

Contents

1. **Variations on a Theme of Uniaxial Orientation: Introductory Remarks on the Past, Present and Future of Fiber Formation** 1
D. R. Salem

2. **Structure Formation During Melt Spinning** 5
J. E. Spruiell

2.1 Concepts and Theories 6

2.1.1 Introduction 6

2.1.2 An Engineering Analysis of the Process 9

2.2 Experimental Observations and Discussion 29

2.2.1 Polyolefins 29

2.2.2 Polyesters 51

2.2.3 Polyamides 66

2.2.4 Other Homopolymers 74

2.2.5 Copolymers Developed for Specialty Applications 76

2.2.6 Polymer Blends and Bicomponent Fibers 82

2.3 Concluding Remarks 86

2.4 References 87

3. **Advances in the Control of Spinline Dynamics for Enhanced Properties** 94
J. A. Cuculo, Joseph F. Hotter and Qiang Zhou

3.1 Introduction 94

3.2 Moving Beyond Imposed Limits as Take-Up Speeds Increase 95

3.2.1 The Dominant Forces 95

3.2.2 Cooling and Crystallization 98

3.2.3 Transient Effects 100

3.3 Recent Development Efforts and Achievements 102

3.3.1 Theoretical Tensile Strengths and the Potential for Vast Improvements 103

3.3.2 The Ideal One-Step Spinning Process 103

3.3.3 Patented Advances in Fiber Melt Spinning 105

3.4 The Preferred Route to Judicious Control of Spinline Dynamics 108

3.4.1 Judicious Control via Radical Change 108

3.4.2 The Response of Spinline Dynamics 109

3.4.3 Unprecedented As-Spun Fiber Properties 111

3.4.4 The Concept of Extended Chains and Enhanced Molecular Connectivity 113

3.5	Potential Applications and Future Development	115
3.6	References	116
4.	Structure Formation During Drawing of Flexible Chain Polymers	118
	<i>D. R. Salem</i>	
4.1	Introduction.....	119
4.2	Overview of Stress-Strain-Structure Relationships	121
4.2.1	Modes of Deformation	121
4.2.2	Constant Extension Rate Deformation	122
4.2.3	Constant Force Deformation	133
4.3	Orientation-Induced Crystallization.....	135
4.3.1	General Concepts.....	135
4.3.2	The Case of Poly(ethylene terephthalate).....	136
4.3.3	Other Polymers	151
4.4	Theory and Modeling	152
4.4.1	Stress-Strain-Orientation Behavior	152
4.4.2	Crystallization	161
4.4.3	Molecular Dynamics Simulations	162
4.5	Morphology.....	164
4.5.1	Range of Order	164
4.5.2	Three Phase Models.....	165
4.6	Structure-Property Relationships	167
4.6.1	Tensile Modulus, Strength, Yield, and Elongation at Break	168
4.6.2	Dimensional Stability	170
4.6.3	Penetrant Diffusion	171
4.7	High Performance Fibers	172
4.7.1	Apolar Polymers	172
4.7.2	Polar Polymers.....	174
4.8	References	178
5.	Basic Aspects of Solution(Gel)-Spinning and Ultra-Drawing of Ultra-High Molecular Weight Polyethylene	185
	<i>P. J. Lemstra, C. W. M. Bastiaansen and S. Rastogi</i>	
5.1	Introduction.....	186
5.2	The Ultimate Stiffness and Strength of Flexible Polymers.....	188
5.2.1	The Ultimate Tensile Modulus.....	188
5.2.2	The Ultimate Tensile Strength	189
5.2.3	Infinite vs. Finite Chains.....	189
5.2.4	Chain Alignment, Orientation vs. Extension	191
5.3	Chain Orientation and Chain Extension	194
5.3.1	The Single Chain	194
5.3.2	An Ensemble of Chains.....	196
5.4	Drawing of Polyethylene in the Solid-State.....	198
5.4.1	Solid-State Drawing of Polyethylenes.....	198

5.4.2	Solution (Gel)-Crystallized Polyethylene	200
5.4.3	Solvent-Free Processing Routes; Nascent Reactor Powder	202
5.4.4	Modeling of the Drawing Behavior	210
5.4.5	Drawing Behavior of Other Polymer Systems	216
5.5	Properties of Polyethylene Fibers, 1-D vs. 3-D	218
5.5.1	Tensile Strength (1-D)	218
5.5.2	Polyethylene Fibers in Composites (3-D)	220
5.5.3	Miscellaneous Properties of PE Fibers	221
5.6	Concluding Remarks	221
5.7	List of Symbols and Abbreviations	222
5.8	References	223
6.	Electrospinning and the Formation of Nanofibers	225
	<i>H. Fong and D. H. Reneker</i>	
6.1	Introduction	225
6.2	Electrospinning Process	227
6.2.1	Jet Initiation and the Diameter of a Single Jet	228
6.2.2	Bending Instability and the Elongation of the Jet	229
6.2.3	Diameter of Nanofibers	233
6.2.4	Observations of Electrospinning of Polyethylene Oxide Solution: Length of the Straight Segment Flow Rate of the Solution, Current, and Voltage	234
6.3	Nanofibers and their Unique Properties	236
6.3.1	Beaded Nanofibers	236
6.3.2	Electrospun Poly (<i>p</i> -phenylene terephthalamide)	237
6.3.3	Composites with Nanofiber Reinforcement	239
6.3.4	Elastomeric Poly(styrene-butadiene-styrene) Nanofibers, Phase Miscibility	240
6.3.5	Carbon Nanofibers	241
6.3.6	Nanofibers for Biomedical, Filtration, Agricultural, and Outer-Space Applications	244
6.4	Acknowledgements	245
6.5	References	245
7.	Fibers from Liquid Crystalline Polymers	247
	<i>S. Z. D. Cheng, F. Li, C. Y. Li, K. W. McCreight, Y. Yoon and F. W. Harris</i>	
7.1	Introduction: Liquid Crystalline Phases	247
7.2	Rheology in Liquid Crystalline Polymers	248
7.3	Fibers from Liquid Crystalline Polymers	253
7.4	Structure Formation and Properties of Liquid Crystalline Polymer Fibers from the Lyotropic Liquid Crystalline State	257
7.4.1	Molecular Parameters, Fiber Spinning, and Heat Treatments	258
7.4.2	PPTA Fiber Structure, Morphology, and Properties	260
7.4.3	PBZT and PBO Fiber Structure, Morphology, and Properties	266

7.5	Structure Formation and Properties of Liquid Crystalline Polymer Fibers from the Isotropic Solution State	271
7.5.1	Molecular Parameters, Fiber Spinning, and Heat Treatments	272
7.5.2	Organo-Soluble Aromatic Polyimide Fiber Structure, Morphology, and Properties	274
7.5.3	Technora [®] Fiber Structure, Morphology, and Properties	280
7.6	Structure Formation and Properties of Liquid Crystalline Polymer Fibers from the Thermotropic State	282
7.6.1	Molecular Parameters, Fiber Spinning, and Heat Treatments	283
7.6.2	HBA/PET Copolyester Fiber Structure, Morphology, and Properties	285
7.6.3	HBA/HNA Copolyester Fiber Structure, Morphology, and Properties	287
7.6.4	Ekonol [®] Copolyester Fiber Structure, Morphology, and Properties .	288
7.7	Concluding Remarks	288
7.8	References	289
8.	Solvent Spun Cellulose Fibers	296
	<i>J. A. Cuculo, N. Aminuddin and M. W. Frey</i>	
8.1	Structure and Properties	296
8.1.1	Introduction	296
8.1.2	Cellulose Structure	297
8.2	Fiber Formation	301
8.2.1	Introduction	301
8.2.2	Liquid Crystalline State	307
8.2.3	Direct Dissolution of Cellulose	309
8.2.4	Fiber Extrusion and Properties	320
8.3	Concluding Remarks	325
8.4	References	325
9.	Carbon Fibers	329
	<i>D. J. Johnson</i>	
9.1	Formation and Structure	329
9.1.1	Introduction	329
9.1.2	Carbon Fibers from PAN Precursors	331
9.1.3	Carbon Fibers from Pitch Precursors	336
9.2	Structure and Properties	339
9.2.1	Tensile Modulus	339
9.2.2	Tensile and Compressive Strength	339
9.2.3	The Structure of Carbon Fibers	340
9.2.4	Failure Mechanisms	349
9.2.5	Disorder in Carbon Fibers	353
9.2.6	Structure-Property Relations	354
9.3	References	356

10. Fibers from Electrically Conductive Polymers	359
<i>R. V. Gregory</i>	
10.1 Introduction.....	359
10.1.1 Polymer Conductivity	360
10.1.2 Measurement of Polymer Conductivity	367
10.1.3 Processing of Conductive Polymers	369
10.1.4 Fiber Formation	372
10.2 Fiber Formation from Emeraldine Base Polyaniline.....	373
10.2.1 Solution Spinning of Emeraldine Base Fiber.....	377
10.2.2 PANI Fiber Properties	385
10.2.3 Viscoelastic Characterization of Spin Dopes	386
10.2.4 Thermal Characteristics of LEB PANI Fibers.....	392
10.3 Conclusions	392
10.4 Future Trends	394
10.5 References	394
11. Fibers from Polymer Blends and Copolymers	397
<i>R. K. Krishnaswamy and D. G. Baird</i>	
11.1 Introduction.....	397
11.2 Polymer Blends	398
11.2.1 Introduction	398
11.2.2 Miscibility.....	398
11.2.3 Multiphase Blends	400
11.2.4 Blends of Thermoplastics and Thermotropic Liquid Crystalline Polymers	401
11.3 Bicomponent Fibers	402
11.4 Fibers from Polymer Blends.....	404
11.5 Thermoplastic Fibers Reinforced with Thermotropic Liquid Crystalline Polymers	406
11.5.1 Fibers Produced by Simultaneous Melting of Blend Components	406
11.5.2 Fibers Generated Using the Dual Extrusion Process	409
11.5.3 Post-Processing of Fibers Generated Using the Dual Extrusion Process	417
11.6 Copolymers	419
11.7 Elastomeric Fibers.....	420
11.8 References	422
12. Thermomechanical Processing: Structure and Properties	425
<i>J.M. Schultz</i>	
12.1 Introduction.....	425
12.2 Commercial Practice	426
12.2.1 General Comments	426
12.2.2 Consumer Textiles	427
12.2.3 Tire Cord and Other Industrial Applications.....	431

12.3	Phenomenology of Thermomechanical Treatments.	433
12.3.1	Mechanical Behavior During Processing; Creation of Internal Stress; Heat-Setting	433
12.3.2	The Development of Orientation of the Crystalline and Amorphous Substituents	440
12.4	Fiber Structure	441
12.4.1	Basic Structure.	441
12.4.2	Crystal Transformation During Heat-Treatment.	442
12.4.3	The Oriented Mesophase.	442
12.5	Kinetics of Structure Development During Heat-Treatment	445
12.5.1	Effect of Orientation on the Crystallization Rate	445
12.5.2	<i>In Situ</i> Studies	446
12.5.3	Treat and Quench Investigations	447
12.6	Some Final Remarks.	453
12.7	References	454
13.	Microstructure Characterization.	457
13.1	Wide Angle X-Ray Diffraction Analysis of Fibers.	457
	<i>J. Blackwell</i>	
13.1.1	Introduction	457
13.1.2	Degree of Crystallinity.	458
13.1.3	Degree of Orientation	460
13.1.4	Crystallite Size	461
13.1.5	Crystal Structure Determination.	462
13.1.6	Aperiodic Scatter from Fibers of Random Copolymers	465
13.1.7	Transesterification in Blends of Copoly(HBA/HNA)	469
13.1.8	Nonlinearity and Distortions	471
13.1.9	References.	473
13.2	Small-Angle Scattering	475
	<i>N.S. Murthy</i>	
13.2.1	Introduction	475
13.2.2	Characteristics of SAS.	477
13.2.3	Instrumentation	479
13.2.4	Data Analysis.	479
13.2.5	Applications	485
13.2.6	Concluding Remark.	491
13.2.7	References.	491
13.3	Density, Birefringence, and Polarized Fluorescence	493
	<i>B. Clauss and D. R. Salem</i>	
13.3.1	Crystallinity from Density.	493
13.3.2	Molecular Orientation from Birefringence	495
13.3.3	Molecular Orientation from Polarized Fluorescence	497
13.3.4	References.	505

13.4 Spectroscopic Methods: Infrared, Raman and Nuclear Magnetic Resonance	507
<i>D.R. Salem and N. Vasanthan</i>	
13.4.1 Introduction	507
13.4.2 Infrared	509
13.4.3 Raman	513
13.4.4 Nuclear Magnetic Resonance	515
13.4.5 References	518
14. Fiber Formation and the Science of Complexity	521
<i>J.W.S. Hearle</i>	
14.1 Introduction	521
14.2 A Historical Account of Structural Complexity	523
14.2.1 The Early Fringed Micelle Models	523
14.2.2 The Common Working Model	528
14.2.3 Alternative Continuous Models	532
14.2.4 Other Complexities	534
14.3 The Science of Complexity	536
14.3.1 Far from Equilibrium	536
14.3.2 Characterizing Structure: Computer Graphics	537
14.3.3 Polymer Dynamics	538
14.3.4 Fractals	540
14.3.5 Kinetics of Homogeneous Processes	541
14.3.6 Nonlinear Irreversible Thermodynamics	542
14.3.7 Chaos Theory	543
14.4 The Possible Role of Quantum Theory	544
14.4.1 Quantum Effects	544
14.4.2 Melt-Spun Fiber Formation	546
14.4.3 Clusters and Quantized Energy Levels	547
14.5 Conclusion: Scientific and Engineering Opportunity	549
14.6 References	551
Index	553