

FLUOROELASTOMERS HANDBOOK

THE DEFINITIVE USER'S GUIDE

SECOND EDITION

Jiri George Drobny

Contents

Preface to the Second Edition	xi
Preface to the First Edition	xiii

PART I FLUOROELASTOMERS OVERVIEW

1 Fundamentals	3
1.1 Introduction	3
1.2 Scope: Fluorocarbon Elastomers	4
1.3 Nature of Fluoroelastomers.....	5
1.4 Fundamental Properties.....	5
1.4.1 VDF Copolymers	5
1.4.2 TFE/Olefin Copolymers.....	6
1.4.3 Perfluoroelastomers.....	6
1.4.4 Other Compositions.....	6
1.5 Developmental History: Compositions, Cure Technology	8
1.6 Major Uses of Fluoroelastomers.....	10
1.7 Producers of Fluoroelastomers.....	11
References.....	14
2 Market and Consumption Statistics and Future Trends	15
2.1 Introduction	15
2.2 Consumption, Demand, and Trends	15
References.....	16
3 Fluoroelastomer Composition and Properties.....	17
3.1 Major Families of Fluorocarbon Elastomers	17
3.2 VDF/HFP/TFE Elastomers	19
3.3 VDF/PMVE/TFE Elastomers.....	20
3.4 TFE/PMVE Perfluoroelastomers	21
3.5 TFE/P Elastomers.....	23
3.6 E/TFE/PMVE Elastomers	24
References.....	26

PART II FLUOROELASTOMERS TECHNOLOGY

4 Fluoroelastomer Monomers.....	29
4.1 Introduction	29
4.2 Vinylidene Fluoride.....	29
4.2.1 VDF Properties.....	29
4.2.2 VDF Synthesis.....	30

4.3	Tetrafluoroethylene	30
4.3.1	TFE Properties.....	31
4.3.2	TFE Synthesis	32
4.4	Hexafluoropropylene.....	33
4.4.1	HFP Properties	33
4.4.2	HFP Synthesis	34
4.5	Perfluoro(methyl vinyl ether)	34
4.5.1	PMVE Properties.....	34
4.5.2	PMVE Synthesis.....	34
4.6	Olefins: Ethylene and Propylene	35
4.7	Cure-Site Monomers	36
4.7.1	Types of Cure-Site Monomers.....	36
4.7.2	Halogenated Vinyl Monomers.....	36
4.7.3	Functional Vinyl Ethers	37
4.8	Safety Aspects of Monomer Handling	37
4.8.1	Toxicity Considerations	37
4.8.2	Flammability	37
4.8.3	Explosivity.....	37
	References.....	38
5	Production of Fluoroelastomers.....	41
5.1	Introduction	41
5.2	General Process Description.....	41
5.3	Free Radical Copolymerization	42
5.3.1	General Reaction Scheme.....	42
5.3.2	Copolymer Composition Relationships.....	43
5.3.3	Monomer Reactivity Ratios.....	44
5.4	Emulsion Polymerization.....	45
5.4.1	Emulsion Polymerization Kinetics	46
5.4.2	Continuous Emulsion Polymerization	53
5.4.3	Semibatch Emulsion Polymerization.....	57
5.5	Suspension Polymerization.....	63
5.5.1	Polymer Compositions.....	65
5.5.2	Polymerization Mechanism and Kinetics	65
5.5.3	Reactor Design and Operation.....	66
5.5.4	Polymerization Control.....	67
5.6	Process Conditions and Polymer Characteristics	69
5.6.1	Molecular Weight Distribution.....	70
5.6.2	End Groups	71
5.6.3	Composition and Monomer Sequence Distributions	72
5.7	Monomer Recovery.....	74
5.8	Isolation.....	75
5.9	Process Safety	76
5.10	Commercial Process Descriptions	77
	References.....	78

6	Cure Systems for Fluoroelastomers.....	81
6.1	Introduction	81
6.2	VDF/HFP/TFE Copolymers: Diamine, Bisphenol, and Peroxide.....	81
6.2.1	Diamine Cure	81
6.2.2	Bisphenol Cure.....	82
6.2.3	Peroxide Cure.....	88
6.3	VDF/PMVE/TFE Elastomers: Peroxide (Bisphenol).....	92
6.4	Perfluoroelastomers—Various Systems.....	94
6.5	TFE/Propylene Elastomers: Peroxide, Bisphenol.....	98
6.6	Ethylene/TFE/PMVE Elastomers: Peroxide, Bisphenol	102
6.7	Cross-Linking by Ionizing Radiation	102
	References.....	103
7	Processing of Fluoroelastomers.....	107
7.1	Introduction	107
7.2	Compounding	107
7.3	Mixing	107
7.3.1	Handling and Storing of Compounding Ingredients	108
7.3.2	Mill Mixing	108
7.3.3	Mixing in Internal Mixers.....	109
7.3.4	Continuous Mixing.....	112
7.4	Extrusion.....	112
7.5	Calendering.....	116
7.6	Curing.....	117
7.7	Molding	118
7.7.1	General Considerations	118
7.7.2	Compression Molding.....	119
7.7.3	Transfer Molding.....	120
7.7.4	Injection Molding.....	120
7.8	Other Processing Methods	125
7.8.1	Latex	125
7.8.2	Thermoplastic Elastomers.....	125
	References.....	129

PART III ENVIRONMENTAL RESISTANCE AND APPLICATIONS OF FLUROELASTOMERS

8	Fluid Resistance of VDF-Containing Fluoroelastomers.....	133
8.1	Introduction	133
8.2	Fluid Resistance Data.....	133
8.3	Discussion of Results	133
8.4	Fluid Service Recommendations	327
	References.....	328
9	Fluid and Heat Resistance of Perfluoroelastomers.....	329
9.1	Introduction	329
9.2	Fluid Resistance Data.....	329

9.3 Heat Resistance Data	404
9.4 Resistance to Special Environment	406
9.5 Major Applications.....	406
References.....	409
10 Fluid Resistance of TFE–Olefin Fluoroelastomers.....	411
10.1 Introduction	411
10.2 Fluid Resistance of TFE/Propylene Elastomers	411
10.2.1 TFE/P Copolymer	411
10.2.2 TFE/P/VDF Terpolymers.....	427
10.2.3 TFE/P/TFP Terpolymers.....	428
10.2.4 Service Recommendations	428
10.3 Fluid Resistance of ETP Elastomers	428
10.3.1 Fluid Resistance Data.....	430
10.3.2 Resistance to Oil Field Environments	430
10.3.3 Cure System Effects.....	430
10.3.4 Service Recommendations	431
References.....	432

PART IV FLUOROELASTOMER APPLICATIONS AND COMPOUNDS

11 Fluoroelastomer Applications	435
11.1 Introduction	435
11.2 Major End Uses.....	436
11.3 Fabrication Methods.....	436
Further Reading	438
12 Compounds for O-Rings and Molded Goods	439
12.1 Compounds for O-Rings.....	439
12.1.1 Specifications	439
12.1.2 Compression Set Measurement.....	439
12.1.3 VDF/HFP Copolymer Compounds.....	441
12.2 VDF/HFP/TFE Compounds.....	447
12.3 VDF/PMVE/TFE Compounds	455
12.4 Seal Design Considerations	457
12.5 Additional Fluoroelastomer Molding Compounds.....	457
References.....	469
13 Compounds for Automotive Fuel Systems.....	471
13.1 Introduction	471
13.2 Fuel Line Veneer.....	472
13.3 Fuel Tank Components	475
13.4 Fuel Injector Seals.....	479
13.5 Development Trends	482
References.....	482

14	Compounds for Automotive Power Train Systems	483
14.1	Introduction	483
14.2	Oil-Seal Requirements	483
14.3	Compounds for Oil Seals.....	486
14.3.1	FKM Elastomers for Oil Seals.....	486
14.3.2	FEPM Elastomers in Engine Seals	487
14.4	Compounds for Transmission Seals	488
	References.....	490
15	Compounds for Power Plant Service	491
15.1	Introduction	491
15.2	Flue Duct Expansion Joints	491
15.3	High-Fluorine Terpolymers.....	491
	References.....	493
16	Other Fluoroelastomer Applications and Processing.....	495
16.1	Introduction	495
16.2	Latex and Coatings.....	495
16.3	Thermoplastic Processing and Fluorinated Thermoplastic Elastomers	495
16.4	Fluoroelastomer Caulks.....	497
16.5	Processing Aids for Hydrocarbon Plastics	497
	References.....	498
17	Fluoroelastomer Safety and Disposal, Sustainability	499
17.1	Introduction	499
17.2	Safety in Production.....	499
17.3	Safety in Applications.....	500
17.4	Disposal	500
17.5	Sustainability	500
	References.....	501
18	New Developments and Current Trends.....	503
18.1	Introduction	503
18.2	New Developments in Chemistry and Processing	503
18.3	New Products	504
18.4	Other Developments.....	505
18.5	C8 Issues.....	506
	References.....	506
	Appendix 1: PDL Resistance Ratings.....	509
	Appendix 2: Examples of FKM-Based Compounds	511
	Appendix 3: Acronyms and Abbreviations.....	515
	Bibliography	517
	Glossary	519
	Index	553