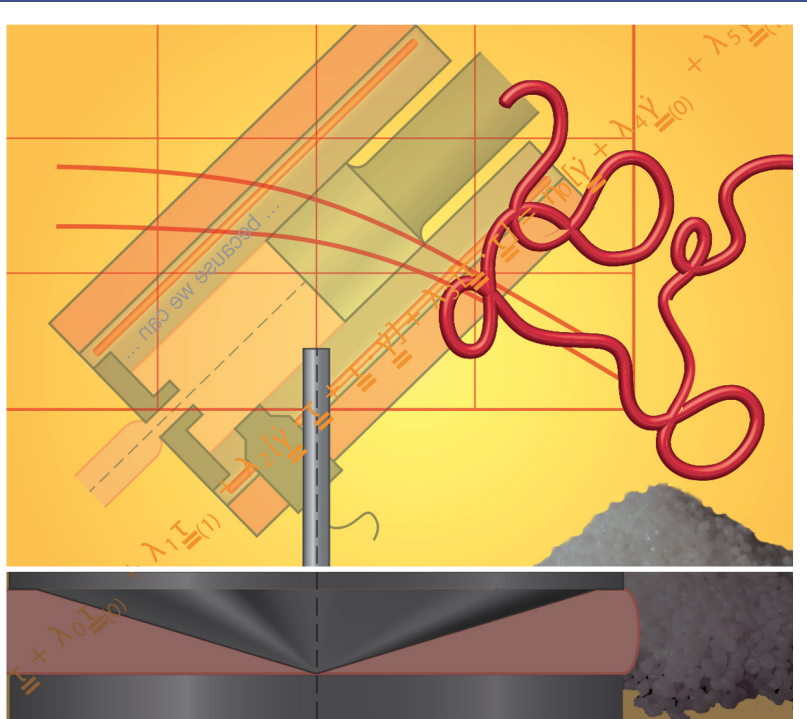


Tim A. Osswald
Natalie Rudolph

Polymer Rheology

Fundamentals and Applications



HANSER

Osswald, Rudolph
Polymer Rheology

Tim Osswald
Natalie Rudolph

Polymer Rheology

Fundamentals and Applications

Hanser Publishers, Munich

HANSER
Hanser Publications, Cincinnati

The Authors:

*Tim Osswald,
Natalie Rudolph,*

Polymer Engineering Center
Department of Mechanical Engineering
University of Wisconsin-Madison
Madison, WI 53706 USA

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 authors 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.

Authors' Disclaimer:

The data and information presented in this book have been collected by the authors and publisher from many sources that are believed to be reliable. However, the authors and publisher make no warranty, expressed or implied, to this book's accuracy or completeness. No responsibility or liability is assumed by the authors and publisher for any loss or damage suffered through reliance on any information presented in this book.
The authors do not purport to give any toxicity or safety information.

The final determination of the suitability of any information for the use contemplated for a given application remains the sole responsibility of the user.

Cataloging-in-Publication Data is on file with the Library of Congress

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 978-1-56990-517-3
E-Book ISBN 978-1-56990-523-4

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 2015
Editor: Christine Strohm
Production Management: Jörg Strohbach
Coverconcept: Marc Müller-Bremer, www.rebranding.de, München
Coverdesign: Stephan Rönigk
Layout: Manuela Treindl, Fürth
Printed and bound by Kösel, Krugzell
Printed in Germany

Dedication

We dedicate this book to our friend, colleague, and mentor Professor Dr.-Ing. Dr. h.c. Gottfried W. Ehrenstein. His lifelong commitment to learning, teaching, and research has inspired more than a generation of students and engineers, and has resulted in a continuous flow of ideas and innovation in plastics technology.

Preface

Designed to provide a polymer rheology background to both engineering students and practicing engineers, this book is written at an intermediate level with the technical information and practical examples required to enable the reader to understand the complex rheological behavior of polymers and its far-reaching consequences. It also provides the necessary decision-making tools for the appropriate choice of rheological testing methods, and the means to troubleshoot rheology related problems encountered in polymer processing. The organization of Polymer Rheology – Fundamentals and Applications and the practical examples throughout the book make it an ideal textbook and reference book, and the information provided is particularly valuable to processors and raw materials suppliers.

The authors would like to acknowledge the invaluable help of many during the preparation of this manuscript: our colleagues at the Polymer Engineering Center at the University of Wisconsin-Madison and at the Institute for Polymer Technology at the Friedrich-Alexander-University in Erlangen, Germany. In particular we would like to thank Dr. Andrew Schmalzer for serving as a sounding board and for his input, John Puentes for helping with the example problems in Chapter 4, Chuanchom Aumnate for the measurements used in the examples in Chapters 2 and 5, and Camilo Perez for reviewing Chapter 3. We are grateful to Tobias Mattner for his outstanding job in not only drawing the figures, but also making excellent suggestions on how to more clearly present the information. Thanks are due to Dr. Christine Strohm for her valuable expertise in editing this book. Dr. Nadine Warkotsch, Dr. Mark Smith and Jörg Strohbach of Carl Hanser Verlag in Munich are thanked for their support throughout this project. Above all, the authors would like to thank their families for their continued support of their work and their input throughout the writing of this book.

Summer 2014

Tim Osswald and Natalie Rudolph
Madison, Wisconsin, USA

Contents

Dedication	V
Preface	VII
1 Introduction to Rheology	1
1.1 The Field of Rheology	5
1.2 Viscous Liquids or the Newtonian Fluid	7
1.3 Linear Elasticity or the Hookean Spring	10
1.4 Viscoelasticity and the Maxwell Model	13
1.5 Time Scale and the Deborah Number	16
1.6 Deformation, Rate of Deformation, and the Deviatoric Stress Tensors ..	18
1.7 Guide to the Book	20
Problems	21
References	21
2 Structure and Properties of Deforming Polymers	25
2.1 Molecular Structure of Polymers	25
2.2 Stress Relaxation Behavior	32
2.3 Shear Thinning Behavior	37
2.4 Normal Stresses in Shear Flow	40
2.5 Stress Overshoot during Start-up Flow	44
2.6 Melt Strength or Melt Fracture	45
2.7 Dynamic Response	47
Problems	56
References	57
3 Generalized Newtonian Fluid (GNF) Models	59
3.1 Temperature Dependence of Viscosity	61
3.2 Viscous Flow Models	65
3.2.1 The Power Law Model	66
3.2.2 The Bird-Carreau-Yasuda Model	68

3.2.3	The Cross-WLF Model	70
3.2.4	The Bingham Model	71
3.2.5	The Herschel-Bulkley Model	72
3.2.6	Accounting for Pressure Dependence in Viscous Flow Models .	73
3.2.6.1	Power Law	73
3.2.6.2	Carreau-WLF	73
3.2.6.3	Cross-WLF	74
3.2.6.4	Universal Temperature and Pressure Invariant Viscosity Function	75
3.3	Elongational Viscosity	80
3.4	Suspension Rheology	82
3.5	Chemo-Rheology	87
	Problems	95
	References	97
4	Transport Phenomena	101
4.1	Dimensionless Groups	102
4.2	Balance Equations	106
4.2.1	The Mass Balance or Continuity Equation	106
4.2.2	The Material or Substantial Derivative	107
4.2.3	The Momentum Balance or Equation of Motion	109
4.2.4	The Energy Balance or Equation of Energy	114
4.3	Model Simplification	117
4.3.1	Reduction in Dimensionality	119
4.3.2	Lubrication Approximation	123
4.4	Viscometric Flows	125
4.4.1	Pressure Driven Flow of a Newtonian Fluid through a Slit ...	125
4.4.2	Flow of a Power Law Fluid in a Straight Circular Tube (Hagen-Poiseuille Equation)	126
4.4.3	Volumetric Flow Rate of a Power Law Fluid in Axial Annular Flow	129
4.4.4	Circular Annular Couette Flow of a Power Law Fluid	131
4.4.5	Squeezing Flow of a Newtonian Fluid between Two Parallel Circular Discs	134
4.4.6	Flow of a Power Law Fluid between Two Parallel Circular Discs	137
	Problems	140
	References	141

5	Viscoelasticity	143
5.1	Linear Viscoelasticity	144
5.1.1	Relaxation Modulus	144
5.1.2	The Boltzmann Superposition Principle	145
5.1.3	The Maxwell Model – Relaxation	147
5.1.4	Kelvin Model	148
5.1.5	Jeffrey’s Model	150
5.1.6	Standard Linear Solid Model	152
5.1.7	The Generalized Maxwell Model	154
5.1.8	Dynamic Tests	160
5.2	Non-Linear Viscoelasticity	164
5.2.1	Objectivity	164
5.2.2	Differential Viscoelastic Models	166
5.2.3	Integral Viscoelastic Models	179
	References	184
6	Rheometry	187
6.1	The Sliding Plate Rheometer	189
6.2	The Cone-Plate Rheometer	191
6.3	The Parallel-Plate Rheometer	194
6.4	The Capillary Rheometer	196
6.4.1	Computing Viscosity Using the Bagley and Weissenberg-Rabinowitsch Equations	198
6.4.2	Viscosity Approximation Using the Representative Viscosity Method	201
6.5	The Melt Flow Indexer	202
6.6	Extensional Rheometry	203
6.7	High Pressure Rheometers	209
6.8	Integrated Mold Sensors for Quality Control	214
	Problems	217
	References	218
	Subject Index	221

1

Introduction to Rheology

On December 9th of 1929, a little over a month after the Wall Street crash, and seven years after he published his book *Fluidity and Plasticity* [1], Eugene Bingham (Fig. 1.1), a chemistry professor at Lafayette College in Easton, Pennsylvania, and a group of chemists, engineers, and physicists met for the first time in Washington D.C.; they called themselves the *Society of Rheology*. Hence, for the first time the word rheology, coined by Markus Reiner and Eugene Bingham in 1920, was officially used¹.



Figure 1.1

Professor Eugene Bingham, in 1945 shortly before his death (Courtesy of Special Collections & College Archives, Skillman Library, Lafayette College)

¹ The roots of the word rheology are the Greek “reo” (flow) and “logos” (study).

However, the history of the field of rheology goes back centuries prior to Bingham and Reiner. A historical review is not complete until the more important events and discoveries through time, and the people who made those events and discoveries possible, have been identified. In Table 1.1 we list these events, discoveries, and important publications. If we inadvertently left out some, we apologize.

Table 1.1 Historical overview of the field of rheology

When	Who	What	Ref
1663	B. Pascal	Published works on inviscid fluids	[2]
1678	R. Hooke	Published work on elastic springs	[3]
1687	I. S. Newton	Published work on viscous fluids	[4]
1705	Bernoulli brothers	Publish the Bernoulli equation	[5]
1807	T. Young	Proposes the elastic (Young's) modulus	[6]
1820	C. Navier	Describes behavior of Newtonian fluids which eventually becomes the Navier-Stokes equation	[7]
1822	A. Cauchy	Describes stress and strain and formulates the Cauchy deformation tensor	[7]
1829	S. Poisson	Describes Poisson's ratio, ν	[8]
1839	G. Hagen	Builds the first capillary viscometer	[9]
1840	J. L. M. Poiseuille	Studies the rheology of blood and builds a capillary viscometer	[10]
1845	G. G. Stokes	Formulates a three dimensional Newtonian fluid model	[11]
1849	G. G. Stokes	Studies the parabolic velocity distribution in a capillary	[5]
1851	G. G. Stokes	Sphere fall experiments	[12]
1859	A. V. Lourenço	Observes viscosity increase with an increase in molecular weight	[13]
1861	A. Lipowitz	Builds a penetrometer to measure the hardness of a gel with a sinking weight	[14]
1861	T. Graham	Coins the word "Colloid"	[15]
1867	J. C. Maxwell	Formulates the viscoelastic Maxwell model	[16]
1873	J. D. Van der Waals	Publishes work on intramolecular forces	[17]
1874	L. Boltzmann	Publishes the superposition principle	[18]
1876	L. Boltzmann	Publishes work on the memory function	[19]
1881	M. Margules	Derives equations that describe the viscosity in the shear flow between two concentric cylinders	[20]
1886	M. M. Couette	Derives equations that describe the viscosity in the shear flow between two concentric cylinders	[21]
1888	M. M. Couette	Builds the first concentric cylinder system to measure viscosity; the drag flow viscometer or the Couette device	[22]
1890	W. Thomson-Kelvin	Describes a "solid viscosity", meaning a viscoelastic solid, known today as the Kelvin model	[5]
1890	W. Voigt	Publishes experiments on viscoelastic solids	[23]
1891	W. Ostwald	Builds a capillary viscometer, Ostwald viscosimeter	[14]