

# Contents

<b>Symbols and Nomenclature</b> . . . . .	xiii
<b>1 Introduction to Rheology</b> . . . . .	1
1.1 What is Rheology? . . . . .	1
1.2 Why Rheological Properties are Important . . . . .	3
1.3 Stress: A Measure of Force . . . . .	4
1.3.1 Foam Rubber Revisited . . . . .	4
1.3.2 Stress: A Normalized Measure of Force . . . . .	4
1.3.3 Role of Normal Stresses in Rheology . . . . .	6
1.4 Strain: A Measure of Deformation . . . . .	7
1.4.1 Strain Measures for Simple (Uniaxial) Extension . . . . .	8
1.4.2 A Strain Measure for Shear . . . . .	9
1.5 Rheological Phenomena . . . . .	10
1.5.1 Elasticity: Hooke's Law . . . . .	10
1.5.2 Viscosity: The Newtonian Fluid . . . . .	11
1.5.3 Viscoelasticity . . . . .	12
1.5.4 Structural Time Dependency . . . . .	15
1.5.5 Plasticity and Yield Stress . . . . .	16
1.6 Why Polymeric Liquids are Non-Newtonian and Elastic . . . . .	17
<b>2 Viscosity and Normal Stress Differences</b> . . . . .	19
2.1 Simple Shear and Steady Simple Shear . . . . .	19
2.2 Viscometric Flow . . . . .	20
2.3 The Viscometric Functions . . . . .	23
2.4 The Viscosity . . . . .	23
2.4.1 Effect of Shear Rate on Viscosity . . . . .	24
2.4.2 The Cox-Merz "Rule" . . . . .	28
2.4.3 Effect of Temperature on Viscosity . . . . .	29
2.4.4 Effects of Pressure and Dissolved Gas on Viscosity . . . . .	30
2.4.5 Effect of Molecular Weight on the Zero-Shear Viscosity . . . . .	32

2.4.6	Effect of Molecular Weight Distribution on Viscosity . . . . .	34
2.4.7	Effect of Tacticity on Viscosity . . . . .	35
2.4.8	Viscosity of Ethylene/Alpha-Olefin Copolymers . . . . .	36
2.4.9	Effect of Long-Chain Branching on Viscosity . . . . .	38
2.5	Normal Stress Differences . . . . .	43
	References . . . . .	45
<b>3</b>	<b>Linear Viscoelasticity . . . . .</b>	<b>49</b>
3.1	Introduction . . . . .	49
3.2	Stress Relaxation and the Relaxation Modulus . . . . .	50
3.3	The Boltzmann Superposition Principle . . . . .	50
3.4	Start-Up of Steady Simple Shear . . . . .	52
3.5	Relaxation Moduli of Rubbers and Molten Polymers . . . . .	53
3.6	The Maxwell Model for the Relaxation Modulus . . . . .	55
3.7	The Generalized Maxwell Model and the Discrete Relaxation Spectrum . . . . .	57
3.8	The Continuous Spectrum . . . . .	58
3.9	Creep and Creep Recovery: The Compliance . . . . .	58
3.10	Uniaxial (Simple) Extension . . . . .	62
	3.10.1 The Net Stretching Stress . . . . .	62
	3.10.2 Extensional Creep . . . . .	62
	3.10.3 Start-Up of Steady Simple Extension . . . . .	63
3.11	Small-Amplitude Oscillatory Shear . . . . .	63
	3.11.1 The Storage and Loss Moduli and the Complex Viscosity . . . . .	64
	3.11.2 The Storage and Loss Compliances . . . . .	66
3.12	Inferring a Discrete Relaxation Spectrum from Storage and Loss Moduli . . . . .	67
3.13	Combining Creep and Oscillatory Shear Data . . . . .	68
3.14	Time–Temperature Superposition . . . . .	68
	3.14.1 Basic Principle . . . . .	68
	3.14.2 The Vertical Shift Factor . . . . .	72
	3.14.3 The Horizontal Shift Factor . . . . .	72
3.15	Cole–Cole and Related Plots of Linear Data . . . . .	73
3.16	Van Gorp–Palmen Plot of Loss Angle Versus Complex Modulus . . . . .	75
3.17	Storage and Loss Moduli of Molten Linear Polymers . . . . .	76
3.18	The Plateau Modulus and the Molecular Weight Between Entanglements . . . . .	77
	3.18.1 Methods for Estimating the Plateau Modulus . . . . .	77
	3.18.2 The Molecular Weight Between Entanglements $M_e$ . . . . .	79

3.19	The Rouse-Bueche Model for Unentangled Melts . . . . .	80
3.20	Tube Models for Entangled Melts . . . . .	84
3.21	Molecular Weights for the Onset of Entanglement Effects . . . . .	86
	References . . . . .	87
<b>4</b>	<b>Nonlinear Viscoelasticity: Phenomena</b> . . . . .	<b>91</b>
4.1	Introduction. . . . .	91
4.2	Nonlinear Phenomena from a Tube Model Point of View. . . . .	92
4.3	Nonlinear Stress Relaxation. . . . .	93
4.3.1	Chain Retraction and the Damping Function. . . . .	93
4.3.2	Normal Stress Relaxation . . . . .	95
4.4	Dimensionless Groups Used to Plot Rheological Data . . . . .	97
4.4.1	The Deborah Number. . . . .	97
4.4.2	The Weissenberg Number. . . . .	97
4.5	The Viscosity in Terms of the Tube Model. . . . .	98
4.6	Transient Shear Tests at Finite Rates . . . . .	99
4.6.1	Stress Growth and Relaxation in Steady Shear . . . . .	99
4.6.2	Nonlinear Creep. . . . .	100
4.6.3	Large-Amplitude Oscillatory Shear . . . . .	101
4.7	Extensional Flow Behavior: Introduction . . . . .	103
4.8	Extensional Flow Characterization of Melts . . . . .	108
4.8.1	Linear Polymers. . . . .	108
4.8.2	Long-Chain Branched Polymers with Known Structures . . . . .	109
4.8.3	Randomly Branched Polymers and LDPE. . . . .	109
4.9	Shear Modification. . . . .	109
4.10	Time-Temperature Superposition of Nonlinear Properties . . . . .	110
	References . . . . .	111
<b>5</b>	<b>Nonlinear Viscoelasticity: Models</b> . . . . .	<b>115</b>
5.1	Introduction. . . . .	115
5.2	Tensor Notation . . . . .	116
5.3	The Stress Tensor . . . . .	117
5.4	A Strain Tensor for Infinitesimal Deformations. . . . .	121
5.5	The Boltzmann Superposition Principle in Tensor Form. . . . .	125
5.6	Strain Tensors for Large, Rapid Deformations. . . . .	126
5.6.1	The Cauchy and Finger Tensors . . . . .	127
5.6.2	Reference Configurations . . . . .	128
5.6.3	Scalar Invariants of the Finger Tensor . . . . .	129
5.7	Integral Constitutive Equations Based on Continuum Mechanics Concepts. . . . .	129
5.7.1	Lodge's Rubberlike Liquid Model . . . . .	130
5.7.2	Strain Dependent Memory Function and the Cauchy Tensor. . . . .	133

5.8	Continuum Differential Constitutive Equations . . . . .	134
5.9	Constitutive Equations from Molecular Models . . . . .	134
5.10	Numerical Simulation of Melt Flows . . . . .	136
	References . . . . .	136
<b>6</b>	<b>Measurement Techniques . . . . .</b>	<b>139</b>
6.1	Introduction. . . . .	139
6.2	Rotational and Other Drag-Flow Rheometers . . . . .	140
6.2.1	Cone-Plate Rheometry . . . . .	143
6.2.2	Parallel Disk Rheometry . . . . .	146
6.2.3	Accessing the Terminal Zone Using Creep and Creep Recovery . . . . .	147
6.3	Pressure-Driven Rheometers . . . . .	149
6.3.1	Capillary and Slit Rheometers . . . . .	149
6.3.2	Extrudate Distortion: Gross Melt Fracture and Sharkskin . . . . .	153
6.3.3	The Spurt Effect, Oscillating Flow, and Wall Slip . . . . .	156
6.3.4	The Extrusion Plastometer (Melt Indexer). . . . .	157
6.4	On-Line Rheometers . . . . .	161
6.4.1	On-Line Detection of Melt Index. . . . .	163
6.4.2	On-Line Determination of Viscosity. . . . .	163
6.5	High-Throughput Rheometry . . . . .	164
6.6	Extensional Rheometers . . . . .	164
6.6.1	Introduction. . . . .	164
6.6.2	Rheometers for Uniaxial (Simple) Extension. . . . .	165
6.6.3	Converging Flow and Melt Strength. . . . .	170
6.7	Torque Rheometers . . . . .	172
6.8	Using Rheology for Statistical Process Control . . . . .	173
6.9	Sample Stability: Thermo-Oxidative Degradation and Hydrolysis. . . . .	173
	References . . . . .	176
<b>7</b>	<b>Rheology and Molecular Structure . . . . .</b>	<b>181</b>
7.1	Rheology and Structure of Linear Polymers . . . . .	181
7.1.1	Effect of Molecular Weight on Zero-Shear Viscosity. . . . .	181
7.1.2	Effect of Molecular Weight Distribution on Shear Behavior . . . . .	182
7.1.3	Effect of Molecular Weight Distribution on Steady State Compliance . . . . .	185
7.1.4	Effect of Tacticity on Viscosity. . . . .	186
7.1.5	Effect of Comonomer on Linear Shear Behavior . . . . .	187
7.1.6	Extensional Flow Behavior of Linear Polymers . . . . .	189

7.2	Long-Chain Branching and Melt Rheology . . . . .	189
7.2.1	Introduction . . . . .	189
7.2.2	Branched Polymers with Monodisperse Structures . . . .	190
7.2.3	Long-Chain Branching in Metallocene Polymers . . . . .	192
7.2.4	Random Branching Introduced by Post-Polymerization Reactions . . . . .	197
7.2.5	Low-Density Polyethylene . . . . .	198
7.2.6	Branching Level from Zero-Shear Viscosity and Molecular Weight . . . . .	199
	References . . . . .	200
<b>8</b>	<b>Role of Rheology in Melt Processing . . . . .</b>	<b>205</b>
8.1	Introduction . . . . .	205
8.2	Flow in Simple Channels and Dies . . . . .	207
8.2.1	Flow in a Circular Channel . . . . .	207
8.2.2	Flow in a Slit Die . . . . .	208
8.2.3	Flow in Channels with Varying Cross-Section . . . . .	209
8.2.4	Flow in Noncircular Channels . . . . .	210
8.2.5	Coextrusion Instabilities . . . . .	211
8.3	Flow in an Extruder . . . . .	212
8.3.1	Basic Considerations . . . . .	212
8.3.2	Effect of Wall Slip on Flow in an Extruder . . . . .	214
8.3.3	Extrudate Phenomena . . . . .	214
8.4	Sheet Extrusion/Film Casting . . . . .	219
8.4.1	Extrusion Coating . . . . .	221
8.5	Film Blowing . . . . .	223
8.5.1	Introduction . . . . .	223
8.5.2	Flow in the Extruder and Die . . . . .	225
8.5.3	Drawability . . . . .	234
8.5.4	Modeling the Film Blowing Process . . . . .	234
8.6	Blow Molding . . . . .	235
8.6.1	Introduction . . . . .	235
8.6.2	Flow in the Die . . . . .	236
8.6.3	Parison Swell . . . . .	237
8.6.4	Parison Sag . . . . .	246
8.6.5	Pleating . . . . .	247
8.6.6	Parison Inflation . . . . .	247
8.6.7	Blow Molding of Engineering Resins . . . . .	248
8.6.8	Stretch Blow Molding . . . . .	248
8.6.9	Resin Selection . . . . .	249
8.7	Injection Molding . . . . .	250
8.7.1	Flow in Runners . . . . .	250
8.7.2	Mold Filling . . . . .	250

- 8.7.3 Formulation and Selection of Injection Molding Resins . . . . . 254
- 8.8 Rotational Molding . . . . . 255
- 8.9 Foam Extrusion . . . . . 256
- References . . . . . 257
  
- Appendix A: Structural and Rheological Parameters of Several Polymers. . . . . 261**
  
- Appendix B: The Displacement Gradient Tensor . . . . . 263**
  
- Author Index . . . . . 269**
  
- Subject Index . . . . . 277**