Rubber Technology and Manufacture

Second Edition

Edited by

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Foreword to the First Edition

BY J. M. BUIST
Chairman of Council, Institution of the Rubber Industry, 1969–1970

The Institution of the Rubber Industry*, since its formation in 1921, has promoted a better understanding of the science and technology of natural rubber and synthetic polymers. By lecture programmes, symposia, publications, and international conferences, the IRI has encouraged and stimulated free interchange of ideas and discussion of methods of solving the many interesting problems which arise in any industry where the technology has often been in advance of the scientific explanations and theories which enable the technology to advance further. In the early 1950s the IRI sponsored and published a series of Monographs designed to assist the growing number of scientists and technologists working with polymers. The IRI has held its examinations for the Associateship since 1925 and the Licenciateship since 1932, and has co-operated fully with educational bodies to provide the necessary preparatory facilities for studying and maintaining a supply of adequately trained technologists for an expanding industry. From time to time the IRI has also supported and encouraged the publication of books on various aspects of rubber and polymer technology in order to disseminate knowledge and encourage students.

With this background, it is highly commendable, but not surprising, that the IRI has sponsored and organised the publication of *Rubber Technology and Manufacture*. In the brief prepared by the Editor, Dr C. M. Blow, it was stated that 'the book is intended for graduates in chemistry, physics and engineering wishing to acquire a sound practical knowledge of rubber technology with emphasis on the processing, compounding and manufacturing of rubber products rather than on the chemistry and physics of rubbers, although the basic facts and theories of the latter must be adequately, though briefly, covered. It is further intended to be a "guide" to undergraduates reading for the AIRI and degrees in polymer science or technology.'

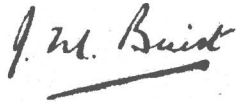
The different chapters of the book have been written by authors who are specialists with considerable familiarity and knowledge of their subject, and

* The IRI and The Plastics Institute amalgamated in 1975 to form the Plastics and Rubber Institute.

Dr Blow is to be congratulated on the team of experts he chose and encouraged to work with him on this project. Personally, I am well aware of the additional effort these authors have had to make over and above their normal business duties, and they deserve our thanks and congratulations. Dr Blow has spent his working life in the polymer industry in a variety of roles, and we are fortunate that a man of his very wide experience has been willing and able to undertake the task of being Editor with such gratifying results.

Although significant advances are made each year in the science and technology of polymers, I believe this book will serve both as a landmark in the recording of the progress of the technology of the polymer industry and as a stimulus to further investigation and research to advance the frontiers of our knowledge in the future.

It has been a privilege and honour to encourage the preparation of this publication during my term of office as Chairman of Council.



Preface to the First Edition

The aim of the book is to provide an up-to-date guide for students, for entrants to the rubber manufacturing and associated supplying industries, and for the users of rubber products in other industries, public corporations, and government departments. Emphasis has been placed on the main scientific facts, technological methods, and manufacturing techniques, with comprehensive coverage of both raw materials and testing methods. Each of the authors has gone straight to the subject of his particular section and written an authoritative contribution. No attempt has been made to eliminate repetition and overlapping completely nor to blend the sections together apart from presenting them in a logical order. Instead, Chapter 2 has been written, as it is entitled, to *outline* the breadth and width of rubber technology and to provide connecting links for the subsequent chapters.

The preparation of a 500 page book on rubber technology and manufacture has been possible only by omitting detailed discussion of certain branches of the subject. Latex, ebonite, and adhesive technologies may be said nowadays to be distinct and separate and have, therefore, been considered outside the scope of this book; short notes on them appear, for reference, in Chapter 2. Because, in recent years, there have been many conferences held and several books published on the use and application of elastomers in engineering, it was decided that this subject should also receive only scant treatment. The third and fourth omissions are the specialised field of chemical analysis in connection with rubbers and rubber products, and the general subject of instrumentation of machines and equipment in such respects as temperature control, or thickness measurement at the calender and spreading plant. Finally, the book is concerned essentially with rubbers; discussion of thermoplastics is in general omitted. It is, of course, realised that the latter materials are processed by rubber manufacturers alongside rubber in certain sections of the industry, notably belting, footwear, and cables, and the authors refer to this in Chapter 10.

The lengthy contents list and indexes, and the abundant cross-references, it is hoped, will be useful in meeting the requirements of those who use the book for reference. For those new to the industry, attention has been paid to nomenclature and to the terms, abbreviations, trade names, etc., in common use. In particular, the code letters for rubbers (ASTM D1418) have been adopted to save repeated use of the full names. Throughout the text,

Registered Trade Names are printed with an initial capital letter. Abbreviations are listed on pp. xxiii–xxiv, and the symbols used in the book appear on pp. xxv.

The glossary of terms published by the British Standards Institution (BS 3558, 1968) not only records the terms used in the industry but suggests reforms by deprecating the use of certain words. Of the deprecated terms, 'compound' is to be found frequently in this book because it is in very common usage to denote a rubber to which have been added all the ingredients necessary for processing and vulcanisate properties. 'Stock', which means much the same and is also deprecated by the BSI, occurs occasionally. The other terms used in this book have the meaning given in the BSI glossary. I have commented in Chapter 2 on the terms 'rubber' and 'elastomer', which, if I interpret the definitions in BS 3558 correctly, are not synonymous. Rubber is 'macromolecular material which *has, or can be given*, properties of (1) at room temperature returning rapidly to the approximate shape from which it has been substantially distorted by a weak stress, and (2) not being easily remoulded to a permanent shape by the application of heat and moderate pressure'; whereas elastomer is 'macromolecular material which can return rapidly to the approximate shape from which it has been substantially distorted by a weak stress'.

These definitions suggest to me that many (rubber) polymers need to be crosslinked to be elastomers and are my justification for confining the term 'elastomer' to vulcanisates only. 'Polymer' and 'rubber' are used for the raw materials, and the latter additionally for mixes, vulcanisates, and products. It is hoped that the context removes any ambiguity.

There has never been any doubt in my mind, or in that of anyone I consulted, that metric units should be used throughout with preference for SI units where these are accepted. The industry, at the time of writing, has not, it appears, made up its mind regarding the use of the newton; furthermore, if the newton is adopted, there seems reluctance to use the recommended meganewton per square metre (MN/m^2) for the tensile strength and stress unit; therefore, kilograms-force per square centimetre (kgf/cm^2) is used. For those who wish to convert to British units, a table is given on p. xxv.

Some explanation is perhaps necessary of the slightly unorthodox way in which the references to the literature and patent specifications have been arranged. Instead of suffixed numbers in the text, the Harvard system has been adopted of identifying in the text the author(s) and the year of publication, with the letters a, b, etc. added if there is more than one publication in one year by an individual author. The references are not listed at the end of each chapter, but are assembled in alphabetical order of first author at the end of the book in what is, in fact, a name index.

As a supplement to the concise Chapter 11 on physical testing, a full list of standards is included. For follow-up reading, a Bibliography, grouped into general and special categories, corresponding to chapter subjects, will be found on pp. 554–561.

Editor's Acknowledgements

Professor R. J. W. Reynolds, Director of the Institute of Polymer Technology, suggested that the IRI should sponsor a textbook on rubber tech-

nology, and I am indebted to him not only for being instrumental in my undertaking the editorship but also for much practical assistance and encouragement. Without his help and that of the small sub-committee in planning the book and suggesting authors, I would never have started. Mr E. W. Madge and Dr D. G. Marshall of The Dunlop Co. enlisted several contributors from their organisation; for that assistance and interest I am grateful. Also I must thank Mr J. M. Buist for suggesting contributors and for so willingly agreeing to write the Foreword.

I thank all contributors for the effort they put into the preparation of their articles and for so readily agreeing to my requests for amendments and additions. I must place on record my gratitude to several of my former colleagues in The Dunlop Co., including Messrs R. N. Thomson and D. W. Southwart for assistance, and to Mr Claude Hepburn who read the text and whose comments enabled me to correct errors and omissions.

Finally, my thanks are due to Miss Mary Lamb and Miss Janet Arnold who worked hard for me at their typewriters, and to my wife who spent many hours checking scripts with me.

Loughborough C.M.R.

Preface to the Second Edition

The last decade has seen many advances in all sections of the industry – materials, processes and products. This second edition, maintaining the aims set out in the preface to the first edition, reflects, it is hoped, these changes and advances.

The opportunity has been taken to eliminate some of the overlapping and duplication; in particular, all discussion of rubber-to-metal bonding is now included in Section 10.5 and of integral bonding additives in Section 6.6.7. Many British Standards are referred to in the text and there seems little value in listing them elsewhere; in the case of methods of test, however, a list of the principal BS, ASTM and ISO standards appear in Chapter 11. Particular attention has been paid to updating the commercial information regarding materials and equipment.

Since the publication of the first edition, the megapascal (MPa) has been adopted as the unit of stress in rubber testing and so all tensile and 'modulus' data are expressed in this unit in this edition. The conversion factor appears in the table on page xxv.

The importance of health and safety in the rubber industry is recognised by the introduction of sections on these two topics, adequate references being included for those readers who are concerned to refer to original papers and reports.

The editors wish to record their gratitude both to those contributors to the first edition who have so willingly and carefully revised their sections of the text and to those who have undertaken the rewriting of sections the first edition authors of which, for a variety of reasons, were not available to do the revision. Thanks are also due to members of the Information Division of the Rubber and Plastics Research Association for providing statistical and other data.

May 1981

C.M.B. & C.H.

Useful Information

Abbreviations

ADC	azodicarbonamide
ADS	air-dried sheet
AHEM	Association of Hydraulic Equipment Manufacturers
APF	all purpose furnace (black)
ACM	polyacrylic rubber
ASTM	American Society for Testing and Materials
AU	polyurethane (ester) rubber
AZDN	azoisobutyronitrile
BASRM	British Association of Synthetic Rubber Manufacturers
BR	polybutadiene rubber
BS	British Standard
BSH	benzene sulphonyl hydrazide
BSI	British Standards Institution
CBS	cyclohexyl benzthiazyl sulphenamide
CCV	catenary continuous vulcanisation
CF	conductive furnace (black)
CIIR	chlorinated butyl rubber
CO	epichlorohydrin rubber (homopolymer)
COD	cyclooctadiene
CR	polychloroprene rubber
CSM	chlorosulphonated polyethylene
CTAB	cetyl trimethyl ammonium bromide
CV	continuous vulcanisation
CV	constant viscosity (natural rubber)
CVNR	constant viscosity natural rubber
DBP	dibutyl phthalate
DBPA	dibutyl phthalate
DCPD	dicyclopentadiene
DETU	diethyl thiourea
DIN	Deutscher Normenausschuss
DNPT	dinitrosopentamethylene tetramine
DOTG	di-*o*-tolylguanidine
DPG	diphenyl guanidine
DPNR	deproteinised natural rubber
DPTS	dipentamethylene thiuram tetrasulphide
ECO	epichlorohydrin rubber (copolymer)
EDTA	ethylene diamine tetraacetic acid
ENB	ethylidene-norbornene
EP	ethylene-propylene rubber
EPC	easy processing channel (black)
EPDM	ethylene-propylene terpolymer rubber
EPM	ethylene-propylene copolymer rubber
ETE	epichlorohydrin rubber (terpolymer)
ETU	ethylene thiourea mercaptoimidazoline
EU	polyurethane (ether) rubber
EV	efficient vulcanisation
EVA	ethylene vinyl acetate
FDA	Federal Drug Administration (USA)
FEF	fast extrusion furnace (black)
FF	fine furnace (black)
FPM*	fluorocarbon rubber
FT	fine thermal (black)
FVMQ	trifluoropropyl vinyl silicone rubber
GMF	quinone dioxime
GPF	general purpose furnace (black)
GPO	polypropylene oxide rubber
GR-S	Government rubber-styrene (SBR)
HAF	high abrasion furnace black
HBS	cyclohexyl benzthiazyl sulphenamide
HCV	horizontal continuous vulcanisation
Hexa	hexamethylene tetramine

HMDA	hexamethylene diamine
HMF	high modulus furnace (black)
HMT	hexamethylene tetramine
HNS	hydroxylamine neutral sulphate
HOFR	heat resisting, oil resisting, and flame retardant
HPC	hard processing channel (black)
HS	high structure (black)
HSMB	hydrosolation masterbatch
IEC	International Electrotechnical Committee
IIR	isobutylene isoprene (butyl) rubber
IISRP	International Institute of Synthetic Rubber Producers
IPPD	*N*-isopropyl *N'*-phenyl-p-phenylene diamine
IR	polyisoprene rubber (synthetic)
IRHD	international rubber hardness degree
IRI	Institution of the Rubber Industry
ISAF	intermediate super abrasion furnace (black)
ISO	International Organisation for Standardisation
LCM	liquid curing medium
LM	low modulus (black)
LS	low structure (black)
LVN	limiting viscosity number
LVNR	low-viscosity natural rubber
MB	masterbatch
MBI	mercaptobenzimidazole
MBS	benzothiazyl-2-sulphene morpholide
MBT	mercaptobenzthiazole
MBTS	dibenzthiazyl disulphide
MDI	diphenylmethane-4,4 -diisocyanate
MOCA	4,4 -methyl-bis-2-chloroamine
MPC	medium processing channel (black)
MPF	medium processing furnace (black)
MQ	dimethyl silicone rubber
MRPRA	Malaysian Rubber Producer's Research Organisation
MRRDb	Malaysian Rubber Research and Development Board
MT	medium thermal (black)
NBR	acrylonitrile-butadiene copolymer (nitrile) rubber
NDPA	4-nitrosodiphenylamine
NDI	naphthalene-1,5-diisocyanate
NR	natural rubber
NS	hydroxylamine neutral sulphate
NS	non-staining (black)
OB	*pp'*-oxy-bis-benzene sulphonylhydrazide
OENR	oil-extended natural rubber
OEP	oil-extended polymer
OESBR	oil-extended styrene butadiene rubber
PAH	polycyclic aromatic hydrocarbons
PAUS	pale amber unsmoked sheet
PBN	phenyl-*β*-naphthylamine
PMMA	polymethylmethacrylate
PP	partially purified
p.p.h.r	parts per hundred of rubber
p.p.m.	parts per million
PRI	plasticity retention index
PRI	Plastics and Rubber Institute
PTFE	polytetrafluorethylene
PVA	polyvinylalcohol
PVC	polyvinylchloride
PVMQ	phenyl vinyl methyl silicone rubber
RAPRA	Rubber and Plastics Research Association
RFL	resorcinol formaldehyde latex
r.h.	relative humidity
RRIM	Rubber Research Institute of Malaysia
RSS	ribbed smoked sheets
SAF	super abrasion furnace (black)
SATRA	Shoe and Allied Trades Research Association
SBR	styrene-butadiene rubber
SC	slow-curing (black)
SCF	super conductive furnace (black)
SCI	scal compatibility index
SMR	standard Malaysian rubber
SP	superior processing (NR)
SPF	super processing furnace (black)
SRF	semi-reinforcing furnace (black)
TBTU	tributyl thiourea
TCR	technically classified rubber
TDI	toluene diisocyanate
TDM	tertiary dodecyl mercaptan
TETD	tetraethyl thiuram disulphide
TLV	threshold limit values
TMTD	tetramethyl thiuram disulphide
TMTM	tetramethyl thiuram monosulphide
TR	polysulphide rubbers
UHF	ultra-high frequency
VCV	vertical continuous vulcanisation
VGC	viscosity gravity constant
VMQ	vinyl methyl silicone rubber
VP	vinyl pyridine
WLF	Williams-Landel-Ferry (equation)
XCF	extra conductive furnace black
XLPE	cross-linked polyethylene
ZDBC	zinc dibutyl dithiocarbamate
ZDEC	zinc diethyl dithiocarbamate
ZDMC	zinc dimethyl dithiocarbamate
ZEPC	zinc ethyl phenyl dithiocarbamate
ZMBT	zinc mercapto benzthiazole

Symbols

A area
B bulkiness (of black)
C driving torque, rate of creep, length of crack, electrical conductivity
c volume fraction of filler
D diffusion coefficient
E Young's modulus, extrusion shrinkage
F force
f shape factor
G' elastic shear modulus
G'' viscous shear modulus
H hysteresis
ΔH latent heat of vaporisation
k Boltzmann's constant
L length, torque
ΔL maximum change in torque during vulcanisation
M molecular weight
M_c number average molecular weight between crosslinks
N number of chains per unit volume
n flow index
P penetration rate
Q anisometry (of black), permeation coefficient
Q_s differential heat of adsorption
R rate of recovery, gas constant
r radius
S rate of stress relaxation, solubility
T absolute temperature, structure factor (of black)
T_g glass transition temperature
t time
v_r volume fraction of rubber in swollen gel
V_s molecular volume of the solvent
V volume adsorbed
V_m volume adsorbed to form monolayer
W stored energy density, work per unit volume
γ strain, surface energy
$\dot{\gamma}$ rate of strain
δ phase angle, solubility parameter
ε strain (tension)
$\dot{\varepsilon}$ rate of strain (tension)
η viscosity
λ extension ratio
ν number of crosslinks (per cubic centimetre)
ρ density
σ stress
$\mathcal{T}$ characteristic energy (per unit area of crack)
τ relaxation time
χ interaction constant (Flory Rehner equation)
Ω angular velocity

Conversion Factors

To convert	*Multiply by*
Millimetres (mm) to inches	0·039
Metres (m) to feet	3·28
Metres (m) to yards	1·09
Square centimetres (cm^2) to square inches	0·155
Cubic centimetres (cm^3) to cubic inches	0·061
Cubic centimetres (cm^3) to pints	0·0018
Grams (g) to ounces	0·035
Kilograms (kg) to pounds	2·205
Kilograms-force per square centimetre (kgf/cm^2) to pounds-force per square inch	14·3
Megapascals (MPa) to kilograms-force per square centimetre (kgf/cm^2)	10·2
Degrees Centigrade (°C) to degrees Fahrenheit	1·8, and add 32

1 megagram (Mg) = 1 ton approx.
1 gigagram (Gg) = 1000 tons approx.