

Contents

Part I Principles: Theory and Practice

1 Physical Principles of Scanning Probe Microscopy Imaging	3
1.1 Introduction	3
1.2 The Physical Principles of Atomic Force Microscopy	4
1.2.1 Forces Between Atomic Species and Surfaces of Solids	5
1.3 Modeling the AFM Force–Distance Curve: Interactions Between Tip and a Planar Half-Space	11
1.4 Static Theory of Deflected Cantilever Beams	13
1.4.1 Vibrating Cantilever Beams	15
References	23
2 Atomic Force Microscopy in Practice	25
2.1 Assembling of AFMs for Operation	25
2.1.1 Scanned Sample AFM (Contact Mode)	25
2.1.2 Stand Alone AFM (Contact Mode)	38
2.1.3 Intermittent Contact (Tapping) Mode	41
2.2 Practical Issues of AFM Operation	45
2.2.1 AFM Cantilevers, Tips, and Their Characteristics	45
2.2.2 Sample Preparation	46
2.2.3 Choice of Operation Modes and Suitable Imaging Environments	50
2.2.4 Tip Handling and Modification Procedures	50
2.2.5 Calibration Issues	51
2.2.6 General Guidelines for AFM Laboratories	58
2.2.7 Data Evaluation	60
2.2.8 Typical AFM Artefacts	66
References	73

Part II Case Studies: Macromolecules, Polymer Morphology and Polymer Surface Properties by AFM

3 Visualization of Macromolecules and Polymer Morphology	79
3.1 Structural Hierarchy in Polymers	79
3.2 Single Component Systems	89
3.2.1 Visualization of Single Macromolecules	89
Visualization of Poly(ethylene imine) (PEI)	
Adsorbed on Mica	92
Visualization of Poly(amidoamine) Dendrimers	
Adsorbed on Mica	94
3.2.2 Lattice Visualization of Crystallized Homopolymers	94
Lattice Visualization of Poly(tetrafluoro ethylene) (PTFE)	
by CM-AFM	96
Lattice Visualization of Poly(oxy methylene) (POM)	
by CM-AFM	98
3.2.3 Amorphous Polymers	99
Imaging of the Surface Morphology of Poly(ethylene terephthalate) (PET) by TM-AFM	101
Imaging of Dewetted Perfluoropolyether Lubricant on Hard Disc Surfaces by TM-AFM	102
3.2.4 Lamellar Crystals (Crystallized from Solution or Melt)	104
Solution-Grown Lamellae of POM and PE by CM-AFM	105
Lamellae in Isotactic Polypropylene (iPP) by TM-AFM	106
Lamellae in Spin-Coated Films of Poly(ethylene oxide) (PEO) by TM-AFM	109
3.2.5 Extended Chain Crystals and Shish-Kebab Structures	110
CM-AFM on Extended Chain Crystals of Cold-Drawn PET	111
TM-AFM on Shish-Kebab Morphology in Drawn Polyethylene Copolymers	112
3.2.6 Hedrites and Spherulites	113
Sample Preparation: Melt Crystallization Followed by Etching	114
CM-AFM on Thin Films of Isotactic Polypropylene (iPP): α -iPP	116
3.3 Biopolymers	118
3.3.1 Imaging of Biological and Biopolymer Specimens Under Liquid	118
3.3.2 Hand-on Examples	127
Visualization of Adsorbed Lipid Vesicles and Bilayers	127
Visualization of Polymerizable Lipid Bilayers	129
Visualization of the Tobacco Mosaic Virus	130

Cellulose Fibers in Pulp	132
Cellulose Microcrystals	133
Polysaccharides: Xanthan Gum	134
Collagen	135
Crystallized Protein Layers: Streptavidin	137
Lambda DNA	138
Biocompatible Polymers	139
3.4 Multicomponent Systems	140
3.4.1 Materials Contrast in AFM Imaging of Multicomponent Systems	140
3.4.2 Block Copolymers	143
Visualization of Microphase Separated Morphology of Films of Polystyrene-b-polyisoprene-b-polystyrene	145
Visualization of Microphase Separated Morphology of Hydrolyzed Films of polystyrene-b-poly(tert-butyl acrylate)	147
3.4.3 Polymer Blends	148
Identification of Phases in Blends of PMMA and PB	150
Identification of Phases in Blends of Impact Polymers by FMM	153
3.4.4 Filled Polymer Systems	154
Distribution of Filler Particles in Elastomers by TMAFM	155
Distribution of Filler Particles in Rubbers by PF mode AFM	157
3.4.5 Interfaces and Interphases in Composites	158
Morphology of Transcrystallized Isotactic PP Induced by Pulling of a Carbon Fiber	159
3.5 Polymers in Applications: Effects of Processing and Processes	161
3.5.1 Polymers in Applications	161
3.5.2 Polymer Processing	163
AFM Imaging of Processed Polymers (1): Blown Films of High Melt Strength Polypropylene (hmsPP)	165
AFM Imaging of Processed Polymers (2): Surface Roughness and Haze	168
Deformation of Block Copolymers	170
3.5.3 Polymer Surface Modifications	171
Surface Oxidized Polypropylene by Oxyfluorination	173
Flame Treatment of LDPE	174
3.5.4 Latexes and Paints	175
3.5.5 Membranes and Porous Films	175
3.5.6 Defects and Failure Analysis	177
AFM Imaging of Rubbed Polyimide	180
References	181

4 Polymer Surface and Interface Properties and (Dynamic) Processes	189
4.1 Adhesion	189
4.1.1 Practical Adhesion Mapping	193
Solution-Grown Lamellae of PE on Mica by FV	194
4.1.2 Correlation of Adhesion Forces and Effects	
of Surface Treatments	197
Surface Treatment of PDMS	198
Force Titrations of Flame-Treated LDPE	201
Force Mapping of Polymer Blends	203
4.2 Friction	204
Sub- T_g Transitions in PMMA	208
Friction Forces on Oxidized PS	209
4.3 Surface Mechanical Properties	211
Nanoindentation of Homopolymers	214
Recovery After Nanoindentation of HDPE	216
4.4 Thermal Properties and Thermal Transitions	217
Crystallization and Melting of PEO by Hotstage Contact	
Mode AFM	222
Crystallization of PCL by Hotstage TM-AFM	225
4.5 Swelling and Solvent Effects	227
Swelling of Polymer Films Ex Situ	228
4.6 Chemical Reactions, Degradation, and Erosion	230
Degradation and Erosion of Biodegradable Polymers	231
Enzymatic Degradation of Polymers	233
References	234
Appendices	237
A. AFM manufacturers	237
B. Probe Tip manufacturers / vendors	239
C. SPM software	241
D. Web-based resources	242
Index	243