

# Carbon Composites

## Composites with Carbon Fibers, Nanofibers, and Nanotubes

Second Edition

Deborah D.L. Chung

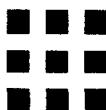
University at Buffalo  
The State University of New York  
Buffalo, NY, United States



AMSTERDAM • BOSTON • HEIDELBERG • LONDON • NEW YORK • OXFORD  
PARIS • SAN DIEGO • SAN FRANCISCO • SINGAPORE • SYDNEY • TOKYO

Butterworth-Heinemann is an imprint of Elsevier





# Contents

Preface	xxiii
1. Carbon Fibers, Nanofibers, and Nanotubes	1
1.1 Introduction to Carbon Science	1
1.1.1 Graphite	1
1.1.2 The Allotropes of Carbon	4
1.1.3 Energy Band Structure	5
1.1.4 Intercalation of Graphite	7
1.1.5 Exfoliation of Graphite	8
1.1.6 Graphite Oxide	12
1.1.7 Lattice Vibrations of Graphite	13
1.2 Carbon Fibers	14
1.2.1 Properties of Carbon Fibers	14
1.2.2 Carbon Fibers vs. Competing Materials	19
1.2.3 Structure of Carbon Fibers	21
1.2.4 Fabrication of Carbon Fibers	26
1.2.5 Classification of Carbon Fibers	45
1.2.6 Functional Properties of Carbon Fibers	51
1.3 Carbon Nanofibers and Nanotubes	52
1.3.1 Structure of Carbon Nanofibers and Nanotubes	54
1.3.2 Properties of Carbon Nanofibers and Nanotubes	66
1.3.3 Fabrication of Carbon Nanofibers and Nanotubes	68
1.4 Activated Carbon Fibers and Nanofibers	81
1.4.1 Structure	81
1.4.2 Processing	82

1.4.3	Activated carbon Fibers With Other Constituents Incorporated	84
1.4.4	Applications Other Than Adsorption	85
1.5	Ceramic Fibers Made From Carbon Fibers	86
2.	<b>Introduction to Carbon Composites</b>	<b>88</b>
2.1	Carbon Fiber/Nanofiber/Nanotube Assemblies	88
2.1.1	Assemblies of Continuous Carbon Fibers	88
2.1.2	Felts	90
2.1.3	Mats	93
2.1.4	Yarns	98
2.1.5	Mixture of Carbon Nanotubes and Graphene Oxide for Dielectric Behavior	101
2.1.6	Vertically Aligned Carbons	101
2.1.7	Carbons With Filled Core Channel	103
2.1.8	Carbons Deposited on Carbons	104
2.1.9	Carbon Grown on Ceramic	107
2.1.10	Carbons Grown on Metals or Attached to Polymers	109
2.1.11	Carbon Foams	109
2.1.12	Doped Carbons	109
2.1.13	Carbons With Embedded Fillers	110
2.1.14	Polymer Fibers With Carbon Filling	111
2.1.15	Coated Carbons	112
2.2	Basic Concepts in Carbon Fiber Composites	124
2.2.1	Configurations of Carbon Fiber Composites	124
2.2.2	Fiber-Matrix Bonding	124
2.2.3	Conductivity Enhancement Using Carbon Fibers	125
2.2.4	Fabrication of Carbon Fiber Composites	125
2.2.5	Carbon Fiber Composites With Various Matrices	126

2.3	Structure and Properties of Carbon Fiber Composites	126
2.3.1	Basic Mechanical Properties	126
2.3.2	Effect of the Fiber-Matrix Bond	126
2.3.3	Effect of the Fiber Volume Fraction	128
2.3.4	Effect of the Fiber Length	128
2.3.5	Effect of the Secondary Reinforcement	128
2.3.6	Short Carbon Fiber Composites	129
2.3.7	Effects of the Method of Composite Fabrication	130
2.4	Coating and Joining of Composites	132
2.5	Hybrid Composites	132
2.6	Recycling	133
2.7	Mechanical Testing Methodology	133
2.8	Applications of Carbon Fibers, Nanofibers, and Nanotubes	135
2.8.1	Structural Applications	135
2.8.2	Nonstructural Applications	145
2.8.3	Applications of Carbon Nanotubes	157
2.8.4	Market of Carbon Fibers, Nanofibers, and Nanotubes	159
3.	Polymer-Matrix Composites: Structure and Processing	161
3.1	Polymer-Matrix Composites According to Polymer Types	161
3.1.1	Thermoset and Thermoplastic Polymers	161
3.1.2	Epoxy	163
3.1.3	Polymers Other Than Epoxy	163
3.1.4	Amorphous vs. Semicrystalline Polymers	166
3.1.5	Examples of Thermoplastic Polymers	167
3.2	Glass Transition and Melting of Polymers	169
3.2.1	Importance to Composite Processing	169

3.2.2	Effects of Glass Transition and Melting on Carbon Fiber Polymer-Matrix Composites	170
3.3	Fiber-Polymer Bonding Effects	173
3.3.1	Fraction of Load Carried by the Fibers in the Composite	173
3.3.2	Apparent Modulus of the Fibers in a Composite	174
3.3.3	Residual Stress in the Fibers of a Composite	174
3.3.4	Fiber Fragmentation Testing	175
3.4	Electrical Resistance Measurement Methodology for Carbon Fiber Polymer-Matrix Composites	175
3.4.1	Four-Probe Method Vs. Two-Probe Method	175
3.4.2	Current Spreading	176
3.5	Continuous Fiber Laminates	178
3.5.1	Forms of Continuous Fiber Laminate	178
3.5.2	Structural Parameters and Their Dependence on the Curing Pressure	179
3.5.3	Fiber Volume Fraction Determination	181
3.6	Interlaminar Interface	181
3.6.1	Basic Structure of the Interlaminar Interface	181
3.6.2	Effect of Stress on the Interlaminar Interface	182
3.6.3	Contact Electrical Resistivity of the Interlaminar Interface	184
3.7	Deicing and Antiicing	194
3.8	Woven Fiber Composites	195
3.9	Microscale Composites, Short Fiber Composites and Continuous Fiber Skeletal Composites	195
3.10	Carbon Nanofiber Composites	197
3.11	Carbon Nanotube Composites	201
3.12	Hybrid Composites	201

3.13	Fabrication of Carbon Fiber Polymer-Matrix Composites	205
3.13.1	General Concepts	205
3.13.2	Molding Methods	206
3.13.3	Filament Winding Process	211
3.13.4	Fiber Prepreg Method	213
3.13.5	Robotic Method	215
3.13.6	Three-Dimensional Printing	216
4.	Polymer-Matrix Composites: Mechanical Properties and Thermal Performance	218
4.1	Concepts of the Mechanical Properties of Composite Materials	218
4.2	Static Mechanical Properties	220
4.2.1	Continuous Carbon Fiber Polymer-Matrix Composites	221
4.2.2	Polymer-Matrix Composites With Discontinuous Carbon Fillers	230
4.3	Dynamic Mechanical Properties	237
4.3.1	Fatigue Behavior	237
4.3.2	Viscoelastic Behavior	238
4.4	Friction and Wear Behavior	243
4.4.1	Short Carbon Fiber Composites	244
4.4.2	Continuous Carbon Fiber Composites	245
4.4.3	Interface Between Unbonded Continuous Carbon Fiber Composites	246
4.5	Thermal Expansion	247
4.6	Elevated Temperature Resistance	248
4.7	Environmental Degradation	250
4.8	Recycling and Upcycling	250

4.9	Joining	251
4.10	Hybrid Composites	251
4.10.1	Hybridization of Reinforcement	251
4.10.2	Hybridization of the Matrix	252
4.10.3	Use of Noncarbon Filler	254
4.10.4	Use of a Polymeric or Metallic Interlayer	254
4.10.5	Concrete Strengthened by Bonding to a Continuous Carbon Fiber Polymer-Matrix Composite	254
5.	Polymer-Matrix Composites: Functional Properties	256
5.1	Electrical Properties	256
5.1.1	Electrical Conductivity	256
5.1.2	Lightning Resistance	263
5.1.3	Effect of Temperature on the Electrical Conductivity	265
5.2	Electromechanical Behavior	267
5.2.1	Piezoresistivity Concept	267
5.2.2	Piezoresistivity in Composites With Discontinuous Carbon Fillers	268
5.2.3	Piezoresistivity in Composites With Continuous Carbon Fibers	270
5.2.4	Effect of Damage on the Electrical Resistivity	273
5.2.5	Self-Sensing of Strain and Damage in Continuous-Carbon-Fiber Polymer-Matrix Structural Composites	273
5.2.6	Method of Electrical-Resistance-Based Self-Sensing	274
5.2.7	Self-Sensing of Strain and Damage in Composites With Continuous Carbon Fiber	279
5.2.8	Self-Sensing of Damage in Hybrid Composites	286

5.2.9	Modeling of the Electromechanical Behavior of Continuous Carbon Fiber Polymer-Matrix Composite	289
5.3	Electromagnetic and Dielectric Behavior	289
5.3.1	Concepts in Electromagnetic and Dielectric Behavior	289
5.3.2	Electromagnetic and Dielectric Behavior Below 30 MHz	291
5.3.3	Electromagnetic and Dielectric Behavior Above 30 MHz	296
5.4	Thermal Conductivity	302
5.4.1	Thermal Conductivity of Continuous Carbon Fiber Polymer-Matrix Composites	302
5.4.2	Thermal Conductivity of Continuous Carbon Fiber Polymer-Matrix Composites in the Through-Thickness Direction	305
5.4.3	Thermal Conductivity of Polymer-Matrix Composites With Discontinuous Carbon Fillers	309
5.5	Thermoelectric Behavior	312
5.5.1	Thermoelectric Behavior of Continuous Carbon Fiber Polymer-Matrix Composites	313
5.5.2	Thermoelectric Behavior of Polymer-Matrix Composites With Discontinuous Carbon Fillers	330
5.6	Other Functional Behavior	332
5.7	Nondestructive Evaluation	332
6.	<b>Cement-Matrix Composites</b>	333
6.1	Cement Science	333
6.1.1	Constituents of Hydraulic Cement	333
6.1.2	Admixtures and Carbon Fiber	334
6.1.3	Pozzolans	336

6.2	Dispersion of Short Carbon Fibers, Nanofibers, or Nanotubes in Cement	336
6.2.1	Methods of Dispersion	338
6.2.2	Effects of the Degree of Dispersion	341
6.2.3	Effects of Carbon Surface Treatment	343
6.3	Electrical Percolation in Cement-Matrix Composites	348
6.3.1	Single Percolation	348
6.3.2	Double Percolation	350
6.3.3	Triple Percolation	351
6.3.4	Using Both Carbon Black and Short Carbon Fiber	351
6.3.5	Using Both CNT and Short Carbon Fiber	352
6.4	Electrical Behavior	352
6.4.1	Electrical Conduction by Ions and Electrons	352
6.4.2	Various Conductive Admixtures in Comparison	353
6.4.3	Cement-Based p–n Junction	353
6.4.4	Controlled Resistivity Materials	354
6.4.5	Electromagnetic Interference Shielding	354
6.4.6	Electric Polarization	355
6.4.7	Joining of New and Old Concretes	358
6.5	Thermal Behavior	358
6.5.1	Thermal Conductivity	358
6.5.2	Specific Heat	359
6.5.3	Effect of Temperature on the Electrical Resistivity	359
6.5.4	Thermoelectric Behavior	361
6.6	Mechanical Behavior	362
6.6.1	Static Mechanical Properties	362
6.6.2	Dynamic Mechanical Properties	364
6.7	Electromechanical Behavior	364
6.7.1	Effect of Strain on the Electrical Resistivity	364
6.7.2	Effect of Strain on the Relative Dielectric Constant	376

6.8 Applications	378
6.8.1 Structural Applications	378
6.8.2 Energy Conservation of Buildings	379
6.8.3 Self-Sensing of Strain/Stress, Damage and Temperature	379
6.8.4 Weighing-In-Motion and Traffic Monitoring	381
6.8.5 EMI Shielding, Antistatic Ability, and Lateral Guidance	381
6.8.6 Deicing, Antiicing, and Heating	382
6.8.7 Cathodic Protection	382
6.8.8 Masonry	383
6.9 Carbon-Reinforced Aluminosilicates	383
6.9.1 Aluminosilicate	383
6.9.2 Aluminoborosilicate	384
6.9.3 Barium Aluminosilicate	385
6.9.4 Lithium Aluminosilicate	386
7. Carbon-Matrix Composites	387
7.1 Introduction	387
7.2 Fabrication	388
7.3 Carbon Matrix Precursors	389
7.4 Choice of Carbon Fiber	391
7.5 Carbon Preforms	392
7.5.1 Carbon Fiber Preform Fabrication	392
7.5.2 Effect of the Carbon Fiber Preform Density	393
7.5.3 Effect of the Pyrolytic Carbon Interfacial Layer Thickness	393
7.5.4 Effect of the Degree of Carbon Fiber Orientation	393
7.5.5 Carbon Fiber Preforms With Nanofiber/Nanotube Incorporation	393
7.5.6 Exfoliated Graphite as the Preform	394

7.6	Liquid Phase Impregnation	394
7.7	Hot Isostatic Pressure Impregnation Carbonization	396
7.8	Hot Pressing	397
7.9	Chemical Vapor Infiltration (Introduction)	397
7.10	Chemical Vapor Infiltration Methodology	398
7.10.1	Isothermal Isobaric CVI	398
7.10.2	Temperature Gradient CVI	398
7.10.3	Pressure Gradient CVI	401
7.10.4	Limitations of CVI	401
7.10.5	CVI of Carbon Fiber Preforms	401
7.10.6	Special Techniques	404
7.11	Fiber-Matrix Interface	406
7.11.1	Effect of the Fiber-Matrix Bond Strength	406
7.11.2	Effect of the Carbon Fiber Surface Treatment	406
7.11.3	Effect of the Carbon Fiber Type	406
7.11.4	Effect of Graphitization	407
7.11.5	Effect of the Interfacial Layer on the Carbon Fibers	407
7.11.6	Microstructural Characterization	408
7.12	Structure of the Carbon Matrix	408
7.12.1	Texture	409
7.12.2	Degree of Graphitization	409
7.13	Structure of the Carbon Fibers	410
7.14	Oxidation Protection (Introduction)	410
7.15	Oxidation Protection Below 1700°C	411
7.15.1	Ceramic Coatings	412
7.15.2	Graphite Coatings	415
7.15.3	Ceramic Incorporation in the Matrix	415
7.15.4	Glass Sealants	421

7.15.5 Inhibitors	422
7.15.6 Dense HfC Nanowire-Toughened Outer Coating on SiC-Coated C/C	422
7.15.7 Phosphoric Acid Impregnation	422
7.15.8 Addition of Fumed Alumina Particle as a Filler in C/C	423
7.15.9 Coating With Mullite	423
7.15.10 Coating With an Alumina-Based Ceramic	426
7.15.11 Coating With a High-Temperature Silicon-Based Alloy	426
7.15.12 Coating With an Antioxidant	427
7.15.13 Other Methods of Oxidation Protection	427
7.16 Oxidation Protection Above 1700°C	427
7.16.1 Coating With Silicon Carbide	427
7.16.2 Coating With Chromium Carbide	427
7.16.3 Coating With Zirconium Oxide and Silica	428
7.16.4 Coating With Hafnium Carbide, Silicon Carbide, and Hafnium Silicide	428
7.16.5 Coating With Four Ceramic Layers	428
7.16.6 Incorporation of Hafnium Diboride in the Matrix	429
7.16.7 Incorporation of Hafnium Carbide in the Matrix	429
7.17 Mechanical Behavior	429
7.17.1 Static Mechanical Properties	430
7.17.2 Dynamic Mechanical Properties	433
7.17.3 Wear Resistance	434
7.17.4 Improving the Wear Resistance of C/C by Incorporating Ceramics to the Matrix	434
7.17.5 Improving the Wear Resistance C/C by Coating the C/C	437
7.17.6 High-Temperature Mechanical Properties	437

7.18	Thermal Expansion	437
7.18.1	Thermal Expansion Anisotropy	437
7.18.2	Effect of Heat Treatment	438
7.18.3	Effect of the Carbon Matrix Precursor	439
7.19	Thermal Conductivity	439
7.19.1	Thermal Conductivity Anisotropy	439
7.19.2	Effect of Heat Treatment	439
7.19.3	Effect of the Carbon Matrix Precursor	441
7.19.4	Effect of the Carbon Fiber Type	441
7.19.5	Low-Temperature Behavior	442
7.19.6	Carbon Nanotube Array Composite	442
7.20	Electrical Conductivity	443
7.21	Electromechanical Behavior	443
7.21.1	Damage Sensing by Electrical Resistance Measurement	443
7.21.2	Strain Sensing by Electrical Resistance Measurement	445
7.22	Joining of C/C Composites	445
7.22.1	Joining Using an Inorganic Phosphate Adhesive	446
7.22.2	Joining Enhanced by SiC Nanofiber Incorporation	446
7.22.3	Joining Enhanced by TiB Whisker Incorporation	446
7.22.4	Joining by Braze	446
7.23	Hybrid C/C Composites	447
7.23.1	C/C with the Matrix Being a Hybrid of Carbon and Ceramic	447
7.23.2	C/C With Two Types of Reinforcement	452
7.23.3	C/C–SiC With SiC Nanofibers	458
7.23.4	C/C With Infiltrated Metal	459
7.23.5	C/C With Filler Incorporation	460

7.24	Carbon Nanotube Composites	464
7.24.1	Vertically Aligned CNT Composites	464
7.24.2	Horizontally Aligned CNT Composites	464
7.24.3	CNT Yarn Composites	465
7.24.4	CNT Compact Composites	465
7.24.5	Joining C/C and Silicate With Aligned CNTs	465
7.25	Applications and Companies	465
7.25.1	Applications	465
7.25.2	Companies	466
8.	<b>Ceramic-Matrix Composites</b>	<b>467</b>
8.1	Introduction to Ceramic-Matrix Composites	467
8.2	Fabrication of Ceramic-Matrix Composites	469
8.2.1	Carbon Fiber Preform Architecture	469
8.2.2	Interfacial Layer on the Carbon Fibers	470
8.2.3	Polymer Impregnation and Pyrolysis	471
8.2.4	Chemical Vapor Infiltration	471
8.2.5	Slurry Infiltration	472
8.2.6	Reactive Liquid Infiltration	473
8.2.7	Reactive Gas Infiltration	475
8.2.8	Liquid Metal Infiltration and Reaction of the Metal With a Gas to Form the Ceramic	475
8.2.9	Sintering of Solids	475
8.2.10	Lattice Composites	476
8.3	Ceramic Matrices	476
8.4	Fiber-Matrix Interface	478
8.4.1	Effect of the Infiltration Pressure	479
8.4.2	Effect of the Infiltrant Viscosity	479
8.4.3	Effect of the Interfacial Layer on the Fiber Surface	479

8.4.4	Effect of the Fiber Preoxidation	481
8.4.5	Effect of Thermal Contraction	482
8.4.6	Interfacial Microstructure	482
8.5	Carbide-Matrix Composites	482
8.5.1	Carbide Science	483
8.5.2	Fabrication	486
8.5.3	Properties	497
8.5.4	Carbon Nanotube Composites	504
8.6	Nitride-Matrix Composites	505
8.6.1	Carbon Fiber Nitride-Matrix Composites	507
8.6.2	Carbon Nanotube/Nanofiber Silicon-Nitride-Matrix Composites	513
8.7	Composites With Silicon Carbonitride Matrix and Related Composites	515
8.7.1	Silicon Carbonitride	515
8.7.2	Silicon Borocarbonitride	516
8.7.3	Silicon Hafnium Borocarbonitride	517
8.8	Oxide-Matrix Composites	517
8.8.1	Aluminum-Oxide-Matrix Composites	517
8.8.2	Silica-Matrix Composites	521
8.8.3	Magnesium Oxide-Matrix Composites	522
8.8.4	Mullite-Matrix Composites	523
8.8.5	Doloma-Matrix Composites	524
8.8.6	Iron-Oxide-Matrix Composite	524
8.9	Hydroxyapatite-Matrix Composites	525
8.10	Hybrid Composites	525
8.10.1	Hybrid Matrices	525
8.10.2	Hybrid Reinforcement	527
8.10.3	Layered Composites	531

<b>9. Metal-Matrix Composites</b>	<b>532</b>
9.1 Introduction	532
9.2 Fabrication	533
9.2.1 Powder Metallurgy	533
9.2.2 Diffusion Bonding	534
9.2.3 Liquid Metal Infiltration and Squeeze Casting	534
9.2.4 Stir Casting	535
9.2.5 Thermal Spraying	535
9.2.6 Semisolid Hot Pressing	536
9.2.7 Physical Vapor Deposition	536
9.2.8 Carbon Preform	536
9.2.9 Shaping	537
9.3 Coatings on Carbon Fibers	537
9.3.1 Wettability and Interfacial Reaction	537
9.3.2 Metal Coatings	537
9.3.3 Ceramic Coatings	538
9.4 Degradation by Heat and Water	542
9.4.1 Thermal Degradation After Composite Fabrication	542
9.4.2 Thermal Degradation During Composite Fabrication	542
9.4.3 Degradation by Water	544
9.5 Aluminum-Matrix Composites	544
9.5.1 Aluminum Carbide Formation	544
9.5.2 Fabrication by Powder Metallurgy or Diffusion Bonding	544
9.5.3 Fabrication by Squeeze Casting or Pressure Casting	546
9.5.4 Thermal Conductivity	546
9.5.5 Thermal Expansion	547

9.5.6	Mechanical Properties	547
9.5.7	Friction and Wear Behavior	549
9.5.8	Radiation Resistance	549
9.6	Magnesium-Matrix Composite	550
9.6.1	Magnesium Alloys	550
9.6.2	Coatings on Carbon Fibers	550
9.6.3	Thermal Expansion	553
9.6.4	Mechanical Properties	554
9.7	Copper-Matrix Composites	554
9.7.1	Fabrication	555
9.7.2	Coatings on Carbon Fibers	555
9.7.3	Thermal Conductivity	555
9.7.4	Electrical Conductivity	556
9.7.5	Thermal Expansion	557
9.7.6	Friction and Wear Behavior	557
9.8	Silver-Matrix Composites	557
9.9	Iron-Matrix Composites	559
9.10	Titanium-Matrix Composites	559
9.11	Tin-Matrix Composites	560
9.11.1	Soldering	560
9.11.2	Contact Angle	560
9.11.3	Thermal Conductivity	561
9.11.4	Thermal Expansion	561
9.11.5	Friction and Wear Behavior	561
9.12	Nickel-Matrix Composites	562
9.13	Comparison of CNT Composites With Various Metal Matrices	562
	References	563
	Index	655