# Contents

**Preface** *xiii*
**List of Contributors** *xv*

**Part I Introduction** *1*

1 **Introduction to Reactive Extrusion** *3*
*Christian Hopmann, Maximilian Adamy, and Andreas Cohnen*
References *9*

**Part II Introduction to Twin-Screw Extruder for Reactive Extrusion** *11*

2 **The Co-rotating Twin-Screw Extruder for Reactive Extrusion** *13*
*Frank Lechner*
2.1 Introduction *13*
2.2 Development and Key Figures of the Co-rotating Twin-Screw Extruder *14*
2.3 Screw Elements *16*
2.4 Co-rotating Twin-Screw Extruder – Unit Operations *22*
2.4.1 Feeding *23*
2.4.2 Upstream Feeding *23*
2.4.3 Downstream Feeding *24*
2.4.4 Melting Mechanisms *24*
2.4.5 Thermal Energy Transfer *24*
2.4.6 Mechanical Energy Transfer *25*
2.4.7 Mixing Mechanisms *25*
2.4.8 Devolatilization/Degassing *25*
2.4.9 Discharge *26*
2.5 Suitability of Twin-Screw Extruders for Chemical Reactions *26*
2.6 Processing of TPE-V *27*
2.7 Polymerization of Thermoplastic Polyurethane (TPU) *29*

2.8 Grafting of Maleic Anhydride on Polyolefines *31*
2.9 Partial Glycolysis of PET *32*
2.10 Peroxide Break-Down of Polypropylene *33*
2.11 Summary *35*
References *35*

**Part III Simulation and Modeling** *37*

**3 Modeling of Twin Screw Reactive Extrusion: Challenges and Applications** *39*
*Françoise Berzin and Bruno Vergnes*
3.1 Introduction *39*
3.1.1 Presentation of the Reactive Extrusion Process *39*
3.1.2 Examples of Industrial Applications *40*
3.1.3 Interest of Reactive Extrusion Process Modeling *41*
3.2 Principles and Challenges of the Modeling *41*
3.2.1 Twin Screw Flow Module *42*
3.2.2 Kinetic Equations *44*
3.2.3 Rheokinetic Model *44*
3.2.4 Coupling *45*
3.2.5 Open Problems and Remaining Challenges *45*
3.3 Examples of Modeling *46*
3.3.1 Esterification of EVA Copolymer *46*
3.3.2 Controlled Degradation of Polypropylene *50*
3.3.3 Polymerization of $\varepsilon$-Caprolactone *55*
3.3.4 Starch Cationization *59*
3.3.5 Optimization and Scale-up *61*
3.4 Conclusion *65*
References *66*

**4 Measurement and Modeling of Local Residence Time Distributions in a Twin-Screw Extruder** *71*
*Xian-Ming Zhang, Lian-Fang Feng, and Guo-Hua Hu*
4.1 Introduction *71*
4.2 Measurement of the Global and Local RTD *72*
4.2.1 Theory of RTD *72*
4.2.2 In-line RTD Measuring System *73*
4.2.3 Extruder and Screw Configurations *75*
4.2.4 Performance of the In-line RTD Measuring System *76*
4.2.5 Effects of Screw Speed and Feed Rate on RTD *77*
4.2.6 Assessment of the Local RTD in the Kneading Disk Zone *79*
4.3 Residence Time, Residence Revolution, and Residence Volume Distributions *81*
4.3.1 Partial RTD, RRD, and RVD *82*
4.3.2 Local RTD, RRD, and RVD *86*

4.4 Modeling of Local Residence Time Distributions *88*
4.4.1 Kinematic Modeling of Distributive Mixing *88*
4.4.2 Numerical Simulation *89*
4.4.3 Experimental Validation *92*
4.4.4 Distributive Mixing Performance and Efficiency *93*
4.5 Summary *97*
References *98*

**5 In-process Measurements for Reactive Extrusion Monitoring and Control** *101*
*José A. Covas*
5.1 Introduction *101*
5.2 Requirements of In-process Monitoring of Reactive Extrusion *103*
5.3 In-process Optical Spectroscopy *111*
5.4 In-process Rheometry *116*
5.5 Conclusions *125*
Acknowledgment *126*
References *126*

**Part IV Synthesis Concepts** *133*

**6 Exchange Reaction Mechanisms in the Reactive Extrusion of Condensation Polymers** *135*
*Concetto Puglisi and Filippo Samperi*
6.1 Introduction *135*
6.2 Interchange Reaction in Polyester/Polyester Blends *138*
6.3 Interchange Reaction in Polycarbonate/Polyester Blends *143*
6.4 Interchange Reaction in Polyester/Polyamide Blends *148*
6.5 Interchange Reaction in Polycarbonate/Polyamide Blends *155*
6.6 Interchange Reaction in Polyamide/Polyamide Blends *159*
6.7 Conclusions *166*
References *167*

**7 *In situ* Synthesis of Inorganic and/or Organic Phases in Thermoplastic Polymers by Reactive Extrusion** *179*
*Véronique Bounor-Legaré, Françoise Fenouillot, and Philippe Cassagnau*
7.1 Introduction *179*
7.2 Nanocomposites *179*
7.2.1 Synthesis of *in situ* Nanocomposites *181*
7.2.2 Some Specific Applications *183*
7.2.2.1 Antibacterial Properties of PP/$TiO_2$ Nanocomposites *183*
7.2.2.2 Flame-Retardant Properties *184*
7.2.2.3 Protonic Conductivity *186*
7.3 Polymerization of a Thermoplastic Minor Phase: Toward Blend Nanostructuration *188*

7.4 Polymerization of a Thermoset Minor Phase Under Shear *196*
7.4.1 Thermoplastic Polymer/Epoxy-Amine Miscible Blends *197*
7.4.2 Examples of Stabilization of Thermoplastic Polymer/Epoxy-Amine Blends *202*
7.4.3 Blends of Thermoplastic Polymer with Monomers Crosslinking via Radical Polymerization *202*
7.5 Conclusion *203*
References *204*

**8 Concept of (Reactive) Compatibilizer-Tracer for Emulsification Curve Build-up, Compatibilizer Selection, and Process Optimization of Immiscible Polymer Blends** *209*
*Cai-Liang Zhang, Wei-Yun Ji, Lian-Fang Feng, and Guo-Hua Hu*
8.1 Introduction *209*
8.2 Emulsification Curves of Immiscible Polymer Blends in a Batch Mixer *210*
8.3 Emulsification Curves of Immiscible Polymer Blends in a Twin-Screw Extruder Using the Concept of (Reactive) Compatibilizer *213*
8.3.1 Synthesis of (Reactive) Compatibilizer-Tracers *213*
8.3.2 Development of an In-line Fluorescence Measuring Device *214*
8.3.3 Experimental Procedure for Emulsification Curve Build-up *216*
8.3.4 Compatibilizer Selection Using the Concept of Compatibilizer-Tracer *219*
8.3.5 Process Optimization Using the Concept of Compatibilizer-Tracer *220*
8.3.5.1 Effect of Screw Speed *220*
8.3.5.2 Effects of the Type of Mixer *221*
8.3.6 Section Summary *221*
8.4 Emulsification Curves of Reactive Immiscible Polymer Blends in a Twin-Screw Exturder *222*
8.4.1 Reaction Kinetics between Reactive Functional Groups *222*
8.4.2 (Non-reactive) Compatibilizers Versus Reactive Compatibilizers *223*
8.4.3 An Example of Reactive Compatibilizer-Tracer *224*
8.4.4 Assessment of the Morphology Development of Reactive Immiscible Polymer Blends Using the Concept of Reactive Compatibilizer *225*
8.4.5 Emulsification Curve Build-up in a Twin-Screw Extruder Using the Concept of Reactive Compatibilizer-Tracer *229*
8.4.6 Assessment of the Effects of Processing Parameters Using the Concept of Reactive Compatibilizer-Tracer *233*
8.4.6.1 Effect of the Reactive Compatibilizer-Tracer Injection Location *233*
8.4.6.2 Effect of the Blend Composition *235*
8.4.6.3 Effect of the Geometry of Screw Elements *238*
8.5 Conclusion *241*
References *241*

**Part V Selected Examples of Synthesis** *245*

**9 Nano-structuring of Polymer Blends by *in situ* Polymerization and *in situ* Compatibilization Processes** *247*
*Cai-Liang Zhang, Lian-Fang Feng, and Guo-Hua Hu*
9.1 Introduction *247*
9.2 Morphology Development of Classical Immiscible Polymer Blending Processes *248*
9.2.1 Solid–Liquid Transition Stage *249*
9.2.2 Melt Flow Stage *251*
9.2.3 Effect of Compatibilizer *253*
9.3 *In situ* Polymerization and *in situ* Compatibilization of Polymer Blends *255*
9.3.1 Principles *255*
9.3.2 Classical Polymer Blending Versus *in situ* Polymerization and *in situ* Compatibilization *255*
9.3.3 Examples of Nano-structured Polymer Blends by *in situ* Polymerization and *in situ* Compatibilization *257*
9.3.3.1 PP/PA6 Nano-blends *257*
9.3.3.2 PPO/PA6 Nano-blends *264*
9.3.3.3 PA6/Core–Shell Blends *264*
9.4 Summary *267*
References *268*

**10 Reactive Comb Compatibilizers for Immiscible Polymer Blends** *271*
*Yongjin Li, Wenyong Dong, and Hengti Wang*
10.1 Introduction *271*
10.2 Synthesis of Reactive Comb Polymers *272*
10.3 Reactive Compatibilization of Immiscible Polymer Blends by Reactive Comb Polymers *274*
10.3.1 PLLA/PVDF Blends Compatibilized by Reactive Comb Polymers *274*
10.3.1.1 Comparison of the Compatibilization Efficiency of Reactive Linear and Reactive Comb Polymers *274*
10.3.1.2 Effects of the Molecular Structures on the Compatibilization Efficiency of Reactive Comb Polymers *278*
10.3.2 PLLA/ABS Blends Compatibilized by Reactive Comb Polymers *282*
10.4 Immiscible Polymer Blends Compatiblized by Janus Nanomicelles *289*
10.5 Conclusions and Further Remarks *293*
References *293*

**11 Reactive Compounding of Highly Filled Flame Retardant Wire and Cable Compounds** *299*
*Mario Neuenhaus and Andreas Niklaus*
11.1 Introduction *299*
11.2 Formulations and Ingredients *300*
11.2.1 Typical Formulation and Variations for the Evaluation *300*
11.2.2 Principle of Silane Crosslinking by Reactive Extrusion *301*
11.2.3 Production of Aluminum Trihydroxide (ATH) *301*
11.2.4 Mode of Action of Aluminum Trihydroxide *302*
11.2.5 Selection of Suitable ATH Grades *303*
11.3 Processing *306*
11.3.1 Compounding Line *306*
11.3.2 Compounding Process for Cross Linkable HFFR Products *308*
11.3.2.1 Two-Step Compounding Process *308*
11.3.2.2 One-Step Compounding Process *309*
11.3.2.3 Advantages and Disadvantages of the Two Process Concepts (Two-Step vs One-Step) *313*
11.4 Evaluation and Results on the Compound *314*
11.4.1 Crosslinking Density *314*
11.4.2 Mechanical Properties *315*
11.4.3 Aging Performance *315*
11.4.4 Fire Performance on Laboratory Scale *317*
11.4.5 Results of the Non-Polar Compounds *318*
11.5 Cable Trials *322*
11.5.1 Fire Performance of Electrical Cables According to EN 50399 *322*
11.5.2 Burning Test on Experimental Cables According to EN 50399 *323*
11.6 Conclusions *328*
References *329*

**12 Thermoplastic Vulcanizates (TPVs) by the Dynamic Vulcanization of Miscible or Highly Compatible Plastic/Rubber Blends** *331*
*Yongjin Li and Yanchun Tang*
12.1 Introduction *331*
12.2 Morphological Development of TPVs from Immiscible Polymer Blends *333*
12.3 TPVs from Miscible PVDF/ACM Blends *334*
12.4 TPVs from Highly Compatible EVA/EVM Blends *338*
12.5 Conclusions and Future Remarks *342*
References *342*

**Part VI Selected Examples of Processing** *345*

**13 Reactive Extrusion of Polyamide 6 with Integrated Multiple Melt Degassing** *347*
*Christian Hopmann, Eike Klünker, Andreas Cohnen, and Maximilian Adamy*
13.1 Introduction *347*
13.2 Synthesis of Polyamide 6 *347*
13.2.1 Hydrolytic Polymerization of Polyamide 6 *347*
13.2.2 Anionic Polymerization of Polyamide 6 *348*
13.3 Review of Reactive Extrusion of Polyamide 6 in Twin-Screw Extruders *352*
13.4 Recent Developments in Reactive Extrusion of Polyamide 6 in Twin-Screw Extruders *354*
13.4.1 Reaction System and Experimental Setup *354*
13.4.2 Influence of Number of Degassing Steps and Activator Content on Residual Monomer Content and Molecular Weight *356*
13.4.3 Influence of Amount and Type of Entrainer on Residual Monomer Content and Molecular Weight *365*
13.4.4 Influence of Polymer Throughput on Residual Monomer Content *367*
13.5 Conclusion *368*
References *369*

**14 Industrial Production and Use of Grafted Polyolefins** *375*
*Inno Rapthel, Jochen Wilms, and Frederik Piestert*
14.1 Grafted Polymers *375*
14.2 Industrial Synthesis of Grafted Polymers *376*
14.2.1 Melt Grafting Technology *377*
14.2.2 Solid State Grafting Technology *378*
14.3 Main Applications *380*
14.3.1 Use as Coupling Agents *380*
14.3.2 Grafted Polyolefins for Polymer Blending *392*
14.3.2.1 Reactive Blending of Polyamides *392*
14.3.3 Grafted TPE's for Overmolding Applications *400*
14.4 Conclusion and Outlook *403*
References *404*

**Index** *407*