

Contents

Preface *XV*

List of Contributors *XIX*

List of Contacts *XXIII*

Part I Introduction to Plasma Technology for Surface Functionalization *1*

1	Introduction to Plasma and Plasma Technology	3
	<i>Massimo Perucca</i>	
1.1	Plasma: the Fourth State of Matter	3
1.2	Historical Highlights	4
1.3	Plasma Fundamentals	6
1.3.1	Free Ideal Gas	7
1.3.2	Interacting Gas	8
1.3.3	The Plasma as a Fluid	11
1.3.4	Waves in Plasmas	12
1.3.5	Relevant Parameters that Characterize the State of Plasma	14
1.4	Classification of Technological Plasmas	17
1.4.1	Hot (Thermal) Plasmas and Their Applications	18
1.4.2	Cold (Nonthermal) Plasmas and Their Applications	19
1.5	Reactive Plasmas	22
1.5.1	Elementary Plasma–Chemical Reactions	22
1.5.2	Elastic Scattering and Inelastic Thomson Scattering: Ionization Cross-section	24
1.5.3	Molecular Ionization Mechanisms	25
1.5.4	Stepwise Ionization by Electron Impact	26
1.6	Plasma Sheaths	28
1.7	Summary	31
	References	31

2	Plasma Systems for Surface Treatment	33
	<i>Guy Buyle, Joachim Schneider, Matthias Walker, Yuri Akishev, Anatoly Napartovich, and Massimo Perucca</i>	
2.1	Introduction	33
2.2	Low Pressure Plasma Systems	34
2.2.1	Microwave Systems	35
2.2.1.1	Introduction	35
2.2.1.2	Standard Microwave System for Textile Treatment	36
2.2.1.3	Example: Duo-Plasmaline—a Linearly Extended Plasma Source	36
2.2.1.4	Electron Cyclotron Resonance Heated Plasmas	40
2.2.2	Capacitively Coupled Systems	43
2.2.2.1	Introduction	43
2.2.2.2	Capacitive Coupled Plasma for Biomedical Applications	44
2.2.3	Physical Vapor Deposition Plasma: LARC [®]	45
2.2.3.1	Background	45
2.2.3.2	Cathodic Arc PVD Systems	45
2.2.3.3	Example: Treatment of Food Processing Tools by LARC [®] PVD System	48
2.3	Atmospheric Pressure Plasma Systems	49
2.3.1	Corona-type Surface Treatment	51
2.3.1.1	Standard Corona Treatment	51
2.3.1.2	Controlled Atmosphere Corona Treatment—Aldyne Treatment	52
2.3.1.3	Liquid Deposition	52
2.3.2	Remote Surface Treatment	54
2.3.2.1	Plasma Sources Used for Modeling	55
2.3.2.2	Example: AcXys Plasma Jet	57
2.4	Summary	58
	Acknowledgment	59
	References	59
3	Plasma-surface Interaction	63
	<i>Domenico D'Angelo</i>	
3.1	Introduction	63
3.2	Polymer Etching	65
3.3	Plasma Grafting	66
3.4	Chemical Kinetics	68
3.4.1	Chain Polymerization	68
3.4.2	Plasma Polymerization	70
3.5	Example: Plasma Polymerization	71
3.5.1	Plasma Polymerization of HEMA	72
3.5.1.1	Theoretical Background	72
3.5.1.2	Example: Polymerization of HEMA on PET Fabric	73
3.5.2	Plasma Polymerization of HDMSO	75
3.6	Conclusion	76
	References	77

4	Process Diagnostics by Optical Emission Spectroscopy	79
	<i>Giacomo Piacenza</i>	
4.1	Introduction	79
4.2	Optical Emission Spectroscopy	79
4.2.1	Theory of Optical Emission	80
4.2.2	Spectroscopy	82
4.2.3	OES Bench and Set-up	83
4.3	Optical Absorption Spectroscopy	85
4.3.1	Actinometry	86
4.4	Laser Induced Fluorescence (LIF)	87
4.5	Conclusion	88
	References	88
5	Surface Analysis for Plasma Treatment Characterization	91
	<i>Amandine David, Yves de Puydt, Laurent Dupuy, Séverine Descours, Françoise Sommer, Minh Duc Tran, and Jocelyn Viard</i>	
5.1	Introduction to Surface Characterization Techniques	91
5.2	X-ray Photoelectron Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA)	94
5.2.1	Principles of XPS	95
5.2.2	XPS Core Level Chemical Shift	96
5.2.3	Quantitative Analysis	97
5.2.4	Quantitative Analysis of Nitrogen Plasma-Treated Polypropylene	98
5.2.5	Angle-Resolved XPS Depth Profiling and Surface Sensitivity Enhancement by Grazing Angle XPS Detection	100
5.2.6	Determination of Thin Coating Thickness by Angle-Resolved XPS	100
5.2.7	Mapping	104
5.2.8	Summary of XPS	105
5.3	Static Secondary Ion Mass Spectrometry by Time of Flight (ToF-SSIMS)	106
5.3.1	Principles of ToF-SSIMS	106
5.3.1.1	Secondary Ion Emission	107
5.3.1.2	Static and Dynamic Modes	107
5.3.1.3	Molecular SIMS	107
5.3.2	Applications of ToF-SSIMS	107
5.3.2.1	Spectrometry Mode	108
5.3.2.2	Secondary Ion Imaging	108
5.3.2.3	Depth Profiling	108
5.3.2.4	Data Treatment by Multivariate Methods: Multi-Ion SIMS	108
5.3.2.5	Examples	109
5.3.2.5.1	Poly(ethylene terephthalate) Tissue	109
5.3.2.5.2	Polypropylene Packaging	109
5.3.2.5.3	SiO _x Barrier Coating on PET	111
5.3.2.5.4	Anti-UV Additive qualification on PET Films	112

5.4	Atomic Force Microscopy	114
5.4.1	Operating Modes in AFM	114
5.4.1.1	Contact Mode	115
5.4.1.1.1	Constant Force Mode	115
5.4.1.2	Resonant Modes	117
5.4.1.2.1	The Contact –No Contact Mode	118
5.4.1.2.2	Phase Contrast Mode	118
5.4.1.3	Other Modes	119
5.4.2	Summary and Outlook	119
5.5	Scanning Electron Microscopy (SEM)	121
5.5.1	Principles of SEM	121
5.5.2	Imaging in SEM	122
5.5.3	New Generation of SEM	122
5.5.4	Chemical Analysis	123
5.5.5	Sample Preparation and Applications	124
5.6	Transmission Electron Microscopy (TEM)	124
5.6.1	Principles of TEM	124
5.6.2	Resolution	126
5.6.3	Image Contrast	126
5.6.4	Chemical Analysis	126
5.6.5	Typical Applications of TEM	127
5.6.6	Sample Requirements	127
5.7	Contact Angle Measurement	129
5.7.1	Surface Energy Calculation	130
5.7.1.1	Owens and Wendt Model for Surface Energy Calculation	130
5.7.1.2	Good and Van Oss Model for Surface Energy Calculation	131
5.8	Conclusions	132
	References	132

Part II Hyperfunctional Surfaces for Textiles, Food and Biomedical Applications 133

6	Tuning the Surface Properties of Textile Materials	135
	<i>Guy Buyle, Pieter Heyse, and Isabelle Ferreira</i>	
6.1	Introduction	135
6.1.1	Potential Impact of Plasma on the Textile Industry	135
6.1.2	Plasma Basics	137
6.1.3	Fundamental Advantage of Plasma Processing	138
6.1.4	Classification of Plasmas from the Textile Viewpoint	138
6.1.4.1	Pressure-based	140
6.1.4.2	Substrate-based	141
6.2	Plasma Treatment of Textile Materials	142
6.2.1	Overview of Functionalizations	142
6.2.2	Effect of Plasma Treatment on Textile Substrates	143
6.2.2.1	Interaction of Active Plasma Species with a Surface	143

6.2.2.2	Basic Plasma Effect on Substrate	143
6.2.2.3	Aging	144
6.3	Integration of Plasma Processes into the Textile Manufacturing Chain	146
6.3.1	Fiber Level	147
6.3.2	Filament Level	148
6.3.3	Yarn Level	149
6.3.3.1	Natural Materials	149
6.3.3.1.1	Cotton	149
6.3.3.1.2	Wool	149
6.3.3.1.3	Other Natural Fibers	149
6.3.3.2	Non-natural Materials	150
6.3.4	Fabric Level	150
6.3.4.1	Woven Textiles	151
6.3.4.1.1	Natural Materials	151
6.3.4.1.2	Non-natural Materials	152
6.3.4.2	Knitted Textiles	152
6.3.4.3	Non-wovens	153
6.3.5	Intermediate/Finished Textile Material	154
6.4	Specific Requirements for the Textile Industry	155
6.4.1	Chemical Composition	155
6.4.2	Surface Cleanliness	155
6.4.3	Three-dimensional Structure of Textiles	156
6.4.4	Large Surface Area	157
6.4.5	Moisture Regain and Air Adsorption	158
6.5	Case Studies	158
6.5.1	Assessing the Surface Energy of Textiles	158
6.5.1.1	Introduction to Methods for Evaluating the Surface Energy and Wetting of Textiles	159
6.5.1.1.1	Wilhelmy Method	159
6.5.1.1.2	Washburn Method	160
6.5.1.2	Evaluation of Methods for Measuring Hydrophilic Properties	161
6.5.1.2.1	Wilhelmy Method	161
6.5.1.2.2	Washburn Method	162
6.5.1.2.3	Summary of Evaluation	163
6.5.1.3	Tests and Standards for Evaluating Hydrophobic/Oleophobic Properties	163
6.5.1.3.1	Water Repellency: Spray Test	164
6.5.1.3.2	Water/Alcohol Repellency	165
6.5.1.3.3	Oil Repellency	166
6.5.2	Hydrophilic Properties Imparted by Plasma	167
6.5.2.1	Plasma Experiments at Low Pressure	167
6.5.2.1.1	First Screening of Precursors	168
6.5.2.1.2	Aging of the Samples	169
6.5.2.2	Plasma Experiments at Atmospheric Pressure (Aldyne System)	170

6.5.3	Hydrophobic/Oleophobic Properties Imparted by Plasma	171
6.5.3.1	Preliminary Experiments	171
6.5.3.2	Washing Durability	172
6.5.3.3	Abrasion Durability	173
6.5.3.4	Summary of Oleophobic Properties	174
6.6	Transferring Plasma Technology to Industrial Processes	174
6.6.1	Textile Sector Related Issues	175
6.6.2	Fundamental Aspects Regarding Industrialization	176
6.7	Summary	177
	References	178
7	Preventing Biofilm Formation on Biomedical Surfaces	183
	<i>Virendra Kumar, Hubert Rauscher, Frédéric Brétagneol, Farzaneh Arefi-Khonsari, Jerome Pulpytel, Pascal Colpo, and François Rossi</i>	
7.1	Bacterial Adhesion to Biomaterials: Biofilm Formation	183
7.1.1	‘Biofilm’ and Its Implications in the Biomedical Field	184
7.1.2	Mechanism for Bacterial Adhesion to Surfaces	184
7.1.3	Biofilm Formation – a Multistep Process	186
7.1.4	Factors Influencing Biofilm Formation	187
7.1.4.1	Role of the Conditioning Film	187
7.1.4.2	Material Surface Characteristics	188
7.1.4.3	Micro-organism Characteristics	190
7.1.4.4	Environmental Factors	191
7.2	Biofilm Prevention Strategies	192
7.2.1	Pre-surgery Precautionary Approach	192
7.2.2	Antimicrobial-releasing Biomaterials	193
7.2.3	Surface-engineering Approach	193
7.2.3.1	High Surface Energy Approach	194
7.2.3.2	Low Surface Energy Approach	195
7.2.3.3	Surfaces with Bound Tethered Antimicrobial Agents	196
7.2.4	‘Antibiofilm’ Approach	197
7.3	Role of Plasma Processing in Biofouling Prevention	198
7.3.1	Plasma Surface Functionalization	199
7.3.2	Plasma-Induced Grafting	199
7.3.3	Plasma Polymerization	200
7.3.4	Plasma Sterilization	201
7.4	Case Study: Plasma-deposited Poly(ethylene oxide)-like Films for the Prevention of Biofilm Formation	202
7.4.1	PEO Films and Plasma Deposition	202
7.4.2	Plasma Polymerization by Continuous Wave Plasma	203
7.4.2.1	Retention of the PEO Character and Film Stability	203
7.4.2.2	Protein Adsorption	205
7.4.2.3	Cell Attachment and Proliferation	206
7.4.2.4	Aging	208
7.4.3	Plasma Polymerization in Pulsed Mode	208

7.4.4	Sterilization of PEO-like Films	210
7.4.5	Composite Films: Ag Nanoparticles in a PEO-like Matrix	211
7.4.5.1	Synthesis of Ag Nanoparticles and Deposition on Surfaces	212
7.4.5.2	Composite AgNP/PEO Surfaces and Their Antibacterial Activity	213
7.5	Summary	216
	References	217
8	Oxygen Barriers for Polymer Food Packaging	225
	<i>Joachim Schneider and Matthias Walker</i>	
8.1	Introduction	225
8.2	Fundamentals of Gas Diffusion through Polymers	225
8.2.1	Diffusion, Solubility, and Permeability of Polymers	227
8.2.2	Diagnostic Methods	230
8.2.3	Barrier Concepts	233
8.3	Case Study: Plasma Deposition of SiO _x Barrier Films on Polymer Materials Relevant for Packaging Applications	234
8.3.1	Materials and Measurements	234
8.3.1.1	Selection of Two-dimensional and Three-dimensional Polymer Substrates	234
8.3.1.2	Measurement of the Steady-state O ₂ Particle Flux	235
8.3.1.3	Measurement of the Coating Thickness	235
8.3.2	SiO _x Barrier Films on PET Foil	236
8.3.2.1	SiO _x Barrier Films Deposited from O ₂ : HMDSO Gas Mixtures	236
8.3.2.1.1	O ₂ Permeation Measurements: Determination of the Diffusion Coefficient	237
8.3.2.1.2	O ₂ Permeation Measurements: Variation of the O ₂ : HMDSO Gas Mixture Ratio	238
8.3.2.1.3	FTIR Analysis: Chemical Composition of the Surface of the SiO _x Barrier Films Deposited from Different O ₂ : HMDSO Gas Mixtures	239
8.3.2.2	SiO _x Barrier Films Deposited from O ₂ : HMDSN Gas Mixtures	243
8.3.2.2.1	O ₂ Permeation Measurements: Variation of the O ₂ : HMDSN Gas Mixture Ratio	243
8.3.2.2.2	FTIR Analysis: Comparing Best Performing SiO _x Barrier Films Deposited from O ₂ : HMDSO and from O ₂ : HMDSN Gas Mixtures	245
8.3.2.2.3	O ₂ Permeation Measurements: Variation of the Film Thickness	246
8.3.3	SiO _x Barrier Films on PP Foil	247
8.3.3.1	ECR Plasma Source: Comparing the Barrier Properties of SiO _x Films Deposited on PP and on PET Foil by Variation of the O ₂ : HMDSO Gas Mixture Ratio	247
8.3.3.2	Duo-Plasmaline Plasma Source: SiO _x Barrier Films Deposited from O ₂ : HMDSN Gas Mixtures	249
8.3.4	ECR Plasma Deposition of SiO _x Barrier Films on Polymer Trays Designed for Food Packaging	251

8.3.4.1	ECR Plasma Deposition of SiO _x Barrier Films Without Directed Gas Supply and Customized Magnet Configuration: Variation of the Plasma Deposition Time and of the Distance between Sample and Plasma	252
8.3.4.2	Achieving Industrially Relevant Plasma Deposition Times by Directed Gas Supply and Customized Magnet Configuration	255
8.4	Conclusions	258
	Acknowledgments	259
	References	259
9	Anti-wear Coatings for Food Processing	263
	<i>Maddalena Rostagno and Federico Cartasegna</i>	
9.1	Introduction	263
9.2	Recent Developments in PVD Coatings	264
9.3	Coatings Trends and Market Share	267
9.4	Coatings Application in the Food Processing Sector	268
9.5	Coating Requirements in the Food Sector	269
9.5.1	Wear Resistance	270
9.5.2	Coefficient of Friction (COF)	271
9.6	Selection of Methodologies for Effective Characterization of Coatings for the Food Sector	271
9.6.1	Chemical and Structural Characterization	273
9.6.1.1	Scanning Electron Microscopy (SEM)	273
9.6.1.1.1	Application to Anti-wear Coatings for Food Processing Tools	273
9.6.1.2	Energy Dispersive X-ray Spectrometry (EDX)	274
9.6.1.2.1	Application to Anti-wear Coatings	274
9.6.1.3	Calotest and Optical Microscopy (OM)	275
9.6.1.3.1	Application to Anti-wear Coatings for Food Processing Tools	276
9.6.2	Mechanical Characterization	276
9.6.2.1	Hardness	276
9.6.2.1.1	Application to Anti-wear Coatings for Food Processing Tools	277
9.6.2.2	Pin-on-disk	279
9.6.2.2.1	Application to Anti-wear Coatings for Food Processing Tools	280
9.6.3	Atotoxicity and Corrosion Characterization	280
9.6.3.1	Food Compatibility: Heavy Metals Release	280
9.6.3.2	Food Compatibility: Oxidation Test	280
9.6.3.3	Salt Spray Test	280
9.7	Case Studies: Development and Characterization of Ceramic Coatings for Food Processing Applications	281
9.7.1	Relevant Substrates and Functionalities Required for Cutting Applications	281
9.7.2	Technical Analysis and Choice of the Proper Coating Chemistry and Technique	282
9.7.3	Coating Development	285
9.7.4	Case Study: PVD Coating of Saw Blades	288

9.7.5	Case Study: PVD Coating of Hammers for Food Treatment	291
9.8	Conclusions	294
	References	294
10	Physics and Chemistry of Nonthermal Plasma at Atmospheric Pressure Relevant to Surface Treatment	295
	<i>Yuri Akishev, Anatoly Napartovich, Michail Grushin, Nikolay Trushkin, Nikolay Dyatko, and Igor Kochetov</i>	
10.1	Introduction	295
10.2	Discharge Modeling	297
10.2.1	Full Kinetic Models and Reduced Model for Technological Plasma	297
10.2.2	Electron Kinetics	299
10.2.3	Plasma Chemistry	301
10.2.4	Experimental UV, Optical, and Near Infra-red Emission Spectra	302
10.2.4.1	Air-based Discharges	302
10.2.4.2	Nitrogen-based Discharges	306
10.2.4.3	CF ₄ -based Discharges	309
10.2.5	Influence of Impurities on Composition of Gas Activated by Nonthermal Plasma	310
10.3	Kinetic Model for Chemical Reactions on a Polypropylene Surface in Atmospheric Pressure Air Plasma	314
10.3.1	Description of Kinetic Model	314
10.3.1.1	Description of Chemical Reaction Modeling	314
10.3.1.2	Description of Surface Concentration Modeling	320
10.3.1.2.1	Abstraction of H Atoms from H-sites by OH Radicals	320
10.3.1.2.2	Abstraction of H Atoms from H-sites by Alkoxy Radicals	321
10.3.1.2.3	Chain Backbone Scission Due to Interaction of Alkoxy Radicals with the Polymer Backbone	321
10.3.2	Results of Modeling and Comparison with Experimental Data	321
10.4	Conclusions	328
	Acknowledgement	328
	References	328
	Part III Economical, Ecological, and Safety Aspects	333
11	Economic Aspects	335
	<i>Elisa Aimo Boot</i>	
11.1	Market Analysis: an Overview	335
11.1.1	Textile Market Analysis	335
11.1.1.1	General	335
11.1.1.2	Technical Textiles	336
11.1.1.3	Hydrophobic and Oleophobic Textile Market	336
11.1.2	Biomedical Market Perspective	337
11.1.3	Food Packaging Market Potential	339

11.2	Case Study: Up-Scaling of the Plasma Treatment of Hammers for Meat Milling	340
11.2.1	Analysis of the Reference Scenario	341
11.2.2	Analysis of Scenario 2 – Outsourcing	341
11.2.3	Analysis of Scenario 3 – In-house	342
11.2.4	Investment and Operating Cost	343
11.2.5	Comparative Analysis of All Three Scenarios	344
11.2.6	Final Considerations	345
	References	346
12	Environment and Safety	347
	<i>Massimo Perucca and Gabriela Benveniste</i>	
12.1	Introduction to LCA	347
12.2	Environmental Impact of Traditional Surface Processing: the Reason for Developing Innovative Solutions Supported by Dedicated LCA	350
12.3	LCA Applied to Plasma Surface Processing: Case Studies	353
12.3.1	Scope, Functional Unit, and System Boundaries	354
12.3.2	Life Cycle Inventory (LCI) and Hypothesis	356
12.3.3	Inventory Data and Results	360
12.3.3.1	The Anti-corrosion Process	361
12.3.3.2	Textile Processes	364
12.3.3.2.1	Total Energy Requirement	364
12.3.3.2.2	Output of the Oleophobic PET Processes	366
12.3.3.2.3	Output of the Hydrophobic PET/Cotton Processes	367
12.3.4	Impact Assessment	369
12.3.5	Sensitivity Analysis	371
12.3.5.1	Managing Uncertainties	371
12.3.5.2	Example 1: General Sensitivity Analysis for the LCA Study of the Textile Processes	371
12.3.5.3	Example 2: Design of Plasma Processes via LCA	375
12.3.6	Concluding Considerations on LCA Study	375
12.4	Process Safety for the Working Environment	378
12.4.1	Atmospheric Pressure Plasma Unit: Standard Configuration	379
12.4.2	Devising Safe Processes for Industrial Applications Maintaining the Semi-continuous Feeding	381
12.4.3	Final Considerations on Process Safety	388
	References	389
	Index	391