengthening Useful Shelf Life .....	290
5.13	Mixed Stock Bin Storage: Reducing Bloom .....	291

5.14	Compression/Transfer/Injection Molding: Improving Mold Release	295
5.15	Compression/Transfer/Injection Molding: Reducing or Eliminating Mold Fouling . . . . .	297
5.16	Compression/Transfer/Injection Molding: Improving Mold Flow . . .	301
5.17	Compression/Transfer/Injection Molding: Reducing Shrinkage of Part . . . . .	303
5.18	Compression/Transfer/Injection Molding: Improving Surface Appearance . . . . .	306
5.19	Increasing the Blow Rate During the Curing of a Sponge Compound . . . . .	307
5.20	Eliminating Trapped Air During Molding . . . . .	310
5.21	Reducing Backrinding . . . . .	311
<b>6</b>	<b>Tire Performance Properties . . . . .</b>	<b>313</b>
6.1	Improving Tire Wet Traction . . . . .	313
6.2	Improving Tire Dry Traction . . . . .	321
6.3	Improving Tire Winter Traction or Ice Traction . . . . .	323
6.4	Improving Tire Rolling Resistance . . . . .	325
<b>Appendix 1</b>	<b>Blends . . . . .</b>	<b>335</b>
A.1	Introduction . . . . .	335
A.1.1	SBR/NR Blends . . . . .	338
A.1.2	SBR/IR Blends . . . . .	341
A.1.3	SBR/BR Blends . . . . .	341
A.1.4	NR/BR Blend . . . . .	343
A.1.5	NR/IR Blends . . . . .	345
A.1.6	NR/CIIR Blends . . . . .	345
A.1.7	NR/BIIR Blends . . . . .	346
A.1.8	NR/BIMS Blends . . . . .	346
A.1.9	NR/IIR Blends . . . . .	347
A.1.10	CR/IIR Blends . . . . .	347
A.1.11	NBR/SBR Blends . . . . .	347
A.1.12	NBR/PVC Blends . . . . .	348
A.1.13	XNBR/PVC Blend . . . . .	349
A.1.14	NBR/IR Blends . . . . .	349
A.1.15	NBR/BR Blends . . . . .	350
A.1.16	NBR/NR Blends . . . . .	350
A.1.17	EPDM/SBR Blends . . . . .	350
A.1.18	EPDM/CR Blends . . . . .	351
A.1.19	EPDM/IR Blends . . . . .	351
A.1.20	EPDM/NR Blends . . . . .	351

A.1.21 EPDM/CSM Blends .....	351
A.1.22 EPDM/Silicone Compatibilized .....	352
A.1.23 EPDM/LDPE Blend .....	352
A.1.24 EPDM/EVA Blend .....	352
A.1.25 CR/SBR Blends .....	352
A.1.26 CR/BR Blends .....	353
A.1.27 CSM/BR Blends .....	353
A.1.28 CR/Hydrin Blends .....	354
A.1.29 NBR/FA Polysulfide Rubber .....	354
A.1.30 Triblend .....	354
A.1.30.1 NR/SBR/BR Blends .....	354
A.1.30.2 BR/SBR/IR Blends .....	355
A.1.30.3 NR/IR/SBR Blends .....	355
A.1.30.4 NR/EPDM/BIIR Blends .....	356
A.1.30.5 NR/EPDM/CIIR Blends .....	356
A.1.30.6 NR/CR/CSM Blends .....	356
A.1.30.7 NBR/PVC/SBR Blends .....	356
A.1.30.8 XNBR/PVC/NBR Blends .....	357
A.1.30.9 XNBR/PVC/BR Blends .....	357
A.1.30.10 XNBR/NBR/BR Blends .....	357
A.1.30.11 NBR/SBR/BR Blends .....	357
A.1.30.12 NBR/BR/NR Blends .....	357
A.1.30.13 NR/EPDM/SBR Blends .....	357
A.1.30.14 EPDM/SBR/CR Blends .....	358
A.1.31 Four-Way Blends .....	358
A.1.31.1 NR/EPDM/SBR/CIIR Blends .....	358
<b>Appendix 2: Cure Systems .....</b>	<b>359</b>
A.2 Introduction .....	359
A.2.1 General Purpose Elastomer Cure Packages .....	359
A.2.2 EPDM Cure Packages .....	362
A.2.3 NBR Cure Packages .....	363
A.2.4 Polychloroprene Cure Packages .....	366
A.2.4.1 General Purpose Thiourea Cure Systems for Carbon Black Loaded CR Compounds .....	367
A.2.4.2 Special Purpose Thiourea Cure Systems for Carbon Black Loaded CR Compounds .....	367
A.2.4.3 General Purpose Non-thiourea Cure Systems for Carbon Black Loaded CR Compounds .....	367
A.2.4.4 Special Purpose Non-thiourea Cure Systems for Carbon Black Loaded CR Compounds .....	368

A.2.5 Chlorobutyl Rubber Cure Packages .....	369
A.2.6 Butyl Rubber Cure Packages .....	371
Review Panel Members' Biographies .....	373
Author's Biography .....	383
Subject Index .....	385



# 1

## Introduction

*Rubber compounding is a highly complex endeavor that involves many interactions and includes many ways to achieve the target properties and economic goals while maintaining an acceptable trade-off for these characteristics. The purpose of this book is to provide the reader with various experimental ideas that may guide him or her to develop better compounds and solve technical problems.*

### ■ 1.1 Complexity of Compound Ingredient Selection

Rubber formulations generally are not simple and usually involve the careful selection of several material systems, each of which can have a major impact on the commercial rubber product. The following are examples of some of these systems:

- Base rubber or rubber blend
- Filler/oil system
- Cure system
- Antidegradant system
- Tackifying system (if applicable)
- Adhesion system (if applicable)
- Flame retardant system (if applicable)
- Blow system (for cellular rubber applications)
- Special process-enhancing chemical additives

The selection of a base rubber (elastomer) has the greatest effect on the properties of a compound. There are well over 30 major rubber types. However, literally hundreds of different grades may be available for any one major category of

rubber, each with a different effect. For example, there are at least 150 different grades of SBR, 50 of BR, 150 of EPDM, 280 of NBR, 100 of silicone rubber, and 75 of fluoroelastomers. Each of these different grades imparts different properties to the compound.

To add to this complexity, many commercial rubber formulations are based on blends of two or more elastomers. For example many rubber compounds are based on blends of SBR and BR, natural rubber (NR) and BR, or various blends of SBR, NBR HIR, CR, EPDM, and so forth. Blending different rubber polymers is an effective way to achieve certain compound properties. However, many times these blended polymers, although compatible (covulcanizable), are not very miscible, or soluble, in each other. Therefore, continuous and discontinuous phases or domains are established from mixing. These different phases have different affinities for various fillers such as carbon black during mixing. These differences in distribution of carbon black can have a unique effect on the properties of the compound.

The selection of an effective filler/oil system for the formulation can also have a very strong influence on compound properties. Many different fillers and reinforcing agents can be used in rubber compounding to enhance physical properties. A wide variety of petroleum-based processing oils and hundreds of synthetic ester plasticizers can also be used. Currently more than 42 standard commercial grades of carbon black are available to the rubber compounder. Some rubber formulations will use more than one grade of carbon black to balance the compound performance properties, adding further to the complexity.

Literally thousands of combinations of organic accelerators and sulfur are used to achieve specific vulcanizate properties. In addition to the common sulfur cures, other cure systems such as peroxide or resin cures can be applied. For effective resistance to in-service degradation, hundreds of different antioxidant and/or antiozonant combinations are used commercially. Different commercial grades are available even for very simple and “straightforward” compounding ingredients such as sulfur or zinc oxide. For example, different sulfur grades with different mesh sizes and chemical treatments are available to ensure better dispersion in certain formulations. Zinc oxide grades are used with different average particle sizes and treatments to enhance certain physical properties.

## ■ 1.2 Industrial Complexity

As noted in the preceding, there are virtually an infinite number of ways to select raw materials and write recipes to meet customers' specifications. It is very costly for corporations to develop rubber compounds to meet these customer requirements. Therefore, most rubber fabricators tend to be quite secretive regarding these formulations to maintain what they consider their competitive advantages. Hence the rubber industry possesses literally hundreds of thousands of quite different recipes to meet customer needs.

However, this industrial complexity does not end with just the sheer number of different recipes used in commerce. Even if two companies were using identical recipes and identical raw materials, they could still be producing products with different properties. For example, it is quite possible for the components of the same recipe to be mixed on different types of mixers or to use a different mixing sequence that results in a different state of mix. Identical compounds that are cured under different conditions of time, temperature, or pressure can also acquire different vulcanizate properties.

## ■ 1.3 Complexity of Ingredient Property Relationships

Another difficulty in rubber compounding is the problem of ingredient property relationships. One form of interaction is experienced by the compounder when he or she tries to formulate to a specific property such as durometer hardness, for example. Increasing or changing the curative package to achieve a higher cured crosslink density ( $X_1$ ) will result in a higher durometer hardness value ( $Y_1$ ). On the other hand, increasing the loading of carbon black ( $X_2$ ) will also increase this durometer hardness ( $Y_1$ ) for a different reason. Significantly reducing oil loading ( $X_3$ ) will again increase hardness for still another reason. This is very common in rubber compounding. In addition, these different independent variables usually show an interaction because their effects are not necessarily additive or linear. Changes in the cure system, the filler-oil system, the base rubber, the rubber blending, the method of mixing, and so forth (...  $X_n$ ) will usually affect a specific property such as durometer hardness ( $Y_1$ ). However, any one or a combination of these deliberate compound changes (independent variables) will also affect in very different ways a very wide variety of *other* compound properties such as ultimate tensile strength ( $Y_2$ ), ultimate elongation

( $Y_3$ ), percent rebound ( $Y_4$ ), aging resistance ( $Y_5$ ), tear resistance ( $Y_6$ ), flex fatigue resistance ( $Y_7$ ), oil resistance ( $Y_8$ ), ... ( $Y_n$ ). Another way of describing this type of interaction from a specific compound change is to refer to it as a *multiple response*. There is an old compounder's "saying" that "you can never change just one thing" (RP: R. J. Del Vecchio). These different compound changes that increased hardness also changed elongation, tensile strength, oil resistance, compression set, flex fatigue, and so forth in very different ways for better or worse regarding product performance. The same is true for processability properties that result as well. Processability properties are almost always affected for better or worse by a compound change(s)—another unintended consequence. To add to this complexity is the fact that many of these multiple responses are nonlinear and usually give both better and poorer compound performance properties simultaneously. This type of interaction resulting in multiple responses is extremely common in rubber compounding. Therefore when using this book to develop ideas on how to change or optimize a specific rubber compound property such as durometer hardness, you are virtually guaranteed to affect just about every other compound property that can be measured. Many of these effects may result in poorer rubber compound performance.

Thus for this principle "...of having multiple responses for a single compound change," the compounder must develop an understanding of how these responses can be different for each selected compound change. For example, some ingredient changes are independent of other ingredient changes (no interaction), whereas others show a great deal of interaction. For example, a change in the concentration of two carbon blacks is usually just the sum of the effects of the individual carbon blacks by themselves. But changes in concentration of a combination of sulfur and accelerator can result in many different responses to hardness, and other properties, than the individual response to separate concentration variations of the sulfur only or accelerator only. This is called *chemical interaction* or synergy (RP: R. J. Del Vecchio). This book provides ideas on how to optimize specific compound properties "one property at a time." As indicated earlier, however, when implementing any change in recipe or process to improve a single compound property, it will *always* change other compound properties *for better or for worse*. If the compounder has many other compound or processing properties to consider as well, the complexity of predicting them all from a single recipe change or process change can be very difficult (RP: R. J. Del Vecchio). A skillful compounder can usually work out the necessary acceptable compromise among properties to meet all the compounding property targets. This ability comes from experience and intuition and usually from a series of trial-and-error experiments or a "one change at a time" approach until the correct balance of compound properties is achieved. This is the so-called

“black art” of compounding (RP: R. J. Del Vecchio). This book is intended to aid the compounder in this approach.

A more modern approach to compounding is to use the statistical method of *design of experiments* (DOE) to achieve this optimal set of properties. To carry out a DOE is much simpler than it was a few years ago because more effective user-friendly software is now available. In a DOE, multiple recipe and process changes can be studied simultaneously to analyze multiple responses and generate a mathematical solution. These DOEs will require more initial effort (typically 8 to 16 compound variations to be formulated, mixed, and tested for all relevant properties in the same period of time). However, this DOE technique is more effective at finding the best recipe and/or process combinations to meet all the compound property requirements, which may be better than changing one variable at a time (RP: R. J. Del Vecchio).

Whichever approach is used (“one variable at a time” or DOE), this book should help the compounder in trying different ideas. From reviewing the ideas given in this book, the compounder may develop a better “feel” and understanding of how to possibly change the recipe or process to meet all the property targets.

Even though this book provides many diverse experimental approaches for changing or improving a specific individual compound property, it *does not* necessarily predict the negative effects for the other compound properties that might result from making this change(s). However, by reviewing the other sections of this book that discuss those other properties of concern; the compounder may develop an appreciation of how a specific recipe change or process adjustment might affect these other targeted compound properties. Thus the various experimental ideas given in this book may suggest a combination of experimental variables that the compounder might try out in order to find the best balance in desired compound properties (RP: R. J. Del Vecchio).

Because trying to improve one single rubber compound property will *always* result in changing other rubber compound properties, for better or for worse, the rubber compounder should review the many ways to change or improve a targeted compound property to find the formulation or processing modification that gives the best trade-off against the other required compound characteristics.

In this book, we present experimental ideas on various possible ways to improve or optimize a specific compound property. However, whenever you implement a recipe or process change to modify one property, you are virtually *guaranteed* to change many other compound properties, many times in the wrong direction. It is a truism that almost all compound or process changes implemented to modify one compound property for the “good” will also change many other properties in both favorable and detrimental ways. In other words, trying to change one

property may result in unintended consequences for other properties. This is where the *art* (or black art) of rubber compounding is applied. This “art” reflects a compounder’s skill in finding the best compromise among properties to meet all the required compound specifications, which may require the compounder to make more than one change to achieve the best overall balance. By reviewing many of the suggestions in this book, the compounder may develop a better intuition for how best to achieve this compromise or trade-off with compound properties. In short, a good compounder should acquire a combination of knowledge and skill from the sciences of chemistry, physics, statistics, and both mechanical and process engineering. The application of these sciences is the true art of compounding (RP: R. Dailey).

As noted earlier, this book provides a large number of diverse experimental ideas for enhancing a specific compound property. It does *not* describe the possible ill effects on other compound properties. However, by reviewing the experimental ideas for these other properties, the reader may develop a limited appreciation for some (but certainly not all) of these consequences. In fact, the compounder may try a combination of experimental ideas to achieve his or her rubber compounding goals.

## ■ 1.4 Experimental Ideas

The experimental ideas provided in this book are *general* suggestions that may or may not work in your *specific* compound. Because of the diversity and scope of rubber compounds used in commerce today, these general statements may not always be applicable to every compound, including yours. Certain precautions should always be taken.

- For all ideas and suggestions provided here, consider any possible health, safety, or environmental hazards that might be created at your facility, including all relevant U.S. Occupational Safety and Health Administration (OSHA) and Environmental Protection Agency (EPA) issues.
- Check out the effectiveness of these experimental ideas in your compound(s) by implementing these ideas in a laboratory-scale mix. Measure the effects of this compound change(s) on your specific formulation and target property as well as all other relevant compound properties that determine the effectiveness of the compound in your customer’s end-use application. It is important to check these experimental ideas thoroughly for your specific compound because no two compounds are identical. The only way to know if the idea

may work for your compound is to test it initially in a laboratory and compare the results against a “control” compound. Be sure to measure effects on the subject property as well as effects on all the other relevant properties vs. your control compound. Your compound change may have improved flex fatigue vs. your control, for example; however, it may also be detrimental to such properties as aging resistance and so forth compared to the control.

- Remember that laboratory mixing is not equivalent to factory mixing. Likewise, laboratory cures are not equal to factory cures. In other words, a compound change that may show improvements in the laboratory may not work in the factory. If the laboratory trials are successful, then try limited and controlled factory trials and product field trials to validate this experimental idea or proposed change. This will help to determine if there are any “hidden” problems that could not be detected at the laboratory scale. Further, these evaluations should be followed through the entire product service life to make sure there are no problems that might hurt the product’s performance throughout its use or create any product safety issues.

## ■ 1.5 Sources of Ideas

There are three basic sources of the experimental ideas given in this book:

1. The first primary source of experimental ideas is from the second edition of the earlier “companion” book published in 2009, *Rubber Technology: Compounding and Testing for Performance*, edited by John S. Dick, and published by Hanser Gardner Publications, Cincinnati. These sources are designated by the prefix “RT:” throughout this book.
2. The second source of experimental ideas is from a review of the general literature. At the end of each idea is cited a specific reference(s). These sources are designated by the prefix “GEN:” throughout this book.
3. The third source of experimental ideas is from the direct contribution of members of the “Review Panel” cited in Section 1.6 of this book. These sources are designated by the prefix “RP:” throughout this book.

The reader should thoroughly review these cited references as well as other references not cited in this book before beginning any experiments. These “other references” should be both of a general and specific nature. Thus looking up other references that are not cited in this book but could be relevant to the problems is greatly encouraged.

The following “experimental ideas” for the most part are generalizations. However, rubber compounding is very complex and such generalizations almost *never* work across vastly different formulations. Therefore all these ideas should be thoroughly researched and checked out as outlined in Section 1.4.

## ■ 1.6 Review Panel

The following are members of the Review Panel who have reviewed the text of this book and made suggestions for additions, deletions, or changes. In addition, they have individually provided further experimental ideas for the enrichment of this book.

Name	Affiliation	E-mail Address
Roger Dailey	Goodyear Chemical Co.	roger_dailey@goodyear.com
R. J. Del Vecchio	Technical Consulting Services	techconsultserv@juno.com
Ronald W. Fuest	Uniroyal Chemical (Retired)	ron@fuest.net
James R. Halladay	Lord Corp.	james_halladay@lord.com
Fred Ignatz-Hoover	Flexsys America L.P.	ignatz-hoover@flexsys.com
Mark Lawrence	Indspec	mlawrence@indspec-chem.com
John M. Long	DSM	john.long@dsm.com
Oscar Noel	Luzenac America	oscar.noel@america.luzenac.com
Leonard L. Outzs	DuPont Dow Elastomers	Leonard.L.outzs@dupont-dow.com
Thomas D. Powell	Degussa Corp.	Thomas.powell@degussa.com
Charles P. Rader	Advanced Elastomer Systems (Ret.)	charles_rader@msn.com
Ronald Schaefer	Dynamic Rubber Technology	rschaeferdr@msn.com
Kelvin K. Shen	Borax/Luzenac, Inc.	kelvin.shen@borax.com
John Sommer	Elastech	johnsommer@att.net
James Stevenson	Honeywell	james.stevenson@honeywell.com
Byron H. To	Flexsys America	byron.h.to@flexsys.com
Walter Waddell	ExxonMobil	walter.h.waddell@exxon-mobil.com
Meng-jiao Wang	Cabot Corp.	meng-jiao_wang@cabot-corp.com

# 2

## Improving the Physical Properties of Cured Rubber Compounds

### ■ 2.1 Increasing Tensile Strength

*In the rubber industry, ultimate tensile strength is considered a fundamental material property. This test parameter measures the ultimate strength of the cured vulcanizate. Even though a typical rubber product probably never will be stretched anywhere close to its ultimate tensile strength, many rubber product users still consider it an important indicator of the overall quality of the compound. Therefore, tensile strength is a very common specification property that a compounder typically will need to find a way to meet even though its relevance to the specific product end use is usually poorly defined.*

*A compounder might consider trying the following ideas on an **experimental** basis if an additional improvement in tensile strength is needed. Also, all relevant literature sources, including the ones cited below, should be researched and read.*

**Caution:** *these general experimental ideas may not work in all specific situations. Changes to increase tensile strength will certainly affect other properties as well, for better or for worse, and this book does not purport to show how these other properties are affected. Also, this book does not purport to address safety and health issues.*

#### ■ Generally

To achieve the highest tensile strength, generally one should start with strain crystallizing base elastomers such as natural rubber (NR), polychloroprene (CR), isoprene rubber (IR), hydrogenated nitrile rubber (HNBR), or polyurethane (PU). RP: J. R. Halladay.

#### ■ Natural Rubber

Compounds based on NR generally impart better tensile strength than similar compounds based on CR. RT: Chapter 6, “Elastomer Selection,” R. School, p. 133.

Of the various grades of NR, ribbed smoked sheet no. 1 gives the highest tensile value. RT: Chapter 7, “General Purpose Elastomers and Blends,” G. Day, p. 156.

Ribbed smoked sheet no. 3 reportedly may actually impart higher ultimate tensile strength than ribbed smoked sheet no. 1, at least in blackloaded compounds. RP: J. M. Long.

For NR-based compounds, avoid using a chemical plasticizer (peptizer) such as dibenzamido-diphenyl disulfide or pentachlorothiophenol (PCTP) because it may reduce the ultimate tensile strength of the compound. RT: Chapter 14, “Ester Plasticizers and Processing Additives,” C. Stone, p. 366.

### ■ Polychloroprene

Polychloroprene (CR) is a strain-crystallizing polymer that imparts high tensile strength even without dependency on high loadings of reinforcing fillers. In fact, sometimes the ultimate tensile strength can actually be increased by reducing the filler loading. Selecting a CR with a higher molecular weight may also increase the ultimate tensile strength. RP: L. L. Outzs.

Consider xanthate-modified types of CR for higher levels of tensile strength and elongation. GEN: Nobuhiko Fujii (Denka Corp.), “Recent Technical Improvements of CR and ER in Industrial Applications,” Presented at the Southern Rubber Group, March, 2006.

### ■ SBR

Use emulsion SBR polymerized at +5°C (41°F) (or lower) instead of +50°C (122°F) for a significant improvement in tensile strength. RT: Chapter 7, “General Purpose Elastomers and Blends,” G. Day, p. 149. RP: J. M. Long.

Emulsion SBR usually provides higher tensile strength than solution SBR. RT: Chapter 7, “General Purpose Elastomers and Blends,” G. Day, p. 156.

Substituting an oil-extended high molecular weight SBR for an unextended SBR while making compound adjustments to keep the same oil level may improve the ultimate tensile strength. RP: J. M. Long.

### ■ NBR

Use nitrile rubber (NBR) grades with higher bound acrylonitrile (ACN) content for higher compound tensile strength. RT: Chapter 8, “Specialty Elastomers,” M. Gozdoff, p. 194. Increasing ACN content to an optimal level of about 41 percent should optimize the tensile strength for some NBR compounds. GEN: Andy Anderson, “Keeping It Real with NBR and HNBR Polymers,” Zeon Chemicals, Presented at the Energy Rubber Group, September 12–15, 2011.

Consider NBR grades with narrower molecular weight distribution for higher compound tensile strength. RT: Chapter 8, "Specialty Elastomers," M. Gozdiff, p. 197.

### ■ Molecular Weight Effect

Using raw NBR elastomers with higher Mooney viscosity and molecular weight may increase the compound's ultimate tensile strength through an optimum before it decreases. GEN: D. Ghang, "Investigation of the Structure-Property Relationships of Improved Low Compression Set Nitrile Rubbers," *Rubber Chemistry and Technology*, March–April, 1981, Vol. 54, p. 170.

### ■ Carboxylated Elastomers

Consider using carboxylated elastomers in place of noncarboxylated versions, that is, carboxylated NBR (XNBR) in place of NBR, or XHNBR in place of HNBR. RP: J. R. Halladay.

Use XNBR with the appropriate zinc oxide in place of conventional NBR to achieve a higher compound tensile strength. RT: Chapter 8, "Specialty Elastomers," M. Gozdiff, p. 199.

The hydrogenation of carboxylated nitrile (XNBR) to HXNBR reportedly will improve both room-temperature ultimate tensile strength as well as high-temperature tensile strength. GEN: John E. Dato (Lanxess), "Hydrogenated Nitrile Rubber for Use in Oilfield Applications," Paper No. 57 presented at the Fall Meeting of the Rubber Division, ACS, Cincinnati, OH, October 10, 2006.

### ■ EPDM

Use semicrystalline EPDM grades (with higher ethylene content) to impart higher ultimate tensile strength. RT: Chapter 8, "Specialty Elastomers," R. Vara, J. Laird, p. 191.

Increasing the molecular weight of EPDM can result in an improved ultimate tensile strength. GEN: Arnis Paeglis, "Use of High Molecular Weight EPDM in Blends to Enhance Properties," Paper No. 22 presented at the Spring Meeting of the Rubber Division, ACS, May 17–19, 2004, Grand Rapids, MI.

### ■ EPDM Catalysts

Single-site constrained geometry (CGC) metallocene catalyst technology for commercial polymerization has made it possible to efficiently produce commercial grades of EPDM with very high ethylene content and higher crystallinity. These special grades with higher ethylene content impart higher ultimate tensile strength to the vulcanizate. In addition, by substituting a higher concentration

of ENB for propylene at constant ethylene content, still higher ultimate tensile strength values can be achieved using this unique technology. GEN: D. Parikh, M. Hughes, M. Laughner, L. Meiske, R. Vara, "Next Generation of Ethylene Elastomers," Presented at ACS Rubber Div. Meeting, Fall, 2000.

Consider using Buckminsterfullerene  $C_{60}$  in an EPDM with exposure to ultraviolet light to develop tensile strength significantly higher than that generated by free-radical crosslinking from dicumyl peroxide. This forms a "nanocomposite" from the EPDM/ $C_{60}$  combination. GEN: G. Hamed, "Reinforcement of Rubber," *Rubber Chemistry and Technology*, July–August, 2000, Vol. 73, p. 524.

### Reactive EPDM

Substituting a 2% maleic-anhydride modified EPDM in place of unmodified EPDM in a blend with NR reportedly will improve the ultimate tensile strength of the NR/EPDM compound. GEN: A. Coran, "Blends of Dissimilar Rubbers: Cure-Rate Incompatibility," *Rubber Chemistry and Technology*, May–June, 1988, Vol. 61, p. 281.

### Gas-Phase EPDM

Try compounding with an ultra-low Mooney viscosity gas-phase polymerized EPDM with very high ethylene content and high filler loading. (Higher ethylene content reportedly increases the ultimate tensile strength values to the vulcanizate.) GEN: A. Paeglis, "Very Low Mooney Granular Gas-Phase EPDM," Presented at ACS Rubber Div. Meeting, Fall, 2000, Paper No. 12.

### Gel

Raw synthetic rubber such as SBR usually contains stabilizers. However, mixing SBR compounds at high temperatures such as 325°F (163°C) or above can cause the formation of both redispersible gel (or "loose" gel that can be milled out) and so-called "tight" gel (which cannot be milled out and remains insoluble in the appropriate solvents). Both of these types of gel can reduce the ultimate tensile strength of the rubber compound. Therefore it might be prudent to restrict how high the dump temperature should be. GEN: R. Mazzeo, "Preventing Polymer Degradation During Mixing," *Rubber World*, February 1995, p. 22.

### Cure

Optimize the ultimate crosslink density from curing. RT: Chapter 3, "Vulcanizate Physical Properties, Performance Characteristics, and Testing," J. S. Dick, p. 47.

Avoid undercuring the compound. RT: Chapter 3, "Vulcanizate Physical Properties, Performance Characteristics, and Testing," J. S. Dick, p. 49.

Avoid overcuring the compound. RT: Chapter 3, “Vulcanizate Physical Properties, Performance Characteristics, and Testing,” J. S. Dick, p. 49.

Avoid porosity from curing caused by low pressure, using volatile ingredients, and so forth. RT: Chapter 3, “Vulcanizate Physical Properties, Performance Characteristics, and Testing,” J. S. Dick, p. 49.

Reportedly natural rubber based compounds cured with CBS instead of MBS or TBBS may have higher ultimate tensile strength and even higher ultimate elongation. GEN: M. Brendan Rodgers, Donald Tracey, Walter Waddell, “Production, Classification and Properties of Natural Rubber,” Paper No. 37 presented at the Spring Meeting of the Rubber Division, ACS, San Antonio, TX, May 16, 2005.

For some rubber compounds based on specialty elastomers such as HXNBR or some fluoroelastomers, applying a post-cure may improve the ultimate tensile strength. GEN: Richard Pazur, L. P. Ferrari, E. C. Campomizzi (Lanxess), “HXNBR Compound Property Improvements Through the Use of Post Cure,” Paper No. 70 presented at the Spring Meeting of the Rubber Division, ACS, 2005; “New DAI-EL Fluoroelastomers for Extreme Environments,” Daikin America, Inc., Presented at a meeting of the Energy Rubber Group, September 15–18, 2008, San Antonio, TX.

### ■ Step-Down Cure

For autoclave-cured products, avoid porosity and low tensile strength by slowly reducing pressure toward the end of the cure cycle. This is called a “step-down cure.” RP: L. L. Outzs.

### ■ Cure Time and Temperature

Consider curing at a lower temperature for a longer time to avoid extra network sulfur and achieve better sulfur crosslink density so as to achieve higher ultimate tensile strength. GEN: Flexsys Technical Bulletin, “High Temperature Curing Compounding,” 1996–1997.

### ■ Processing

Avoid contaminating the compounding ingredients, raw elastomers, or the mixing process with dirt. RT: Chapter 3, “Vulcanizate Physical Properties, Performance Characteristics, and Testing,” J. S. Dick, p. 49.

### ■ Polyurethane

For very high ultimate tensile strength properties, base the compound on either polyester or polyether urethane polymers. RT: Chapter 6, “Elastomer Selection,” R. School, p. 126.

The ultimate tensile strength for a two-part cast polyurethane system usually can be increased by adjusting the curative ratio. The curative ratio refers to the relative amounts of prepolymer and curative. The amount of curative [such as methylene-bis-ortho-chloroaniline (MBCA)] needed to match exactly the isocyanate groups on the prepolymer is referred to as a “100% theory” or “100% stoichiometry.” For example, if the curative is reduced by 5%, it is referred to as “95% theory” or “95% stoichiometry.” On the other hand, if the curative is increased by 5% from theory, it is referred to as “105% theory” or “105% stoichiometry.” Generally, going to a lower stoichiometry, such as 95%, may improve ultimate tensile strength. RT: Chapter 9, “Polyurethane Elastomers,” R. W. Fuest, p. 251.

Usually, but not always, selecting an ester-type polyurethane provides an advantage for tensile strength in demanding applications. RT: Chapter 9, “Polyurethane Elastomers,” R. W. Fuest, p. 257.

Consider blending polyurethane with a conventional rubber-based compound to improve tensile strength. GEN: T. Jazlonowski, “Blends of Polyurethane Rubber with Conventional Rubber,” Paper No. 46 presented at the Spring Meeting of the Rubber Division, ACS, April, 1999, Chicago, IL.

### ■ Silicone

To ensure good tensile strength, avoid basing a compound on either silicone or fluorosilicone rubber. RT: Chapter 6, “Elastomer Selection,” R. School, p. 136.

### ■ AEM

To significantly increase the ultimate tensile strength for terpolymers of ethylene-acrylic elastomer (AEM) (under the trade name of Vamac, from DuPont), which uses a traditional diamine cure system based on hexamethylene-diamine carbamate (HMDC) and DPG, consider the addition of dicumyl peroxide and a 1,2-polybutadiene (Ricon, 152) to reportedly increase the ultimate tensile strength. GEN: H. Barager, K. Kammerer, E. McBride, “Increased Cure Rates of Vamac, Dipolymers and Terpolymers Using Peroxides,” Presented at ACS Rubber Div. Meeting, Fall, 2000, Paper No. 115.

### ■ Silicone-EPDM

Consider using compounds based on the new silicone-EPDM in place of the traditional silicone to achieve better ultimate tensile properties. GEN: M. Chase, “Roll Coverings Past, Present, and Future,” Presented at Rubber Roller Group Meeting, New Orleans, May 15-17, 1996, p. 7.

## Reactive BR

Using zinc oxide to crosslink a gum carboxylic butadiene rubber that possesses one carboxyl group for approximately every 100 carbons on the backbone can produce a cured rubber that has higher tensile strength than those produced using normal sulfur cures. This becomes an “ionomeric elastomer” in which ionic crosslink sites form nanometer-sized domains. GEN: G. Hamed, “Reinforcement of Rubber,” *Rubber Chemistry and Technology*, July–August, 2000, Vol. 73, p. 524.

## Mixing

Increase the percent dispersion of reinforcing fillers such as carbon black through better mixing techniques. RT: Chapter 3, “Vulcanizate Physical Properties, Performance Characteristics, and Testing,” J. S. Dick, p. 49. GEN: S. Monthey, T. Reed, “Performance Differences Between Carbon Blacks and CB Blends for Critical IR Applications,” *Rubber World*, April, 1999, p. 42.

Avoid any contamination or undispersed material of relatively large particle size. RT: Chapter 3, “Vulcanizate Physical Properties, Performance Characteristics, and Testing,” J. S. Dick, p. 49.

Prudent use of processing aids with a filler system can be used to achieve better dispersion and thus higher ultimate tensile strength. GEN: Hermann-Josef Weidenhaupt, Kishor Katkar, “Novel Zinc-Free Processing Aid for Silica Compounds,” Paper No. 34 given at the IRE 2011 Rubber Conference, Chennai, India.

## Phase Mixing

For an SBR/BR blend, a lower tensile strength was reported when there was a higher concentration of carbon black in the SBR phase through phase mixing techniques. GEN: W. Hess, C. Herd, P. Vegvari, “Characterization of Immiscible Elastomer Blends,” *Rubber Chemistry and Technology*, July–August, 1993, Vol. 66, p. 329.

It has been reported that through phase mixing techniques of an NR/BR blend, one can achieve an increase in the amount of carbon black dispersed in the BR phase, which may increase the ultimate tensile strength. Other reports have found different effects. Also, Hess reported a large drop in tensile strength if all the carbon black is concentrated in the NR phase. GEN: E. McDonel, K. Baranwal, J. Andries, *Polymer Blends*, Vol. 2, Chapter 19, “Elastomer Blends in Tires,” Academic Press, 1978, p. 282; W. Hess, C. Herd, P. Vegvari, “Characterization of Immiscible Elastomer Blends,” *Rubber Chemistry and Technology*, 1993, Vol. 66, p. 329.