Contents

1. INTRODUCTION 1
A. Polymers and the importance of rheology 1
B. Rheology in its simplest form 9
Problems 12
Suggested references, with commentary 13
2. STRESS 15
A. Stress and pressure 16
B. Organization of the stress components 30
C. Coping with subscripts 31
D. Typical stress tensors 32
Appendix 2-1: Compilation of equations of motion (ssc) 38
Appendix 2-2: Equations of motion—curvilinear quick list (ssc) 40
Problems 40
References 44
3. VELOCITY, VELOCITY GRADIENT AND RATE OF DEFORMATION 45
A. Why velocity is simpler than location—Speedometers vs. GPS 45
B. Velocity gradients 46
C. Rate of deformation 48
Appendix 3-1: Components of the rate-of-deformation tensor 52
Appendix 3-2: Components of the continuity equation. 53
Appendix 3-3: Nomenclature and sign conventions used in popular rheology texts 53

CONTENTS

Problems 54
References 57
4. RELATIONSHIP BETWEEN STRESS AND RATE OF DEFORMATION: THE NEWTONIAN FLUID 59
A Material idealizations in rheology 59
B. The Newtonian fluid 63
Problems 68
References 70
5. GENERALIZED NEWTONIAN FLUIDS—A SMALL BUT IMPORTANT STEP TOWARD A DESCRIPTION OF REAL BEHAVIOR FOR POLYMERS 71
A. Reasons for inventing generalized Newtonian fluids—behavior of polymer melts 72
C. Generalizing the GNF to three dimensions 77
D. Inventing relationships for viscosity vs. shear rate. 82
E. Short primer on finding GNF parameters from data 86
F. Summary of GNF characteristics 90
Appendix 5-1: Fitting data with Excel® 90
Problems 92
References 96
6. NORMAL STRESSES—ORDINARY BEHAVIOR FOR POLYMERS 97
A. Introduction 97
B. What are normal stresses? 98
C. Origin of normal stresses in simple shear 99
D. The second normal-stress difference 102
E. Normal-stress coefficients and empirical findings 103
F. Transient rheological functions 107
D. Temperature effects and superposition of steady-flow data 109
Problems 116
References 122
7. EXPERIMENTAL METHODS 125
A. Measurement of viscosity 126
B. Normal stresses from shearing flows 149
C. Extensional rheology 155
D. Specialized geometries 162
E. Flow visualization and other rheo-optical methods 165
F. Micro and nano rheology 171
Appendix 7-1: Numerical derivatives 174
Appendix 7-2: Velocity-profile correction for non-Newtonian fluids 176

Appendix 7-3: Incorporation of slip into the velocity-profile correction—the Mooney correction 179
Appendix 7-4: Normal stresses using the cone-and-plate geometry 180
Appendix 7-5: Desktop rheo-optical experiment 184
Problems 186
References 193
8. STRAIN, SMALL AND LARGE 197
A. Displacement 197
B. Infinitesimal strain 201
C. Hookean solids 208
D. Finite strain 210
E. The Lodge elastic fluid and variants 214
F. The Cauchy strain measure 219
G. Fixing up integral equations based on **C** and $\mathbf{C}^{-1}$ 222
Appendix 8-1: The relaxation function 226
Appendix 8-2: Constant-rate extension of the LEF 227
Problems 233
References 238
9. MOLECULAR ORIGINS OF RHEOLOGICAL BEHAVIOR 239
A. Description of polymer molecules 239
B. The Rouse chain—a limited description of polymer behavior 241
C. Other chain-like models 242
D. Dealing with entanglements 248
E. Summary of predictions of molecular theory 255
Problems 256
References 259
10. ELEMENTARY POLYMER PROCESSING CONCEPTS 261
A. Simple laboratory processing methods 261
B. Elementary extrusion concepts 271
C. A downstream process—spinning 281
D. Summary 284
Appendix 10-1: Densities of melts at elevated temperatures 284
Problems 286
References 290
11. QUALITY-CONTROL RHEOLOGY 291
A. Examples of methods used by various industries 292
B. Test precision 297
Appendix 11-1: ASTM tests methods for rheological characterization 302
Problems 305
References 308

CONTENTS

12. FLOW OF MODIFIED POLYMERS AND POLYMERS WITH SUPERMOLECULAR STRUCTURE. 311
A. Polymers filled with particulates. 311
B. Liquid crystallinity and rheology 321
C. Polymers with microphase separation in melts or solutions 323
D. Covalent crosslinking of polymers 327
Appendix 12-1: Van 't Hoff equation applied to gelation 329
Problems 330
References 335
ANSWERS TO SELECTED PROBLEMS 337
Chapter 1 337
Chapter 2 339
Chapter 3 342
Chapter 4 345
Chapter 5 350
Chapter 6 352
Chapter 7 357
Chapter 8 362
Chapter 9 371
Chapter 10 372
Chapter 11 375
Chapter 12 377
NOMENCLATURE 381
Greek Symbols: 382
AUTHOR INDEX 385
SUBJECT INDEX 391