VISCOELASTIC PROPERTIES OF POLYMERS

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Preface

The extensive development of the subject of this book between the first edition in 1961 and the second edition in 1970 has progressed unabated in the past decade and is reflected in a further expansion of references and authors cited in this third edition. Even so, the present edition inevitably represents a smaller proportion of the total literature than did those preceding.

The chapters remain the same as in the second edition. As before, the emphasis is still on linear viscoelasticity of amorphous polymers. Although the phenomena of nonlinear viscoelasticity are given more attention, this subject and the properties of crystalline and glassy polymers are treated somewhat superficially and the reader is referred to other treatises and reviews, with the admonition that current developments may lead to a clearer understanding within a few years.

There have been a few minor changes in symbols, and the notation conforms to the recommendations of the Society of Rheology published in 1976. Numerical values are still given mostly in cgs units, but the equivalent values in SI units are frequently added.

As before, I am grateful to my present and former students and associates at the University of Wisconsin for their generous contributions to this edition in the form of general perspective and specific advice. Their researches cited here were supported in part by the agencies named in the preface to the first edition and also by the National Institutes of Health and the NATO Research Grants Programme.

Efforts to prevent this revision from being too far out of date on the day of publication have been greatly facilitated by unpublished data and other information generously made available by Professors D. J. Plazek, W. W. Graessley, R. B. Bird, A. J. Kovacs, J. L. Schrag, C. W. Macosko, N. W. Tschoegl, and G. C. Berry, and by Drs. M. Doi, O. Kramer, C. R. Taylor, and D. S. Pearson. Different portions of the manuscript were read by Professors R. B. Bird, N. W. Tschoegl, D. J. Plazek, J. L. Schrag, W. W. Graessley, J. J. Aklonis, A. S. Lodge, and A. Peterlin; and Drs. R. A. Dickie, D. J. Massa, and T. L. Smith. I am greatly indebted to them for their valuable advice. The manuscript was painstakingly typed by Miss Paulette A. Schlomann.

JOHN D. FERRY

Madison, Wisconsin
March 1980

Preface to the First Edition

It is interesting to observe the evolution of science in microcosm by following the development of a highly specialized fragment of it, especially one which cuts across several conventional fields, such as the subject of this book. The familiar pattern of alternation between experimental and theoretical advances is apparent. Underlying each advance is a conceptual scheme which is an arbitrary and subjective choice of one investigator or school; in this conceptual abstraction, attention is focused on certain aspects of observed behavior that are believed to be particularly important or useful to describe, and other aspects are ignored. The conceptual scheme leads to a set of characteristic physical quantities which can be defined, measured, and correlated by theoretical relationships.

Naturally, in the spontaneous development of the subject, alternative conceptual schemes arise, each with its favored definitions, parameters, and terminology. Sometimes the languages are readily translatable, in other cases with extreme difficulty. In the course of time, a majority of the scientific community may adopt one scheme, and for a while a degree of order prevails.

The subject of the viscoelasticity of polymers has not quite reached this last stage of development, but it has matured to the point where some kind of summarizing treatment seems desirable. The phenomenological theory of linear viscoelasticity is essentially complete. The molecular origin of some aspects of the viscoelastic behavior peculiar to polymers is semi-quantitatively understood, as are their dependences on temperature, molecular weight, concentration, and other variables. Moreover, the relationships are well enough understood to permit rule-of-thumb predictions of behavior in practical situations to a far greater extent, I believe, than has been exploited up to now. Other aspects such as the effects of molecular weight distribution and the properties of highly cross-linked, glassy, and crystalline polymers are very poorly understood, but the direction which further experimental and theoretical developments should take is fairly clear.

This book was written with several objectives in view. First, I have tried to assemble the working information needed by investigators in the field for making measurements and interpreting data—information which has hitherto been scattered in dozens of separate publications. A uniform notation has been used, most

of it in accordance with the recommendations of the Society of Rheology. Second, the exposition is I hope straightforward enough so that new investigators, of whom there are many in industrial laboratories encountering the phenomena of polymer viscoelasticity without any previous experience, can use it to familiarize themselves with the subject. Third, certain needs for further theoretical and experimental advances are pointed out. Finally, a few examples of practical applications are given in the hope that these will stimulate a much wider use of approximate interconversions of viscoelastic functions, and reduced variables describing effects of temperature, pressure, and concentration, to predict viscoelastic behavior and correlate it with other properties under a wide variety of conditions.

I owe a profound debt to my former students and associates who, over the years, have participated in studies of the viscoelastic properties of polymers at the University of Wisconsin, and whose collective experience has contributed greatly to writing this book. The work cited from our own laboratory was supported by the Research Committee of the Graduate School of the University of Wisconsin; the Ordnance Corps, Department of the Army; National Science Foundation; Office of Naval Research; Allegany Ballistics Laboratory; and Union Carbide Chemicals Company.

In addition to the many citations of published investigations from other laboratories, unpublished data and theoretical calculations were generously made available by the late Professor E. Jenckel and by Drs. A. Kovacs, J. Lamb, R. S. Marvin, A. R. Payne, and K. Ninomiya.

Most of the manuscript was written during tenure of a National Science Foundation Senior Postdoctoral Fellowship at the University of Brussels in 1959. I am deeply indebted to Professor L. de Brouckère for the kind hospitality of the Laboratoire de Chimie Analytique et Minérale at the University, and to European Research Associates for the use of library facilities. Different chapters were read by Professor Edwin R. Fitzgerald of Pennsylvania State University and by Drs. Robert F. Landel, Thor L. Smith, Robert S. Marvin, Kazuhiko Ninomiya, Donald J. Plazek, Malcolm L. Williams, and André J. Kovacs; I am grateful for their constructive criticism. The proof of the entire book was painstakingly read by Professor Fitzgerald and Dr. Plazek.

JOHN D. FERRY

December, 1960

Viscoelastic Properties of Polymers

Contents

1. The Nature of Viscoelastic Behavior 1

A. Introduction, 1

B. Strain, Stress, and Linear Constitutive Equations for Simple Shear, 3

1. Equations of Change, 4
2. Infinitesimal Strain Tensor, 4
3. Stress Tensor, 5
4. Constitutive Equation for Linear Viscoelasticity in Simple Shear, 6

C. Description of Linear Time-Dependent Experiments in Shear, 8

1. Stress Relaxation after Sudden Strain, 8
2. Stress Relaxation after Cessation of Steady Shear Flow, 9
3. Stress Growth after Initiation of a Constant Shear Rate, 9
4. Creep after Sudden Stress, 10
5. Other Types of Transient Experiments, 10
6. Periodic or Dynamic Experiments, 11
7. Correlation of Experimental Data to Provide Information over Wide Ranges of Time Scale, 14

D. Mechanical Model Analogies of Linear Viscoelastic Behavior, 15

E. The Boltzmann Superposition Principle; Elastic Recovery, 17

F. Linear Stress-Strain Relations for Other Types of Deformation, 20

1. Bulk Compression or Dilatation, 21
2. Simple Extension, 22
3. One-Dimensional Extension in Infinite Medium (Bulk Longitudinal Deformation), 25
4. Inhomogeneous Deformations, 25

G. Finite Strains and Large Strain Rates, 26

1. Normal Stress Differences, 27
2. Non-Newtonian Flow, 29
3. Other Time-Dependent Phenomena, 29

Supplement 1: Summary of Moduli and Compliances, 29

Supplement 2: Complex Notation for Dynamic (Sinusoidal) Stress-Strain Relations, 30

2. Illustrations of Viscoelastic Behavior of Polymeric Systems **33**

A. Linear Viscoelastic Behavior in Shear or Simple Extension, 33

1. Description of the Polymers Chosen for Illustration, 34
2. The Creep Compliance, 37
3. The Stress Relaxation Modulus, 40
4. The Storage Modulus, 41
5. The Loss Modulus, 42
6. The Dynamic Viscosity, 43
7. The Storage Compliance, 44
8. The Loss Compliance, 45
9. The Loss Tangent, 46

B. Linear Viscoelastic Behavior in Bulk (Voluminal) Deformation, 48

C. Nonlinear Viscoelastic Phenomena in Shear, 49

1. Normal Stress Differences, 49
2. Non-Newtonian Flow, 51
3. Stress Relaxation after Large Sudden Strains, 52
4. Stress Relaxation after Cessation of Steady-State Non-Newtonian Flow, 52

D. Conclusions, 54

3. Exact Interrelations among the Viscoelastic Functions **56**

A. Mechanical Model Analogies, 57

1. The Maxwell Element, 57
2. The Voigt Element, 58
3. Discrete Viscoelastic Spectra, 58

B. The Relaxation and Retardation Spectra, 60

1. The Relaxation Spectrum, 60

2. The Retardation Spectrum, 61
3. Interrelations between the Spectra, 63

C. Calculation of Viscoelastic Functions and Constants from the Spectra, 64

D. Calculation of Relaxation and Retardation Spectra from Experimentally Determined Viscoelastic Functions, 67

E. Calculation of One Experimentally Observable Viscoelastic Function from Another, 68

1. Interrelation of the Two Transient Functions, 68
2. Interrelation of a Transient with the Corresponding Dynamic Functions, 68
3. Interrelations between the Components of a Complex Dynamic Function, 69
4. Evaluation of Viscoelastic Constants, 70

F. Calculation of More Complicated Experimental Functions, 71

1. Deformation at Constant Rate of Strain, 71
2. Deformation at Constant Rate of Stress Loading, 72
3. Stress Relaxation after Cessation of Steady-State Flow, 73
4. Creep Recovery or Elastic Recoil, 73
5. Recovery after Partial Stress Relaxation, 74

G. Comments on the Phenomenological Theory of Linear Viscoelasticity, 74

H. Relations from Nonlinear Constitutive Equations, 76

4. Approximate Interrelations among the Linear Viscoelastic Functions **80**

A. Calculation of Spectra from Experimental Functions, 81

1. Relaxation Spectrum from Relaxation Modulus, 81
2. Retardation Spectrum from Creep Compliance, 82
3. Relaxation Spectrum from Storage Modulus, 83
4. Retardation Spectrum from Storage Compliance, 84
5. Relaxation Spectrum from Loss Modulus, 85
6. Retardation Spectrum from Loss Compliance, 86
7. Criteria of Applicability of Various Approximations, 86

B. Interrelations between the Spectra, 87

1. One Spectrum and Transient Known, 87
2. One Spectrum and Dynamic Data Known, 88
3. One Spectrum Known with Constant Logarithmic Slope, 88

C. Calculation of Viscoelastic Functions from the Spectra, 88

D. Calculation of One Experimentally Observable Viscoelastic Function from Another, 89

1. Interrelation of the Two Transient Functions, 89
2. Interrelation of a Transient with the Corresponding Dynamic Functions, 90
3. Interrelation between the Components of a Complex Dynamic Function, 92
4. Criteria of Applicability, 92

E. Calculation of Spectra from More Complicated Experimental Functions, 92

F. Table of Correction Factors, 94

5. Experimental Methods for Viscoelastic Liquids 96

A. Creep, 99

1. Rotation between Coaxial Cylinders, 99
2. Torsion between Parallel Plates or Cone and Plate, 101
3. Calculation of η_0 and J_e^0 from Creep Measurements in the Terminal Zone, 103
4. Nonlinear Creep and Non-Newtonian Viscosity, 104

B. Shear Stress Relaxation and Stress Growth, 104

C. Normal Stress Measurements, 105

1. Measurements of Total Thrust, 106
2. Measurements of Pressure Gradients, 106
3. Measurements Involving Hole Pressures, 107

D. Dynamic (Oscillatory) Measurements without Sample Inertia Effects ("Gap Loading"), 107

1. Direct Measurements of Sinusoidally Varying Stress and Strain, 108
2. Measurements Involving the Mechanical Impedance of a Moving Element, 110
3. Transducer Measurements by Electrical Impedance, 114

E. Dynamic (Oscillatory) Measurements of Characteristic Impedance ("Surface Loading"), 116

F. Shear Wave Propagation, 121

G. Dynamic Measurements on Liquids in Solid Matrices, 124

H. Measurement of Dynamic Viscoelastic Functions by Eccentric Steady Flow Instruments, 124

I. Isothermal and Adiabatic Measurements, 125

1. Difference between Adiabatic and Isothermal Moduli for Perfect Elastic Materials, 125
2. Critical Frequencies for Isothermal-Adiabatic Transitions, 126
3. Time-Dependent Effects Associated with Heat Flow, 126

6. Experimental Methods for Soft Viscoelastic Solids and Liquids of High Viscosity **130**

A. Creep, 132

B. Stress Relaxation, 133

C. Dynamic Measurements without Sample Inertia Effects, 135

1. Direct Measurements of Sinusoidally Varying Stress and Strain, 135
2. Transducer Measurements by Electrical Impedance, 136
3. Compound Resonance Devices with Forced Oscillations, 139
4. Compound Resonance Devices with Free Oscillations, 142

D. Wave Propagation, 144

E. Methods with Other Features, 148

1. Simple Extension at Constant Strain Rate, 148
2. Impact Measurements, 149
3. Sinusoidal Deformations with Large Amplitudes, 149
4. Combined Static and Dynamic Measurements, 150
5. Dynamic Mechanical Measurements Combined with Other Physical Properties, 150

7. Experimental Methods for Hard Viscoelastic Solids **154**

A. Creep and Stress Relaxation, 156

B. Direct Measurements of Sinusoidally Varying Stress and Strain, 157

C. Resonance Vibrations, 158

D. Compound Resonance Vibration Devices, 160

E. Wave Propagation, 161

F. Methods Adapted to Fibers, 161

1. Creep and Stress Relaxation, 162
2. Dynamic Measurements, 163

8. Experimental Methods for Bulk Measurements 168

A. Bulk Transient Measurements 168

B. Bulk Dynamic Measurements, 169

1. Homogeneous Deformation with Direct Measurement of Pressure, 169
2. Homogeneous Deformation by Longitudinal Waves in a Confining Liquid, 170
3. Longitudinal Bulk Wave Propagation, 171

9. Dilute Solutions: Molecular Theory and Comparison with Experiments 177

A. Rigid Solute Molecules, 179

1. Elongated Rodlike Models, 179
2. Other Rigid Models, 182
3. Jointed Bead-Rod Model, Three Beads, 183

B. Linear Flexible Random Coils: The Bead-Spring Model, 183

1. The Bead-Spring Model with No Hydrodynamic Interaction among Beads, 185
2. The Bead-Spring Model with Dominant Hydrodynamic Interaction, 191
3. Partial Hydrodynamic Interaction, 192
4. Non-Θ-Solvents, 193
5. Comparisons of Characteristic Parameters for Bead-Spring Model Theories, 194
6. Comparison of Theory for Linear Molecules with Experiment, 194
7. Effect of Molecular Weight Distribution, 198
8. Branched Flexible Random Coils, 200

C. Partially Flexible Elongated Molecules, 204

1. Helical Macromolecules, 205
2. Polyelectrolytes, 207

D. Behavior at Finite Concentrations, 209

1. Effects of Domain Overlap, 209
2. Onset of Entanglement Coupling, 212
3. Rigid Rodlike Macromolecules, 213

E. Behavior at High Frequencies and in High-Viscosity Solvents, 214

F. Non-Newtonian Flow, 219

G. Practical Aspects of Viscoelasticity of Dilute Solutions, 219

10. Molecular Theory for Undiluted Amorphous Polymers and Concentrated Solutions; Networks and Entanglements **224**

A. Undiluted Polymers of Low Molecular Weight, 224

1. Modified Rouse Theory, 225
2. Closed Form of Rouse Theory: Ladder Networks, 228
3. Effect of Molecular Weight Distribution, 229
4. Effect of Branching, 232

B. Cross-Linked Networks, 233

1. Idealized Network with Fixed Cross-Links, 234
2. Network with Mobile Cross-Links, 237
3. Network with Random Distribution of Strand Lengths, 239
4. Role of Network Defects, 240

C. Uncross-Linked Polymers of High Molecular Weight, 241

1. The Nature of Entanglement Coupling, 241
2. Behavior in the Transition Zone, 247
3. Behavior in the Terminal Zone, 247
4. Transient Network Models for Viscoelastic Properties in the Terminal Zone, 252
5. Practical Aspects of Behavior in the Terminal Zone, 253
6. Behavior in the Plateau Zone, 254

D. Behavior in and near the Glassy Zone, 254

1. Limiting Behavior at High Frequencies, 255
2. Persistence of Relaxation and Retardation Spectra into the Glassy Zone, 256

E. Nonlinear Behavior in Uncross-Linked Polymers of High Molecular Weight, 257

1. Apparent Viscosity in Non-Newtonian Flow, 257
2. Steady-State Compliance and Normal Stress Differences, 259
3. Other Manifestations of Nonlinear Behavior, 259

11. Dependence of Viscoelastic Behavior on Temperature and Pressure **264**

A. Origin of the Method of Reduced Variables, 266

1. Deduction from the Dilute-Solution Theories for Flexible Random Coils, 266
2. Deduction from Theory for Undiluted Polymers, 267
3. Empirical Development of the Use of Reduced Variables, 270
4. Reduced Variables for Undiluted Polymers in Terms of Steady-Flow Viscosity, 271
5. Reduced Variables Applied to Polymers of High Molecular Weight, 271
6. Application of Reduced Variables near the Glassy Zone of Time or Frequency, 272

B. Procedure and Criteria for Applicability of the Method of Reduced Variables, 273

C. The WLF Equation and the Relation of Temperature Dependence of Relaxation Times to Free Volume, 280

1. The Glass Transition and Free Volume, 280
2. Relation of Molecular Mobility to Free Volume, 285
3. The WLF Equation, 287
4. Modification of the WLF Equation with an Energy Term, 289

D. Free-Volume Interpretation of the Dependence of Relaxation Times on Pressure and Other Variables, 291

1. Pressure Dependence of Relaxation Times, 291
2. Interrelation of Effects of Temperature and Pressure on Relaxation Times, 294
3. Changes in Relaxation Times during Isothermal Contraction near the Glass Transition, 298
4. Effects of Molecular Weight and Other Variables on Free Volume and Relaxation Times, 298

E. Reduced Variables and Free-Volume Parameters from Other Than Viscoelastic Measurements, 301

1. Dielectric Dispersion, 301
2. Nuclear Magnetic Resonance Relaxation, 302
3. Diffusion of Small Molecules in Polymers, 303

F. Examples of More Limited Applicability of the Method of Reduced Variables, 304

1. Glassy and Highly Crystalline Polymers, 304
2. Multiple Viscoelastic Mechanisms with Different Temperature Dependences, 305
3. Changes in Internal Structure due to Crystallinity, 312

G. Treatment of Data at Fixed Frequency or Time and Varying Temperature, 312

H. Application of Reduced Variables to Bulk and Nonlinear Viscoelastic Properties, 314

1. Bulk (Volume) Viscoelasticity, 314
2. Normal Stresses, 314
3. Non-Newtonian Viscosity, 315
4. Ultimate Properties and Other Practical Aspects of Behavior, 315

12. The Transition Zone from Rubberlike to Glasslike Behavior **321**

A. The Location of the Transition Zone on the Time or Frequency Scale, 322

B. The Monomeric Friction Coefficient, 328

1. Comparisons at Constant Temperature, 329
2. Relation of Friction Coefficient to Free Volume in the Methacrylate Series, 333
3. Comparisons at Corresponding Temperatures, 335
4. Estimation of ζ_0 from the Steady-Flow Viscosity, 337
5. Correlation of ζ_0 with Data from Diffusion of Small Foreign Molecules, 338
6. Relation of ζ_0 to the Onset of the Transition Zone, 342

C. Shapes of the Spectra and Viscoelastic Function in the Transition Zone, 343

1. Relaxation Spectra Reduced to Corresponding States, 343
2. Relation of the Shape of H to Those of Other Viscoelastic Functions, 346
3. Behavior of Copolymers and Polymer Mixtures, 348
4. Behavior of Filled Systems, 356

D. The Transition Zone in Polymers of Low Molecular Weight, 359

13. The Plateau and Terminal Zones in Uncross-Linked Polymers **366**

A. Manifestations of Entanglement Networks, 366

1. Maxima in the Loss Compliance and Retardation Spectrum, 366
2. Storage Modulus and Loss Tangent, 368
3. Relaxation and Retardation Spectra, 369

B. Estimations of Entanglement Spacings, 372

1. Integration of Retardation Spectrum or Loss Compliance, 372

2. Other Methods for Estimating M_e, 376
3. The Critical Molecular Weight M_c from Viscosity or Viscoelastic Time Scale, 377
4. The Critical Molecular Weight M_c' from Steady-State Compliance, 378

C. Behavior in the Terminal Zone, 379

1. Viscosity at Vanishing Shear Rate, 379
2. Dependence of Non-Newtonian Shear Viscosity on Shear Rate, 380
3. Terminal Relaxation Time and Steady-State Compliance, 382
4. Effects of Branching, 385
5. Effects of Molecular Weight Distribution, 387

D. Behavior in the Plateau Zone, 391

1. Width of Plateau Zone on Time Scale, 392
2. Andrade Creep, 392
3. Effects of Molecular Weight Distribution, 393

E. Nonlinear Behavior in Uniaxial Extension, 395

1. Stress Relaxation, 396
2. Uniaxial Extension at Constant Strain Rate, 398
3. Creep and Creep Recovery, 400

14. Cross-Linked Polymers and Composite Systems **404**

A. Effects of Cross-Linking in the Transition Zone, 404

B. Effects of Cross-Linking in the Plateau and Terminal Zones, 407

1. Maxima in the Loss Compliance and Retardation Spectrum, 407
2. Additivity of Contributions of Cross-Links and Trapped Entanglements to the Equilibrium Modulus, 408
3. Changes in the Retardation Spectrum during Early Stages of Cross-Linking, 411
4. Approach to Elastic Equilibrium in Lightly Cross-Linked Systems, 414
5. Slow Relaxation Mechanisms and the Plateau Modulus G_N, 417
6. Relaxation of Unattached Macromolecules in Networks, 419
7. Densely Cross-Linked Polymers, 420

C. Nonlinear Behavior in Cross-Linked Polymers, 420

1. Nonlinear Behavior at Equilibrium, 420
2. Stress Relaxation and Creep, 422
3. Stress-Strain Behavior at Constant Rate of Deformation, 423
4. Small Dynamic Strains Superimposed on Large Static Strains, 424