

Contents

<i>Preface to Fourth Edition</i>	v
<i>Preface to First Edition</i>	vii
1 The Historical Development of Plastics Materials	1
1.1 Natural Plastics	1
1.2 Parkesine and Celluloid	3
1.3 1900-1930	4
1.4 The Evolution of the Vinyl Plastics	5
1.5 Developments since 1939	6
1.6 Raw Materials for Plastics	9
1.7 The Market for Plastics	10
1.8 The Future for Plastics	14
2 The Chemical Nature of Plastics	18
2.1 Introduction	18
2.2 Thermoplastic and Thermosetting Behaviour	22
2.3 Further Consideration of Addition Polymerisation	23
2.3.1 Elementary kinetics of free radical addition polymerisation	27
2.3.2 Ionic polymerisation	32
2.4 Condensation Polymerisation	36
3 States of Aggregation in Polymers	38
3.1 Introduction	38
3.2 Linear Amorphous Polymers	38
3.2.1 Orientation in linear amorphous polymers	42
3.3 Crystalline Polymers	44
3.3.1 Orientation and crystallisation	47
3.4 Cross-linked Structures	48
3.5 Polyblends	50
3.6 Summary	52
4 Relation of Structure to Thermal and Mechanical Properties	54
4.1 Introduction	54
4.2 Factors Affecting the Glass Transition Temperature	54
4.3 Factors Affecting the Ability to Crystallise	59
4.4 Factors Affecting the Crystalline Melting Point	65

x Contents

4.5	Some Individual Properties	67
4.5.1	Melt viscosity	67
4.5.2	Yield strength and modulus	68
4.5.3	Specific gravity	68
4.5.4	Impact strength	68
5	Relation of Structure to Chemical Properties	70
5.1	Introduction	70
5.2	Chemical Bonds	70
5.3	Polymer Solubility	73
5.3.1	Plasticisers	80
5.3.2	Extenders	82
5.3.3	Determination of solubility parameter	83
5.3.4	Thermodynamics and solubility	86
5.4	Chemical Reactivity	88
5.5	Effects of Thermal , Photochemical and High Energy Radiation	89
5.6	Aging and Weathering	92
5.7	Diffusion and Permeability	93
5.8	Toxicity	96
5.9	Fire and Plastics	97
6	Relation of Structure to Electrical and Optical Properties	102
6.1	Introduction	102
6.2	Dielectric Constant, Power Factor and Structure	102
6.3	Some Quantitative Relationships of Dielectrics	109
6.4	Optical Properties	111
7	Additives for Plastics	114
7.1	Introduction	114
7.2	Fillers	116
7.2.1	Coupling agents	118
7.3	Plasticisers and Softeners	121
7.4	Lubricants and Flow Promoters	122
7.5	Anti-aging Additives	124
7.5.1	Antioxidants	124
7.5.2	Antiozonants	133
7.5.3	Stabilisers against dehydrochlorination	133
7.5.4	Ultra-violet absorbers and related materials	133
7.6	Flame Retarders	135
7.7	Colourants	139
7.8	Blowing Agents	140
7.9	Cross-linking Agents	143
7.10	Photodegradants	143
8	Principles of the Processing of Plastics	146
8.1	Introduction	146
8.2	Melt Processing of Thermoplastics	147
8.2.1	Hygroscopic behaviour	148
8.2.2	Granule characteristics	149
8.2.3	Thermal properties influencing polymer melting	149
8.2.4	Thermal stability	150
8.2.5	Flow properties	150
8.2.5.1	Terminology	151
8.2.5.2	Effect of environmental and molecular factors on viscous flow properties	154

8.2.5.3	Elastic effects in polymer melts	157
8.2.6	Thermal properties affecting cooling	158
8.2.7	Crystallisation	160
8.2.8	Orientation and shrinkage	161
8.3	Melt Processing of Thermosetting Plastics	162
8.4	Processing in the Rubbery State	165
8.5	Solution, Suspension and Casting Processes	166
8.6	Summary	167
9	Principles of Product Design	169
9.1	Introduction	169
9.2	Rigidity of Plastics Materials	169
9.2.1	The assessment of maximum service temperature	171
9.3	Toughness	172
9.3.1	The assessment of impact strength	174
9.4	Stress–Strain–Time Behaviour	177
9.4.1	The WLF equations	179
9.4.2	Creep curves	180
9.4.3	Practical assessment of long term behaviour	182
9.5	Recovery from Deformation	183
9.6	Distortion, Voids and Frozen-in Stress	184
9.7	Conclusions	186
10	Polyethylene	187
10.1	Introduction	187
10.2	Preparation of Monomer	189
10.3	Polymerisation	189
10.3.1	High pressure polymerisation	190
10.3.2	Ziegler processes	191
10.3.3	The Phillips process	191
10.3.4	Standard Oil Company (Indiana) process	192
10.3.5	Processes for making linear low density polyethylene	193
10.4	Structure and Properties of Polyethylene	193
10.5	Properties of Polyethylene	198
10.5.1	Mechanical properties	198
10.5.2	Thermal properties	201
10.5.3	Chemical properties	204
10.5.4	Electrical properties	207
10.6	Additives	208
10.7	Processing	212
10.8	Polyethylenes of Low and High Molecular Weight	217
10.9	Cross-linked Polyethylene	218
10.10	Chlorinated Polyethylene	219
10.11	Applications	220
11	Aliphatic Polyolefins other than Polyethylene, and Diene Rubbers	225
11.1	Polypropylene	225
11.1.1	Preparation of polypropylene	226
11.1.2	Structure and properties of polypropylene	227
11.1.3	Properties of isotactic polypropylene	230
11.1.4	Additives for isotactic polypropylene	235
11.1.5	Processing characteristics	237
11.1.6	Applications	240
11.1.7	Atactic polypropylene	243
11.1.8	Chlorinated polypropylene	243

xii **Contents**

11.2	Polybut-1-ene	244
11.2.1	Atactic polybut-1-ene	244
11.3	Polyisobutylene	245
11.4	Poly-(4-methylpent- -ene)	245
11.4.1	Structure and properties	246
11.4.2	General properties	247
11.4.3	Processing	248
11.4.4	Applications	248
11.5	Other Aliphatic Olefin Homopolymers	249
11.6	Copolymers Containing Ethylene	250
11.7	Diene Rubbers	254
11.7.1	Natural rubber	258
11.7.2	Synthetic polyisoprene (IR)	262
11.7.3	Polybutadiene	263
11.7.4	Styrene-butadiene rubber (SBR)	264
11.7.4.1	High styrene resins	267
11.7.5	Nitrile rubber (NBR)	267
11.7.6	Chloroprene rubbers (CER)	268
11.7.7	Butadiene-pentadiene rubbers	269
11.8	Thermoplastic Diene Rubbers	269
11.9	Aliphatic Olefin Rubbers	272
11.9.1	Thermoplastic polyolefin rubbers	275
11.10	Rubbery Cyclo-olefin (Cyclo-alkene) Polymers	276
11.10.1	Aliphatic polyalkenamers	276
11.10.2	Polynorbornene	277
11.10.3	Chlorine-containing copolymers	278
11.11	1,2-Polybutadiene	279
12	Vinyl Chloride Polymers	281
12.1	Introduction	281
12.2	Preparation of Vinyl Chloride	283
12.3	Polymerisation	284
12.4	Structure of Poly(vinyl chloride)	287
12.4.1	Characterisation of commercial polymers	289
12.5	Compounding Ingredients	295
12.5.1	Stabilisers	295
12.5.2	Plasticisers	300
12.5.3	Extenders	302
12.5.4	Lubricants	306
12.5.5	Fillers	307
12.5.6	Pigments	310
12.5.7	Polymeric impact modifiers and processing aids	310
12.5.8	Miscellaneous additives	312
12.5.9	Formulations	312
12.6	Properties of PVC Compounds	314
12.7	Processing	316
12.7.1	Plasticised PVC	316
12.7.2	Unplasticised PVC	319
12.7.3	Pastes	320
12.7.4	Copolymers	324
12.7.5	Latices	324
12.8	Applications	325
12.9	Miscellaneous Products	328
12.9.1	Crystalline PVC	328
12.9.2	Chlorinated PVC	328
12.9.3	Graft polymers based on PVC	329

12.9.4	Vinyl chloride–propylene copolymers	329
12.9.5	Vinyl chloride–N-cyclohexylmaleimide copolymers	329
13	Fluorine-containing Polymers	332
13.1	Introduction	332
13.2	Polytetrafluoroethylenq	333
13.2.1	Preparation of monomer	333
13.2.2	Polymerisation	333
13.2.3	Structure and properties	334
13.2.4	General properties	335
13.2.5	Processing	338
13.2.6	Additives	340
13.2.7	Applications	340
13.3	Tetrafluoroethylene–Hexafluoropropylene Copolymers	341
13.4	Tetrafluoroethylene–Ethylene Copolymers (ETFE)	342
13.5	Polychlorotrifluoroethylene Polymers (PCTFE) and Copolymers with Ethylene (ECTFE)	342
13.6	Poly(vinyl fluoride) (PVF)	344
13.7	Poly(vinylidene fluoride)	344
13.8	Perfluoroalkoxy Polymers	345
13.9	Hexafluoroisobutylene–Vinylidene Fluoride Copolymers	346
13.10	Fluorine-containing Rubbers	346
13.11	Miscellaneous Fluoropolymers	350
14	Poly(vinyl acetate) and its Derivatives	351
14.1	Introduction	351
14.2	Poly(vinyl acetate)	351
14.2.1	Preparation of the monomer	351
14.2.2	Polymerisation	353
14.2.3	Properties and uses	353
14.3	Poly(vinyl alcohol)	354
14.3.1	Structure and properties	355
14.3.2	Applications	356
14.4	The Poly(vinyl acetals)	356
14.4.1	Poly(vinyl formal)	357
14.4.2	Poly(vinyl acetal)	358
14.4.3	Poly(vinyl butyral)	358
14.5	Poly(vinyl cinnamate)	359
14.6	Other Organic Vinyl Ester Polymers	360
15	Acrylic Plastics	362
15.1	Introduction	362
15.2	Poly(methyl methacrylate)	363
15.2.1	Preparation of monomer	363
15.2.2	Polymerisation	365
15.2.3	Structure and properties	368
15.2.4	General properties of poly(methyl methacrylate)	369
15.2.5	Additives	372
15.2.6	Processing	373
15.2.7	Applications	375
15.3	Impact Resistant Methyl Methacrylate Polymers	376
15.4	Nitrile Resins	378
15.5	Acrylate Rubbers	379
15.6	Thermosetting Acrylic Polymers	380
15.7	Acrylic Adhesives	380

xiv Contents

15.8	Poly(methacrylamide)	381
15.9	Miscellaneous Methacrylate and Chloroacrylate Polymers and Copolymers	382
15.10	Other Acrylic Polymers	384
16	Plastics Based on Styrene	386
16.1	Introduction	386
16.2	Preparation of the Monomer	387
	16.2.1 Laboratory preparation	387
	16.2.2 Commercial preparation	388
16.3	Polymerisation	390
	16.3.1 Mass polymerisation	390
	16.3.2 Solution polymerisation	391
	16.3.3 Suspension polymerisation	392
	16.3.4 Emulsion polymerisation	393
	16.3.5 Characterisation and routine control	393
	16.3.6 Grades available	393
16.4	Properties and Structure of Polystyrene	394
16.5	General Properties	395
16.6	High-Impact Polystyrenes (HIPS)	398
16.7	Styrene–Acrylonitrile Copolymers	402
16.8	ABS Plastics	402
16.9	Miscellaneous Rubber-modified Styrene–Acrylonitrile and Related Copolymers	407
16.10	Butadiene–Styrene Block Copolymers	409
16.11	Miscellaneous Polymers and Copolymers	410
16.12	Stereoregular Polystyrene	411
16.13	Processing of Polystyrene	412
16.14	Expanded Polystyrene	413
	16.14.1 Structural foams	416
16.15	Oriented Polystyrene	417
16.16	Applications	419
17	Miscellaneous Vinyl Thermoplastics	423
17.1	Introduction	423
17.2	Vinylidene Chloride Polymers and Copolymers	423
	17.2.1 Properties and applications of vinylidene chloride–vinyl chloride copolymers	425
	17.2.2 Vinylidene chloride–acrylonitrile copolymers	427
17.3	Coumarone–Indene resins	427
17.4	Poly(vinyl carbazole)	429
17.5	Poly(vinyl pyrrolidone)	431
17.6	Poly(vinyl ethers)	432
17.7	Other Vinyl Polymers	433
18	Polyamides and Polyimides	435
18.1	Polyamides: Introduction	435
18.2	Intermediates for Aliphatic Polyamides	436
	18.2.1 Adipic acid	436
	18.2.2 Hexamethylenediamine	437
	18.2.3 Sebacic acid and Azelaic acid	438
	18.2.4 Caprolactam	438
	18.2.5 ω-Aminoundecanoic acid	440
	18.2.6 ω-Aminoenanthic acid	440
	18.2.7 Dodecanolactam	441

18.3	Polymerisation for Aliphatic Polyamides	442
18.3.1	Nylons 66, 69, 610 and 612	442
18.3.2	Nylon 6	443
18.3.3	Nylon 11	443
18.3.4	Nylon 12	443
18.3.5	Nylon 7	443
18.4	Structure and Properties of Aliphatic Polyamides	444
18.5	General Properties of the Nylons	446
18.6	Additives	452
18.7	Glass-filled Nylons	453
18.8	Processing of the Nylons	454
18.9	Applications	455
18.10	Polyamides of Enhanced Solubility	458
18.11	Other Aliphatic Polyamides	460
18.12	Aromatic Polyamides	461
18.13	Polyimides	466
18.14	Modified Polyimides	471
18.15	Elastomeric Polyamides	475
19	Polyacetals and Related Materials	476
19.1	Introduction	476
19.2	Preparation of Formaldehyde	477
19.3	Acetal Resins	478
19.3.1	Polymerisation of formaldehyde	478
19.3.2	Structure and properties of acetal resins	481
19.3.3	Properties of acetal resins	482
19.3.4	Processing	487
19.3.5	Additives	488
19.3.6	Applications of the acetal polymers and copolymers	488
19.4	Miscellaneous Aldehyde Polymers	489
19.5	Polyethers from Glycols and Alkylene Oxides	490
19.6	Oxetane Polymers	492
19.7	Polysulphides	494
20	Polycarbonates	499
20.1	Introduction	499
20.2	Production of Intermediates	500
20.3	Polymer Preparation	501
20.3.1	Ester exchange	501
20.4	Relation of Structure and Properties	504
20.4.1	Variations in commercial grades	506
20.5	General Properties	508
20.6	Processing Characteristics	514
20.7	Application of Bis-phenol A Polycarbonates	516
20.8	Alloys based on Bis-phenol A Polycarbonates	518
20.9	Miscellaneous Carbonic Ester Polymers	518
21	Other Thermoplastics Containing <i>p</i>-Phenylene Groups	522
21.1	Introduction	522
21.2	Polyphenylenes	522
21.3	Poly- <i>p</i> -xylylene	523
21.4	Poly(phenylene oxides) and Halogenated Derivatives	524
21.5	Alkyl Substituted Poly(phenylene oxides) including PPO	524
21.5.1	Structure and properties of poly-(2,6-dimethyl-<i>p</i>-phenylene oxide) (PPO)	525

21.5.2	Processing and applications of PPO	527
21.5.3	Blends based in polyphenylene oxides	527
21.6	Polyphenylene Sulphides	529
21.7	Polysulphones	531
21.7.1	Properties and structure of polysulphones	534
21.7.2	General properties of sulphones	535
21.7.3	Processing of polysulphones	536
21.7.4	Applications	537
21.8	Aromatic Polyether Ketones	537
21.9	Phenoxy Resins	539
21.10	Linear Aromatic Polyesters	540
21.11	Polyhydantoin Resins	542
21.12	Poly(parabanic acids)	543
21.13	Summary	544
22	Cellulose Plastics	546
22.1	Nature and Occurrence of Cellulose	546
22.2	Cellulose Esters	549
22.2.1	Cellulose nitrate	549
22.2.2	Cellulose acetate	553
22.2.3	Other cellulose esters	560
22.3	Cellulose Ethers	562
22.3.1	Ethyl cellulose	562
22.3.2	Miscellaneous ethers	564
22.4	Regenerated Cellulose	565
22.5	Vulcanised Fibre	566
23	Phenolic Resins	568
23.1	Introduction	568
23.2	Raw Materials	568
23.2.1	Phenol	569
23.2.2	Other phenols	571
23.2.3	Aldehydes	572
23.3	Chemical Aspects	572
23.3.1	Novolaks	573
23.3.2	Resols	574
23.3.3	Hardening	574
23.4	Resin Manufacture	576
23.5	Moulding Powders	578
23.5.1	Compounding ingredients	579
23.5.2	Compounding of phenol–formaldehydemoulding compositions	581
23.5.3	Processing characteristics	582
23.5.4	Properties of phenolic mouldings	584
23.5.5	Applications	585
23.6	Phenolic Laminates	587
23.6.1	The properties of phenolic laminates	589
23.6.2	Applications of phenolic laminates	591
23.7	Miscellaneous Applications	591
23.8	Resorcinol–Formaldehyde Adhesives	595
23.9	Friedel–Crafts and Related Polymers	595
23.10	Phenolic Resin Fibres	599

24	Aminoplastics	601
24.1	Introduction	601
24.2	Urea-Formaldehyde Resins	602
24.2.1	Raw materials	602
24.2.2	Theories of resinification	602
24.2.3	U-F moulding materials	604
24.2.4	Adhesives and related uses	610
24.2.5	Foams and firelighters	611
24.2.6	Other applications	612
24.3	Melamine-Formaldehyde Resins	613
24.3.1	Melamine	613
24.3.2	Resinification	615
24.3.3	Moulding powders	616
24.3.4	Laminates containing melamine-formaldehyderesin	620
24.3.5	Miscellaneous applications	621
24.4	Melamine-Phenolic Resins	622
24.5	Aniline-Formaldehyde Resins	622
24.6	Resins Containing Thiourea	624
25	Polyester Resins	626
25.1	Introduction	626
25.2	Unsaturated Polyester Laminating Resins	628
25.2.1	Selection of raw materials	628
25.2.2	Production of resins	633
25.2.3	Curing systems	634
25.2.4	Structure and properties	636
25.2.5	Polyester-glass fibre laminates	637
25.2.6	Allyl resins	639
25.3	Polyester Moulding Compositions	640
25.4	Fibre and Film-forming Polyesters	644
25.5	Poly(ethylene terephthalate) Moulding Materials	650
25.6	Poly(butylene terephthalate)	653
25.7	Poly-(1,4-cyclohexylenedimethylene terephthalate-CO- isophthalate)	654
25.8	Highly Aromatic Linear Polyesters	655
25.9	Polyester Thermoplastic Elastomers	659
25.10	Poly(pivalolactone)	660
25.11	Polycaprolactones	661
25.12	Surface Coatings, Plasticisers and Rubbers	662
25.13	Water-extended Polyesters	664
26	Epoxide Resins	666
26.1	Introduction	666
26.2	Preparation of Resins from Bis-phenol A	667
26.3	Curing of Glycidyl Ether Resins	672
26.3.1	Amine hardening systems	674
26.3.2	Acid hardening systems	676
26.3.3	Miscellaneous hardener systems	682
26.3.4	Comparison of hardening systems	682
26.4	Miscellaneous Epoxide Resins	683
26.4.1	Miscellaneous glycidyl ether resins	683
26.4.2	Non-glycidylether epoxides	685
26.5	Diluents, Flexibilisers and other Additives	689
26.6	Structure and Properties of Cured Resins	693
26.7	Applications	693

xviii **Contents**

27	Polyurethanes and Polyisocyanurates	698
27.1	Introduction	698
27.2	Isocyanates	699
27.3	Fibres and Crystalline Moulding Compounds	702
27.4	Rubbers	703
27.4.1	Thermoplastic polyurethanes and Spandex fibres	707
27.5	Flexible Foams	709
27.5.1	One-shot polyester foams	710
27.5.2	Polyether prepolymers	711
27.5.3	Quasi-prepolymer polyether foams	712
27.5.4	Polyether one-shot foams	712
27.5.5	Properties and applications of flexible foams	716
27.6	Rigid and Semi-rigid Foams	717
27.6.1	Self-skinning foams and the RIM process	719
27.7	Coatings and Adhesives	721
27.8	Polyisocyanurates	721
27.9	Polycarbodi-imide Resins	724
27.10	Polyurethane–Acrylic Blends	724
28	Furan Resins	726
28.1	Introduction	726
28.2	Preparation of Intermediates	726
28.3	Resinification	727
28.4	Properties of the Cured Resins	728
28.5	Applications	728
29	Silicones and Other Heat-resisting Polymers	730
29.1	Introduction	730
29.1.1	Nomenclature	731
29.1.2	Nature of chemical bonds containing silicon	732
29.2	Preparation of Intermediates	733
29.2.1	The Grignard method	734
29.2.2	The direct process	735
29.2.3	The olefin addition method	736
29.2.4	Sodium condensation method	736
29.2.5	Rearrangement of organochlorosilanes	736
29.3	General Methods of Preparation and Properties of Silicones	737
29.4	Silicone Fluids	739
29.4.1	Preparation	739
29.4.2	General properties	740
29.4.3	Applications	742
29.5	Silicone Resins	744
29.5.1	Preparation	744
29.5.2	Properties	745
29.5.3	Applications	745
29.6	Silicone Rubbers	748
29.6.1	Preparations of dimethylsilicone rubbers	748
29.6.2	Special purpose rubbers	748
29.6.3	Compounding	751
29.6.4	Fabrication and cross-linking	752
29.6.5	Properties and applications	752
29.6.6	Liquid silicone rubbers	754
29.7	Polymers for use at High Temperatures	754
29.7.1	Fluorine-containing polymers	755
29.7.2	Inorganic polymers	756

29.7.3	Cross-linked organic polymers	760
29.7.4	Linear polymers with <i>p</i> -phenylene groups and other ring structures	760
29.7.5	Ladder polymers and spiro polymers	762
29.7.6	Co-ordination polymers	764
29.7.7	Summary	765
30	Miscellaneous Plastics Materials	767
30.1	Introduction	767
30.2	Casein	767
30.2.1	Chemical nature	768
30.2.2	Isolation of casein from milk	769
30.2.3	Production of casein plastics	770
30.2.4	Properties of casein	772
30.2.5	Applications	773
30.3	Miscellaneous Protein Plastics	774
30.4	Derivatives of Natural Rubber	774
30.5	Gutta Percha and Related Materials	779
30.6	Shellac	781
30.6.1	Occurrence and preparation	781
30.6.2	Chemical composition	782
30.6.3	Properties	783
30.6.4	Applications	784
30.7	Amber	784
30.7.1	Composition and properties	785
30.8	Bituminous Plastics	785
	Index	789